JCNS Jülich Centre for Neutron Science

MLZ Heinz Maier-Leibnitz Zentrum

JÜLICH FORSCHUNGSZENTRUM

Sample environment for reflectometers

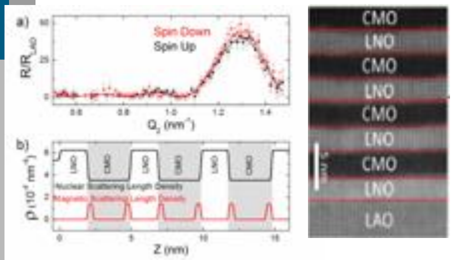
14th of May 2018, Cremlin WP4 Workshop

Stefan Mattauch, Jülich Centre for Neutron Science at MLZ

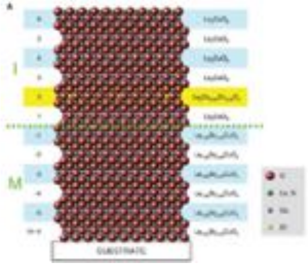
Science case selects SE

- **Resolving small length scales around interfaces regions**
- in thin film materials - **small amount of material in thin film systems**

\- with **lateral homogeneous distribution**: (specular reflectivity) (today $\Delta z>1\text{nm}$)



A. J. Grutter et al,
PRL 111, 087202 (2013)



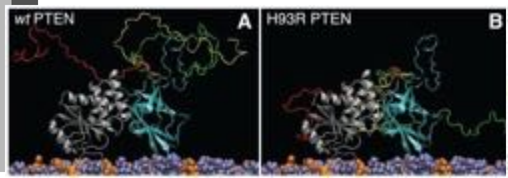
G. Logvenov et al., Science
326, 699 (2009).

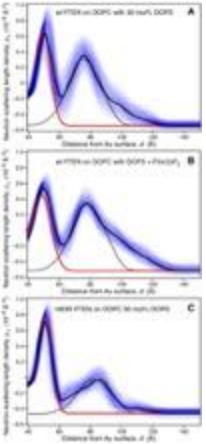
Magnetism, Ferroelectricity and Superconductivity at interfaces between two non-magnetic, non-ferroelectric and non-superconducting materials, the reconstruction or interaction at interfaces may create these states. **(below 1nm – Å region)**

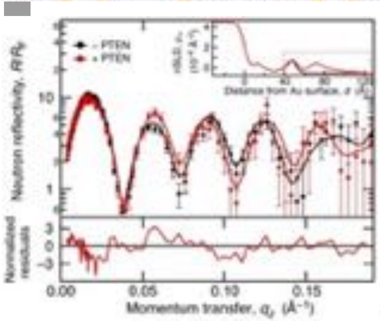
$\Rightarrow$ innovation, path to future spintronic devices

$\Rightarrow$ fundamental understanding of the phenomena

- also interplay between these states .





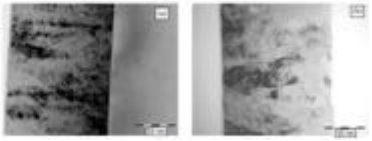


H. Nanda, S.A.K. Datta, F. Heinrich,
et al., Biophys. J., 2010, 99, 2516-
2524

Structural biology of membrane proteins

\- membrane-incorporated or membrane-associated proteins:

- membrane association of the protein depends strongly on membrane composition.
- **spatial resolution is crucial (below 1nm) to understand the binding of the protein on the membrane**



Harald Schmidt J. Phys. Cond. Matter
105303 (2011) JMS 2012

Material science: self-diffusion of atoms in solids is a fundamental point-defect mediated matter transport process

$\rightarrow$ **(Å level $\rightarrow$ high Q)**

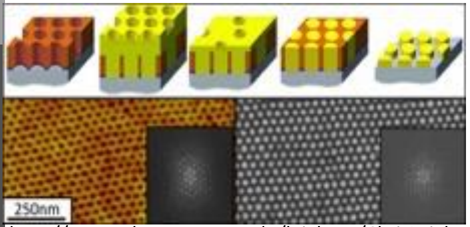
- **key role** for the design and optimization of materials as well as for the performance of devices in various branches of technology like energy storage, electronic devices, sensor technology and nanostructured materials design.

Science case selects SE

Resolving small length scales around interfaces regions
in thin film materials - **small amount of material in thin film systems**

- with **lateral inhomogeneous distribution**: (length scale sub-nm - μm)

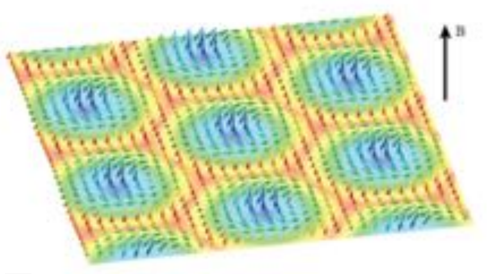
(today in thin film systems mostly not feasible due to the low available intensity)



http://research.cems.umn.edu/leighton/ChrisLeighton_MinnesotaCurrentProjects.html

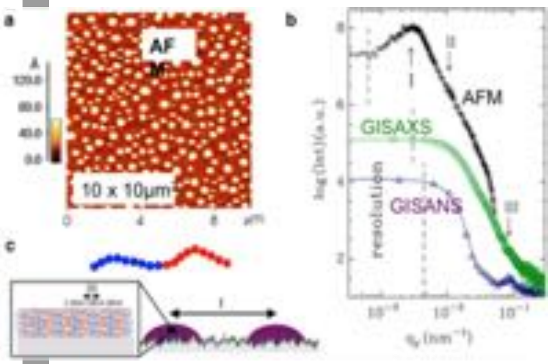
Magnetic nanoparticles assembled in a non-magnetic matrix in thin films

- stabilized by a polymer: the interaction between the particles can be tuned => tuning magnetic properties a system in a wide range => engineering of magnetism in nanostructures
- Obtaining polymer films with new magnetic, optical or mechanical properties is one of the most rapidly growing research areas in current material science
- Nanoparticle size flexible (**1-100nm, often typically 5nm**)



Novel topologically protected magnetic states, e.g. skyrmions

- recently discovered in MnSi bulk samples by SANS techniques, will be in main focus of intensive research for the next decades; extremely interesting for applications, but materials need to be investigated in thin films:
- the confinement changes the properties, e.g. increase the parameter range to higher transition temperatures. Particularly interesting, the lateral dimension of the skyrmion structure - between **a few and several hundreds of nanometers**



Self assembly of colloidal particles e.g. at the solid-liquid boundary, e.g. colloids or polymers stabilized by charge. Interesting is here the ability to tune the self-assembly by external parameters like temperature, shear etc.

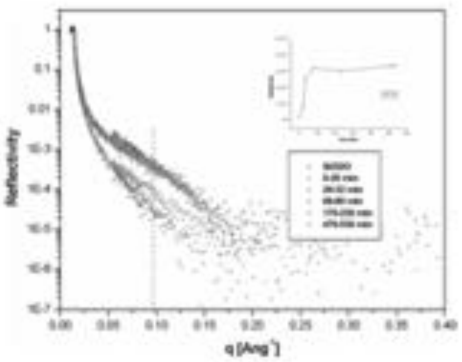
Polymer blends

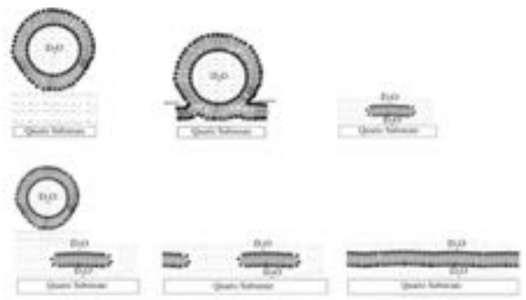
- large scale structures with utmost interest for industry-related samples of adhesives, thin foils and injection molded plastics. Typical structures composed of PB are inaccessible for neutrons.
- Due to the processing technology the surface structures are expected to be very different from the inner structures
- size ranges **from larger nm to the micrometer range**

Science case selects SE

Fast kinetic processes in life science, chemistry, biology

- time resolution from below seconds to minutes, typically for processes in cells, drug delivery, etc. (today is impossible in thin films)



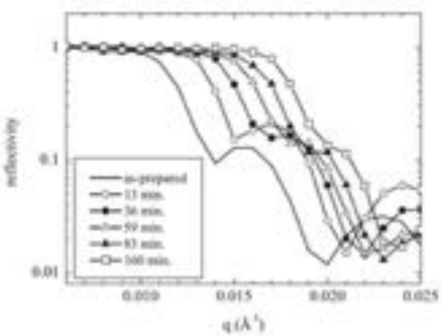


Drug delivery

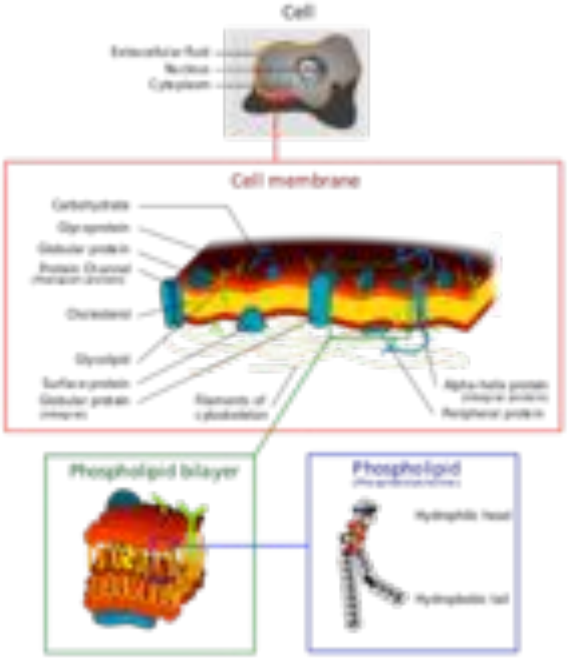
- **biocompatible interfaces** or **biosensors based on membrane receptors**, and as biophysical model systems for studying the **interaction of biomolecules with membrane surfaces.**

Energy Materials used e.g. in supercapacitors, batteries, or hydrogen storage materials

- **In-situ monitoring of chemical reactions**: e.g. deuterium absorption of thin Mg-based alloys
- fast measurements on **sub-seconds time to several seconds scale are required** to probe the system under realistic conditions



H. Fritzsche et al., Int. Journal of Hydrogen Energy 37, 3540 (2012)



Cell processing, lipid raft formation processes: gain essential insight into the dynamics of membrane organization.

Membranes are occupied by fluctuating nanoscale assemblies of sphingolipids, cholesterol and proteins stabilized into platforms that are important in signaling, viral infection and membrane trafficking.

Rafts in cells of **10 to 100 nm**, dynamic process, form and decompose by diffusion on a time scale of a **few ms to several seconds** depending on size.

Before we start with SE

You need a dedicated instrument designed for a scientific task

Vertical sample reflectometer:

Good: hard matter (esp. magnetism), soft matter, biology, solid/liquid interfaces, in general optimised for 1cm^2 sample

Not Good: liquid/liquid interfaces, liquid/gas interfaces

Horizontal sample reflectometer:

Good: liquid/liquid interfaces, liquid/gas interfaces, solid/liquid interfaces, soft matter, biology

Not so Good: hard matter (esp. magnetism), in general optimised for 16cm^2 sample

Before we start with SE

You need a dedicated instrument designed for a scientific task

You have good users with good samples

You have standard sample environment

⇩

You will get good publications

Before we start with SE

You need a dedicated instrument designed for a scientific task

You have good users

You have unique sample environment
with unique samples

↓

You will get excellent high ranked publications

Before we start with SE

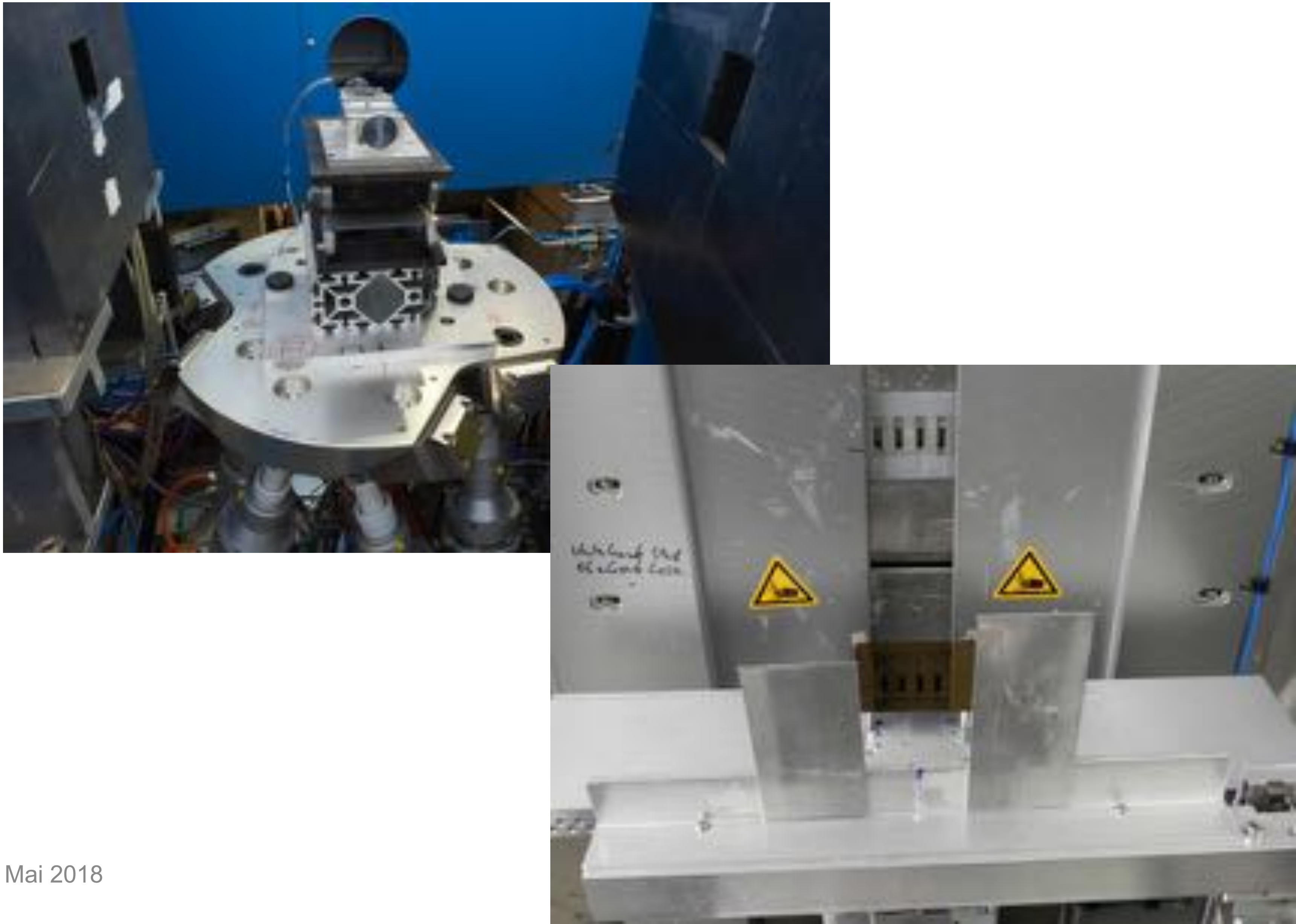
In the end you need both

You need good standard push button sample environment

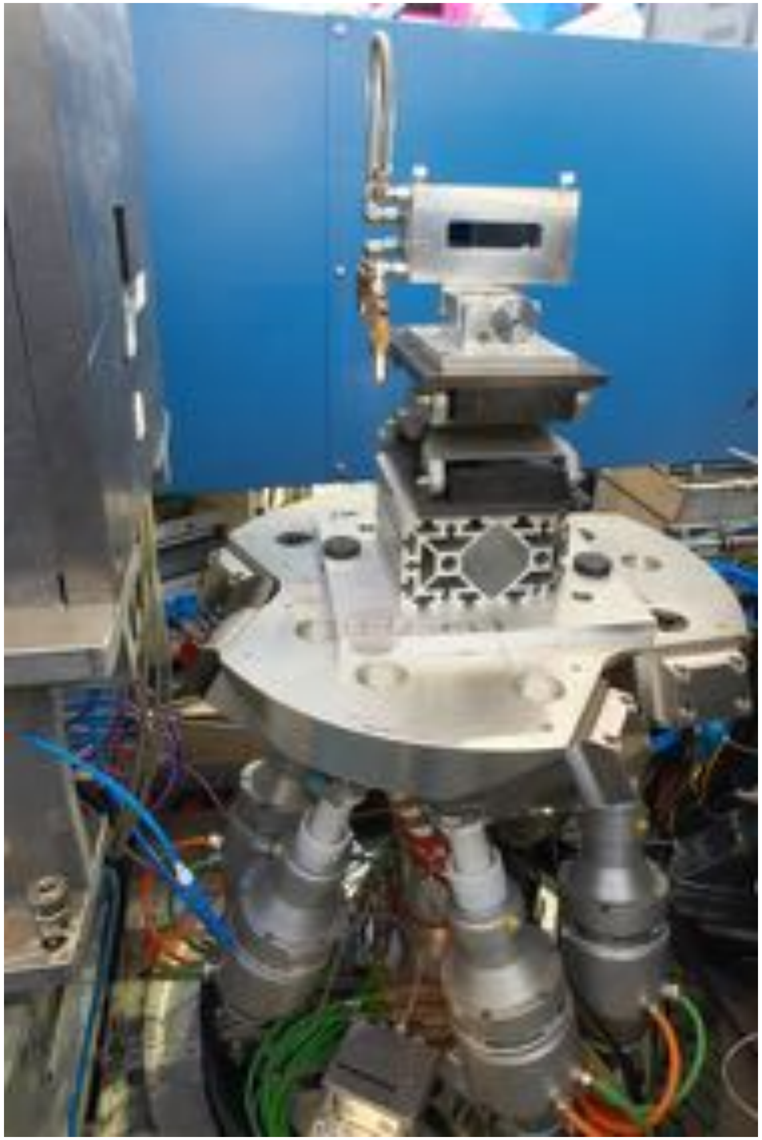
and

You need unique sample environment

Simple sample holders



Simple solid liquid cell at MARIA

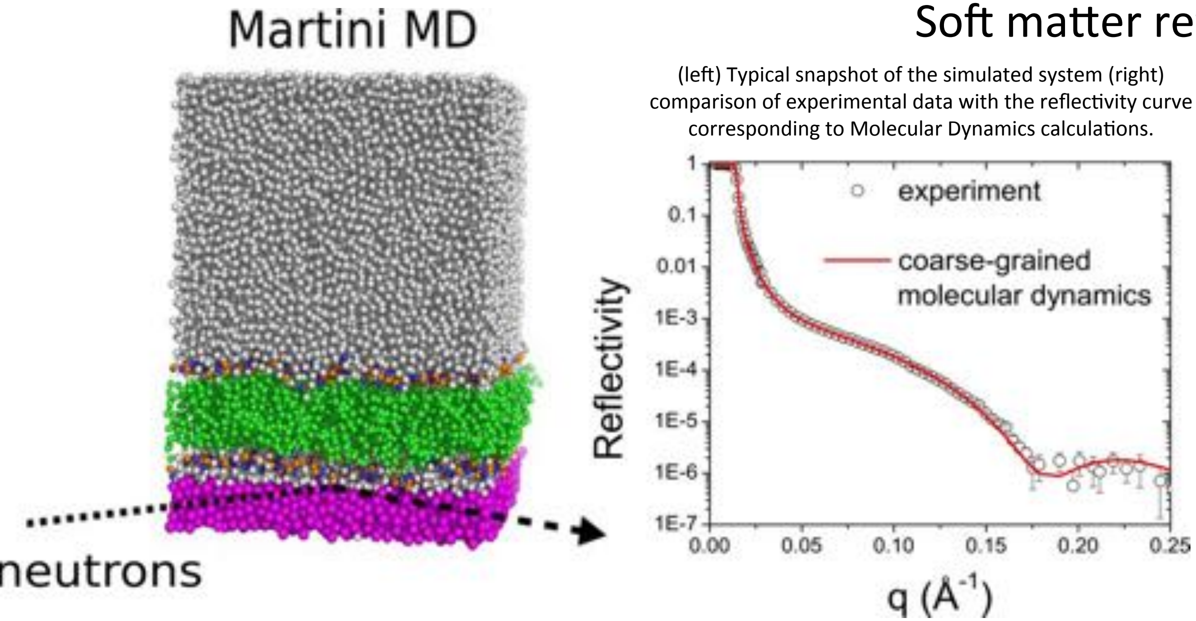


- Can be moderatly heated and cooled
- Can be investigated by in-situ Dynamic light scattering
- ....

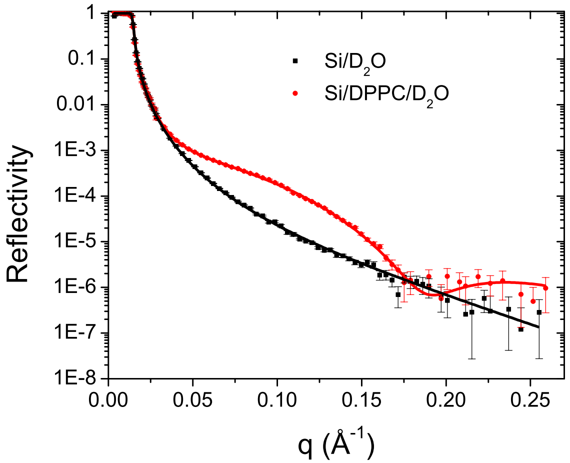
Such curves are measured in 2h

Soft matter reflectivity

(left) Typical snapshot of the simulated system (right) comparison of experimental data with the reflectivity curve corresponding to Molecular Dynamics calculations.



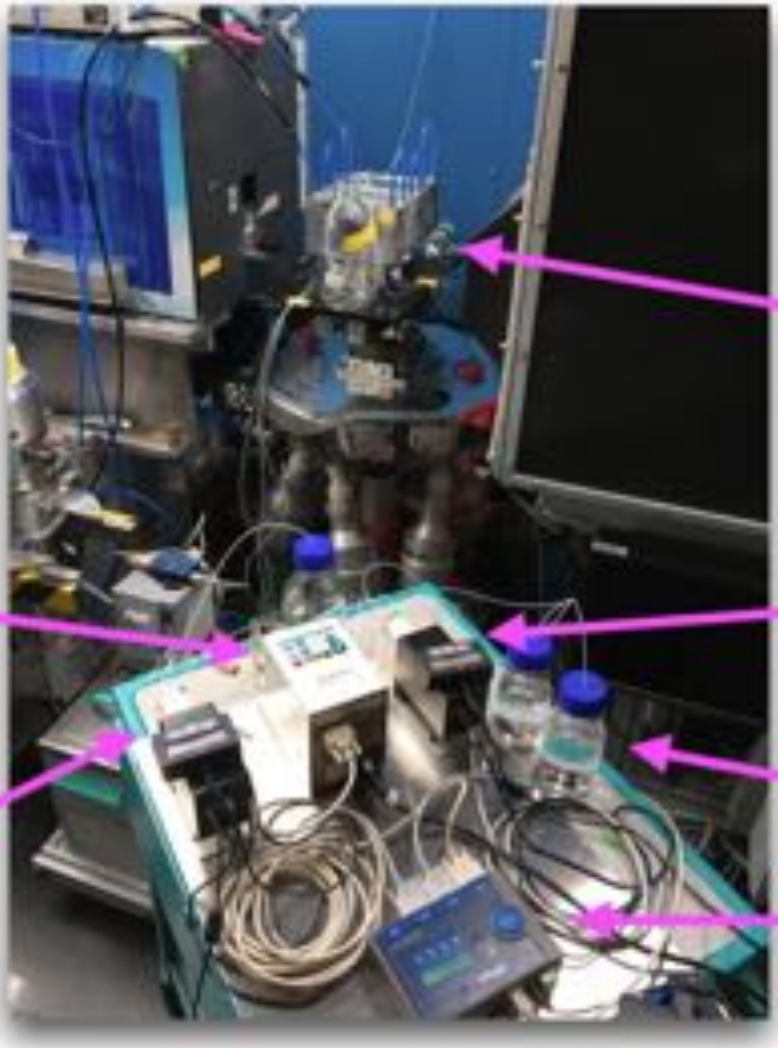
Neutron reflectivity of the silicon/D2O interface before and after the formation of supported DPPC bilayer by vesicle fusion. Full lines represent model fits of the experimental data using a head/tail/head model of the membrane.



Alexandros Koutsioubas, “Combined Coarse-Grained Molecular Dynamics and Neutron Reflectivity Characterization of Supported Lipid Membranes”; *J. Phys. Chem. B*, **2016**, 120 (44), pp 11474–11483, DOI: 10.1021/acs.jpcb.6b05433

Solid/Liquid interfaces

Today more advanced



multiple solid/liquid cells
mounted on the
sample changer

peristaltic pump

solution selection valve

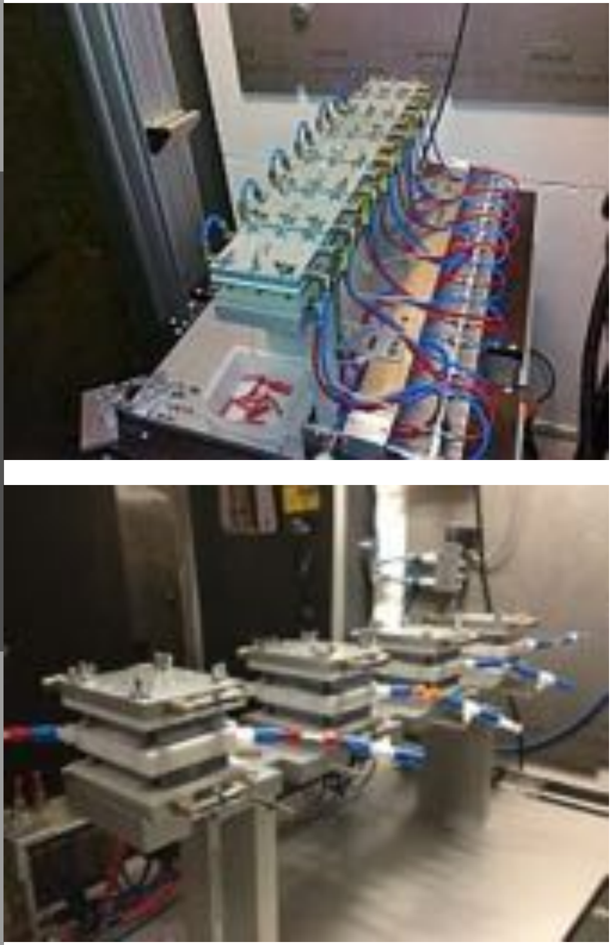
up to 6 input solutions

cell selection valve

NICOS control

The same on other machines

FIGARO ILL



REFSANS MLZ

MARIA MLZ

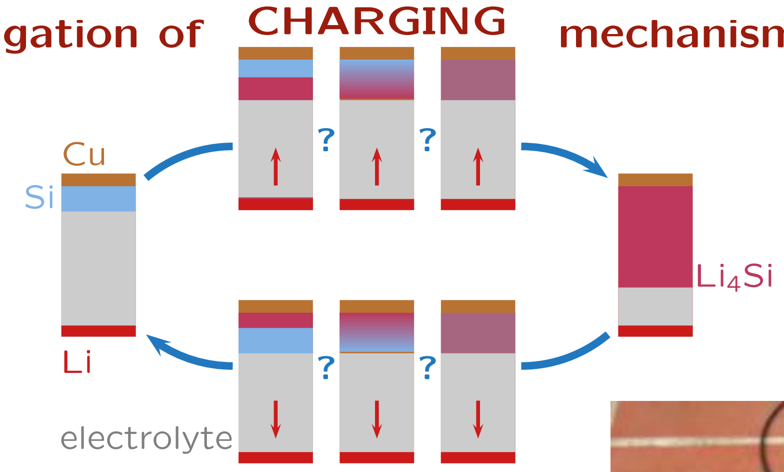
Nrex$^+$ MLZ

Electro chemical cell on AMOR

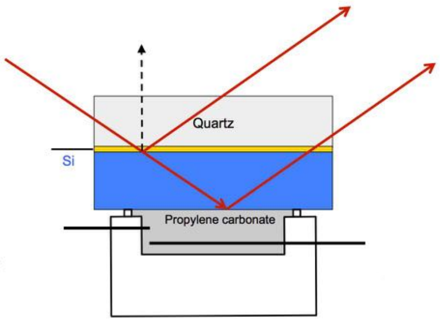
in-operando battery studies

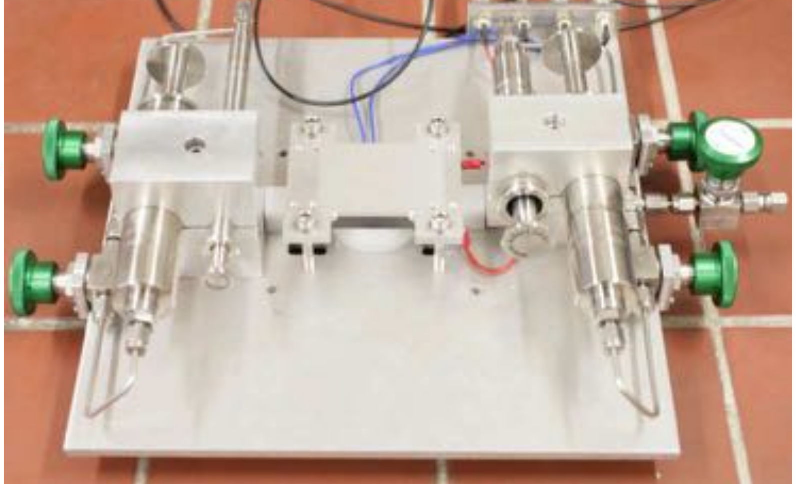
H. Schmidt, E. Hüger, B. Jerliu

In-operando investigation of CHARGING mechanism in Si/Li batteries



DIS-CHARGING



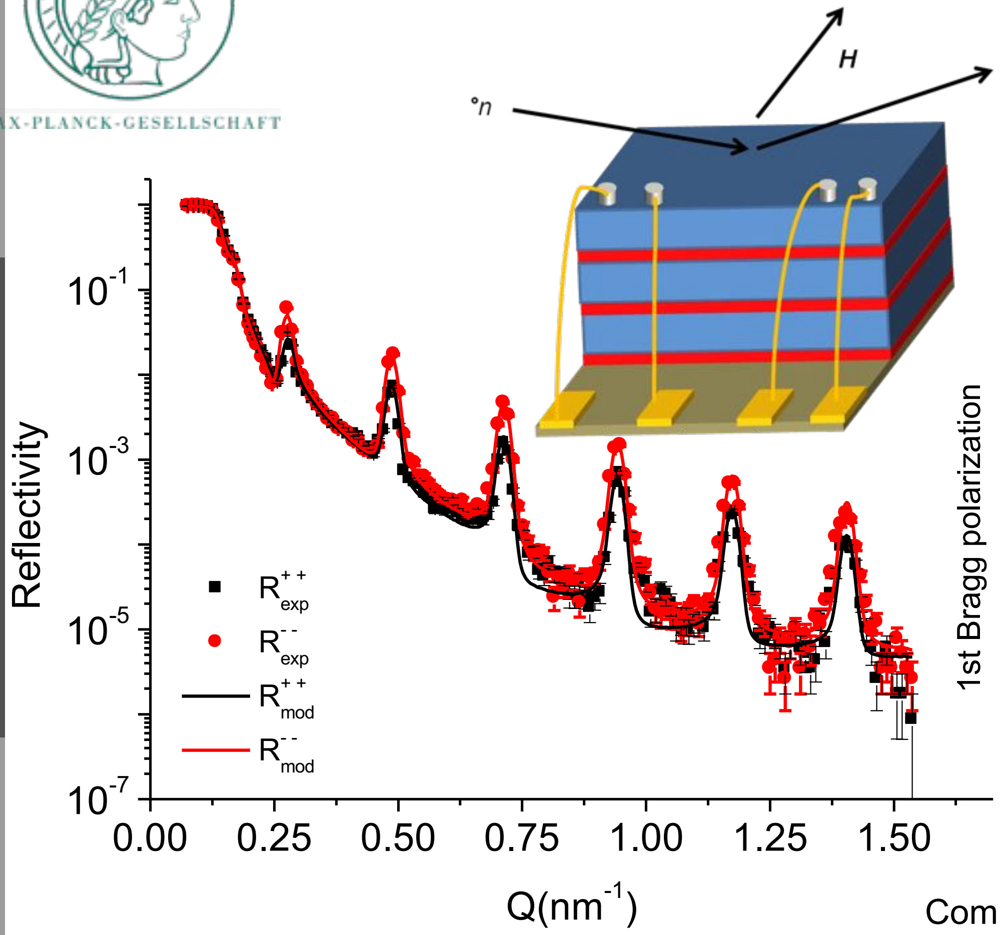


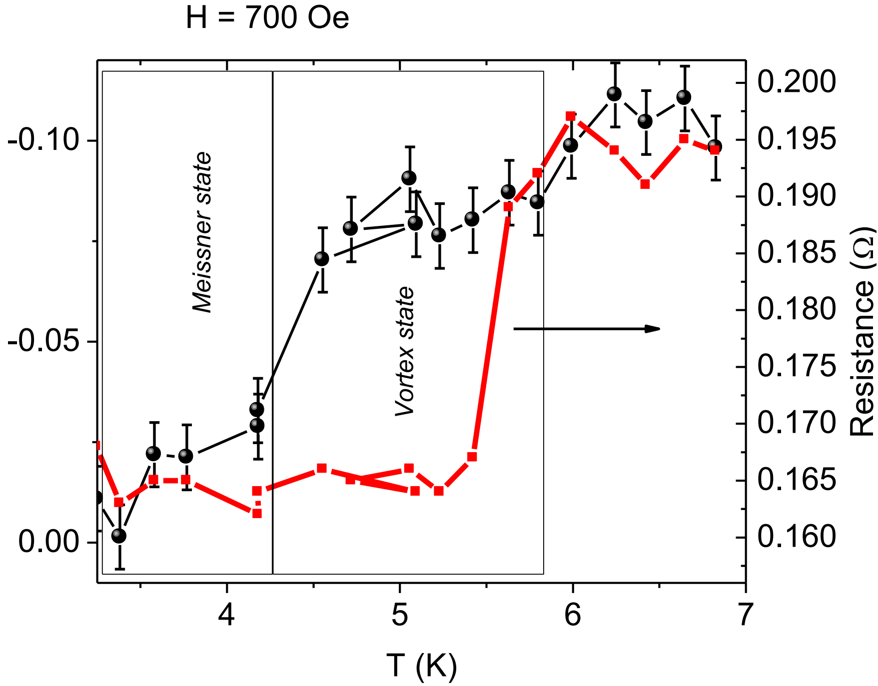
Electrochemical cell on NREX⁺

Low-temperature in-situ transport at NREX reflectometer

With courtesy of Y. Khaydukov

In collaboration with Institute of Electronic Engineering and Nanotechnologies Kishinev, Moldova





Sample:
Superconducting-ferromagnetic superstructure
[Gd(1.3nm)/Nb(25nm)]$_{12}$/Al2O3

Magnetron sputtering @ Institute of Metal Physics
(Ekaterinburg, Russia)

Comprehensive study of magnetic and transport phenomena:

- Superconducting transition in SF heterostructures
- Relation of transport and magnetic properties in spin valves
- Spin current and spin-diffusion

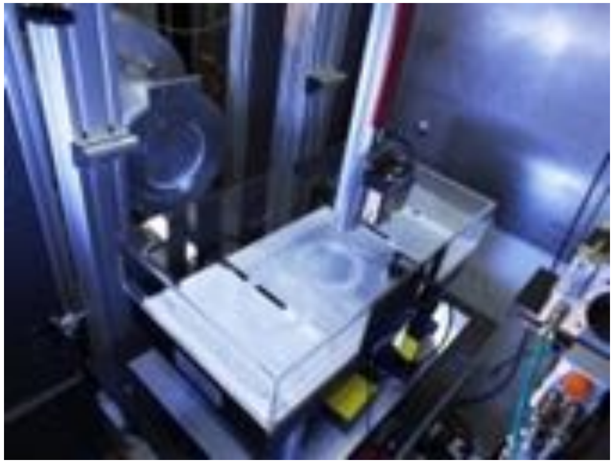
Homemade electrochemical cell

AMOR (PSI) Jochen Stahn

Surface chemistry: Langmuir Blodgett trough

insoluble monolayers at the air/water interface: the monolayer is made from a spreading solution of the material in a carrier solvent, and then barriers are used to compress the film

FIGARO (ILL)



In surface chemistry the results include adsorption of surfactants at the air-solution interface, insoluble monolayers and polymers at the air-liquid interface, soap films and adsorption at the liquid-solid and liquid-liquid interfaces


REFSANS (MLZ)

- surface pressure in situ
- trough area is 500 x 250 mm
- volume ~600 ml of liquid
- heatable

Surface chemistry: Langmuir Blodgett trough

insoluble monolayers at the air/water interface

CRISP (ISIS)

REFSANS (MLZ)

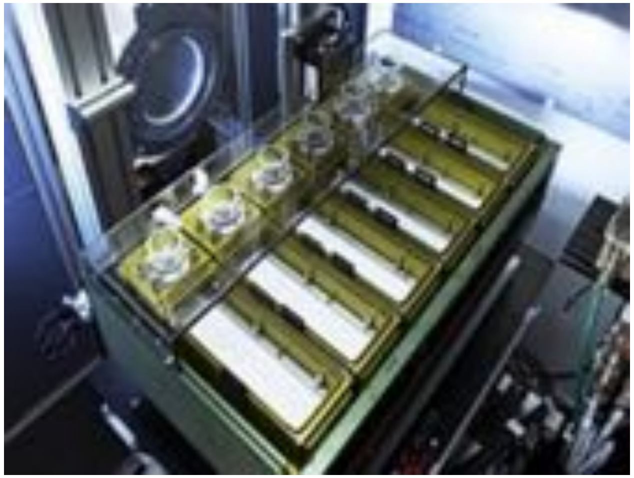
A summary of the key features of the Nima troughs follows:

Small Nima Trough	
Internal dimensions	200 × mm
Average area coverage	90 - 540 cm^2
Typical subphase volume	300 cm^3
Temperature range	-50 - 100 C
Large Nima Trough	
Internal dimensions	200 × mm
Average area coverage	90 - 1080 cm^2
Typical subphase volume	up to 1500 cm^3
Temperature range	-50 - 100 C

Surface chemistry: Adsorption trough

Interfacial layers of molecules self-assembled from solution

FIGARO (ILL)



The troughs assembly involves six sample positions each of which contains a PTFE trough of dimensions 220 mm x 50 mm. The volume required are 45 ml for liquids of high surface tension (such as water) and 25 ml for liquids of low surface tension (such as a concentrated surfactant solution)

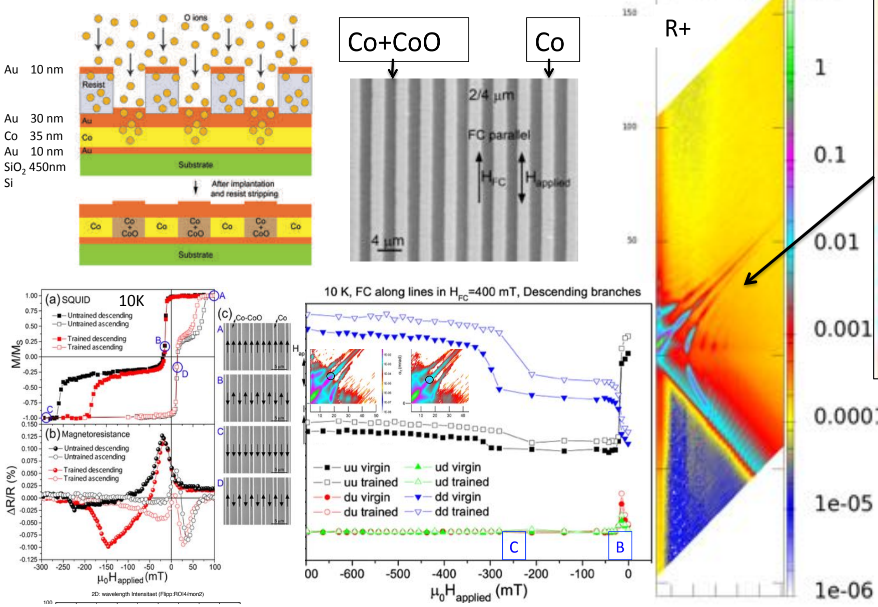
Figaro homepage

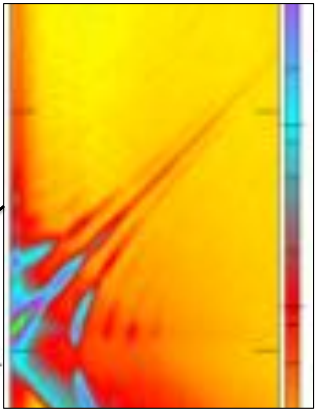
Magnetic examples

Polarized reflectometry

Magnetic configuration in laterally modulated exchange-biased microstructures

Courtesy of: E. Menendez Dalmau K.U.Leuven (Belgium)

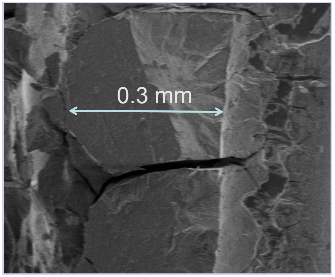




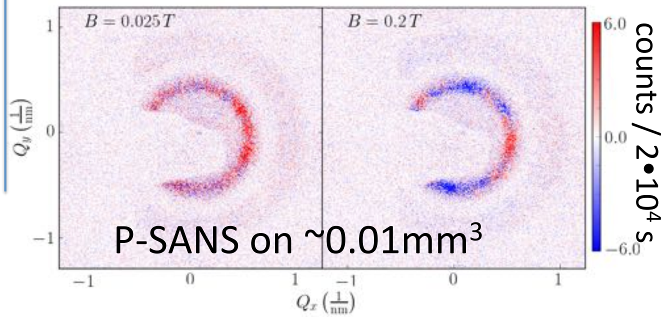
- Sample size : 15x15 mm
- After saturation
- 8 Gaus
- RT

Enric Menéndez, et.al., „Lateral Magnetically Modulated Multilayers by Combining Ion Implantation and Lithography„; **small** 2017, 1603465 , DOI: 10.1002/smll.201603465

Polarized GISANS/SANS



Centrifuge assisted sedimentation from spherical iron oxide nanoparticles with a diameter of 15nm.

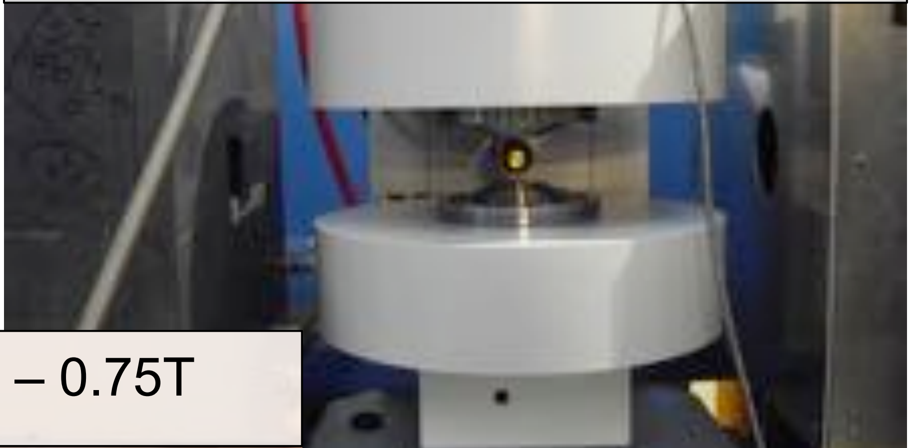


P-SANS on ~0.01mm^3

Michael Smik, Elisa Volkmann, Genevieve Wilbs, Alexandros Koutsioumpas, Stefan Mattauch, Emmanuel Kentzinger,, Jörg Perßon, Ulrich Rücker, Oleg Petracic, Thomas Brückel; Jülich Centre for Neutron Science JCNS

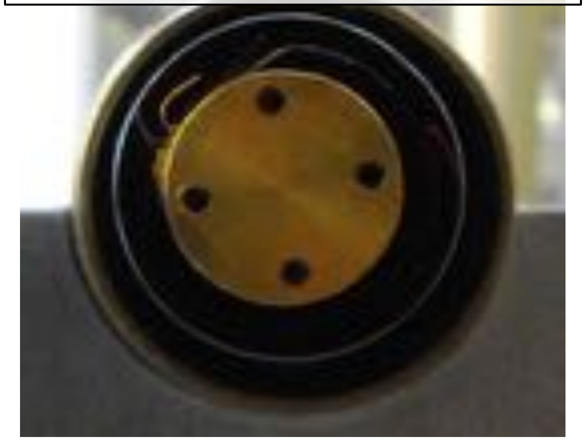
Magnets and cryos on MARIA

2cm – 2.5K – 1.2 T



2” - 4K – 0.75T

0.8cm - 10K – 2T



0.05K – 5 T - 270°

Same magnet and
cryostat at magnetic
reflectometer (ORNL)

Magnets AMOR (PSI)

options

1T electromagnet
large gap

polarisation
polarisation analysis

cryomagnet
(horizontal, 6 T)

Magnets AMOR (PSI)

equipment

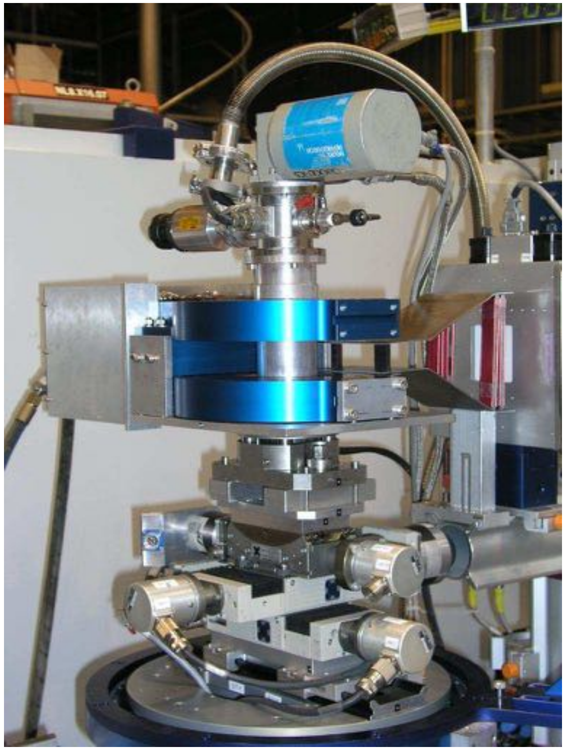
sample environment

e.g. cooling with a

closed cycle refrigerator $8\,\mathrm{K} < T < 300\,\mathrm{K}$

application of an external magnetic field with

Helmholtz coils $-1000\,\mathrm{Oe} < H < 1000\,\mathrm{Oe}$



tilt- and translation stages for alignment

ω rotation stage

sample

within sample-holder

Magnets REMUR (JINR)

- Three-circle goniometer with electromagnet: 0-20 kOe field direction ± 90°.
- Set poles with cross sections: 40 × 20 mm^2 (20kOe), 110 × 70 mm^2 (10KOe) and 60 × 40 mm^2.
- Cryostat with a vertical magnetic field of up to 3 Tesla and T=1.45-600 K. The maximum sample size is 40x40 mm^2.


Electromagnet


Cryostat

with courtesy of Viktor Bodnarchuk and Vladimir Zhaketov

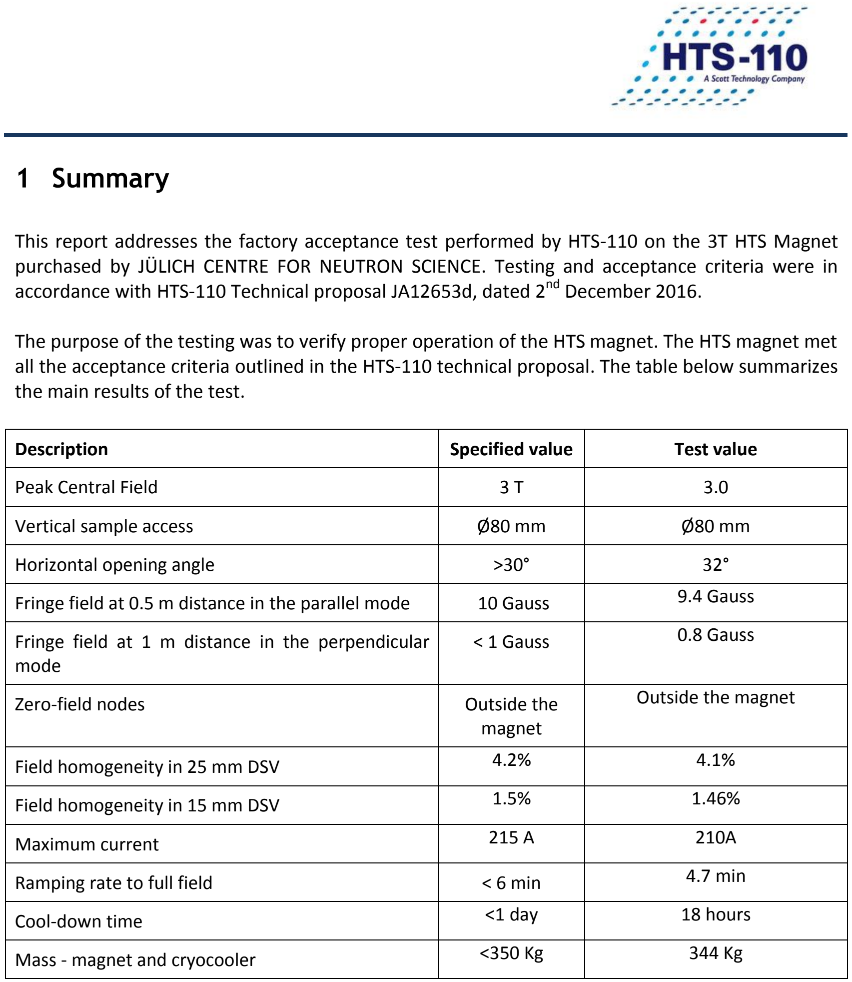
More Magnets and cryos atD17

- Quartz window vertical field cryomagnet <7T, 1.5 K < T < 320 K (50mK dilution insert optional): standard magnet for higher fields
- Quartz window horizontal field cryomagnet (XY) <8T, 1.5 K < T < 320 K (50mK dilution insert optional): Just in case you need the field geometry, not so much
- Electromagnet <1T: each cycle
- CCR insert for electromagnet 30 K < T < 600 K: New system but is increasimngly more used, as it is quicker in cooling and heating and can heat to 600 K
- XYZ coil setup <0.01T (with quartz window cryostat): rare

More about cryos in the talk of Harald Schneider according to the Harald Schneider scale:

- Hand warm (3K)
- Fresh to cool (1,5K)
- Cold (mK)

Change for Electromagents?



HTS-110
A Scott Technology Company

1 Summary

This report addresses the factory acceptance test performed by HTS-110 on the 3T HTS Magnet purchased by JÜLICH CENTRE FOR NEUTRON SCIENCE. Testing and acceptance criteria were in accordance with HTS-110 Technical proposal JA12653d, dated 2nd December 2016.

The purpose of the testing was to verify proper operation of the HTS magnet. The HTS magnet met all the acceptance criteria outlined in the HTS-110 technical proposal. The table below summarizes the main results of the test.

Description	Specified value	Test value
Peak Central Field	3 T	3.0
Vertical sample access	Ø80 mm	Ø80 mm
Horizontal opening angle	>30°	32°
Fringe field at 0.5 m distance in the parallel mode	10 Gauss	9.4 Gauss
Fringe field at 1 m distance in the perpendicular mode	< 1 Gauss	0.8 Gauss
Zero-field nodes	Outside the magnet	Outside the magnet
Field homogeneity in 25 mm DSV	4.2%	4.1%
Field homogeneity in 15 mm DSV	1.5%	1.46%
Maximum current	215 A	210A
Ramping rate to full field	< 6 min	4.7 min
Cool-down time	<1 day	18 hours
Mass - magnet and cryocooler	<350 Kg	344 Kg

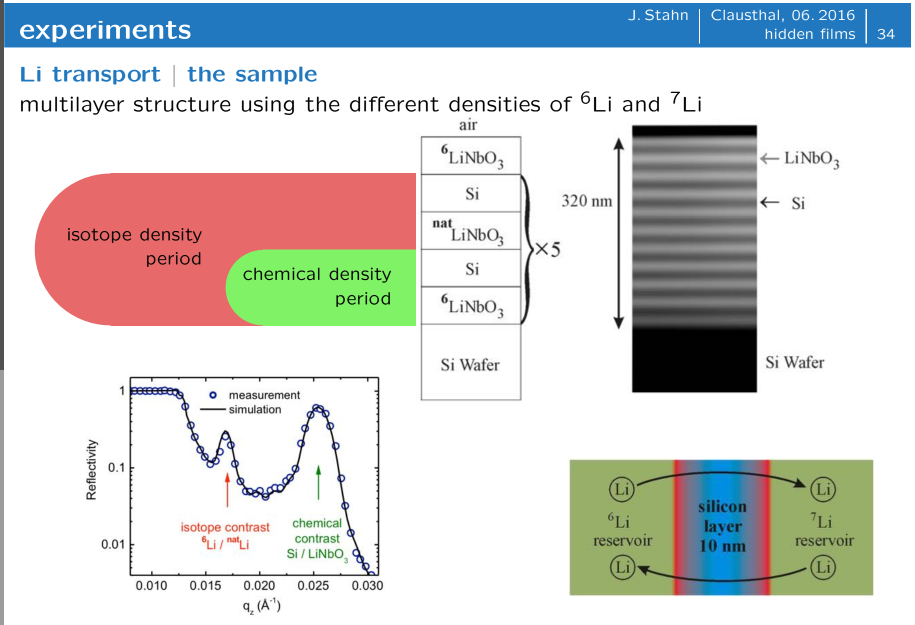
Heaters/Furnaces

- Heater stage < 400°C: max ~5 times in the year
- Furnace <1000°C: rare

D17

- In-situ furnace for fast heating and cooling RT to 500 deg C (being upgraded to 600 deg C) for diffusion studies.
- In-situ furnace for higher temperatures, slowly heating, very slowly cooling.

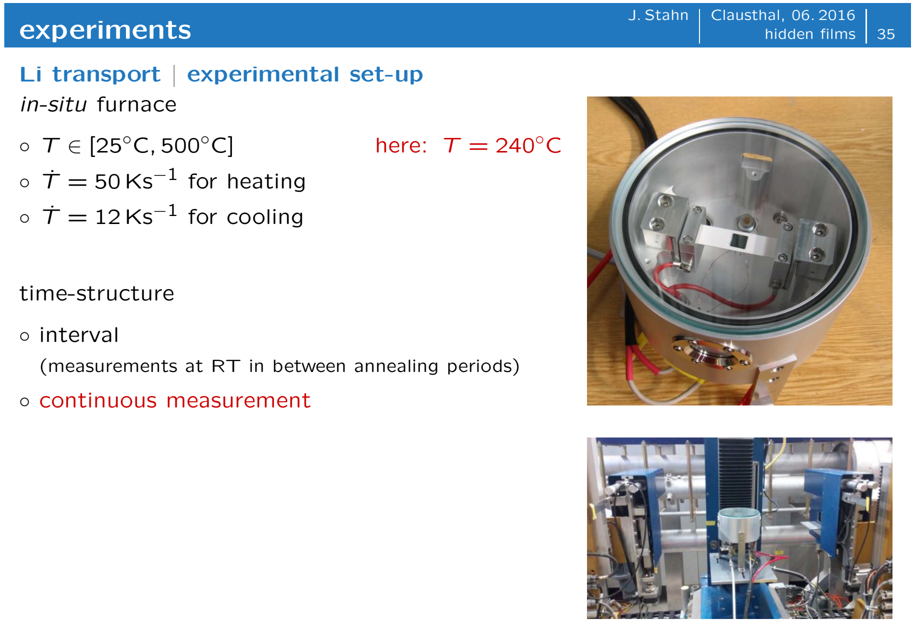
AMOR



experiments J. Stahn | Clausthal, 06. 2016 | hidden films | 34

Li transport | the sample

multilayer structure using the different densities of ^{6}Li and ^{7}Li



experiments J. Stahn | Clausthal, 06. 2016 | hidden films | 35

Li transport | experimental set-up

in-situ furnace

- $T \in [25°\mathrm{C}, 500°\mathrm{C}]$ here: $T = 240°\mathrm{C}$
- $\dot{T} = 50\,\mathrm{Ks}^{-1}$ for heating
- $\dot{T} = 12\,\mathrm{Ks}^{-1}$ for cooling

time-structure

- interval
  (measurements at RT in between annealing periods)
- continuous measurement

Molecular Beam Epitaxy setup

Base pressure < 10^{-10} mbar

Sources: 6 Effusion cells, 2 e-guns (each 4 crucibles), plasma source

Growth control via Quartz micro balances and Reflection High Energy Electron Diffraction (RHEED)

Substrate manipulator temperatures up to 1000 °C, sample size: up to Φ 2" and 20 mm x 20 mm

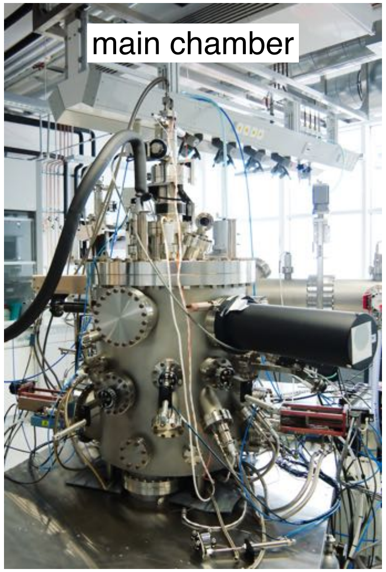
High reproducibility of sample growth:

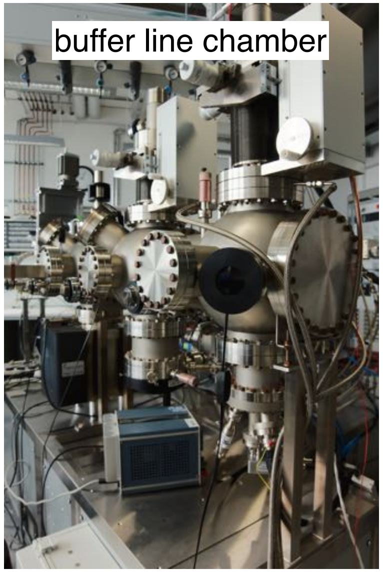
Automated control of the growth procedure by "recipes" in the MBE system software

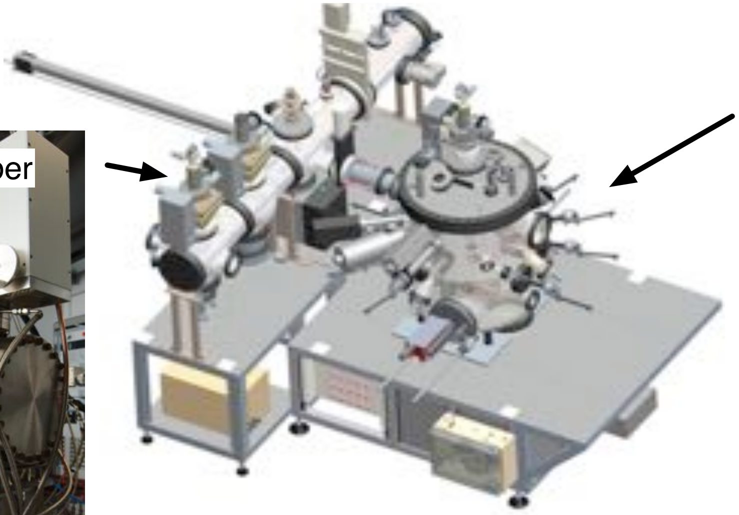
Supplied evaporation material:

Ag, Al, Au, Co, Cr, Cu, Fe, La, Mn, Ni, Nb, Pt, Sr, and Ti, other material on request

MBE: http://mlz-garching.de/mbe







Buffer line chamber:

surface structure analysis via Low Energy Electron Diffraction (LEED)

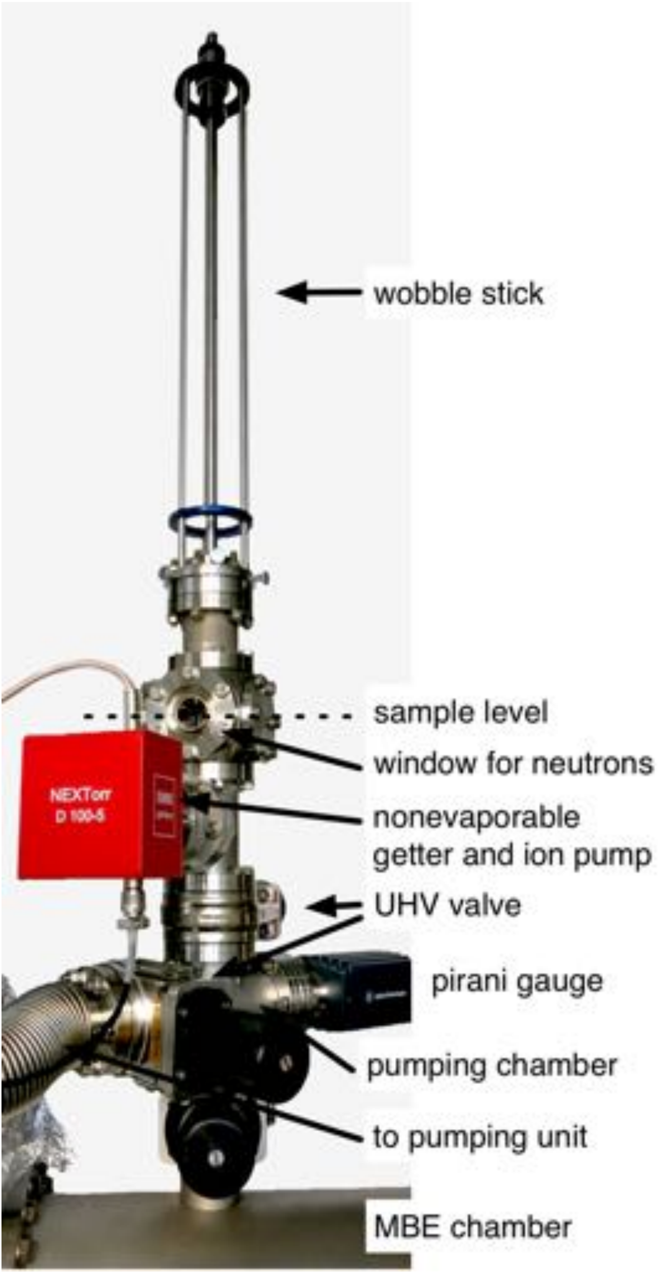
chemical surface analysis via Auger Electron Spectroscopy (AES)

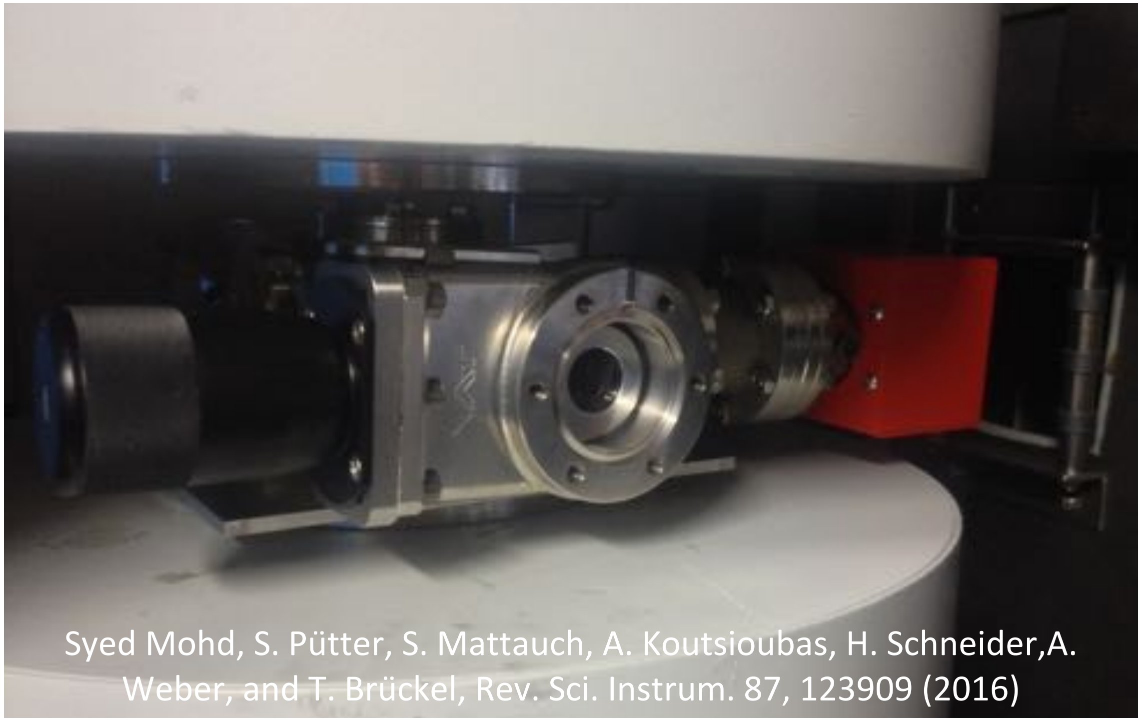
storage of up to 12 samples

UHV-Transfer: quasi in-situ

- DN CF-40 cube serves as main chamber
- two sapphire windows for the neutron beam
- a wobble stick, which serves also as a sample holder for samples of up to 1 cm2
- a DN CF-40 tee
- a nonevaporable getter and ion pump type Nextorr D 100-5 (SAES Getters SpA)
- DN CF-40 valve with window (for adjusting

➜base pressure 2・10-10 mbar



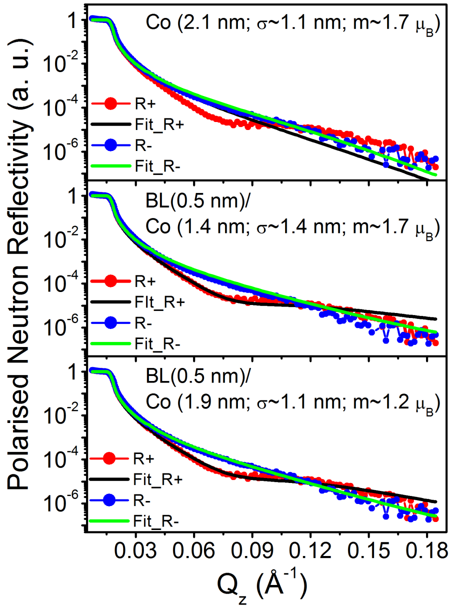


Syed Mohd, S. Pütter, S. Mattauch, A. Koutsioubas, H. Schneider,A. Weber, and T. Brückel, Rev. Sci. Instrum. 87, 123909 (2016)

UHV-Transfer: quasi in-situ

Sample 2.1 nm Co film on nontreated MgO(001) substrate, grown by MBE technique
PNR measurements at room temperature in a magnetic field of max. 600 mT

Assume pure Co thin film



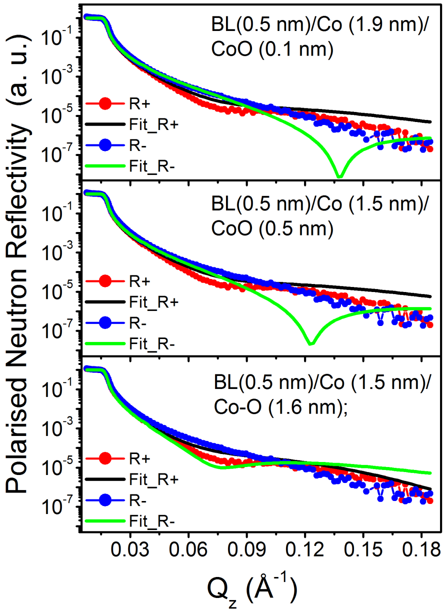
Expected film parameters do not fit

Introduce intermixing bottom layer (BL) [4,5]

Introduce lower magnetic moment [5]

Best values: BL 0.5 nm and
1.9 nm Co with σ≈1.1 nm and m= 1.2 μ_B

Assume CoO_x layers of different thickness



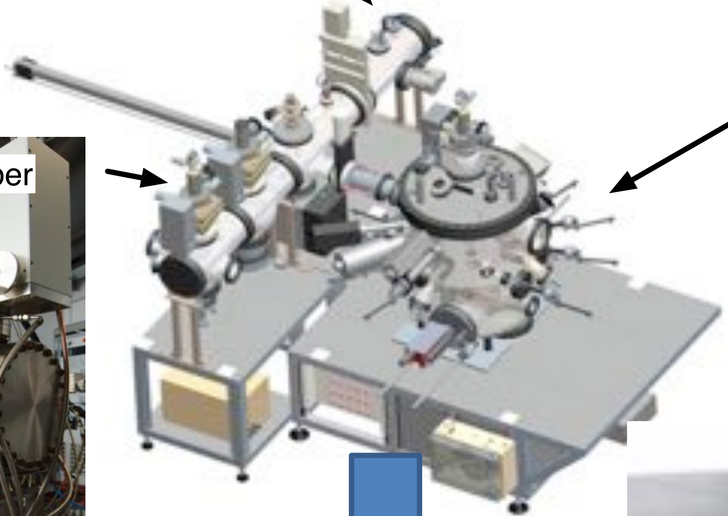
Small Co oxide layer of 0.1 nm

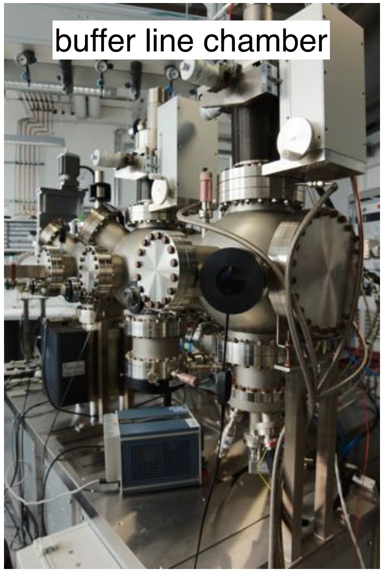
Intermediate Co oxide layer of 0.5 nm

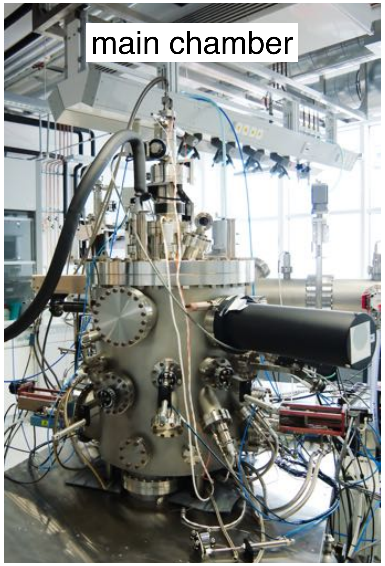
Maximum Co oxide layer of 1.6 nm

With CoO_x layer the data are not satisfied

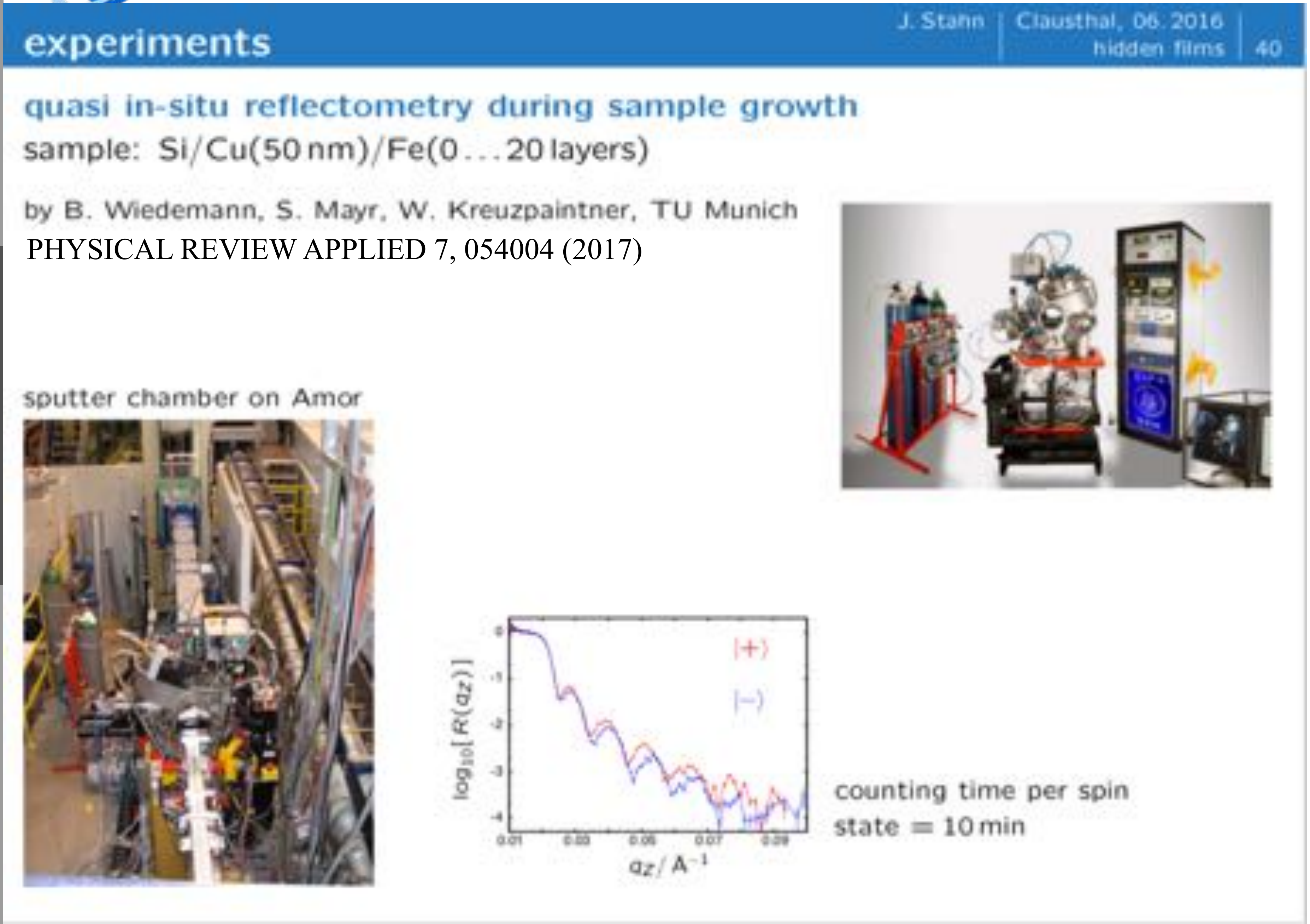
In the future PLD-chamber: Talk Alexander Goikhmann







Quasi in-situ sputtering at ARMOR (PSI)



quasi in-situ reflectometry during sample growth

sample: Si/Cu(50 nm)/Fe(0 . . . 20 layers)

by B. Wiedemann, S. Mayr, W. Kreuzpaintner, TU Munich

PHYSICAL REVIEW APPLIED 7, 054004 (2017)

sputter chamber on Amor

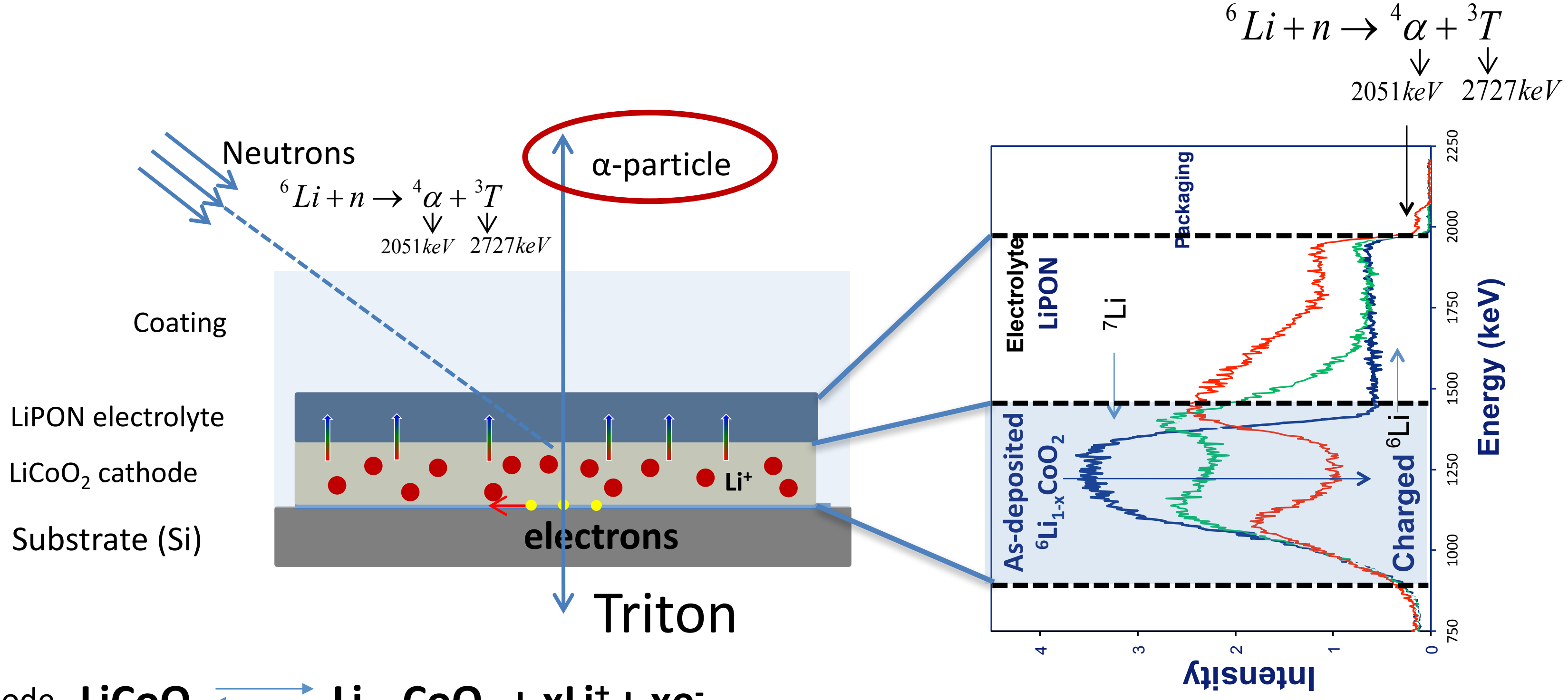
counting time per spin state = 10 min

and at REFSANS (MLZ)

with courtesy of Mathias Pomm and Wolfgang Kreutzpaintner

NDP setup at MARIA

All-solid-state thin film microbattery



$$\underset{2051\,keV}{{}^{6}Li + n \rightarrow {}^{4}\alpha} + \underset{2727\,keV}{{}^{3}T}$$

J.F.M. Oudenhoven *et al.*, Adv. Mater., 23 (2011) 4103.

Cathode **$LiCoO_2 \rightleftarrows Li_{1-x}CoO_2 + xLi^+ + xe^-$**

Anode **$xLi^+ + xe^- \rightleftarrows xLi$**

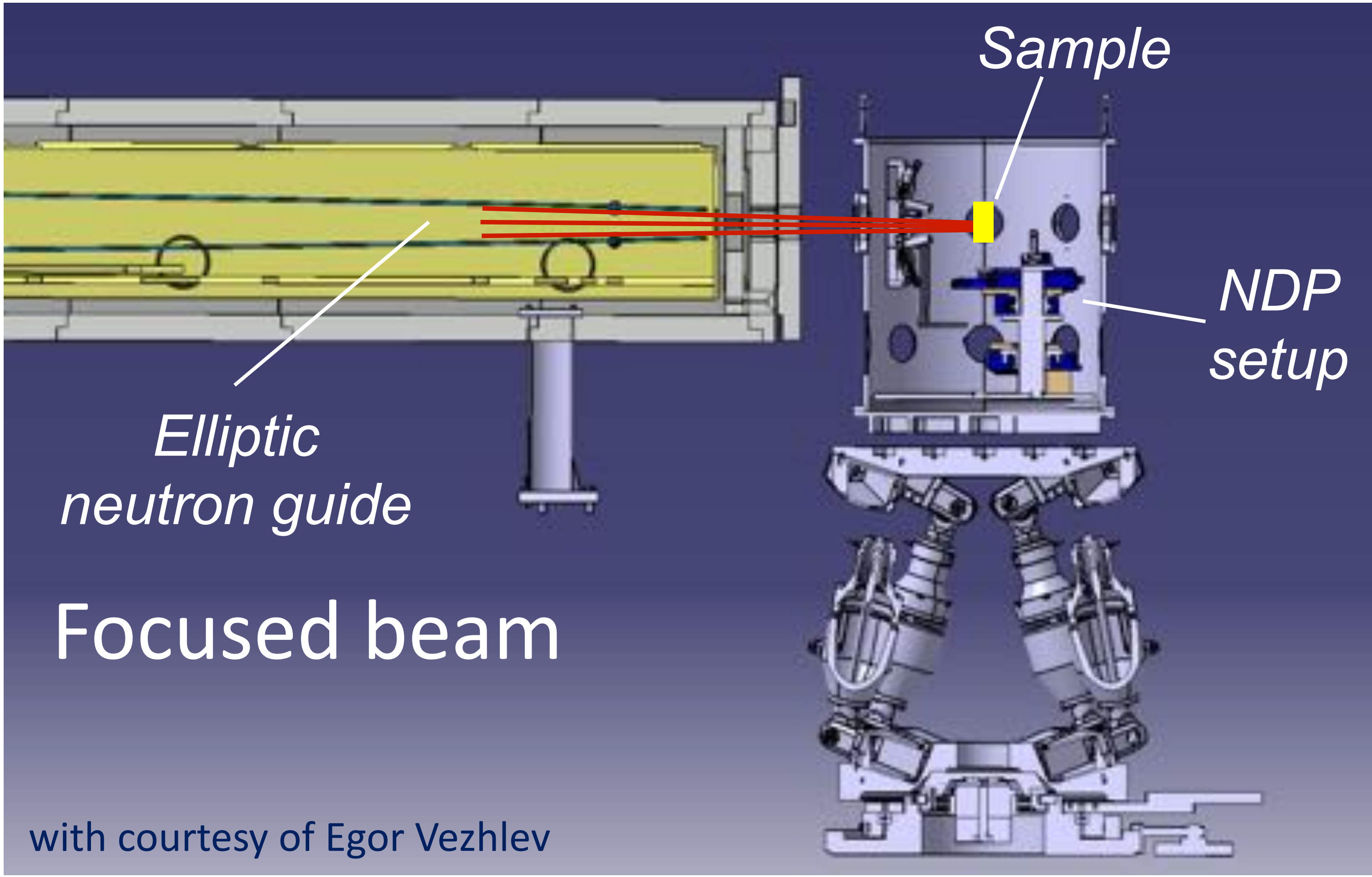
During charging/discharging of the battery Li ions are migrating back and forth inside the battery cell – one can monitor this process with Neutron Depth Profiling

with courtesy of Egor Vezhlev

NDP setup at MARIA

higher charging rate => shorter collection time:

- focused beam => Intensity increase
- stronger source => Intensity increase
- keeping low background (reflectometer)



Focused beam

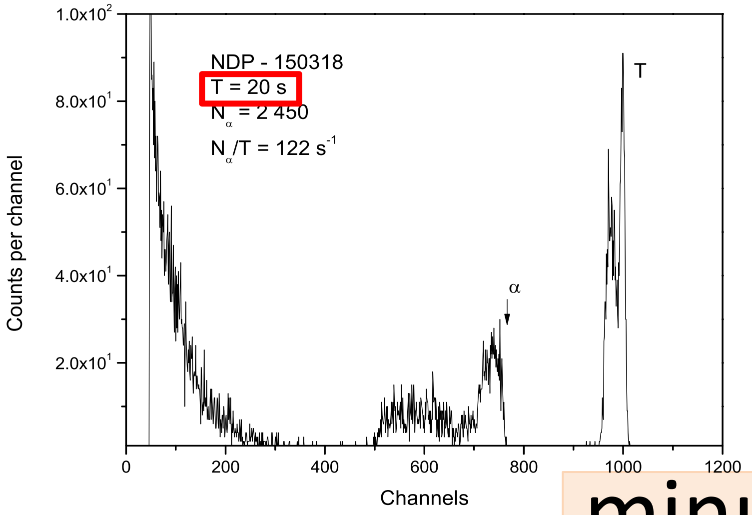
with courtesy of Egor Vezhlev

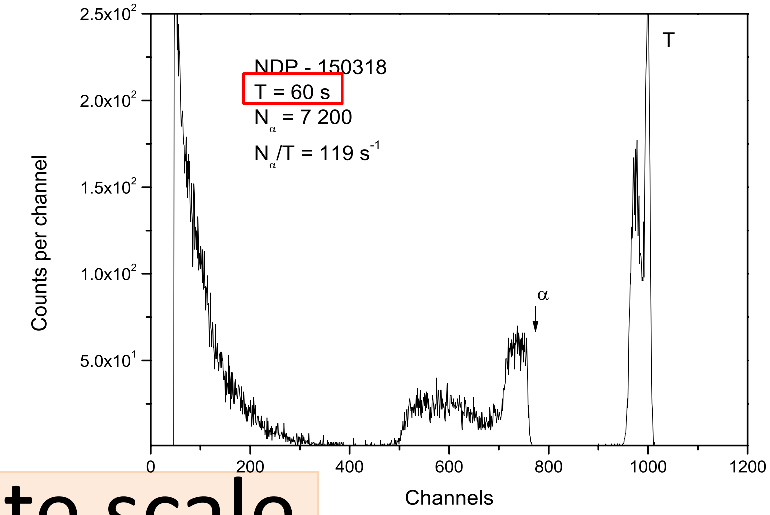
NDP setup at MARIA

In cooperation with:

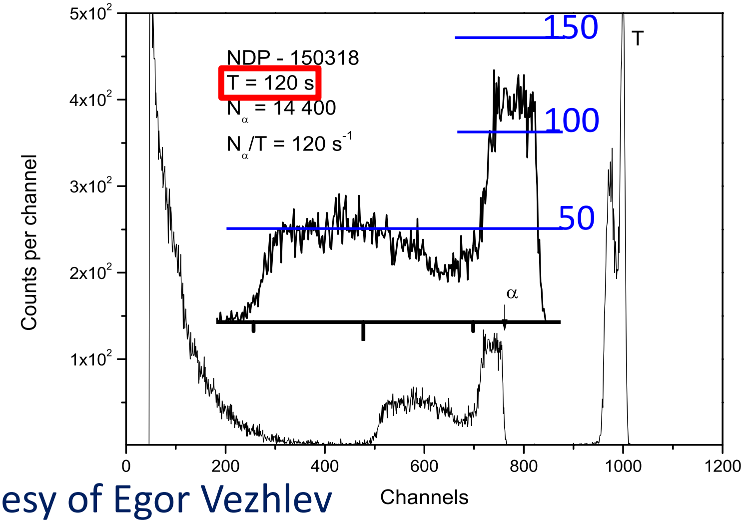
TU Eindhoven, the Netherlands
Peter Notten
Dmitry Danilov
Jie Xie

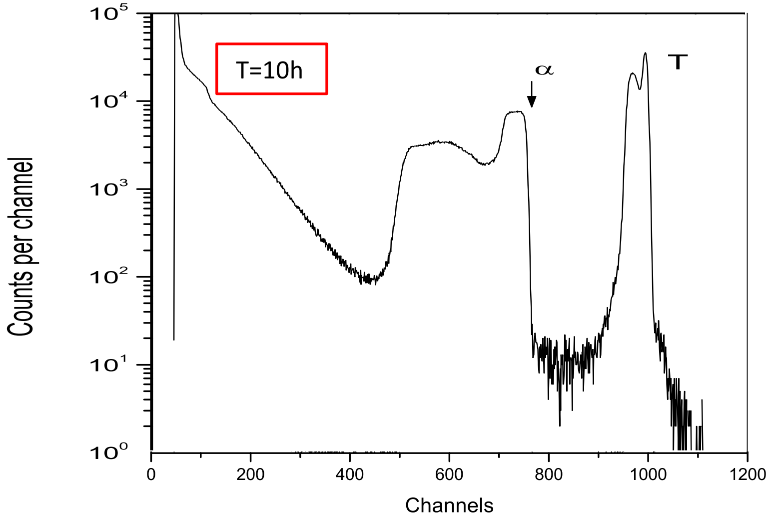
Nuclear Physics Institute, Czech Republic
Jiri Vacik
Vladimir Hnatowicz
Ivo Tomandl





minute scale

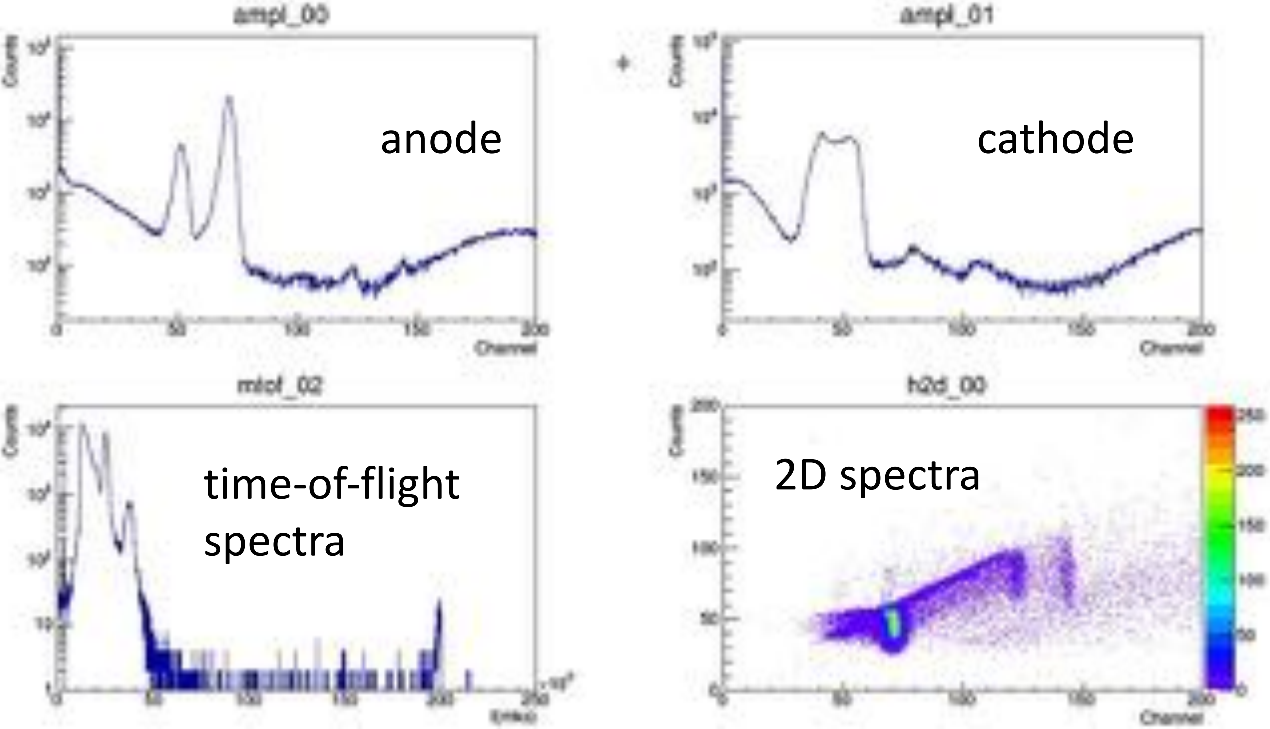




with courtesy of Egor Vezhlev

Isotope-identifying neutron reflectometry on REMUR

Ionization chamber for charge particles registration



Spectra of α-particles and tritons as signal from ^{6}Li
Sample:
Cu(10nm)/V(55nm)/CoFe(5nm)/**LiF(5nm)/**V(15nm)//glass
Grazing angle: 3 mrad

Conclusion Reflectometer SE

V6 (HZB) – CRISP, Inter, Offspec, Polref and Surf (ISIS) - PRISM and HERMES (LLB) - D17 and FIGARO (ILL) - ARMOR (PSI) - NREX+, REFSANS and MARIA (MLZ) - Remur, GRAINS and REFELX (FLNP) – Liquid Reflectometer and Magnetic Reflectometer (ORNL)

Standard SE in the end very similiar for all reflectometers

BUT

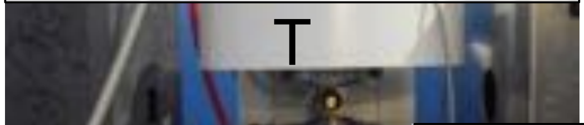
Specialised SE is quite different because individual groups are designing it for a special scientifc case

Thanks to
Jochen Stahn, Mathias Pomm, Thomas Saerbeck,
Wolfgang Kreutzpaintner, Yuri Khaydukov,
Viktor Bodnarchuk, Vladimir Zhaketov, Egor Vezhlev,
Alexandros Koutsioumpas, Amir Syed Mohd

Thank you for your attention!

Sample Environment on MARIA

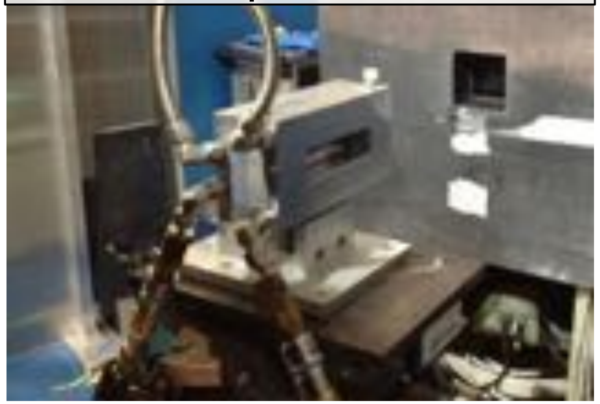
2cm – 2.5K – 1.2 T



2” - 4K – 0.75T

0.8cm - 10K – 2T

Liquid cell



0.05K – 5 T - 270°

Before we start with SE

Before we start with SE

Before we start with SE

Before we start with SE

Before we start with SE