Neutron reflectometry at CMRR reactor and its applications

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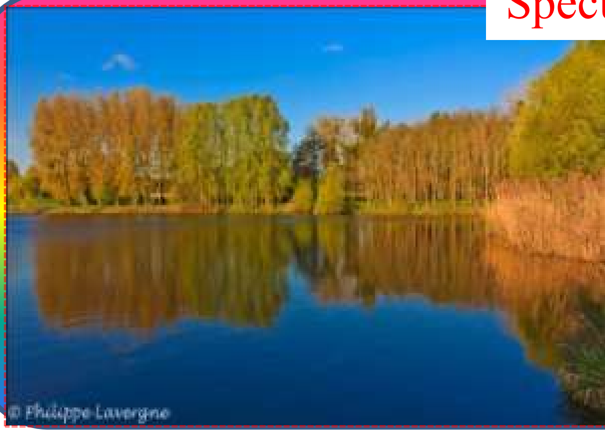
What you will know

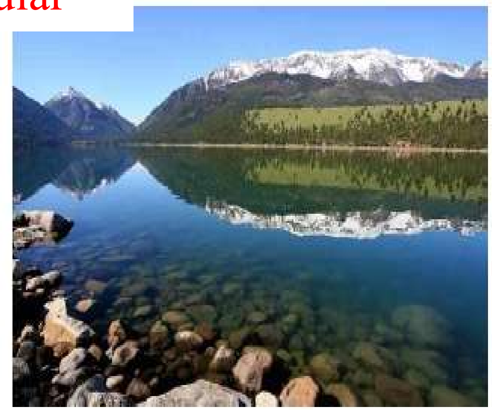
1. Introduction of neutron reflectometry
2. Diting - a reflectometer at CMRR
3. The helium behavior in materials
4. Acknowledgement

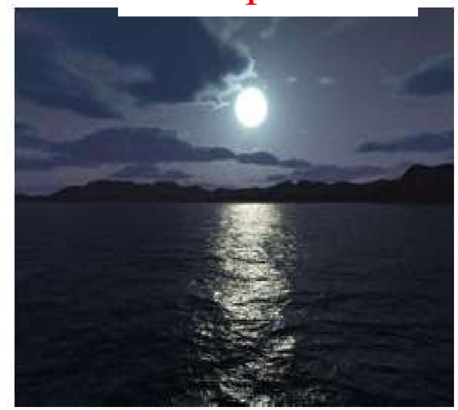
What is reflectometry?

Specular

Off-Specular

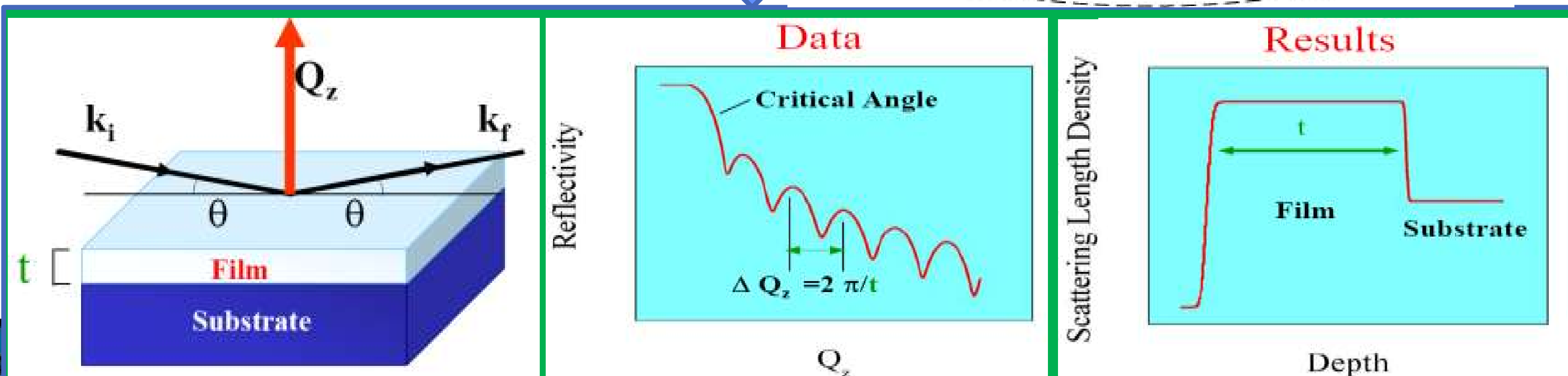




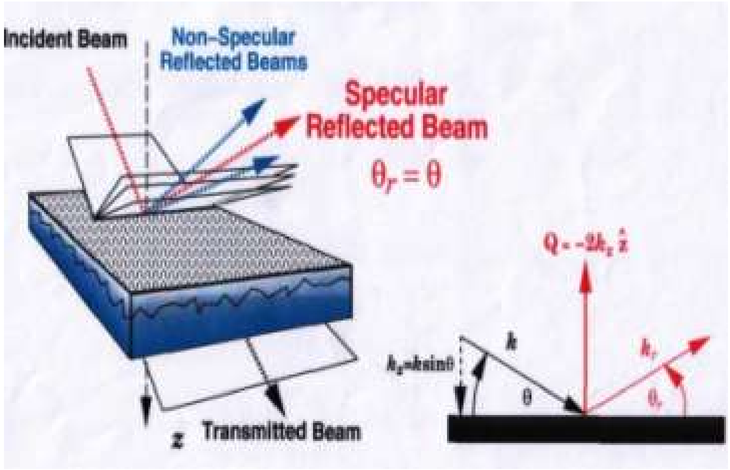


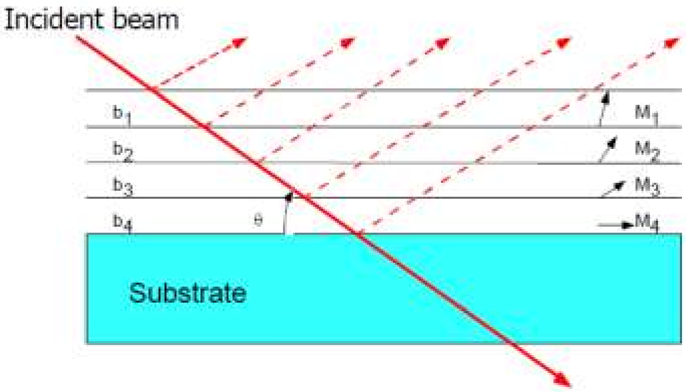
Neutron

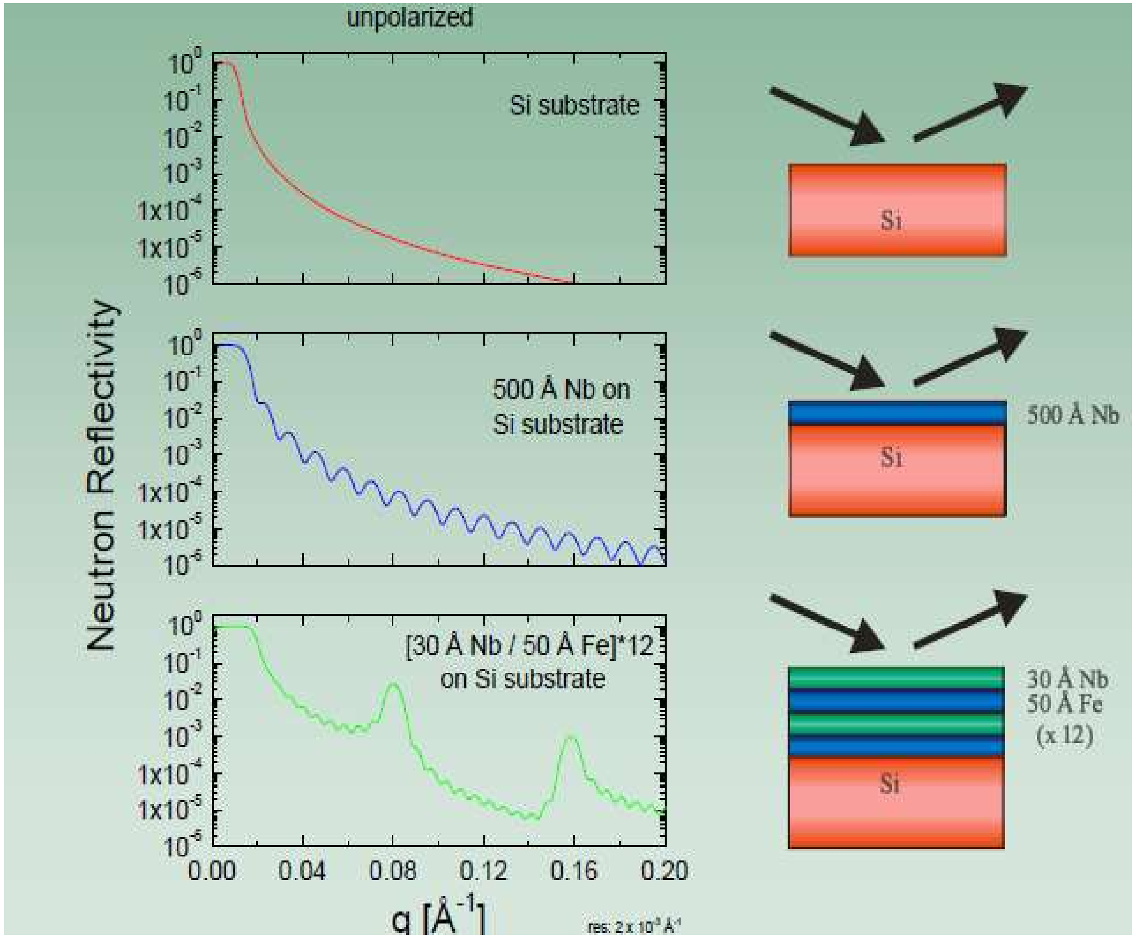
- Neutron WAVELENGTH ~ atomic/molecular dimensions:
  - interference
  - reflection
  - refraction
- Neutrons are NEUTRAL particles:
  - highly penetrating
  - nondestructive probe
  - sample environments



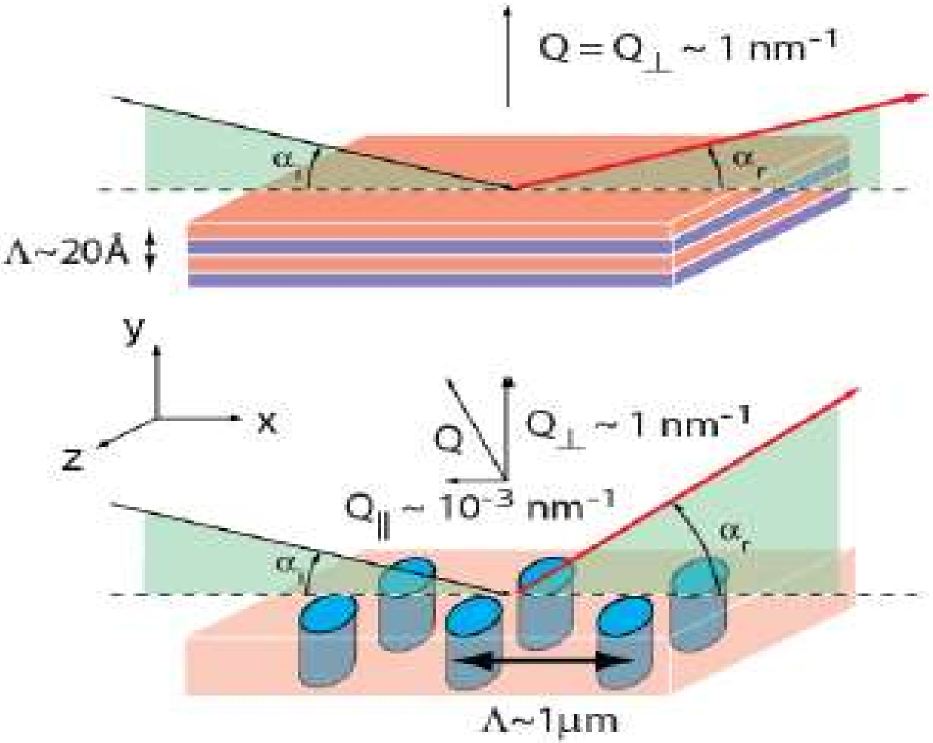
What is reflectometry?







Glancing angle neutron reflection



Specular reflectometry
Depth profiles
(nuclear and/or magnetic)

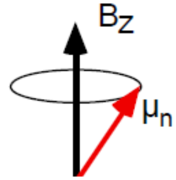
Off-specular (diffuse) scattering
In-plane correlated roughness
Magnetic stripes
Phase separation (polymers)

Polarized neutron reflection

- spin 1/2 particle (→ associated magnetic moment μ_n)

  $|+\rangle$ *and* $|-\rangle$ *are the eigenstate s*

- Interacts with the magnetic fields **B** (aligned along z):
  - *Neutron in an eigenstate* ($|+\rangle$ *ou* $|-\rangle$) :
    stays in this state
  - *Quantified neutron along (Ox)* ($\frac{1}{\sqrt{2}}(|+\rangle+|-\rangle)$) *:*
    precession around B_z



The neutron:

spin 1/2 particle (Fermion)

=> its component along a given direction z can only be "up" (+) or "down" (-)

Nuclear magnetic dipole moment:

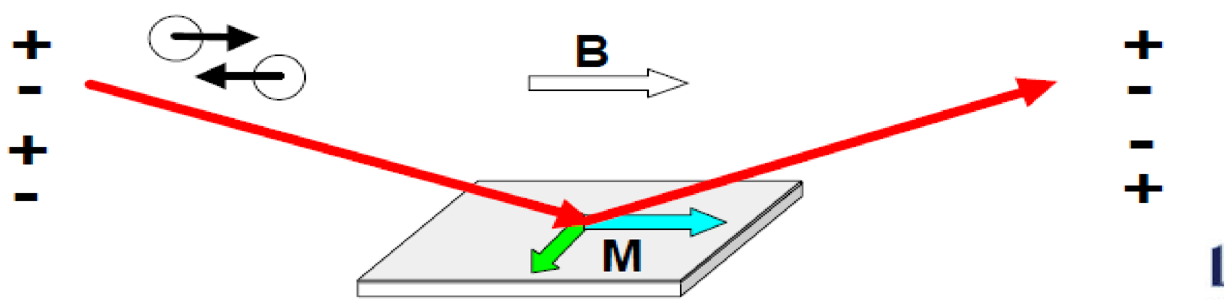
μ_N = -1.913 nuclear magnetons = 5.4 x 10^{-4} μ_B

(comparison: Fe atom = 2.2 μ_B)

=> neutrons have strong direct interaction with atomic and nuclear spins

polariser – flipper – sample – flipper – analyser – detector

- 4 cross-sections $R^{++}, R^{--}, R^{+-}, R^{-+}$



A brief theory of Neutron reflectometry

- Neutron reflectometry (**NR**) can provide the profile of scattering length density along the depth(**SLD(z)**), which relates to the scattering length(**b**) and number density(**n**) of nuclides

$$SLD(z) = \sum_{j=1}^{k} c_j n(z) b_j$$

From Database: nucleus or magnetic (b_j)

$$n(z) = \frac{\rho}{M} N_a ,$$

Density (ρ)

Avogadro Constant (N_a)

$$M = \sum_{j=1}^{k} m_j \cdot c_j ,$$

atomic weight (m_j)

Equivalent formula

$$A_{c_1} B_{c_2} \cdots X_{c_k}$$

The concentration (c_j)

J. Atom. Mole.Phys. 2008, 25(5):1017 (in chinese)

Typical use of NR

- Inter-diffusion of polymers
- Phase separation in block copolymers
- Amphiphilic molecules at air-water interfaces
- Effect of shear on films of complex fluids
- Grafting of polymers to surfaces (mushrooms and brushes)
- Swelling of films exposed to vapor
- Magnetic structure of multilayers
- CMR/GMR films
- Exchange bias and exchange springs
- Nuclear polarization in spintronic materials

What you will know

1 Introduction of neutron reflectometry

2 Diting - a reflectometer at CMRR

3 The helium behavior in materials

4 Acknowledgement

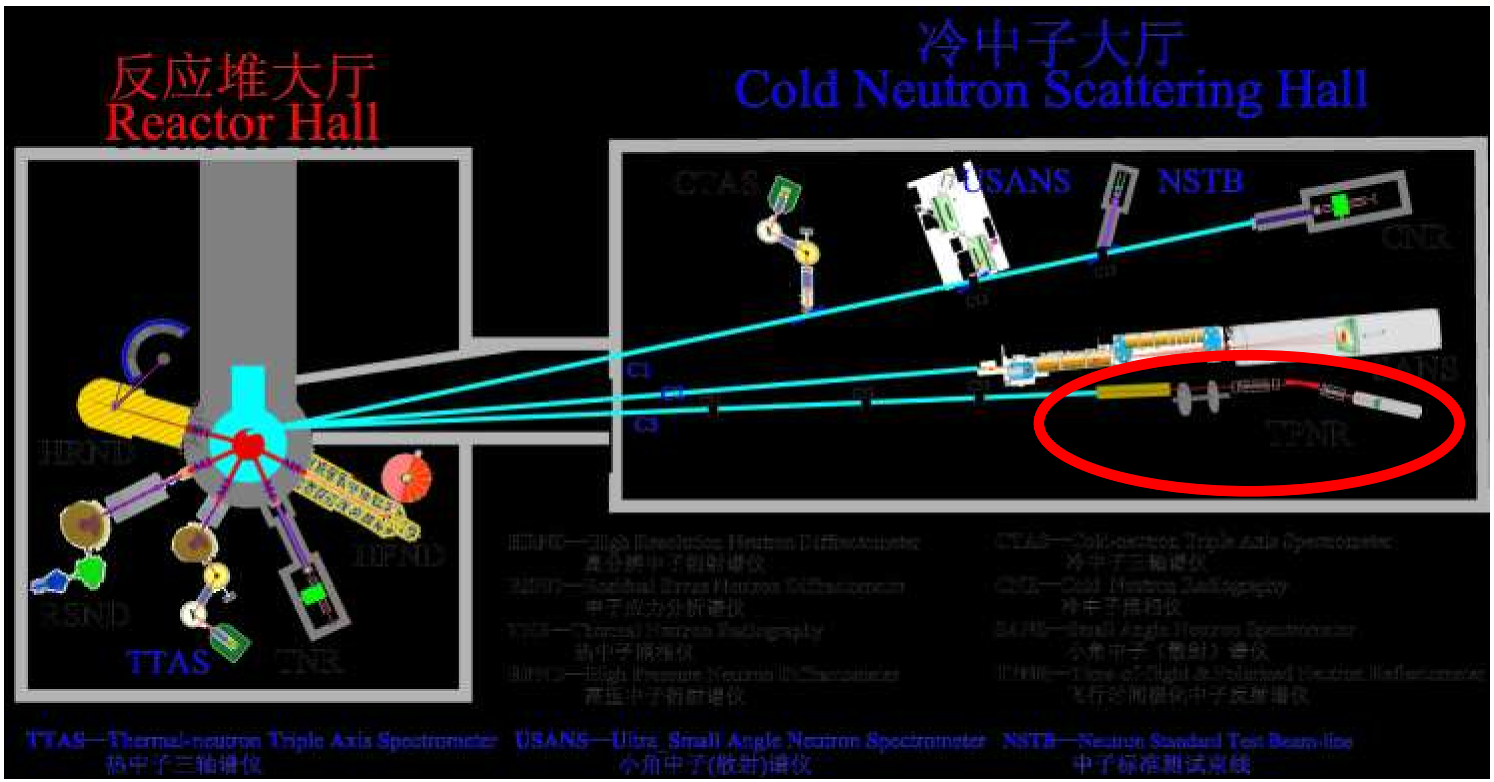
Diting - a reflectometer at CMRR

- **Name : Diting or TPNR**
- **In commission : April, 2014**

> - Time of flight;
> - Polarized option;
> - Horizontal neutron scattering plane.

谛 听

Diting



Specifications of Diting

Parameter	Specifications
Characteristic	Time of Flight (TOF) + Polarization
Neutron scattering plane	Horizontal
Magnetic field in sample position	0-1.2T
Range of neutron wavelength	0.2nm-1.25nm
Available range of momentum transfers	0 ~5.13nm^{-1}
Measurable minimum reflectivity	10^{-6}
Δλ for 0.4nm	0.0023nm
Peak flux at sample position	7.5×10^4 n/cm^2·s
Polarizer and analyzer efficiency	≥95%
Flip probability of flipper	≥99%

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Layout of Diting

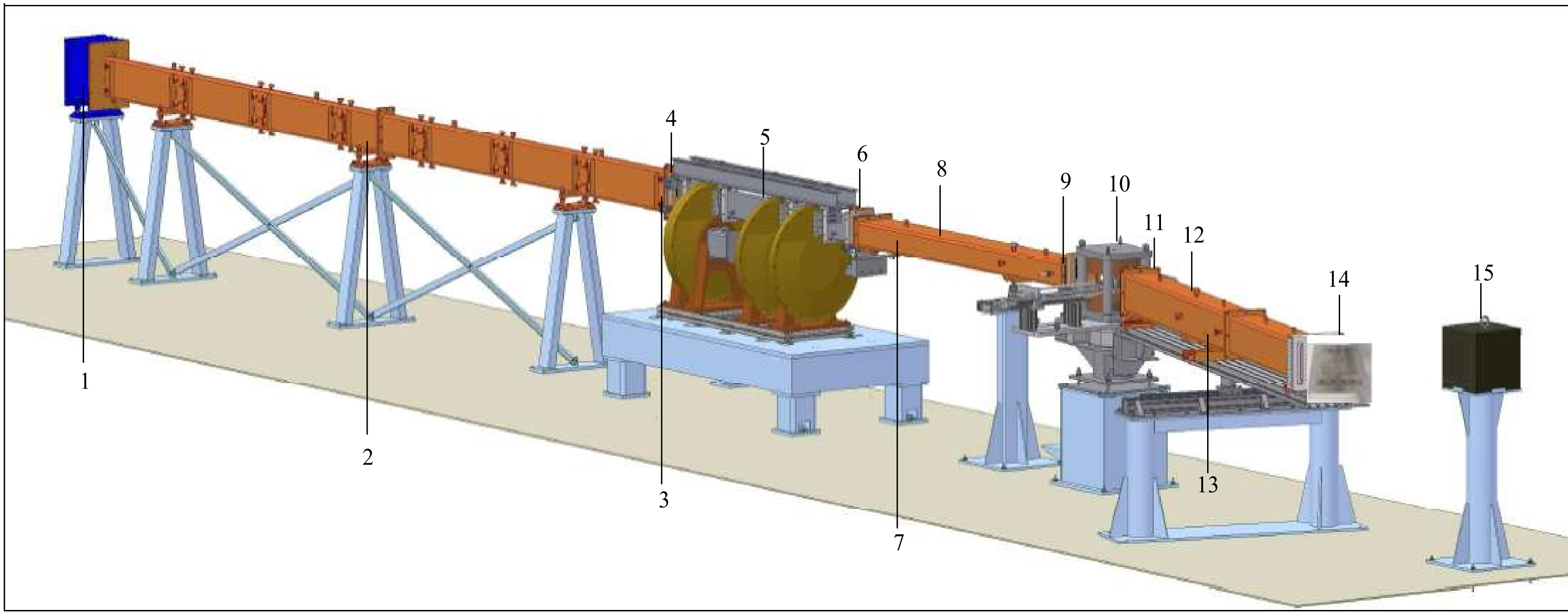
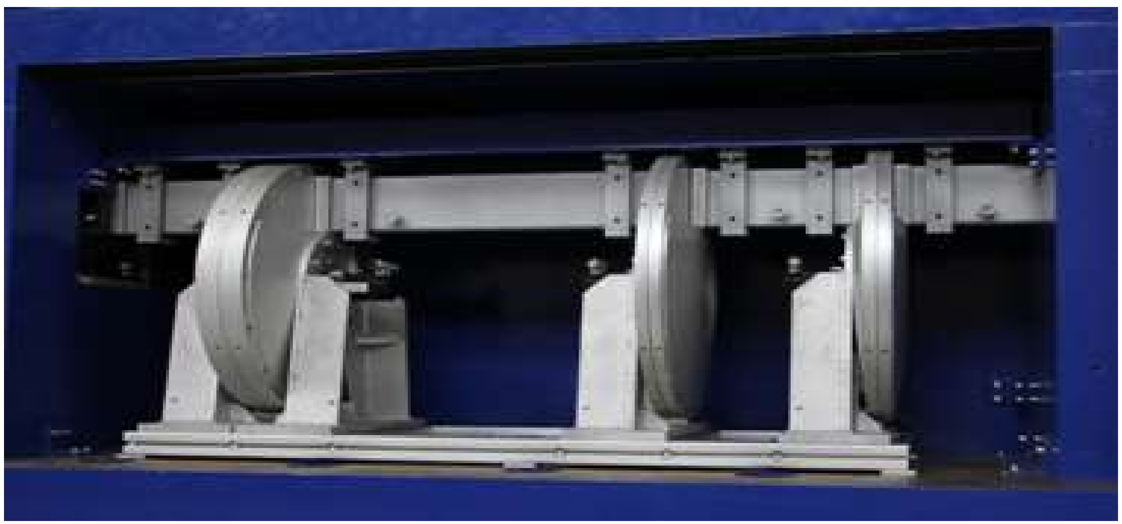
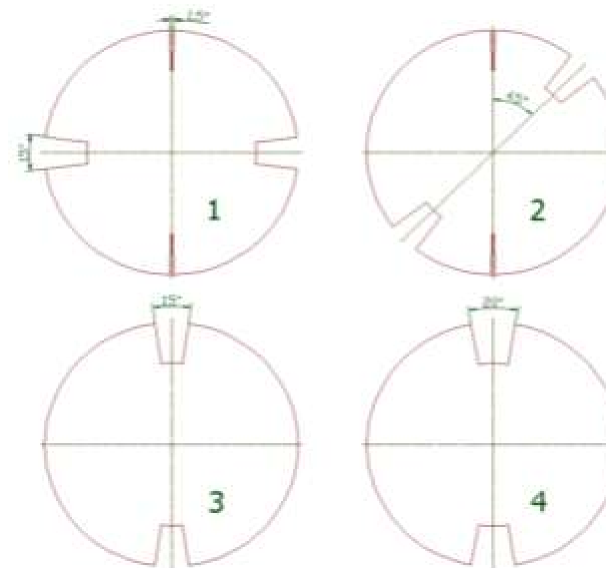


Fig. 1. Perspective view of TPNR reflectometer, the main components(numbers): 1.second shutter, 2. focus neutron guide, 3. neutron beam monitor, 4. 1# slit, 5. four-disk chopper system, 6. 2# slit, 7. front vacuum tube, 8. polarized system(polarizer and 1# flipper), 9. 3# slit, 10. sample unit with electromagnet, 11. 4# slit, 12, back vacuum tube, 13. analyzer syster(2# flipper and analyzer), 14. ^{3}He filled two-dimensional position sensitive detector, 15. beam stop.

Main Component: Four-Disk Chopper

- More wavelength resolution choice
- Convenient wavelength band selection
- Matching the requirements of polarizer
- Suitable to position sensitive sample





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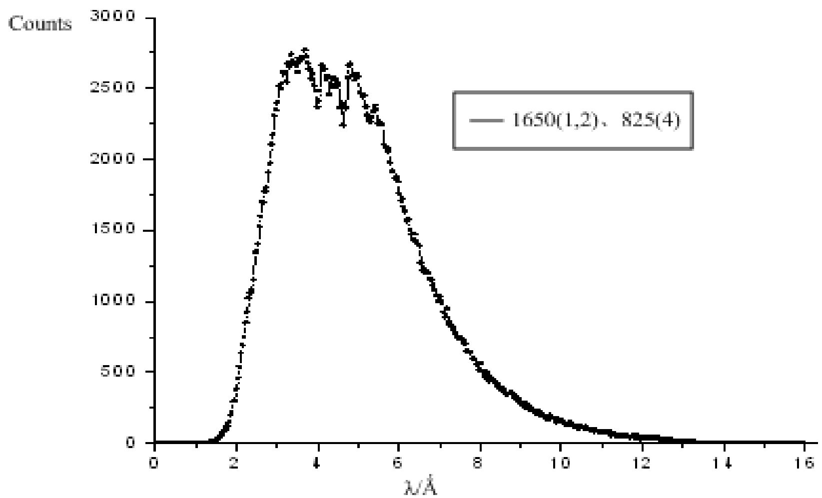
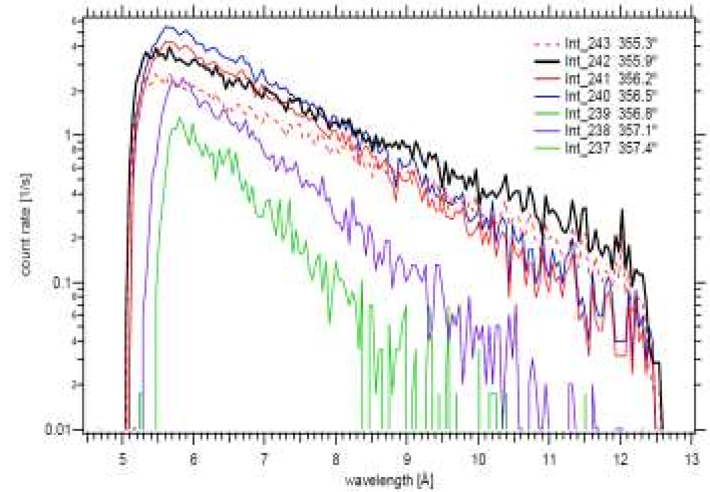
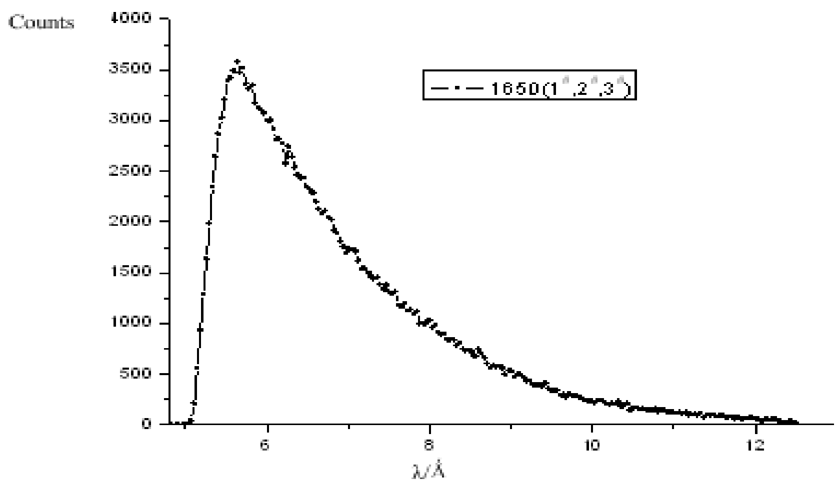
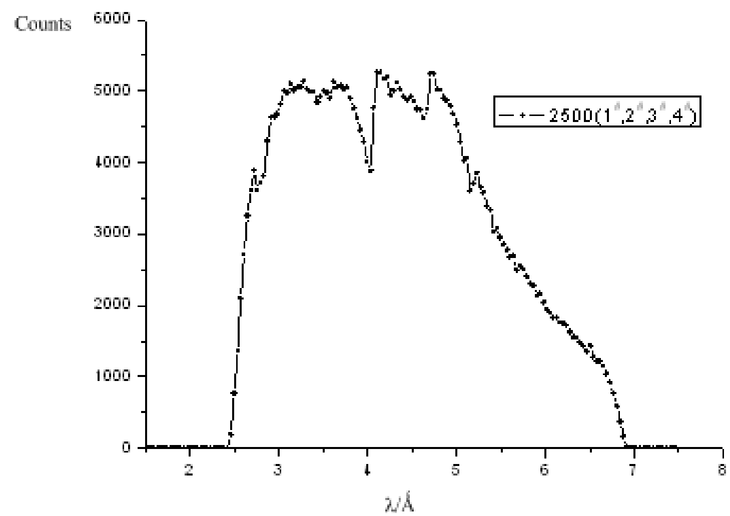
Neutron Spectrum

- Wavelength resolution at 0.4 nm: 0.0023nm









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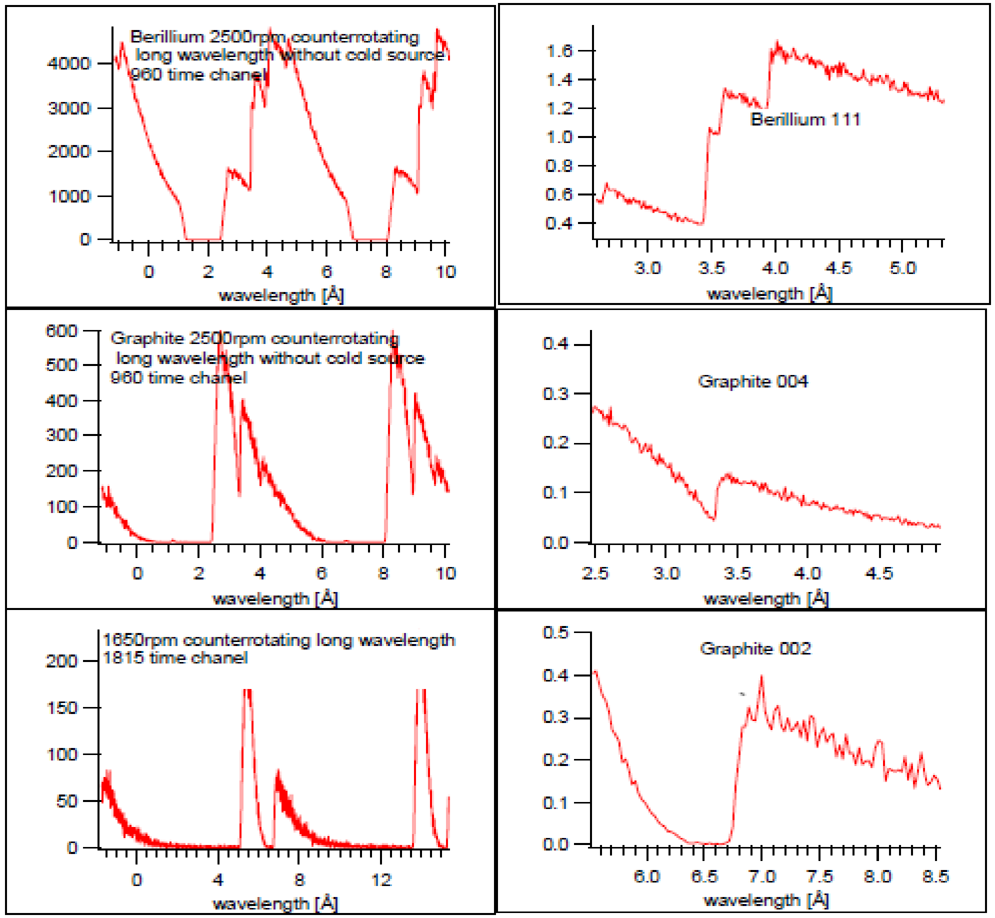
Neutron Spectrum

- The wavelength resolution is determined from the half width of the Bragg edge from beryllium (the edge of the graphite sheet has significant width).



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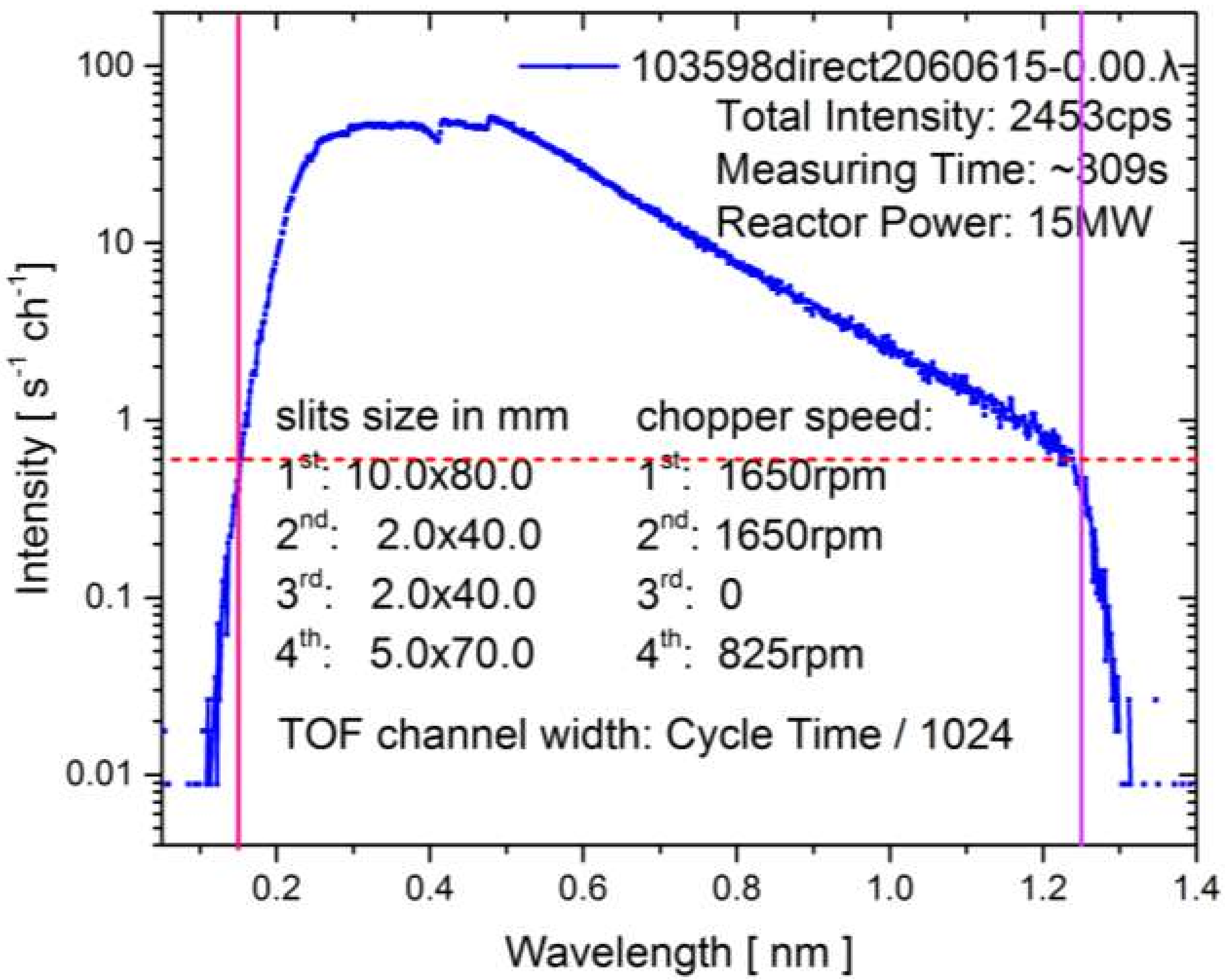
Neutron Spectrum

- Available wavelength: 0.16nm ~ 1.25 nm



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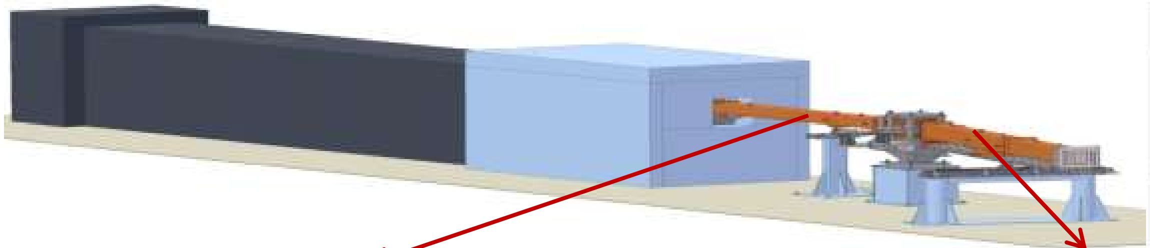
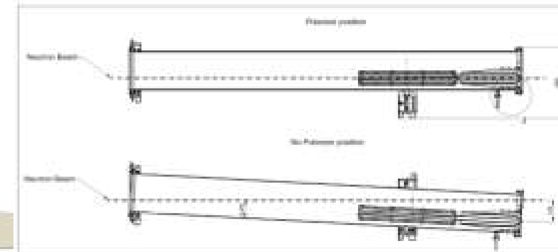
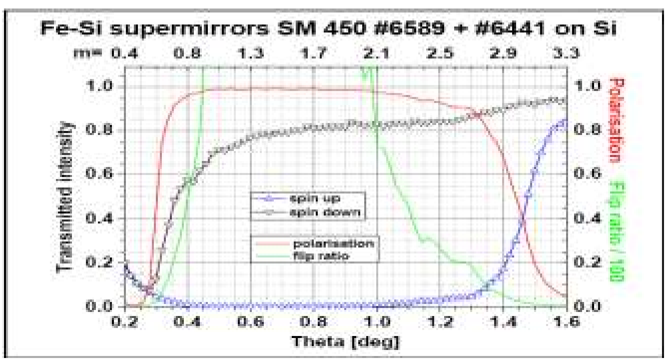
Main Component: Polarization system

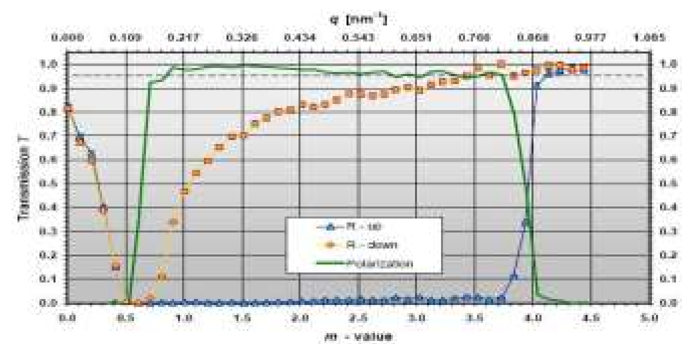




Polarizer+Flipper1

Flipper2 + Analyzer





Polarizer：m=2.7

Analyzer：m=3.85

- L wavelength band：0. 25nm-0. 68nm 0. 55°
- H wanglength band：0. 49nm-1. 25nm 1. 1°

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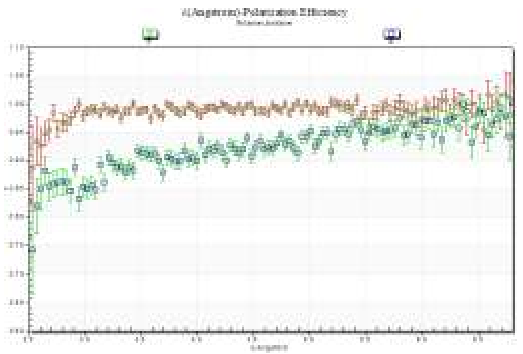
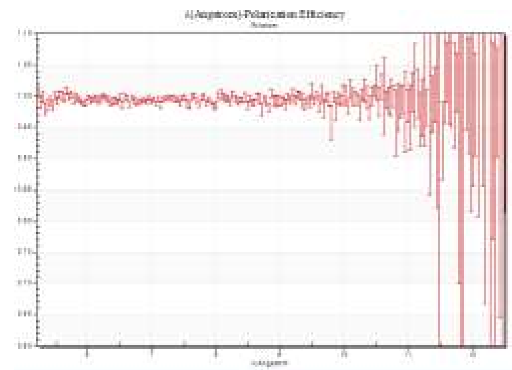
Main Component: Polarization system

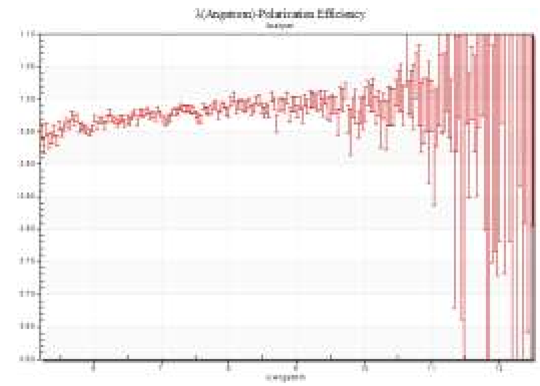
➢ **Calibration at Oct 10, 2014.**



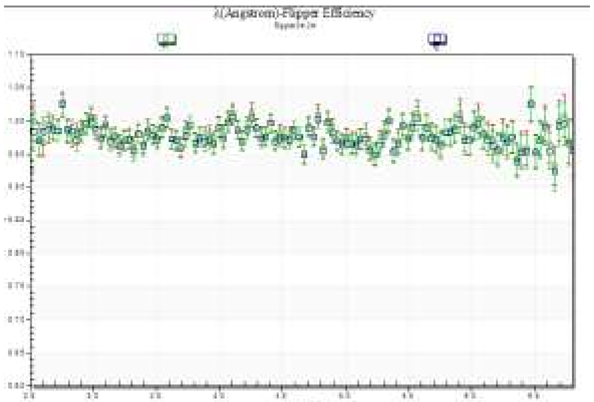
Polarizer(red)+Analyzer(green) [L]



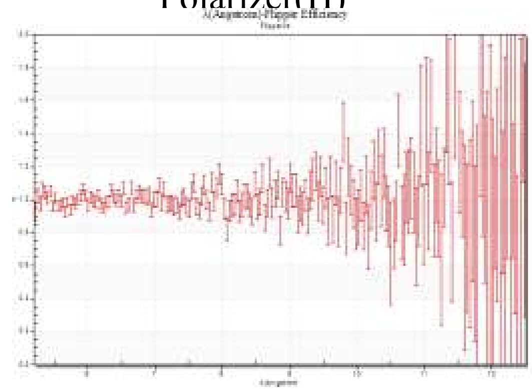
Polarizer(H)

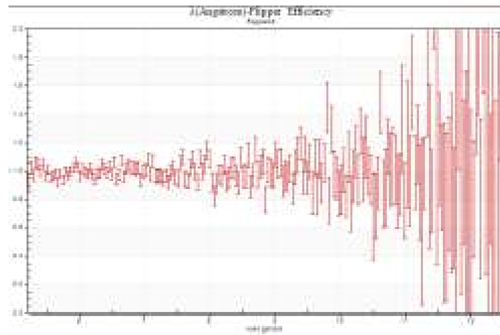


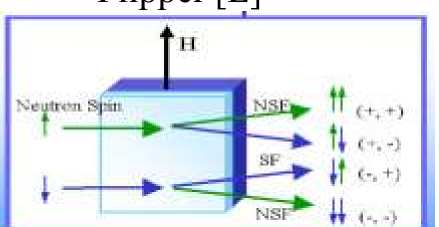
Analyzer(H)

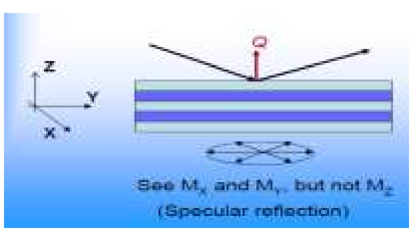


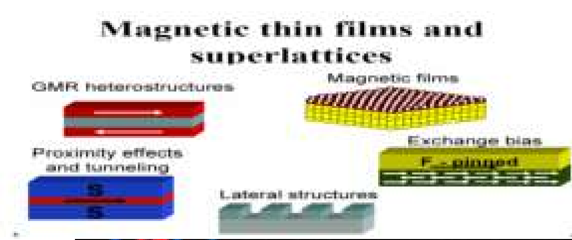
Flipper [L]





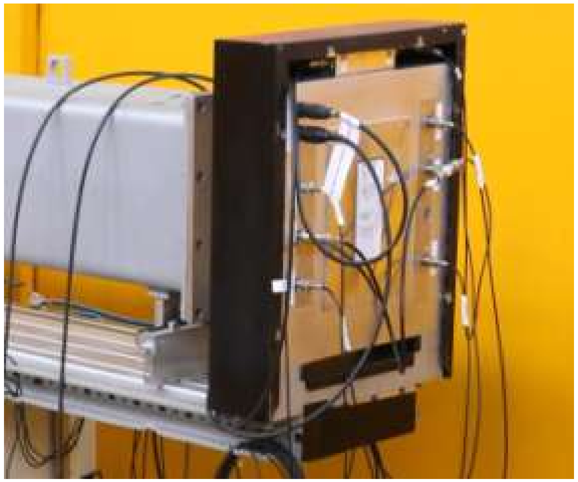


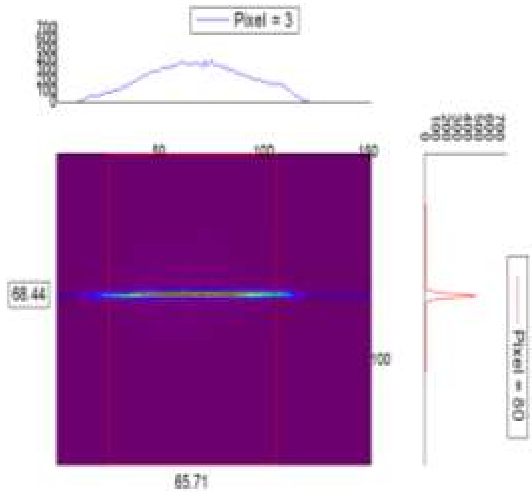




Main Component: PSD Detector

- Very suitable to off-specular studies

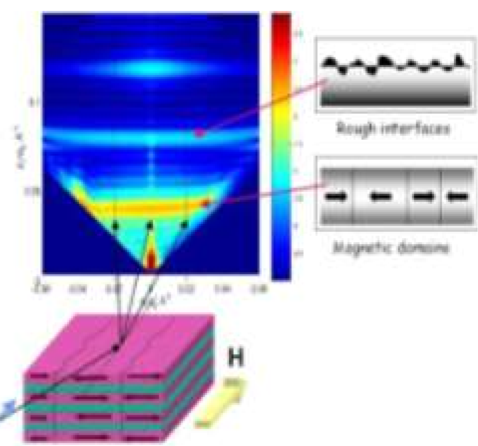


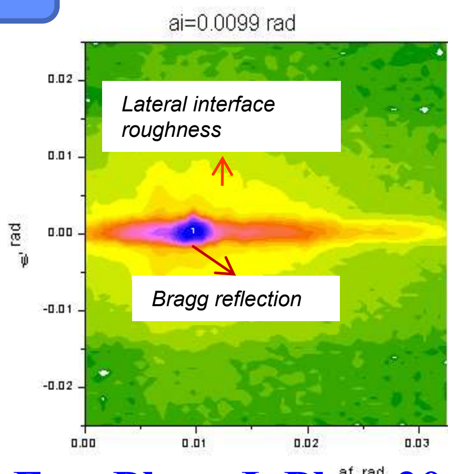


Specifications

Parameter	Specifications
Active area	200mm× 200mm
Maxmal global count rate	4×10^5 cps
Spatial resolution	1.8mm×1.8mm
Efficiency (λ=0.25-1.25 nm)	≥80 %

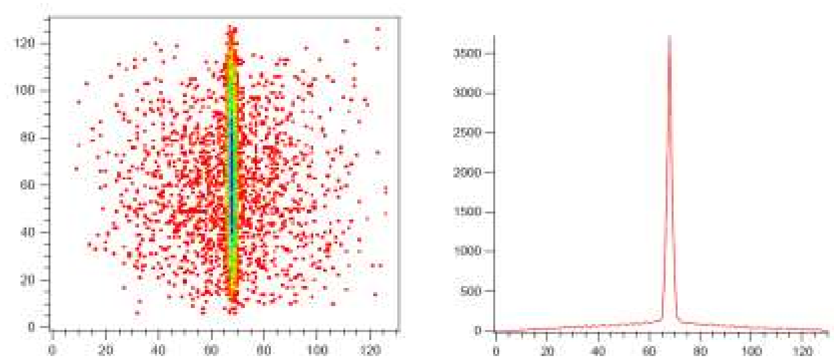
Off-specular





The detector spatial resolution was determined by an 0.5mm Cd slit placed in front of the sample. The pixel size was determined by measuring the beam placing the detector at different positions close to the slit 3, opened it to 0.2mm.

pixel size at 132 pixel mode: 1.73x1.73mm



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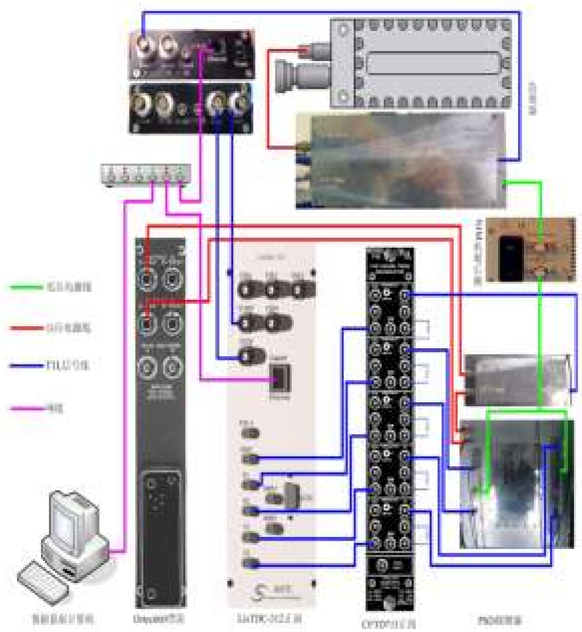
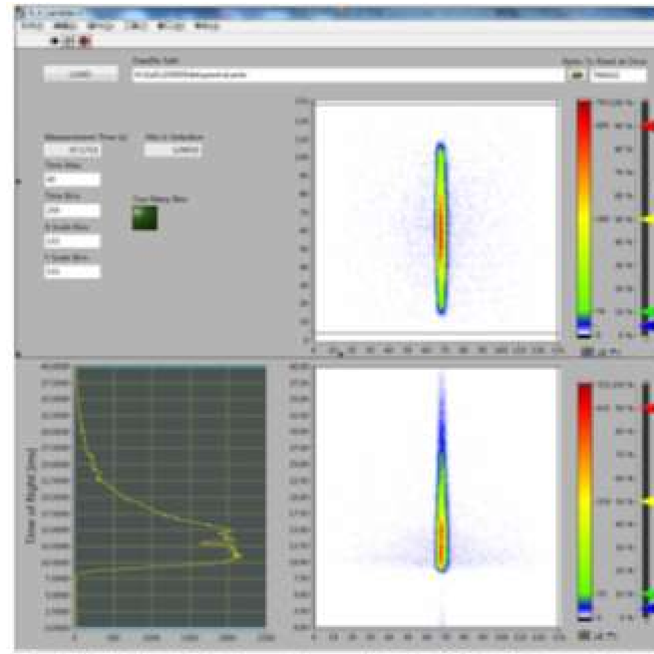
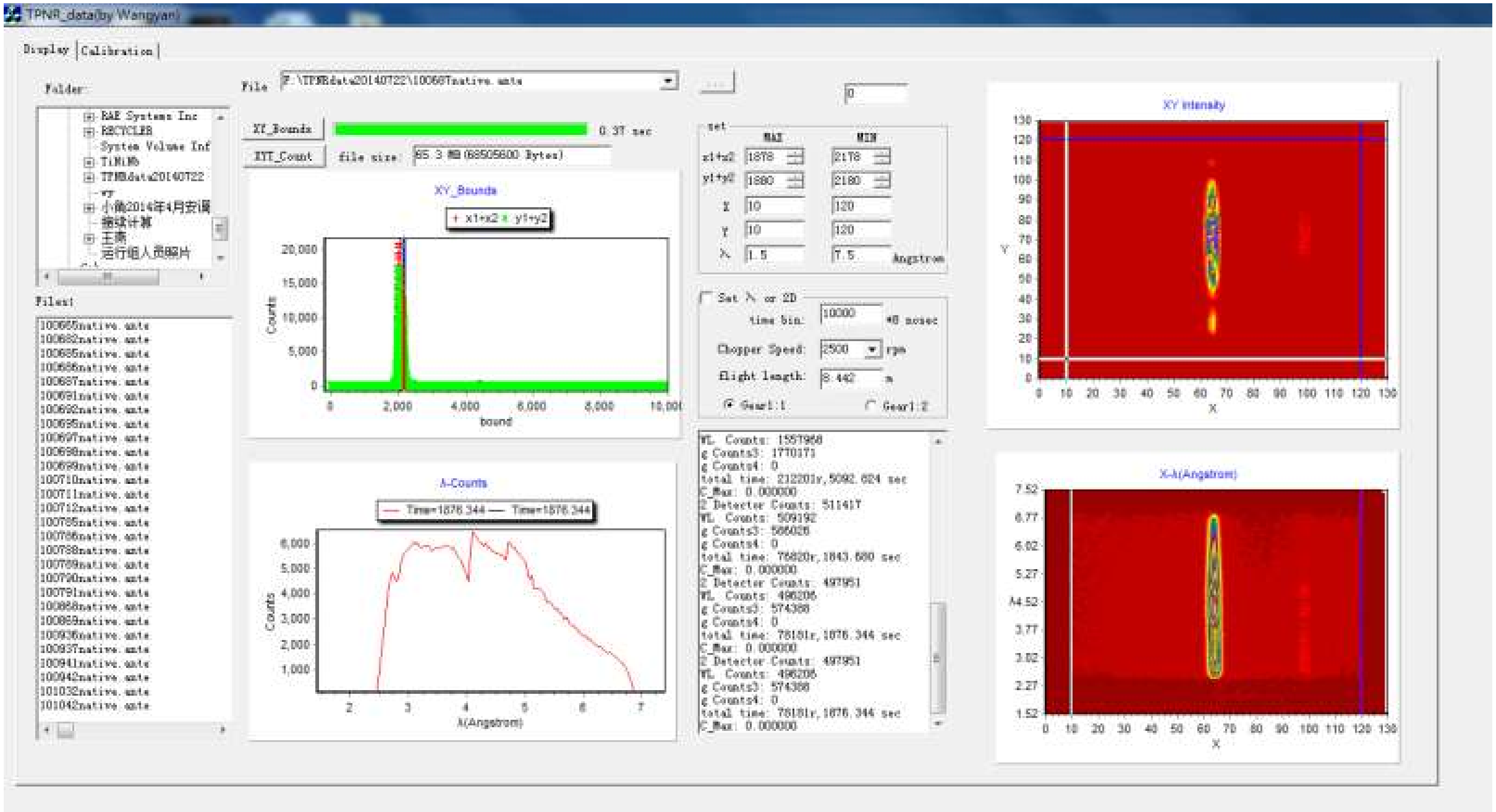
Main Component: DAQ system





Main Component: DAQ system

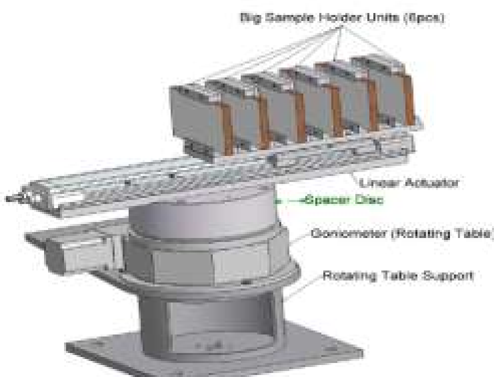


Main Component: Environmental Device

Sample Unit

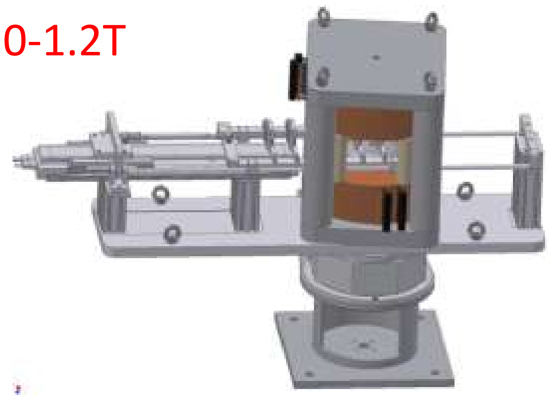
1、 Small sample unit

2、 Large sample unit



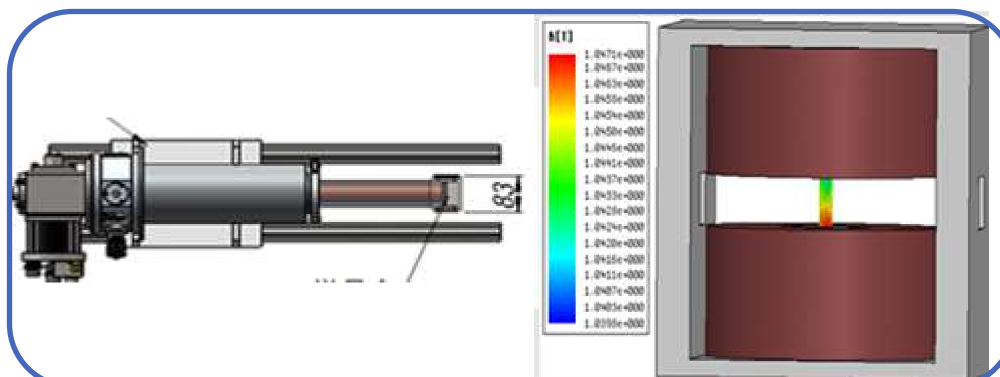
Environment Unit

0-1.2T

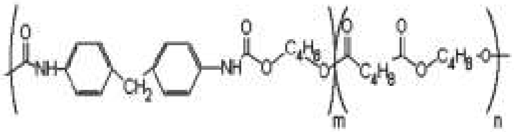


Cryostat+ Furnace+Magnet

5K-800K; 0-1.2T 。

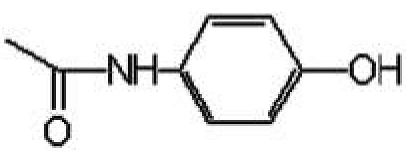


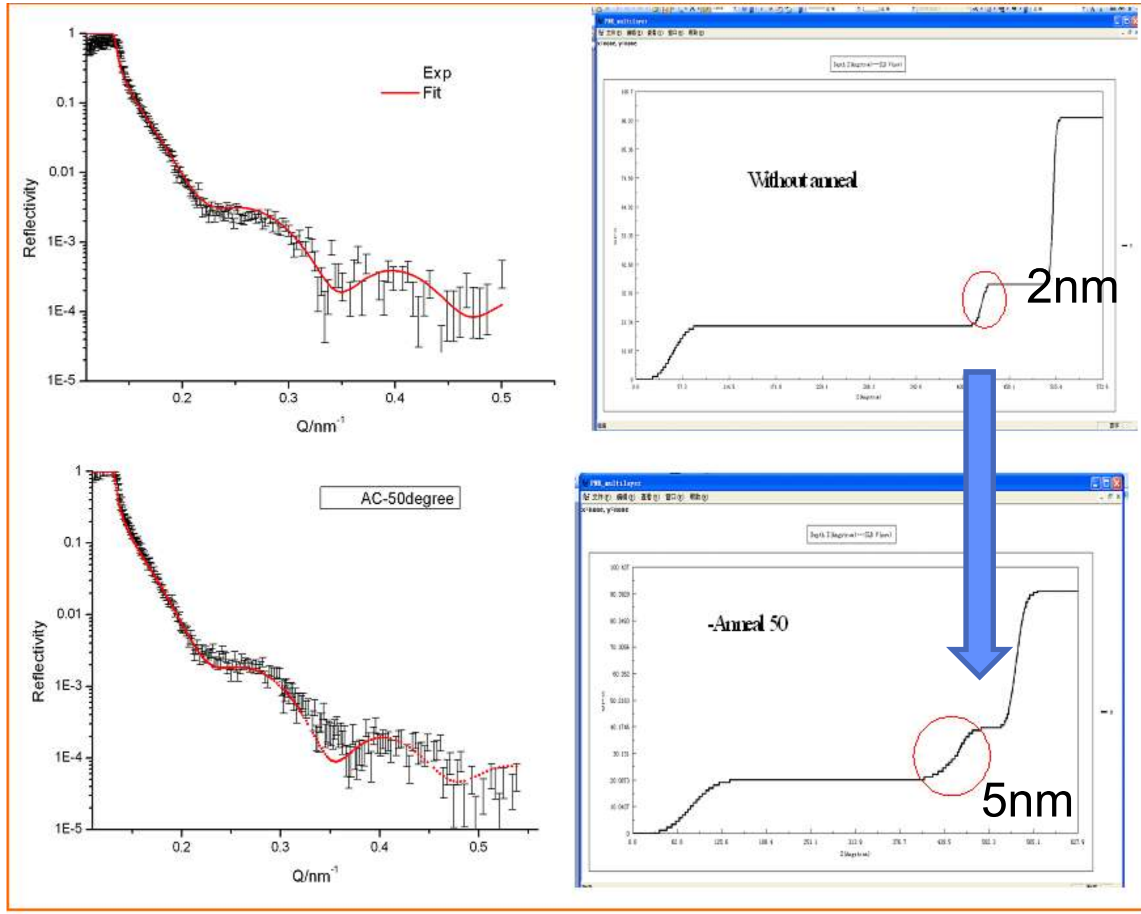
Use: Temperature effect on the Estane Film



Estane 5703 m:n=1:4

Acetaminophen

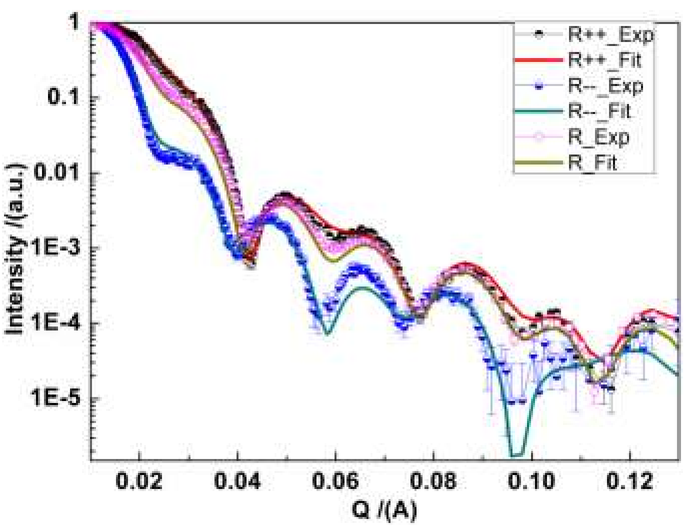


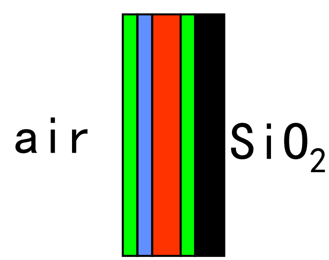


Annealing at 50°C increased the thickness of diffusion layer

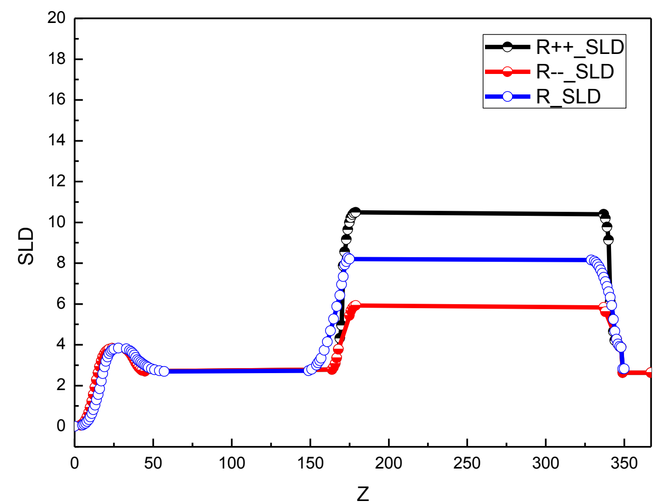
Use: Exchange Bias Effect in Magnetic Nano-film

The saturation magnetic flux density in the direction parallel to the antiferromagnetic is 0.98T, which is consistent with the results of Vibrating Sample Magnetometer. Obviously, the interlayer diffusion is found, and the different microstructure-performance correlations are established to enhance the electromagnetic stealth





B=0.98 T



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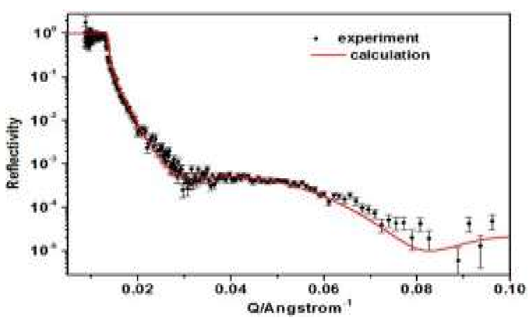
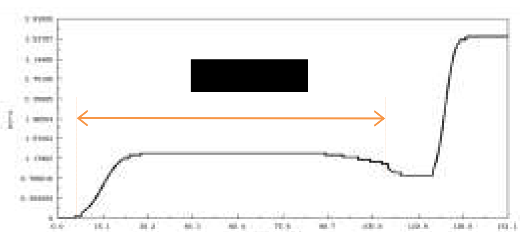
Key Laboratory of Neutron Physics, CAEP

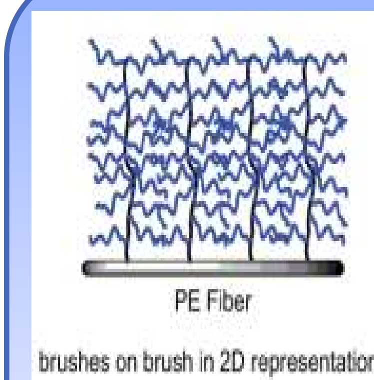
核物理与化学研究所
INSTITUTE OF NUCLEAR PHYSICS AND CHEMISTRY

Use: U absorption depending on Conformation

Accurate extraction of the molecular chain in the aqueous solution of the extension of the thickness of 250 nm and density, the establishment of different environments under the performance - microstructure - process can enhance the material to enhance the performance of uranium

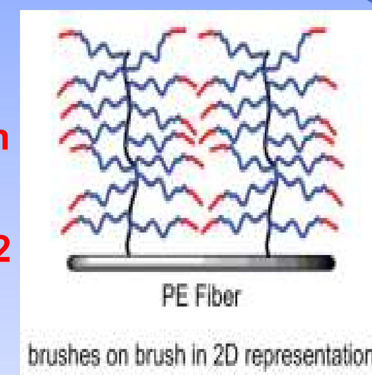






U Absorption (mg/g)

1.56 ⇨ 3.02



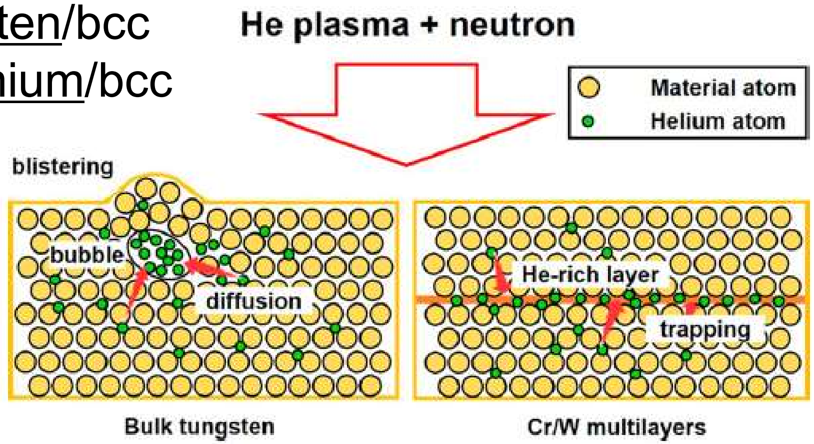
J. Mater. Chem. A, 2014, 2, 14674–14681

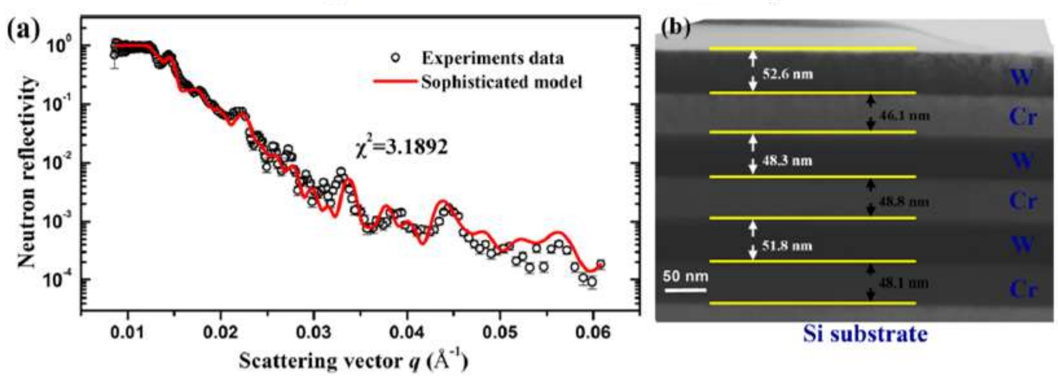
The conformation of fiber plays an important role in the absorption of uranium

Use: He Capture Behavior of Cr / W Multilayers

Cr / W multilayers are the fusion reactor plasma wall materials. The neutron reflectometry gives the helium location in the multilayers, and proves the aggregation of the helium atoms at the interface.

Tungsten/bcc
Chromium/bcc
silicon





layer	element	thickness (Å)	scattering potential energy (neV)
1	C	10	100.476
2	W–He	51.59	79.13
3	W	382.54	83.87
4	W–He	79.37	77.06
5	Cr–He	187.42	50.18
6	Cr	164.96	95.1
7	Cr–He	45.67	78.3
8	W–He	96.85	62.4
9	W	382.35	83.53
10	W–He	42.52	72.6
11	Cr–He	167.46	51.77
12	Cr	258.73	94.44
13	Cr–He	23.23	70.69
14	W	517.42	79.77
15	Cr	477.77	94.2
16	SiO_2	18.53	95
17	Si substrate	∞	54

ACS Appl. Mater. Interfaces 2016, 8, 24300

What you will know

1 Introduction of neutron reflectometry

2 Diting - a reflectometer at CMRR

3 The helium behavior in materials

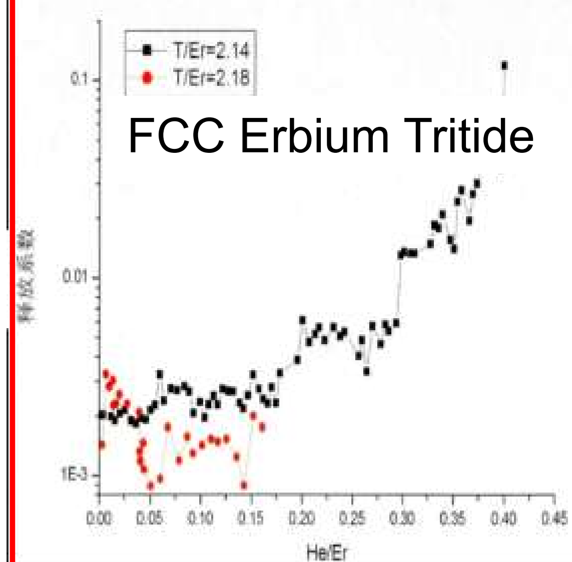
4 Acknowledgement

Motivation

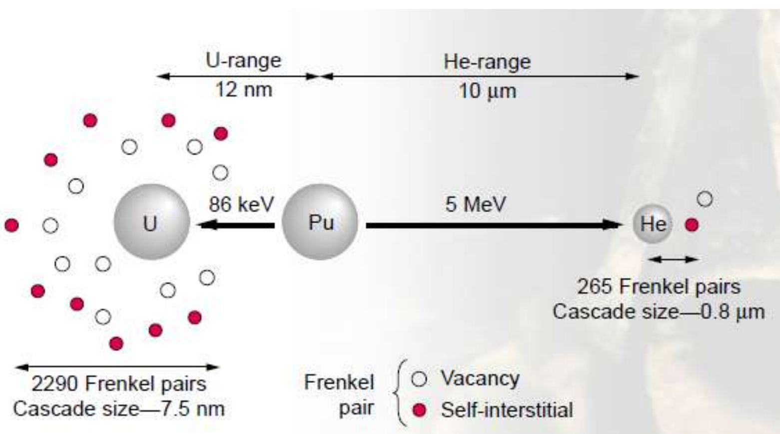
He induced fracture

Helium:

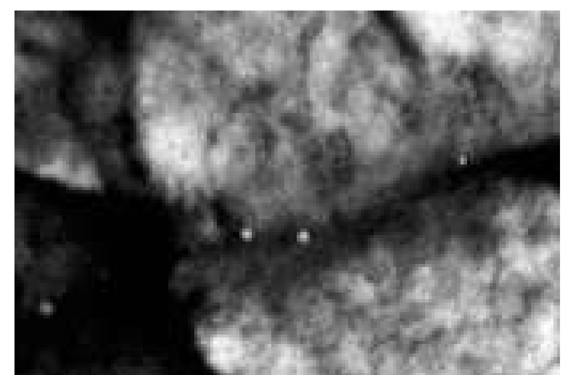
- Nuclear Device
- He induced embrittlement
- Decrement Performance



Accelerating release



Pu: fission produce He. ~10a , voids and bubbles are visible , induce swelling and worsen performance

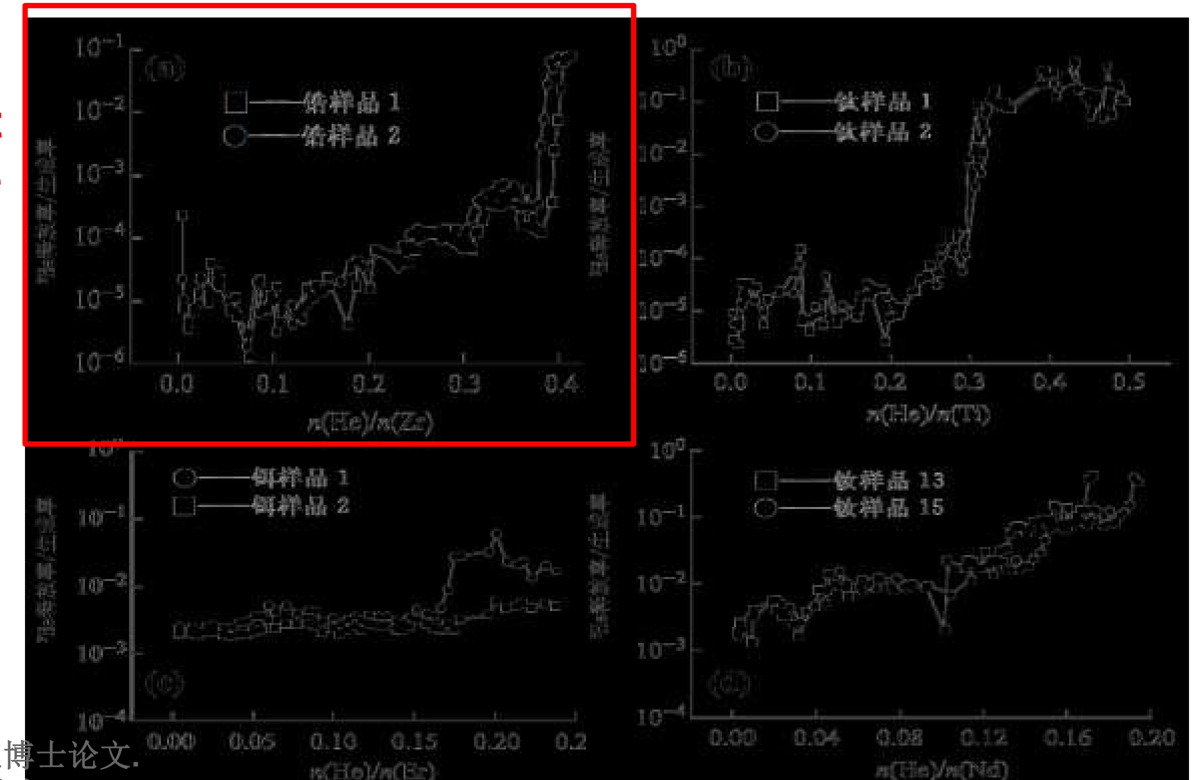


21a Pu-Ga, 400℃@1h

Motivation

He accelerated release of metal tritides has a great impact on its performance, such as brittlement, surface powder, etc., its storage and application environment will also be affected.

Highest Release Threshold



周晓松, 2012, 中物院博士论文.

丁伟等. 原子能科学技术. 2008, 42(10):944

Zirconium alloy has the highest He release threshold, the best solid helium capability

Motivation

Ion Implantation

Adv：Simple and quick features

Disadv：Low energy: small infiltration depth, fewer body characteristics; high energy: serious damage,

Tritium Decay

Adv：body uniform, fewer atomic damage

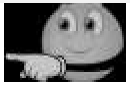
Disadv：Longer accumulation, half-life of 12.32 years, not easy to access

Magnetron sputtering

Adv：fast formation, uniform He, easy to control helium concentration

Disadv：The deposited film is thin and loose, difficult to prepare the bulk sample

Nuclear(n, α) reaction



activation

Adv： Simultaneous simulation of helium accumulation and atomic displacement damage, body distribution

Disadv： Helium accumulation is very slow, needs "cool” time

Sample preparation by magnetron Sputtering

Si/TiHe & Si/ZrHe multilayer

parametes

Ti(He)Film

TiFilm. He:Ar = 0:10
Ti (HeAr3). He:Ar = 30:10
Ti(HeAr9). H:Are = 90:10

Zr(He)Film

ZrFilm. He:Ar = 0:10
Zr(HeAr3). He:Ar = 30:10
Zr(HeAr6). He:Are =60:10

Sample preparation by magnetron Sputtering

$SiO_{2[substrate]}/ZrH_{x[40\sim60\ nm]}/Ta_{[40\ nm]}$ multilayer

Tech Para

Initial sample

ZrH3030. Ar:H2=30:30
ZrH3020. Ar:H2=30:20
ZrH3010. Ar:H2=30:10

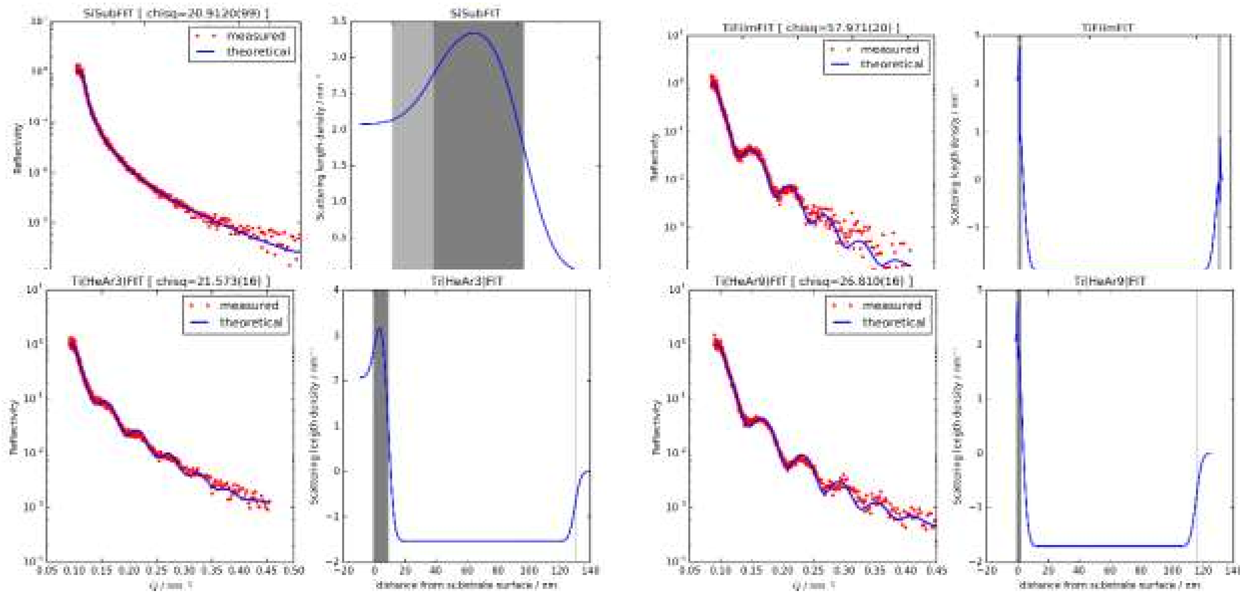
Annealed sample

ZrH3030_VA. 2h@300℃
ZrH3020_VA. 2h@300℃
ZrH3010_VA. 2h@300℃

chemical	Phase/structure	Density/ g cm^{-3}	SLDr $10^{-4}nm^{-2}$
ZrH2	ε-phase/BCT	5.617	-0.12
ZrH1.66	δ-phase/FCC	5.646	0.35
ZrH	γ-phase/FCT	5.837	1.30

NR analysis（Ti-He）

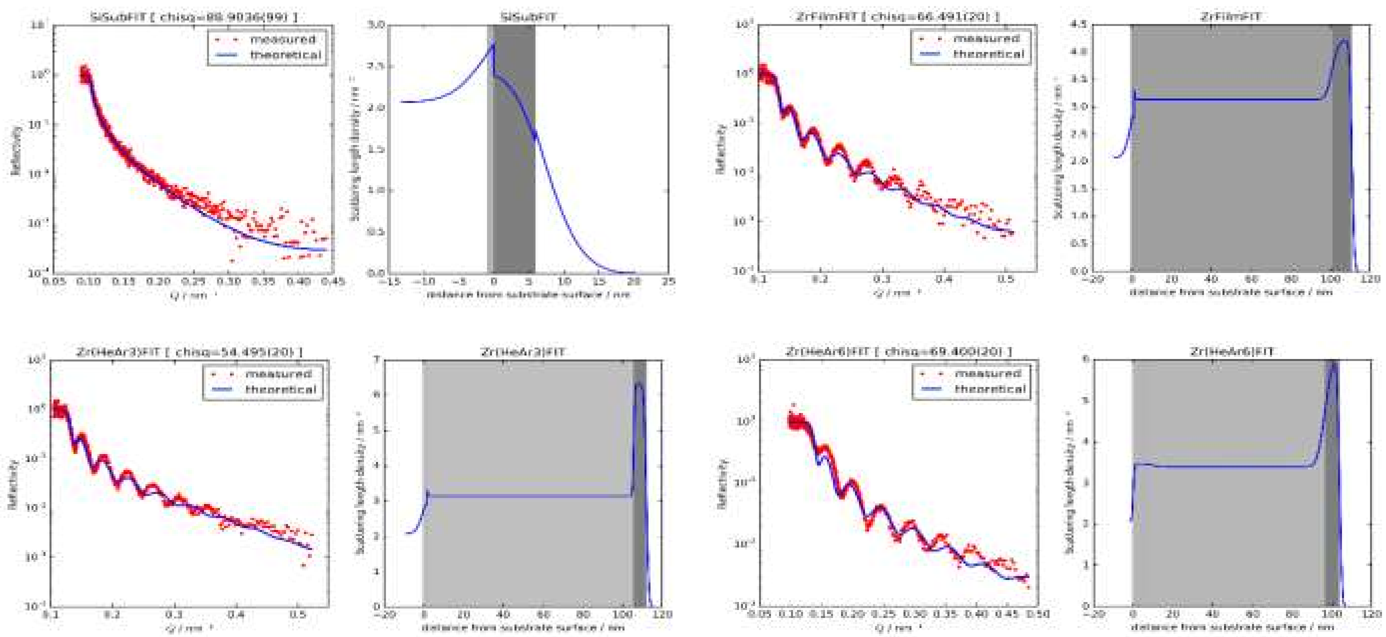
- The atomic ratio of helium atoms in helium-doped Ti films is 28.06% when the He / Ar ratio is 3, and the higher the He is in the atmosphere, the more helium atoms are embedded.



sample	density (g/cm^3)	SLD@25.3meV (10^{-4}nm^{-2})	SLD (10^{-4}nm^{-2})	He density (10^{21}cm^{-3})	Zr density (10^{22}cm^{-3})	He ratio (%)
Ti bulk	4.540	-1.9242	-	-	5.71	-
TiFilm	4.628	-1.9615	-	-	5.82	-
Ti (HeAr3)	3.640	-1.5428	0.4188	12.85		28.06
Ti (HeAr9)	4.027	-1.7066	0.2549	7.82	-	15.44

NR analysis (Zr-He)

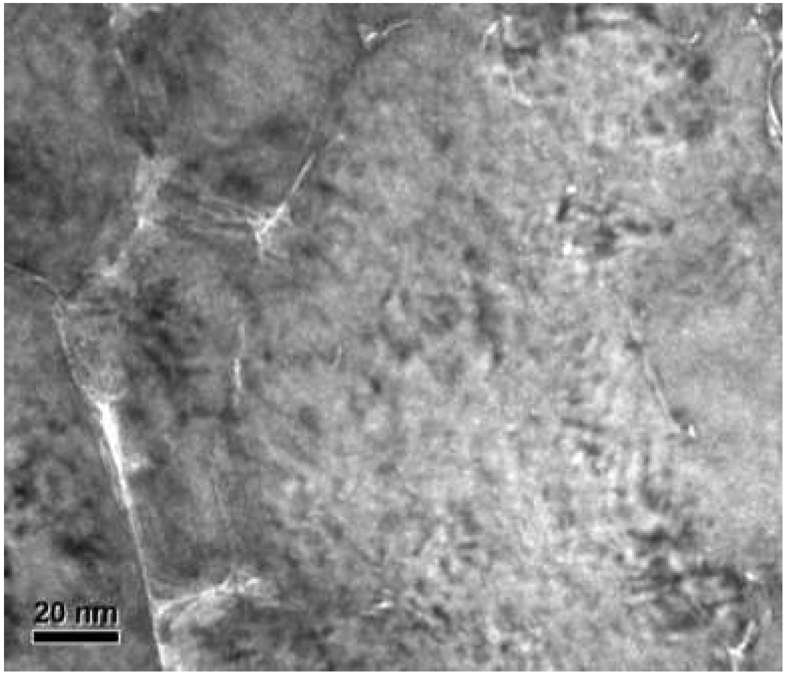
- The ratio of He to Ar is introduced into the atmosphere, and when the He: Ar atmosphere ratio is 6, the atomic ratio is increased to 18.17% 。



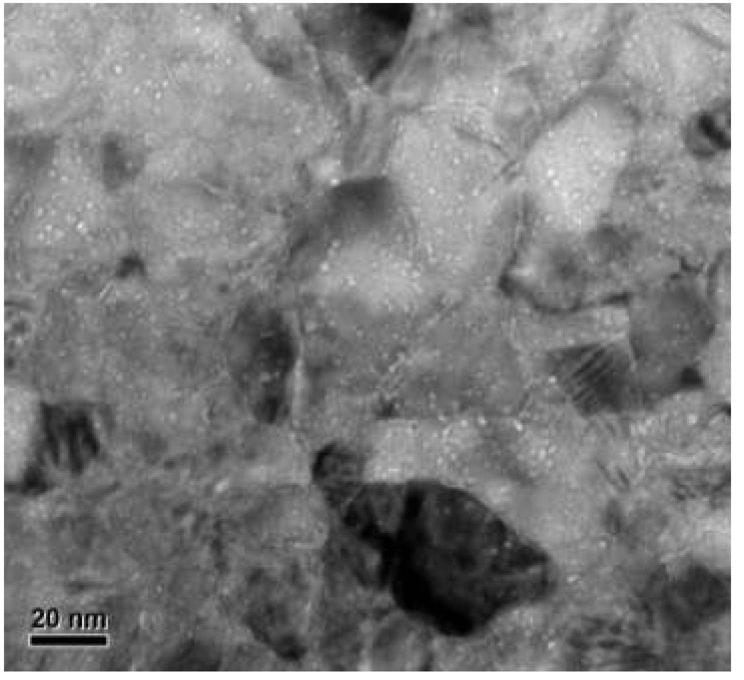
Sample	density (g/cm^3)	SLD@25.3meV (10^{-4}nm^{-2})	SLD增量 (10^{-4}nm^{-2})	He density （10^{21}cm^{-3}）	Zr density （10^{22}cm^{-3}）	He ratio (%)
Zr bulk	6.506	3.0734	-	-	4.29	-
ZrFilm	6.642	3.1376	-	-	4.38	-
Zr(HeAr3)	6.657	3.1447	0.0071	0.22	-	0.50
Zr(HeAr6)	7.191	3.3971	0.2596	7.96	-	18.17

NR analysis（Zr-He）

- **The TEM observation of ZrHe3030 sample before and after annealing showed that the Zr-He sample was prepared with fine helium bubbles. The annealing treatment not only increased the size of helium bubble, but also increased the number of helium bubbles.**



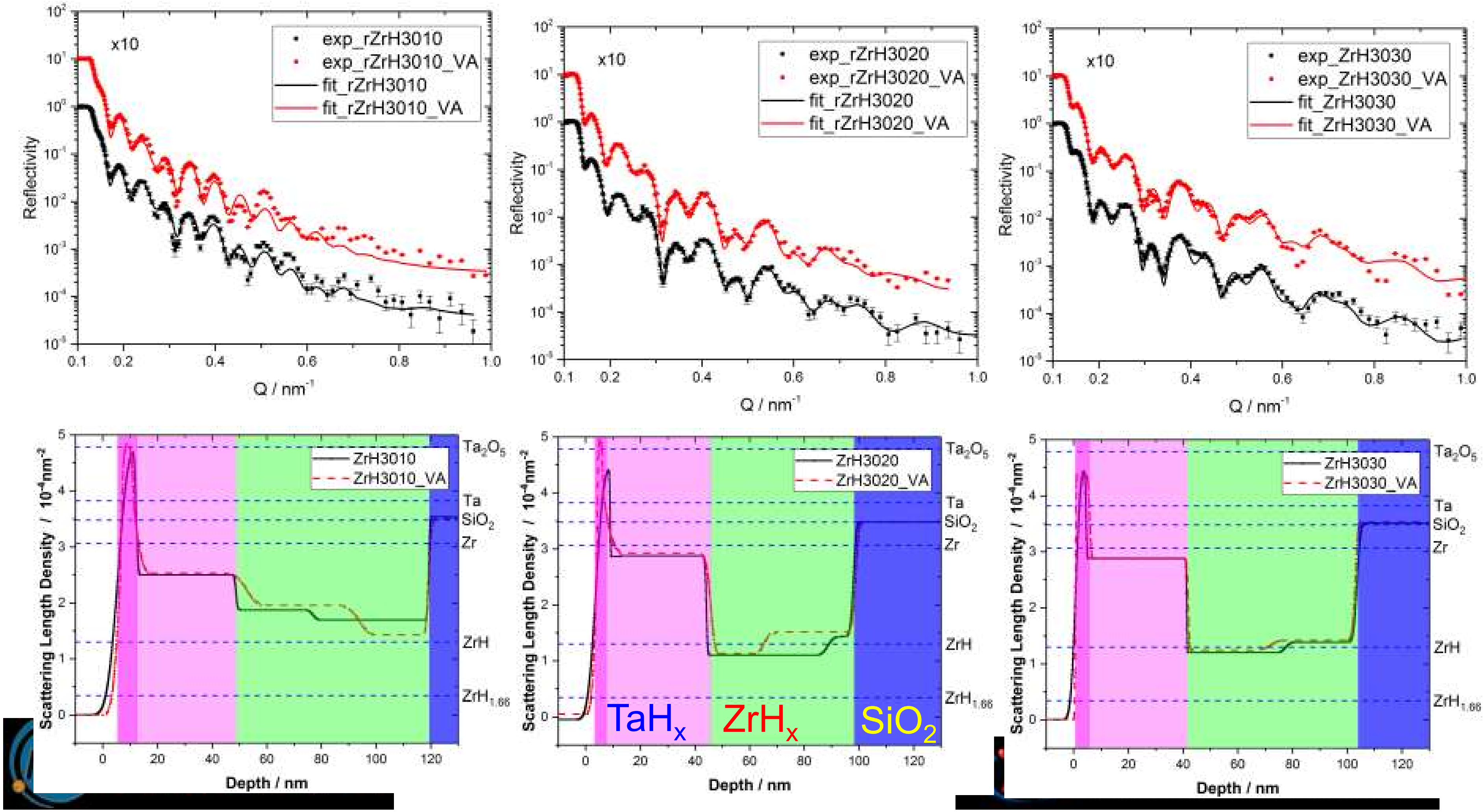
TEM of as the sputtered



TEM of as the annealed

NR analysis (Zr-H)

- Different layers of Ar: H, the protective layer Ta and Zr are hydrogenated, slightly different thickness ZrH_x ($x < 1$) composition, low H content Ta oxide film is protected, high H to be thicker Ta protective layer



Conclusion

- Ti films and hydrides containing Ti and Zr were prepared on SiO_2 substrates by control of the ratio of Ar:H atmosphere. The films were characterized by neutron reflection (NR).
- NR shows the ZrD_X layer appeared stratified and the H distribution was not uniform. In the low H, H has a relatively lower SiO2 / Zr interface at the Zr / Ta interface, and the Zr / Ta interface increases at high H. The content of H increased with the increase of H content in the atmosphere.
- The annealed same sample shows, γ-ZrH was formed near the interface of SiO2 / Zr, and different ZrHX compounds were formed at the Zr / Ta interface with the relative content of H. After annealing, H in the high hydrogen content sample (similar to 3030 and 3020) is relatively large at the Zr / Ta interface; the low content sample (3010) at the Zr / Ta interface will migrate to the near substrate.

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4 Acknowledgement

Acknowledgement(Our Team, Lab)

INPC+NPL，CAEP

Neutron Scattering Lab

Instrument | Application | High Pressure | Macro | Stress | ……

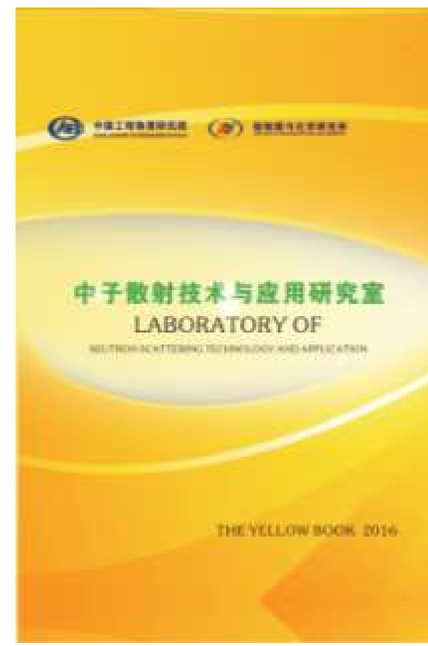
^{3}He Physics

47 stuffs, 14 (associate)Prof, 27 Dr., 34.5y average age MS&PHD Students: 15

How to get neutron beam?

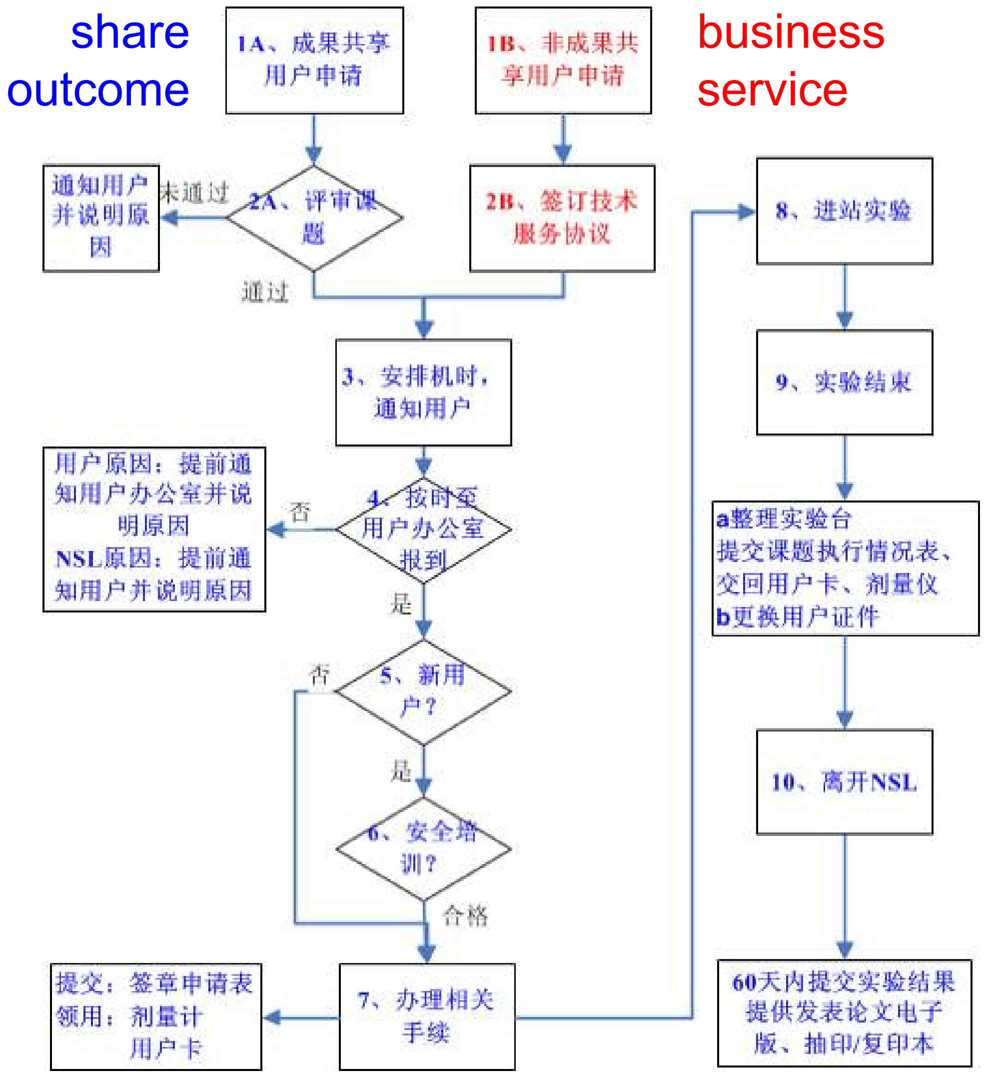
npl.caep.cn

- status
- Proposal



中子散射谱仪介绍

How to get neutron beam?



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Thank you for your attention!

Comments are welcome!

NSL INPC

Neutron Scattering Laboratory

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