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Sputter-engineering a first-order magnetic phase transition in sub-15-nm-thick single-crystal FeRh films

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Abstract

Equiatomic FeRh alloys undergo a fascinating first-order metamagnetic phase transition (FOMPT) just above room temperature, which has attracted reinigorated interest for applications in spintronics. Until now, all attempts to grow nanothin FeRh alloy films have consistently shown that FeRh layers tend to grow in the Volmer-Weber growth mode. Here we show that sputter-grown sub-15-nm-thick FeRh alloy films deposited at low sputter-gas pressure, typically ~ 0.1 Pa, onto (001)-oriented MgO substrates, grow in a peening-induced Frank-van der Merwe growth mode for FeRh film thicknesses above 5 nm, circumventing this major drawback. The bombardment of high-energy sputtered atoms, the atom-peening effect, induces a re-balancing between adsorbate-surface and adsorbate-adsorbate interactions, leading to the formation of a smooth continuous nanothin FeRh film. Chemical order in the films increases with the FeRh thickness, t_{FeRh} , and varies monotonically from 0.75 up to 0.9. Specular x-ray diffraction scans around Bragg peaks show Pendellösung fringes for films with $t_{\text{FeRh}} \geq 5.2$ nm, which reflects in smooth well-ordered densified single-crystal FeRh layers. The nanothin film's roughness varies from 0.6 down to about 0.1 nm as t_{FeRh} increases, and scales linearly with the integral breadth of the rocking curve, proving its microstructured origin. Magnetometry shows that the FOMPT in the nanothin films is qualitatively similar to that of the bulk alloy, except for the thinnest film of 3.7 nm.

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10 I. INTRODUCTION

11 First-order phase transitions typically entail abrupt changes in a material's properties
12 [1], which potentially open up new opportunities for tailoring functional devices[2]. FeRh
13 alloys belong to a unique class of technologically sought-after materials, as they possess
14 a fascinating first-order metamagnetic phase transition (FOMPT) originally discovered by
15 Fallot in 1937, while conducting studies on Fe-X (X=Ru [3], Ir [4] and Rh [5]) intermetallic
16 alloys. However, it was later on that Kouvel *et al.* [6], showed that the FOMPT in FeRh
17 alloy can be observed if it is heated up above room temperature. In particular, $\text{Fe}_x\text{Rh}_{1-x}$
18 alloys close to equiatomic compositions ($48 \leq x \leq 56$ at% Fe) form a B2 ordered CsCl-
19 type crystallographic structure and undergo an intriguing multi-stimuli tuned first-order
20 magnetic phase transition [6]. At low temperature, FeRh adopts an anisotropic collinear
21 type-II [7] antiferromagnetic (AF) phase, where nearest-neighbour Fe sites ordered antifer-
22 romagnetically within (001)-planes and ferromagnetically within (111)-planes, transforming
23 to a weakly anisotropic ferromagnetic (F) phase at around about $T \sim 370$ K, which shows
24 the usual thermal hysteresis of a first-order transition. On cooling, the FOMPT in FeRh
25 alloys is accompanied by a massive decrease in volume [8] of $\sim 1\%$ and by large changes
26 in its fundamental physical properties, including for instance a giant magnetoresistance [9]
27 ($\Delta R/R \sim 50\%$) and a giant magnetostriction [8] ($\sim 0.82\%$).

28 Interestingly for applications, the FOMPT in FeRh alloys shows a wide tunability by a
29 variety of stimuli [10], *e.g.* magnetic field, strain, or chemical doping, among others. Build-
30 ing on such rich phenomena, novel power-efficient spintronics concepts have been recently
31 demonstrated, *e.g.* a robust AF-based memory resistor [11], a voltage-controlled hybrid stor-
32 age memory [12] device and an exchange-spring coupled heterostructure [13] for near-future
33 heat-assisted magnetic recording technology [14]. However, in order to develop real-world
34 spintronic device prototypes based on active FeRh layers, smoother fully functional thinner
35 FeRh layers will be much needed, typically below 15 nm. Nowadays, conventional physi-
36 cal vapor deposition approaches to growing nanothin FeRh alloy layers are far away from
37 meeting these stringent requirements.

38 In this Rapid Communication, we show that, in sharp contrast to previous attempts in
39 which nanothin FeRh alloy films were shown to grow in the Volmer-Weber growth mode
40 [15–19], smooth chemically well-ordered single-crystal fully functional nanothin FeRh alloy

41 films can be synthesized if proper dc-magnetron sputtering deposition parameters are cho-
 42 sen. In particular, we demonstrate that sputter-grown sub-15 nm thick FeRh alloy films
 43 deposited at an Ar pressure of about 0.1 Pa onto (001)-oriented MgO substrates grow in an
 44 induced Frank-van der Merwe growth mode for $t_{\text{FeRh}} > 5$ nm, as consequence of the *atom-*
 45 *peening* [20] effect, *i.e.* the bombardment by highly energetic sputtered atoms. Specular
 46 x-ray diffraction (XRD) scans around typical (001) and (002) Bragg peaks for B2 ordered
 47 FeRh alloys show Pendellösung [21] fringes for films with $t_{\text{FeRh}} \geq 5.2$ nm, which indicates
 48 nanothin FeRh alloys are very smooth and well-ordered densified single-crystal layers. The
 49 analysis of Pendellösung fringes reveals an offset thickness in the nanothin films, *i.e.* an
 50 Fe-enriched layer of ~ 1.0 - 1.5 nm, as confirmed by the chemical mapping. Its origin resides
 51 in the segregation of Rh at the MgO/FeRh interface at elevated temperatures. Furthermore,
 52 chemical order increases with the FeRh thickness, t_{FeRh} , and the chemical order parameter,
 53 S , varies monotonically from 0.75 up to 0.9. The nanothin film's roughness varies from 0.6
 54 down to about 0.1 nm as t_{FeRh} increases, and scales linearly with the integral breadth of the
 55 rocking curve, proving its microstructured origin. We show that the FOMPT is qualitatively
 56 similar to that of the bulk alloy, except for the nanothin film with $t_{\text{FeRh}} = 3.7$ nm.

57 II. EXPERIMENTAL METHODS

58 Ultrathin FeRh films with thicknesses ranging from 3.7 nm up to 14.1 nm were deposited
 59 using a DC magnetron sputtering high vacuum (HV) chamber (typical base pressure \sim
 60 1×10^{-6} Pa) onto (001)-oriented epi-polished MgO substrates 0.5-mm-thick, with a typical
 61 (001) deviation angle of 0.3° and surface roughness ≤ 0.5 nm. The deposition procedure
 62 is in essence similar to that previously reported [22]. Briefly, after degreasing and cleaning
 63 the MgO substrates in ultrasonic baths using acetone and isopropanol baths for 30 mins
 64 each at 308 K, these were baked and degassed at a temperature of 973 K for 1.5 hours
 65 in the HV chamber; after that, the substrate temperature was reduced to 873 K prior to
 66 deposition and maintained during the FeRh growth; immediately after finishing the FeRh
 67 alloy deposition, the as-grown nanothin films were annealed in HV at 1023 K for 2 h. At
 68 the deposition temperature, the sputtering chamber base pressure prior to deposition was
 69 $\sim 9 \times 10^{-6}$ Pa. The films were grown using a sputter gas (Ar) pressure of ~ 0.1 Pa, with
 70 an Ar flow rate of ~ 30 sccm. The dc voltage and current supplied by the magnetron power

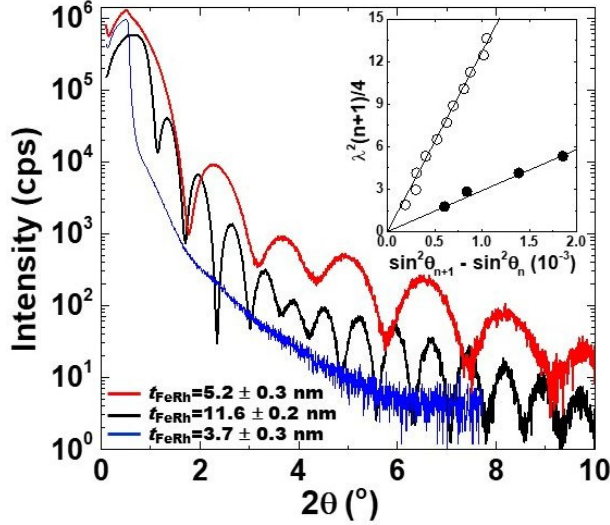


FIG. 1. X-ray reflectometry (XRR) scans for nanothin FeRh alloy films with FeRh thickness $t_{\text{FeRh}} = 5.2$ nm and 11.6 nm. t_{FeRh} was determined from the Kiessig fringe spacings [29]. The blue line corresponds to the XRR scan for the nanothin film with $t_{\text{FeRh}} = 3.7$ nm. Because of the absence of Kiessig fringes, its thickness was subsequently determined by using scanning transmission electron microscopy. The inset shows a linear fit of the Kiessig fringe spacing analysis for the films with $t_{\text{FeRh}} = 5.2$ nm (full dots) and 11.6 nm (empty dots).

71 source are about 365 V and 70 mA, respectively, resulting in a typical deposition rate of
 72 0.25 nm s^{-1} . The FeRh target used was 2 inch in diameter and 3 mm thick and had a
 73 composition of $\text{Fe}_{47}\text{Rh}_{53}$ in at.% with a purity of 99.99%. In sputter-grown FeRh films, the
 74 composition in the deposited film measurably differs from that in the FeRh target used, so
 75 that the composition shift depends on the sputter gas pressure [23]. By extrapolating that
 76 measured sputter gas pressure dependence, we estimate from our known target composition
 77 that, in our case, the nanothin FeRh alloy film's composition is close to $\text{Fe}_{52}\text{Rh}_{48}$.

78 We opted not to use any capping layer to protect the nanothin FeRh films, in order to
 79 avoid it exerting influence upon the magnetic properties [24]. In fact, this common practice
 80 is unnecessary, provided the FeRh films are dense and compact enough. The formation of
 81 any significant native oxide layer at the FeRh surface is self-terminating since, if it were to
 82 form, then it would leave Rh-rich layers which are inert to oxidation. This way, the top
 83 outermost Rh layers in the FeRh alloy film act as an excellent corrosion resistance layer [27]
 84 for the underneath FeRh layers and native oxides are limited to only nanometer thickness

85 [24].

86 X-ray reflectometry (XRR) and diffractometry (XRD) θ - 2θ scans, as well as ω - 2θ rock-
87 ing curves were collected in a four-circle diffractometer using a Cu $K\alpha$ source. This has a
88 V-Göbel mirror as a beam conditioner and a 2-bounce germanium monochromator, which
89 results in an extremely parallel (divergence 0.007°) and monochromatic beam for high res-
90 olution measurements.

91 Atomic force micrographs were collected in non-contact mode, at a resolution of 512×512
92 pixels with a scanning frequency of 1 Hz. Commercial cantilever probes with a resonance
93 frequency around 320 kHz were used. Raw data processing (background subtraction, flatte-
94 nening and filtering) and the subsequent analysis of the AFM micrographs was performed
95 using GWYDDION software[28].

96 A cross-sectional transmission electron microscopy (TEM) specimen of the 3.7 nm-thick
97 FeRh film was prepared from the bulk substrate, transferred onto a copper Omniprobe grid
98 and ion-milled using an FEI Nova focused ion-beam (FIB) instrument. Standard Ga^+ FIB
99 operating procedures were followed (including final polishing steps, adding a Pt protective
100 e-beam deposited layer and to reduce thickness of damaged sections) to produce an electron
101 transparent FeRh/MgO lamella. TEM imaging and spectroscopy described in this paper
102 were carried out on a JEOL Atomic Resolution Microscope (JEM-ARM200F) TEM, oper-
103 ating at 200 kV. Conventional and high-resolution high angle annular dark field (HAADF)
104 scanning TEM (STEM) were performed on the cross-sectional TEM lamella and electron
105 energy loss spectroscopy (EELS) provided chemical analysis.

106 Magnetization versus temperature scans were collected at a fixed applied magnetic field
107 using a SQUID-VSM magnetometer. The temperature was swept at a typical rate of
108 2 K/min.

109 III. RESULTS AND ANALYSIS

110 We attempted to use the XRR technique [29] to experimentally determine the thickness
111 of nanothin FeRh alloy films presented in this study, instead of relying on their estimated
112 nominal thickness. Data are shown in Fig. 1. However, Kiessig fringes were absent from the
113 XRR scan collected from the thinnest ($t_{\text{FeRh}}=3.7$ nm). In that case, the STEM technique
114 was employed to determine its thickness by direct imaging of the cross-section of the film,

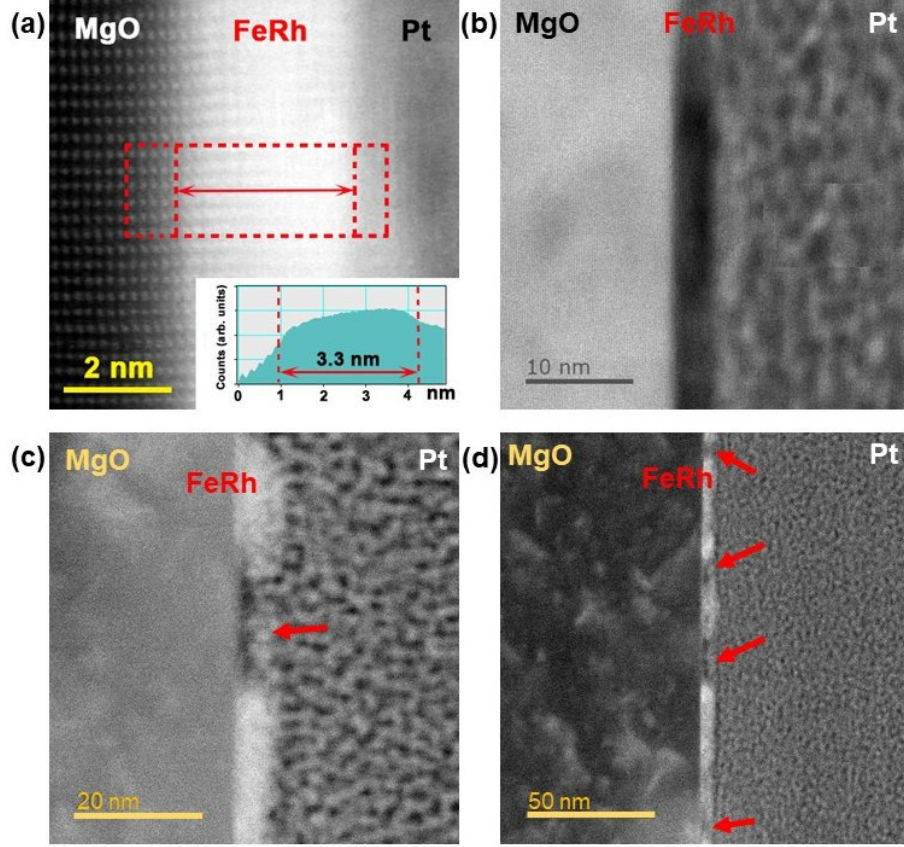


FIG. 2. HAADF-STEM images of a cross-sectional TEM lamella showing the FeRh thin film (middle of each image) grown on the MgO substrate (left), with an average thickness of 3.7 nm, and protective Pt layer (right). (a) High resolution HAADF-STEM image showing the localized structure of the FeRh and its epitaxial interface with the MgO substrate, as well as an average thickness profile (inset). HAADF-STEM images showing (b) a zone with uniform thickness and (c-d) others with non-uniform FeRh thin film, the discontinuous growth features denoted with red arrows.

115 shown in Fig. 2. Thus, the thicknesses of the remaining FeRh alloy films were determined
 116 from the Kiessig fringe spacings, so that the positions, *i.e.* θ values, for the maxima of
 117 the interference fringes are linked to the t_{FeRh} by the modified Bragg equation, which reads
 118 as [29]: $\sin^2 \theta_n = \theta_c^2 + (n + 1/2)^2 \lambda^2 / 4t_{\text{FeRh}}^2$ where θ_n is the position of the maximum of
 119 the n^{th} interference fringe, θ_c is the critical angle for total reflection, n is an integer, and
 120 $\lambda = 1.54184 \text{ \AA}$ is the x-ray wavelength. This way, plotting $\lambda^2(n + 1)/4$ vs $\sin^2 \theta_{n+1} - \sin^2 \theta_n$
 121 removes the dependence on θ_c , so that the slope of the linear fit provides t_{FeRh} (see Fig. 1),
 122 which was determined to be $t_{\text{FeRh}} = 4.1, 5.2, 8.1, 9.2, 11.6$ and 14.1 nm. As shown in

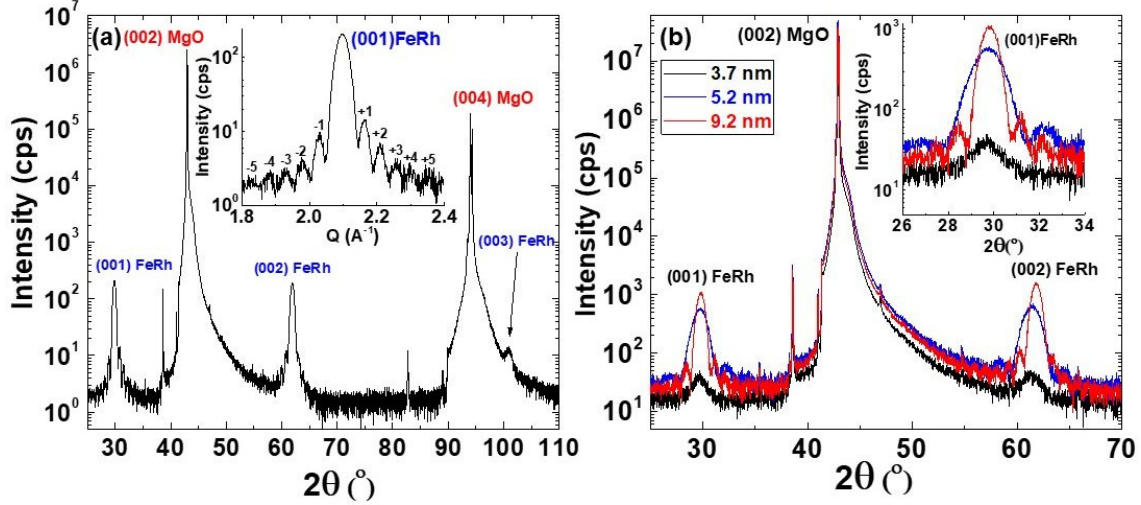


FIG. 3. Specular x-ray diffraction (XRD) θ - 2θ scans for (001)-oriented FeRh alloy films grown onto (001)-oriented MgO single crystal substrates for FeRh thickness (a) $t_{\text{FeRh}} = 14.1$ nm, where the inset shows a close-up of the XRD scan around the (001) Bragg peak as a function of the scattering wave-vector Q . Well-developed Pendellösung fringes up to fifth-order are labeled. (b) As above for $t_{\text{FeRh}} = 3.7$, 5.2, and 9.1 nm, where the inset displays a close-up of the XRD scan around the (001) Bragg peak.

123 Figure 1, XRR profiles collected for FeRh nanothin films with $t_{\text{FeRh}} \geq 5$ nm clearly show
 124 well-defined Kiessig fringes up to high 2θ values, despite the reflectivity intensity decays
 125 as θ^4 . This observation is an early indication of a smooth top surface, since Kiessig fringe
 126 intensity tends to decay quite rapidly with increasing surface roughness [30]. We note that
 127 the Kiessig fringe amplitude presents a subtle convoluted modulation (see Figure 1), which
 128 suggests the FeRh films possess a chemical modulation.

129 Figure 2(a) shows a high resolution HAADF-STEM image of the epitaxy across the
 130 MgO/FeRh interface for the nanothin film with $t_{\text{FeRh}} = 3.7$ nm; the inset displays an average
 131 thickness profile in a slightly thinner zone of the film [see Fig. 2(a)]. As the field of view
 132 (FOV) of the HAADF-STEM increases, the FeRh film, which looked smooth and continuous
 133 at a FOV of 40 nm [see Fig. 2(b)], start to show regions of non-growth and inhomogenous
 134 thickness [see Figs. 2(c) and 2(d)]. The lateral dimensions of these regions range from 5 nm
 135 to a few tens of nm.

136 All sputter-grown nanothin FeRh alloy films are excellent-quality B2-ordered single
 137 crystals, as can be inferred from the specular XRD scans displayed in Fig. 3, wherein

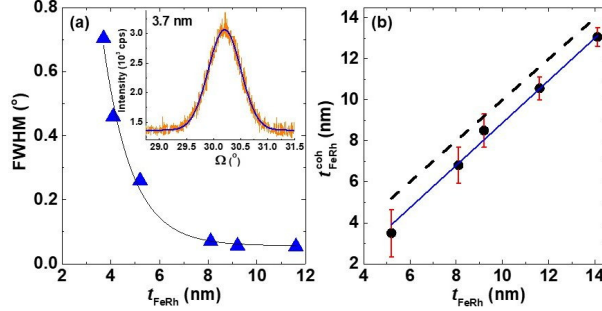


FIG. 4. Rocking curve analysis. (a) Dependence of the full-width-half-maximum (FWHM), measured over the rocking curve scan collected on the (002) FeRh Bragg peak, with the FeRh thickness, t_{FeRh} . The line is a guide to the eye. The inset shows the rocking curve scan collected on the film with $t_{\text{FeRh}} = 3.7$ nm. The line corresponds to a Gaussian fit with FWHM= 0.7° (b) Coherent FeRh thickness, $t_{\text{FeRh}}^{\text{coh}}$, determined as $2\pi/\Delta Q$ [31, 32], where ΔQ is the spacing between adjacent Pendellösung fringes, as a function of the experimental t_{FeRh} values. The dashed line corresponds to a plot where $t_{\text{FeRh}}^{\text{coh}}=t_{\text{FeRh}}$ and the continuous one is a guide to the eye.

138 (00 l) for $l=1, 2$, and 3, Bragg diffraction peaks are observed. The expected epitaxial
 139 relationship between the MgO substrate and FeRh overlayer along the growth direction,
 140 MgO(002)||FeRh(002), is observed, as can be inferred from Fig. 3. Furthermore, the (001)
 141 and (002) Bragg diffraction peaks for the B2-ordered FeRh alloys appear at values of the scat-
 142 tering angle, 2θ , around about 29.5° and 61.5° , respectively. Specular XRD scans collected
 143 in films with $t_{\text{FeRh}} \geq 5.2$ nm showed clear Pendellösung interference fringes[21] (*i.e.* Laue
 144 oscillations) around (001) and (002) Bragg peaks, but these are missing for $t_{\text{FeRh}} < 5.2$ nm
 145 (see insets in Fig. 3). Thus, Pendellösung fringes firstly emerge as weak satellite peaks
 146 around (001) and (002) Bragg peaks in the 5.2 nm-thick FeRh film, wherein up to 2nd-order
 147 satellites are visible, and these grow in number and intensity as t_{FeRh} increases. Figure 3(a)
 148 shows well-developed Pendellösung fringes around (001) Bragg peak up to fifth-order in the
 149 film of 14.1 nm thickness. Pendellösung fringes are absent in films with $t_{\text{FeRh}} = 3.7$ and
 150 4.1 nm, which may result from a crystallinity degradation of the FeRh films as these get
 151 thinner, resulting from a rougher top-surface, a smaller grain size and a larger mosaicity.
 152 However, we highlight that the appearance of Pendellösung fringes in our nanothin films is
 153 a feature not found at all in prior studies reporting on nanothin FeRh films [15–19]. Addi-
 154 tionally, these XRD scans show no trace of the Bragg peak associated with the fcc γ -FeRh

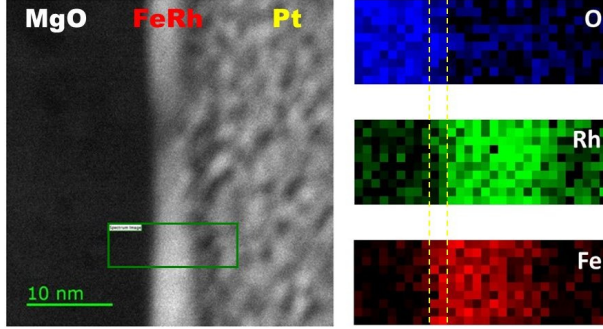


FIG. 5. HAADF-STEM analysis. (Left-panel) HAADF-STEM image showing the MgO substrate (lefthand portion of the image), FeRh layer (middle) and protection Pt layer (right) for the film with $t_{\text{FeRh}} = 3.7$ nm. (Right-panel) Chemical composition mapping for oxygen, rhodium, and iron, obtained using EELS (pixel lateral size is 5 \AA) over the area enclosed by the green box (longside length is ~ 15 nm) in the left-panel. The 1 nm-thick Fe-enriched layer is denoted by yellow dashed lines.

155 phase, which should appear at around about $2\theta \sim 47^\circ$ (assuming that $a_{\text{fcc-FeRh}} \sim 0.37$ nm).

156 Rocking curve ω - 2θ scans have been collected over the (002) FeRh Bragg peaks to check
 157 the film's grain size and mosaicity along growth direction, *i.e.* the measure of the spread
 158 or tilt of (001) crystal plane orientations, which gives an accurate indication of the degree
 159 of crystallinity of the nanothin films. As displayed in Fig. 4(a), the variation of the full-
 160 width-half-maximum (FWHM) of the rocking curve with t_{FeRh} shows two distinct regimes.
 161 It is found that the integral-breadth or FWHM is around 0.06° for $t_{\text{FeRh}} \geq 8.1$ nm, but this
 162 increases rapidly for $t_{\text{FeRh}} \leq 5.2$ nm yielding FWHM= 0.7° for $t_{\text{FeRh}} = 3.7$ nm. Fig. 4(b)
 163 shows the coherent FeRh thickness, $t_{\text{FeRh}}^{\text{coh}}$, determined as [31, 32], $t_{\text{FeRh}}^{\text{coh}} = 2\pi/\Delta Q$, where
 164 ΔQ is the spacing between consecutive Pendellösung fringes emerging around the (001)
 165 Bragg peak in reciprocal space. We notice that unlike the (002) Bragg peak, which has its
 166 origin in the bcc lattice, the (001) one is exclusively linked to the B2 ordering. Thus, we
 167 observed that in all cases $t_{\text{FeRh}}^{\text{coh}} < t_{\text{FeRh}}$; moreover, the difference between the FeRh thickness
 168 and the coherent one, $\Delta t = t_{\text{FeRh}} - t_{\text{FeRh}}^{\text{coh}}$ ranges from 1.6 nm ($t_{\text{FeRh}} = 5.2$ nm) down to
 169 1 nm ($t_{\text{FeRh}} = 14.1$ nm). The emergence of such “offset” thickness, Δt , which to first-order
 170 approximation could be considered as thickness-independent (notice the uncertainty in the
 171 data in Fig. 4(b)), it is tentatively ascribed to a MgO/FeRh interface effect, resulting from
 172 the segregation of Fe and Rh metal species at the interface, as confirmed by the chemical

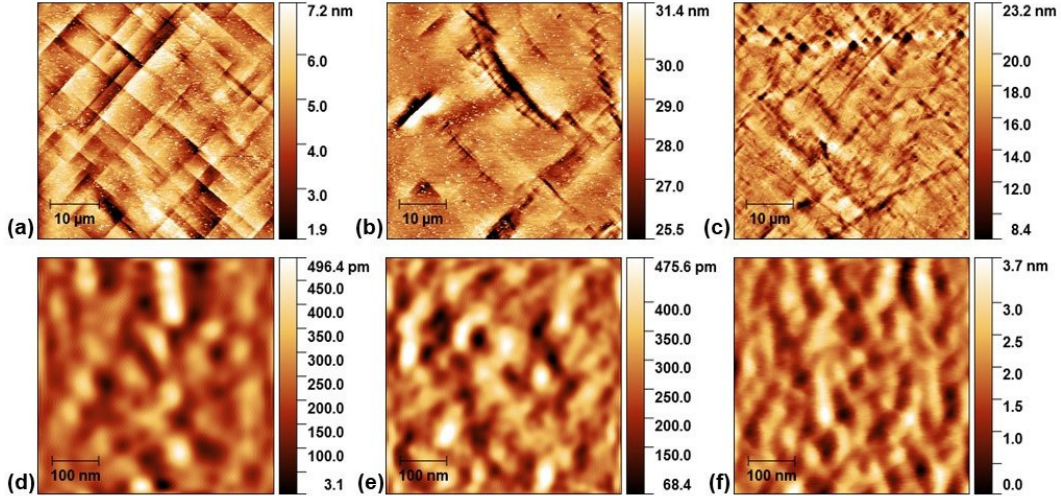


FIG. 6. Atomic force micrographs taken on nanothin FeRh alloy films with FeRh thickness, $t_{\text{FeRh}} = 14.1$ nm, (a) and (d), $t_{\text{FeRh}} = 9.2$ nm, (b) and (e), and $t_{\text{FeRh}} = 3.7$ nm, (c) and (f). AFM scan size is $50 \times 50 \mu\text{m}^2$ (top row) and $0.5 \times 0.5 \mu\text{m}^2$ (bottom row); micrographs edges are aligned along the $[110]\text{MgO}||[100]\text{FeRh}$ and $[\bar{1}10]\text{MgO}||[010]\text{FeRh}$ directions. Height scales have been set to optimize image contrast.

173 mapping across the MgO/FeRh interface (see Fig. 5). Thus, within the resolution provided
 174 by EELS, we estimate that the thickness of the FeRh layer near to the MgO/FeRh interface,
 175 which seems to be richer in Fe, is ~ 1.0 - 1.5 nm, which is consistent with Δt . Segregation-
 176 driven processes at the interfaces of bimetallic alloy systems, resulting from the dissimilar
 177 stability of metal species in oxidizing environments, is a familiar mechanism in catalysis [33].
 178 Building on that, we attribute the segregation of Fe and Rh at the MgO/FeRh interface
 179 during film growth and annealing to the instability of Rh-O bonds [25, 34] at $T > 600^\circ\text{C}$.
 180 Therefore, we can conclude that there exists in principle a good correlation between the
 181 increase of the integral-breadth of the rocking curve in the thinnest films and the absence
 182 of Pendellösung fringes. We note that little noticeable evidence for any native oxide layer,
 183 suggesting that it must be extremely thin if present at all.

184 In sharp contrast to prior studies [15–19], our sputter-grown nanothin FeRh films show
 185 a smooth surface morphology, as shown in Fig. 6. There we show atomic force micrographs
 186 that show that the FeRh layer wets completely the MgO surface with the exception of the
 187 very thinnest films, *i.e.* for those with $t_{\text{FeRh}} < 5$ nm. These very thin films present a rougher
 188 morphology than the thicker ones and show small regions of incomplete coverage or pits,

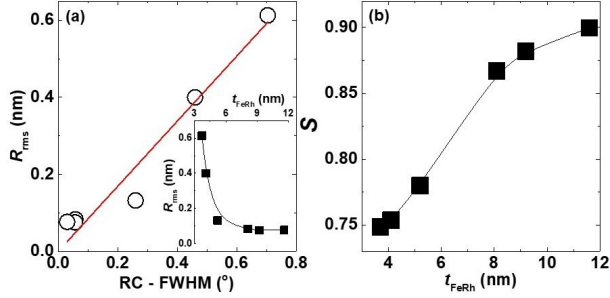


FIG. 7. Structural analysis. (a) Average root-mean-square roughness, R_{rms} , versus full-width-half-maximum (FWHM) of the rocking curve. The line corresponds to a linear fit, where the intercept is zero and the slope is to 0.845 ± 0.056 nm/deg. Standard deviation values for the R_{rms} are smaller than or similar to the dots size. The inset shows the variation of R_{rms} with t_{FeRh} . (b) Thickness dependence of the nanothin FeRh alloy films order parameter, S , determined according to Ref. 35.

189 with lateral dimensions ranging from 5 to ~ 30 nm, as shown for the 3.7 nm-thick film.
 190 Strikingly, this observation suggests that the sputter-grown nanothin FeRh layers deposited
 191 at low Ar pressure tend to grow in an induced Frank-van der Merwe growth mode for
 192 thicknesses above 5 nm, in marked contrast to the Volmer-Weber growth mode reported
 193 previously [15–19]. The atomic force microscopy (AFM) images taken for a scan size of
 194 $50 \times 50 \mu\text{m}^2$ reveal that the FeRh overlayers develop a terrace-like pattern, which could
 195 be mistakenly assigned to the expected presence of atomic-steps at the bottom epi-polished
 196 (001) MgO surface. However, as the experiment shows, these terrace-like features are t_{FeRh}
 197 dependent [see Figs. 6(a)-6(c)], starting to emerge for $t_{FeRh} > 5$ nm and vanishing for the
 198 thinnest films. Therefore, we conclude from this observation that terrace-like features are
 199 not carried through from the substrate, but emerge from the crystallographic structure of
 200 the FeRh films as the surface smooths out. Bear in mind that AFM image edges are aligned
 201 ($\pm 5^\circ$ misalignment) along the $[110]\text{MgO} \parallel [100]\text{FeRh}$ and $[\bar{1}10]\text{MgO} \parallel [010]\text{FeRh}$ directions in
 202 the MgO substrate and FeRh film (notice the 45° rotation between the MgO and FeRh
 203 cubic lattices [19]). AFM micrographs with scan size $0.5 \times 0.5 \mu\text{m}^2$ exhibit an astonishing
 204 similarity, except for the depth of the regions of inhomogeneous thickness, which become pits
 205 through the whole thickness for the thinnest film [see Figs. 6(d)-6(f)]. Therefore, the surface
 206 morphology features revealed by the AFM micrographs are consistent with the STEM images
 207 taken on the thinnest FeRh film.

208 The average root-mean-square roughness, R_{rms} , was determined using the GWYDDION

209 software [28] over several $0.5 \times 0.5 \mu\text{m}^2$ AFM micrographs taken at different places on each
 210 film's surface. This scan size ensures the R_{rms} is determined within an FeRh terrace. As
 211 shown in Fig. 7(a), there is a clear correlation between the integral-breadth of the rocking
 212 curve, *ie* FWHM, and R_{rms} in the nanothin FeRh films, which suggests the R_{rms} has its origin
 213 in the film microstructure, this is grain size and mosaicity. The chemical order parameter
 214 S is a measure of the ordering quality possessed by the nanothin FeRh alloy films, and is
 215 defined as the fraction of Fe/Rh lattice sites in the B2 crystallographic structure that obey
 216 the ordering condition, $S = r_{\text{Fe}} + r_{\text{Rh}} - 1$ where $r_{\text{Fe(Rh)}}$ is the fraction of Fe(Rh) lattice
 217 sites occupied by Fe(Rh) atoms. From the specular XRD scans, S can be determined as,
 218 $S = \left(\left[I_{(001)}/I_{(002)} \right] / \left[I_{(001)}^*/I_{(002)}^* \right] \right)^{1/2}$, where $I_{(002)}$ and $I_{(001)}$ are the integrated intensities
 219 of the fundamental and superlattice Bragg peaks, respectively, and the $I_{(001)}^*$ and $I_{(002)}^*$ refer
 220 to the theoretical ones, calculated for each sample [35]. We note that I^* is a function of
 221 t_{FeRh} , the integral-breadth of the Bragg peaks, and the divergence and goniometer radius of
 222 the x-ray diffractometer. If S is calculated otherwise [22], S will attain values well above
 223 unity for all the nanothin films in this study, which lacks meaning, as $S \leq 1$ by definition.
 224 As displayed in Fig. 7(b), S decreases as films are thinner, ranging from nearly 0.9 for the
 225 thickest films down to 0.75 for the thinnest, which indicates that the chemical order degrades
 226 as films get thinner, although these are chemically well ordered B2 FeRh alloys, despite their
 227 finite-size.

228 Fig. 8(a) shows in-plane magnetization as a function of temperature (M - T) curves for
 229 nanothin FeRh alloy films with $t_{\text{FeRh}} = 3.7, 5.2, 8.1$ and 9.2 nm, wherein the sharp rise
 230 in M associated the FOMPT in FeRh[6] is clearly observed. The criterion for determining
 231 the FOMPT temperature, T_{MPT} , from the M - T curves consists of obtaining the point over
 232 the M - T locus that yields the maximum slope. It turns out that T_{MPT} is shifted towards
 233 lower temperatures, consistent with prior studies[16], and the FOMPT width, ΔT , becomes
 234 broader as t_{FeRh} decreases. Although further research is needed, this latter aspect may
 235 reflect in the impact that finite-size effects have upon the FOMPT [36]. We find that
 236 $T_{\text{MPT}} = 359, 302, 281$ and 298 K and $\Delta T = 30, 68, 136$ and 170 K for $t_{\text{FeRh}} = 9.2, 8.1,$
 237 5.2 and 3.7 nm, respectively, measured all over the M - T curve on cooling. The residual
 238 M in the AF phase, which is linked to the presence of B2 disordered FeRh phase clusters
 239 and, therefore, intimately related to S [37], appears to increase as the films become thinner
 240 [see Fig. 8]. A plausible reason for that could be that there is a small region of crystalline

241 degradation of the B2 ordered structure near the interface that forms a larger and larger
 242 proportion of the film as it becomes thinner, which is also reflected in the diminishing value
 243 of S as film's thickness decreases (see Fig. 7(b)). Besides, the M values for films with
 244 $t_{\text{FeRh}} \geq 5.2$ nm attain in excess of 900 emu cm^{-3} in the FM phase, smaller than that in bulk
 245 FeRh [6], $\sim 1200 \text{ emu cm}^{-3}$, but notably larger than those values obtained in similar FeRh
 246 films [16–19].

247 Building on the suppression of the AF-FM transition in FeRh nanoparticles [38], we
 248 foresee that the likely presence of strain gradients in our nanothin films, anticipated by the
 249 thickness-dependence of the (001) and (002) Bragg peak breadths as seen in Fig. 3(b), may
 250 surely contribute to increase the observed residual FM moment in the AF phase. Following
 251 with this analogy, the existence of a strain-induced lattice parameter relaxation mainly
 252 along the growth direction, would affect the highly sensitive interatomic distance dependent
 253 AF-FM exchange coupling balance, resulting in setting a non-uniform thickness-dependent
 254 AF-FM phase coexistence. Studying this matter in more depth is well beyond the scope of
 255 the present study; we hope however that our work might inspire further studies to shed light
 256 on this issue using advanced characterization tools, *i.e.* Bragg coherent diffraction imaging
 257 or differential nano-X-ray absorption spectroscopy.

258 Likewise, it is remarkable that the large diminishment of the in-plane M shown by the
 259 3.7 nm-thick FeRh film, in comparison to those values attained in thicker films (see Figure
 260 8), was also observed in similar nanothin films, displaying a rough morphology and having a
 261 smaller order parameter [19]. In first instance, we should consider that nanothin FeRh films
 262 deposited onto single-crystal MgO substrates are prone to developing a strong perpendicular
 263 magnetic anisotropy originated at the FeRh/MgO interface, caused by the formation of an
 264 Fe-enriched layer close to the MgO substrate [39]. This way, we envisage competing surface
 265 and volume magnetic anisotropy terms would induce a tendency for the magnetisation to tilt
 266 out-of-plane as the film thickness becomes small. Whilst for films with $t_{\text{FeRh}} \geq 5.2$ nm, the
 267 easy direction for M clearly lies in-plane, for the film with $t_{\text{FeRh}} = 3.7$ nm, the remanent M
 268 for $\mathbf{H} \parallel [001]$, *i.e.* $M_{\text{r}}^{[001]}$, is twice as much as $M_{\text{r}}^{[110]}$. In this thinnest film, M attains dissimilar
 269 saturation values for H applied in- and out-of-plane (see Fig. 8(b)), resulting in a nearly 40%
 270 larger M for $\mathbf{H} \parallel [001]$, which would partially contribute to the substantial reduction of the
 271 M values in Fig. 8(a), when compared to those in the thicker films. On the other hand, the
 272 $M(H)$ loop for $\mathbf{H} \parallel [110]$ is more upright and saturates at a lower field than that for $\mathbf{H} \parallel [001]$,

273 where there is a long gradual approach to saturation. This mixed evidence for where the
 274 easy direction lies suggests that the anisotropy is also mixed and lateral inhomogeneities are
 275 likely to exist in this very thin film. This may in part be do to with variations in the degree
 276 of oxidation: the thinness of any oxide layer, as discussed above, means that is not likely to
 277 be continuous and uniformly well-developed everywhere across the whole film surface.

278 Another crucial aspect to consider in FeRh nanosystems is the influence that non-uniform
 279 strains and low-dimensionality effects may have, both on the anisotropy and also upon
 280 reducing M . Thus for instance, in unstrained 3.3 nm diameter FeRh nanoparticles, a 10%
 281 reduction of the magnetic moment is observed [38]. (Notice that a broader spread of the
 282 lattice parameter is intrinsically expected for the highly-strained 3.7-nm-thick film.) We
 283 anticipate the origin of the anisotropy of M resides in a strain-induced spin-orbit-mediated
 284 anisotropic $3d$ - $4d$ hybridized [42] orbital filling [43] in tetragonally distorted FeRh films.
 285 We notice that the anisotropy of the magnetic moment is not an atypical phenomenon,
 286 especially when dealing with strained nanostructures [44] or materials that hold a strong
 287 spin-orbit coupling [45]. Ultrathin FeRh films provide a fertile ground for investigating
 288 emergent strain-induced anisotropies, given that they combine a relatively large spin-orbit
 289 coupling [42] with the feasibility of developing substantial epitaxial strains [19].

290 IV. DISCUSSION

291 The microstructure of sputter-grown thin films can be tailored, to a great extent, by ad-
 292 equately choosing sputtering deposition parameters, mainly sputter-gas (Ar) pressure, p_{Ar} ,
 293 and substrate temperature [50, 51], T_{subs} . From earlier studies [15–19], it is known that
 294 epitaxial nanothin FeRh films deposited onto single-crystal MgO substrate tend to grow in
 295 the Volmer-Weber growth mode [52]. These experimental results can be qualitatively un-
 296 derstood, neglecting the effect associated to the misfit strain ($< 0.5\%$) between FeRh and
 297 MgO, in terms of the surface free energy [53], γ , associated to the system formed by the
 298 (001) MgO substrate surface [54], $\gamma_{\text{subs}}^{\text{MgO}} = 1.1 \text{ Jm}^{-2}$, (001)Fe [55] and (001)Rh [55] overlay-
 299 ers/film, $\gamma_{\text{f}}^{\text{Fe}} = 2.94 \text{ Jm}^{-2}$ and $\gamma_{\text{f}}^{\text{Rh}} = 2.83 \text{ Jm}^{-2}$ respectively, and substrate-overlayer inter-
 300 face, $\gamma_{\text{int}}^{\text{MgO-FeRh}}$. In this case, the Volmer-Weber growth mode occurs because $\gamma_{\text{subs}}^{\text{MgO}} < \gamma_{\text{f}}^{\text{Fe}}$
 301 (or $\gamma_{\text{f}}^{\text{Rh}}$) + $\gamma_{\text{int}}^{\text{MgO-FeRh}}$, where the FeRh overlayer tends not to wet the MgO surface, randomly
 302 nucleating dome-like atom clusters. As the effective thickness increases, the initially FeRh

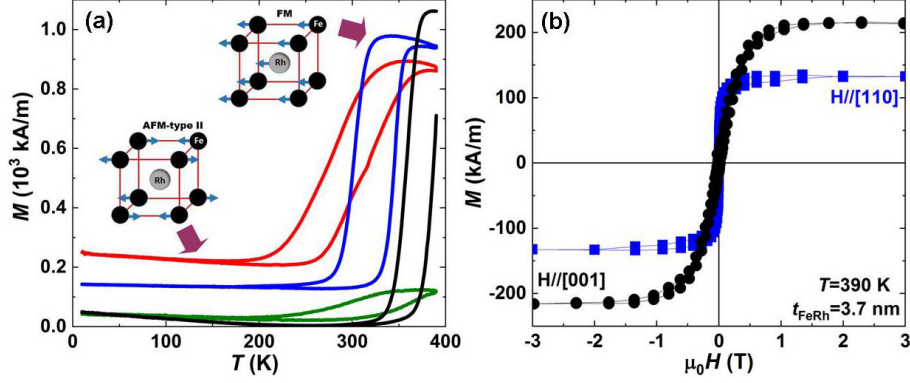


FIG. 8. Magnetic properties. (a) Magnetization as a function of temperature for FeRh alloy films with thickness, $t_{\text{FeRh}} = 9.2$ (black), 8.1 (blue), 5.2 (red) and 3.7 nm (green) for an applied magnetic field, $\mu_0 H_{\text{app}} = 0.1$ T so that $\mathbf{H} \parallel [110]$. (b) M - H loops for $\mathbf{H} \parallel [110]$ (blue squares) and $\mathbf{H} \parallel [001]$ (black dots) for the thinnest film in the FM phase.

303 clusters increase in size, developing into islands, which grow predominately faster in height
 304 than in lateral size, and eventually forming an almost continuous layer only for thick FeRh
 305 films, where FeRh islands coalesce.

306 A plausible way to circumvent the unwanted Volmer-Weber growth mode observed in
 307 FeRh overlayers consists of sputter-growing FeRh at low p_{Ar} . During sputtering deposition,
 308 the sputtered atoms are ejected with average energies of the order of ~ 10 eV [56–59], which
 309 compare well with the sublimation energy for Fe/Rh metal species, ~ 4 -7 eV [60]. A substan-
 310 tial loss of kinetic energy by the ejected sputtered atoms is expected at elevated p_{Ar} , typically
 311 > 0.65 Pa in most cases, due to collisions (thermalization effect) with plasma particles and
 312 sputter-gas atoms while travelling from the cathode towards the substrate. However, such
 313 energy loss at low p_{Ar} , typically < 0.15 Pa in most cases, is in turn negligible, which entails
 314 major microstructural transformations for the condensed overlayer, since its surface is re-
 315 lentlessly bombarded by highly-energetic particles, including the ejected sputtered atoms, an
 316 effect known as *atom-peening* [20]. This unique aspect of sputtering deposition technology
 317 has been experimentally [61] and theoretically [62, 63] tested.

318 Besides T_{subs} and p_{Ar} , morphology and microstructure of sputter-grown FeRh films finely
 319 depend on other sputtering deposition parameters [64], such as the deposition power P , in
 320 addition to substrate-to-target distance, L , which together with P determines the deposition
 321 rate, $\sim P/L$, and the magnetron design, which determines the minimum p_{Ar} needed to

322 sustain the plasma. To illustrate that point, in our sputtering facility Ar gas is injected
 323 directly over the face of the target, which enables us to sustain the plasma even for $p_{\text{Ar}} =$
 324 0.06 Pa at $P = 20$ W. It is enlightening at this point to introduce the mean free path of the
 325 FeRh sputtered atoms, \bar{l}_{FeRh} , *i.e.* the mean distance that the sputtered atoms travel in the
 326 plasma and Ar gas before suffering a collision and start losing kinetic energy. \bar{l}_{FeRh} can be
 327 related to p_{Ar} as [65, 66]: $\bar{l}_{\text{FeRh}} = \frac{k_{\text{B}}T}{\sqrt{2\pi p_{\text{Ar}}}d_{\text{m}}^2}$, where k_{B} is the Boltzmann constant, T is the
 328 sputtering gas temperature and d_{m} is the molecular diameter of Ar gas (~ 0.4 nm). Thus,
 329 for $p_{\text{Ar}} = 0.1$ Pa and at room temperature, $\bar{l}_{\text{FeRh}} \simeq 6.44$ cm. Moreover, the dimensionless
 330 Knudsen number, K_{n} , is defined as [65], $K_{\text{n}} = \bar{l}_{\text{FeRh}}/L$, for sputtering deposition, and
 331 characterizes the regime at which the sputtering deposition takes place. Thus, for $K_{\text{n}} \geq 1$,
 332 the sputtering deposition process occurs in the high vacuum regime, *i.e.* the sputtered Fe
 333 and Rh atoms bombard the condensed layer on the substrate as highly energetic atoms.
 334 Conversely, for $K_{\text{n}} < 0.01$ sputtering deposition takes place in the fluid flow regime, this is
 335 the sputtered atoms are mostly thermalized. For intermediate K_{n} values, which is the most
 336 common situation, the sputtering deposition takes place in the transition regime. Thus, K_{n}
 337 is largely a sputtering deposition conditions independent value, which could be envisioned
 338 as a quantitative manner of comparing sputtering deposition processes. In our sputtering
 339 facility and for $p_{\text{Ar}} = 0.1$ Pa, K_{n} is 0.915, which clearly denotes that the atom-peening
 340 effect is the dominant factor that determines the morphology and microstructure of the
 341 sputter-grown layer.

342 During the deposition at low p_{Ar} (~ 0.1 Pa) of the FeRh nanothin films, they are constantly
 343 bombarded by energetic sputtered Fe and Rh atoms, which concomitantly incorporate to the
 344 condensed FeRh layer. This *atom-peening* effect [20] decisively affects the deposited FeRh
 345 layer microstructure [20, 61, 67], *e.g.* it induces layer densification, significantly improves
 346 the crystallinity, as well as introduces compressive strain in the deposited overlayer. This
 347 is because the kinetic energy which sputtered Fe and Rh atoms impact with on the FeRh
 348 overlayer is high enough to displace previously deposited Fe and Rh atoms from their equi-
 349 librium positions at the surface. In a way, the atom-peening effect forces a re-balancing of
 350 the thermodynamic equilibrium between adsorbate-surface and adsorbate-adsorbate inter-
 351 actions, originally leading to the Volmer-Weber growth mode. For the sake of clarity, we
 352 notice that at the FeRh deposition temperature used here, *i.e.* $T_{\text{dep}} = 873$ K, the reduced
 353 temperature $T_{\text{dep}}/T_{\text{melt}} \simeq 0.46$, where $T_{\text{melt}} \sim 1900$ K [68] is the melting temperature for

354 FeRh alloy, which indicates that during the FeRh deposition thermodynamic equilibrium is
 355 reached, where atom diffusion at the surface is the dominant process [50, 51]. Therefore, by
 356 depositing at low sputter-gas pressures, the atom-peening effect causes the initially nucleated
 357 FeRh islands to undergo a smoothing and planarization process. Thus, the FeRh islands are
 358 forced to grow mainly in the lateral dimensions, rather than in height, as a result of the bom-
 359 bardment pressure exerted by the highly energetic sputtered atoms, so that the deposited
 360 FeRh layer covers most of the MgO surface by forcing FeRh islands to coalesce at very low
 361 nominal deposition thickness. Simultaneously, the FeRh layer is densified and its degree of
 362 single-crystal perfection increased [69]. Our nanothin FeRh films present a microstructure
 363 and surface morphology, revealed by XRD, AF micrographs and STEM images, that is fully
 364 compatible with the aftermath of the atom-peening effect. Moreover, the strikingly good
 365 crystallinity observed in the sputter-grown FeRh nanothin films described here, *i.e.* the ap-
 366 pearance of Pendellösung fringes, a smooth surface, and the induced Frank-van der Merwe
 367 growth mode, which takes place for $t_{\text{FeRh}} > 5$ nm, is therefore a direct consequence of the
 368 above-mentioned atom-peening effect.

369 According to kinetic roughening theory [70, 71], the root-mean-square surface roughness,
 370 R_{rms} , scales with the thin films thickness, T , as a power-law [72], $R_{\text{rms}} \propto t^\beta$, where β takes
 371 different values, typically between 0 and 1, depending on the growth mode [71, 73]. This
 372 implies that R_{rms} increases as thin films grows thicker, since $\beta > 0$. However, we experi-
 373 mentally observe an opposite behavior in our nanothin FeRh films, so that R_{rms} decreases
 374 as t increases, as displayed in Fig. 7(a). Besides, we find that the R_{rms} scales linearly with
 375 the rocking curve FWHM (see Fig. 7(a)), which indicates that the film surface roughness
 376 originates in its microstructure, *i.e.* grain size and mosaicity. Notice that the finite-size of
 377 the diffraction volume and tilt of crystal planes both inseparably contribute to the broad-
 378 ening of the rocking curves [31]. We tentatively assign this unusual trend to the smoothing,
 379 flattening and densification processes that occur in the nanothin FeRh film as result of the
 380 atom-peening effect [69]. Film thickness is controlled by deposition time, and both are
 381 linearly related, so that the thicker the film the longer the FeRh overlayer is exposed to
 382 the atom-peening effect. We can therefore infer from the above that the island coalesce,
 383 overlayer densification and surface smoothing are thickness-dependent effects, since atom-
 384 peening process impacts primarily on the outermost FeRh layers. Thus, we interpret the
 385 data shown in Fig. 7(a) as a growth regime transition from a rougher almost continuous film

386 (Volmer-Weber type growth mode) at low nominal t_{FeRh} to a smoother densified continuous
387 (peening-induced Frank-van der Merwe growth mode) for thicker films, with an inflection
388 point for about $t_{\text{FeRh}} = 5$ nm. Lastly, the thickness variation of the chemical order parameter
389 displayed in Fig. 7(b) is most likely related to the formation of an Fe-enriched layer, caused
390 by the Rh segregation at the MgO/FeRh interface, which may also affect the B2 ordering
391 in the FeRh layers above.

392 V. CONCLUSIONS

393 In summary, we have shown that, in sharp contrast to prior studies [15–19], sputter-grown
394 sub-15-nm-thick FeRh alloy films deposited at low sputter-gas pressure, typically ~ 0.1 Pa,
395 onto (001)-oriented MgO substrates grow in a modified Volmer-Weber type growth mode,
396 turning this into an atom-peening-induced [20] Frank-van der Merwe growth mode for thick-
397 nesses above 5 nm. This growing procedure considerably improves the film crystallinity,
398 which decisively contributes to preserving the first-order magnetic phase transition in the
399 nanothin films. Thus, the chemical order increases with the FeRh thickness, t_{FeRh} , and
400 varies monotonically from 0.75 up to 0.9. Furthermore, specular XRD scans around Bragg
401 peaks display Pendellösung interference fringes [21] for films with $t_{\text{FeRh}} \geq 5.2$ nm, which
402 reflects in smooth well-ordered densified single-crystal FeRh layers. Surface morphology in
403 the nanothin FeRh alloy films is smooth and FeRh layers tend to form a continuous film,
404 even at very low thicknesses, uniformly wetting the whole MgO surface for $t_{\text{FeRh}} > 5$ nm.
405 Additionally, the root-mean-square roughness varies from 0.6 nm down to about 0.1 nm as
406 t_{FeRh} increases, and scales linearly with the integral-breadth of the rocking curve measured
407 on the (002) FeRh Bragg scattering peak, proving that its origin resides in the film's mi-
408 crostructure. Iso-field magnetization measurements show that the first-order metamagnetic
409 phase transition is qualitatively similar to that of the bulk alloy, i.e. is sharp and shows little
410 thermal hysteresis, in all nanothin films, although for the 3.7 nm-thick film this becomes
411 broader, less sharp and is accompanied by a significant diminishing in the saturation mag-
412 netization value. Lastly, we would like to highlight that the thin film growth approach laid
413 down here is of wide applicability and can be reliably used to grow, by means of sputtering
414 techniques, smooth continuous compact densified nanothin metal overlayers onto insulating
415 substrates, which will eventually enable to undertake novel exciting spintronics studies.

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