Neutron Reflectometry

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Jun-04-2013
Canadian Neutron Scattering Summer School

Outlook

Application/advantages of neutron reflectometry

Theoretical background

Instrumental setup

Experiments:
- **Photoactive azobenzene films**
- **Hydrogen absorption in Mg-based films**

Supermirrors (non-polarizing and polarizing)

What can be measured?

Film thickness (2 – 200 nm):
swelling of polymer films due to water uptake
film expansion during illumination of photoactive films
film expansion during hydrogen absorption
growth of oxide layer

Scattering length density profile:
profile of absorbed gas/liquid
interdiffusion
magnetic structures
magnetic field penetration into superconductors

In-plane structures on nm and μm scale

Specific advantages of NR

Large penetration depth (for most materials):

Buried layers

In-situ measurements (cryostats, cryomagnets, high-pressure cells, furnaces)

High sensitivity to hydrogen:

Determine hydrogen profile in hydrogen storage materials

Change of contrast by using isotopes:

swelling of films during water (vapor or liquid) uptake (H_2O / D_2O)

expansion of films during hydrogen absorption (H_2 / D_2)

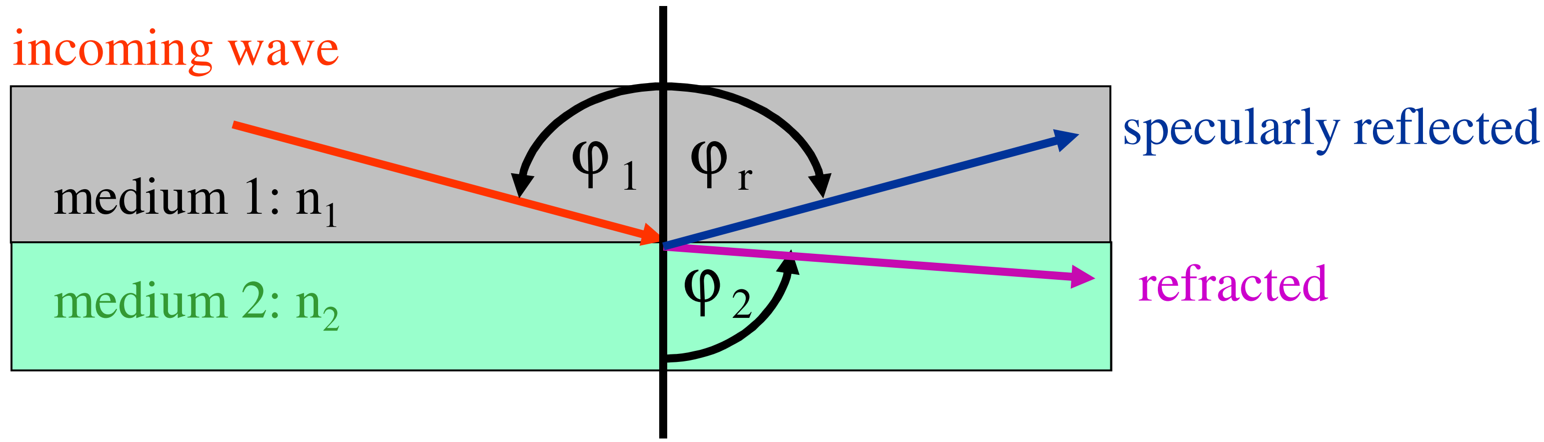
No diamagnetic background of substrate for ferromagnetic samples:

Determination of absolute magnetic moment

Spin and non-spin flip reflectivity:

Magnetization reversal, magnetic structure

Reflection and Refraction



<u>Physical origin:</u>

different index of refraction for two media

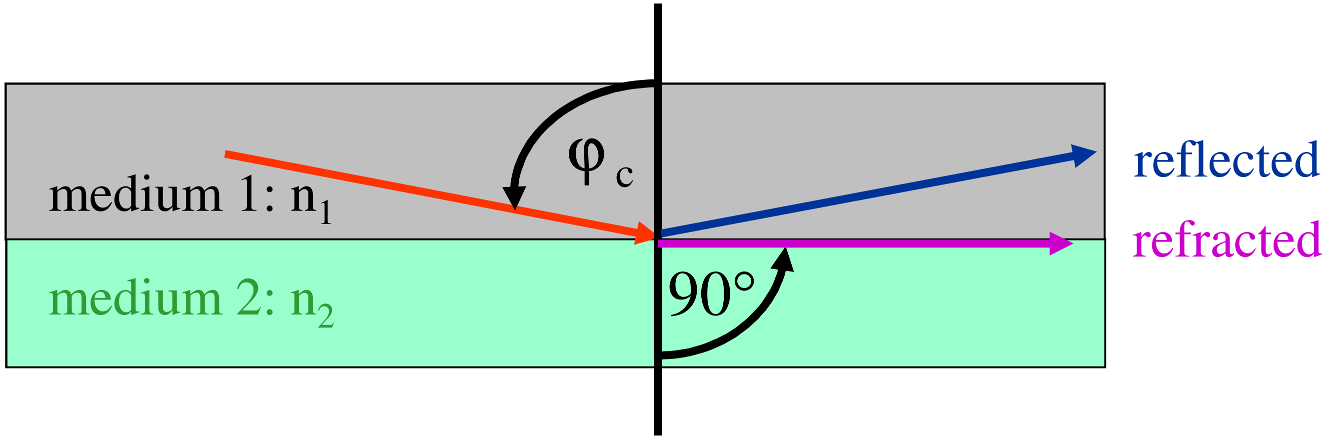
<u>Reflection:</u>

$\varphi_r = \varphi_1$

<u>Refraction: Snell's law</u>

$n_1 \sin \varphi_1 = n_2 \sin \varphi_2$

The critical angle



Critical angle: $n_1 \sin \varphi_1 = n_2 \sin 90° \Rightarrow \sin \varphi_c = n_2 / n_1$

For $\varphi_1 > \varphi_c$: no refracted beam exists, only a reflected beam

Total reflection (100% reflectivity) occurs in the medium with the larger n

Index of refraction for light

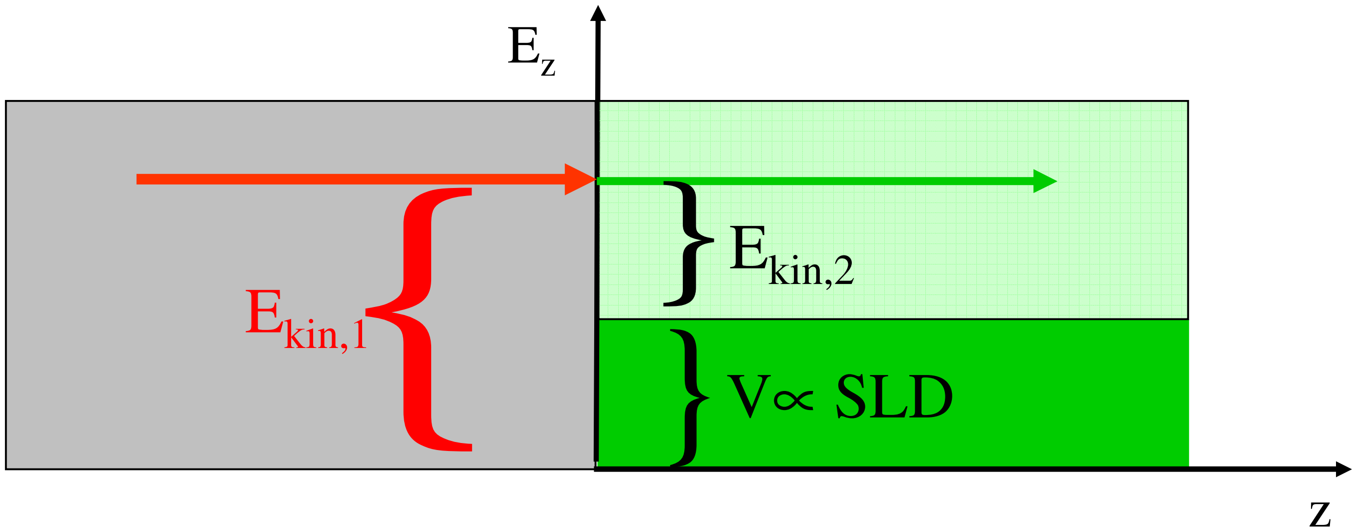
For **light** with λ= 656 nm:

Material	**n**	**φ_c (for n_2=1)**
Vacuum	**1.00**	**-**
Water	**1.33**	**48.8°**
Quartz glass	**1.46**	**43.2°**
Benzene	**1.50**	**41.8°**

Note: the index of refraction depends on the wavelength

What is the index of refraction for neutrons?

Index of refraction for neutrons



$$\frac{\hbar^2 k_1^2}{2m} = \frac{\hbar^2 k_2^2}{2m} + V \quad \Rightarrow \quad n = \frac{k_2}{k_1} = \sqrt{1 - \frac{2m \cdot V}{\hbar^2 k_1^2}} = \sqrt{1 - \frac{\lambda^2}{\pi}\rho b}$$

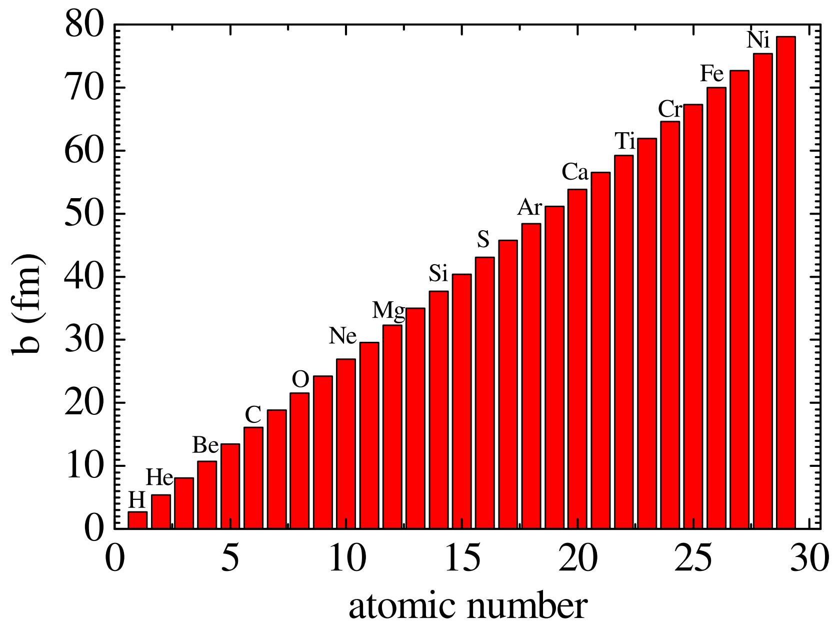
m: neutron mass
λ: neutron wavelength
b: nuclear scattering length
ρ: density of atoms
ρb: scattering length density (SLD)

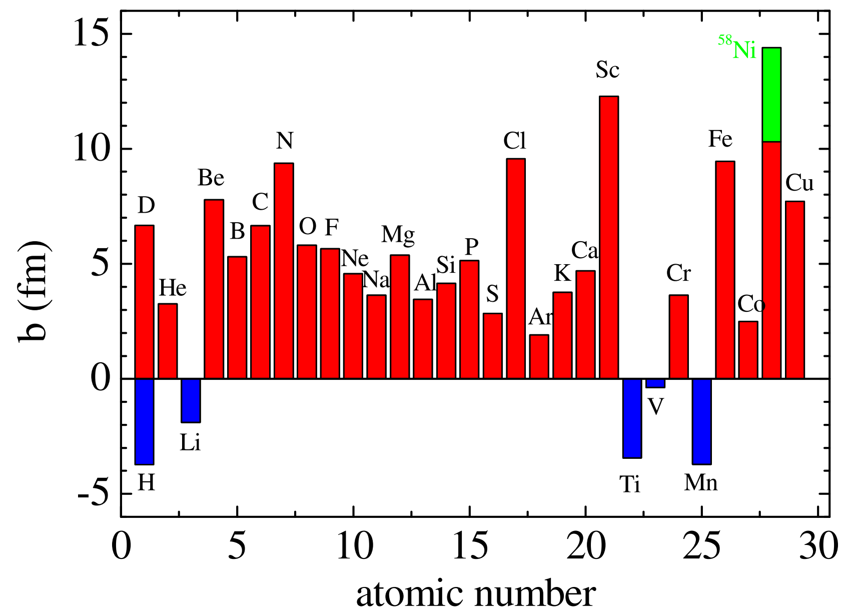
Fermi's pseudopotential: $V = \frac{2\pi\hbar^2}{m}\rho b$

Scattering length

X-rays

Neutrons





X-rays: b ∝ Z (electron density)

Neutrons: no systematics

Important: not absolute number but contrast of SL
X-rays and neutrons are complementary probes

Index of refraction: some examples

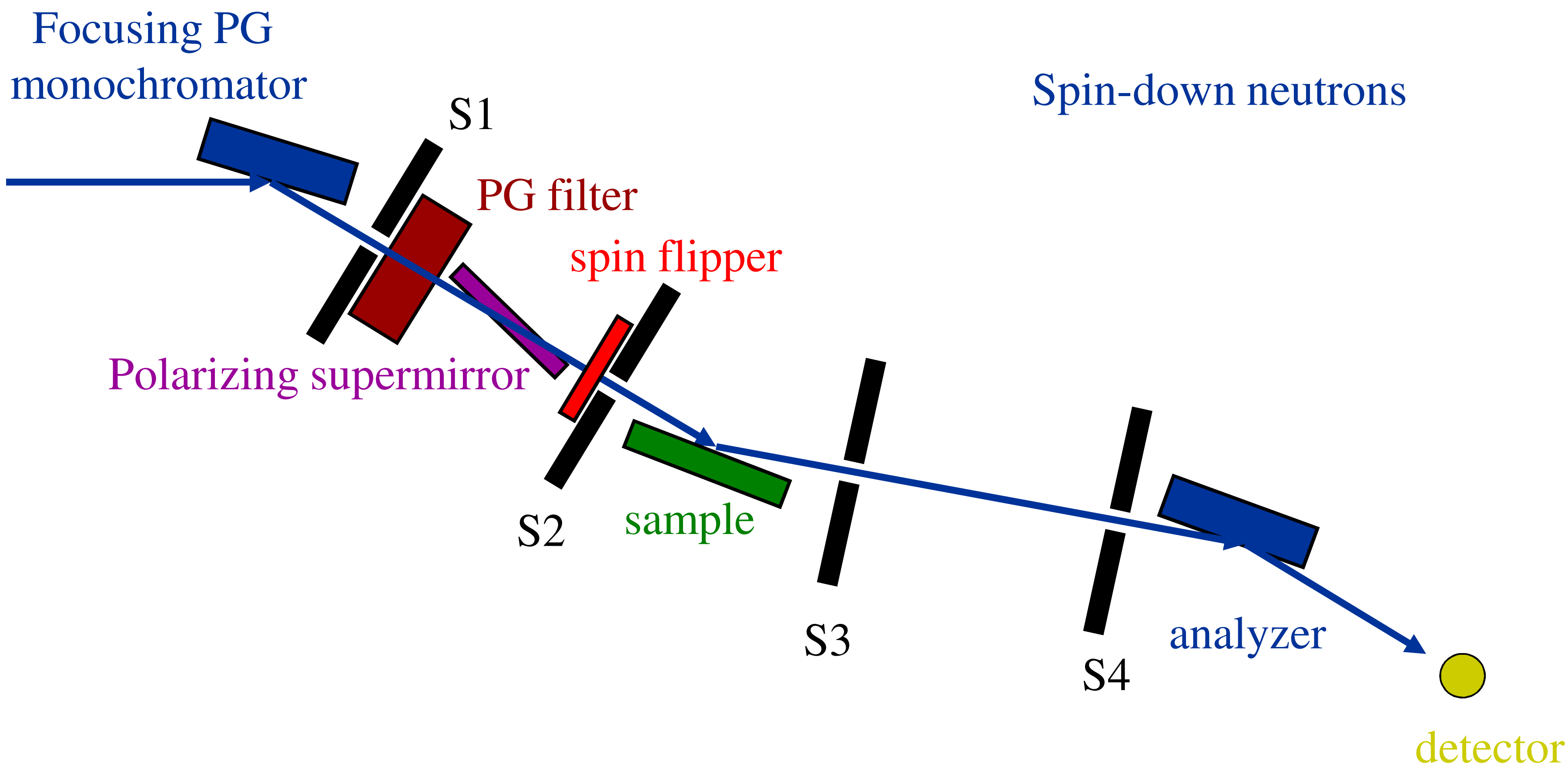
For **neutrons** with λ= 0.237 nm:

Material	**n**	ρ ***b*** (10^{-4} 1/nm^2)
Vacuum	1.00	0
Water (H_2O)	1.000001	-0.561
Si	0.999998	2.073
Quartz glass	0.999997	4.185
Heavy water (D_2O)	0.999994	6.366
^{58}Ni	0.999988	13.16

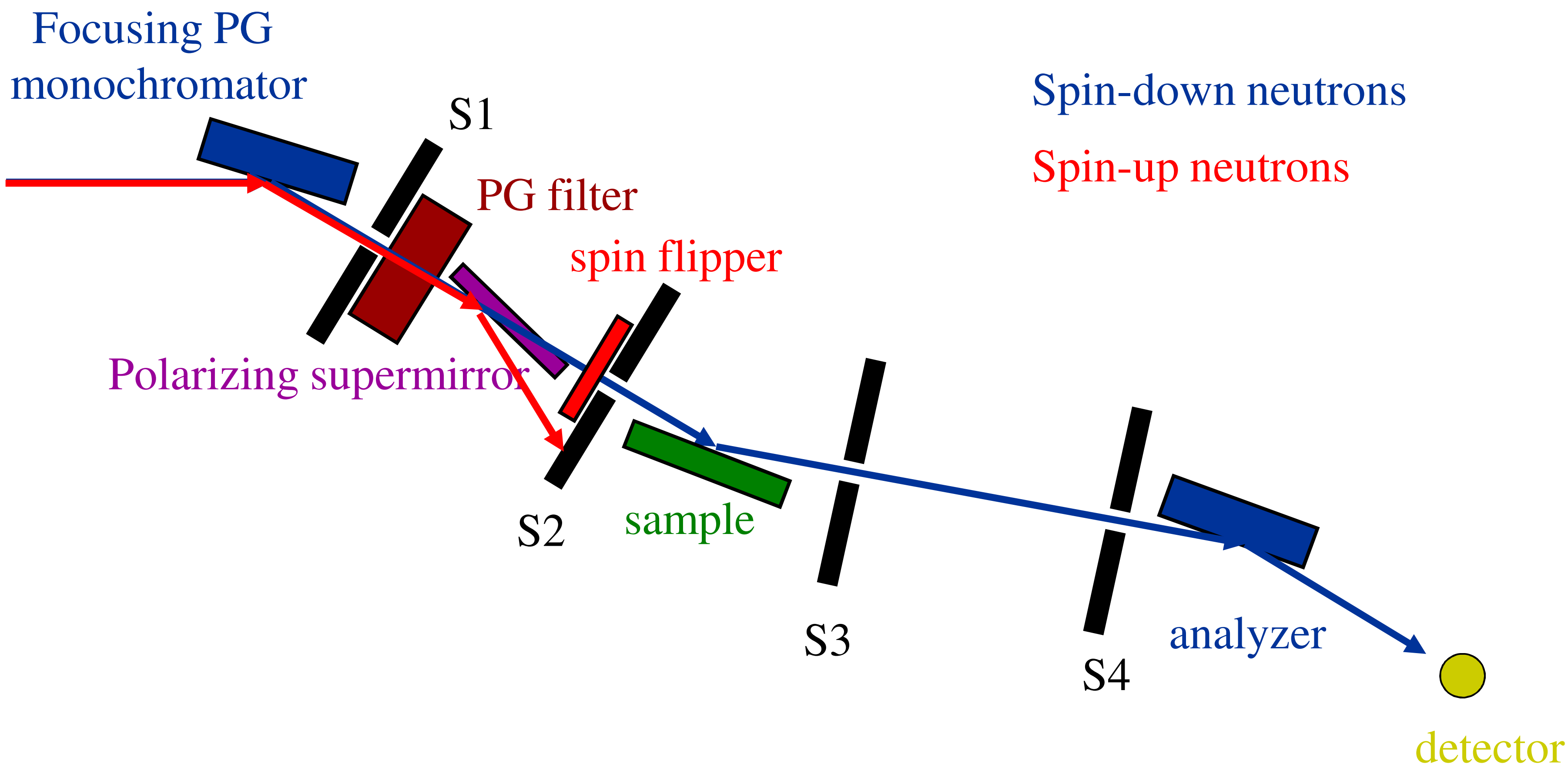
Note: $n \approx 1-10^{-5}$

The deviation of $n_{neutron}$ from 1 is much smaller than for light, because the interaction of neutrons with matter is much weaker

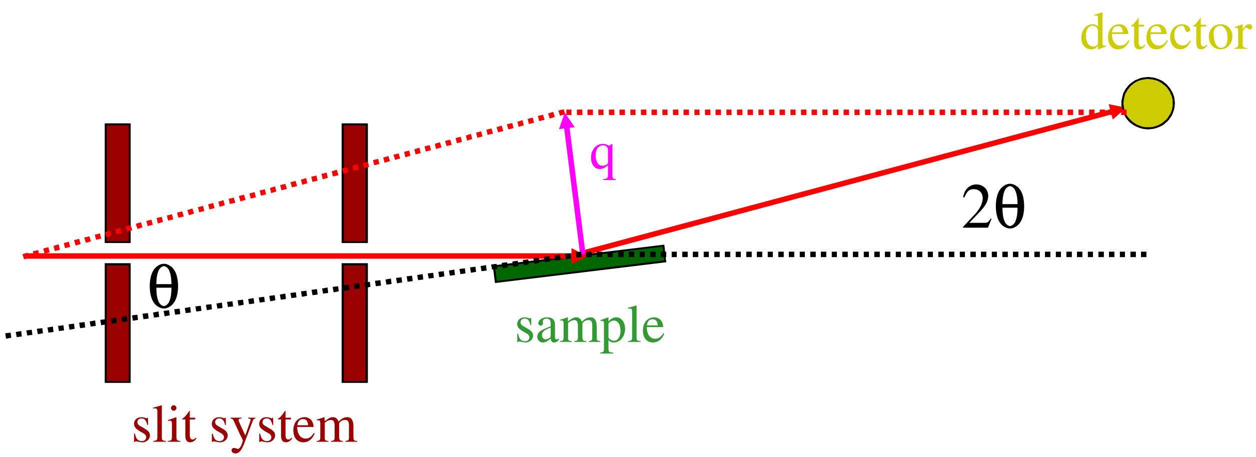
Reflectometry setup on D3



Reflectometry setup on D3



The reflectometry experiment

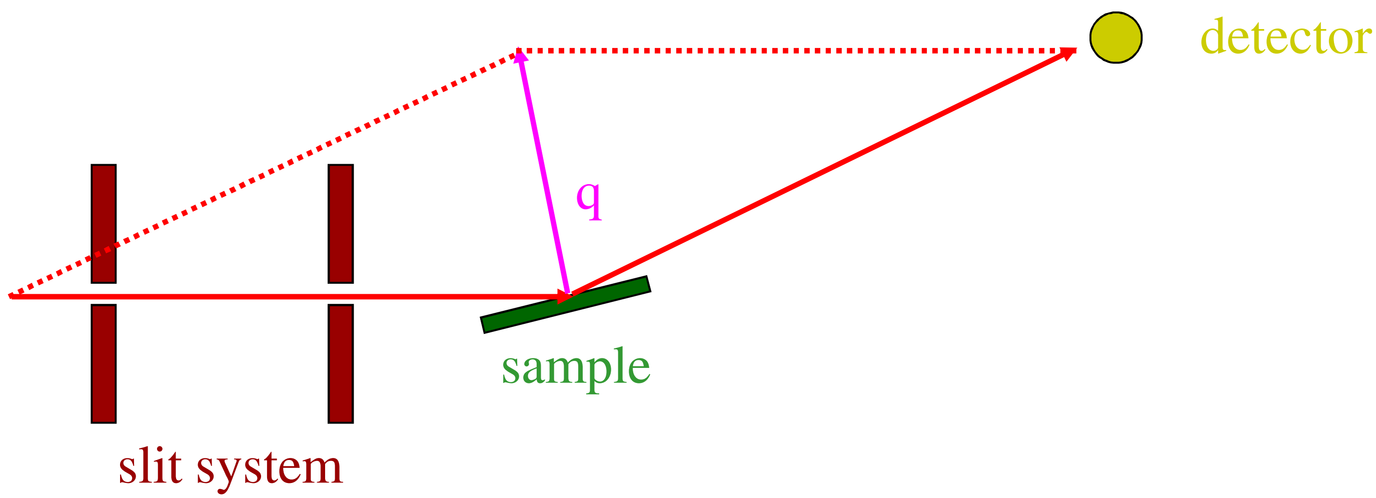


<u>θ–2θ geometry:</u>
sample moves by θ
detector moves by 2θ

$$\vec{q} = \vec{k}_r - \vec{k}_i = \frac{4\pi}{\lambda}\sin\theta$$

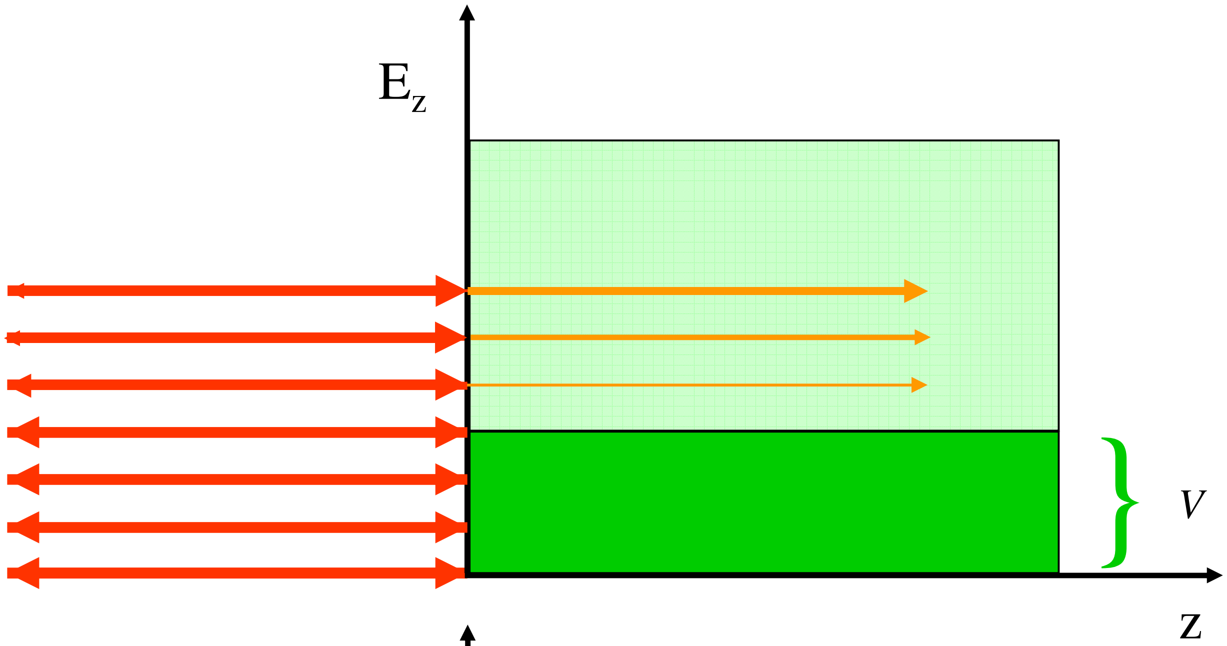
q: scattering vector
2θ: scattering angle

The reflectometry experiment

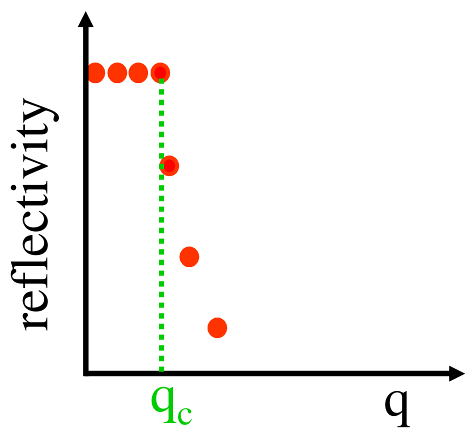


Reflectometry:
Measuring the reflected intensity as a function of q

Visualization of a reflectivity curve



$$V = \frac{2\pi\hbar^2}{m}\rho\, b_{nuc}$$

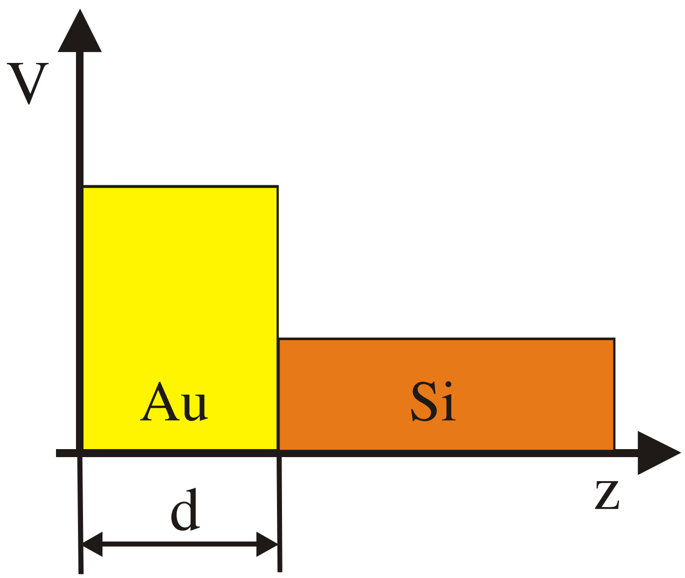


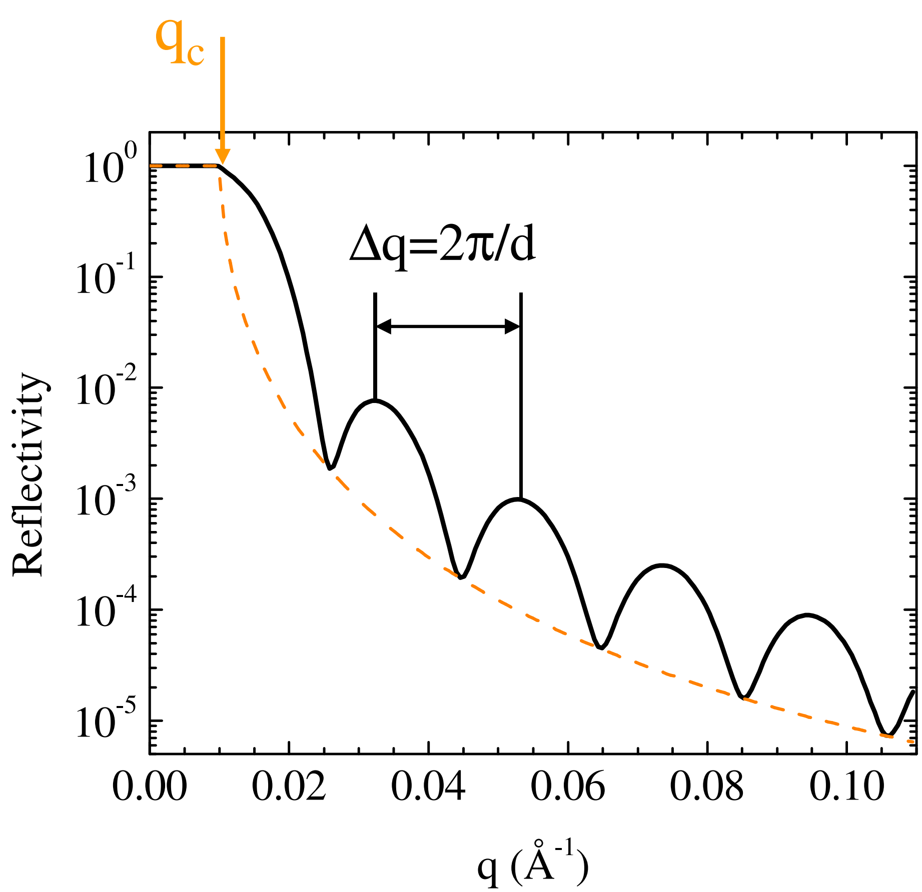
$$q_c = \frac{4\pi}{\lambda}\sin\theta_c \qquad \theta_c = \lambda\sqrt{\frac{\rho b}{\pi}}$$

Si: θ_c=0.11° (for λ=2.37 Å)

^{58}Ni: θ_c=0.28° (for λ=2.37 Å)

Kiessig fringes





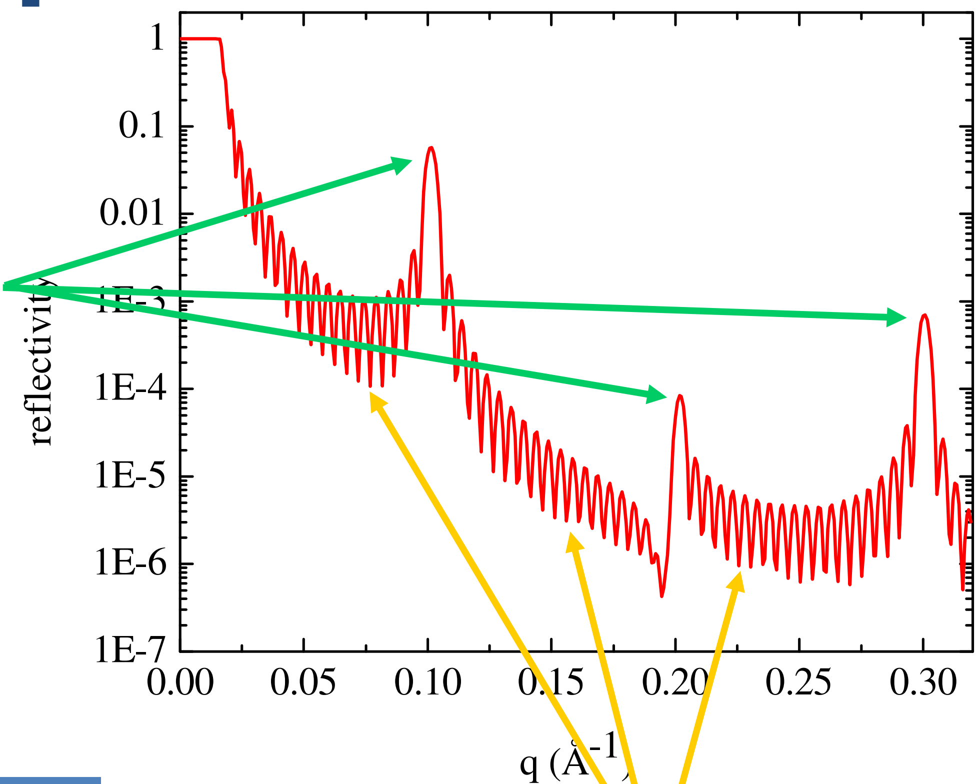
Oscillations due to total film thickness

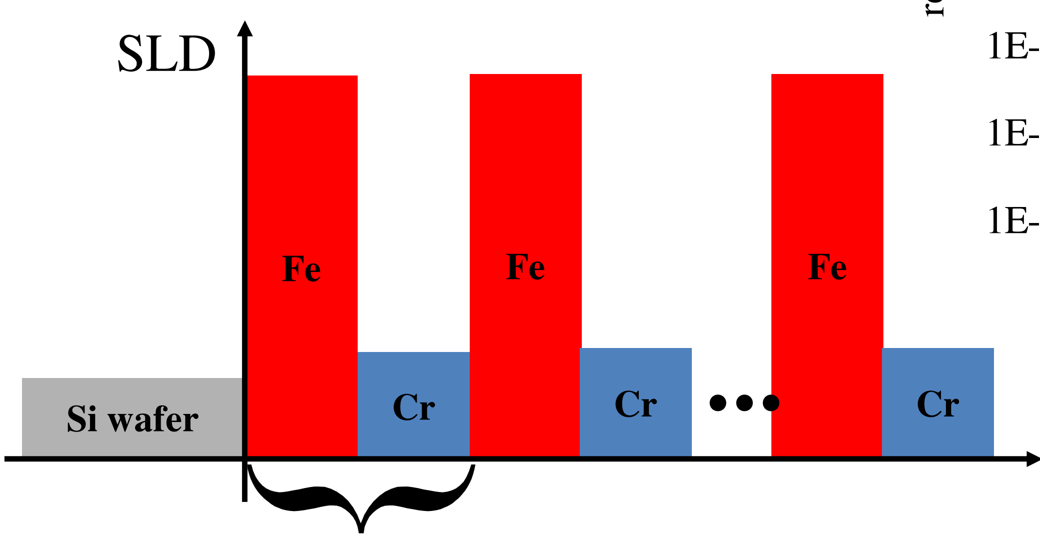
$\Delta q \propto 1/d$

Multilayer Bragg peaks

bilayer Bragg peaks at $q=2\pi/t$

$q = n \cdot 2\pi/62.8\ Å^{-1} = n \cdot 0.1\ Å^{-1}$



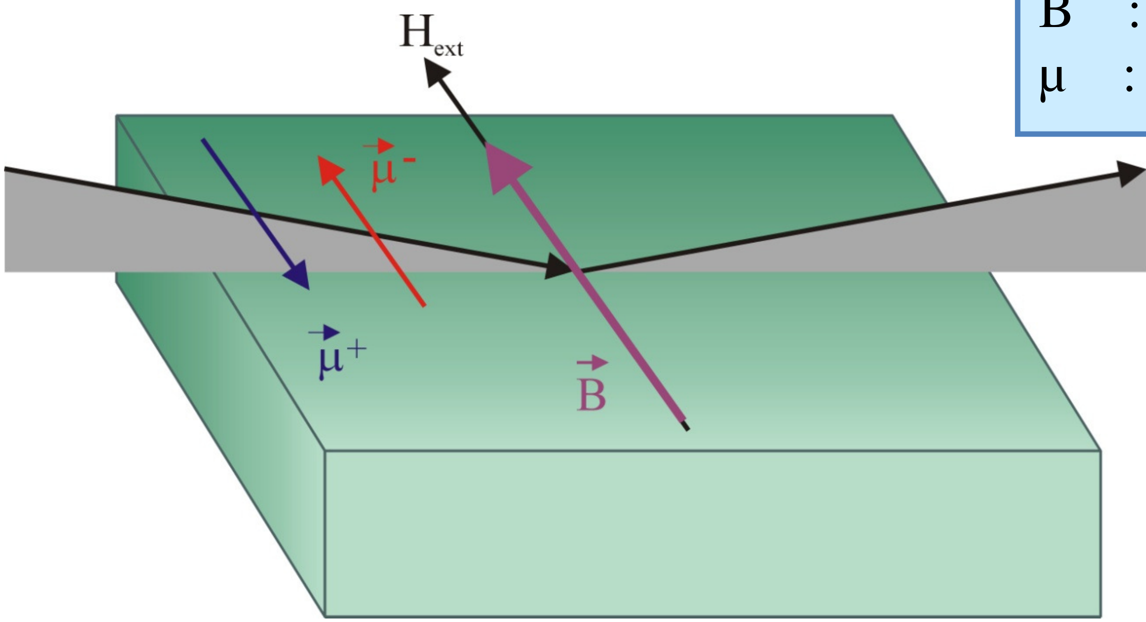


Bilayer thickness t
t = 32.8 Å + 30 Å = 62.8 Å
In total: 20 repetitions

Short period oscillations:
Kiessig fringes

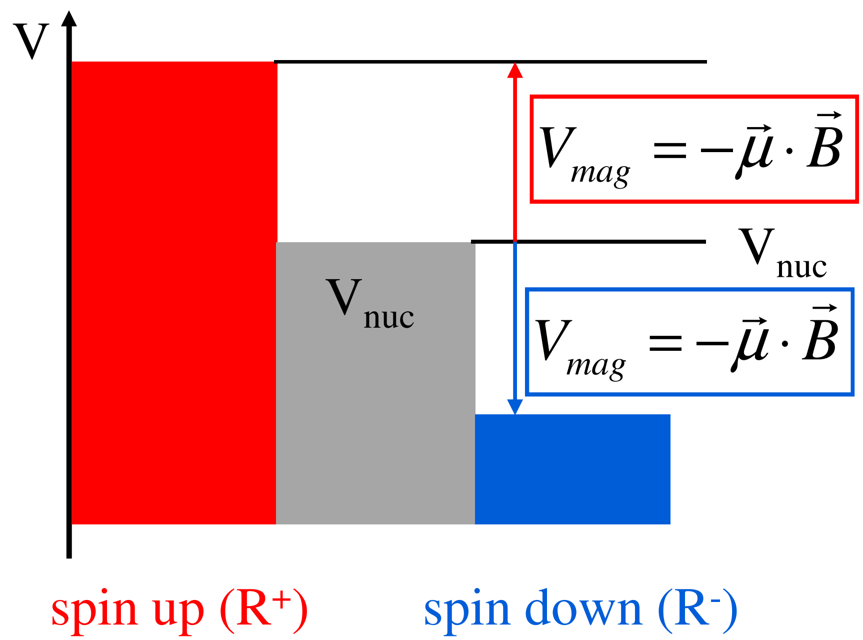
Magnetic interaction

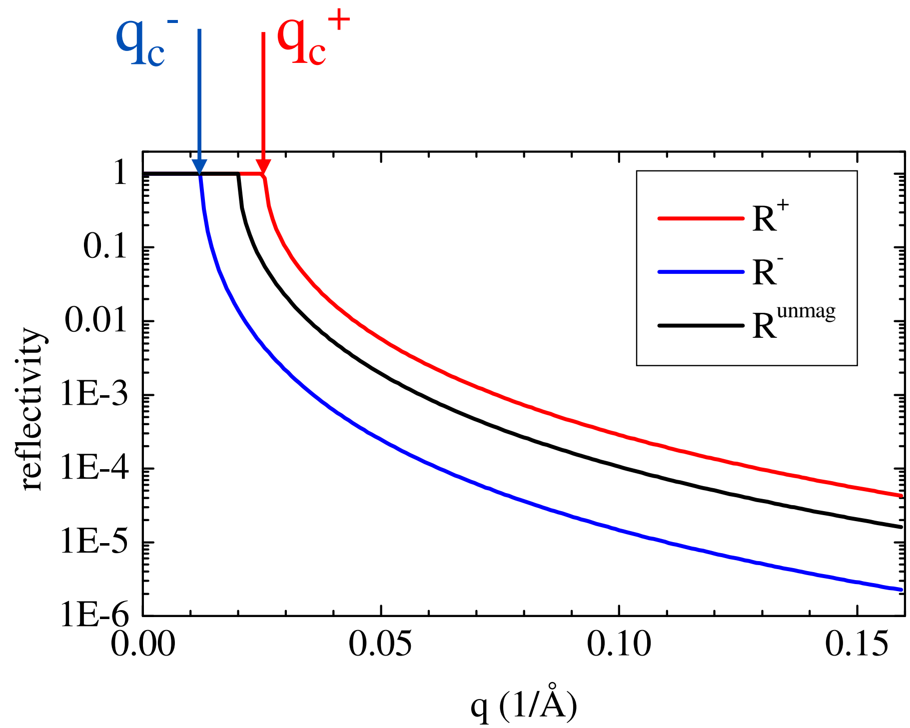
H_{ext}: external magnetic field
B : magnetic induction
μ : magnetic moment of neutrons



$$V = V_{nuc} + V_{mag} = \frac{2\pi\hbar^2}{m}\rho b - \vec{\mu}\vec{B} = \frac{2\pi\hbar^2}{m}\rho\left(b_{nuc} \pm b_{mag}\right)$$

PNR: bulk Fe



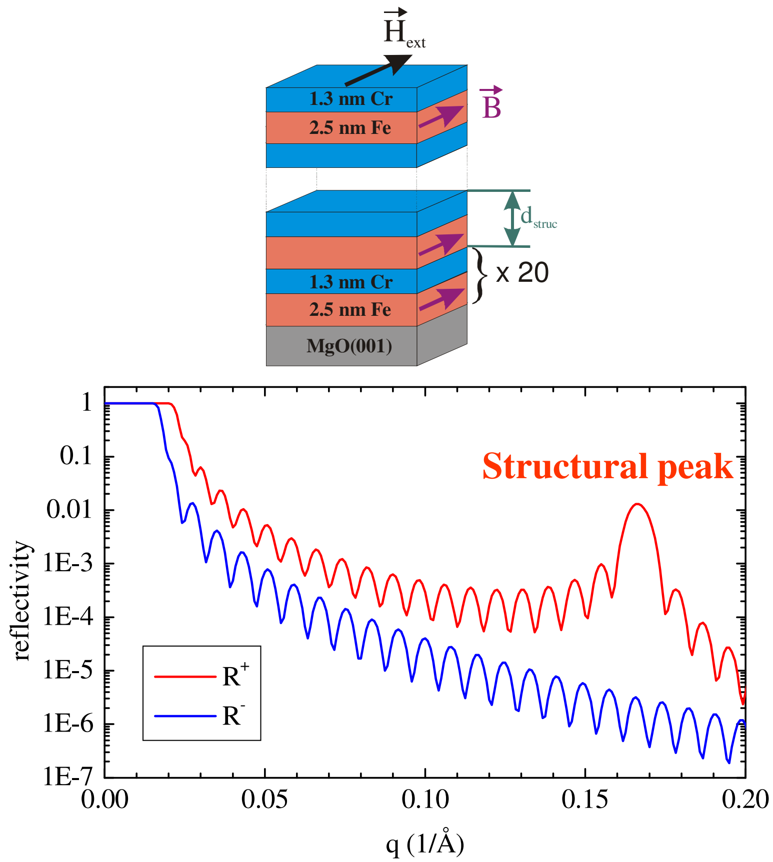


Different reflectivity for spin-up and spin-down neutrons

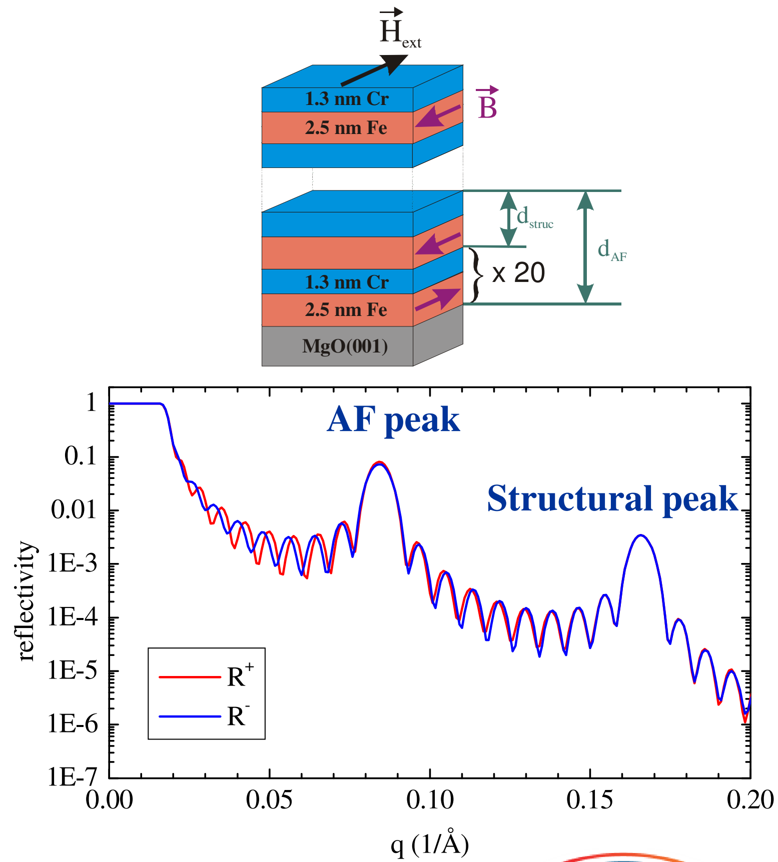
⇒ Determination of the absolute magnetic moment possible

PNR: Fe/Cr multilayers

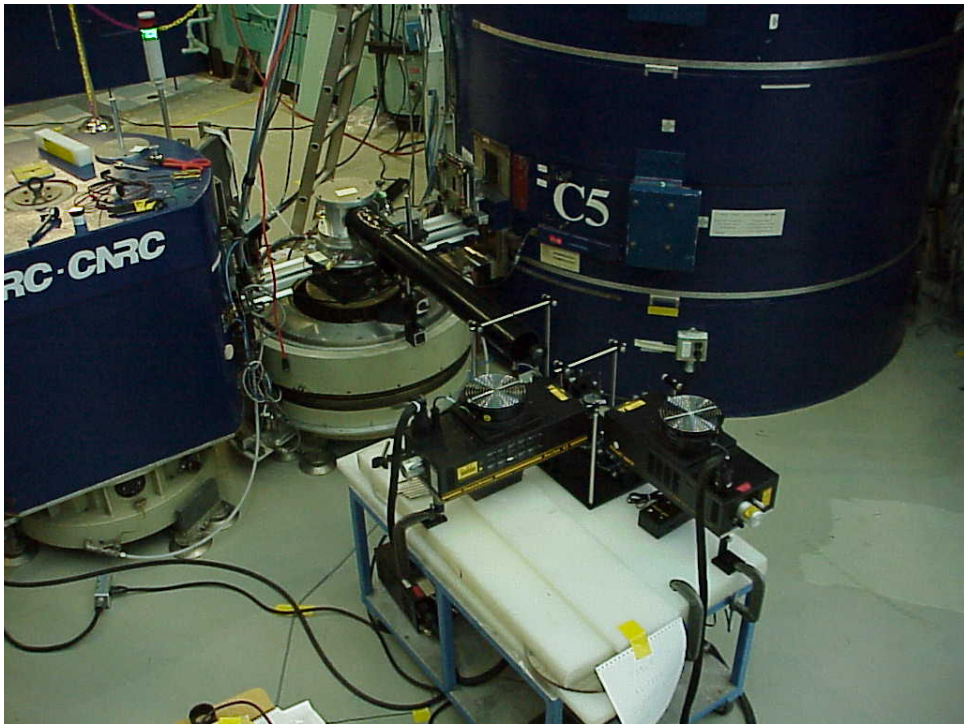
Ferromagnetic coupling:
Magnetic period = chemical period

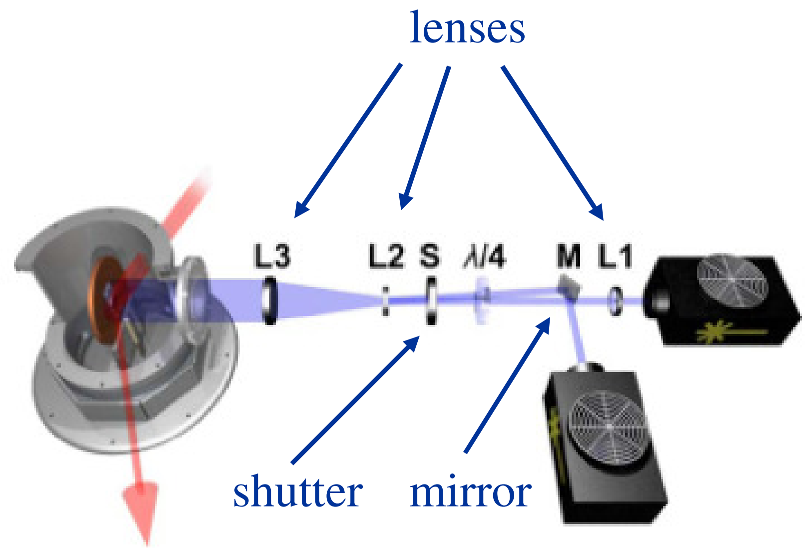


Antiferromagnetic coupling:
Magnetic period = 2 x chemical period



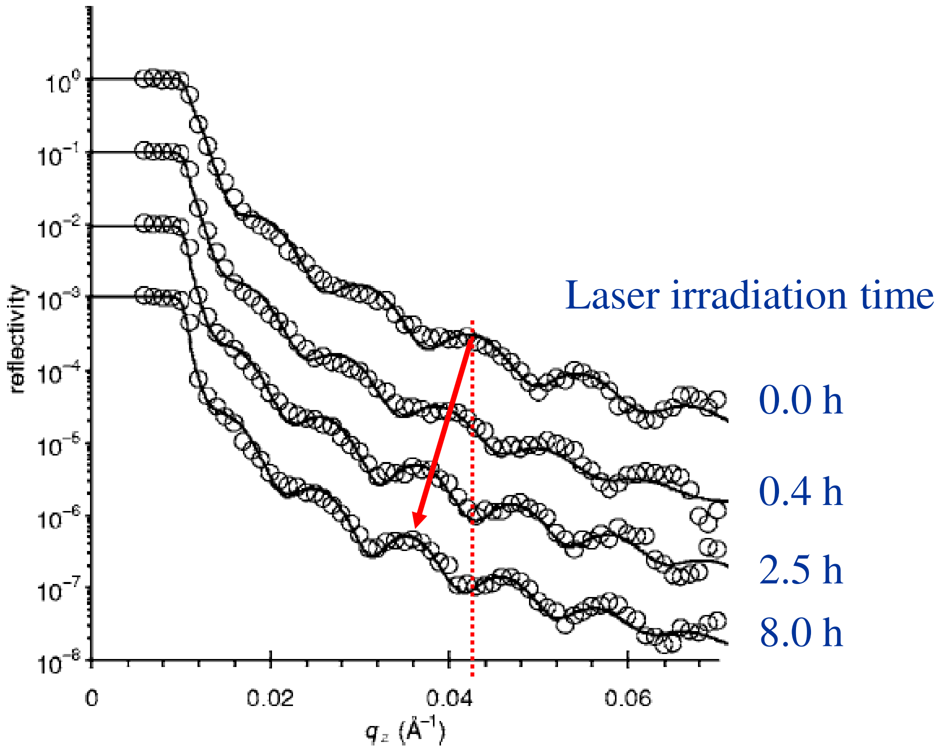
In-situ setup for photoactive films

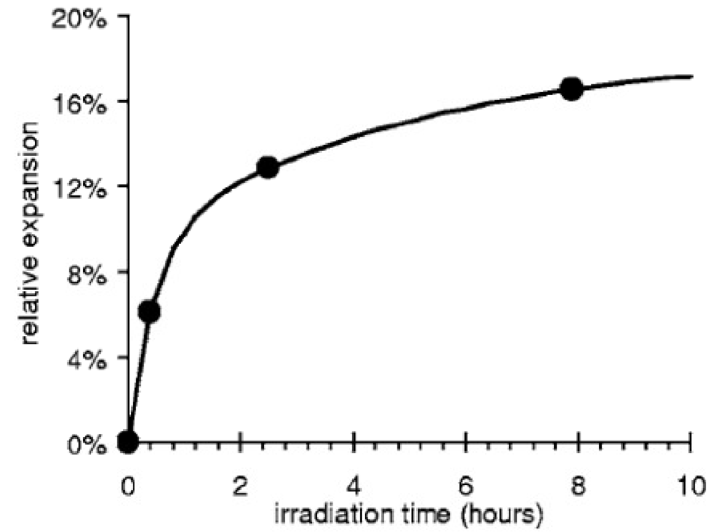




Neutron reflectometry and Laser illumination at the same time

Results for azobenzene films





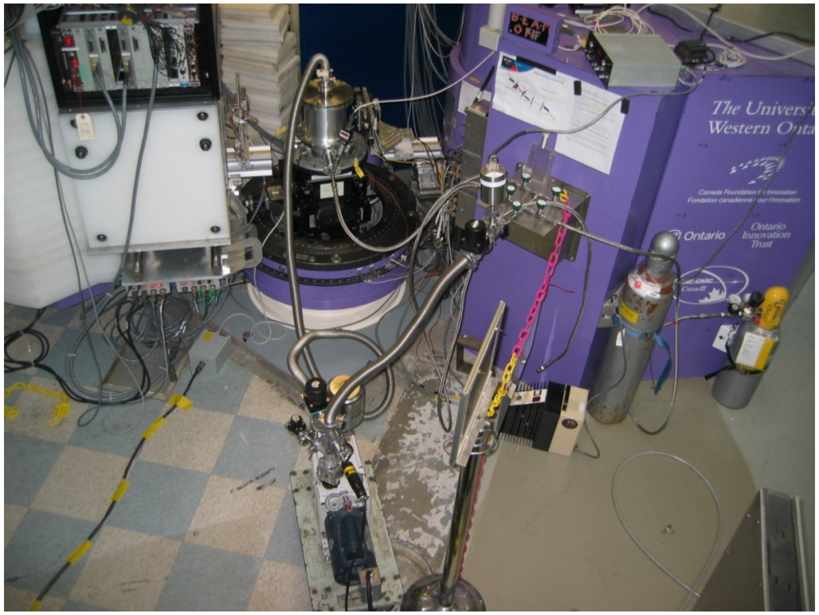
Smaller Δq ⇒ larger film thickness

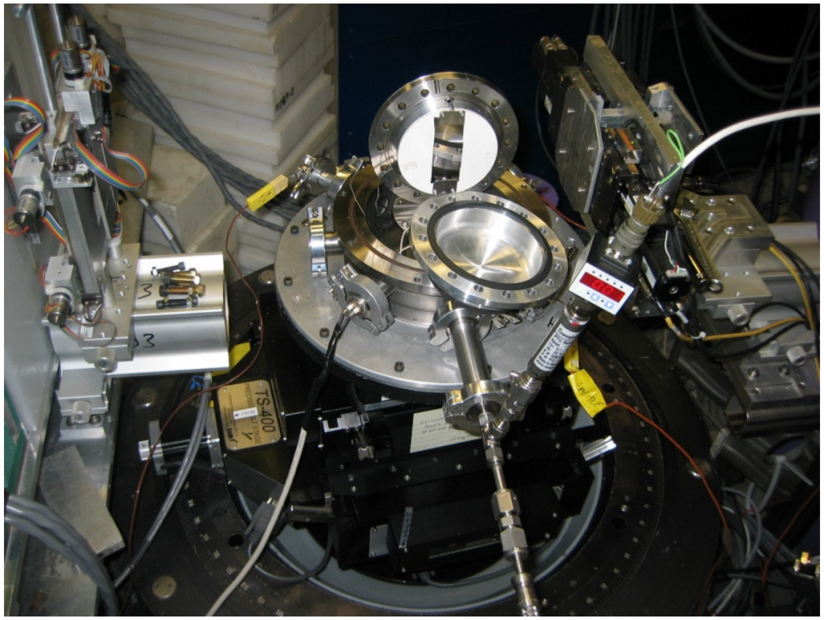
K. Yager, O. M. Tanchak, C. Godbout, H. Fritzsche, and C. Barrett
Photomechanical effects in azo-polymers studied by neutron reflectometry
Macromolecules **39**, 9311 (2006); citations: 42

From summer school to real experiments in 2 months

Kevin Yager, Oleh Tanchak:
Neutron summer school: June 2004
First experiments: August 2004

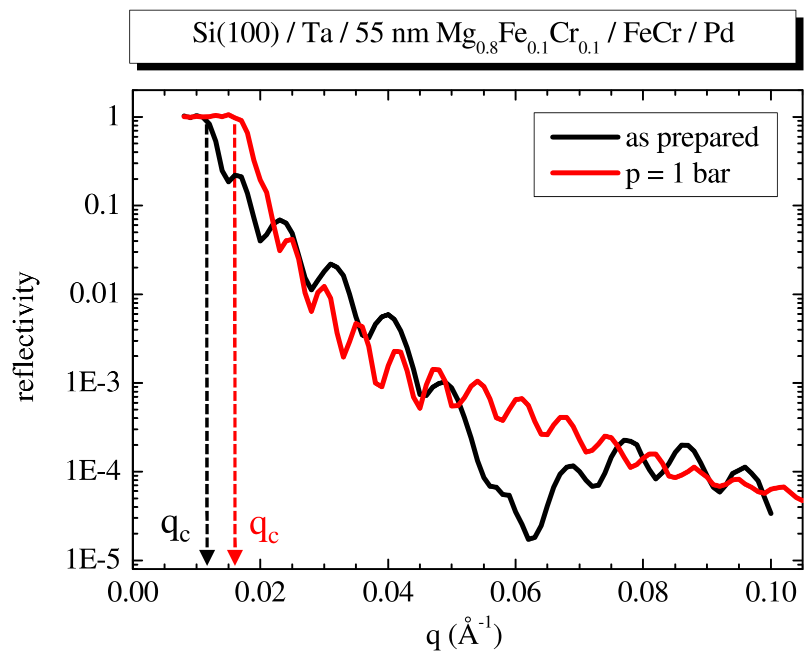
sample cell for hydrogen absorption

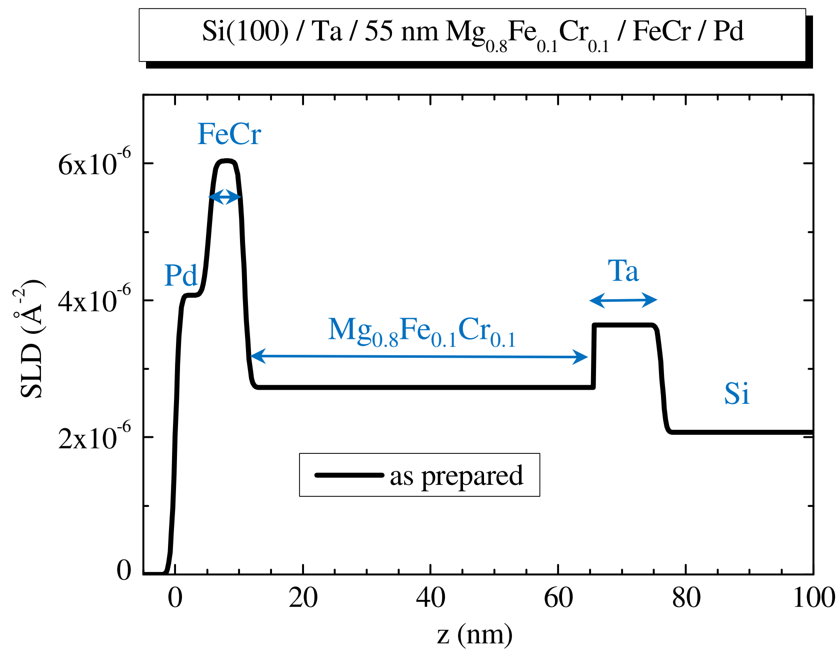




In-situ hydrogen absorption:
Up to 400º C, 40 bar

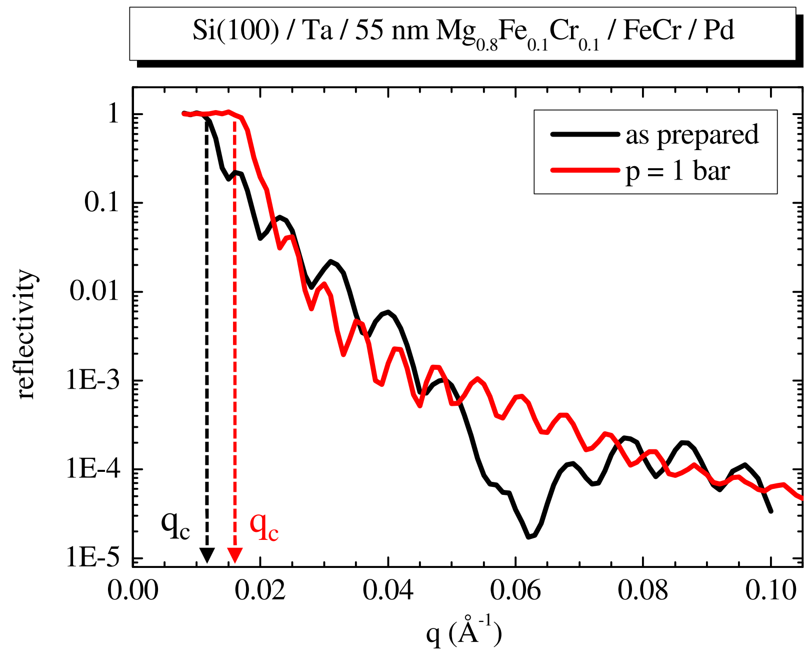
Deuterium absorption at RT

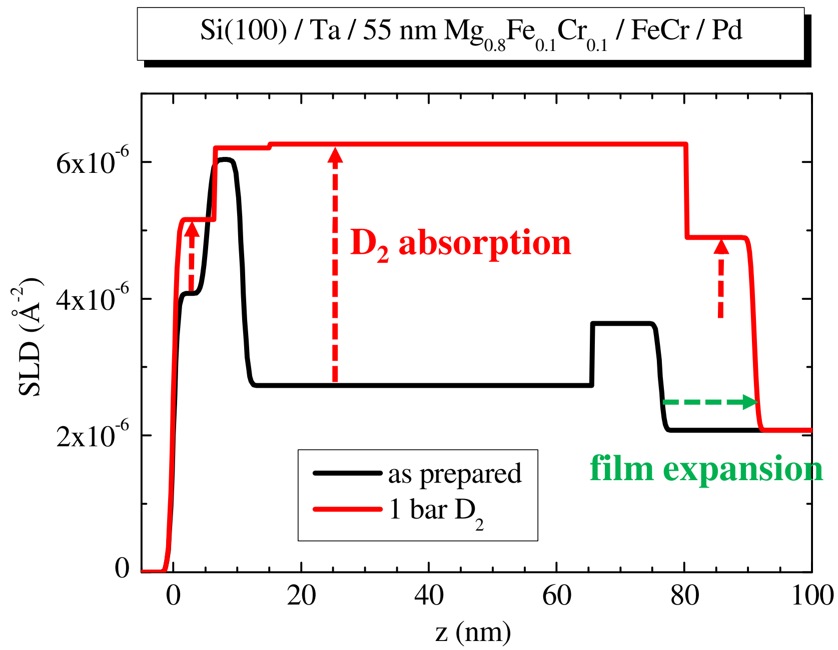




i) q_c increases upon D_2 absorption $\Rightarrow$ MgFeCr is absorbing D_2
ii) The frequency of the Kiessig oscillation increases $\Rightarrow$ film is expanding

Deuterium absorption at RT





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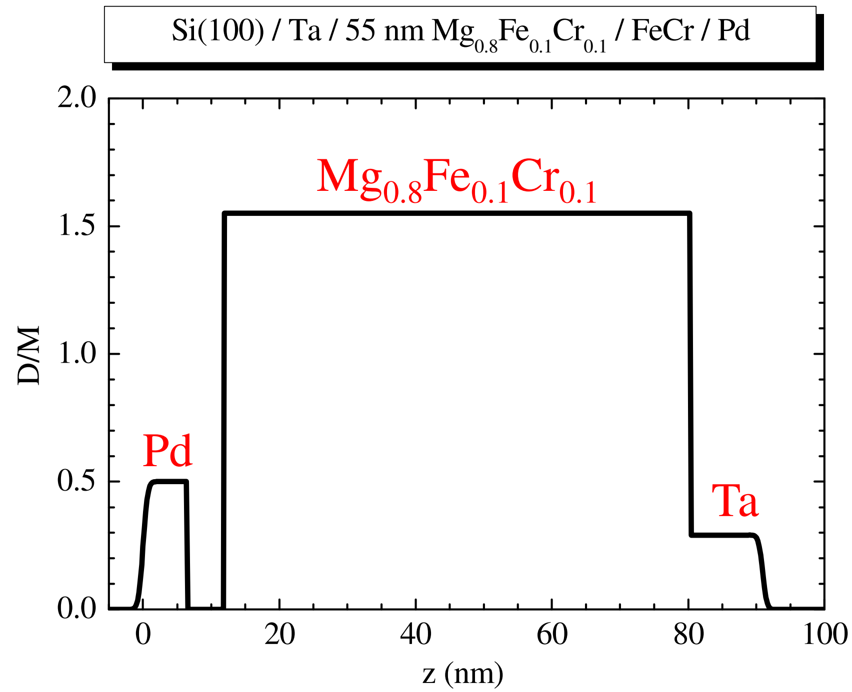
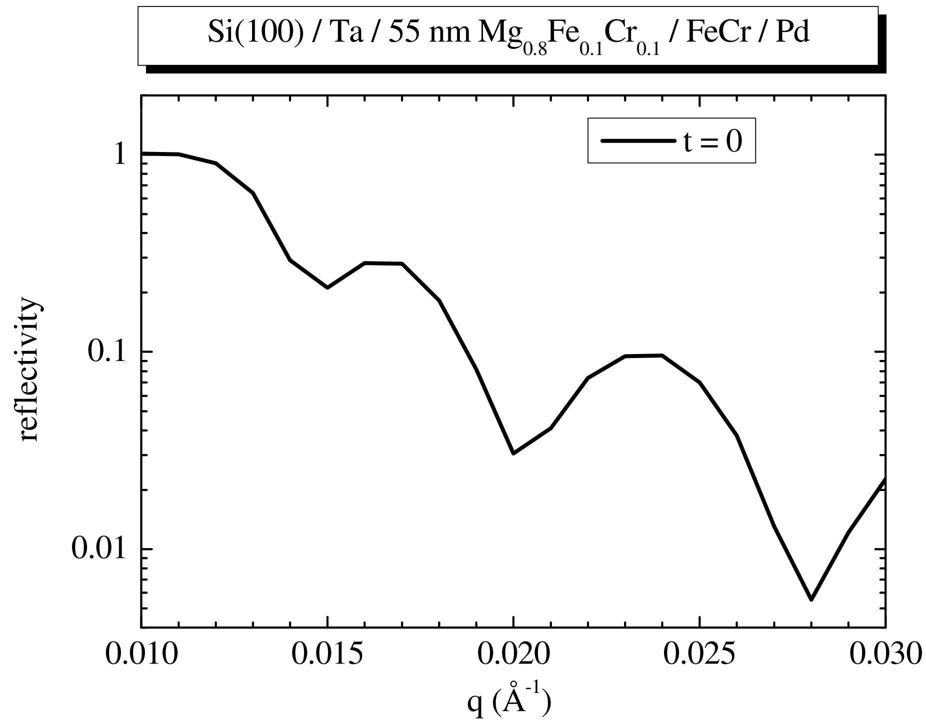
Deuterium concentration profile

$$c_{deut} = \left(\frac{SLD_{deut}}{SLD_M} \cdot \frac{t_{deut}}{t_M} - 1\right)\frac{b_M}{b_D}$$



- Absorption in $Mg_{0.8}Fe_{0.1}Cr_{0.1}$ up to D/M=1.55 (almost all Mg reacts to MgD_2)
- Film expands by 20%

Kinetics at RT and 8 mbar D_2: The reflectivity curve



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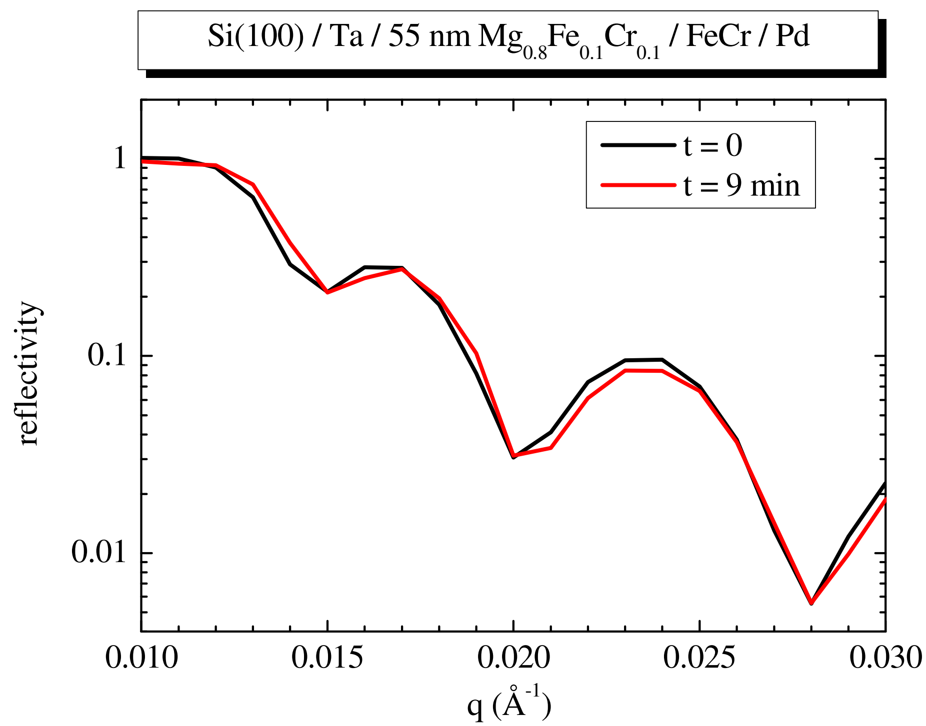

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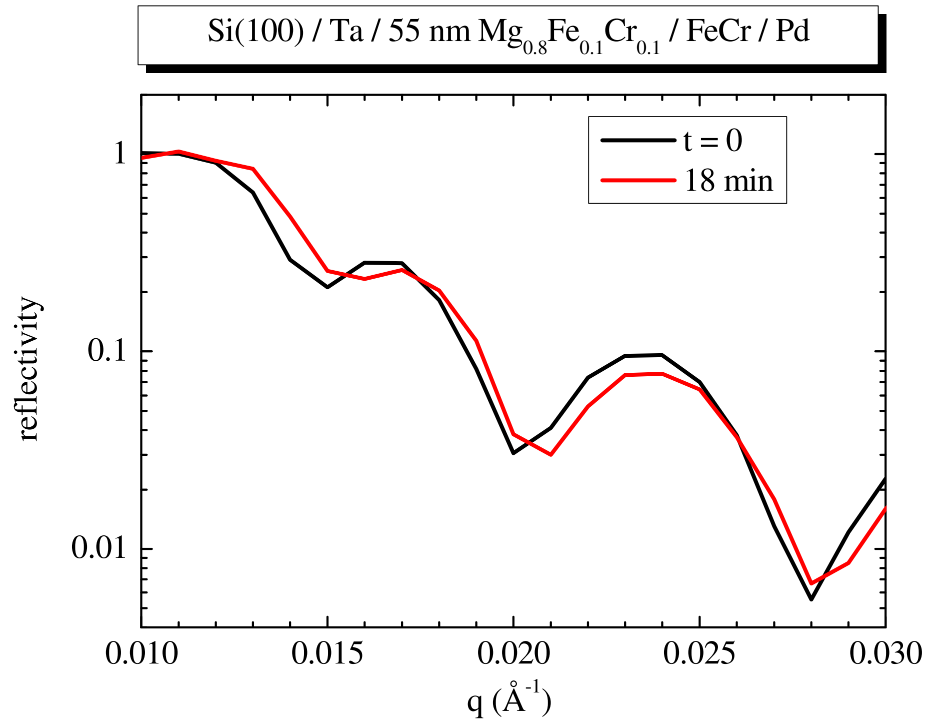

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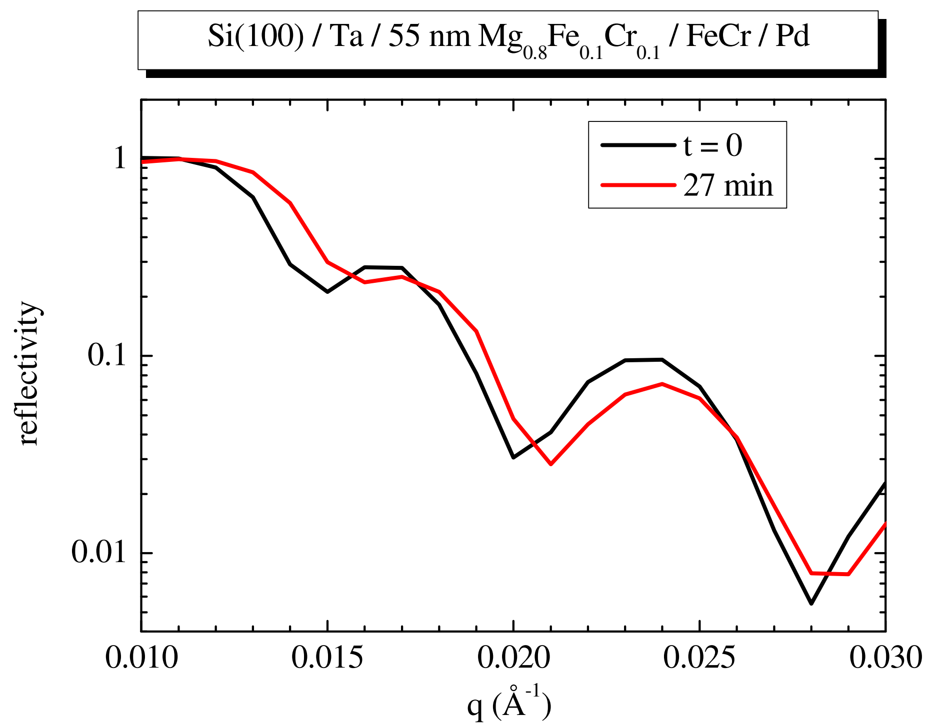

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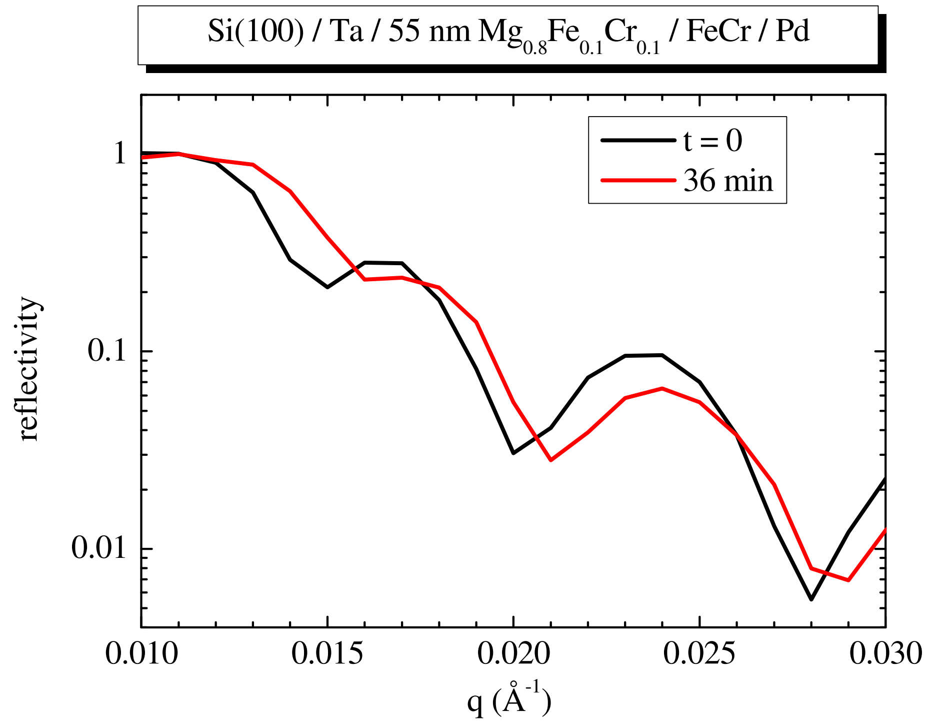

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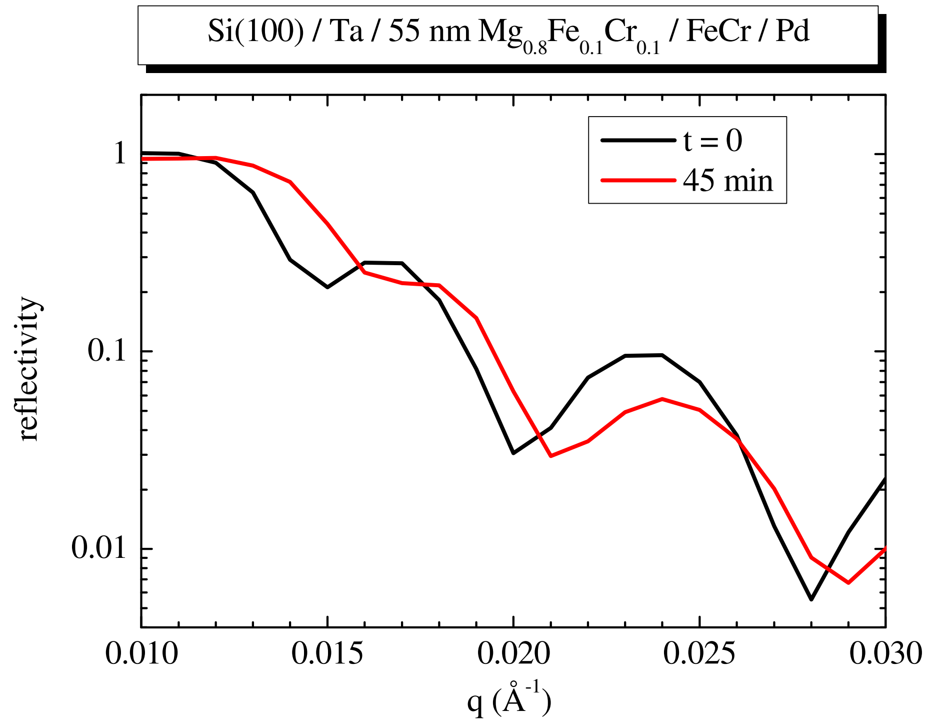

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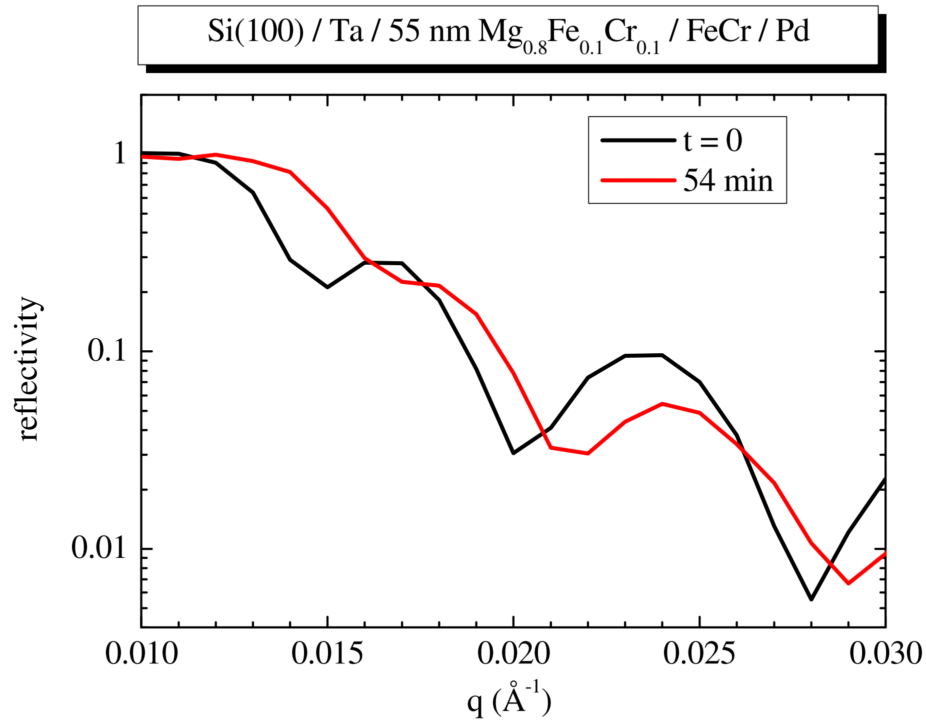

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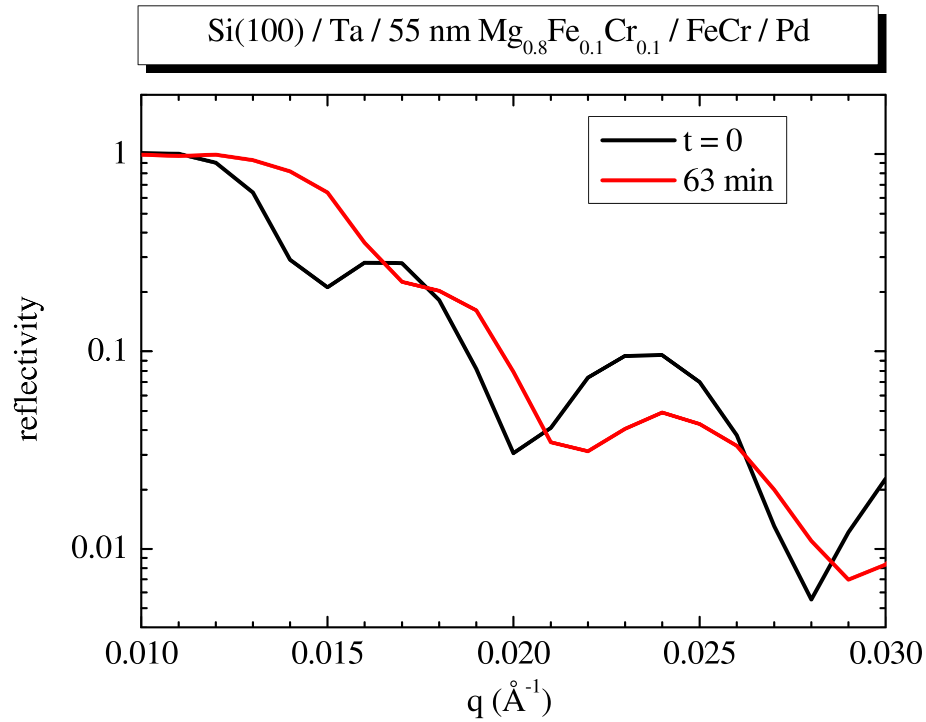

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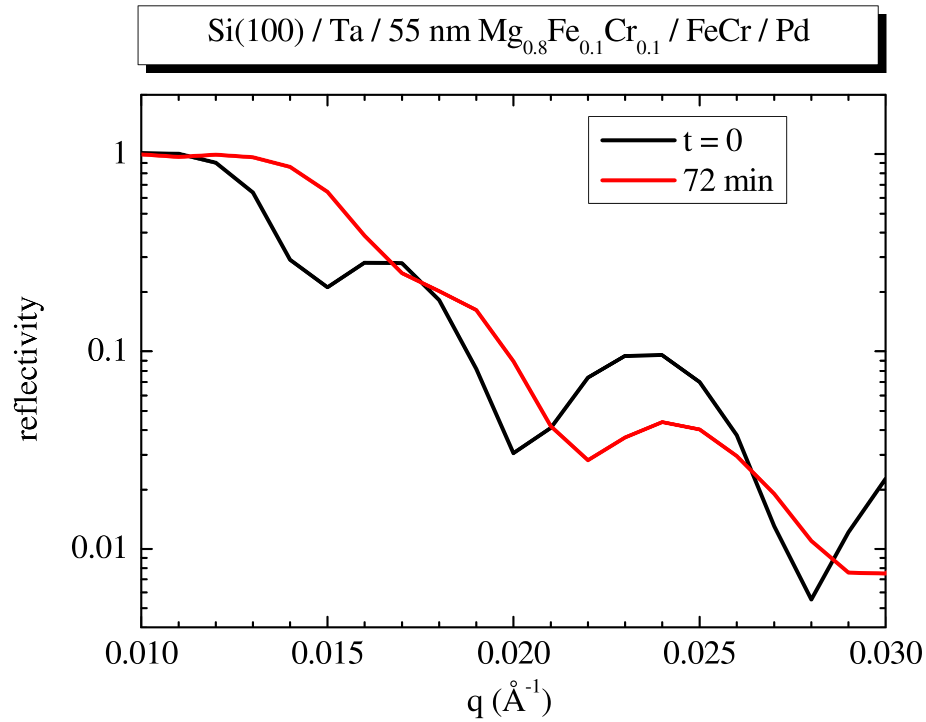

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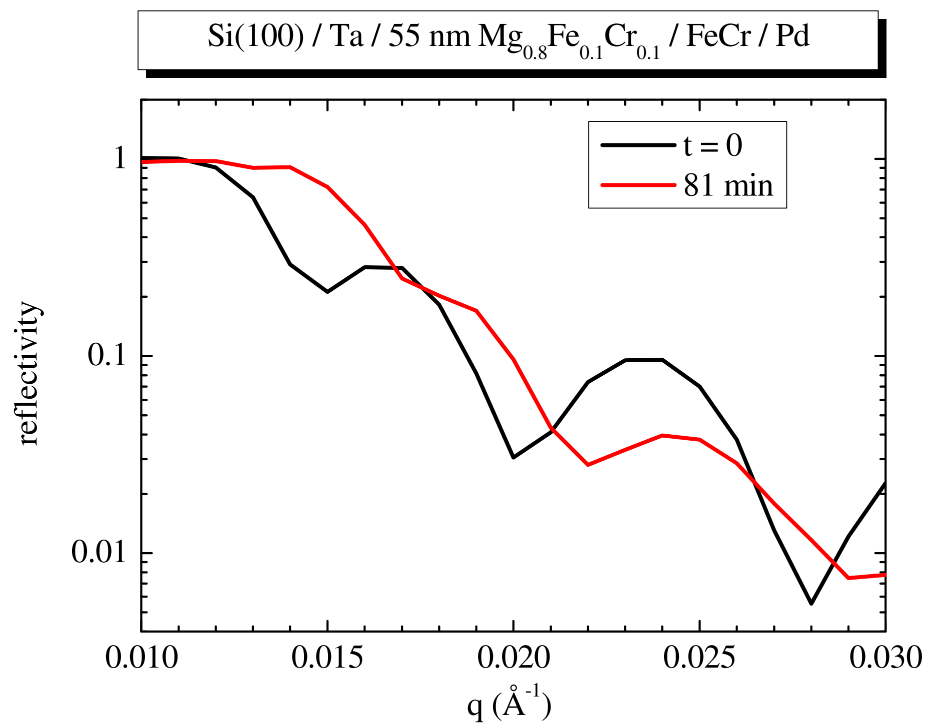

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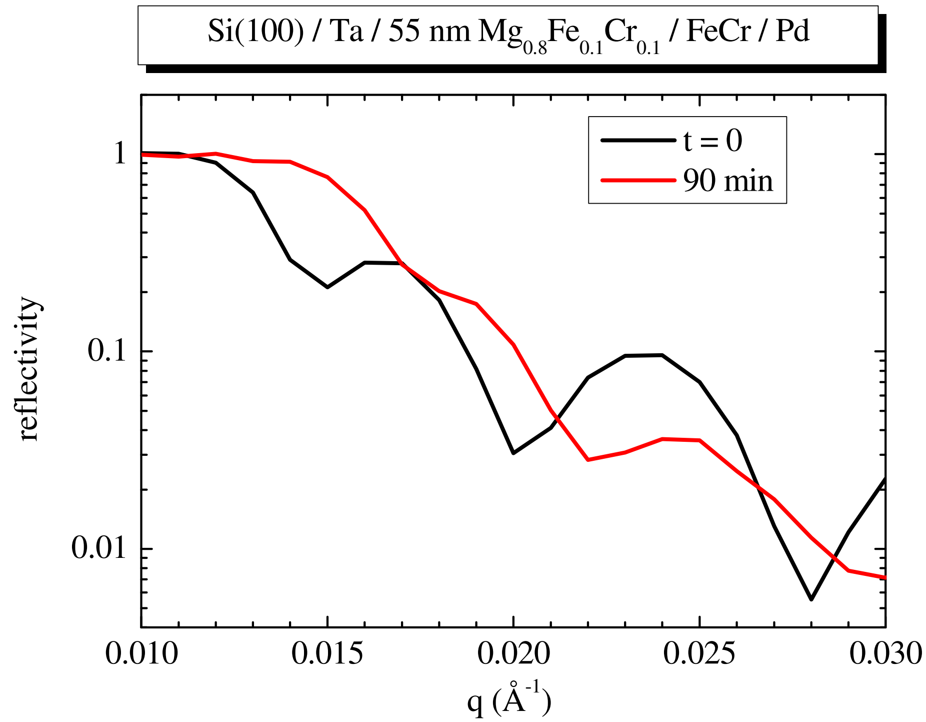

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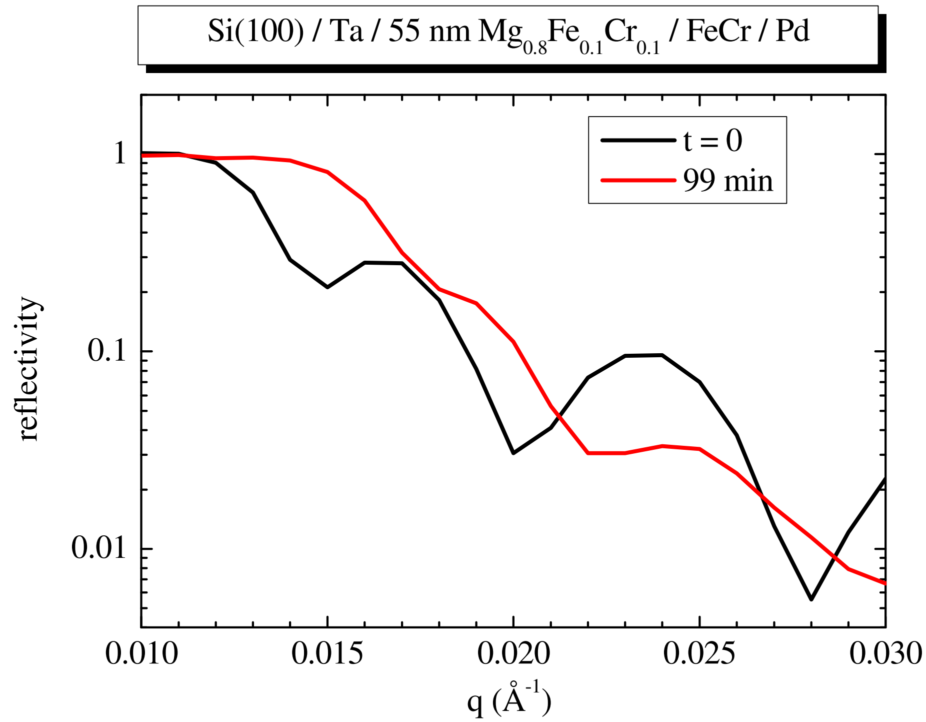

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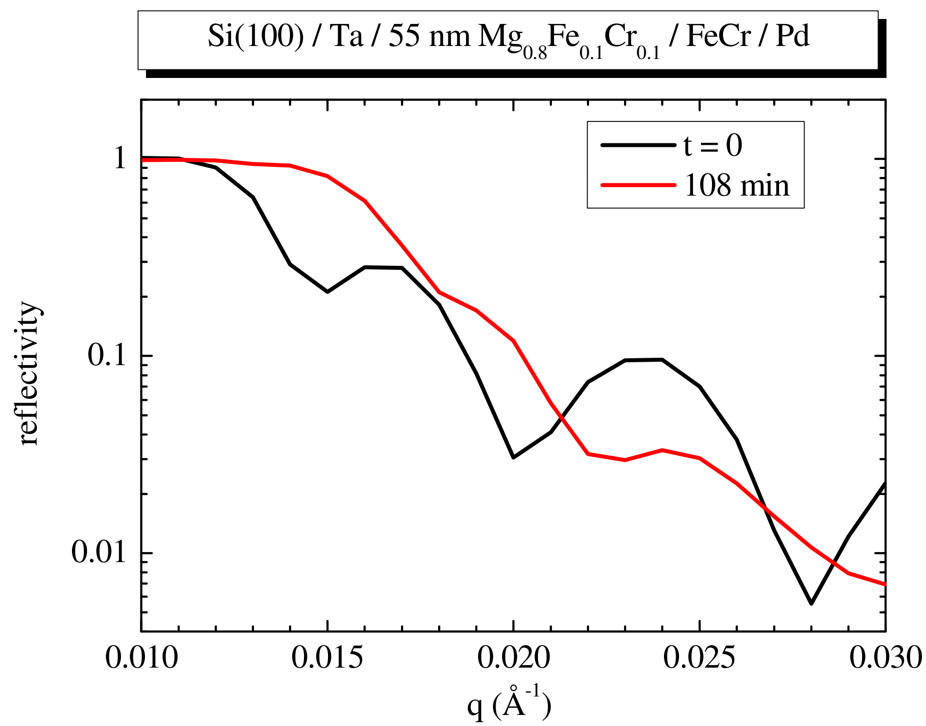

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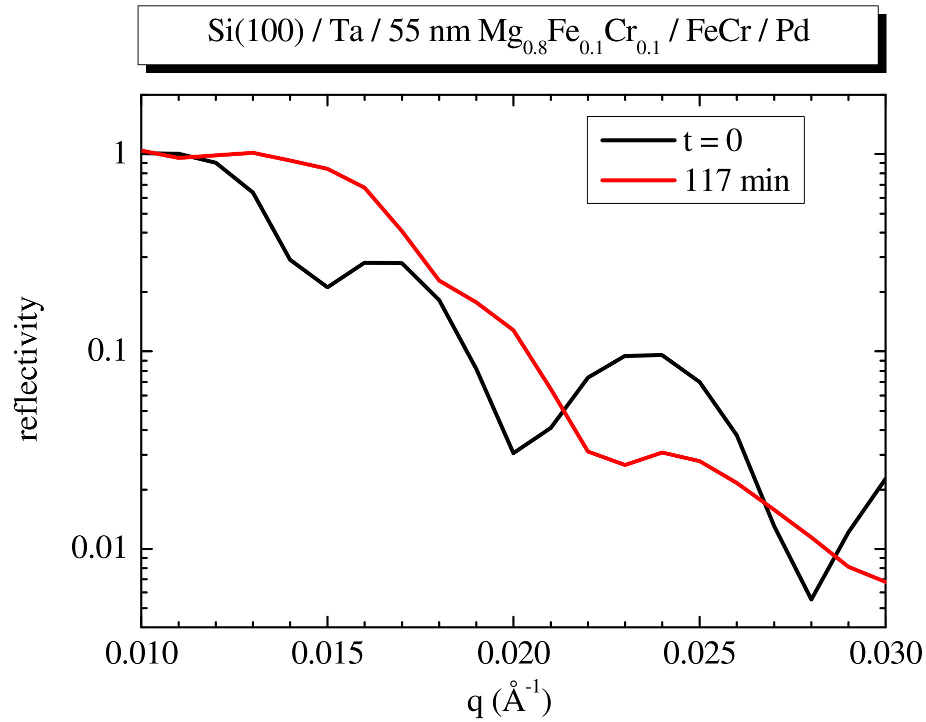

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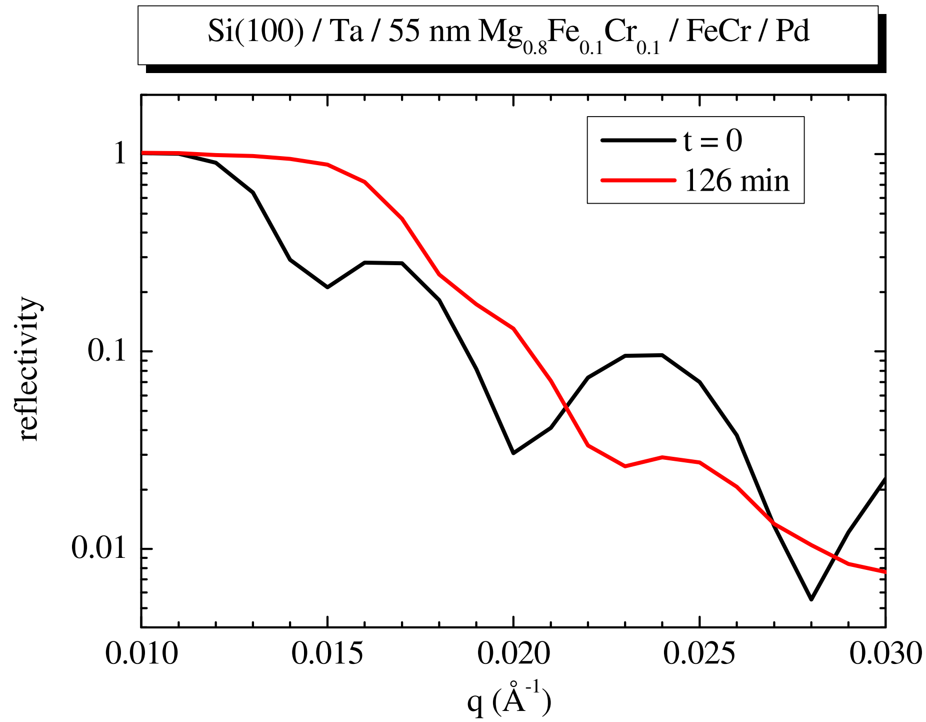

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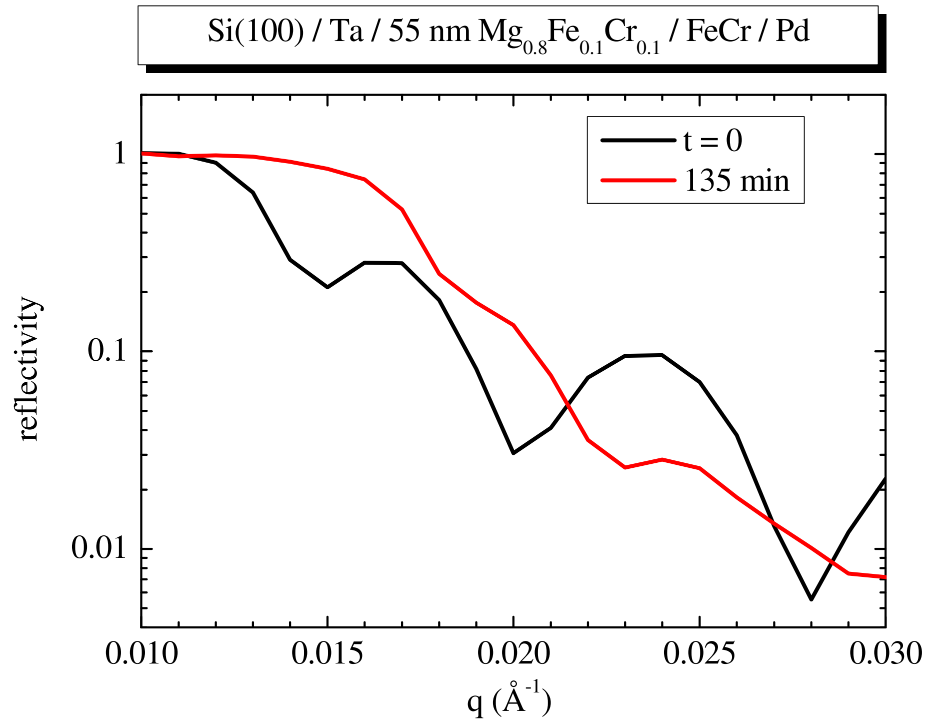

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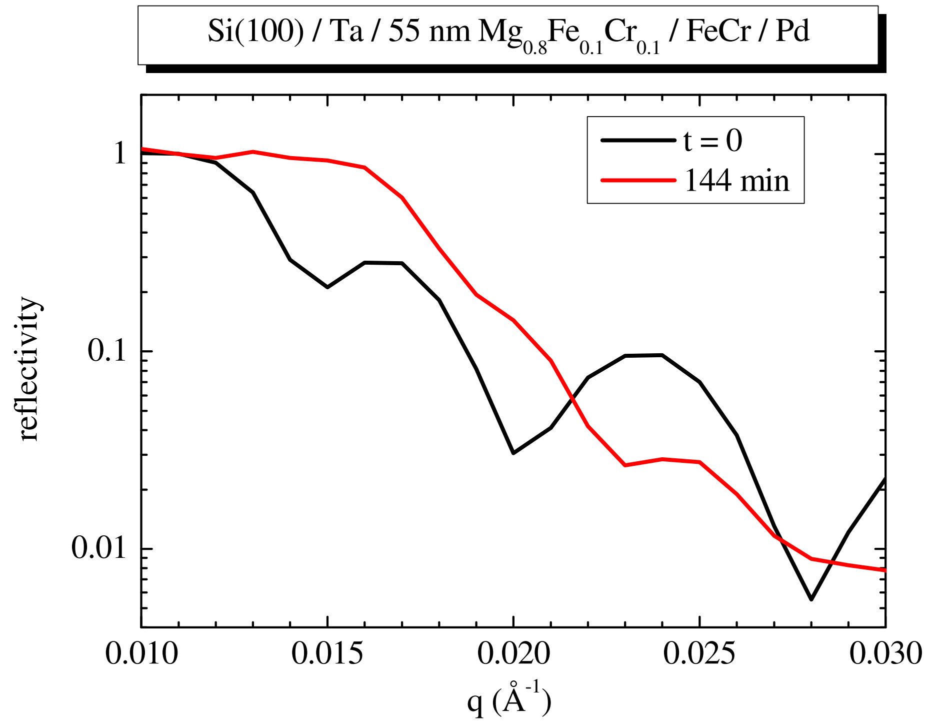

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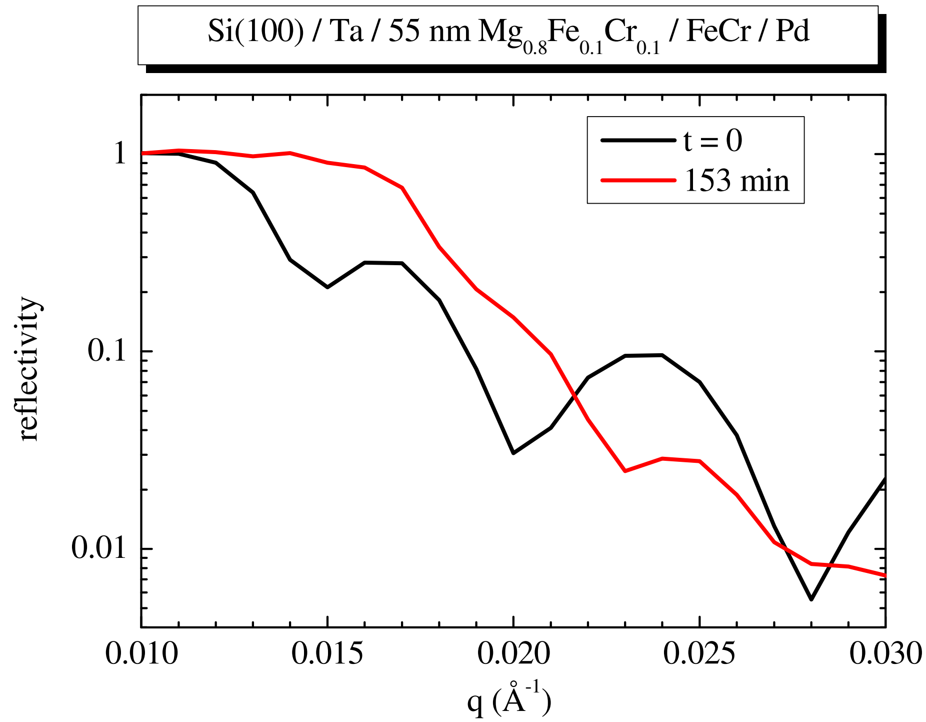

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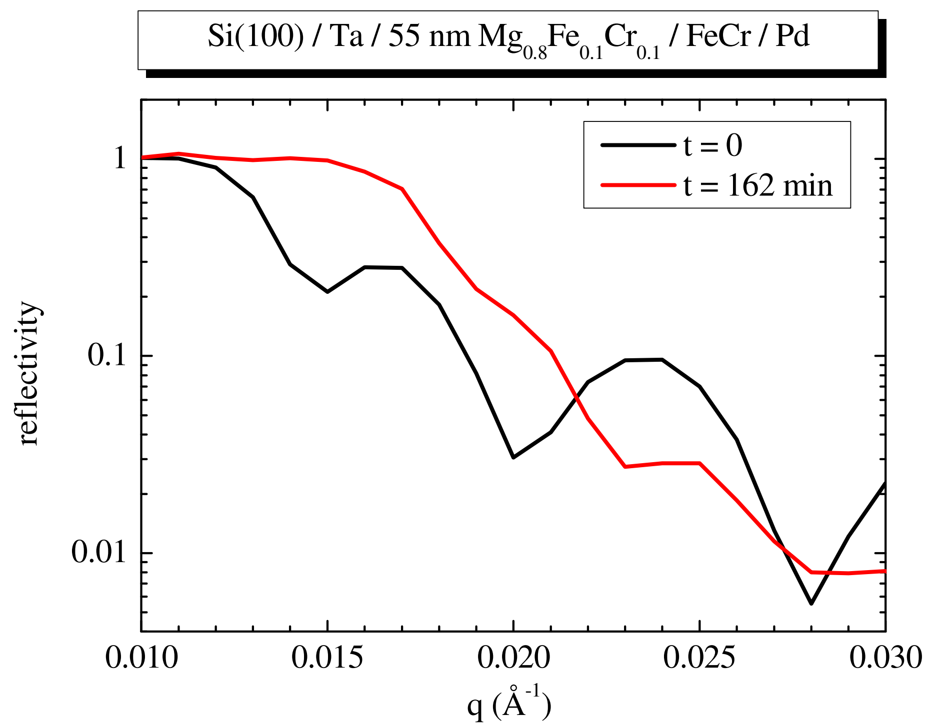

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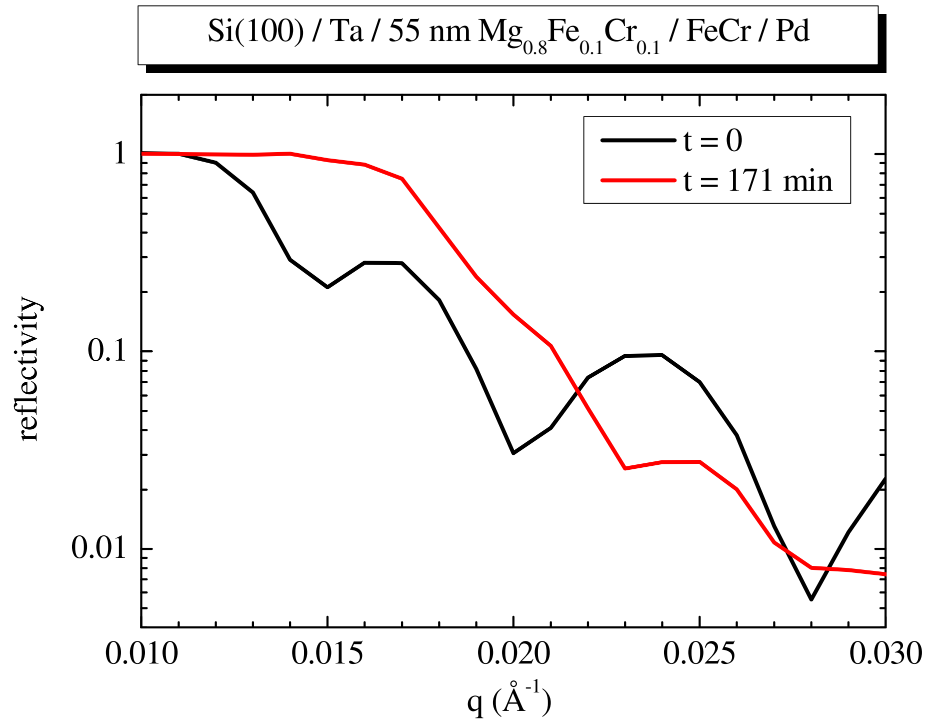

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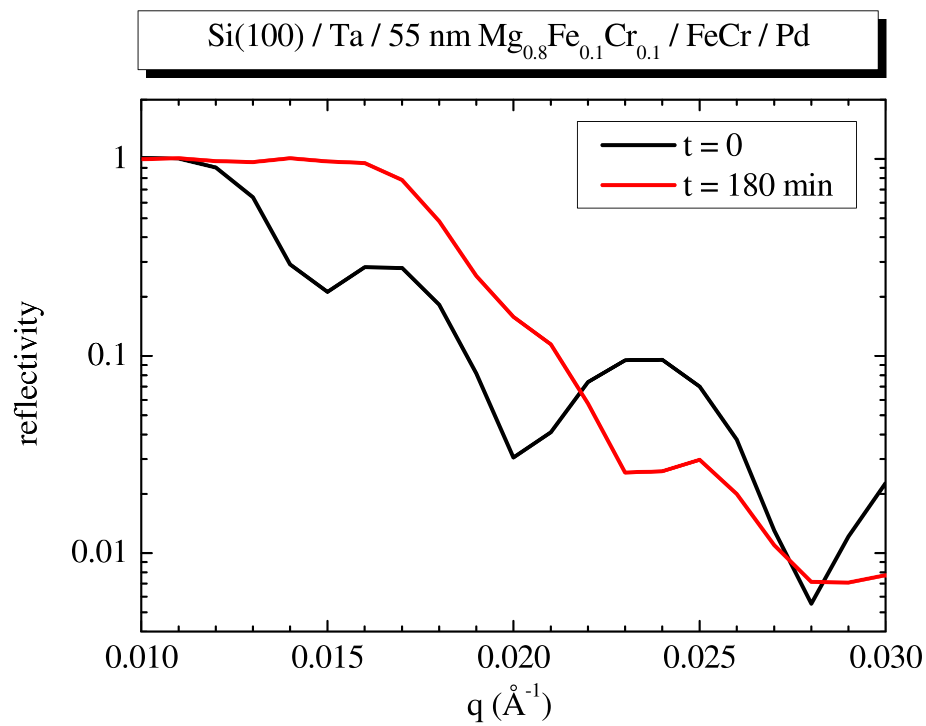
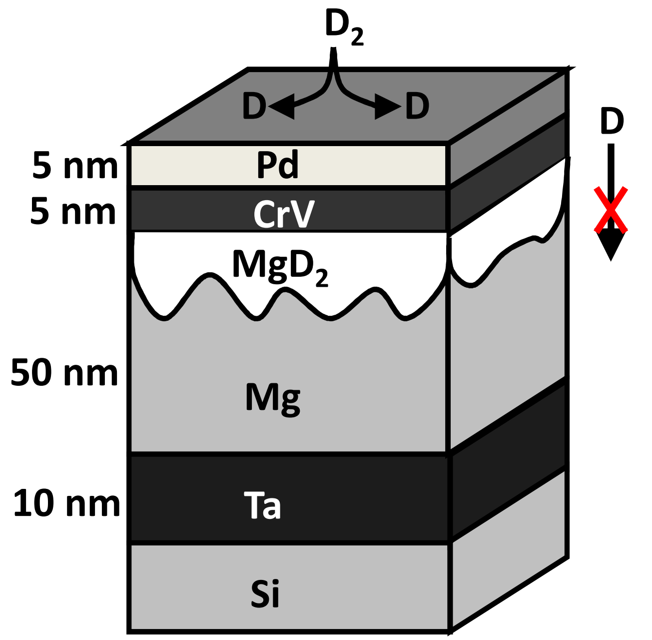


Mg vs. MgFeCr: different mechanisms



Mg: formation of blocking MgD_2 layer

P. Kalisvaart, E. Luber, H. Fritzsche, D. Mitlin, Chem. Commun. **47**, 4294 (2011)

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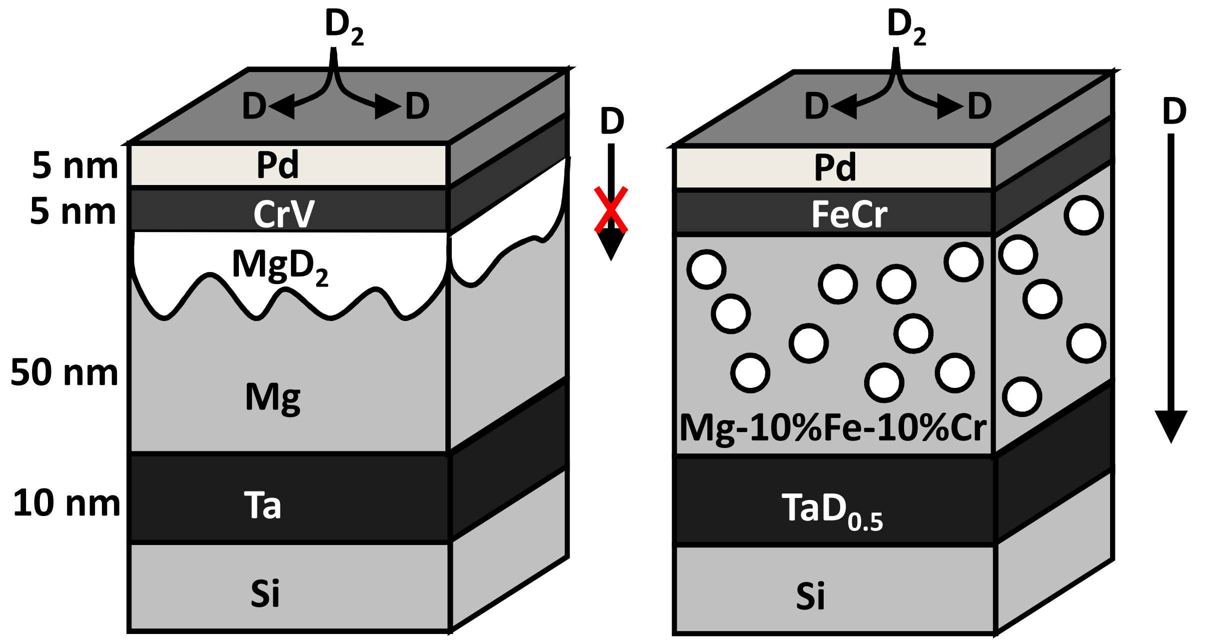


Mg: formation of blocking MgD_2 layer

Fe and Cr segregation leads to:

- many nucleation sites
- homogeneous hydrogenation

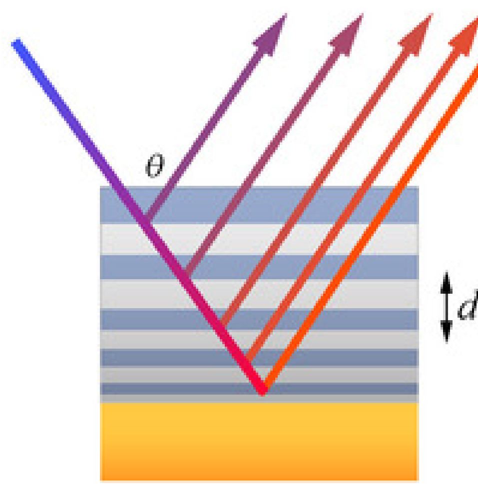
H. Fritzsche, W. P. Kalisvaart, B. Zahiri, R. Flacau, and D. Mitlin, Int. J. Hyd. Energy **37**, 3540 (2012)

supermirror

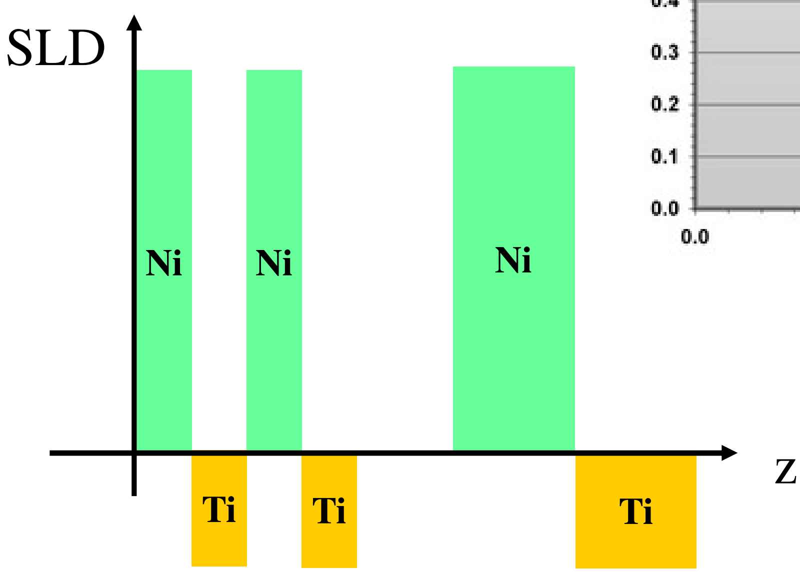
goal:
Extend the range of neutron reflection beyond the regime of total reflection

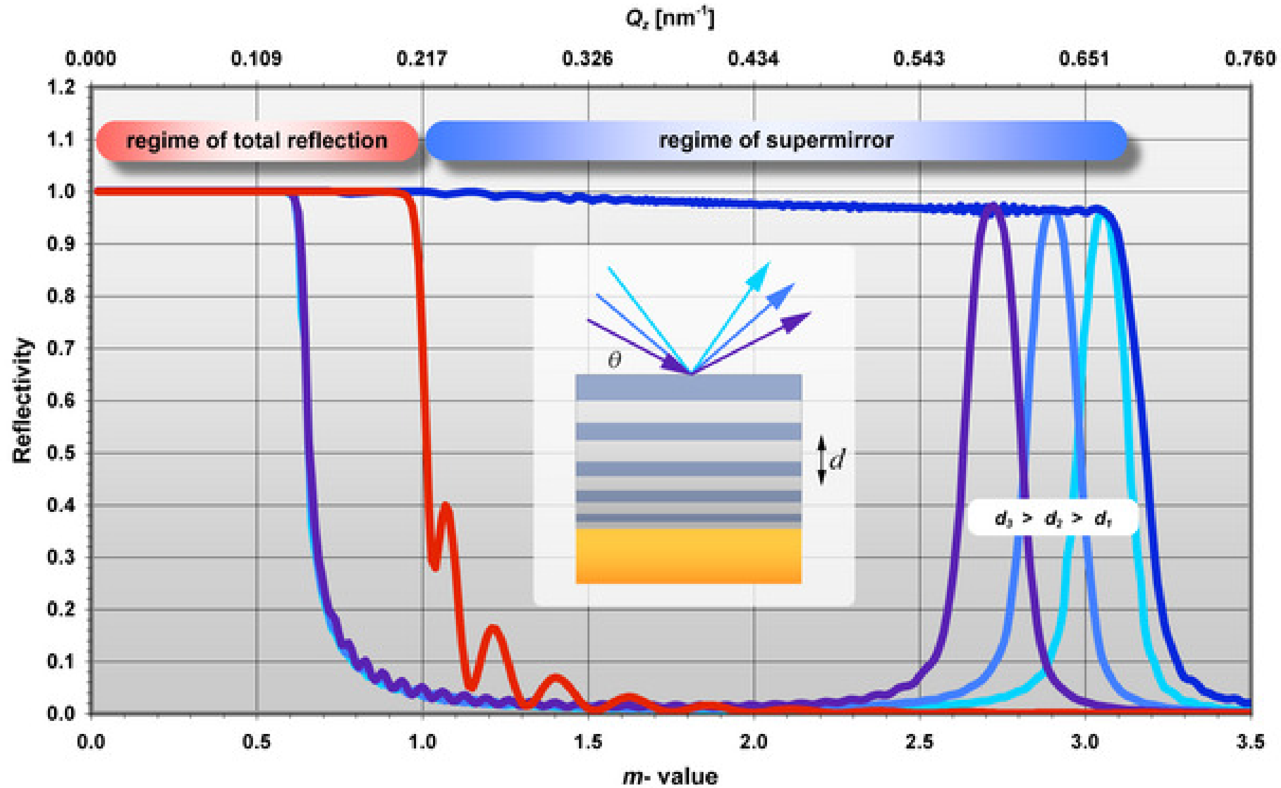
concept:
continuous Bragg reflection from a multilayer composed of bilayers with a variation of the thickness

realization:
Ni/Ti multilayer, b_{Ni} = 10.3 fm, b_{Ti} = -3.4 fm
100 bilayers,
$q_c = 2 \times q_{c,\, Ni}$



supermirror



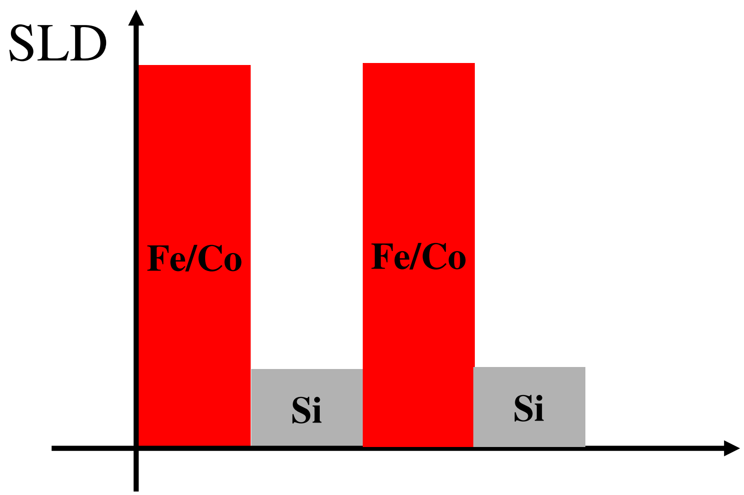


m-value: $m = q_c / q_{c, Ni}$

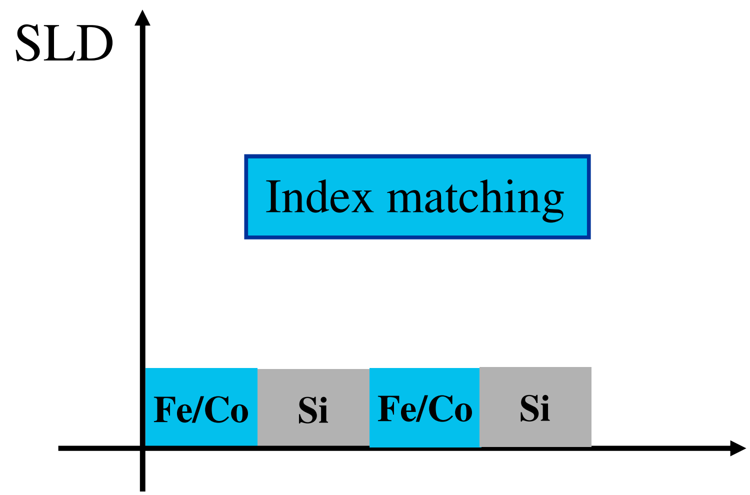
Polarizing supermirror

<u>concept:</u>
Using the supermirror concept with a magnetic/non-magnetic bilayer
The SLD of the bilayer is index-matched for spin-down neutrons
no multilayer Bragg peaks for down-neutrons
Spin-up neutrons show supermirror behavior with extended critical edge

spin-up neutrons

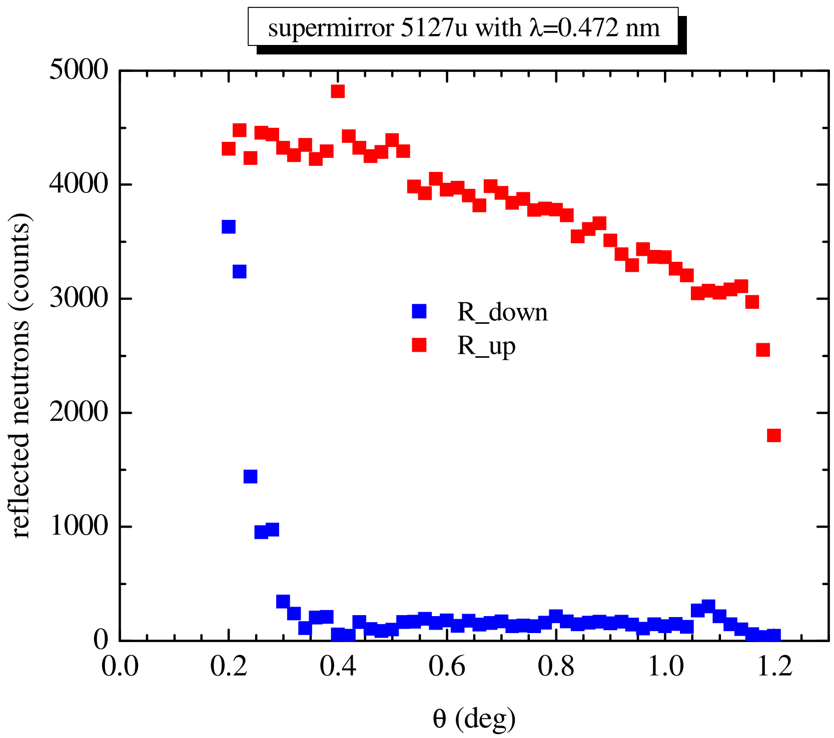


spin-down neutrons

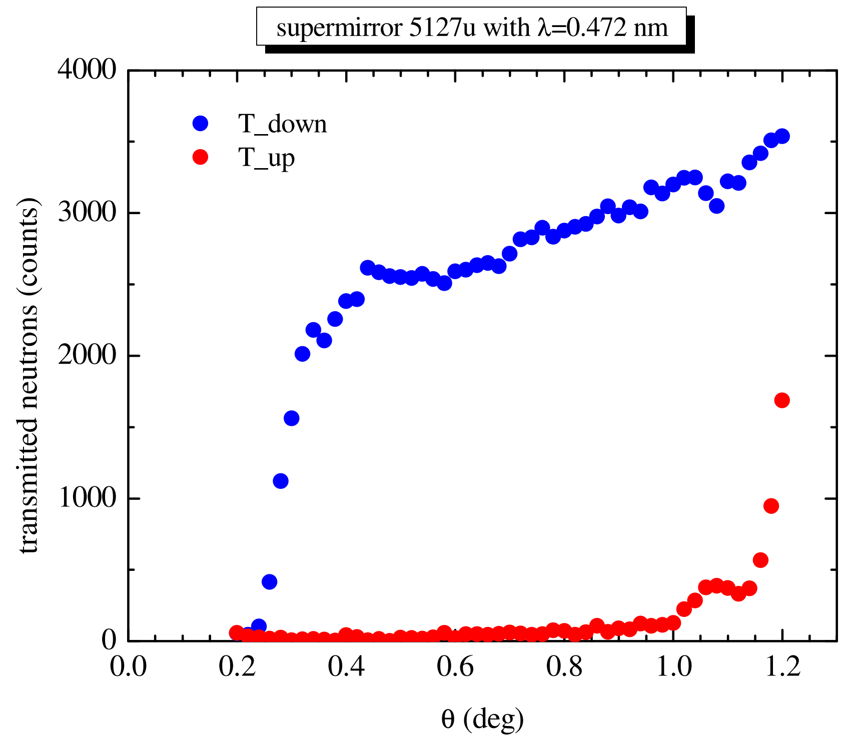


Fe-Co/Si polarizing supermirror

Reflected intensity

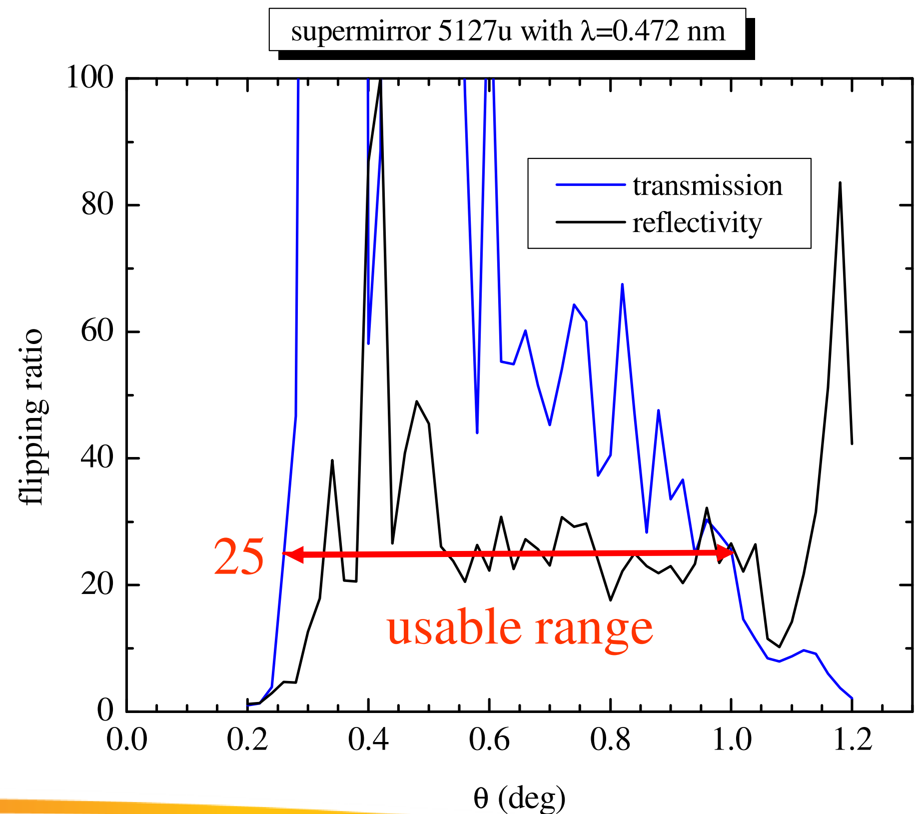


Transmitted intensity



Supermirror: flipping ratio

$$\text{Flipping ratio} = \frac{R^+ - R^-}{R^+ + R^-}$$



Discussion

Thank-you