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Laboratory for Neutron Scattering and Imaging

seminar *Neutrons for Science and Industry*

TU Munich, 07.05.2018

# Electrochemistry & Reflectometry

**In-situ investigation of charging**

- in batteries and
- for magnetic switching

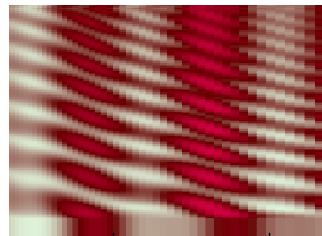
## reflectometry



- in general
- focusing
- Amor

## charging of batteries

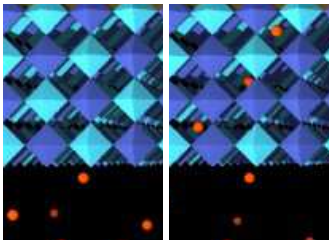
**H. Schmidt, TU Clausthal**



- principle
- measurements & data analysis
- outlook

## magnetic switching by electrochemical doping

**G. Bimashofer, PSI**



- motivation / principle
- state of the work
- outlook

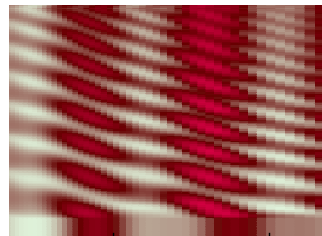
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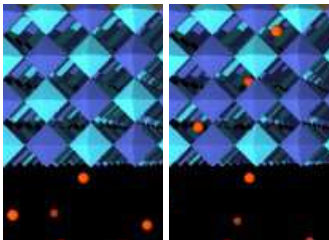
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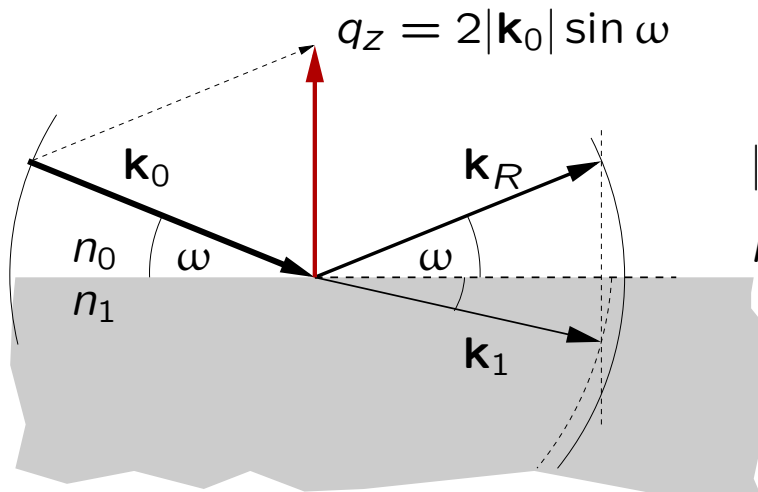


## analogy to visible light

flat surfaces partly reflect light  
 → picture of the boot

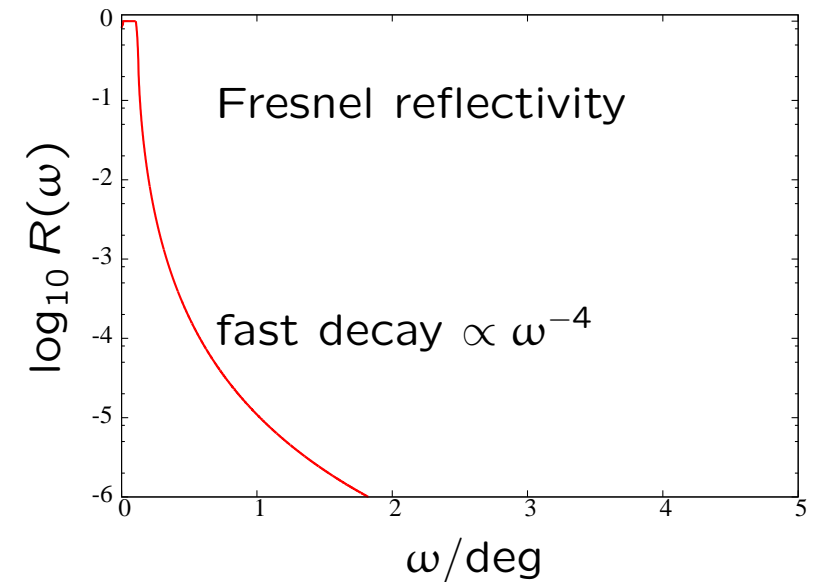
some media also transmit light  
 → ground below the water

parallel interfaces  
 → colourful soap bubbles



$|\mathbf{k}| = 2\pi/\lambda$

$n = \text{index of refraction}$



## reflected intensity of a multilayer

$$R(q_z) \approx |\mathcal{F}[\rho(z)]_{q_z}|^2$$

⇒ all phase information is lost

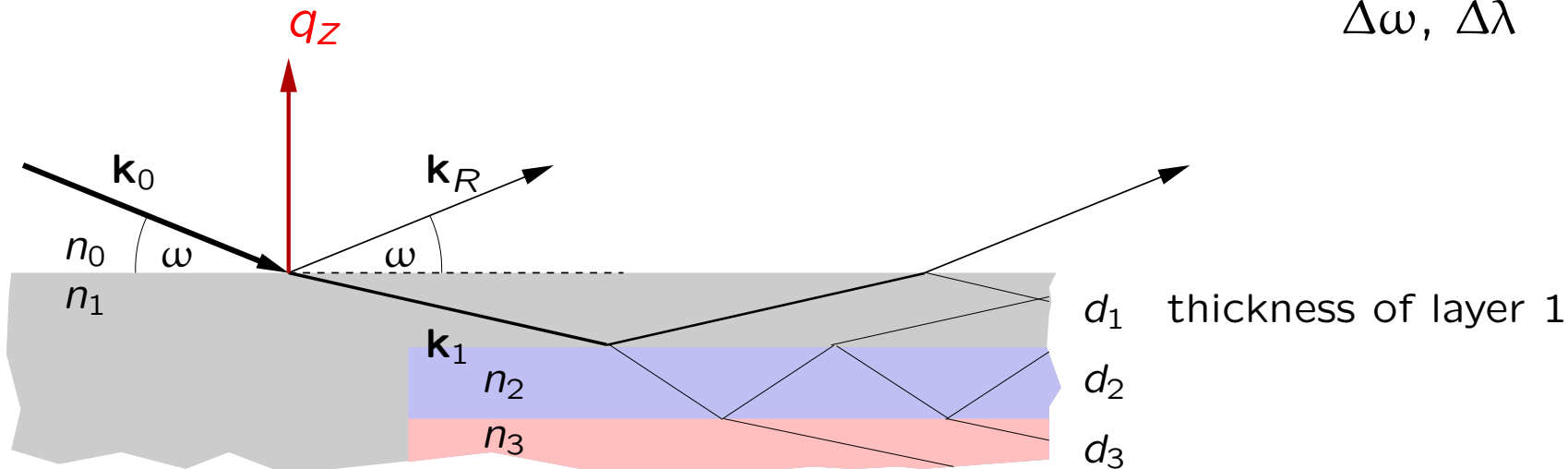
⇒ one way road:

⇒ calculation of  $R(q_z)$  using a model  
and  
comparison to measured curve(s)

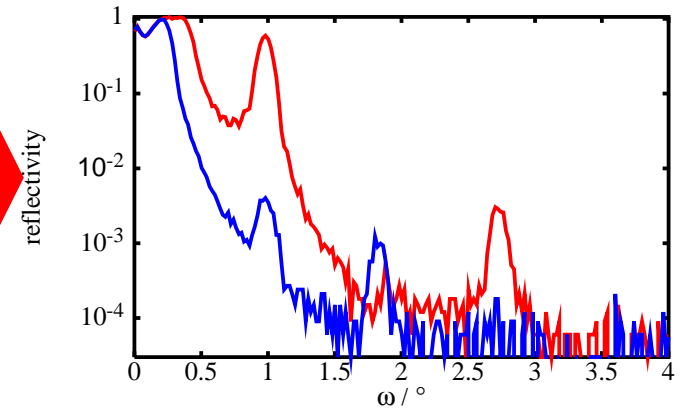
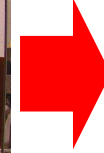
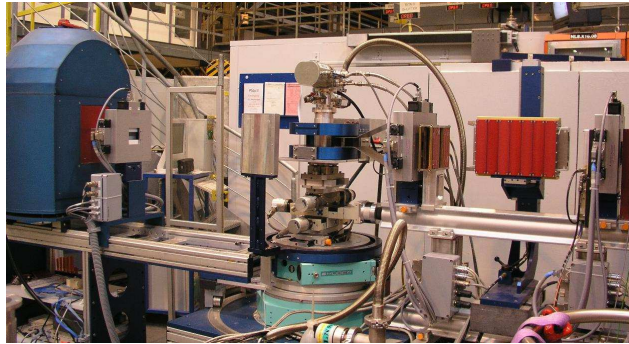
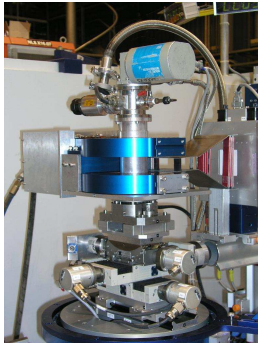
real effects

to be taken into account:

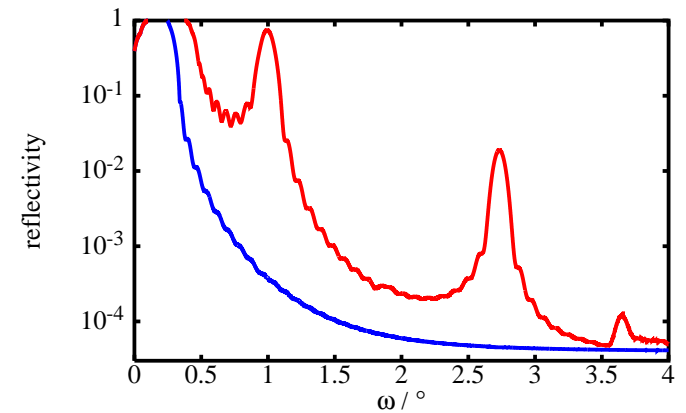
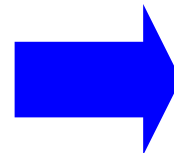
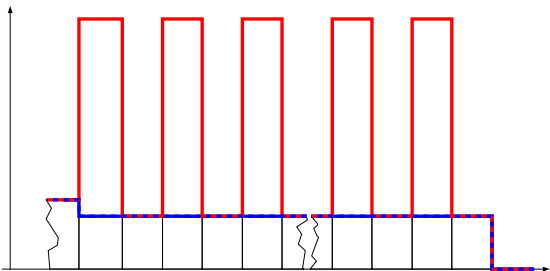
- non-sharp interfaces
- inhomogeneous layers
- illumination of the sample
- resolution of the set-up  
 $\Delta\omega, \Delta\lambda$



## data acquisition and interpretation



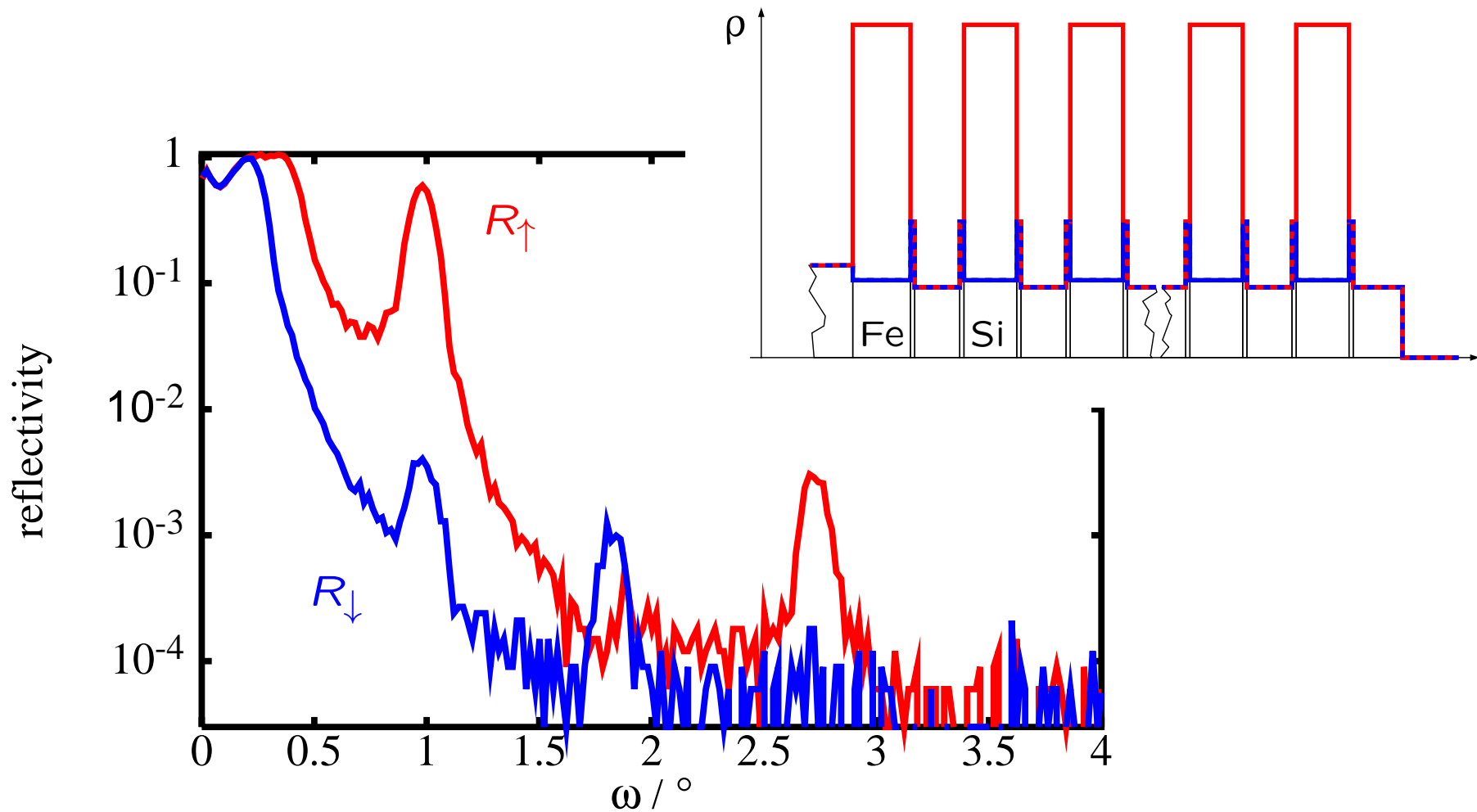
?



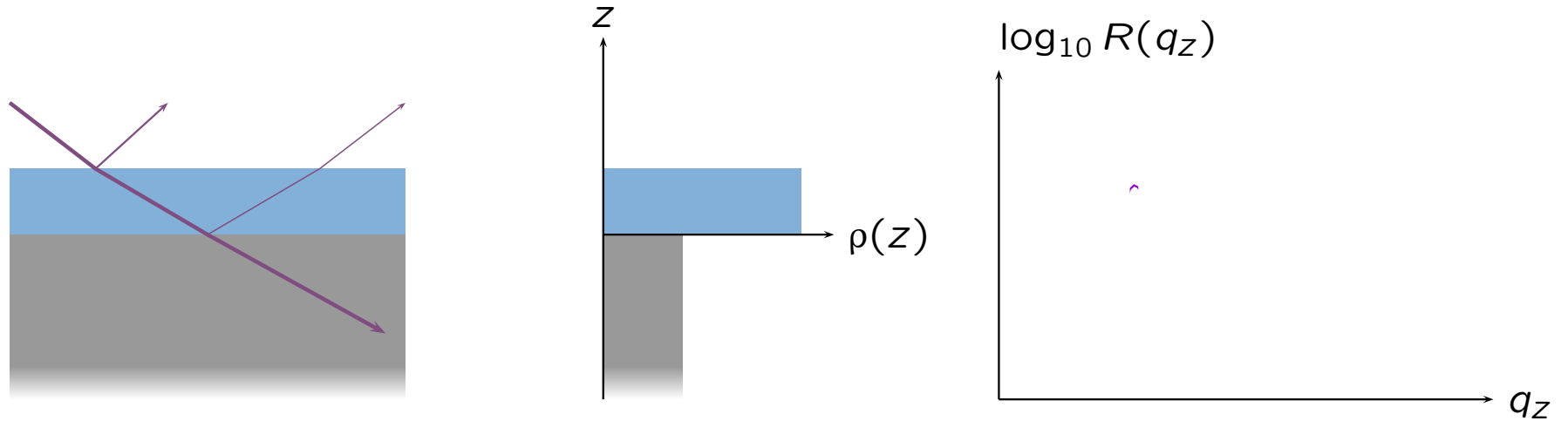
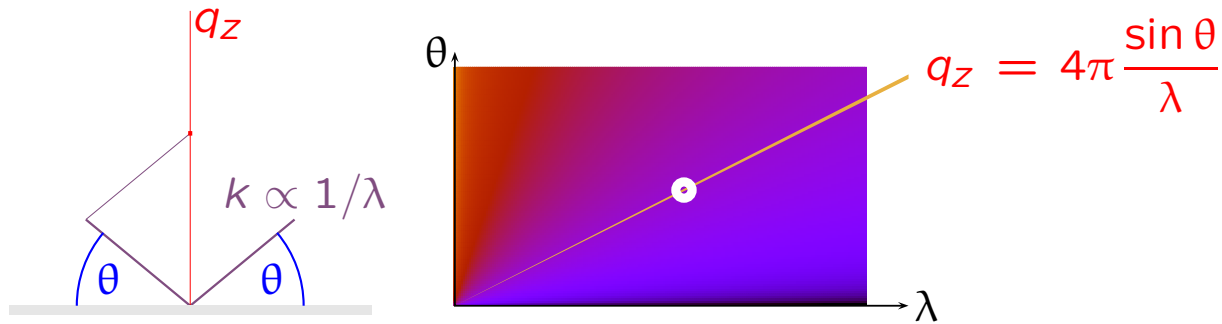
## data acquisition and interpretation

### Fe/Si multilayer

interdiffusion leads to 5 Å thin magnetically dead Fe : Si layers

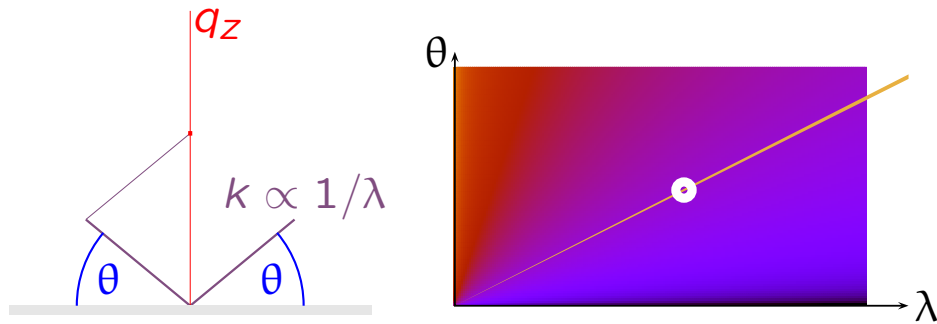


## specular reflectometry

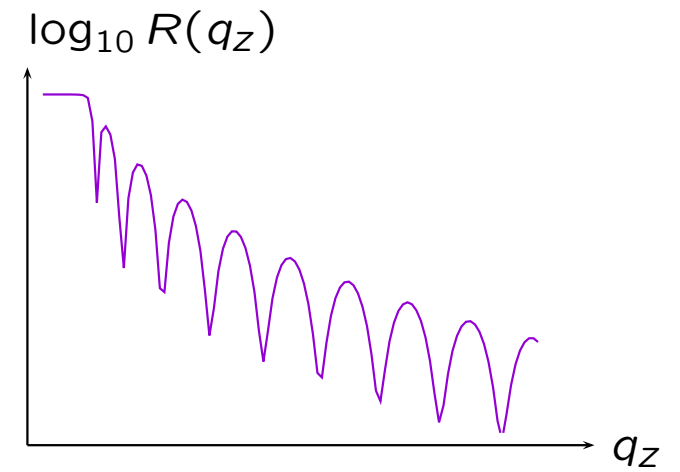
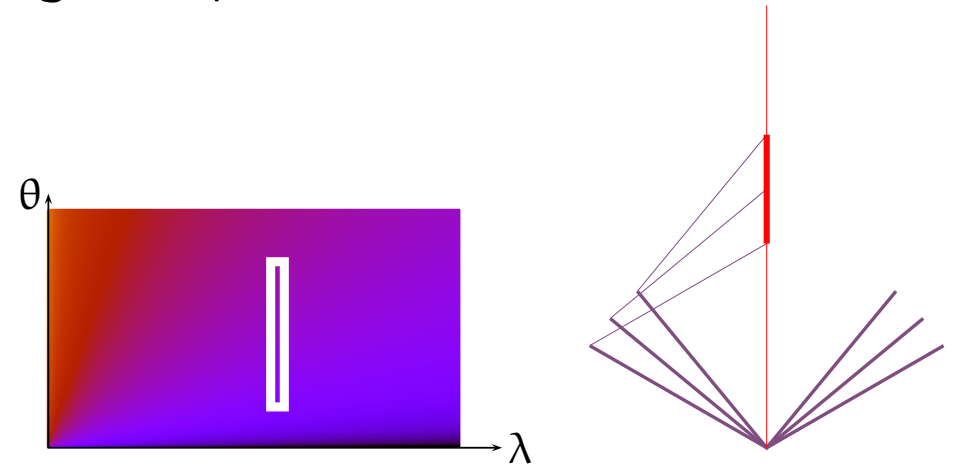




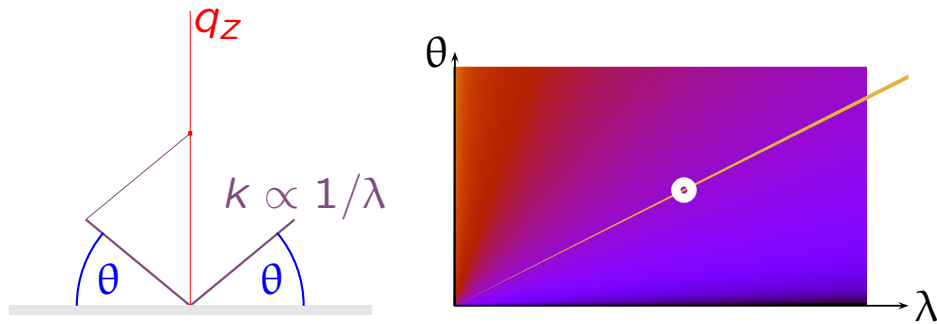
## specular reflectometry



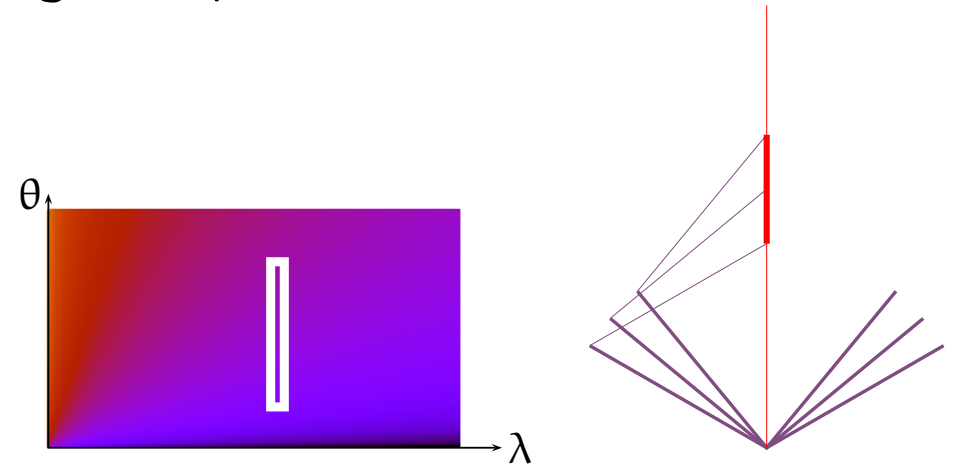
## angle-dispersive



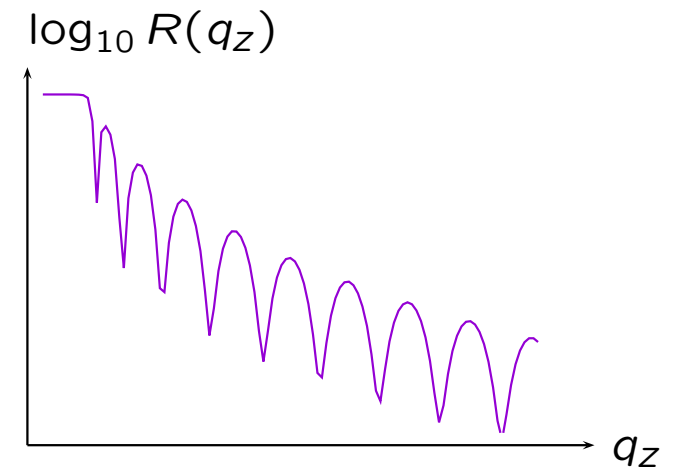
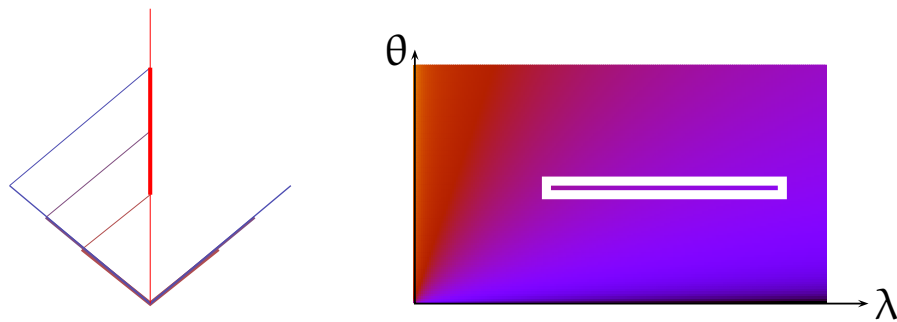
## specular reflectometry



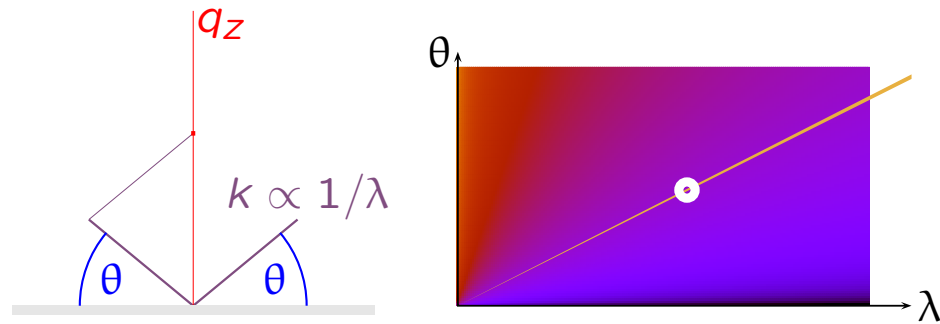
## angle-dispersive



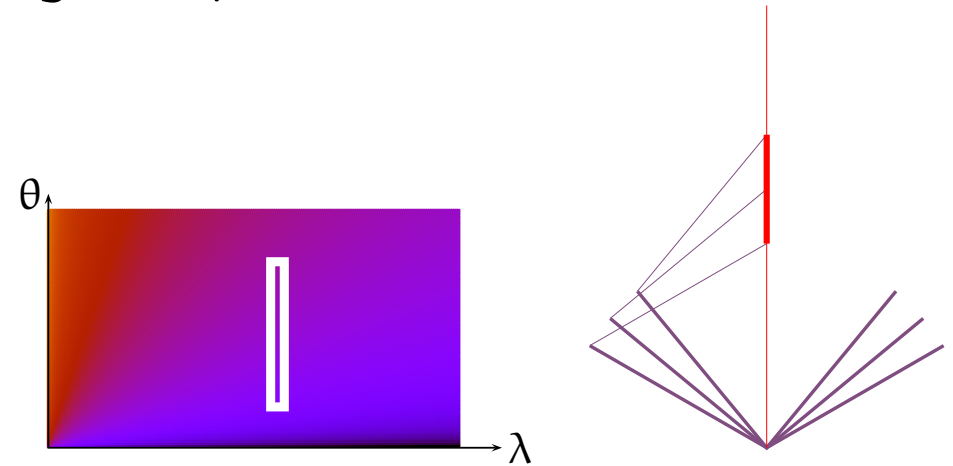
## energy-dispersive



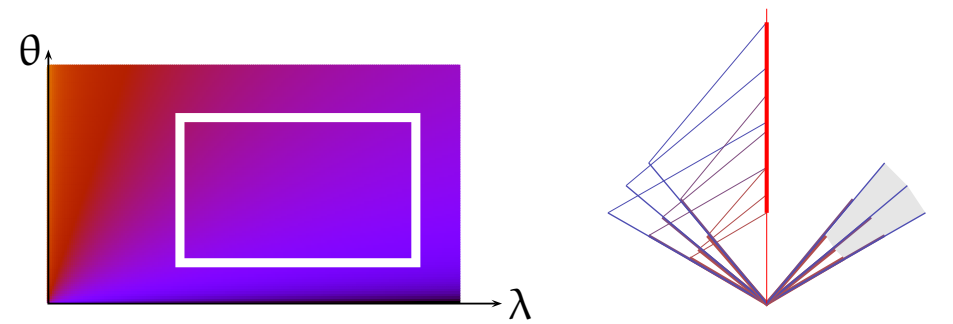
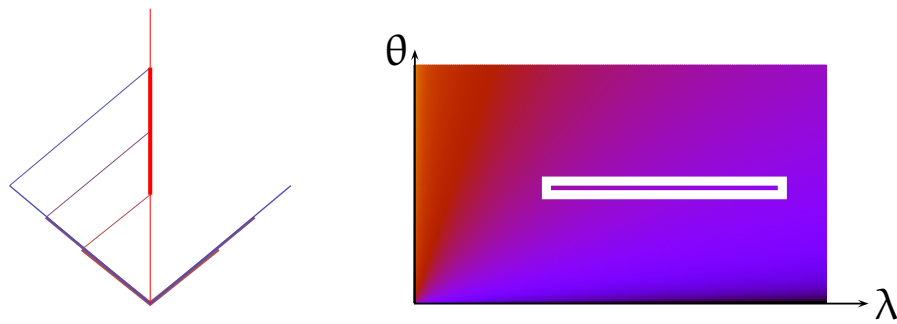
## specular reflectometry



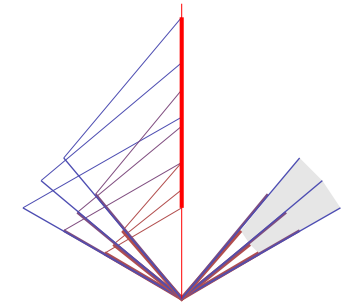
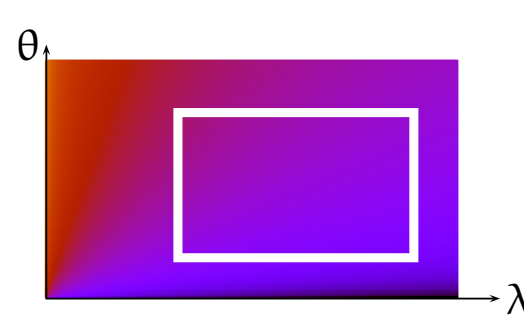
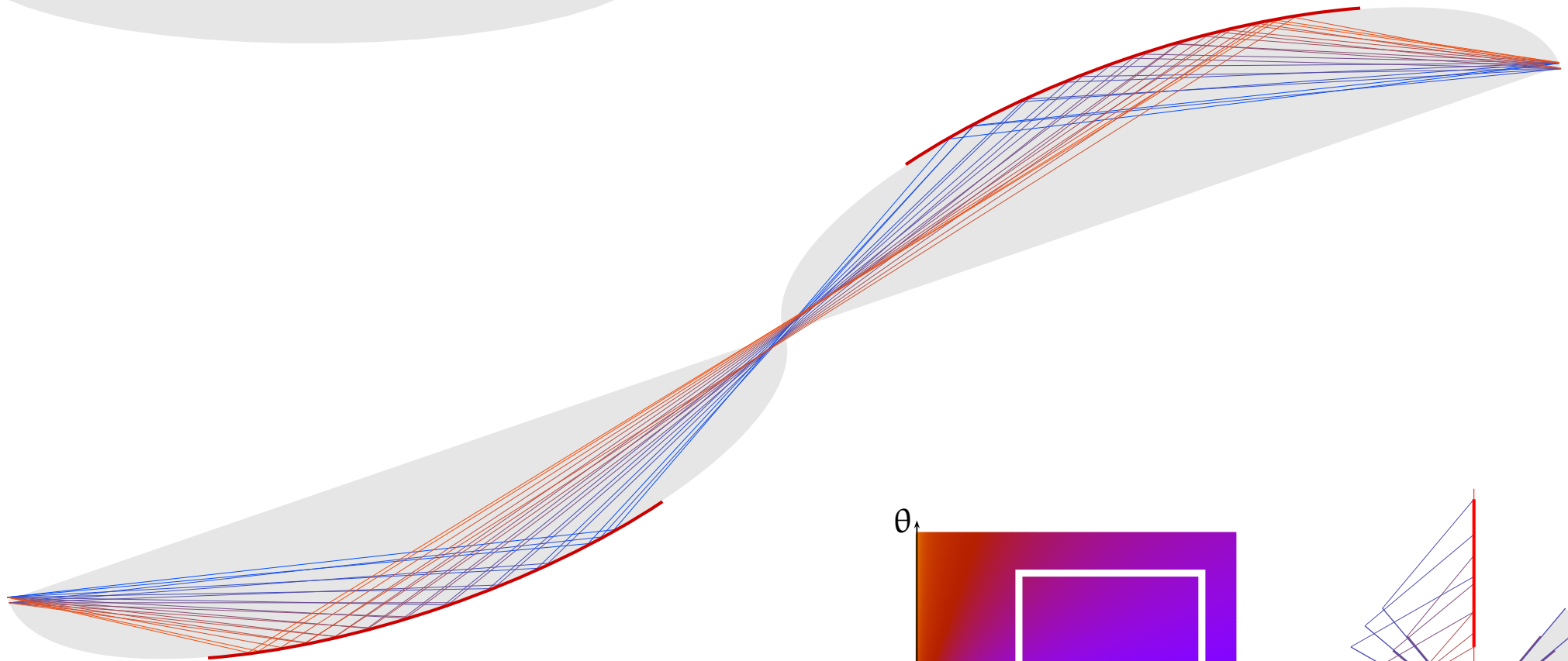
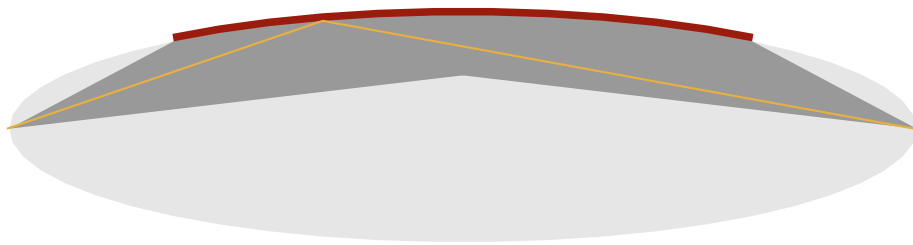
## angle-dispersive



## energy-dispersive



## angle-dispersion by focusing



## the *Selene* guide

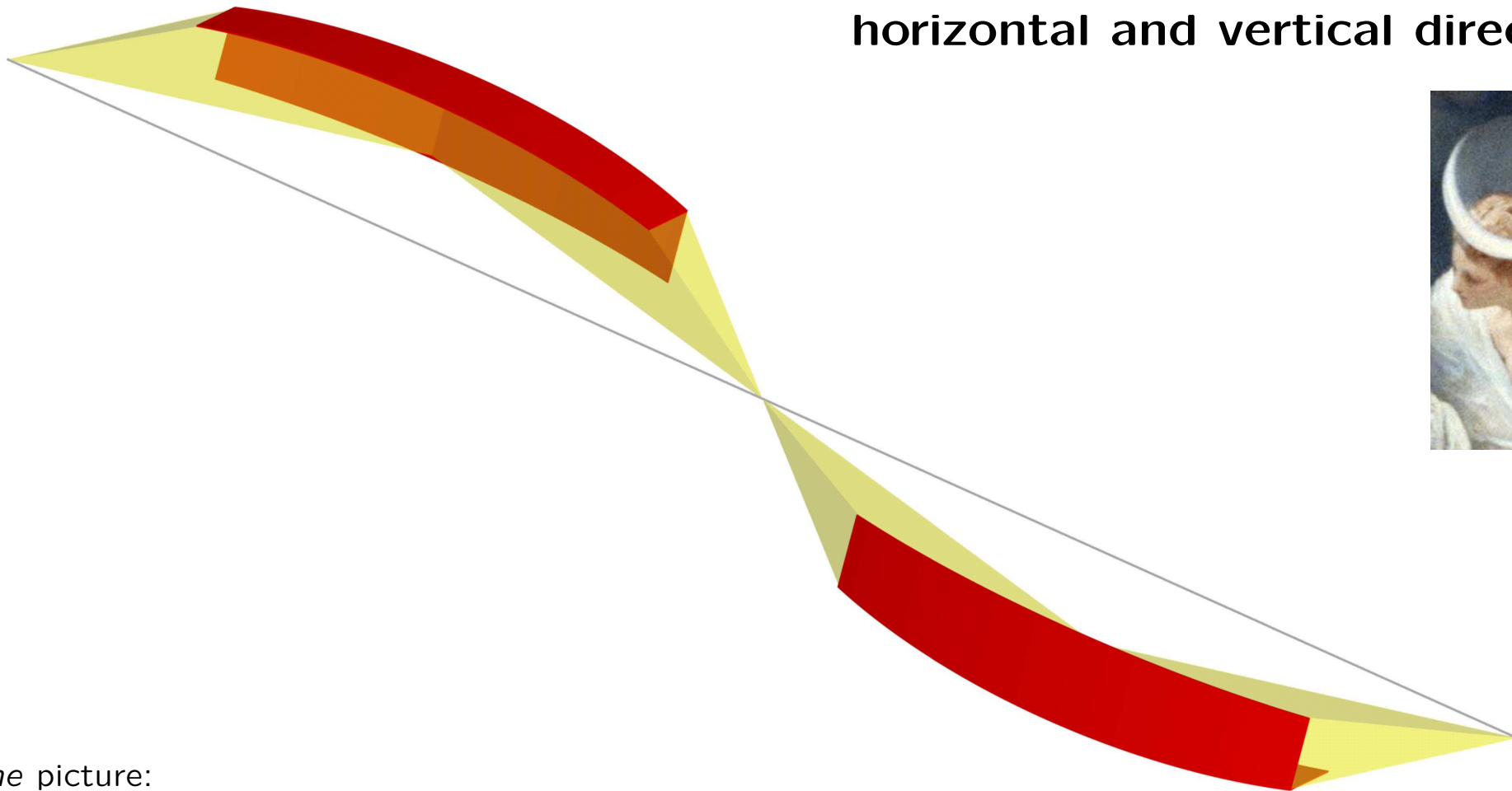
point-to-point focusing

with

2 subsequent elliptical reflectors

for

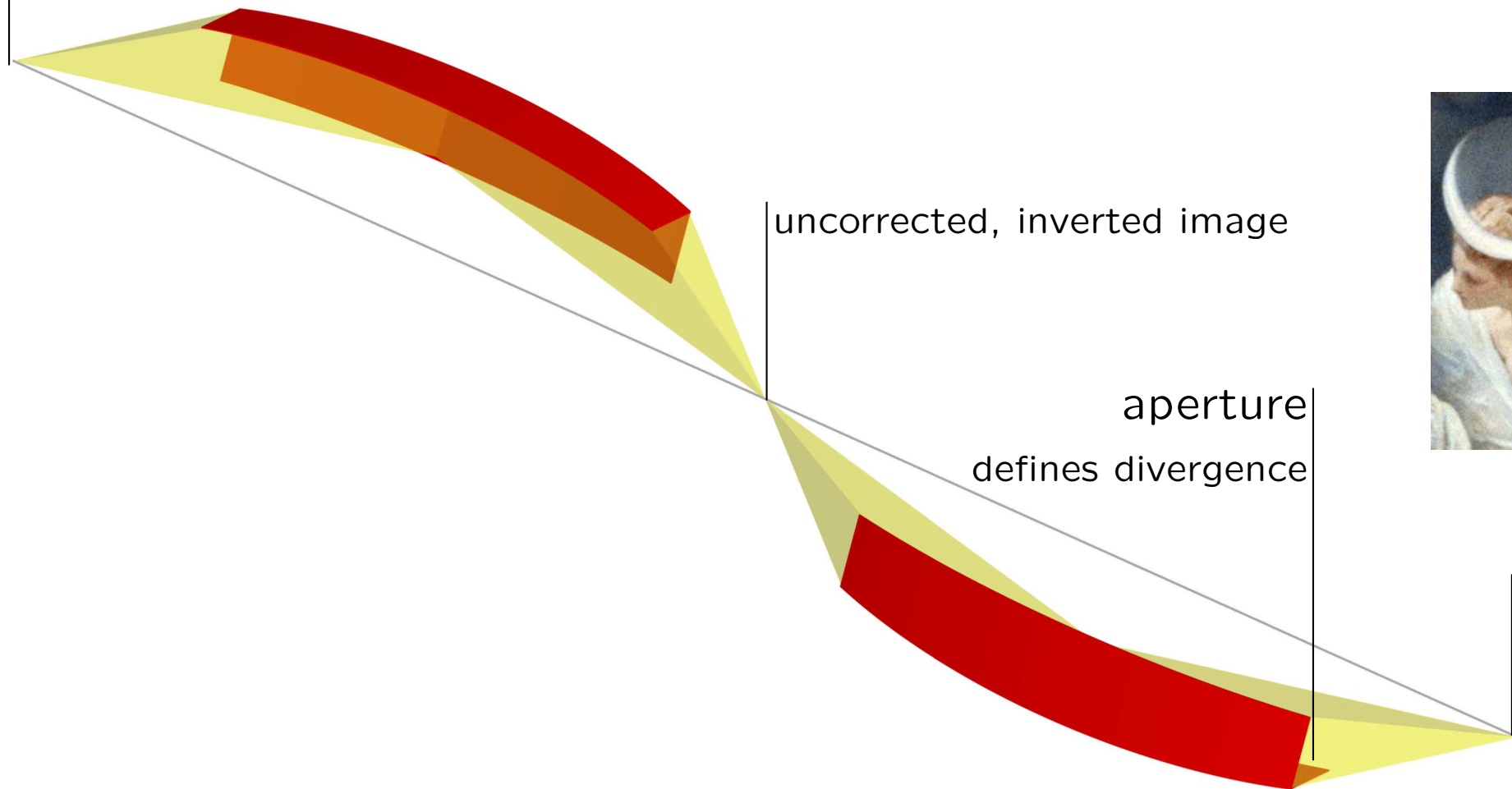
horizontal and vertical direction



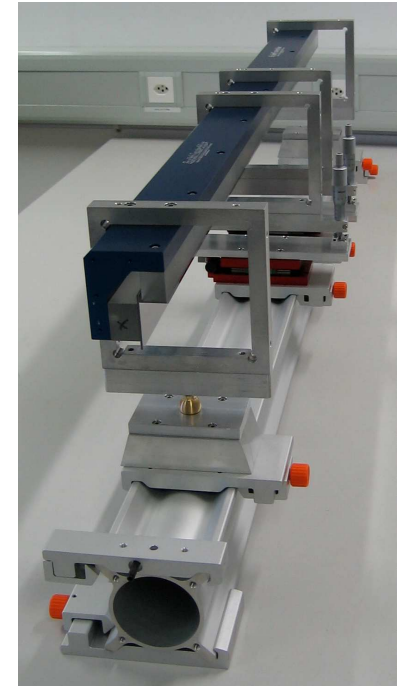
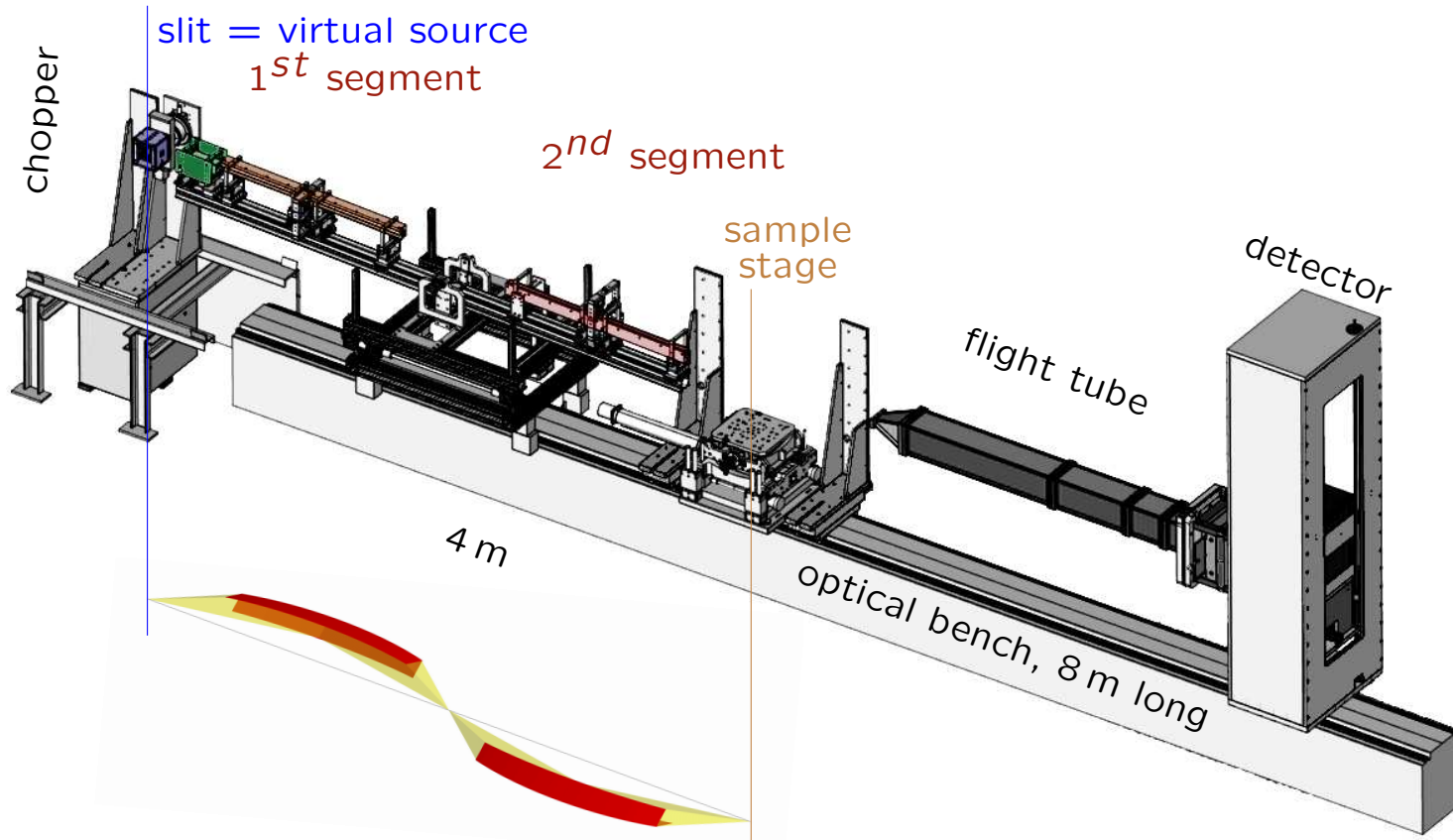
*Selene* picture:  
ceiling painting in the Ny Carlsberg Glyptotek, København

## the *Selene* guide

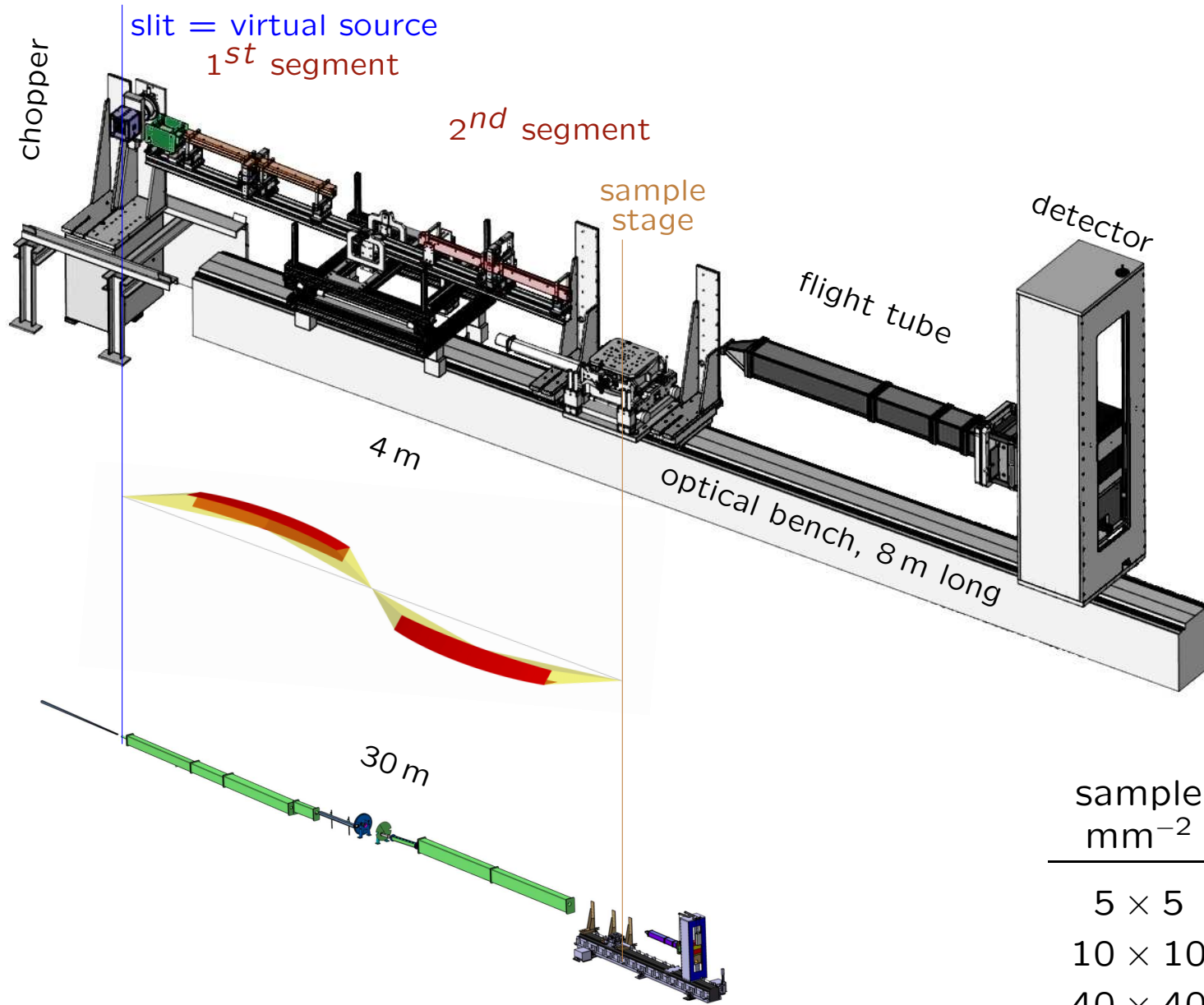
light-field-diaphragm  
control of footprint



# Selene guide demonstrator on Amor@PSI



# Selene guide demonstrator and full-scale implementation on Amor@PSI



sample mm <sup>-2</sup>	gain / old Amor divergent	collimated
5 × 5	20	3
10 × 10	30	5
40 × 40	10	2



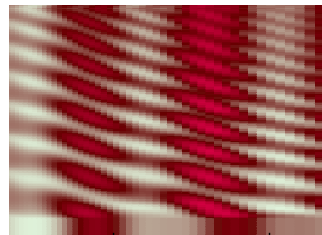
## reflectometry



- in general
- focusing
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## charging of batteries

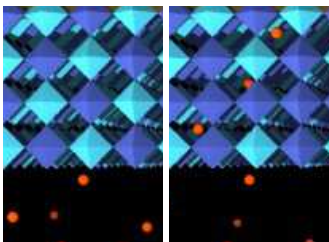
H. Schmidt, TU Clausthal



- principle
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## magnetic switching by electrochemical doping

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- motivation / principle
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## How are the cations distributed in the electrode?

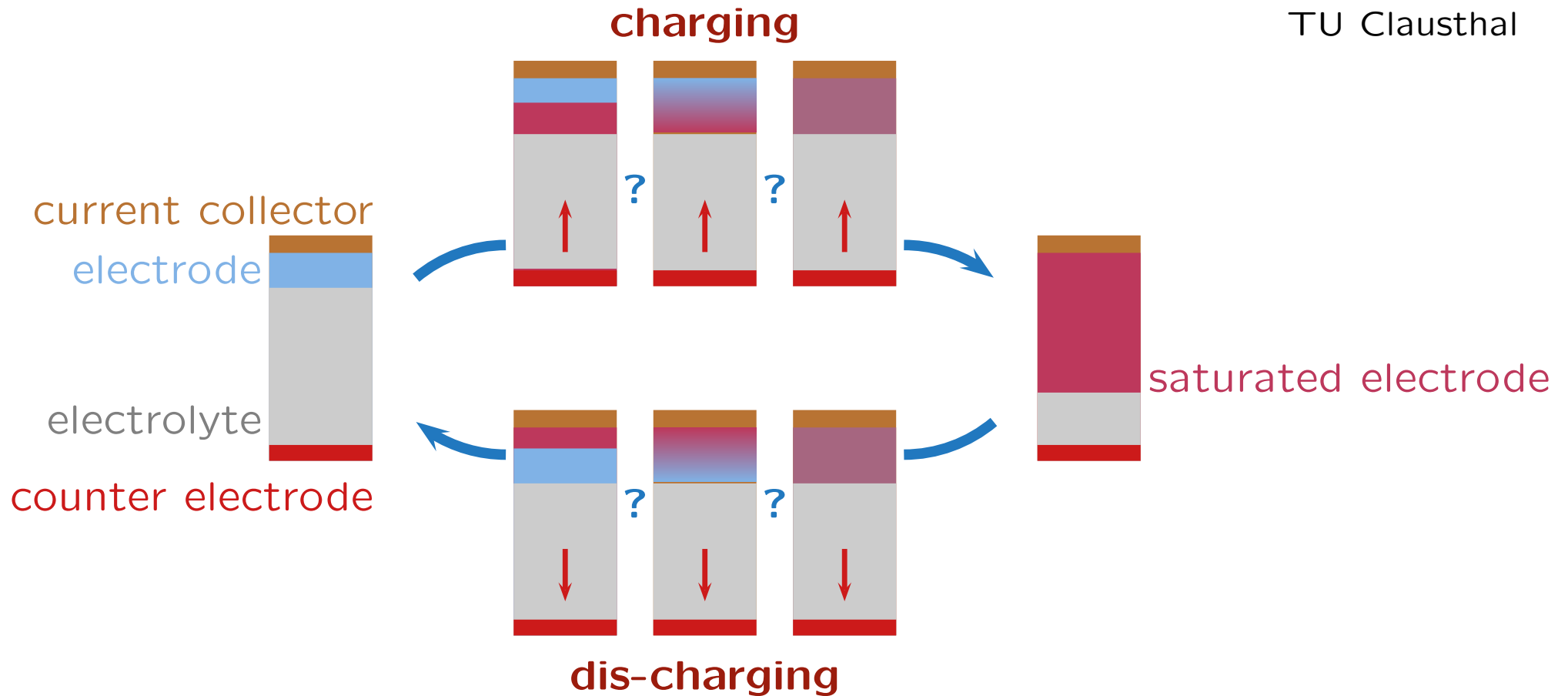
cooperation with

H. Schmidt

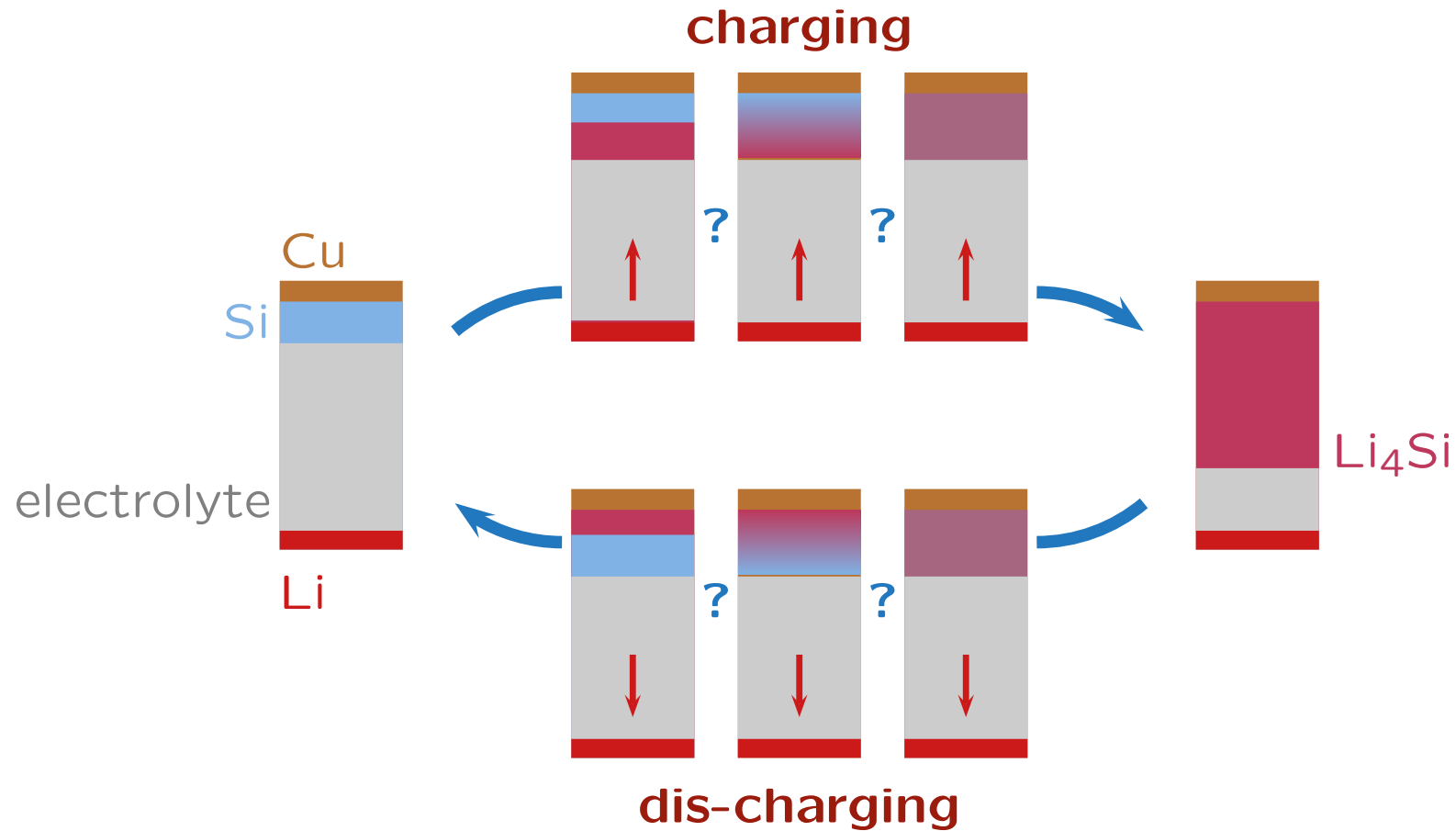
E. Hüger

B. Jerliu

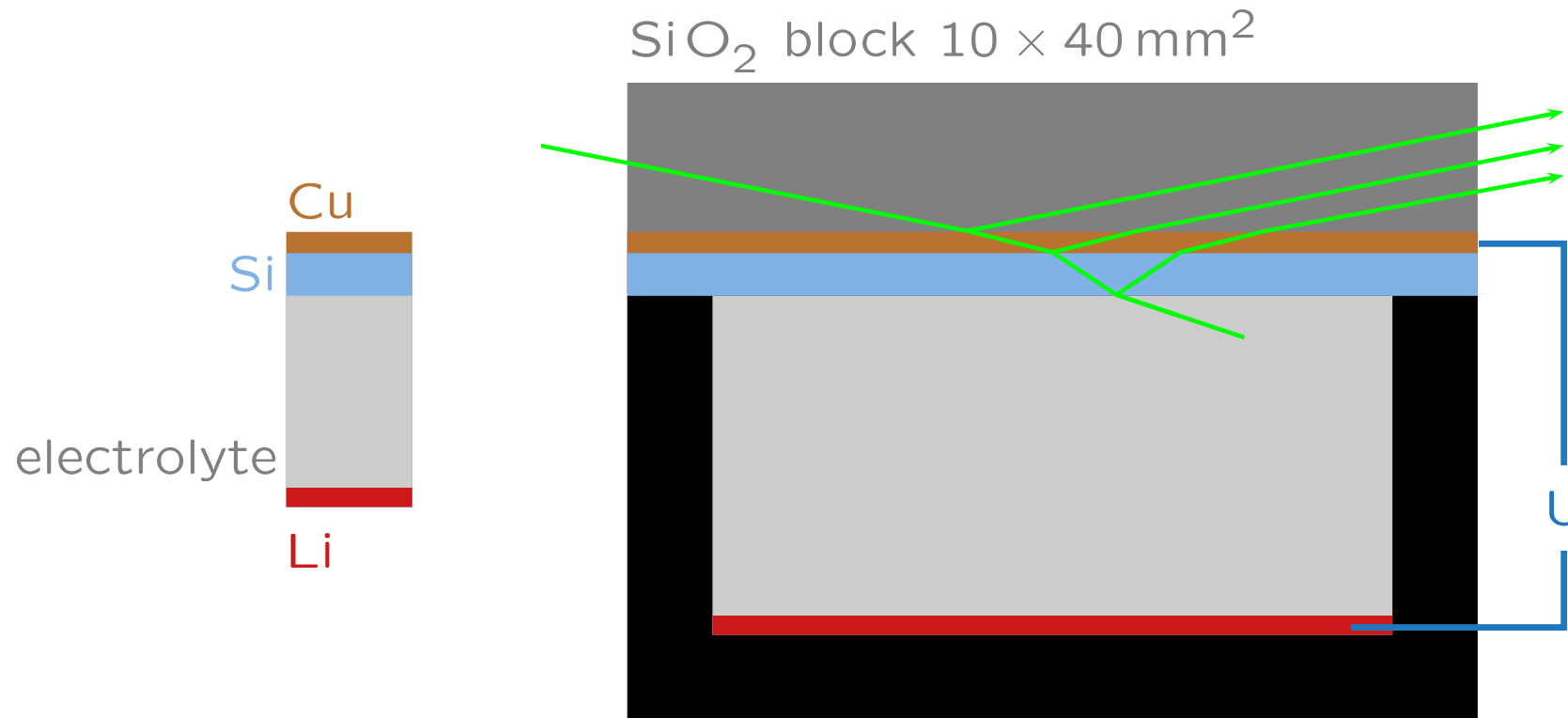
TU Clausthal



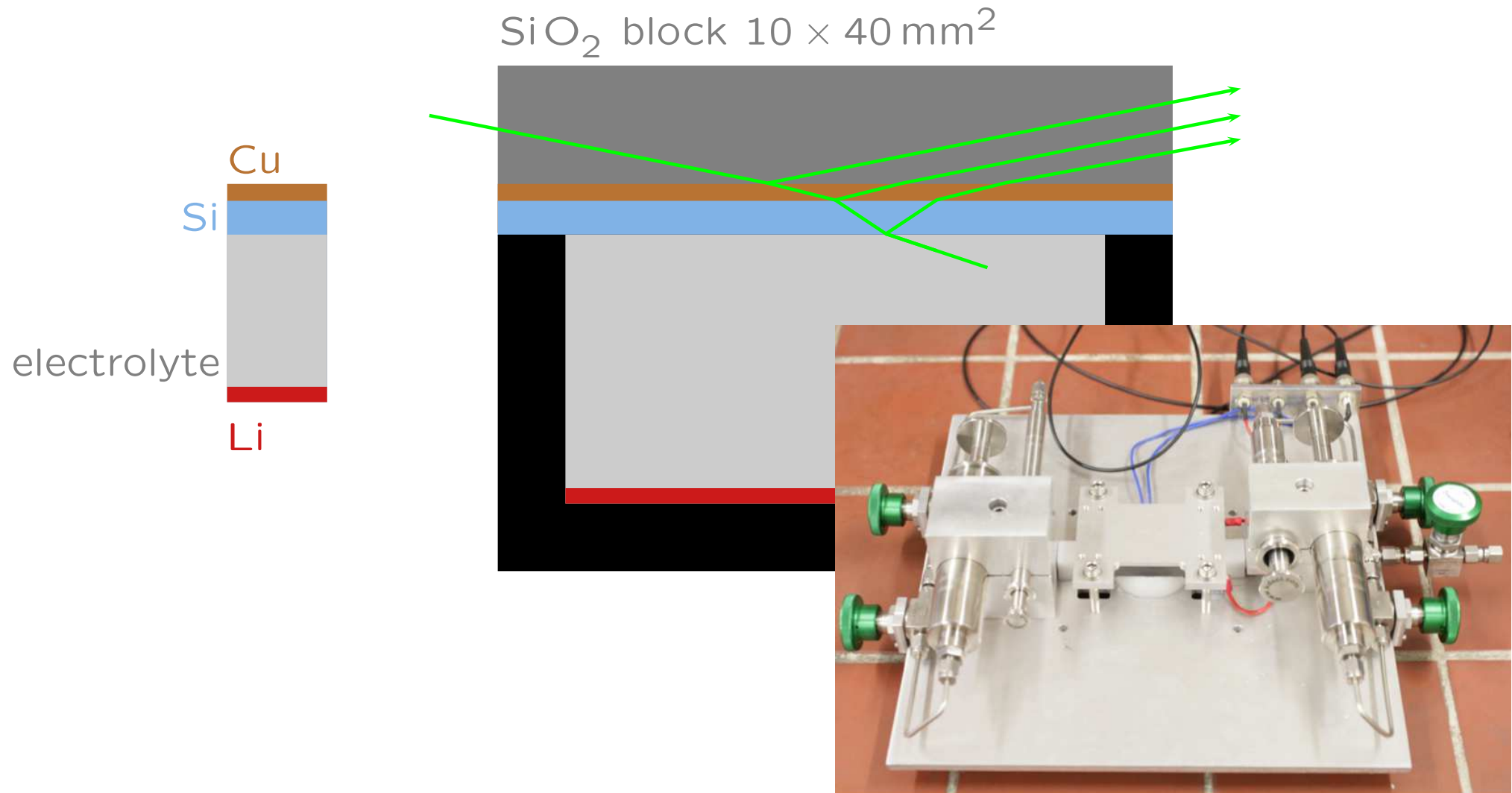
How are the **Li cations** distributed in a Si electrode?



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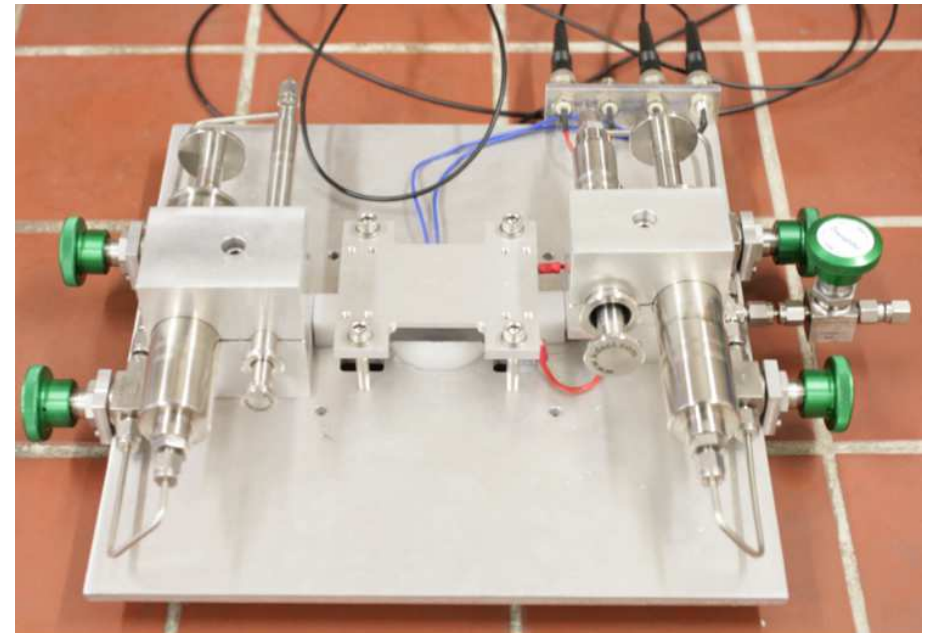
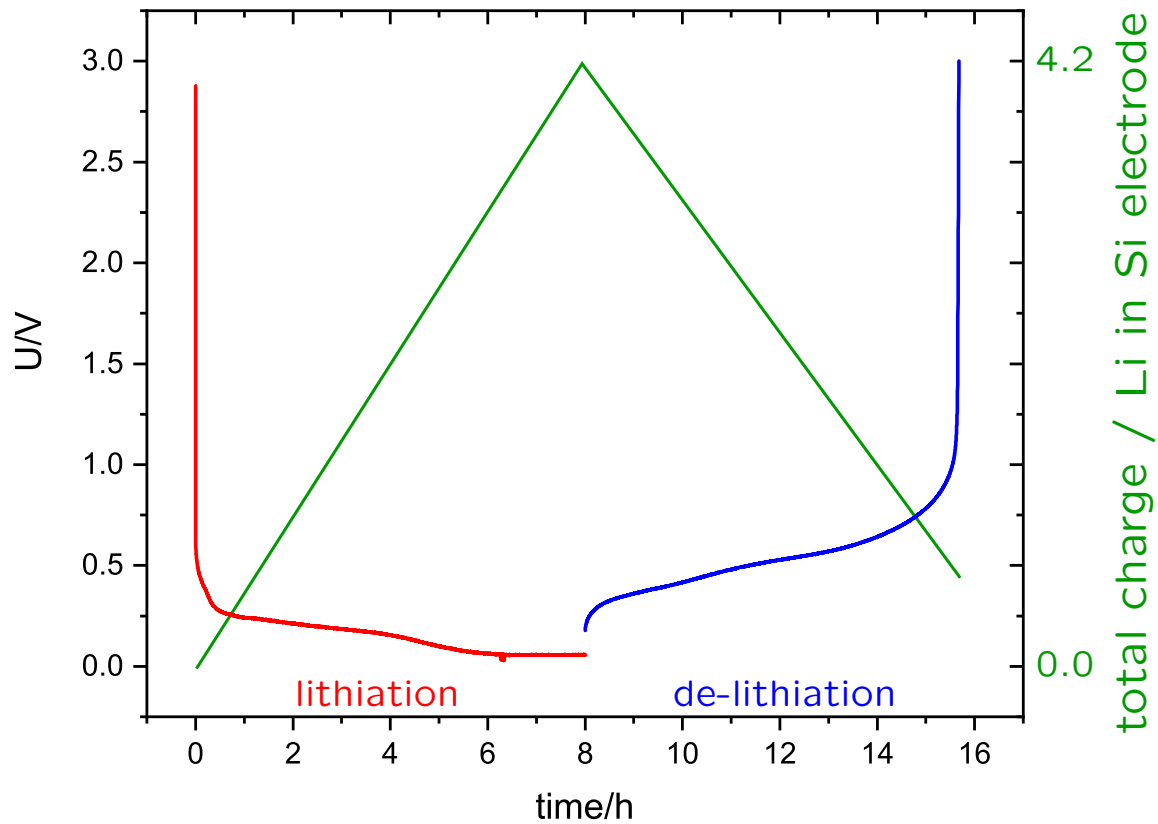
## measurements

electronic part

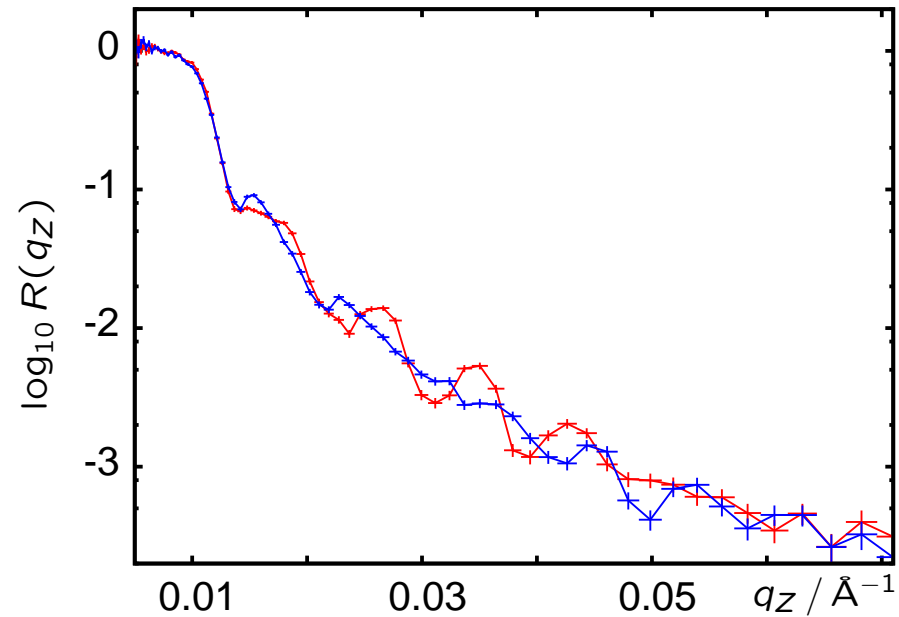
potentiostat / galvanostat

Bio Logic SP50

$U$  and  $Q$  vs. time for 1 cycle



## neutron reflectometry measurements

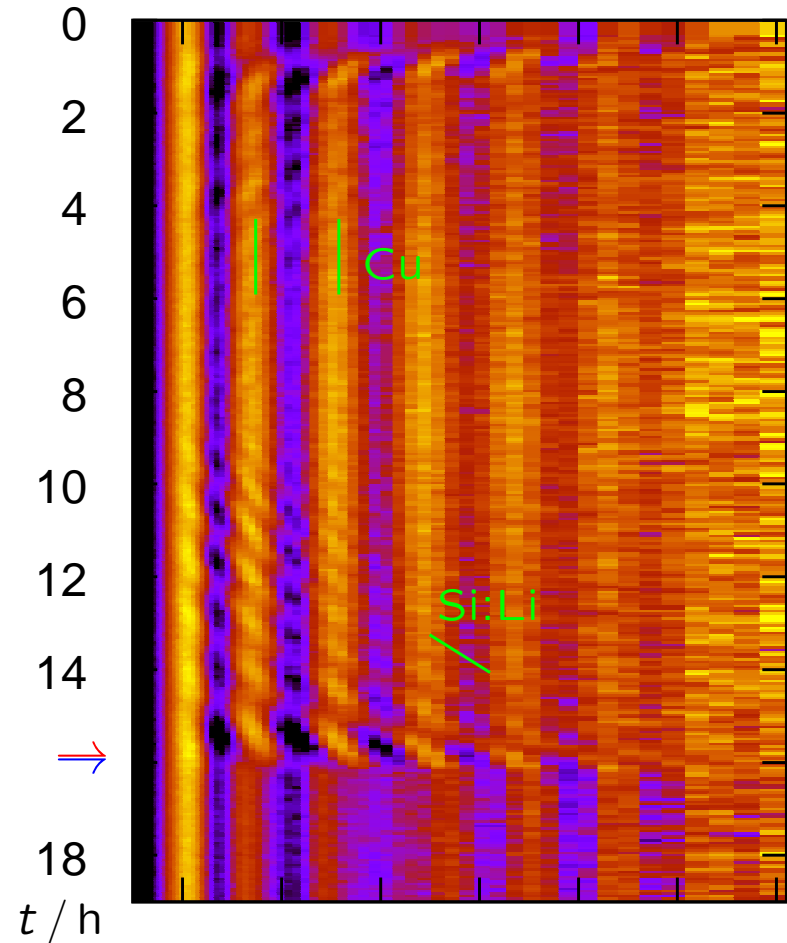


time-resolution: 1 ... 6 min

$\approx$  400 measurements per cycle

$\approx$  4000 measurements per beamtime

$\Rightarrow$  new data analysis strategy required



**Cu contact**  $\Rightarrow$  oscillations

**Si electrode**  $\Rightarrow$  adds phase factor

**Li in Si**  $\Rightarrow$  swelling

$\Rightarrow$  phase shift

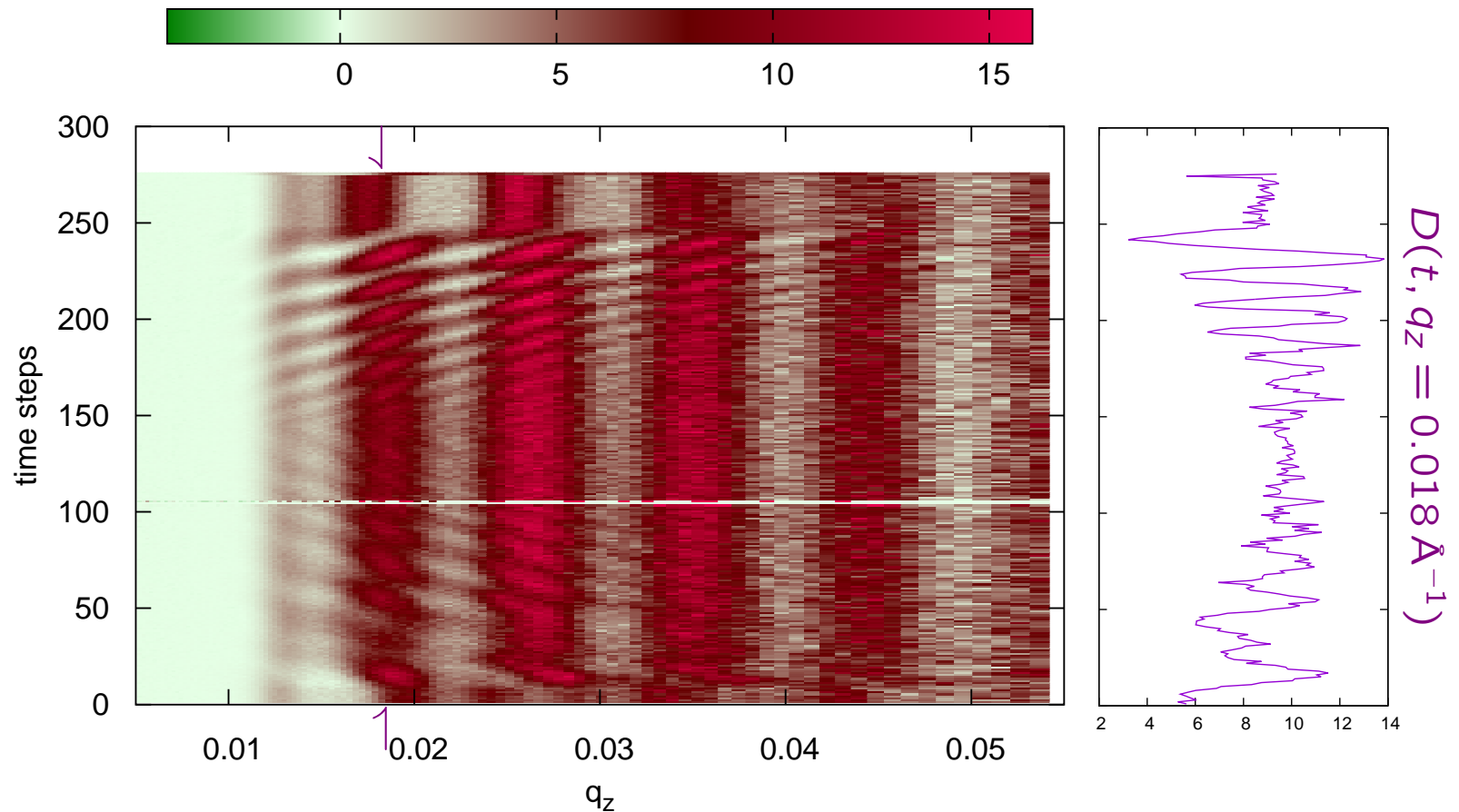
$\Rightarrow$  density change

$\Rightarrow$  contrast variation

## neutron reflectivity measurements

comparison to  $R_{\text{Fresnel}}$   
for better visibility

$$D(t) = \frac{R(t) - R_{\text{Fresnel}}}{R_{\text{Fresnel}}}$$

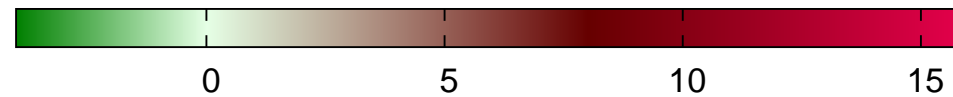




## neutron reflectivity analysis

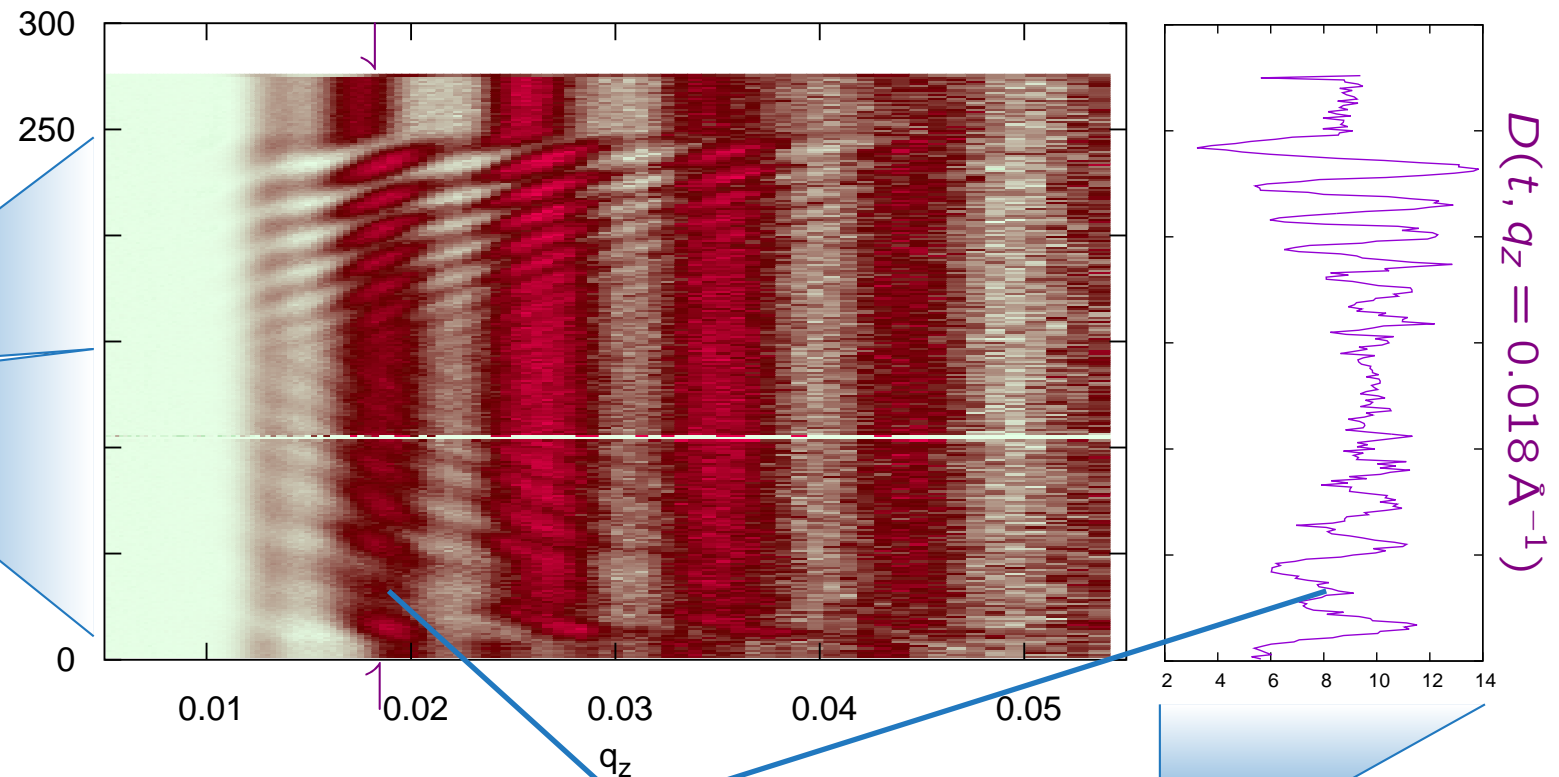
comparison to  $R_{\text{Fresnel}}$   
for better visibility

$$D(t) = \frac{R(t) - R_{\text{Fresnel}}}{R_{\text{Fresnel}}}$$



visible features:

asymetrie  
in time  
in number  
of fringes

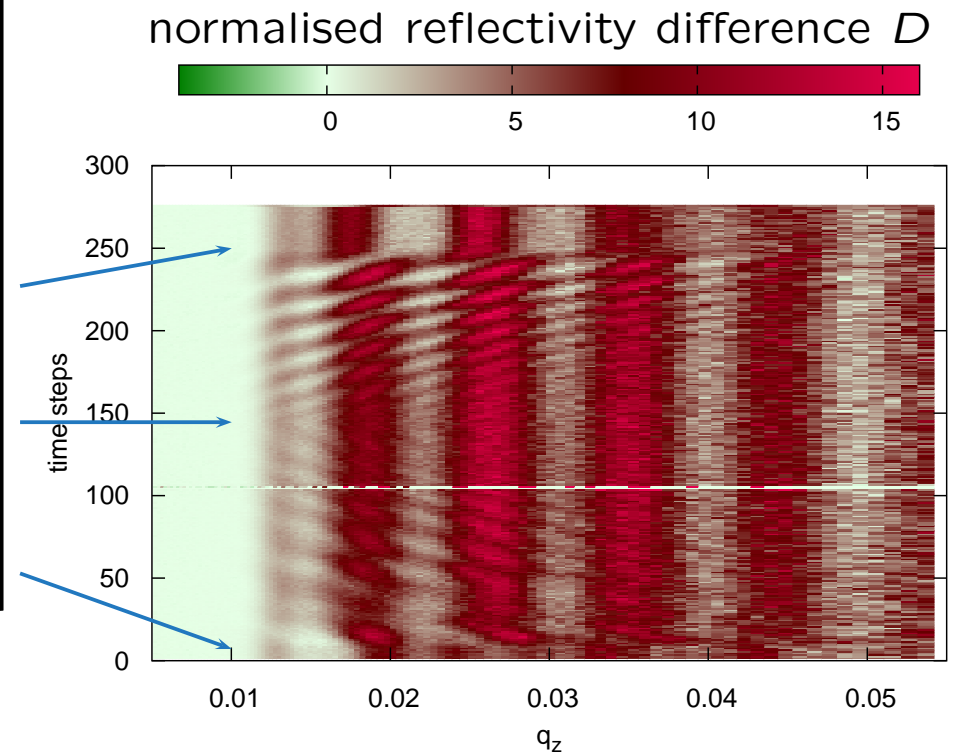
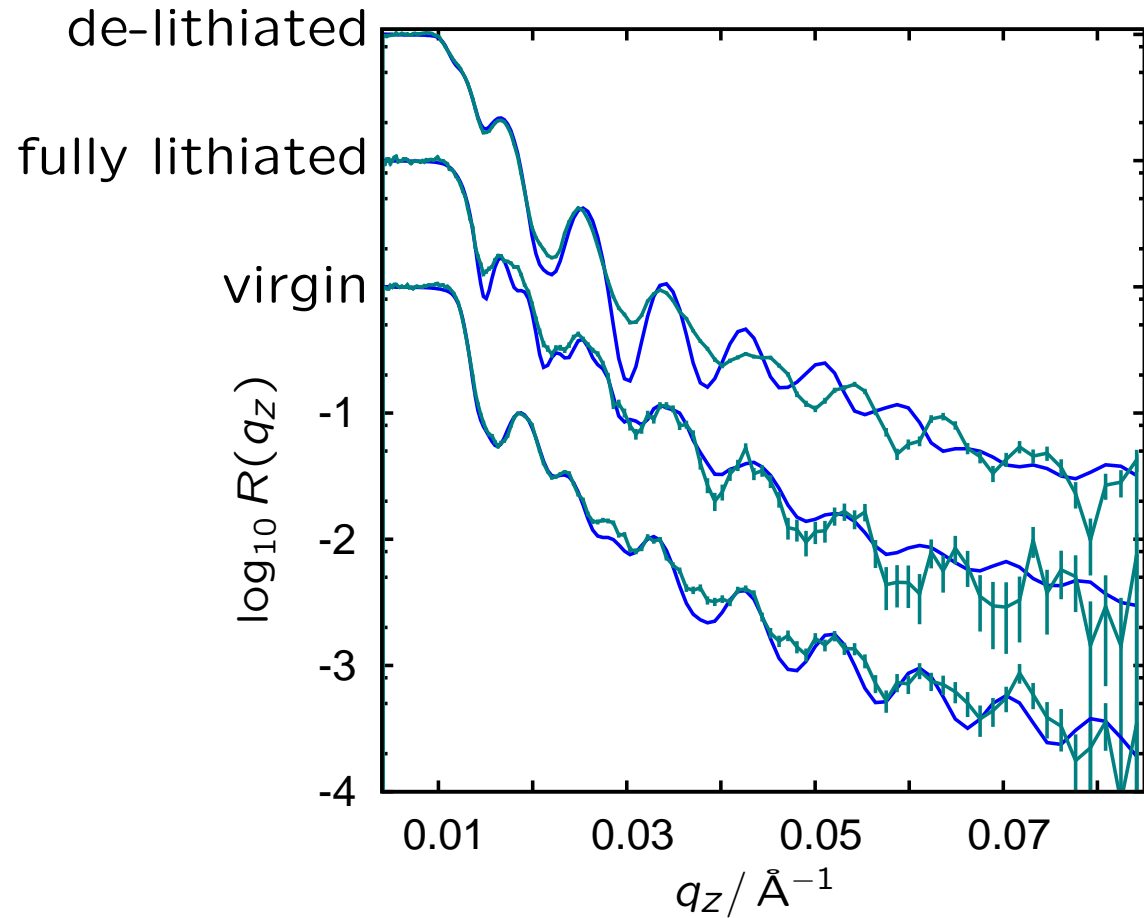


weak fringe

fringes not equidistant

## neutron reflectometry analysis

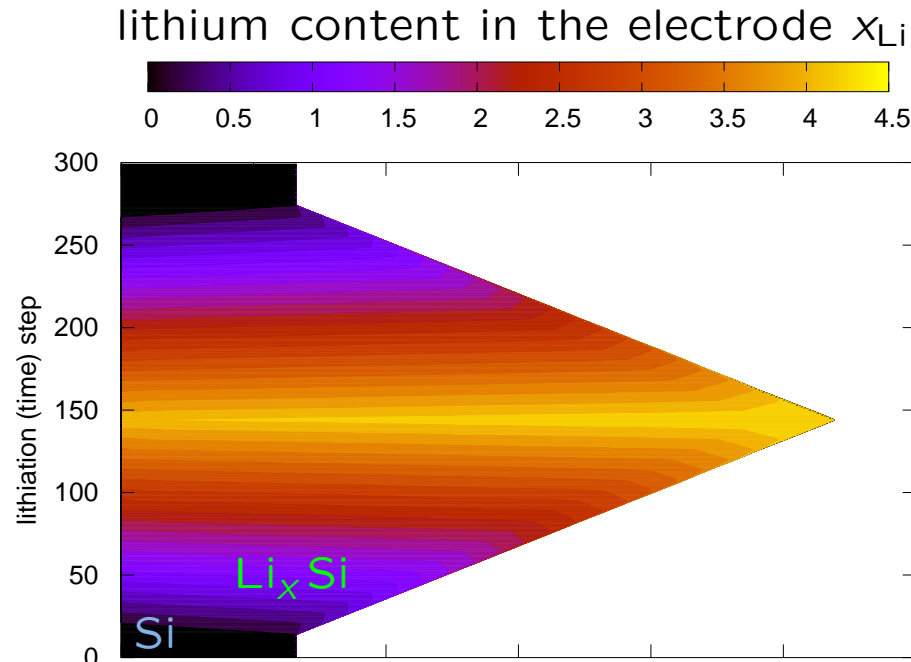
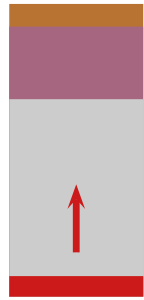
simulation of *pure* states



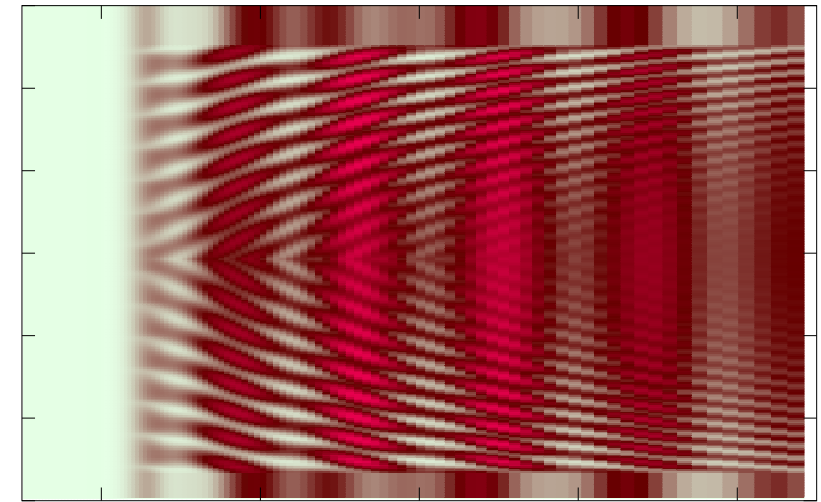
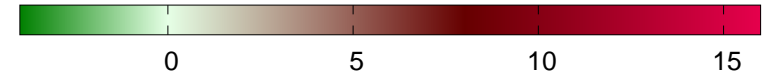
model assumptions for process in-between

## modelling

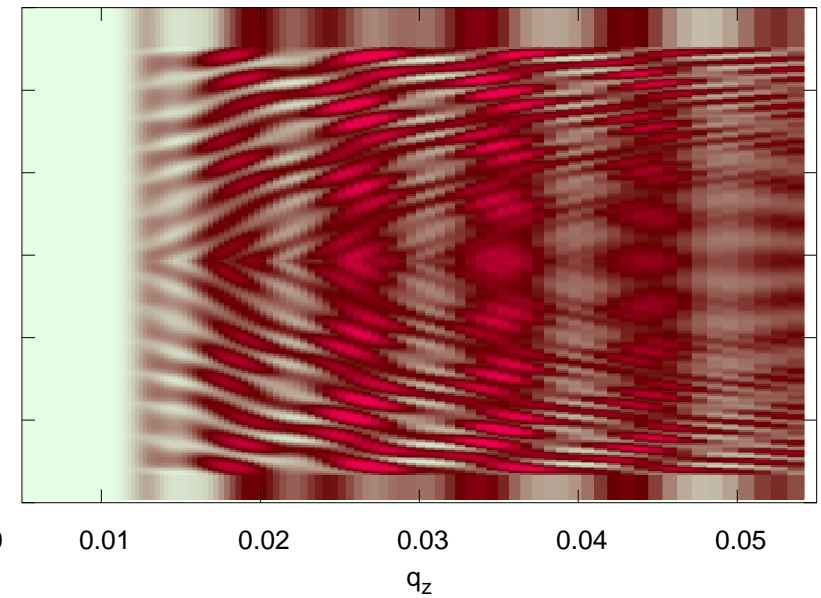
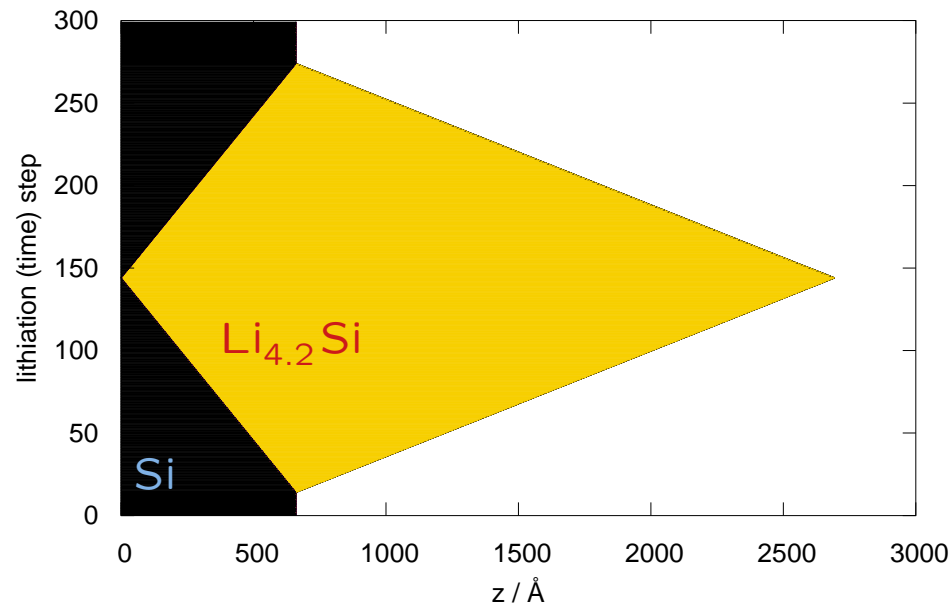
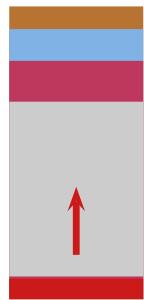
homogeneous



normalised reflectivity difference  $D$



2 phases

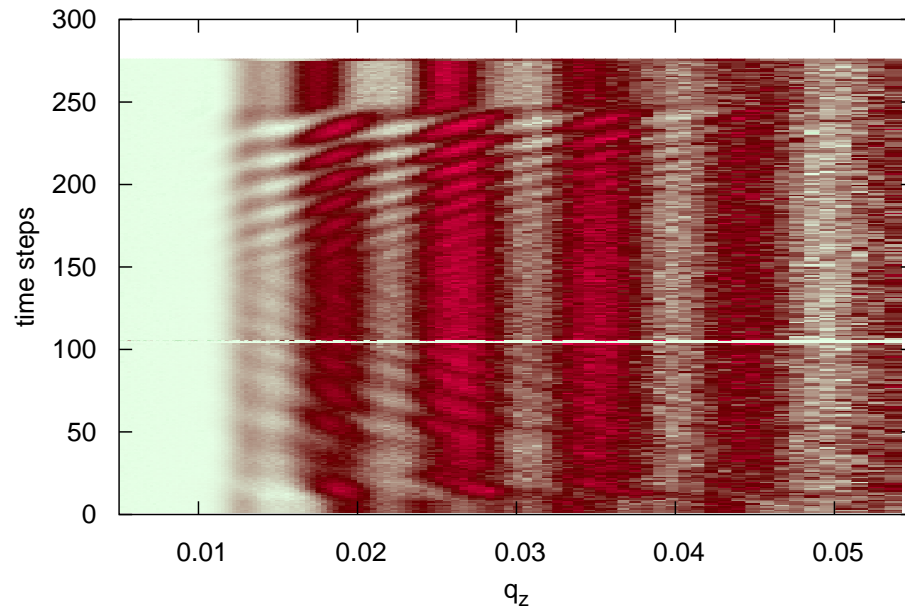
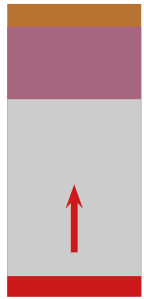


## modelling

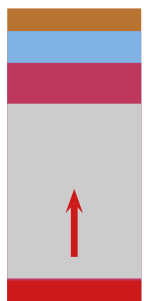
direct comparison

experiment vs. model

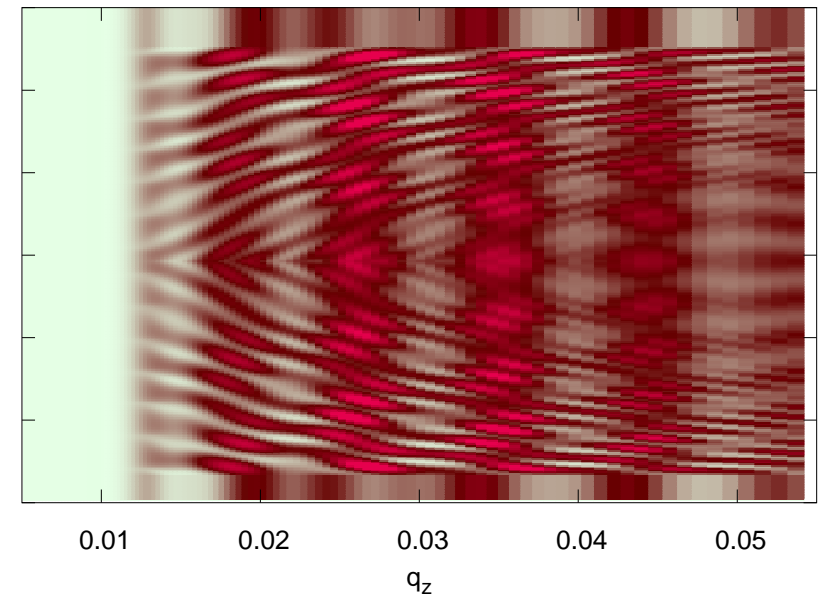
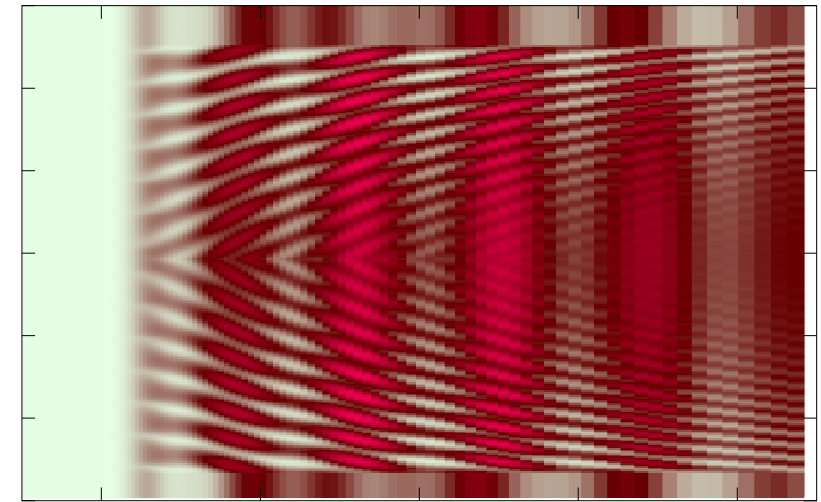
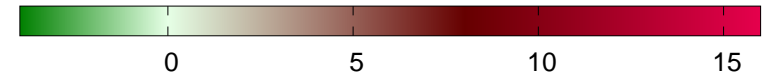
homogeneous



2 phases

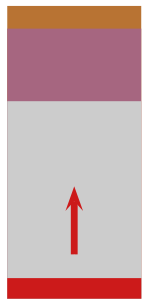


normalised reflectivity difference  $D$

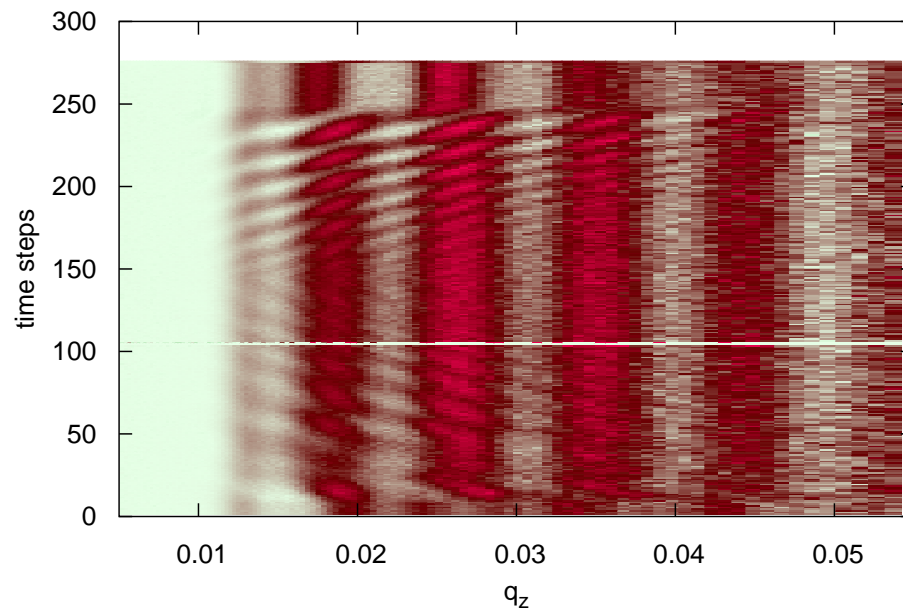


## modelling

homogeneous

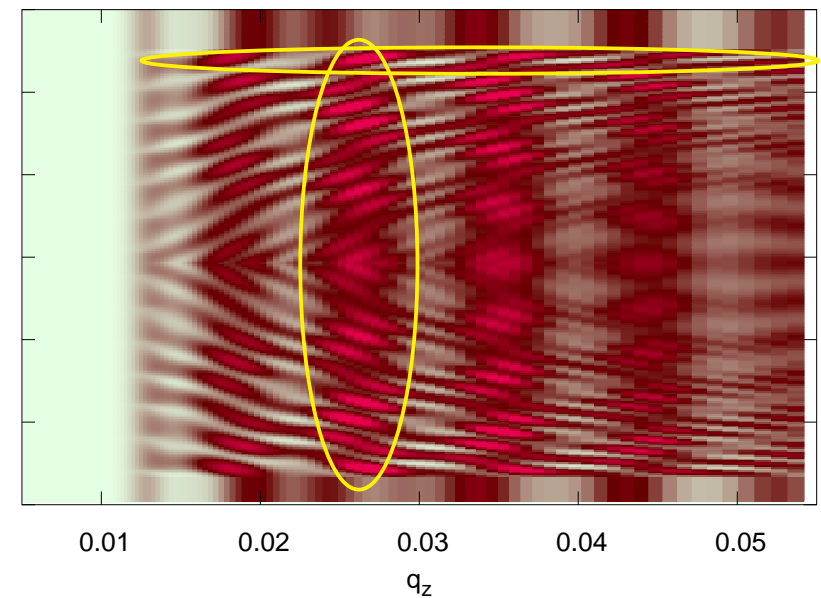
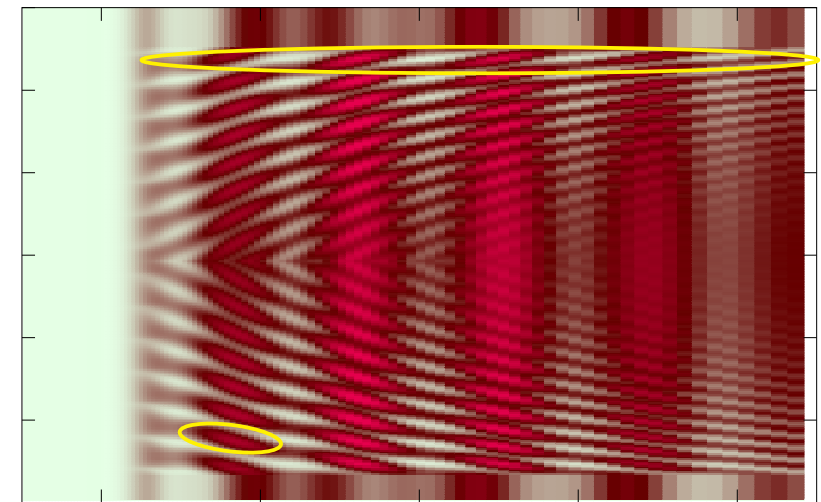
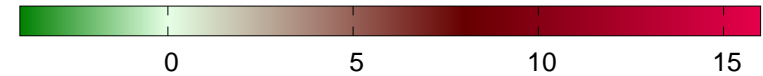


homogeneous Li distribution

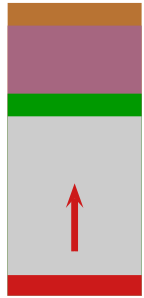


- + *something* at the beginning
- + non-linear thickness increase
- + Li trapped in the end

normalised reflectivity difference  $D$



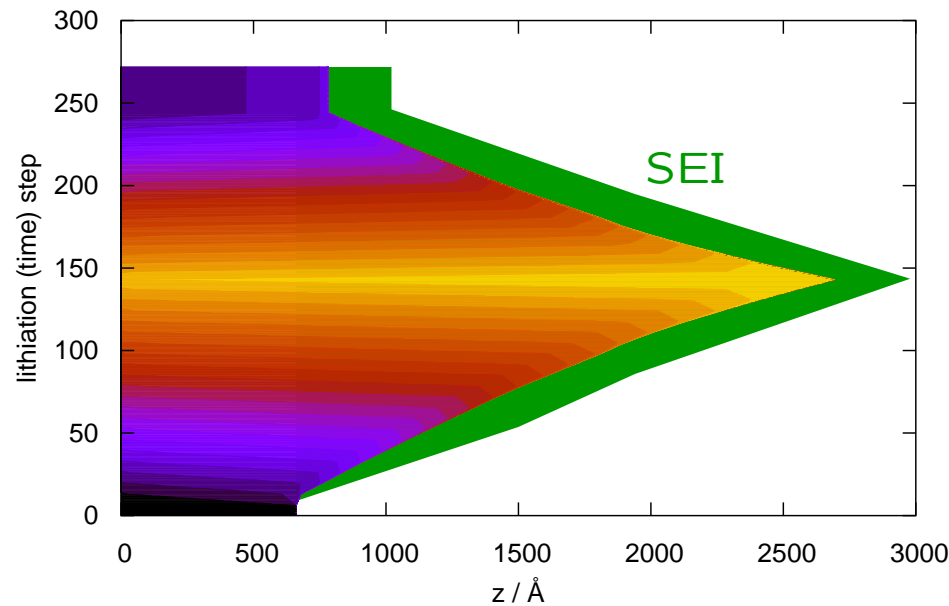
## modelling



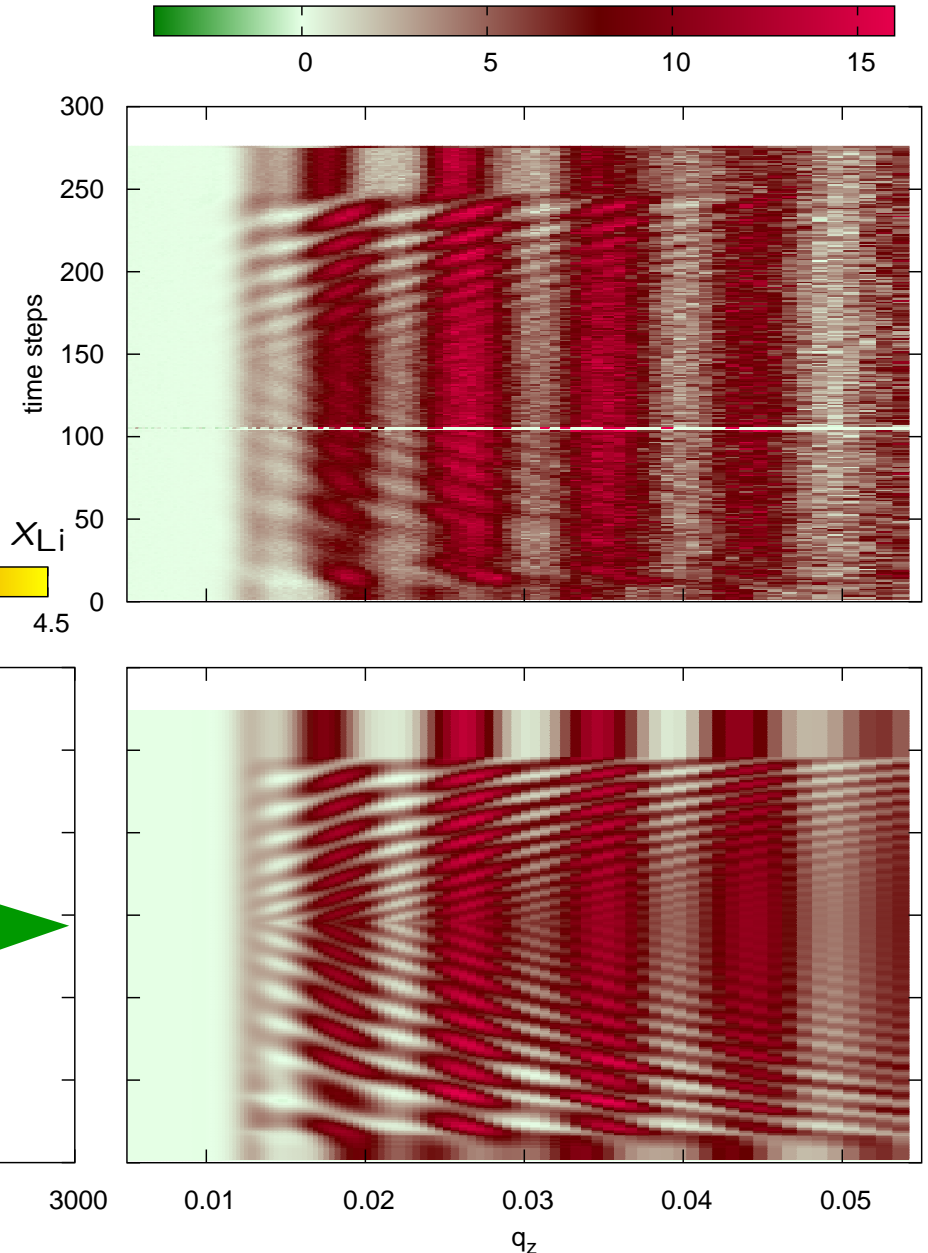
homogeneous Li distribution  
 solid electrolyte inter-phase (SEI)  
 within electrolyte

- + good fit (3 parameters)
- SEI too thick

lithium content in the electrode  $x_{Li}$



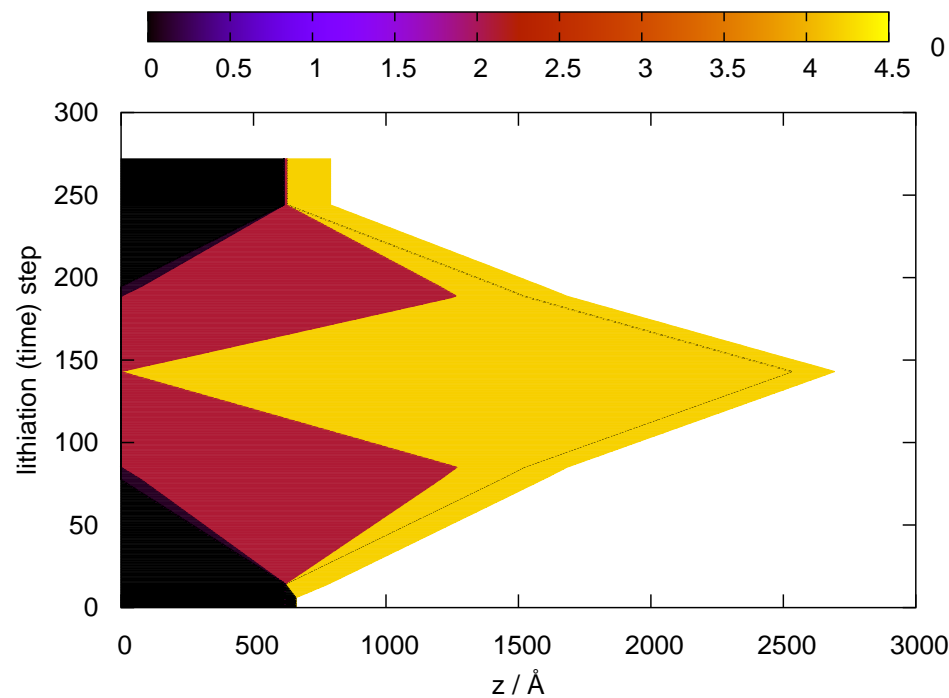
normalised reflectivity difference  $D$



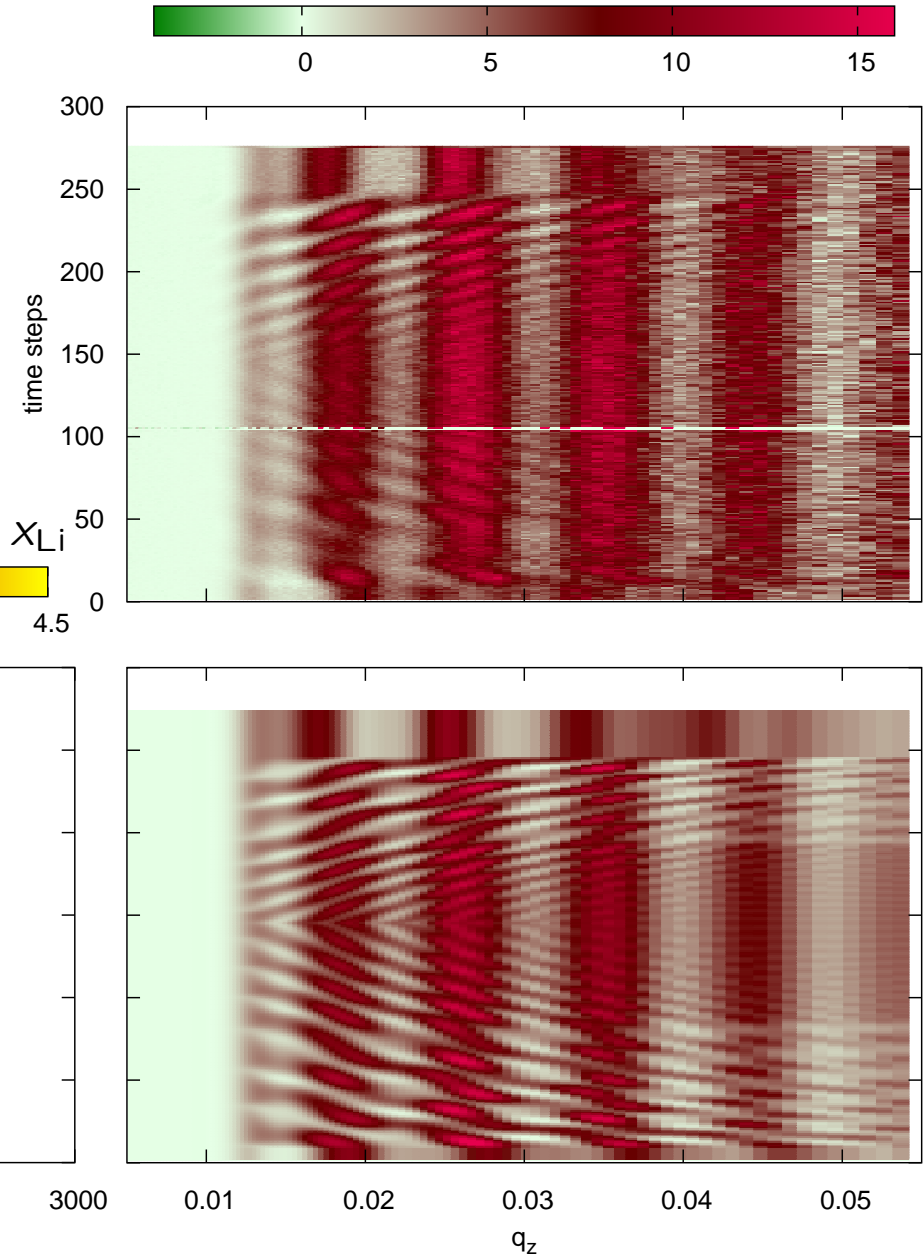
## modelling without SEI

- gradient Li distribution
  - various multi-phase models
  - lateral inhomogeneities
  - combination of models
- ⇒ plenty of parameters  
⇒ no satisfactory fit yet

## 3 phase model lithium content in the electrode $x_{\text{Li}}$



## normalised reflectivity difference $D$

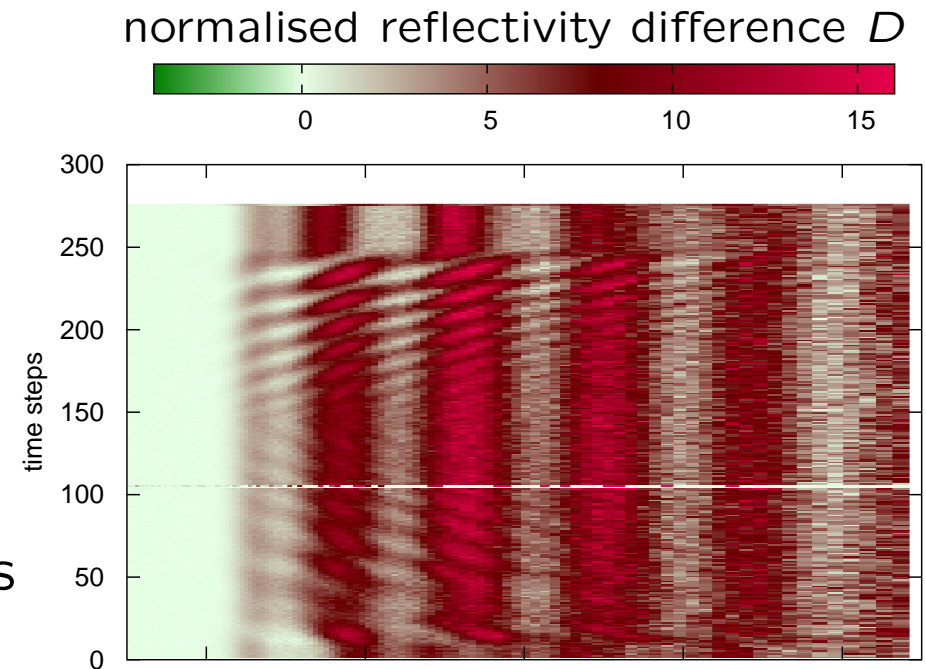


## state of the project

- some unknown initial process  
SEI formation?
- followed by homogeneous Li distribution
- non-linear increase in thickness
- de-lithiation is faster
- de-lithiation incomplete
- cycling is reversible besides initial process

## next steps

- variation of sample composition  
electrolyte / isotope labelling
- variation of sample geometry  
thicknesses of Cu and Si
- complementary methods  
determination of SEI mass with microbalance and impedance spectroscopy





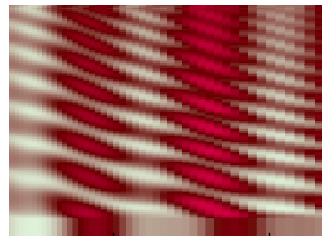
## reflectometry



- in general
- focusing
- Amor

## charging of batteries

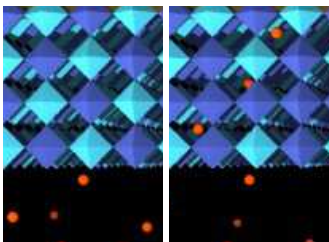
H. Schmidt, TU Clausthal



- principle
- measurements & data analysis
- outlook

## magnetic switching by electrochemical doping

G. Bimashofer, PSI



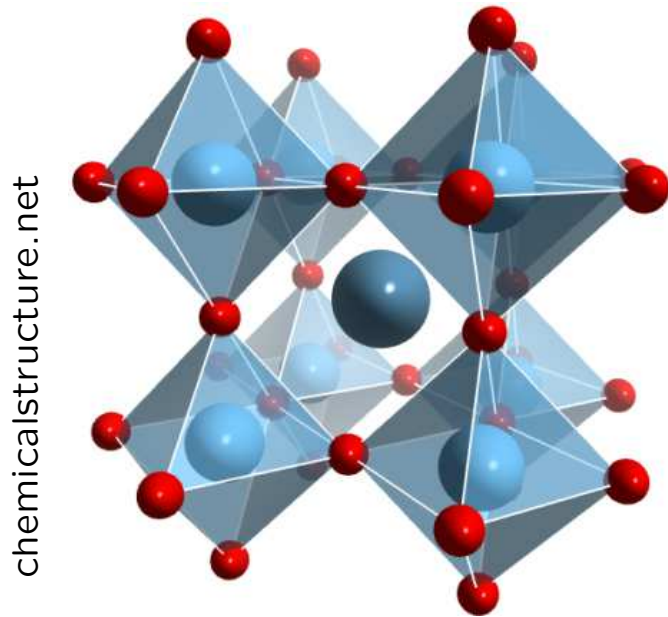
- motivation / principle
- state of the work
- outlook





corner-sharing  $\text{MnO}_6$  octahedra

random occupation of void by La or Sr

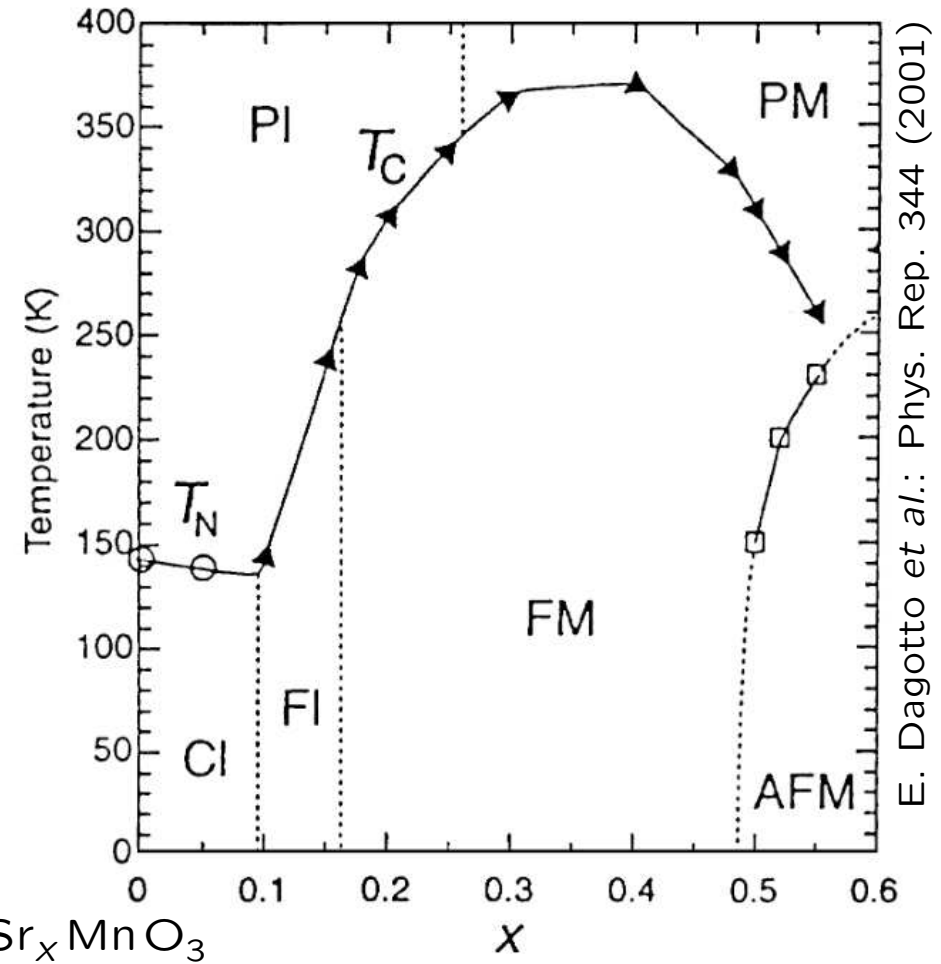


⇒ wide variety of electronic, magnetic and steric environments for  $\text{MnO}_6$

+ various competing coupling mechanisms

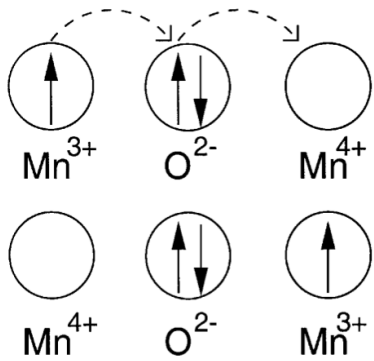
⇒ weak perturbation might drive phase transition

magnetic phase diagram

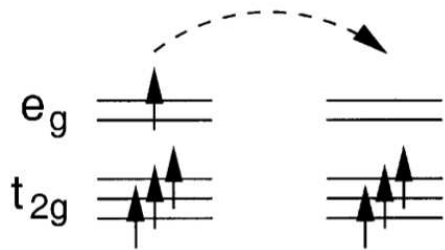


## explanation FM

“double exchange”  
historic picture



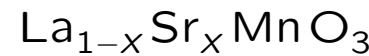
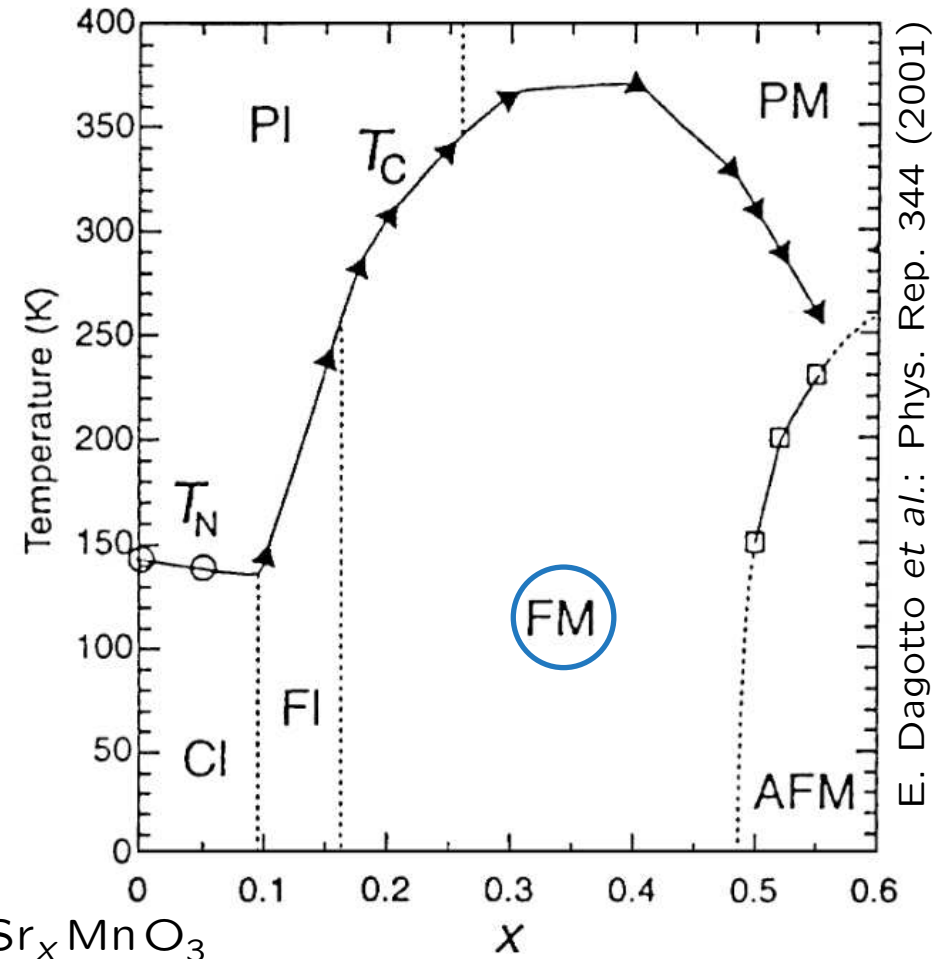
new explanation without O



⇒ parallel spins favoured

⇒ fast and random change of Mn<sup>3+</sup> and Mn<sup>4+</sup>

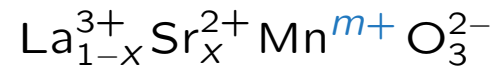
## magnetic phase diagram



3

m

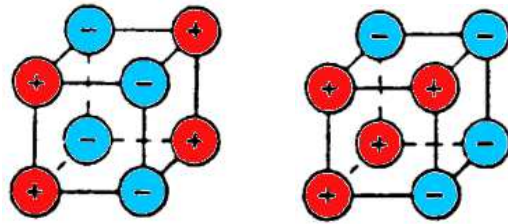
3.5



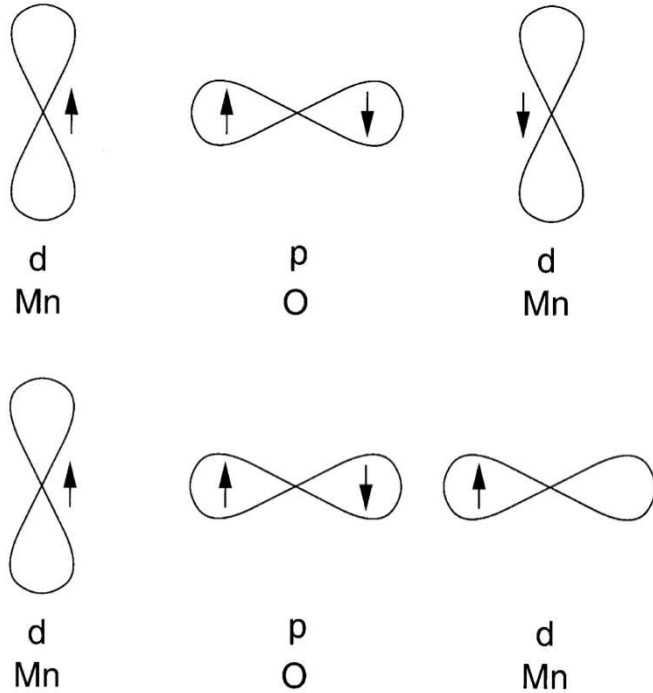
$m = 3 - 5x$

E. Dagotto et al.: Phys. Rep. 344 (2001)

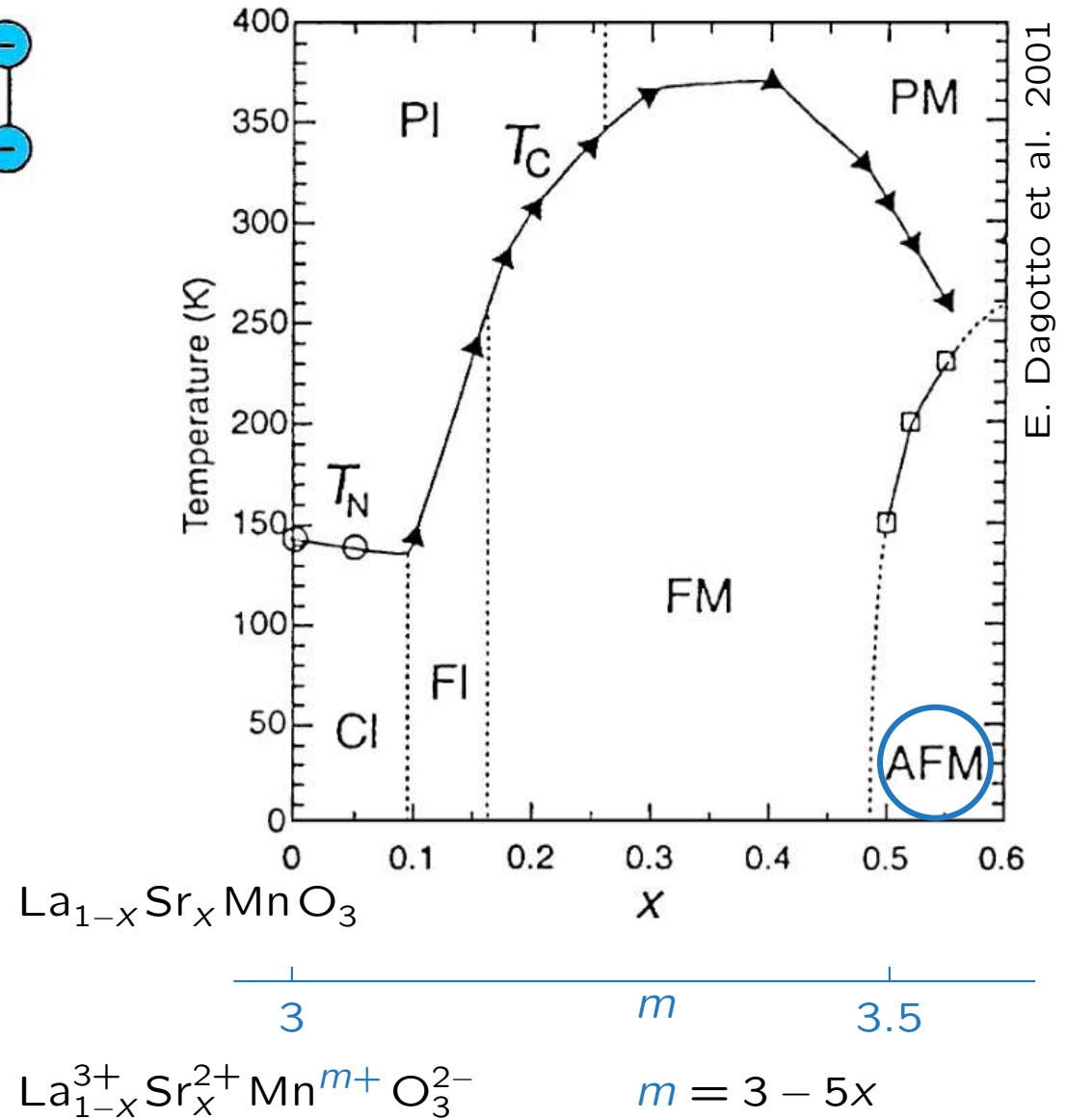
## explanation AFM of type CD



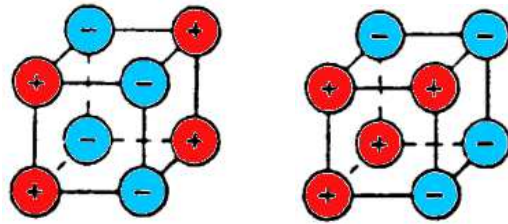
“semi-covalent exchange”



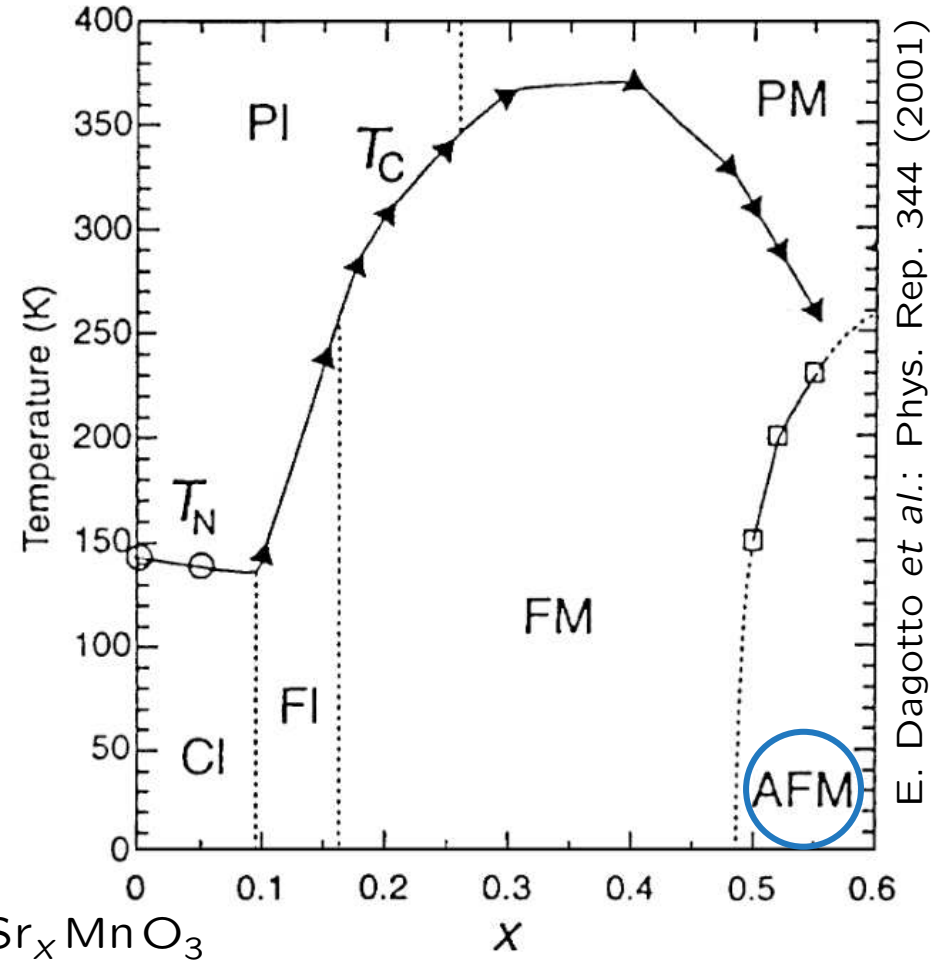
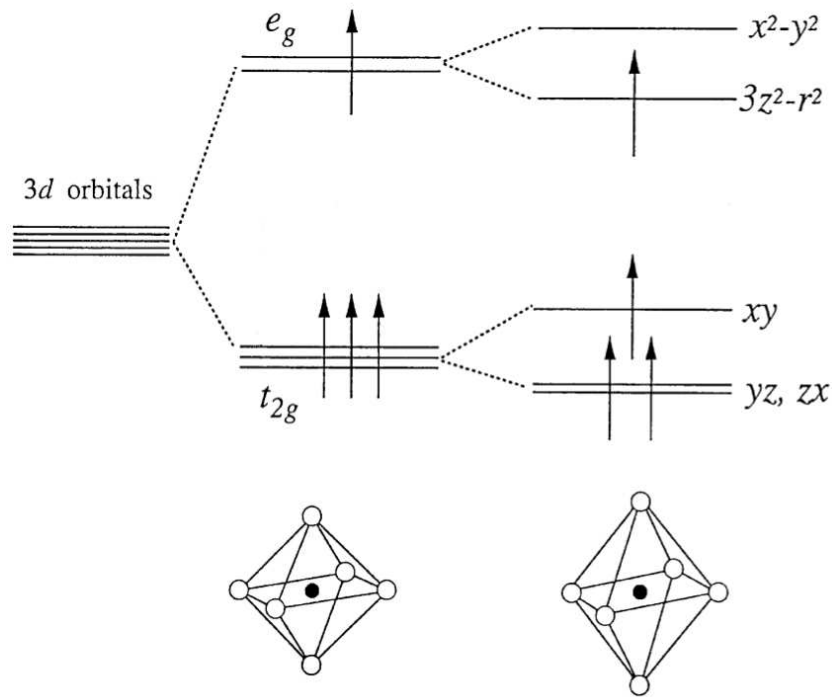
- ⇒ orbital ordering
- ⇒ charge ordering



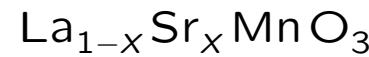
## explanation AFM of type CD



steric effects + strain



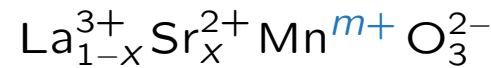
E. Dagotto et al.: Phys. Rep. 344 (2001)



3

m

3.5



$m = 3 - 5x$

⇒ charge ordering

## problem

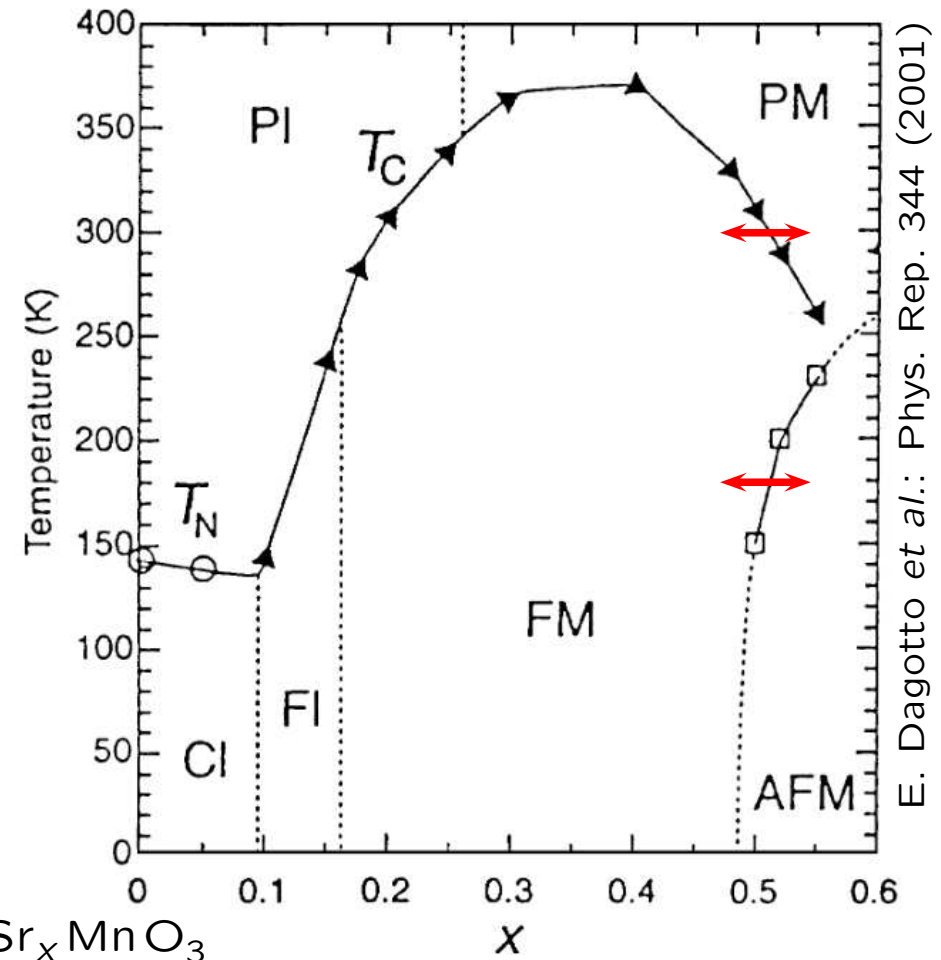
each  $m$  means a new sample

## idea

move horizontally in the phase diagram by adding / removing  $e^-$

i.e. electrochemical (de-)lithiation

new system:  $\text{La}_x\text{Sr}_y\text{Li}_z\text{Mn}^{m+}\text{O}_3$

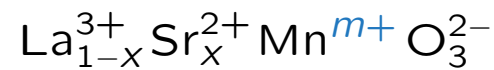


$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

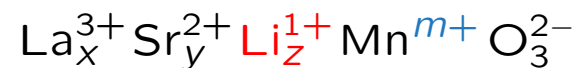
3

$m$

3.5



$m = 3 - 5x$

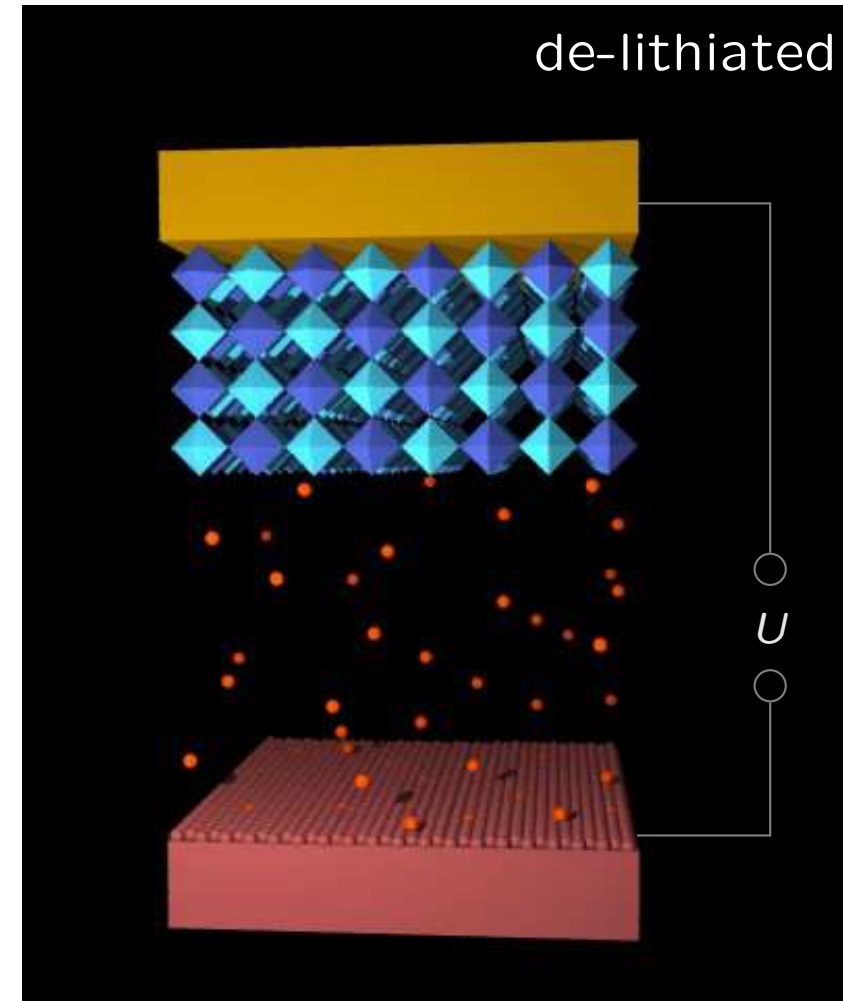
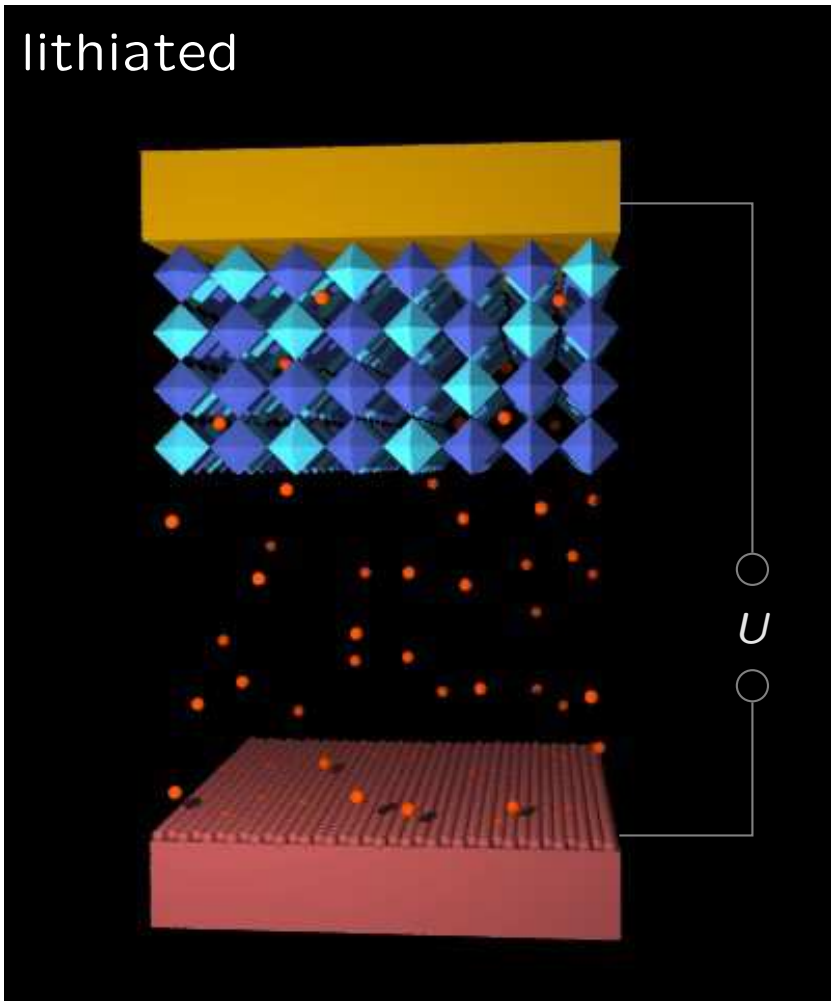
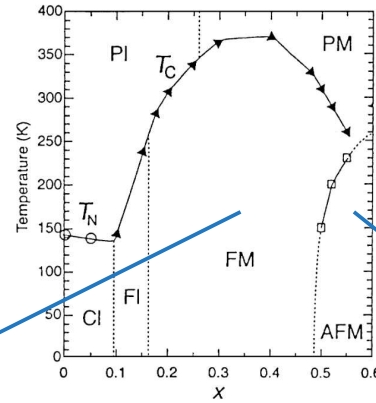


$m = 6 - 3x - 2y - z$

## idea

$Mn^{3+}/Mn^{4+}$  dis-ordered  
(bad) metal  
FM

charge ( $Mn^{3+}/Mn^{4+}$ ) ordered  
(bad) insulator  
AFM



current collector  
substrate

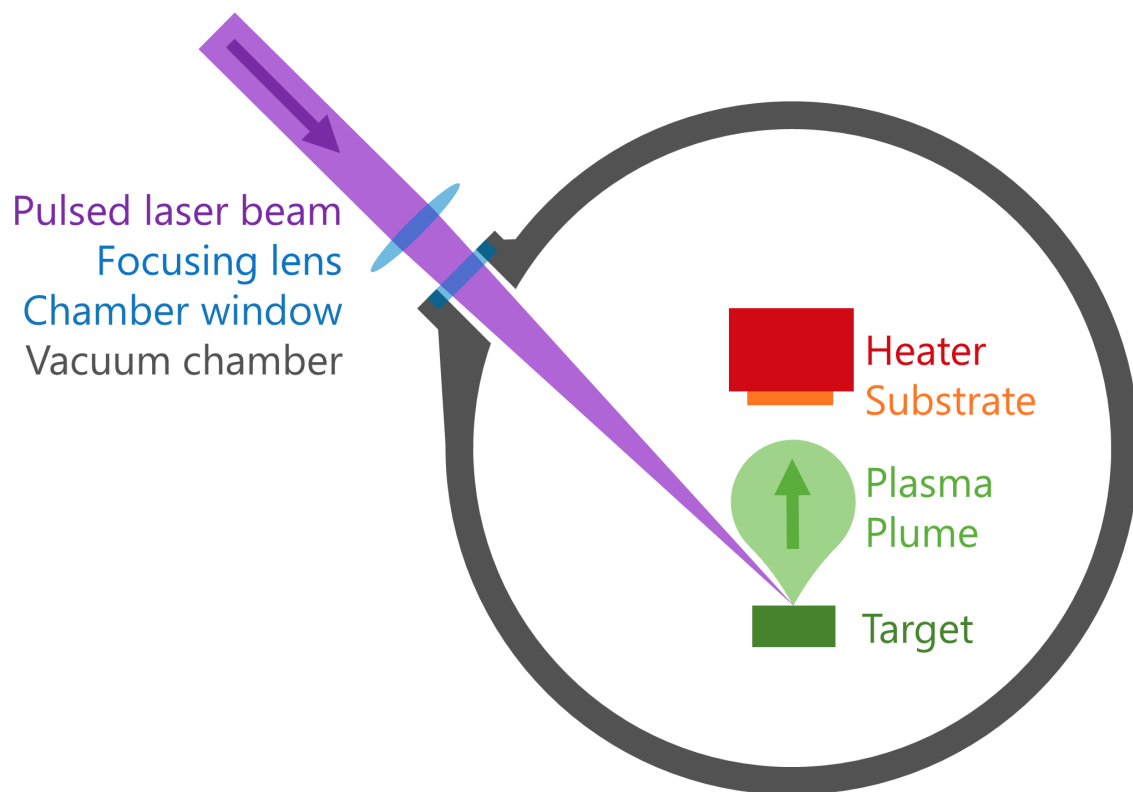
LSMO electrode

electrolyte

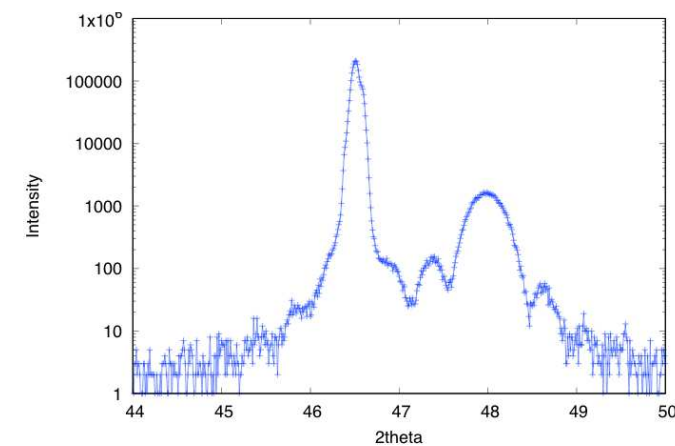
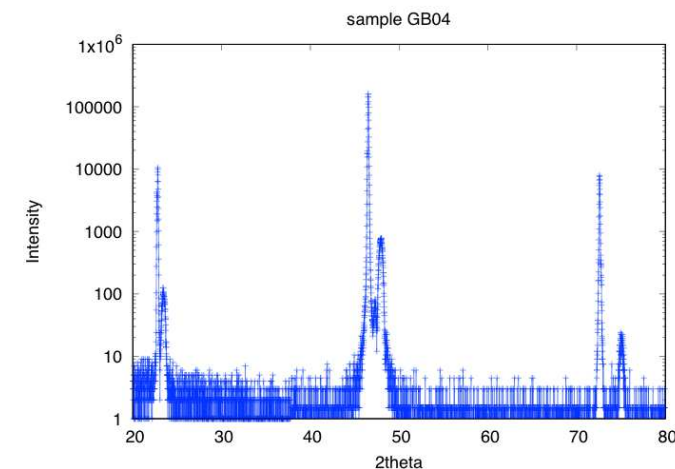
Li reservoir (metal)

## sample growth by pulsed laser deposition (PLD)

with group of T. Lippert, PSI



## X-ray diffraction

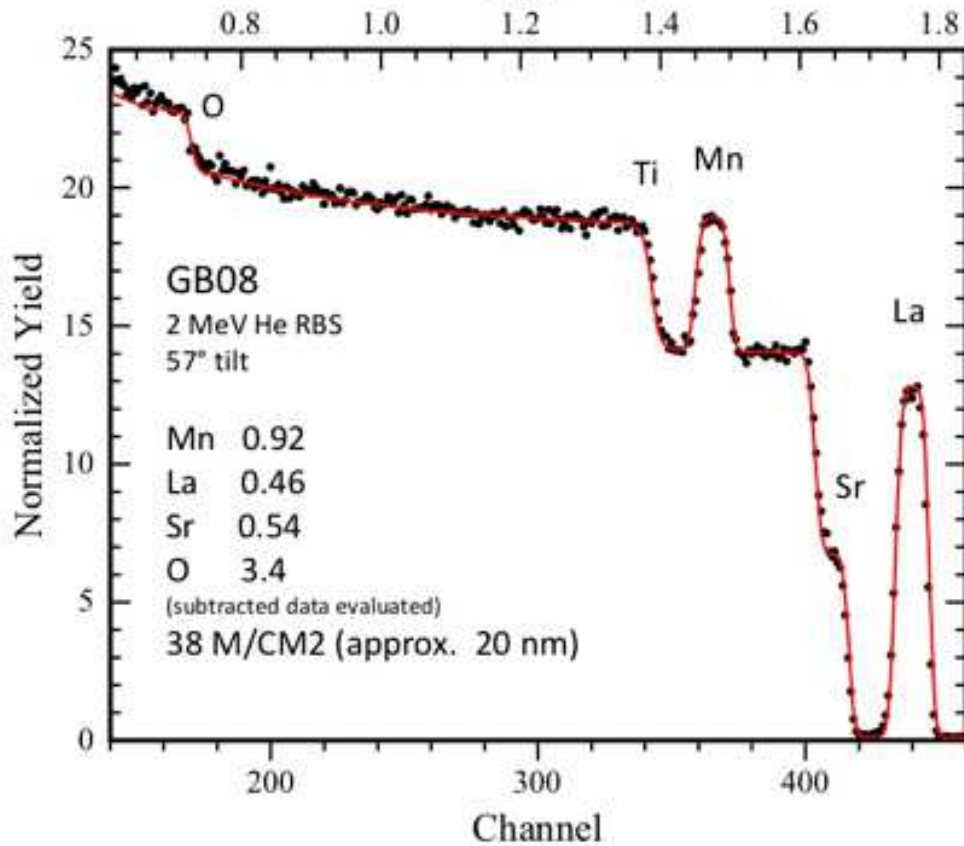
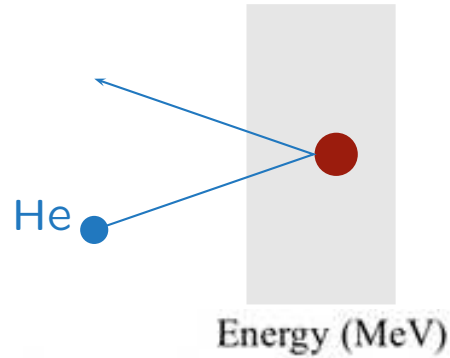




## characterisation

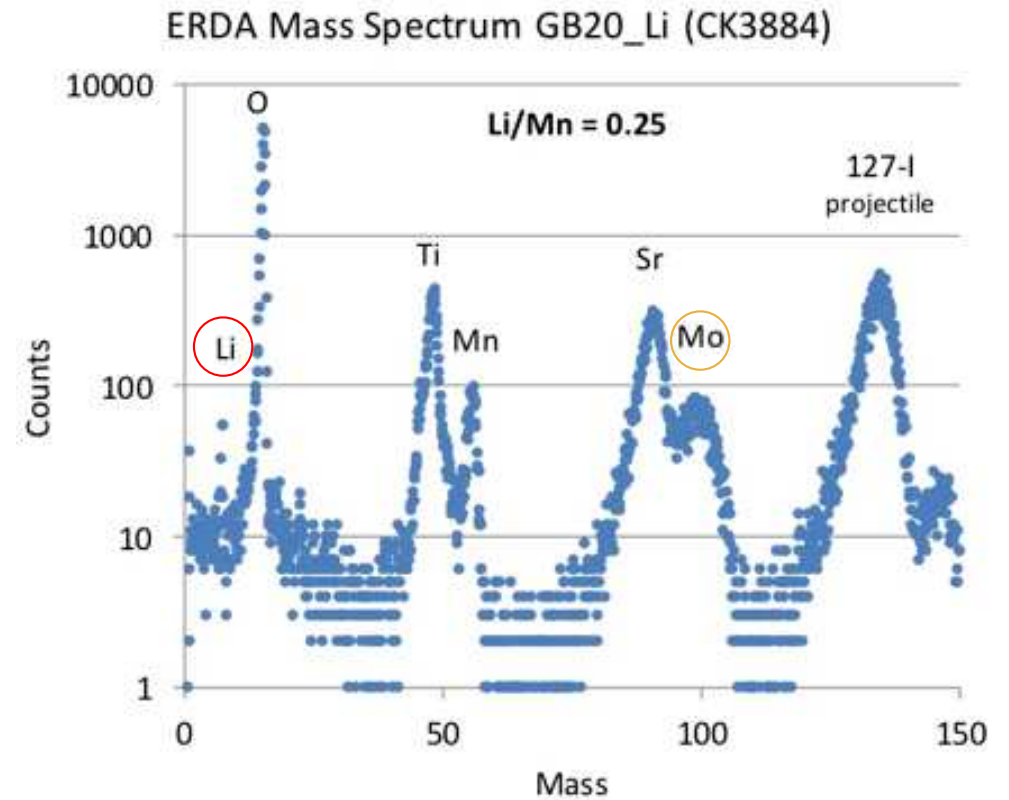
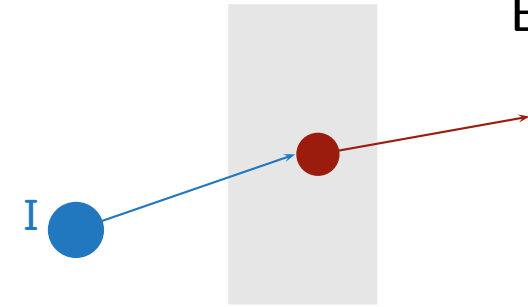
Rutherford back scattering

RBS

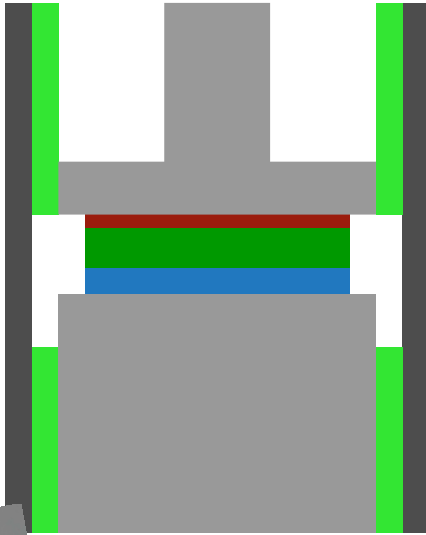


by M. Döbeli, ETHZ  
elastic recoil detection analysis

ERDA



## in-situ cell



upper piston  
insulator (PEEK)  
steel housing

Li metal  
electrolyte  
substrate

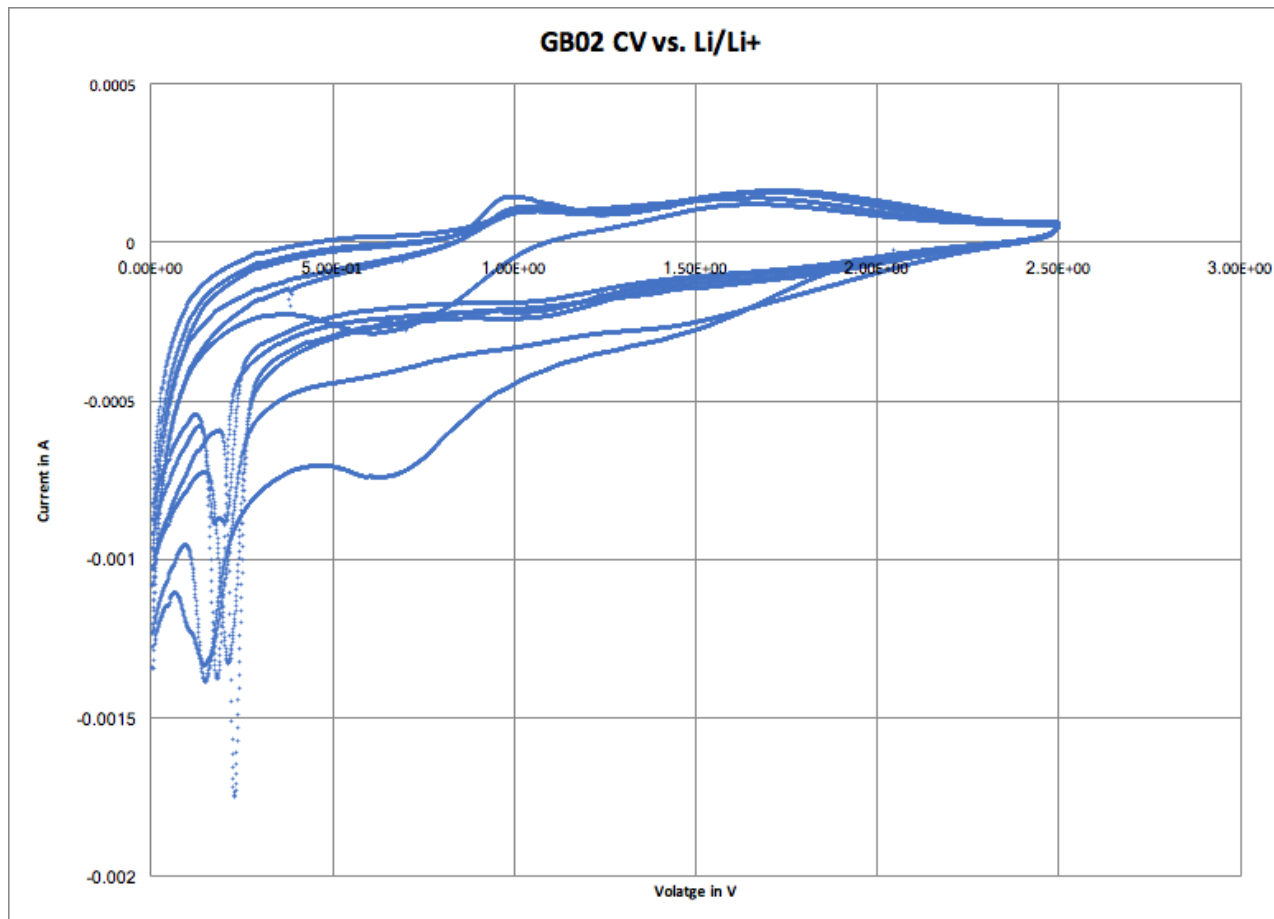
lower piston



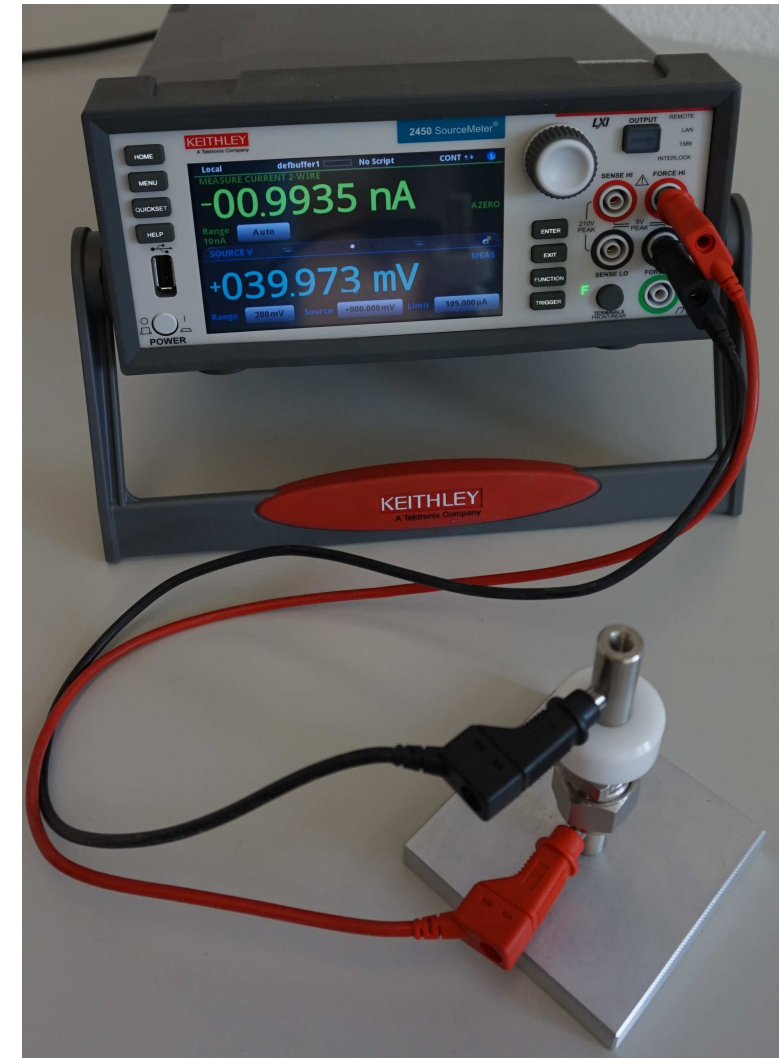
## CV measurements

cyclic voltammetry

ramping  $U$  while measuring  $I$



voltage  $U/V$



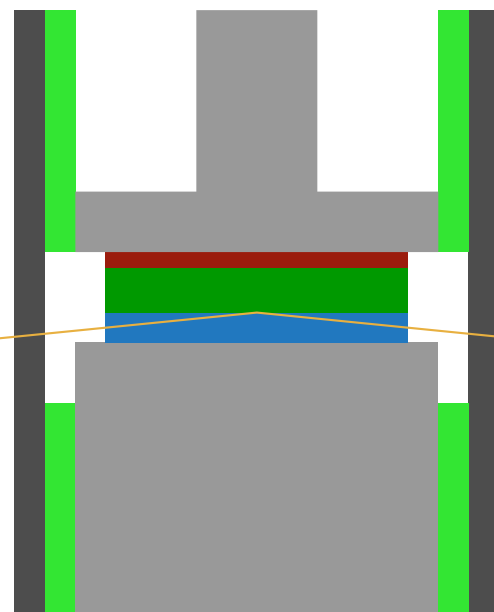
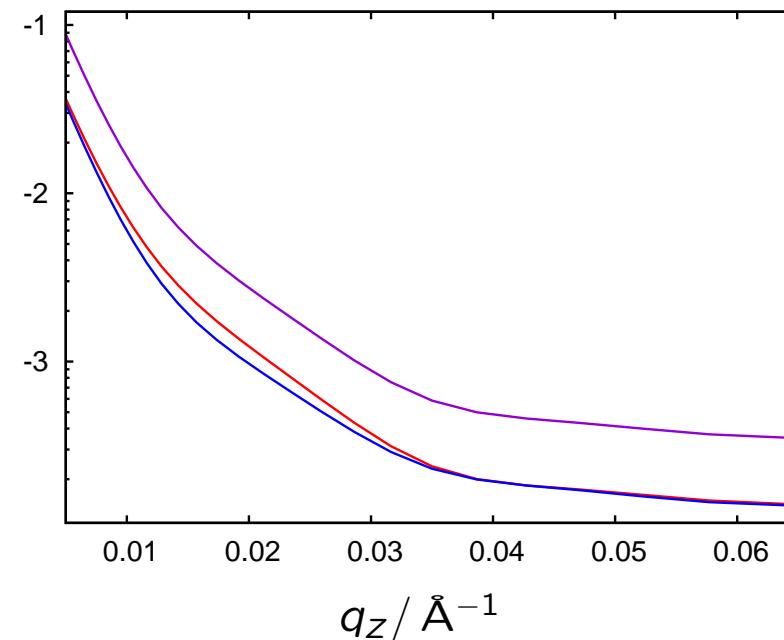
## polarised neutron reflectometry PNR

conditions

$H = 1 \text{ T}$

$T \approx 290 \text{ K}$

$\log_{10} R(q_z)$



upper piston

insulator (PEEK)

steel housing

⇒ absorption & scattering

Li metal

electrolyte

substrate

⇒ incoherent background

⇒ absorption & scattering

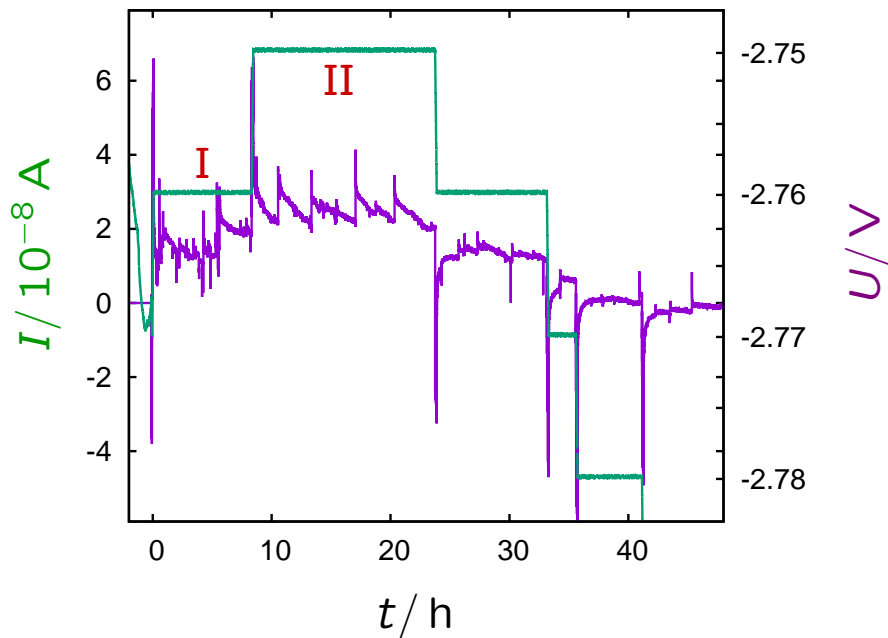
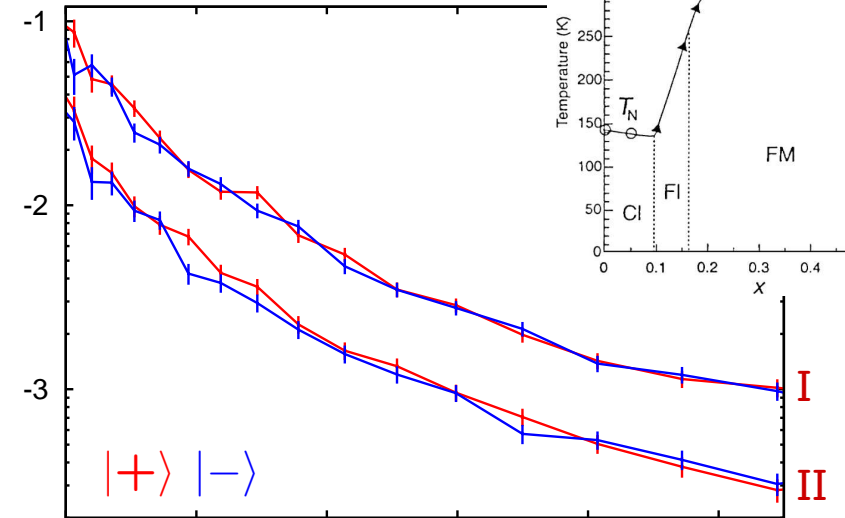
difficult to align

lower piston

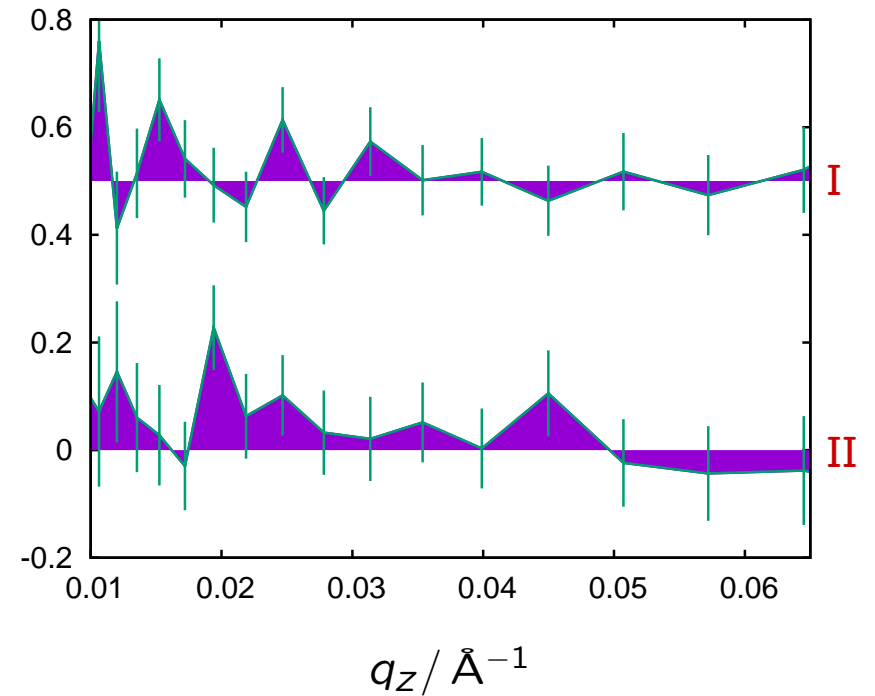
## PNR on $\text{La}_{0.5-\delta}\text{Sr}_{0.5+\delta}\text{MnO}_3 + \text{Li}$

switching PM/FM just significant

$\log_{10} R(q_z)$



$$\frac{R^+ - R^-}{R^+ + R^-}$$

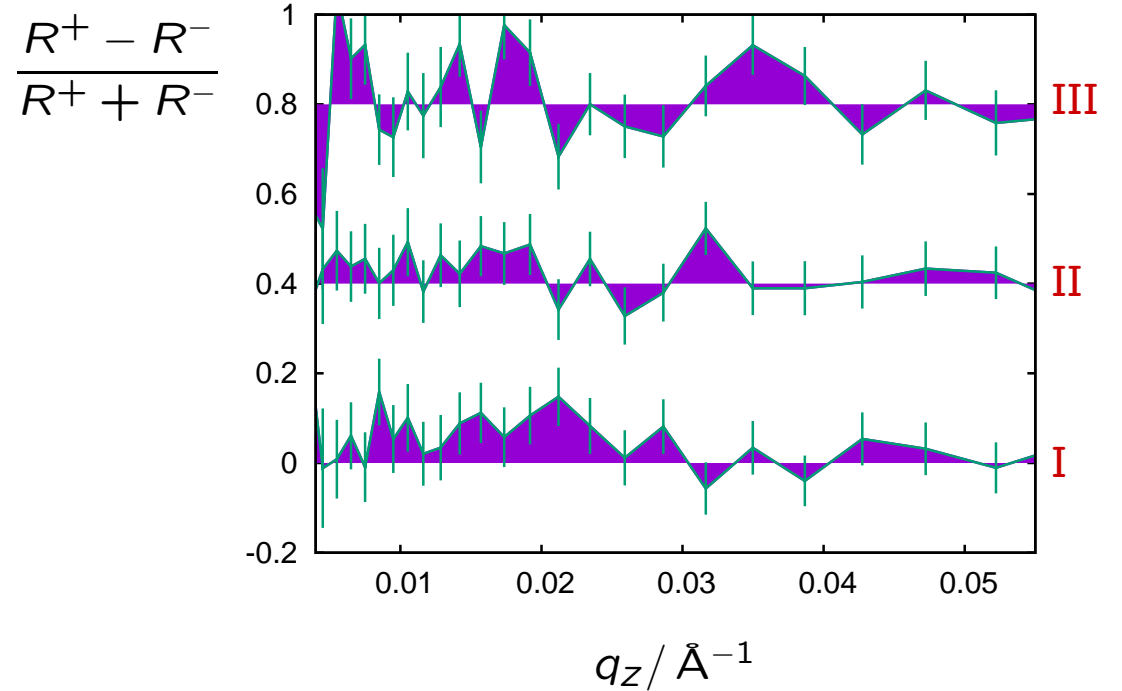
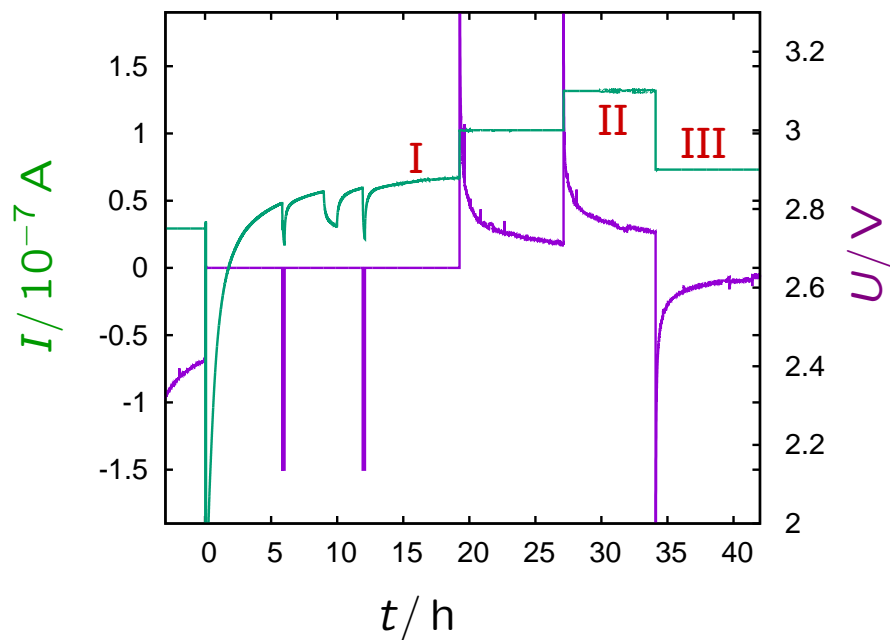
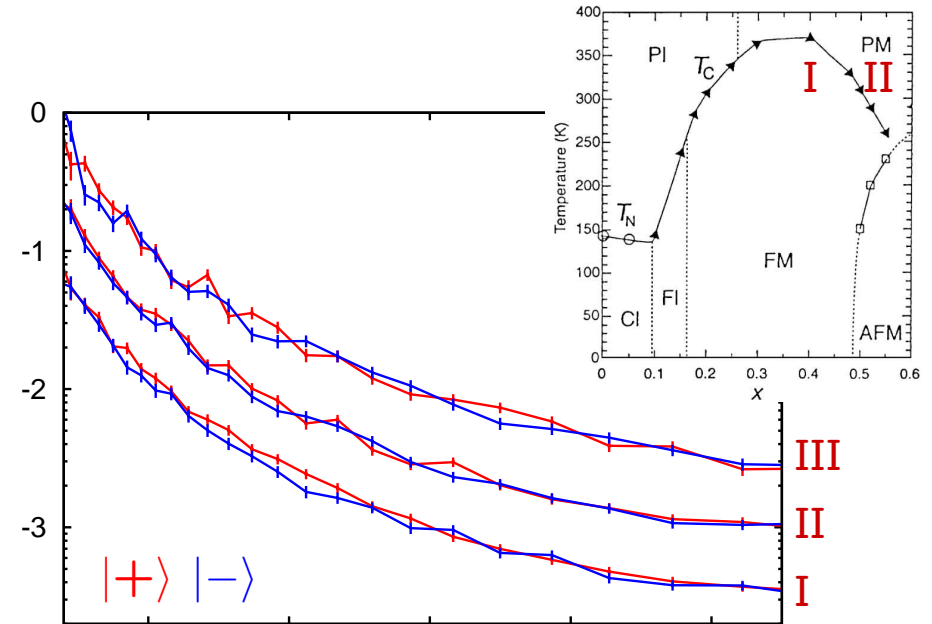


## PNR on $\text{La}_x\text{Sr}_y\text{Li}_z\text{MnO}_3 - \text{Li}$

switching FM/PM just significant  
switching PM/FM with low statistics

sample was Mo-contaminated

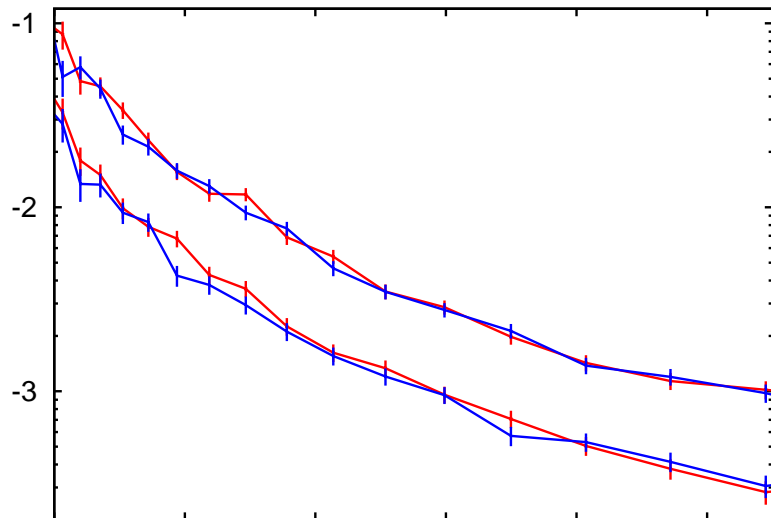
$\log_{10} R(q_z)$



## so far

samples prepared by PLD

cell built and used



PNR at RT

proof of principle



## problems

low intensity / high background due to liquid cell

pure lithiated sample by PLD not yet realised

## next steps

new PLD target for  $\text{La}_x\text{Sr}_y\text{Li}_z\text{MnO}_3$

solid-state cell

current collector with contact A

Li reservoir

solid electrolyte

working electrode

non-conducting substrate

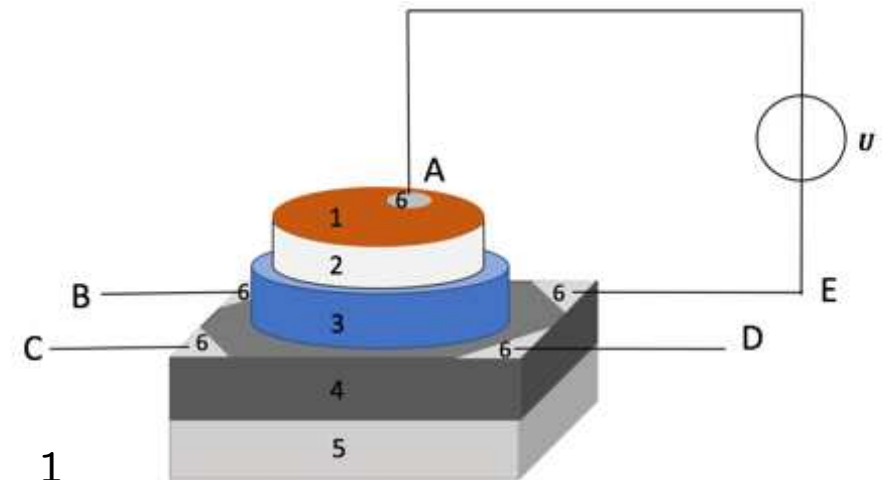
contacts B,C,D,E for 4-point measurements

⇒ less absorption

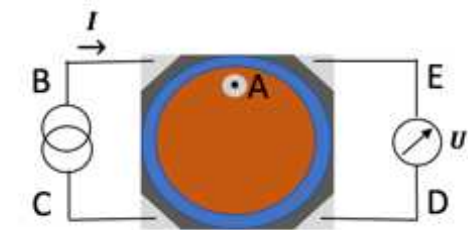
⇒ low  $T$  enabled

⇒ total reflection plateau for alignment

	Au	1
	$\text{LiNbO}_3$	2
	$\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$	3
	$\text{La}_x\text{Sr}_y\text{Li}_z\text{MnO}_3$	4
	$\text{SrTiO}_3$	5



1  
2  
3  
4  
5  
6



## far future

resonant X-ray techniques to probe charge and orbital ordering



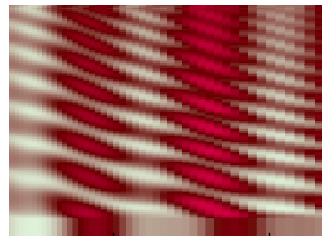
## reflectometry



- short intro
- focusing
- Amor now and 2020

## charging of batteries

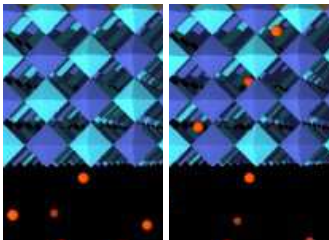
**H. Schmidt, TU Clausthal**



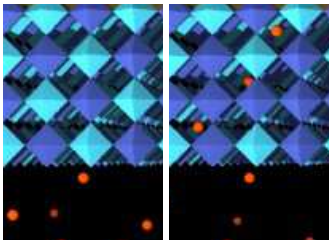
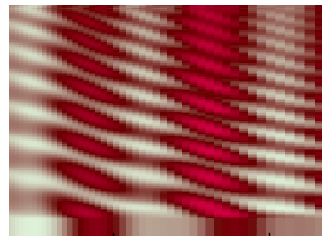
- ... handle huge amount of data
- follow cathode thickness and density
- uncertainty in the initial process

## magnetic switching by electrochemical doping

**G. Bimashofer, PSI**



- feasibility proved
- solid state cell in preparation
- might be applied to other systems



**Thank you  
for listening**