Chemical and Magnetic order of FeRh nanoparticles in epitaxy on $SrTiO_3$ (001)

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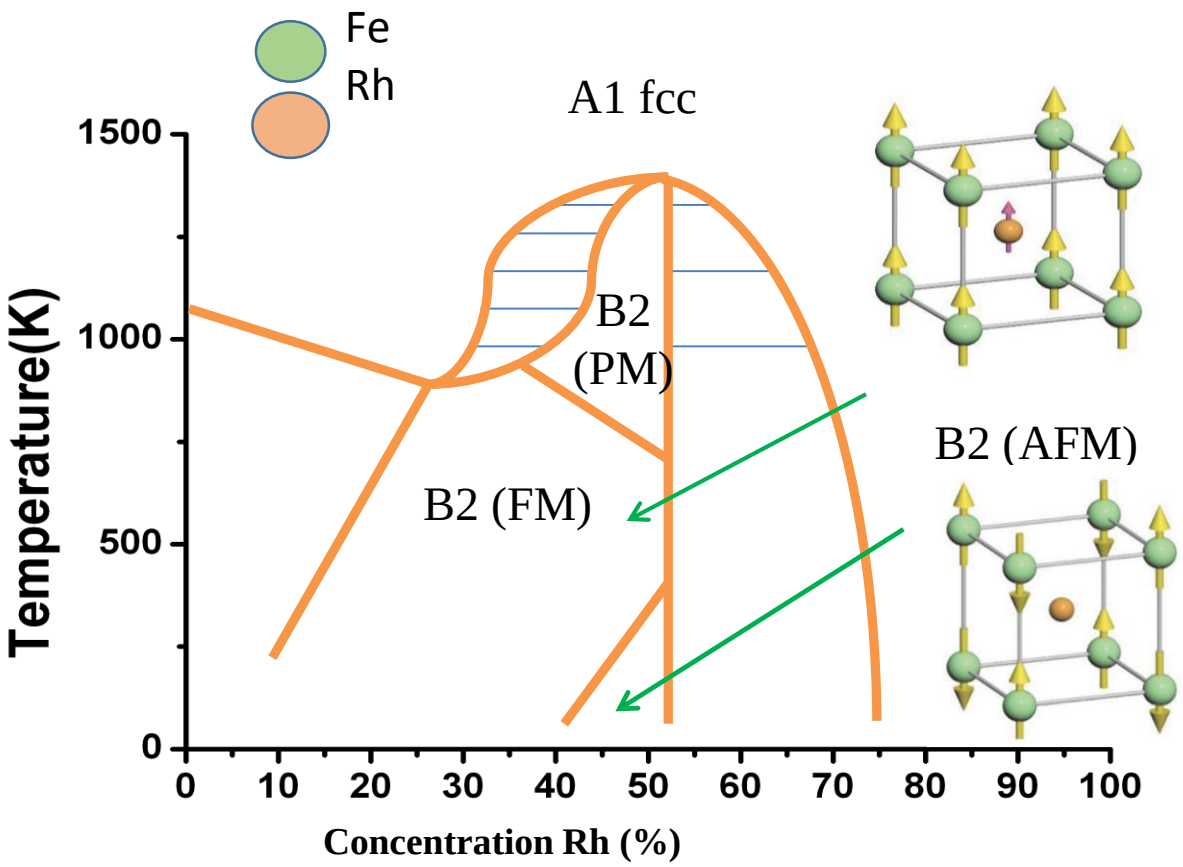
Chemical and magnetic order in B2 cubic FeRh bulk phase



Bulk FeRh Phase-diagram

Metamagnetic transitions in bulk FeRh *(AFM → FM → PM)*
350 K *650 K*

Nano-heterostructure
for Multiferroic Refrigeration applications

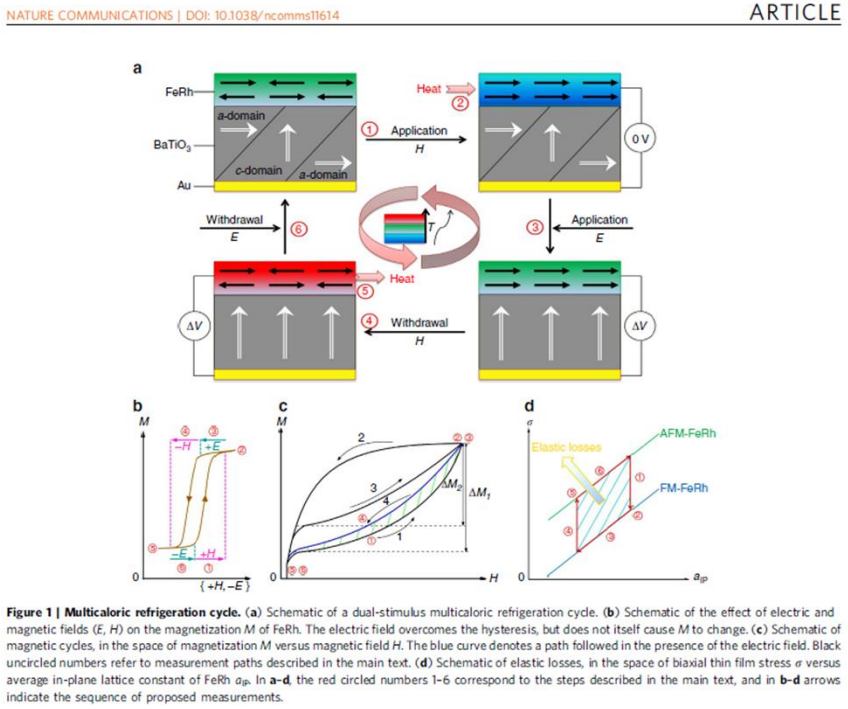


Figure 1 | Multicaloric refrigeration cycle. (**a**) Schematic of a dual-stimulus multicaloric refrigeration cycle. (**b**) Schematic of the effect of electric and magnetic fields (*E*, *H*) on the magnetization *M* of FeRh. The electric field overcomes the hysteresis, but does not itself cause *M* to change. (**c**) Schematic of magnetic cycles, in the space of magnetization *M* versus magnetic field *H*. The blue curve denotes a path followed in the presence of the electric field. Black uncircled numbers refer to measurement paths described in the main text. (**d**) Schematic of elastic losses, in the space of biaxial thin film stress σ versus average in-plane lattice constant of FeRh a_{ip}. In **a**–**d**, the red circled numbers 1–6 correspond to the steps described in the main text, and in **b**–**d** arrows indicate the sequence of proposed measurements.

At Nanoscale, **chemical order** can be obtained by UHV annealing **at high T**

Structural parameters **related to magnetic properties** ?

Mass-Selected Low Energy Cluster Beam Deposition

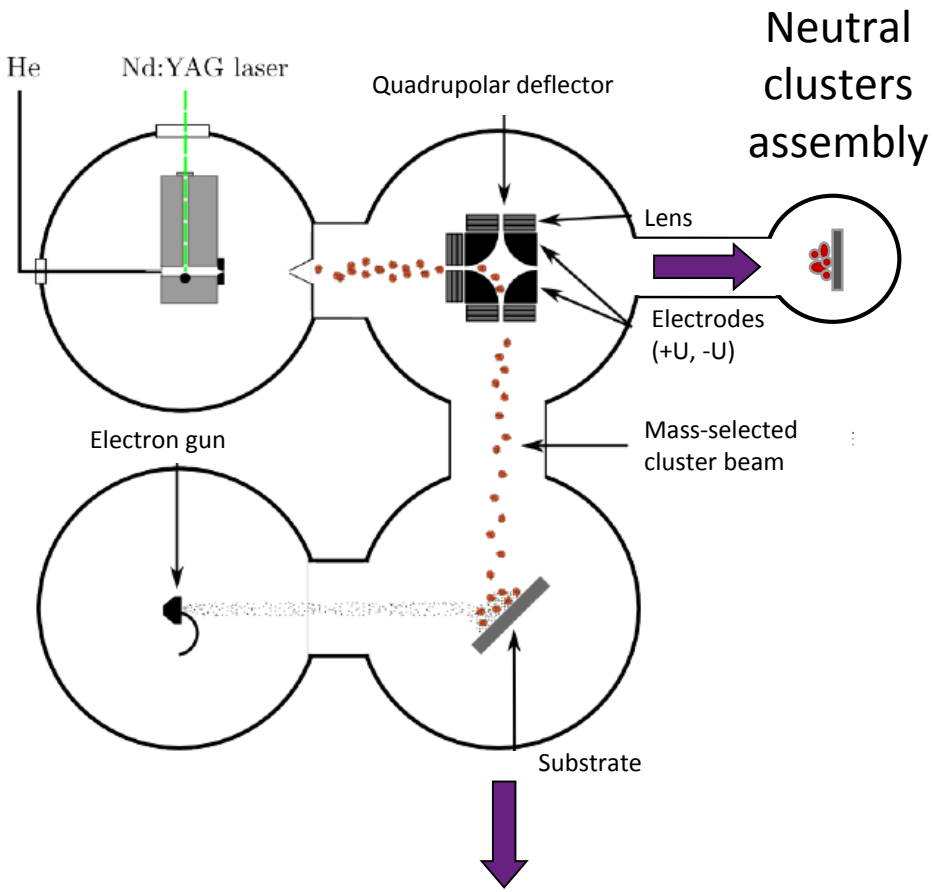
Platform PLYRA

LECBD Technique :
Low Energy Cluster
Beam Deposition

Deposition under UHV of mass-selected ionized clusters

Laser Vaporisation Source
+ Electrostatic quadrupole

- Mixed clusters via Target composition
- Random UHV deposition on Surface
- co-deposited Matrix or capping layer
- Coverture rate independent of size



M-S Low energy cluster beam deposition

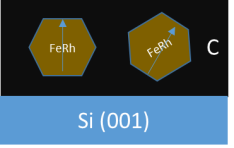
Soft-landing regime
with narrow size cluster distribution

Objectives

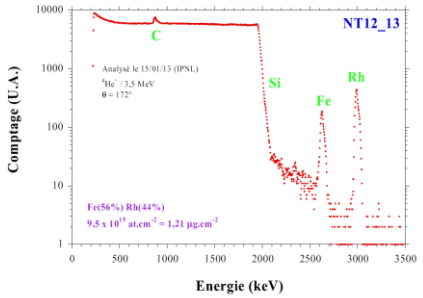
How do the properties of FeRh nanoparticles change when deposited on perovskite substrates?

- Prepare FeRh nanoparticles with 3 nm and 7 nm monomere size
- *In situ* deposited over Si and BTO/STO in UHV + C-capping
- Determine chemical and crystallographic orders.
- Describe magnetic behavior.

or

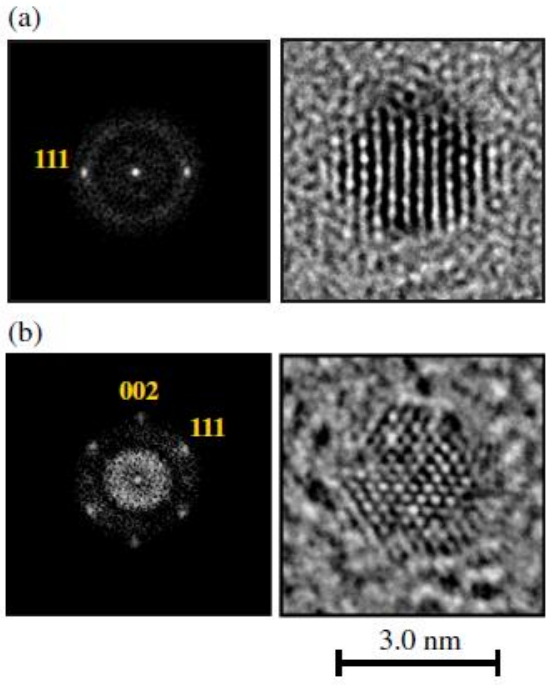


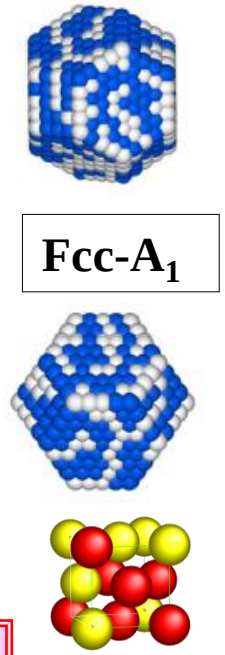
Intrinsic Properties of Mass-selected **3nm-FeRh** clusters@C



RBS analysis FeRh@C

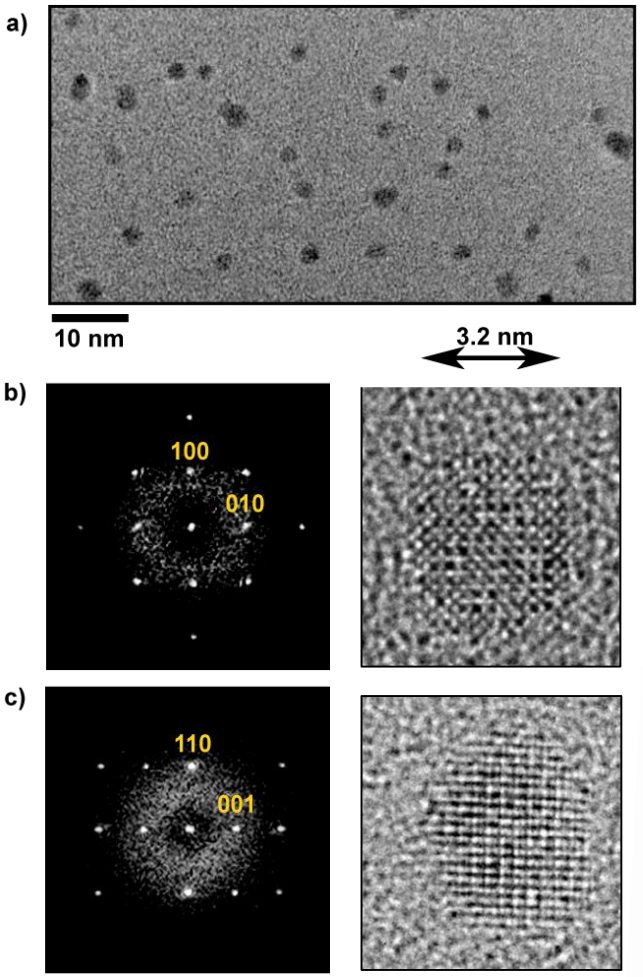
Fe56%Rh44% (± 5%)





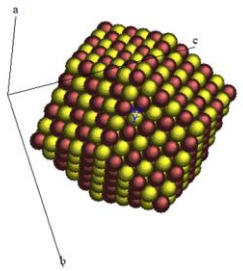
Fcc-A_1

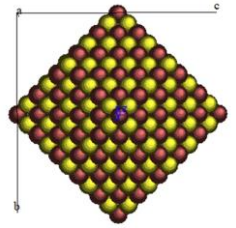
As-prepared FeRh clusters



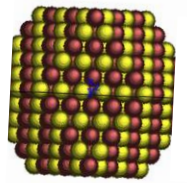
Annealed 3nm-FeRh clusters

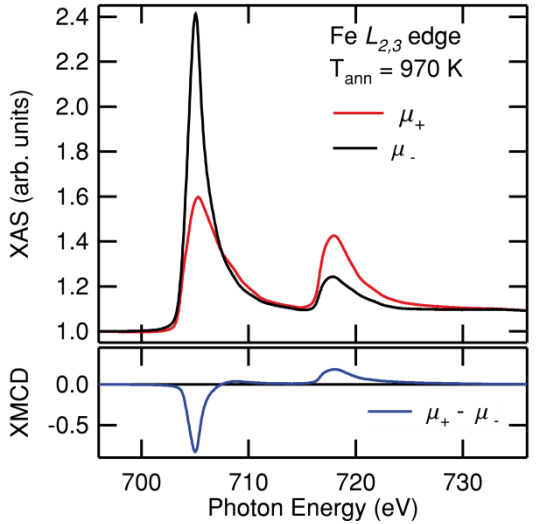
CS HRTEM, Coll. K. Sato, Sendaï Japon



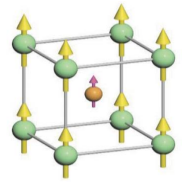


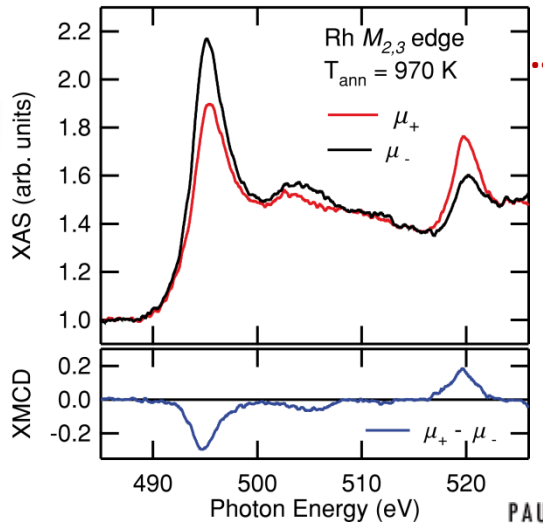
CsCl- B_2





XMCD at 2K
Fe $L_{2,3}$ edge





… But FM from 2K - 350 K

Rh M $_{2,3}$ edge

PAUL SCHERRER INSTITUT

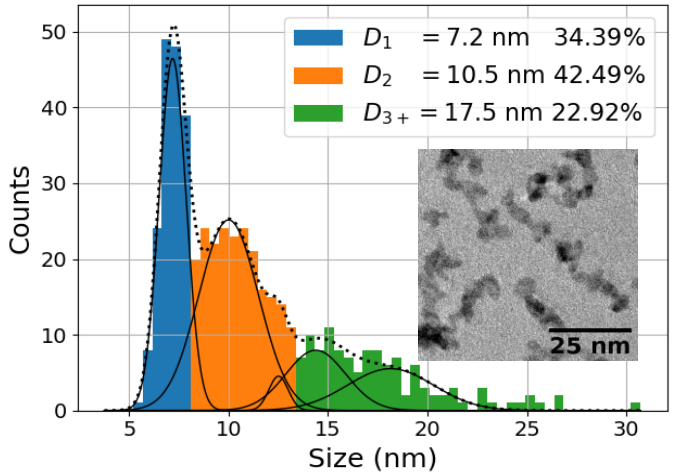
Fcc- A1 chemically disordered → Cubic B2 chemically ordered FeRh NPs …

A. Hillion et al. *PRL 2013*

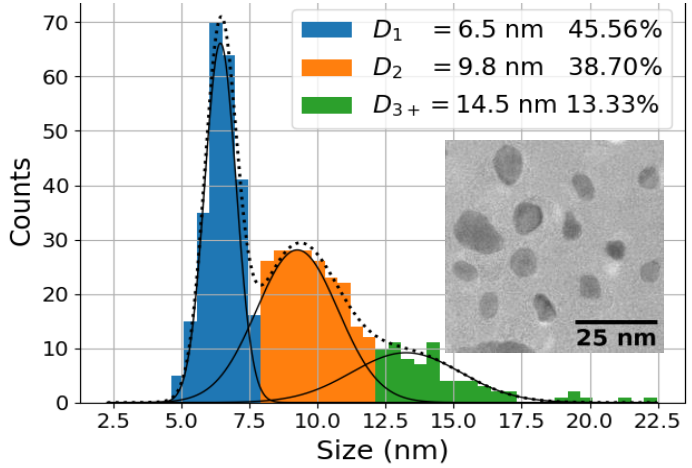
TEM/HRTEM on thin Mass-selected **7nm-FeRh** clusters@C

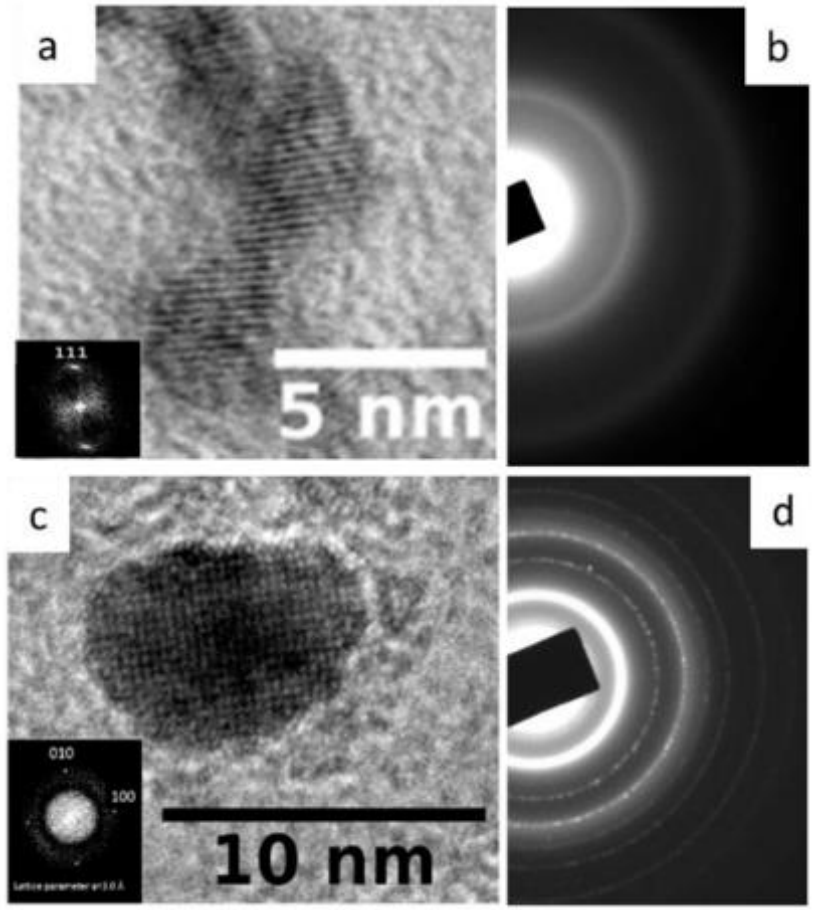
- FeRh nanoparticles of 7 nm (nominal monomer size on TEM grid)
- After annealing, nanoparticles are in B2 phase and become rounder.

As prepared



Annealed at 700 °C





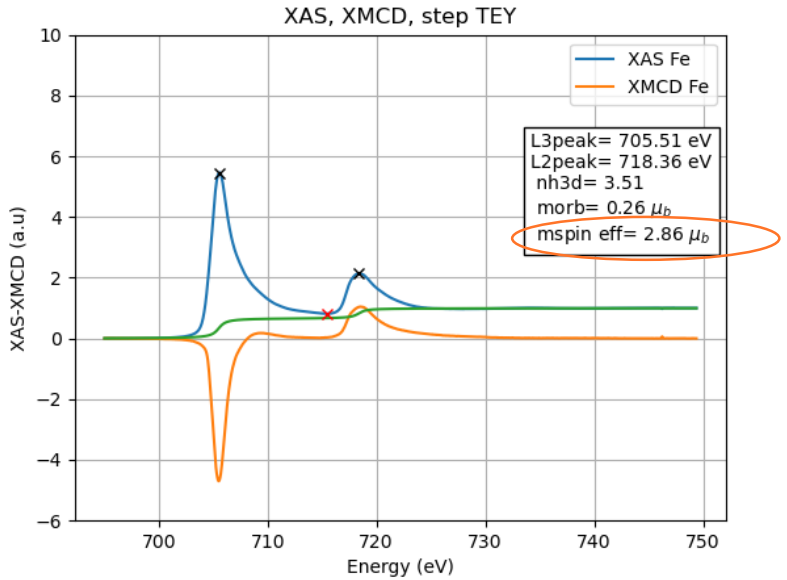
A1 FeRh FCC

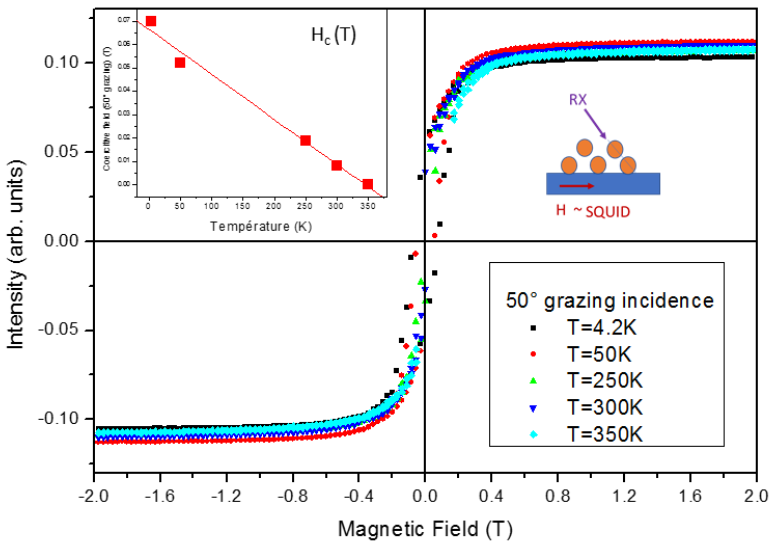
B2 FeRh cubic

Guillermo Herrera et al. *EPJAP (2022)*

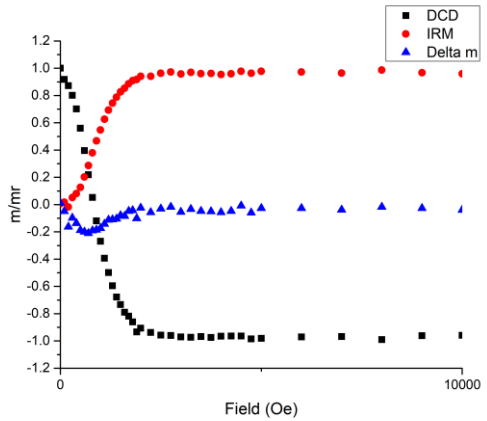
Intrinsic Magnetic Properties of **Large** B2 FeRh Clusters in C matrix

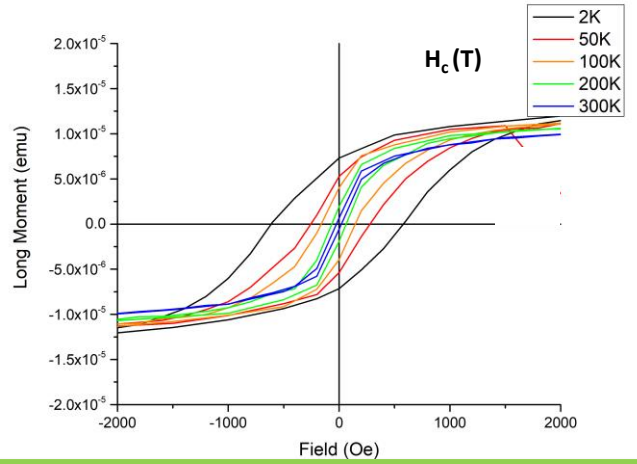
XMCD at 4.2K at Fe $L_{2,3}$ edge on annealed 7nm-FeRh B2 clusters@C on Si at DEIMOS





In agreement with SQUID magnetometry: FM behaviours up at 2K for moderate NPs interaction



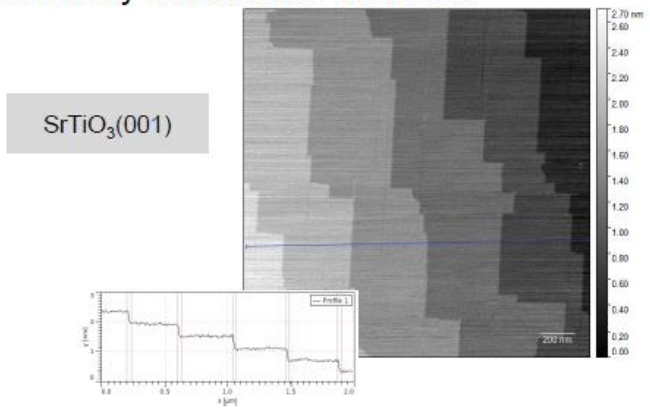


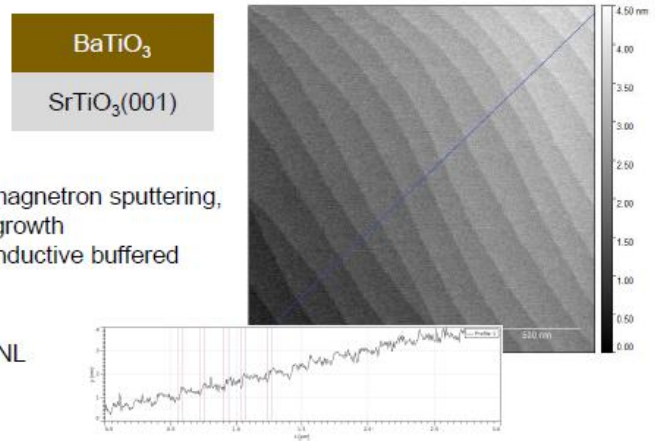
Ferromagnetic order at Low T for B2 FeRh NPs up to 10 nm in diameter !

Mass-selected **FeRh** clusters deposited on **perovskite oxide**

SrTiO3, BaTiO3 films (001) @INL

Atomically flat titanate surfaces

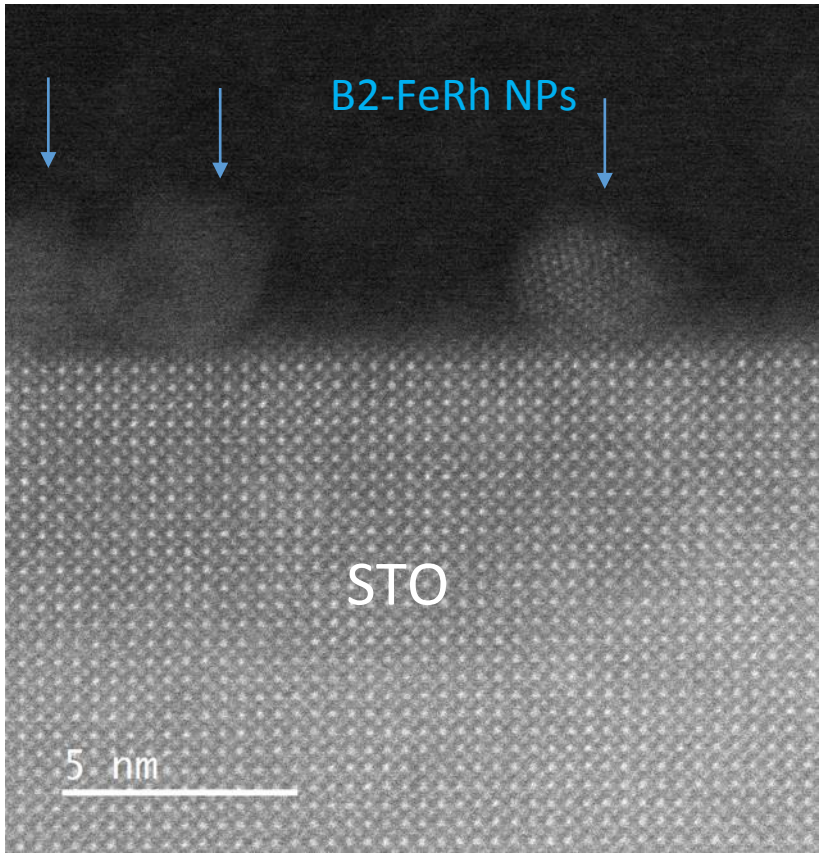




BaTiO3: Radio-frequency magnetron sputtering, high temperature, thin film growth
Different substrates and conductive buffered substrates under study

Atomic Force Microscopy, INL

Institut des Nanotechnologies de Lyon UMR 5270



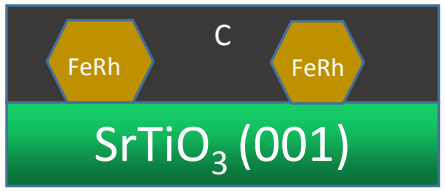
STEM HAADF, CLYM St Etienne

VOLtage COntrol of NANOmagnet ANR-19-CE09-0023

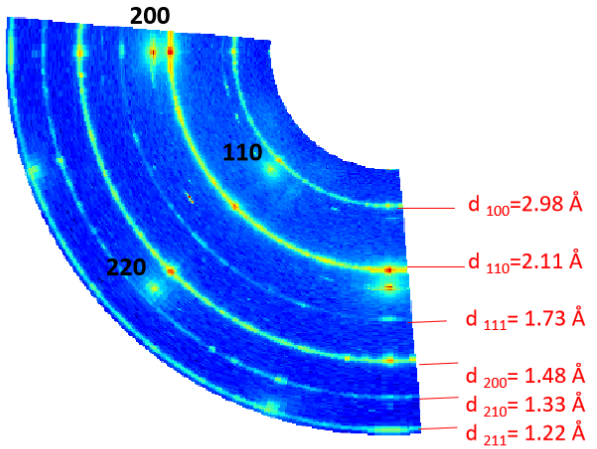
B2 **FeRh** NPs on **perovskite substrate**

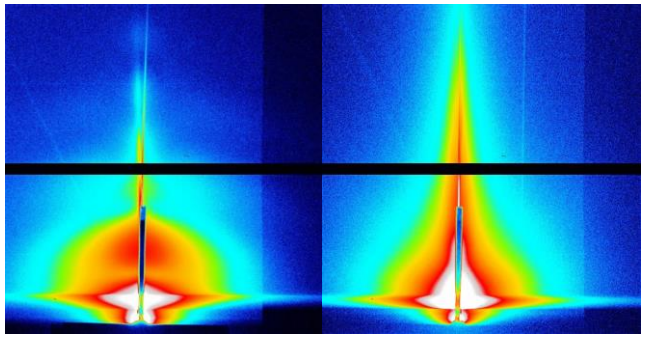
at BM32-ESRF beamline

In situ UHV annealed 2C/FeRh 3 nm monomer/$SrTiO_3$



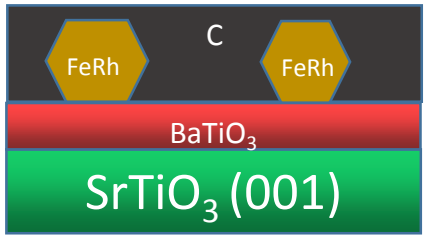
FeRh[110] / $SrTiO_3$[020]



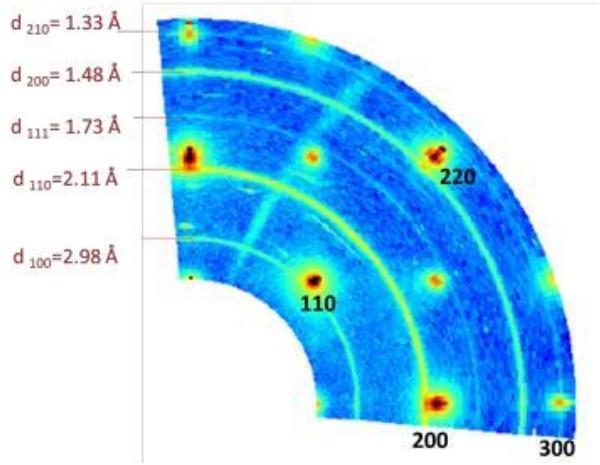


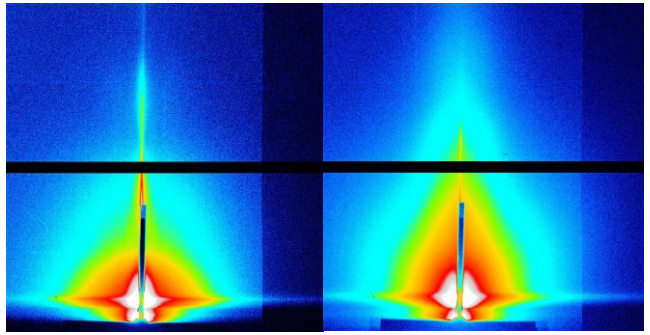
as prepared 700 °C

In situ UHV annealed 2C/FeRh 7 nm monomer/thin $BaTiO_3$/$SrTiO_3$



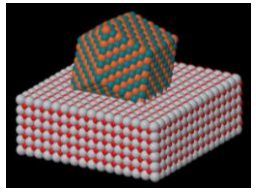
FeRh[110] / thin $BaTiO_3$[020] on STO



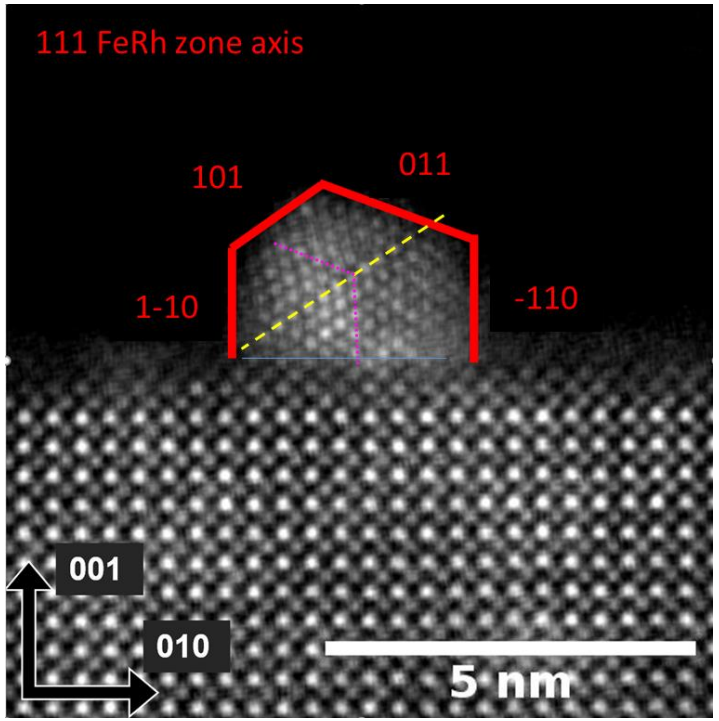


as prepared 700 °C

B2 **FeRh** NPs on **perovskite** evidence of several Epitaxies

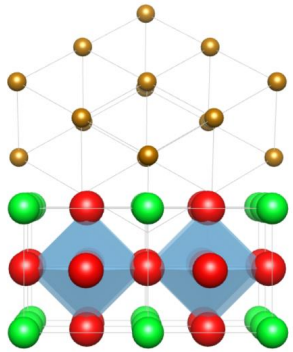


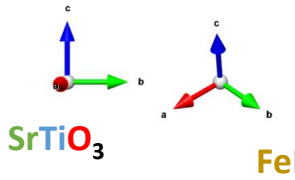
STEM-HAADF @ 200 kV
(Cs-corrected Jeol NeoARM)
Cross-section sample by FIB



Epitaxy FeRh [1-10]/$SrTiO_3$[100] seen by STEM and GIXRD

New epitaxy (1)
[1-10] FeRh //[100] $SrTiO_3$
[111] FeRh //[010] $SrTiO_3$





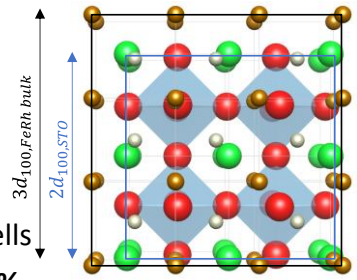
→(11-2) FeRh plane contact
Anisotropic in-plane strain

$$\varepsilon_{1-10/100} = \frac{d_{100,STO} - 2d_{1-10,FeRh\ bulk}}{2d_{1-10,FeRh\ bulk}} = \textbf{-7.42\%}$$

New epitaxy (2)
[100] FeRh //[100] $SrTiO_3$
[110] FeRh //[110] $SrTiO_3$

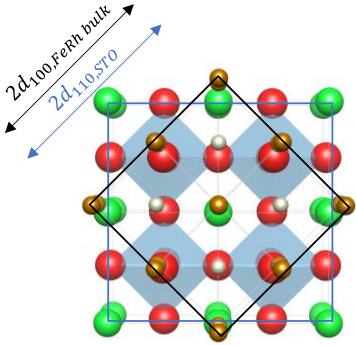
→(001) FeRh plane contact
3 FeRh cells cube-on-cube on 2 $SrTiO_3$ cells

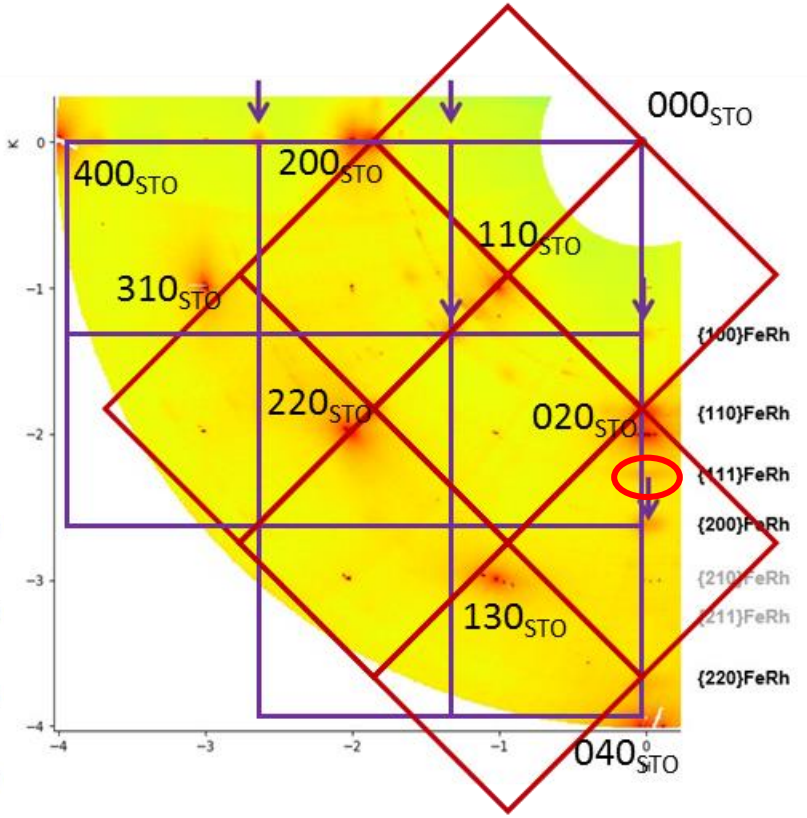
$$\varepsilon_{100/100} = \frac{2d_{100,STO} - 3a_{FeRh\ bulk}}{3a_{FeRh\ bulk}} = \textbf{-12.73\%}$$



Conventional epitaxy
[110] FeRh//[100] $SrTiO_3$
[1-10] FeRh//[010] $SrTiO_3$

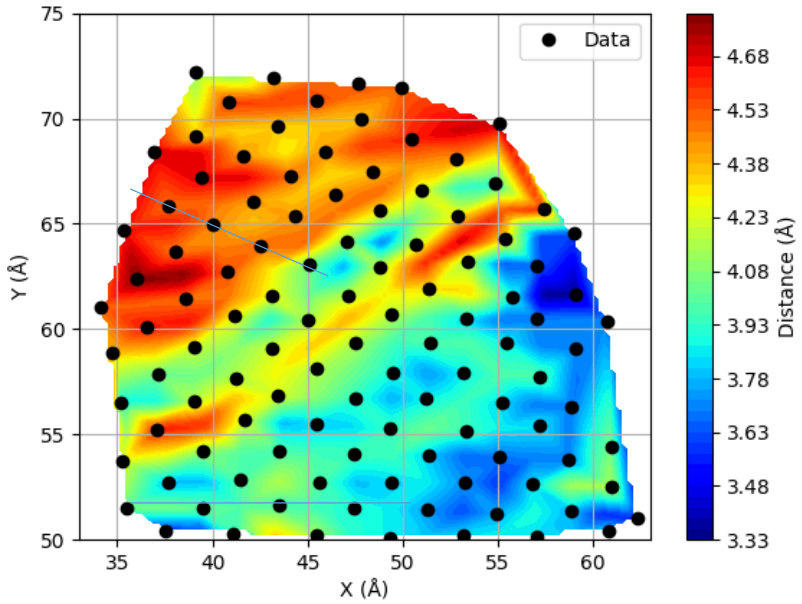
→(001) FeRh plane contact
FeRh cell axes at 45°





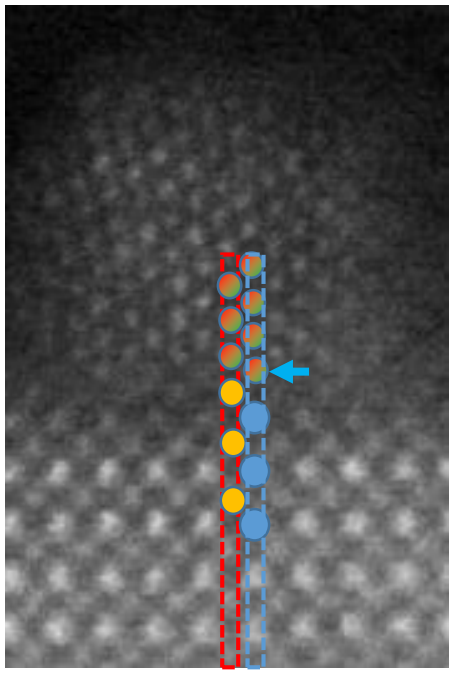
Single B2 **FeRh** NP on **STO** substrate

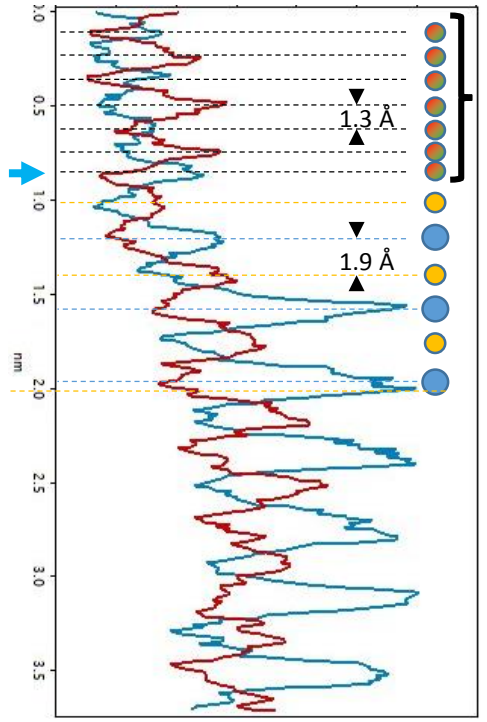
STEM-HAADF @ 200 kV
(Cs-corrected Jeol NeoARM)
Cross-section sample by FIB



- Is possible to identify positions.
- Possible twining and deformation.
- Epitaxy at the interface.

STEM-HAADF



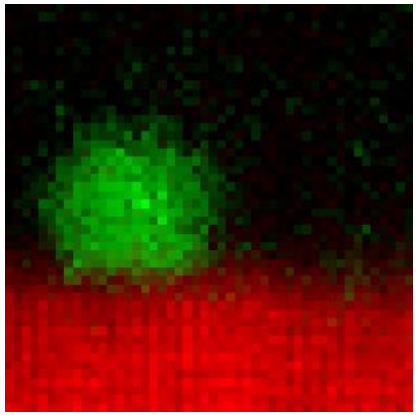


Fe/Rh

Ti
Sr
Ti
Sr
Ti

$SrTiO_3$ (001) surface is Ti terminated

STEM-EELS



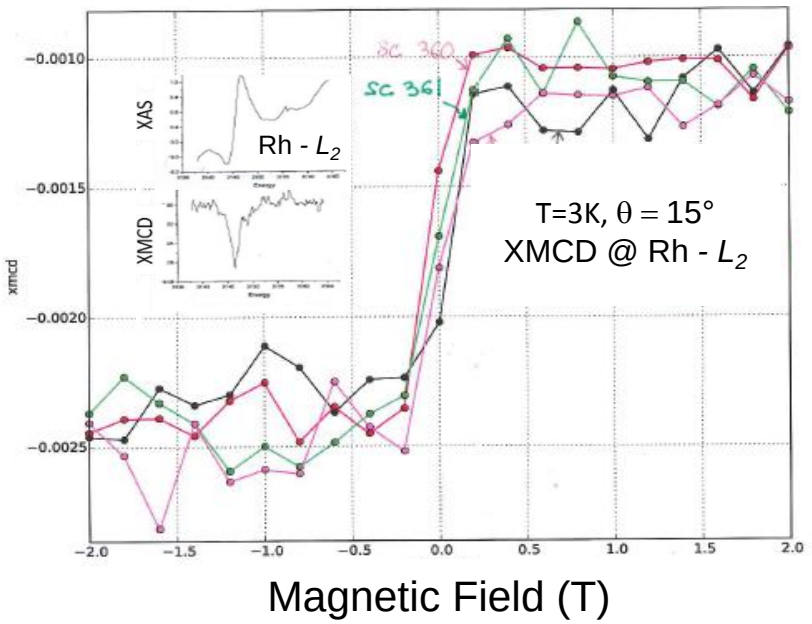
Fe-L_{23}, Ti-L_{23}

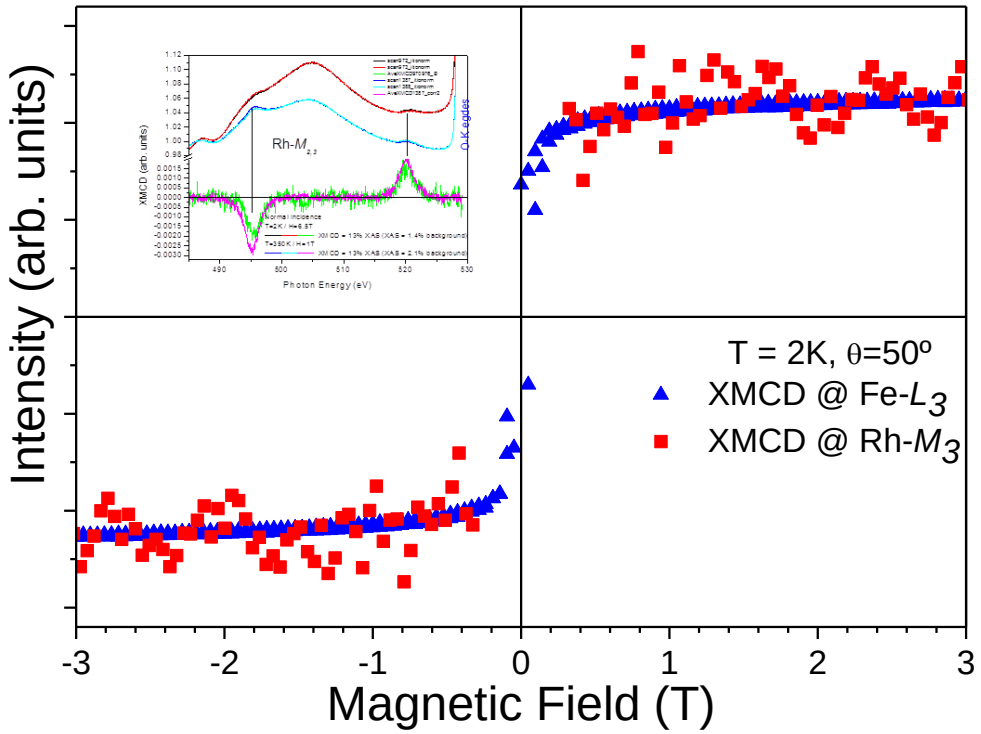
There is no diffusion of Ti or Fe

Sharp Interface and strain
→(11-2) FeRh plane contact
Anisotropic in-plane strain

Magnetic Properties of B2 FeRh NPs on perovskite

XMCD at Rh-L edge (ID12 –ESRF) and at Fe-L and Rh-M edges (DEIMOS –SOLEIL)

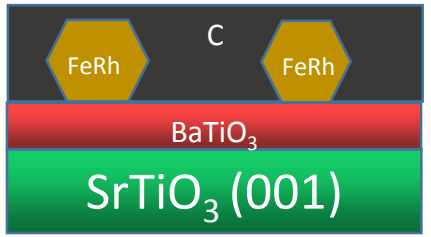




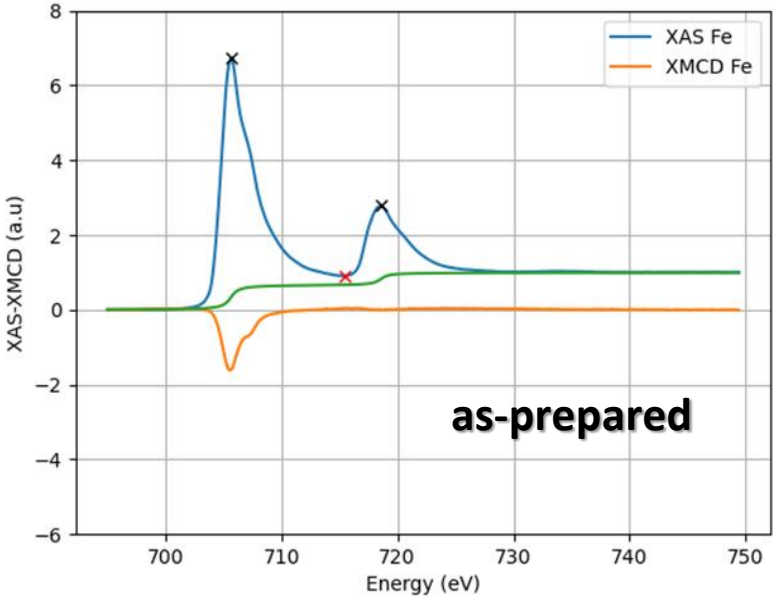
- **Strong FM coupling between Fe and Rh moment even at low temperature**

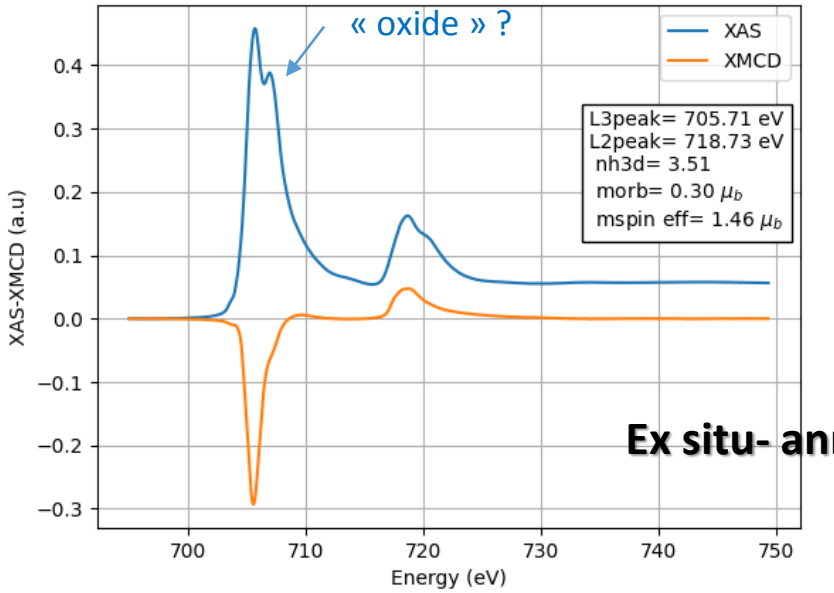
Magnetic Properties of B2 FeRh NPs on perovskite

As-prepared and UHV annealed sample avec C-capping :
2C/FeRh 7 nm monomer/$BaTiO_3$/$SrTiO_3$

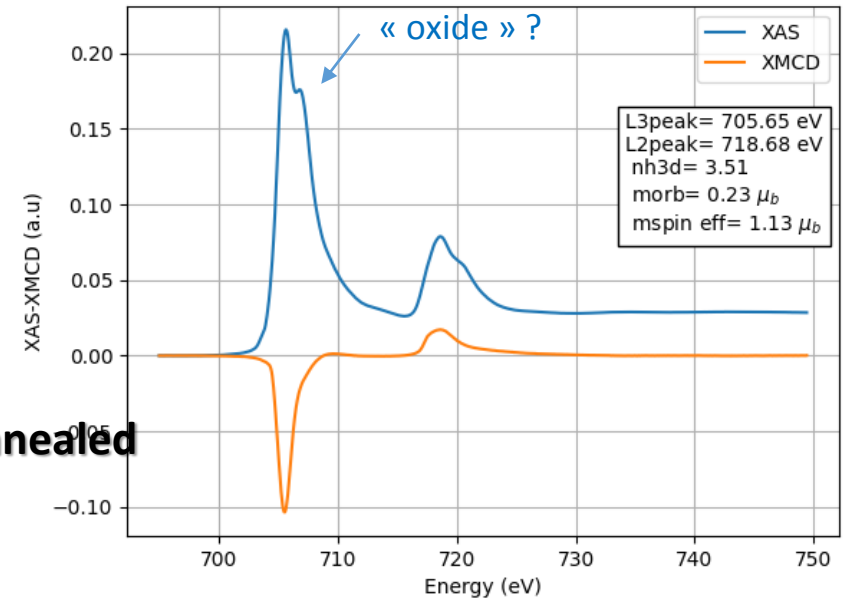


XMCD at Fe-$L_{2,3}$ edge @ 2 K





@ 350 K

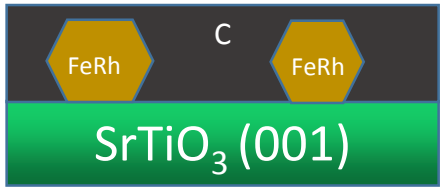


Magnetic Properties of B2 FeRh NPs on perovskite

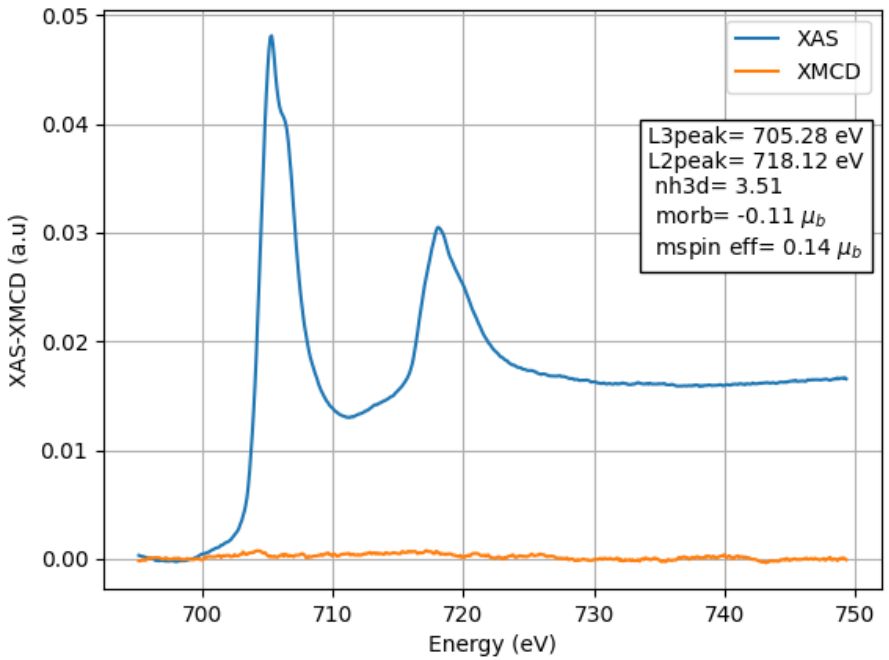
Deoxidation of FeRh NPs possible from :

In situ UHV annealing FeRh 3 nm monomer/$SrTiO_3$

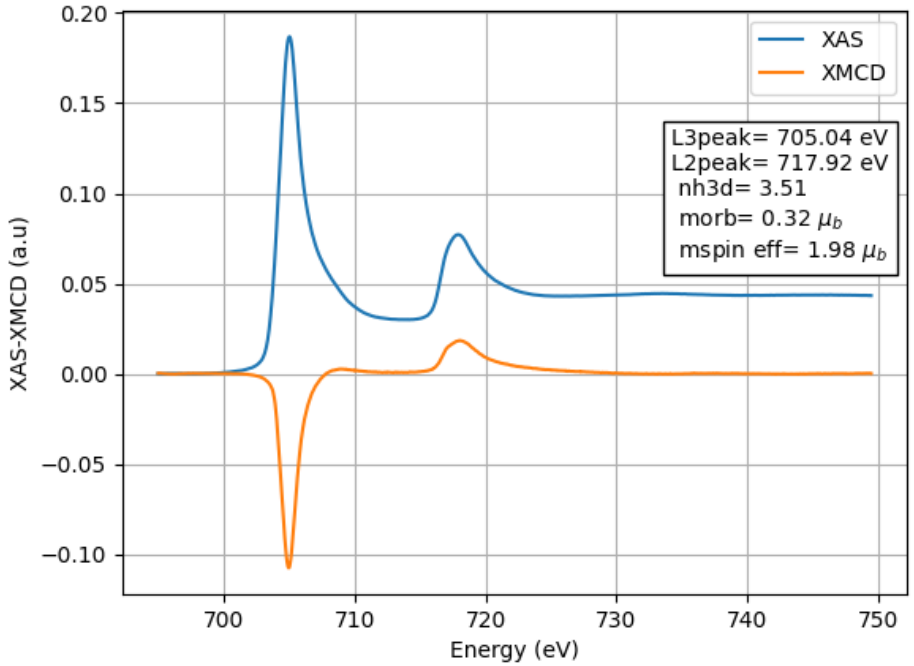
ms is reduced compared to same sample on Si : Fe magnetic dead layer on STO ?



Sample as prepared

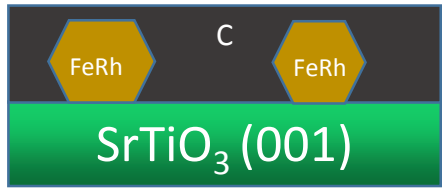


Sample *in situ* annealed 600°C

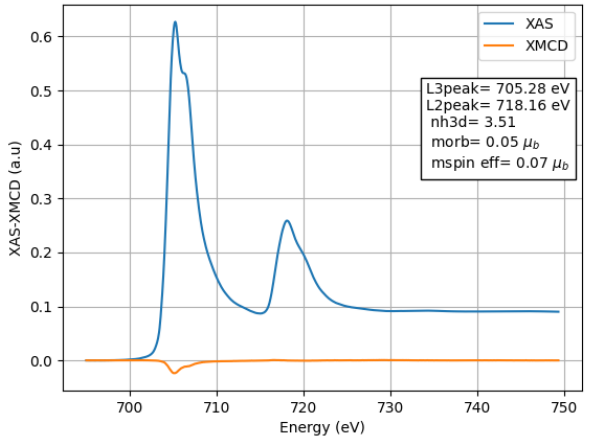


Magnetic Properties of B2 FeRh NPs on perovskite

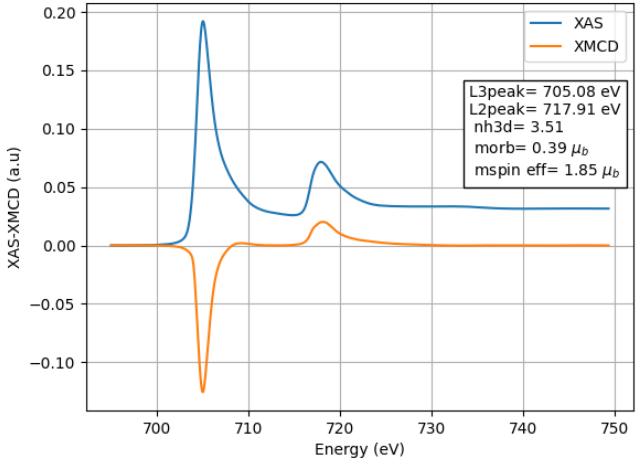
Deoxidation of FeRh NPs on STO



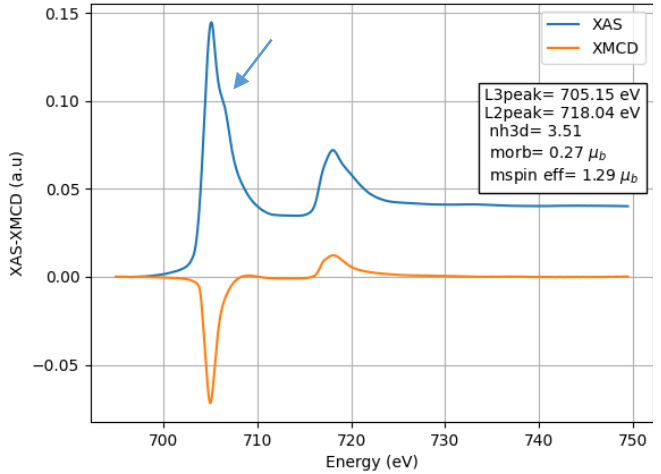
Sample as-prepared



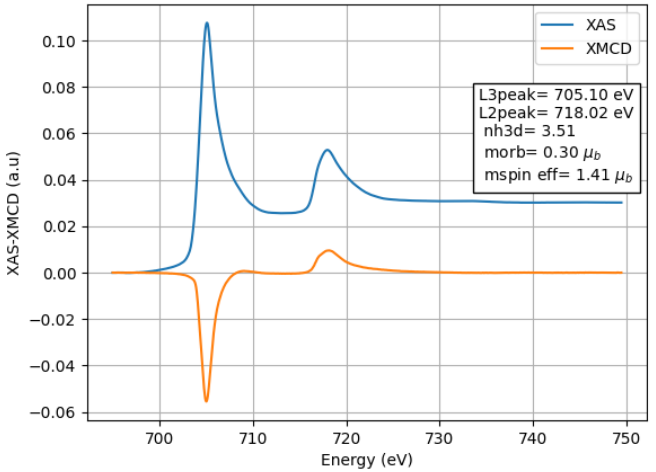
in situ UHV annealed up to 800°C



after transfer in air (after 2 months)



in situ UHV reduced at 500°C



In situ UHV annealing FeRh 3 nm monomer/$SrTiO_3$
But *ms* reduced (magnetic dead layer on STO ?)

Conclusion
on chemically ordered FeRh NPs over Perovskite oxides

- B2-FeRh nanoparticles present several **epitaxy over $SrTiO_3$ and thin $BaTiO_3$**
- with **strong** Lattice parameter **strain**
- FeRh NPs get partially oxided, but **can be deoxidized from in situ annealing at 600°C.**
- **No migration of Fe or Ti at Interface**.
- **Relaxation** and **size effect** still present on avoiding **AntiFerromagnetic** state at low temperature

PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR
ANR

VOLtage COntrol of NANOmagnet

ANR-19-CE09-0023

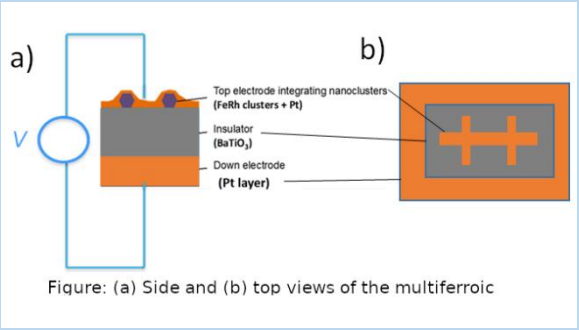
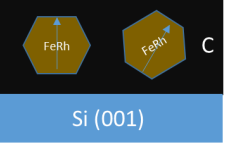


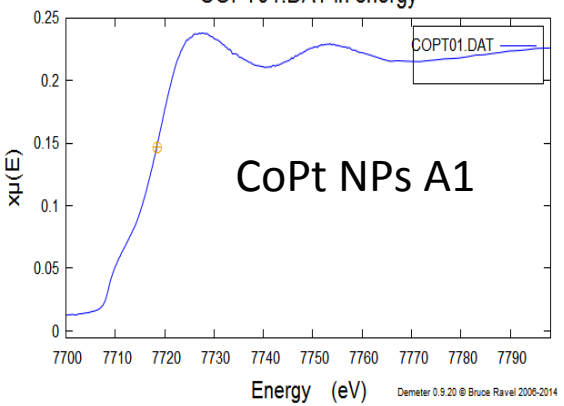
Figure: (a) Side and (b) top views of the multiferroic

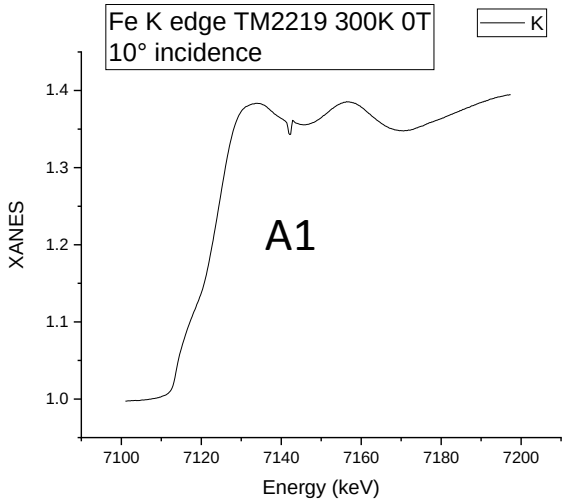
Acknowledgment

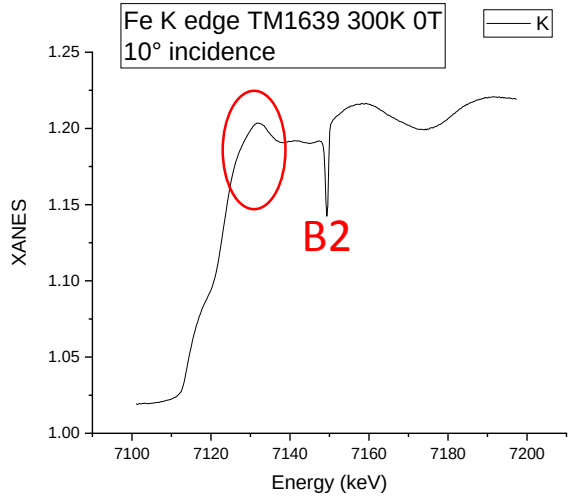
-ANR project VOLCONANO
-DEIMOS-SOLEIL Synchrotron
-SIXS-SOLEIL Synchrotron
-BM32-ESRF Synchrotron
-ID12-ESRF Synchrotron
-CLYM

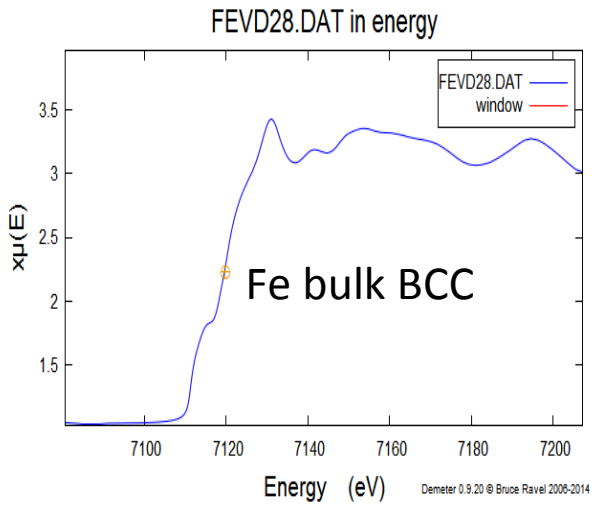


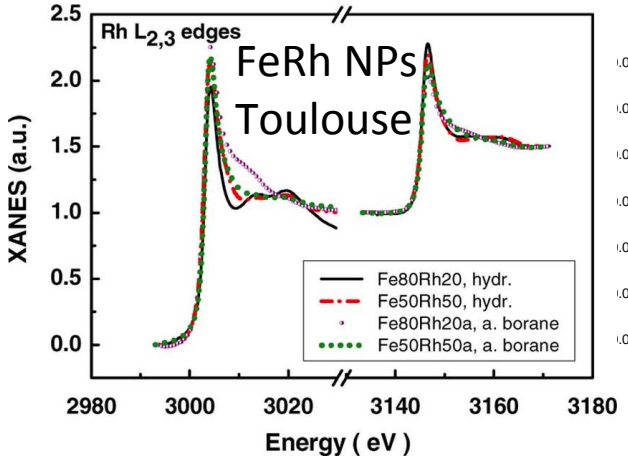
XANES thin Mass-selected 7nm-FeRh@ C samples / Si

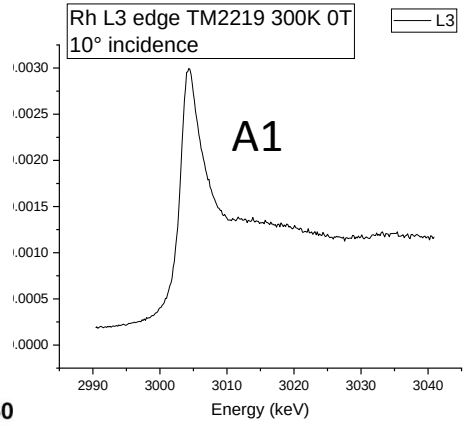


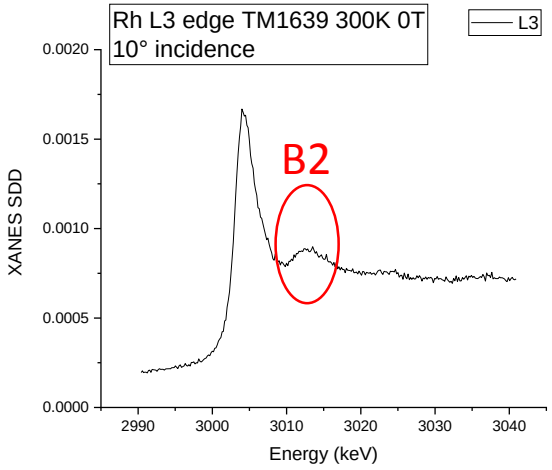








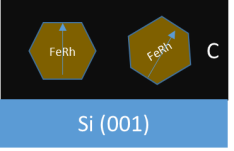




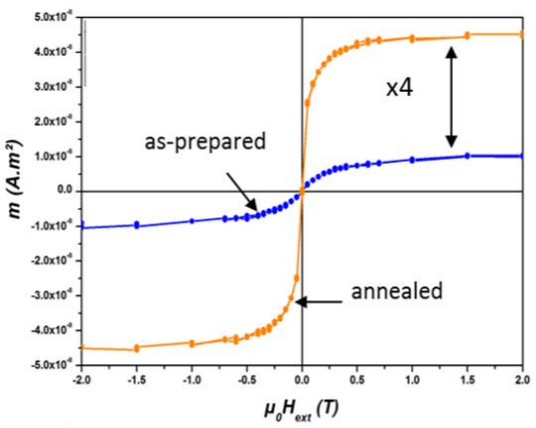
Rh L_2-edge

as-prepared / annealed

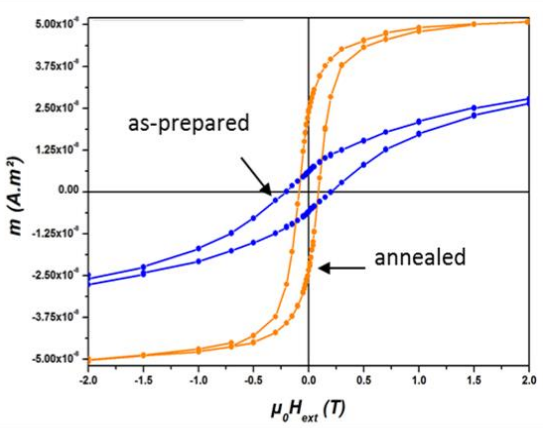
at ID12 - ESRF beamline



SQUID on Mass-selected 7nm-FeRh@ C / Si
Low density : 4 %

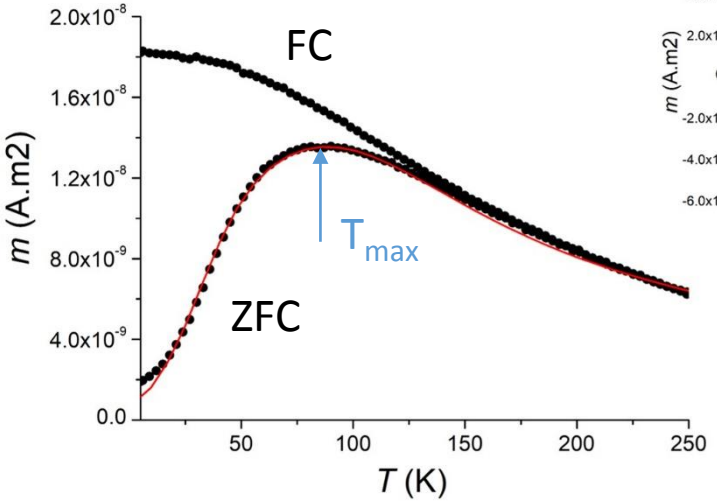


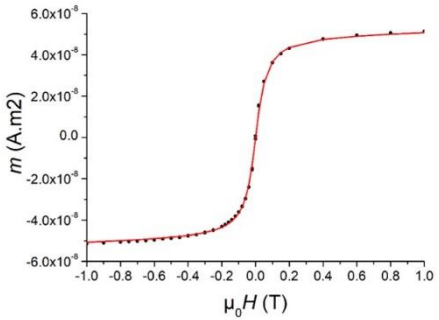
SP @100 K



FM @ 2 K

TM 16-39 FeRh environ 4 %





Dm1 = 6.3 nm
w = 0.08
74 % de monomère (fixé par rapport au TEM)
Dm2 = 1.26*Dm1
w2 = 0.08
K1 = 123 kJ/m3
wK1 = 0.38 ;
il y a une large distribution de constante d'anisotropie (comme pour le Co)

ZFC/FC susceptibility and Hysteresis loops @ 300 K
for annealed sample

- No Metamagnetic transition for annealed thin mass-selected FeRh @ C with 7 nm in diameter

Large mass-selected FeRh sample @ C, Guillermo Herrera et al. EPJAP (2022)

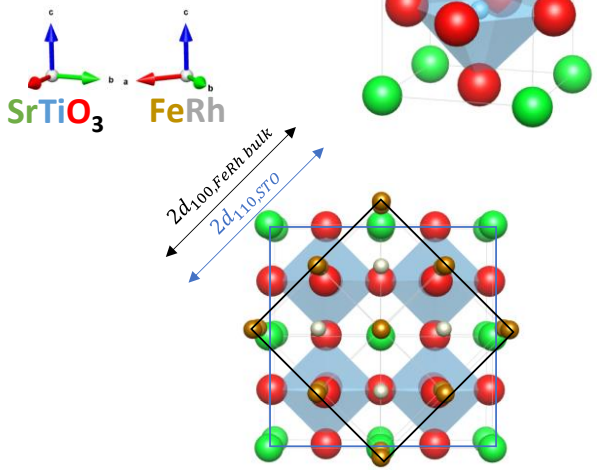
FeRh / STO epitaxy : details

Epitaxial relationships
Lattice mismatch, cell matching

Conventional epitaxy
[110] FeRh//[100] $SrTiO_3$
[1-10] FeRh//[010] $SrTiO_3$

→(001) FeRh plane contact
FeRh cell axes @ 45deg from $SrTiO_3$ ones

$$\varepsilon_{110/100} = \frac{2d_{110,STO} - 2d_{100,FeRh\ bulk}}{2d_{100,FeRh\ bulk}} = \textbf{-7.43\%}$$

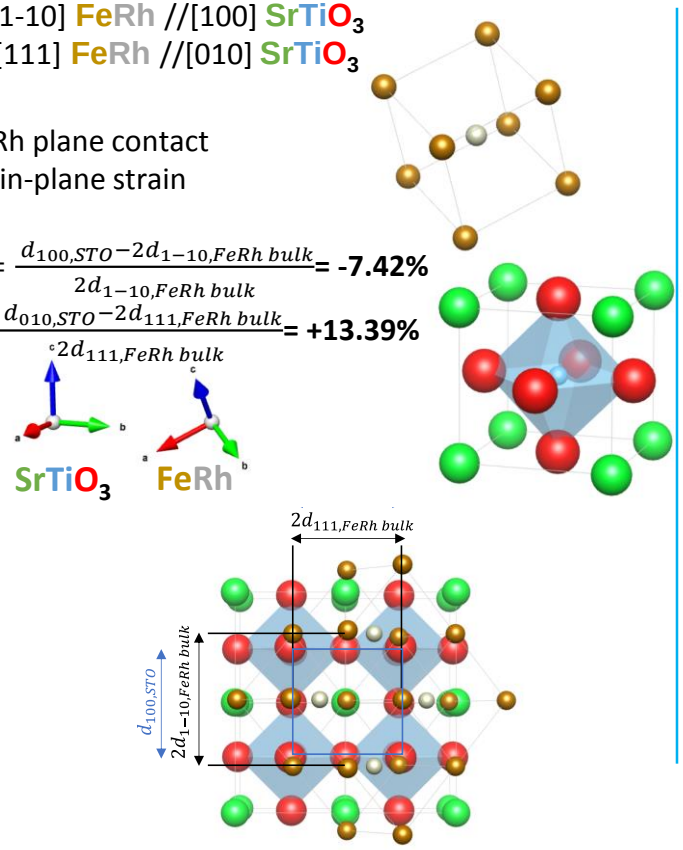


New epitaxy (1)
[1-10] FeRh //[100] $SrTiO_3$
[111] FeRh //[010] $SrTiO_3$

→(11-2) FeRh plane contact
Anisotropic in-plane strain

$$\varepsilon_{1-10/100} = \frac{d_{100,STO} - 2d_{1-10,FeRh\ bulk}}{2d_{1-10,FeRh\ bulk}} = \textbf{-7.42\%}$$

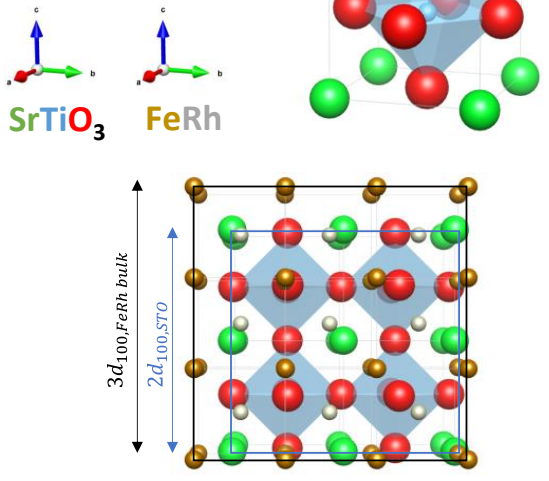
$$\varepsilon_{111/010} = \frac{d_{010,STO} - 2d_{111,FeRh\ bulk}}{2d_{111,FeRh\ bulk}} = \textbf{+13.39\%}$$



New epitaxy (2)
[100] FeRh //[100] $SrTiO_3$
[110] FeRh //[110] $SrTiO_3$

→(001) FeRh plane contact
3 FeRh cells cube-on-cube on 2 $SrTiO_3$ cells

$$\varepsilon_{100/100} = \frac{2d_{100,STO} - 3a_{FeRh\ bulk}}{3a_{FeRh\ bulk}} = \textbf{-12.73\%}$$



Under large lattice mismatch: unusual epitaxies can be stabilized in small volume objects, *ie* NCs

Bulk crystals
FeRh B2 phase, Pm-3m, a = 2.983A
$SrTiO_3$ Pm-3m, a = 3.905A

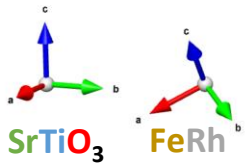
FeRh / STO epitaxy : STEM-HAADF

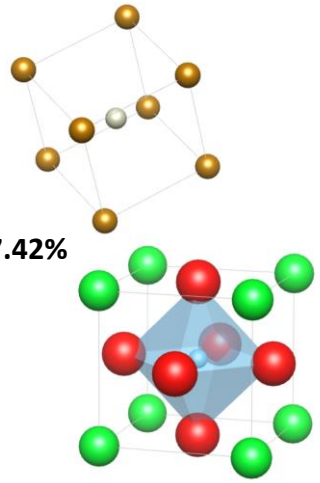
Epitaxial relationships
Lattice mismatch, cell matching

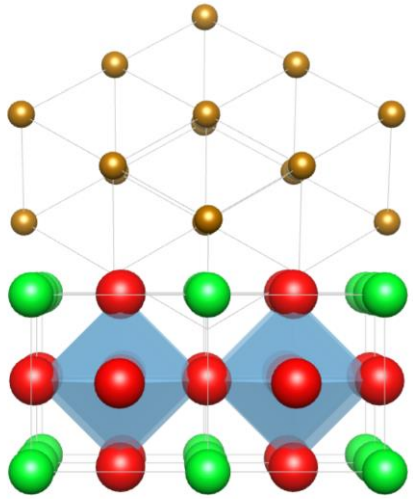
New epitaxy (1)
[1-10] FeRh //[100] $SrTiO_3$
[111] FeRh //[010] $SrTiO_3$

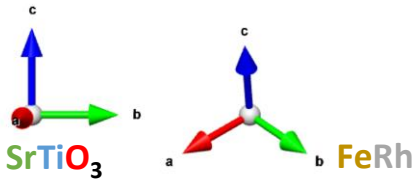
→(11-2) FeRh plane contact
Anisotropic in-plane strain

$$\varepsilon_{1-10/100} = \frac{d_{100,STO} - 2d_{1-10,FeRh\ bulk}}{2d_{1-10,FeRh\ bulk}} = \textbf{-7.42\%}$$

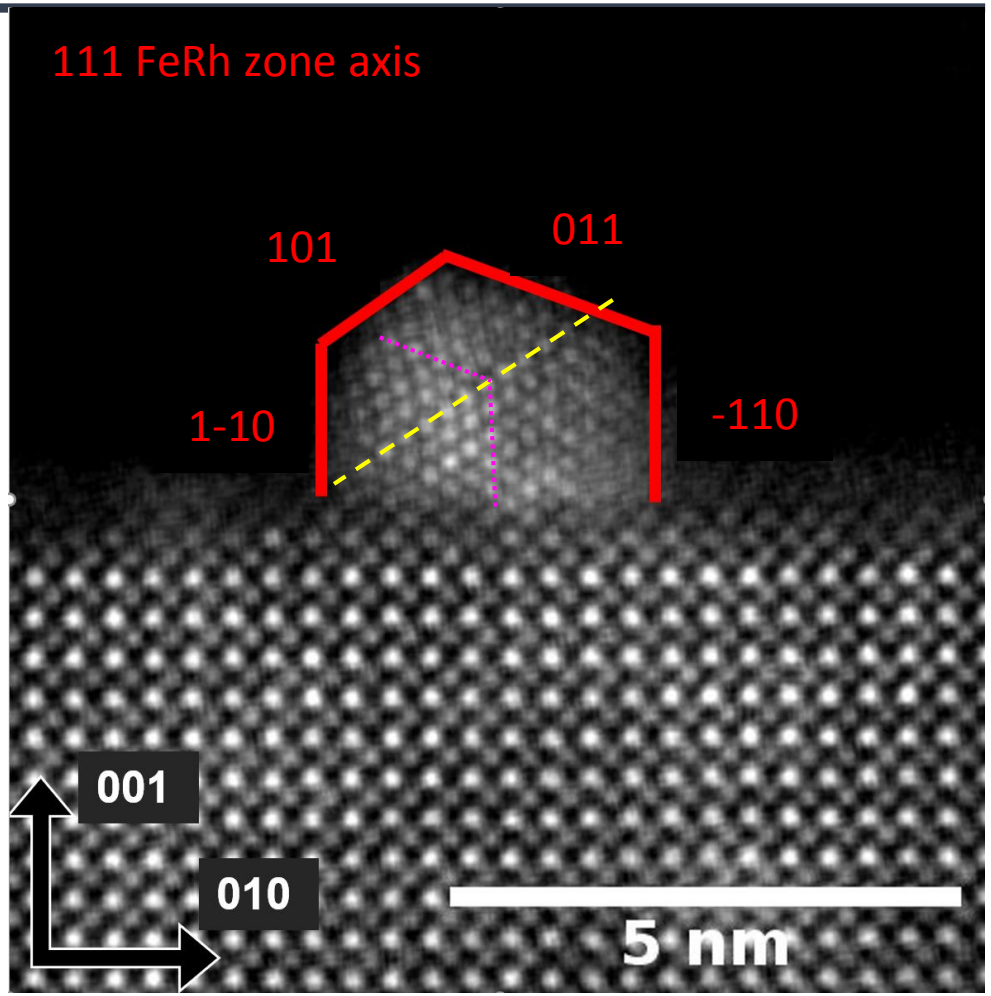






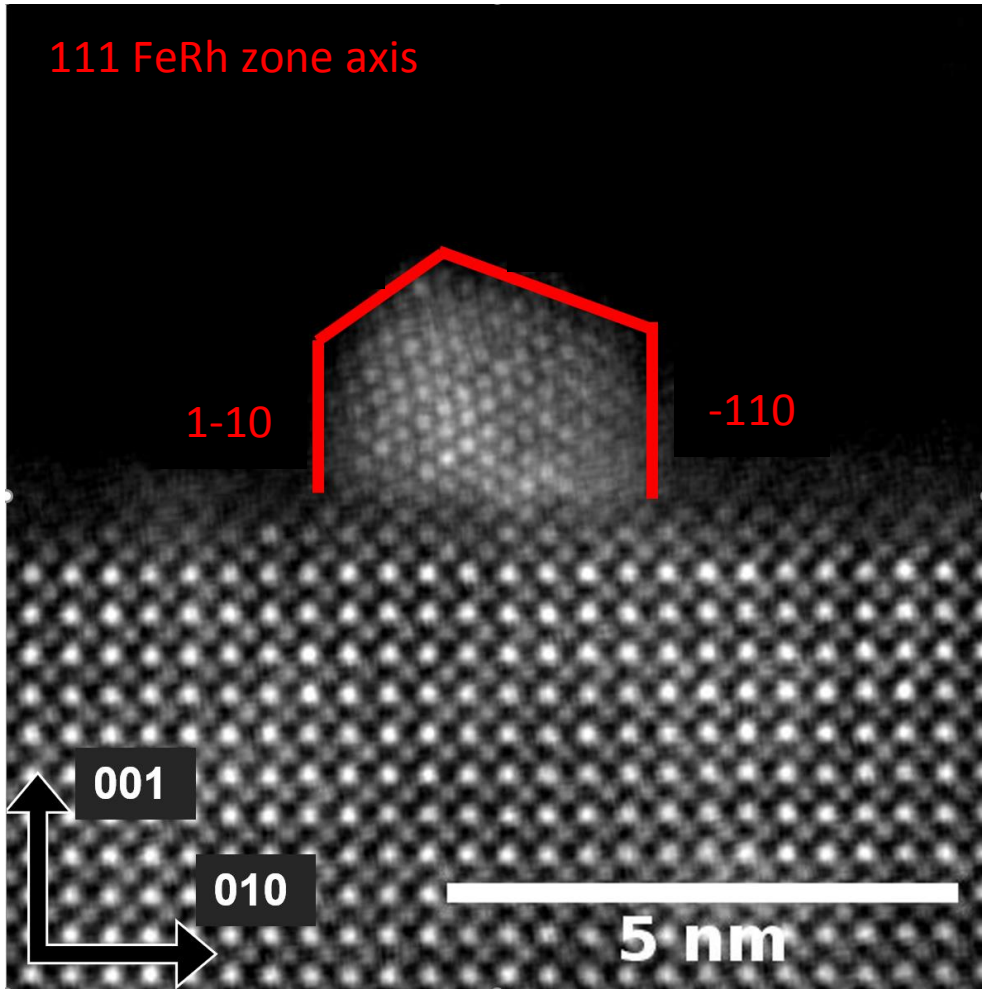


STEM HAADF
New epitaxy (1)



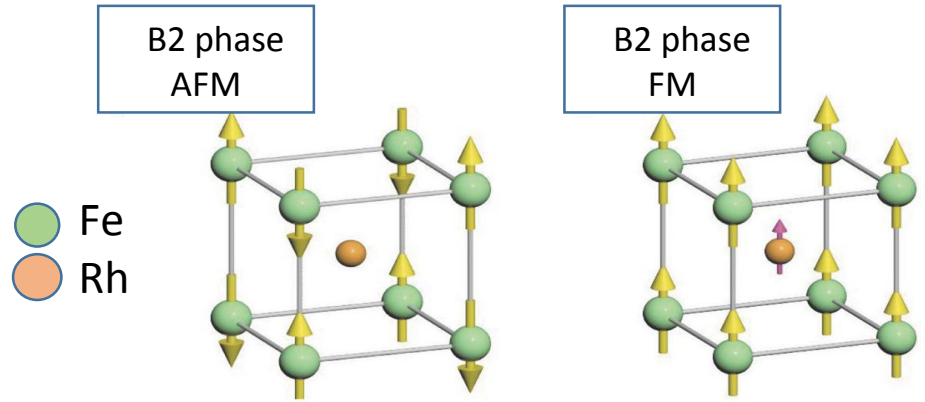
Under large lattice mismatch: unusual epitaxies can be stabilized in small volume objects, *ie* NCs

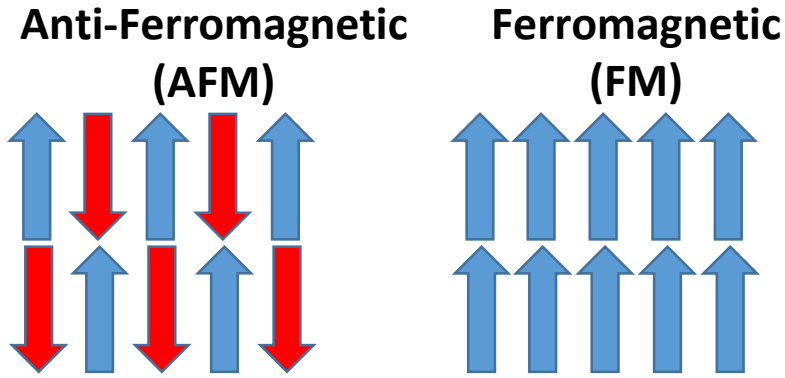
Bulk crystals
FeRh B2 phase, Pm-3m, a = 2.983A
$SrTiO_3$ Pm-3m, a = 3.905A


111 FeRh zone axis
1-10
-110
001
010
5 nm

Iron Rhodium (FeRh)

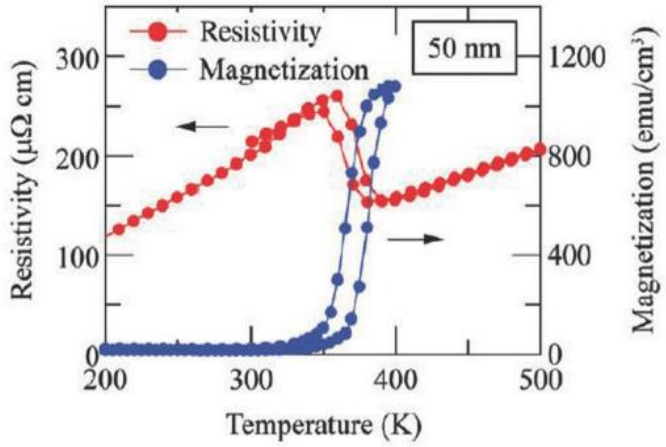
- FeRh bulk in the chemically ordered B2 phase presents metamagnetic transition: it is antiferromagnetic at temperatures lower than 370 K and ferromagnetic at higher temperatures.
- This metamagnetic transition happens along with a lattice parameter expansion.
- In thin film form, the B2 phase can be achieved after annealing at 700° C, presenting the metamagnetic transition.





T < 370 K

T > 370 K



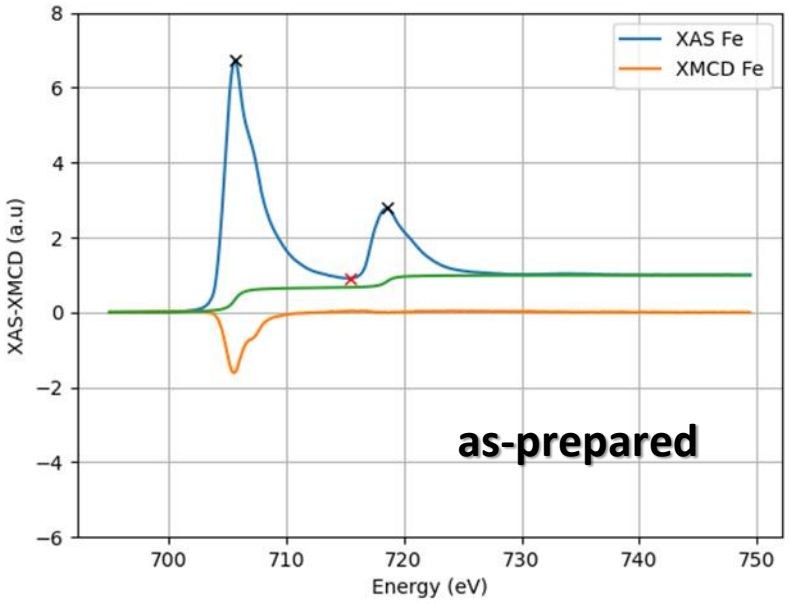
[1] Z. Feng et al, Adv. Electron. Mater. 2018

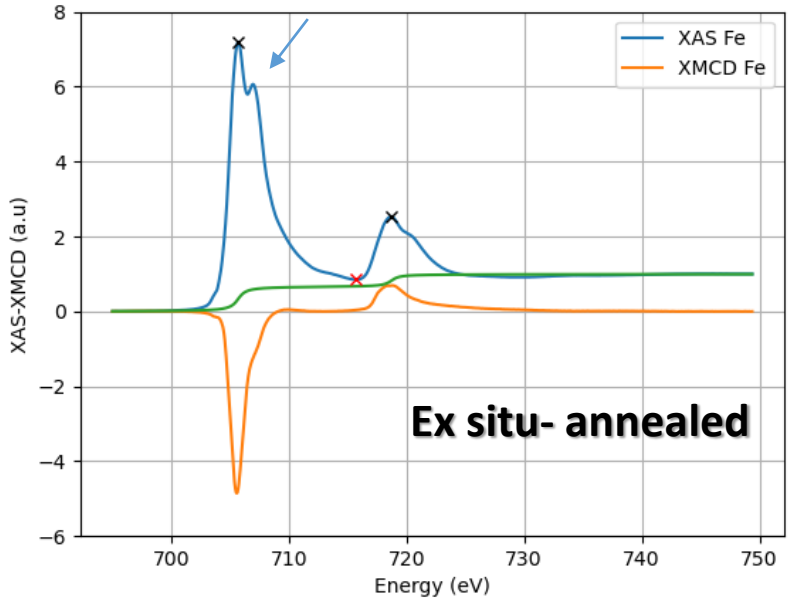
Magnetic Properties of B2 FeRh NPs on perovskite

XAS/XMCD at Fe-$L_{2,3}$ edges as-prepared, after annealing and transfer in air

7nm-FeRh clusters **on (001) BTO thin film on STO crystal**

« oxide »

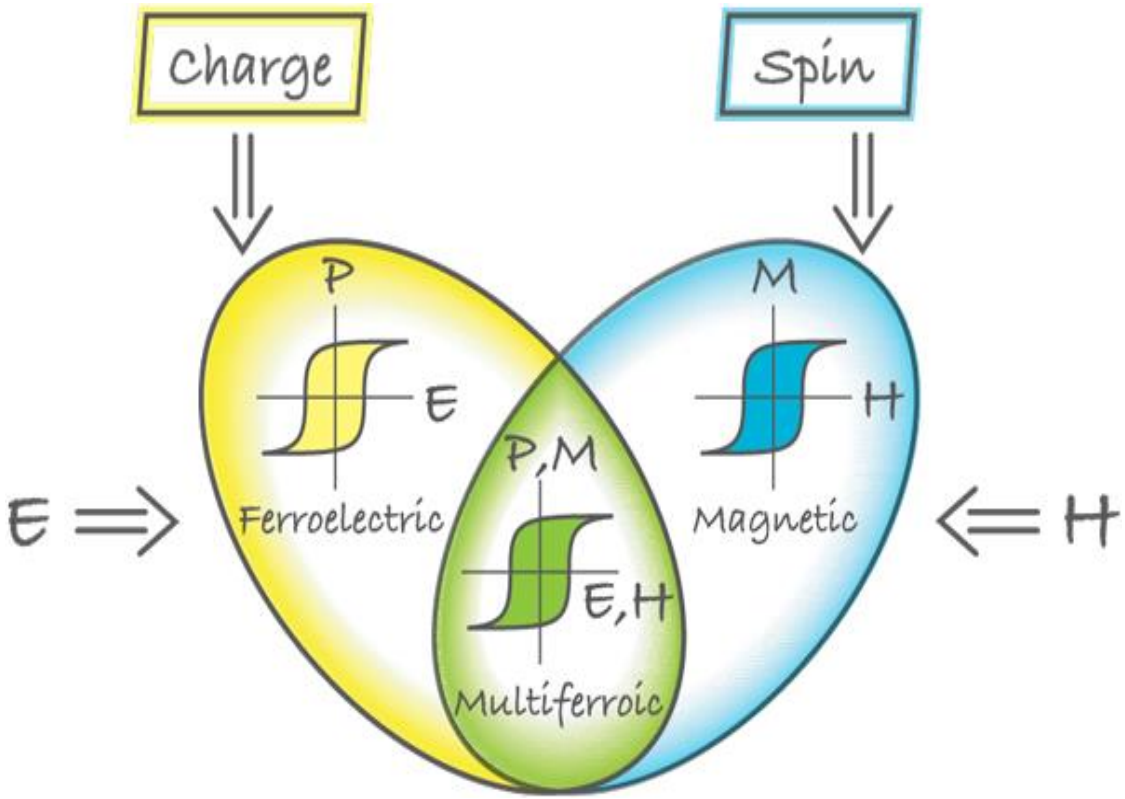




Hybrid multiferroic

- Hybrid multiferroic corresponds to a system that contains a Ferroelectric material and a Ferromagnetic material.

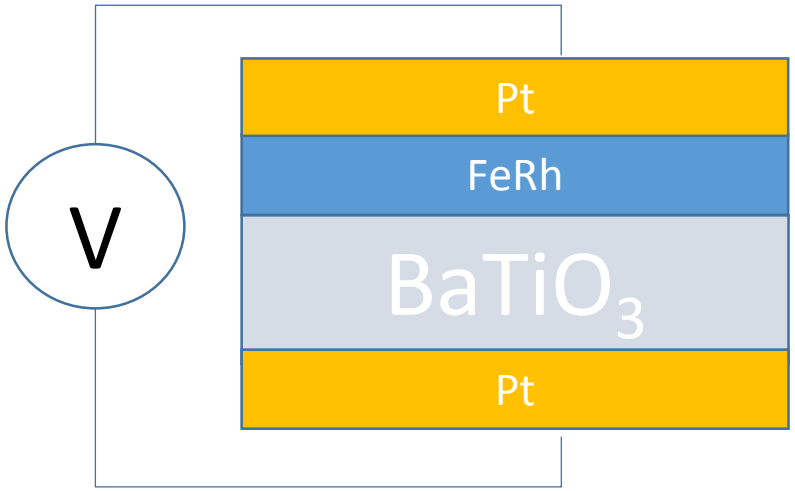
- FeRh metamagnetic transition can be controlled by other external stimuli not only by temperature.

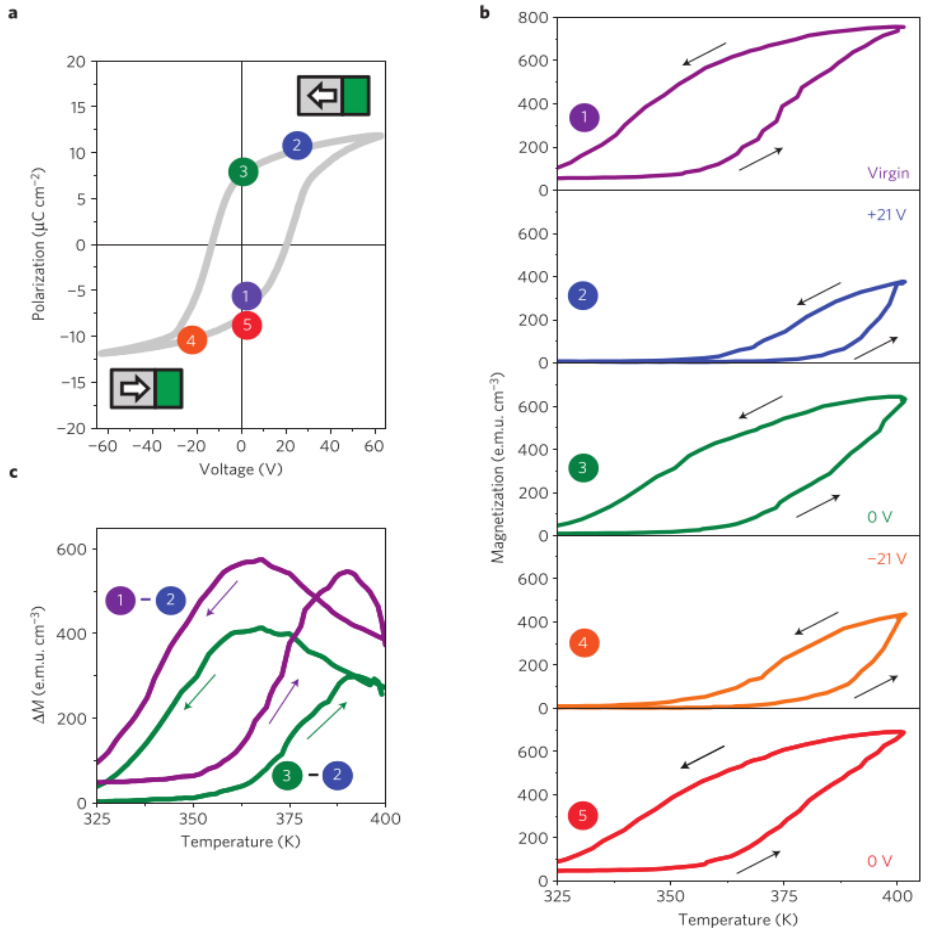


[2] Classifying multiferroics: Mechanisms and effects, Daniel Khomskii, 2009

FeRh film over $BaTiO_3$

- It is possible to shift the transition temperature of FeRh layers over $BaTiO_3$ using voltage.
- $SrTiO_3$ is interesting because is similar to $BaTiO_3$.

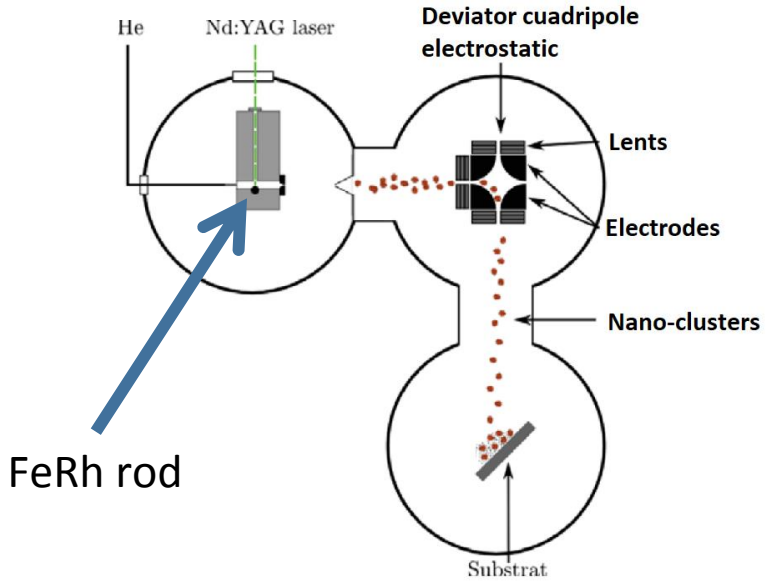




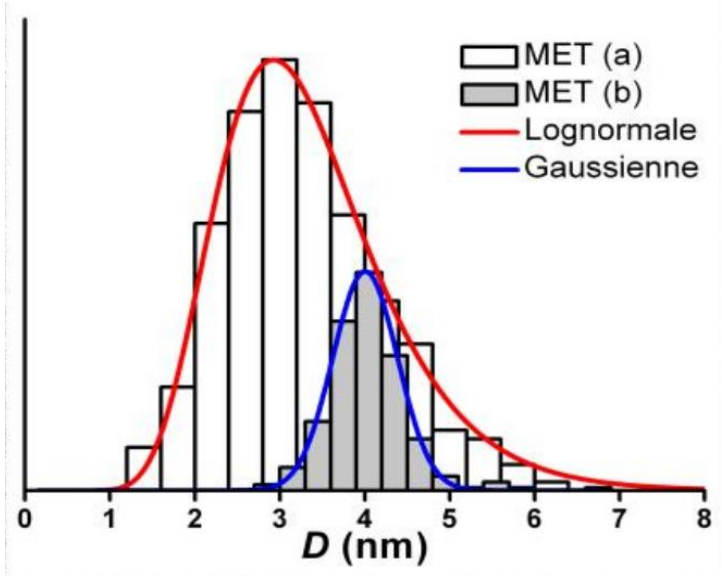
[3] Cherifi et al, Nat. Mater. 2014

Sample preparation

- Low energy cluster beam deposition mass-selected.
- Pulsed laser heats an FeRh rod.
- Nanoparticles are formed in gas phase.
- Charged nanoparticles can be deviated using a quadrupole.



Scheme of the nano cluster deposition chamber



Size distribution for mass-selected (blue) and not mass selected (red)