

## Experimental report on Proposals ID : 20160911 (BM32)

### *Interfacial coupling for FeRh clusters deposited on a BaTiO<sub>3</sub> crystalline surface*

#### **Scientific Background**

Controlling magnetism by means of an electric field is a key issue for future developments of low power spintronic that would reconcile electronic and magnetic devices. The major importance of surface atoms in small nanoparticles offers the opportunity to tailor the magnetic properties by playing with the interface between a nanomagnet and its surrounding. FeRh has attracted a lot of attention because, when it is in the chemically ordered B2 phase (CsCl-like), it presents an antiferromagnetic to ferromagnetic order (AFM-FM) transition close to room temperature. Moreover, in this system the crystalline and magnetic properties are intimately linked (magneto-elastic effects). Recently for epitaxially grown FeRh films [1] both strain and field effects from an underneath BaTiO<sub>3</sub> ferroelectric crystal has been exploited to electrically drive, with only a few volts, the FeRh metamagnetic transition temperature (just above room temperature).

#### **Sample preparation and Characterization**

We have previously studied the structural and intrinsic magnetic properties of FeRh nanoclusters, prepared using Mass-Selected Low Energy Cluster Beam Deposition (MS-LECBD) available at the PLYRA platform of Institut Lumière Matière. In sharp contrast to film and bulk studies, we have put into evidence the persistence of FM order down to 3 K (ferromagnetic alignment of the Fe and Rh magnetic moments of respectively 3 and 1  $\mu_B$  in size-selected 3.3 nm diameter FeRh clusters crystallized in the B2 phase [2]. This anomalous magnetic order has been ascribed to finite size induced structural relaxation.

In the present case, FeRh nanoclusters have been deposited on a crystalline BaTiO<sub>3</sub> layer epitaxially grown on a Nb-doped SrTiO<sub>3</sub> layer, using a MBE technique (at INL-ECL). Different particle sizes have been studied (3 and 6 nanometers) thanks to the size-selection capabilities of the MSLECBD setup, with a relative diameter dispersion lower than 10 % on the surface (see Fig. 1), but ensuring a large enough diffraction signal. Samples deposited at room temperature have been compared with deposition at higher temperature (200-300°C). The nanoparticle samples are then capped by amorphous carbon (protection against oxidation) before x-ray measurements at ESRF but also by Pt capping layer which can be used as the top electrode for measurements involving electric manipulation. We have also studied uncapped samples transferred under UHV between Lyon and Grenoble (thanks to a UHV suitcase, already successfully used for previous experiments at BM32 on our deposited clusters).

In the following table, are listed the samples probed by GISAXS and XRD during this experiment

Sample name	NPs size	Substrate	deposition T°	Capping
TM17-31	6 nm	BTO (20 nm)	RT	a-C
TM17-32	6 nm	Si	RT	a-C
TM17-33	3 nm	BTO (20 nm)	RT	a-C
TM17-34	3 nm	Si	RT	a-C
TM17-37	6 nm	BTO (20 nm)	500°C	a-C
TM17-41	3 nm	BTO (20 nm)	500°C	a-C + Pt

TABLE I: Summary of all the samples characterized during the run.

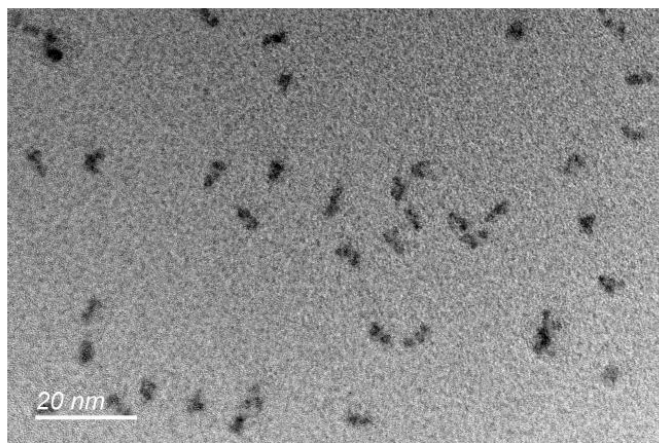


FIG. 1: TEM image of the 3 nm FeRh nanoparticles on a carbon/copper TEM grid. The nanoparticles are formed from several small clusters.

### **Experimental results**

The sample which gave us the best results was TM17-33. At the moment, only results on this sample have been meticulously analyzed, as follow:

1. GISAXS (figure 2 on the left) and XRD before annealing
2. Incremental thermal treatment from 250°C to 600°C
3. During annealing, characterization of the sample with GISAXS and fast HKL scans in  $\langle 100 \rangle$  and in  $\langle 110 \rangle$  directions
4. After annealing at 600°C for several hours (typically a night), back to RT and GISAXS and XRD characterizations

As seen in Fig. 1 from TEM observations, performed prior to the run at ESRF, the 3 nm in diameters FeRh nanoparticles (NPs) are composed of several smaller clusters. We hoped that the morphology would become more spherical upon annealing. The thermal evolution of the GISAXS patterns is presented in Fig. 2. First of all, the absence of remarkable form factor which could be due to the partitioning of the as-prepared sample is seen on the left. While after annealing, a monodisperse shape can be assumed from the form factor evidenced on the right pattern with the apparition of an intense form factor around the direct beam. On the figure 3, from XRD scans performed before annealing, we can see the BTO peaks surrounded by a lot of features and small peaks which are mostly artifacts (at the top). The peak situated at 0.22 nm corresponds to the Molybdenum sample holder. While after annealing (figure 3 at the bottom), it is possible to see some changes in the two peaks situated at 0.15 nm and 0.212 nm both on the  $\langle 010 \rangle$  (red curve) and  $\langle -1-10 \rangle$  (blue curve) directions, which correspond to two epitaxial relationships as presented on the right of Fig. 3. Indeed, the peaks at 0.212 nm on the red curve and at 0.15 nm on the blue curve, represent the well-known epitaxial relationship as shown on the top of Fig. 3 [2]. While the peaks at 0.15 nm on the red curve and the one at 0.212 nm on the blue curve, are coherent with a new relationship rotated to the previous configuration, depicted on the bottom. Such 'cube on cube' relationship has never been observed on thin films. In order to confirm those relationships, we did omega scans and omega maps. A map has been taken in the  $[HK0]$  plane starting from  $[H,K,L] = [0,1.68,0]$  to  $[H,K,L] = [0,2.88,0]$ . On this map, at  $K = 1.85$  it is possible to see highlight every 45° corresponding to the known epitaxy and the new epitaxy. The omega scan has been probed out of the plane, at the  $[111]$  bragg peak and visible on the Fig. 5.

One can underline that it is the first evidence of epitaxial relationship between the faces of nanocrystallites pre-formed in gas phase and a mono-crystalline oxide surface. Moreover, these specific interface coupling between FeRh clusters and the  $\text{BaTiO}_3$  surface would pave the way towards the manipulation of the atomic structure, and hence the magnetic properties, through a voltage-driven control of the ferroelectric (and piezoelectric) substrate.

### **References**

- [1] A. Hillion et al., Phys. Rev. Letters 110, 087207 (2013)
- [2] R. O. Cherifi et al., Nature Materials 13, 345–351 (2014)

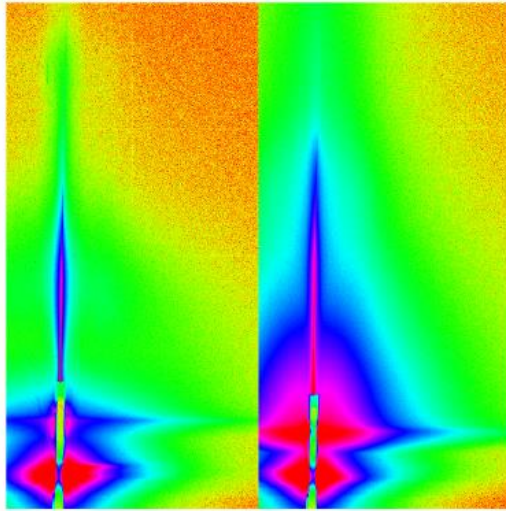


FIG. 2: Evolution of the GISAXS pattern of 3 nm FeRh nanoparticles deposited on BaTiO<sub>3</sub> substrate (sample TM17-33).

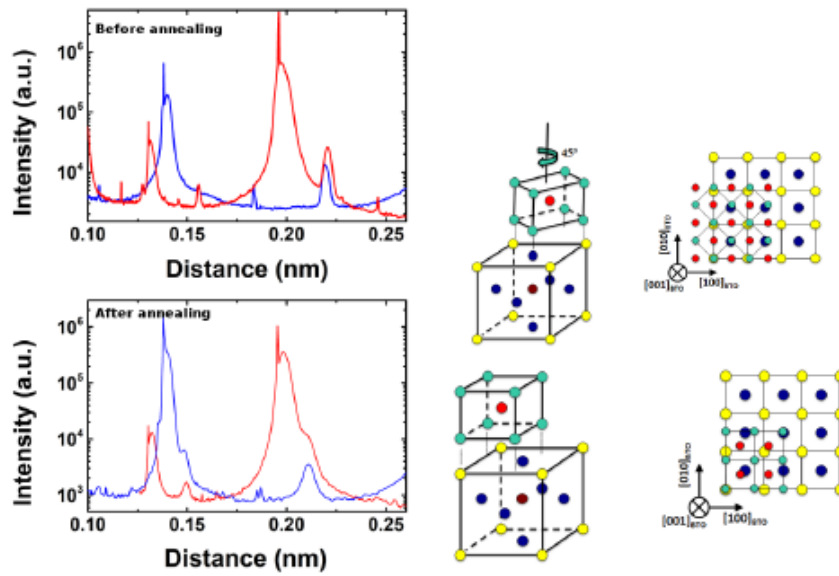


FIG. 3: XRD scans in two directions,  $\langle 010 \rangle$  in red and  $\langle -1-10 \rangle$  in blue. The peaks at the distance 0.212 nm in the  $\langle 010 \rangle$  direction and 0.15 nm in the direction  $\langle -1-10 \rangle$  corresponds to the known epitaxy of FeRh on BTO. However the peaks at 0.212 nm in the direction  $\langle -1-10 \rangle$  and 0.15 nm in the direction  $\langle 010 \rangle$  relate a 'new' epitaxy. A sketch of this epitaxy is drawn on the right at the bottom.

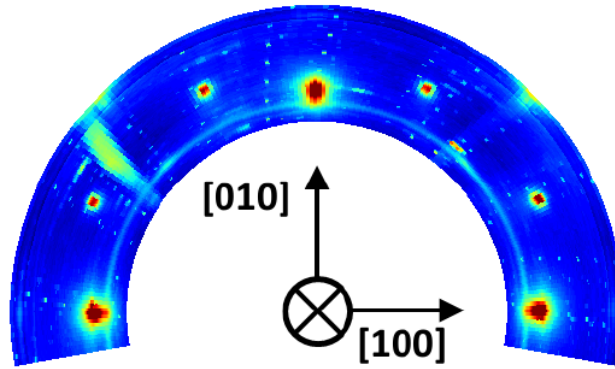


FIG. 4: Omega map taken between  $-100^\circ$  and  $+100^\circ$  starting from  $[H,K,L] = [0,1.68,0]$  to  $[H,K,L] = [0,2.88,0]$ . The interesting part is situated for omega scans at  $K = 1.85$ . It is possible to see spots in the omega scan at  $0, 90$  and  $-90$  which corresponds to BTO spots with shoulders extending at  $K = 1.85$ . The shoulders are the FeRh known epitaxy diffraction spots. Situated at  $45^\circ$  and  $-45^\circ$ , highlights can be seen and correspond to the new epitaxy.

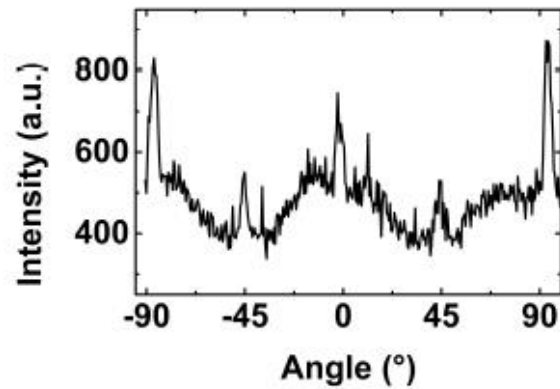


FIG. 5: Omega scan on the Ewald sphere at  $[111]$  FeRh bragg peak,  $[H,K,L] = [1.305,1.305,1.305]$ . It is possible to see both 4 fold symmetry epitaxies with peaks around  $-90, -45, 0, 45$  and  $90$ .