Magnetism of ultra-thin iron films seen by the nuclear resonant scattering of synchrotron radiation

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Abstract. Conversion electron Mössbauer spectroscopy proved in the past to be very useful in studying surface and ultrathin film magnetism with monolayer resolution. Twenty years later, its time-domain analogue, the nuclear resonant scattering (NRS) of synchrotron radiation, showed up to be orders of magnitude faster and more efficient. The evolution of the spin structure in epitaxial $^{57}$Fe films on a tungsten W(110) was studied via the accumulation of the NRS time spectra directly during Fe film deposition. In the 0.5 - 4 monolayers Fe thickness range, the complex non-collinear magnetic structure was derived from the NRS data, resulting from the deviation from the layer by layer growth mode. For thicker Fe films, the in-plane thickness induced spin reorientation transition could be clearly identified. Based on the NRS analysis it is shown that SRT process originates at the Fe/W(110) interface and proceeds through a transient fan-like magnetization structure.

1. Introduction
Magnetic properties of nanoscale materials are nowadays of great scientific and technological interest. Complex magnetic structures often found for low-dimensional systems, such as ultra-thin iron films, present a challenge for experimental methods. They have been studied by scanning probe microscopy (SPM) [1], spin sensitive electron scattering techniques [2], X-ray magnetic dichroism [3], magneto-optic Kerr effect (MOKE) [4], magnetometry [5], and $^{57}$Fe Conversion Electron Mössbauer Spectroscopy (CEMS) [6]. Except the last one, all of these methods suffer from limited depth resolution: spin-polarized scanning tunneling is strictly surface sensitive, while the others integrate magnetic properties over the entire sample or over an element. In this respect, CEMS and, recently, the Grazing Incidence Nuclear Resonant Scattering (NRS) of synchrotron radiation are exceptional since, owing to their isotopic selectivity, they make it possible to study of magnetic properties with spatial resolution using isotopic probe-layers.

2. NRS technique
NRS is a synchrotron analogue of Mössbauer spectroscopy (MS), in the sense that recoilless excitation (induced by the resonant x-rays with energy 14.4 keV for $^{57}$Fe) of the nuclear energy levels,
split due to the hyperfine interactions, is involved. In this method, the hyperfine parameters can be obtained from a characteristic beat pattern seen in the time evolution of the intensity of nuclear resonant scattering (the so called time spectrum). In conventional MS methods, such as Conversion Electron Mössbauer Spectroscopy (CEMS), the hyperfine interactions are measured in an incoherent process, in which the decay of a nucleus resonantly excited by a γ-quant occurs via resonance fluorescence or internal conversion. The resulting spectrum is the incoherent sum of those single events. In contrast, the NRS signal, measured after the simultaneous excitation of an ensemble of nuclei by a synchrotron radiation pulse, results from the coherent superposition of the probability amplitude for scattering from all nuclei of the ensemble. This coherent character of the scattering process, in combination with the outstanding properties of the synchrotron radiation from third generation synchrotron sources (high brilliance, tunability in energy with monochromatization down to 0.5 meV, defined time structure, and polarization) opened new possibilities for time resolved nuclear spectroscopy based on hyperfine interactions. Magnetic properties in the nanoscale can be studied with sub-monolayer sensitivity. The isotopic sensitivity, in combination with the $^{57}$Fe probe layer concept, gives local structural and magnetic information from a sample region pre-selected during the preparation process. Furthermore, the well defined polarization of the synchrotron x-rays allows for an enhanced (with respect to CEMS) sensitivity to the orientation of the hyperfine magnetic field and electric field gradient. Extensive description of the method and its application can be found in several review papers [7] and a comprehensive book [8].

NRS on thin films or surfaces is a nuclear diffraction technique performed under specular reflection geometry at grazing incidence (GI) as shown in Fig. 1a.

![Figure 1](image)

**Figure 1.** (a) Geometry of a grazing incidence nuclear resonance scattering experiment. Angles $\Theta$ and $\Phi$ give relative orientation of the incident synchrotron beam wave vector $k_0$ to magnetization $M$. $\sigma$ and $\pi$ are the linear polarization basis vectors. The grazing angle $\phi$ is typically a few milliradians. (b) Schematics of the UHV NRS scattering chamber at ID 18 of the ESRF.

A newly constructed ultra high vacuum (UHV) system [9] at the beamline ID 18 at ESRF Grenoble [10] permits diverse GI-NRS experiments *in situ*, and also during or shortly after $^{57}$Fe deposition. This multichamber UHV system ensures state-of-the-art preparation and characterization of single crystalline surfaces and epitaxial films, offering evaporation of several metals (including Fe isotopes). Unique features of the GI-NRS technique were for the first time demonstrated in the in-situ nuclear inelastic scattering [11] and GI-NRS experiments for epitaxial Fe nanostructures on a single crystalline tungsten substrate.

### 3. Results and Discussion

For the epitaxial Fe(110) film on W(110), there are two different thickness regimes where the most intriguing properties have been found: i) ultrathin Fe films with thickness in the range of 0.5 - 4 ML, where the onset of ferromagnetic behavior is expected [2], and ii) Fe films with thicknesses of a few
tens of ML in the vicinity of the in plane spin reorientation transition (SRT) [12]. Using the UHV system at ID 18 these regimes could be studied with unprecedented spatial resolution.

As shown in Fig. 1b, $^{57}$Fe could be deposited on a freshly cleaned and pre-aligned (to the X-ray beam) W(110) crystal. The first pseudomorphic monolayer was deposited at 600 K. The rest of the layer, beyond 1 ML, was deposited at room temperature, and all GI-NRS time measurements were also made at room temperature. Using a remote-operated shutter and a precision $^{57}$Fe flux monitor, the whole preparation process could be operated on-line from the control hutch, without stopping the X-ray beam. Thus, the time of the experiment could be minimized, ensuring clean preparation and impurity-free films. It is also important that virgin magnetic states can be accessed, since, in contrast with most magnetic measurements, no magnetic field is necessary for the NRS. The measurement procedure that allows the acquisition of the GI-NRS time spectra along with the film deposition makes the method extremely fast. It was possible to complete the entire experimental run for the $^{57}$Fe films in the thickness range 1.6 Å to 6.5 Å (step 0.4 Å) in 1.5 hours.

Figure 2 shows a selection of the fitted time spectra for $k_\theta$ parallel to the [1 T 0] and [001] directions in the W(110) plane, as well as the evolution of the magnetic structure derived from the best fits obtained with the software package CONUSS [13]. For the given coverage, the fits for both the sample orientations were obtained assuming identical contributions of all components (represented by the areas of rectangles in the fig.2) as well as magnitudes of hyperfine parameters. The in-plane angles

![Figure 2](image_url)
between hyperfine magnetic fields and $k_\theta$ were fixed to 0 and 90 degree for $k_\theta$ parallel to the [1 1 0] and [001] respectively, consistently with the [1 1 0] easy magnetization axis in this thickness range [2]. The spectrum of the 1.64 Å film [corresponding to 1.0 pseudomorphic Fe(110) monolayer (psML)] shows no quantum beat pattern, in agreement with the literature data that the monolayer Curie temperature is of about 240K [2]. A quantum beat structure that appears in the time spectra when the nominal Fe thickness reaches 2.84 Å (1.8 psML) is of a magnetic origin. For this coverage, formation of the magnetic double layer islands surrounded by the nonmagnetic monolayer areas is expected [1]. In fact, from the obtained spin structure more complicated film morphology could be deduced (see fig.2) yielding coexistence of the two types of the double layer patches (one with the homogenous out-of-plane magnetization and the second with non-collinear magnetic order) with an in-plane magnetized tri-layer areas. In addition, a nonmagnetic component corresponding to the uncoated monolayer had to be included. With increasing coverage the in-plane magnetic anisotropy becomes dominant as tri-layer areas expand. Finally, for coverage above 5Å (~3 psML), the out of plane magnetic anisotropy disappears and homogenous in-plane magnetization establishes as it can be concluded from the fit parameters and distinctly different spectra for the [001] and [1 1 0] directions.

Our results reveal the complex character of this well known thickness induced SRT [2], from the out-of-plane to the in-plane magnetization direction. The non-collinear magnetic structure appears due to the exchange interaction between the mono-, double-, and trilayer areas coexisting due to the deviation from the layer-by-layer growth mode. The obtained profiles of the local magnetization across the film are unique and were not accessible with any other method.

As mentioned above, because of the reduced surface symmetry, the Fe(110) films provide an example where in-plane surface anisotropies occur in addition to the usual out-of-plane anisotropies. These in-plane anisotropies may induce an in-plane SRT, as it was observed by Gradmann et al. for film thicknesses increasing 30 and 50 ML, where the magnetization switching from [1 1 0] to [001] was found [12]. The nature and mechanism of the transition is not fully explained. During the film growth, when approaching the critical film thickness, it can be considered either as continuous coherent magnetization rotation from [1 1 0] to [001] or as coexistence of the [1 1 0] and [001] oriented magnetic domains with different occupation. In-field measurements [14] or remanent measurements after saturating field pulses [15] point to the domain model. On the other hand, the early conversion electron Mössbauer study does not exclude the scenario of continuous rotation occurring without external field [12]. It is also plausible that the applied field could change the character of transition. The present GI-NRS experiment allowed us to get insight into the mechanism of the in-plane SRT. In a single experimental run, multiple transition steps induced by the increase of the film thickness could be studied. Methodology of the thickness induced SRT studies was similar to that described above. $^{57}$Fe was evaporated on the W(110) crystal held at 330 K with the rate of 0.3 ML/min to the final thickness of 30 ML. During the preparation, a set of NRS time spectra were collected (acquisition time per spectrum was only several seconds), thus probing the hyperfine parameters in thickness steps corresponding to the fraction of Fe monolayer. The fitted time spectra are shown in Fig.3 for the selected film thicknesses. A regular beat structure that is exemplified in Fig. 3a reflects, according to the theoretical fits, the uniform magnetization state with the easy axis along the [1 1 0] direction that persists up to the thickness $d \approx 50$ Å. Similarly, the spectra for the coverage above 56 Å (Fig.3f) can be simply fitted assuming homogeneous magnetization along [001]. It is clear that SRT extends over large thickness range $\delta \approx 6$ Å, corresponding to about 3ML Fe. The time spectra accumulated across the SRT process (Fig.3b-d) were unique and presented a challenge for the numerical analysis. Assuming a homogeneous magnetization depth profile across the Fe(110) films, the coherent magnetization and domain models, as described above were considered. Both models showed distinctly different spectra, however any combination of the magnetization configuration resulting from the models could give a satisfactory description of the NRS time spectra series. Moreover, various combinations of these models, such as for example simple coexistence of domains
magnetized along [1̅ 0̅ 0], [001] and with magnetization continuously rotating with increasing thickness from [1̅ 0̅ 0] towards [001], were also excluded, as not reproducing the measured time spectra. Only when a depth-dependent magnetization structure was assumed, the perfect fits of the time spectra from Fig. 3 could be obtained (thin solid line).

Figure 3. NRS time spectra measured with \( k_0 \) parallel to [1̅ 0̅ 0] direction are shown for selected ⁵⁷Fe/W(110) films, demonstrating in-plane SRT.

To implement the depth variation of the magnetization direction, for each nominal coverage \( d_{\text{nom}} \) the iron film was divided into eight equivalent sub-layers, with the same thickness \( d=d_1=d_2=...=d_8=d_{\text{nom}}/8 \). Each sub-layer was characterized by the identical magnetic hyperfine field \( B_{\text{HF}} = 33 \text{T} \), while its in-plane orientation was defined by the angles \( \phi_1, \phi_1, ..., \phi_8 \) with respect to the [1̅ 0̅ 0] direction. In this way, the number of free parameters could be limited to the absolute minimum and, with increasing thickness, the subsequent spectra could be fitted assuming only the corresponding increase of \( d_{\text{nom}} \) and adjusting the set of the \( \phi_1, \phi_1, ..., \phi_8 \) values. From the best fits the evolution of the angular distribution of the magnetization along the film normal could be determined. We found that
the spin structure evolves with increasing thickness in the smooth and continuous manner and that the SRT from [1 1 0] to [0 0 1] is initiated by the deepest layers (neighboring to the tungsten substrate). In the transition a non-collinear magnetization structure appears. With increasing thickness, the magnetization of the subsequent layers rotates, and finally the transition is completed by the top-most surface layers.

4. Conclusions
In conclusions, the magnetic and structural properties of epitaxial Fe films were studied with in situ NRS technique. In the low Fe thickness regime NRS provided unique information about the correlation between the spin structure evolving with the increasing thickness and film morphology resulting from the peculiar growth mode. For thicker films, details of the in-plane spin reorientation transition could be accessed revealing existence of the non-collinear magnetic structure at the thickness driven SRT. Combination of the NRS technique and standard UHV methodology resulted in the high perfection and surface cleanness of the investigated films eliminating unwanted effects of the residual gas adsorption. Finally, the described experiments were performed in the absence of the external magnetic field, which can strongly alter the intrinsic magnetism at the spin reorientation transition process.

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6. References
[1] Pietzsch O, Kubetzka A, Bode M, Wiesendanger R 2000 Phys. Rev. Lett. 84 5212.
[2] Elmers H. J., Hauschild J., Hoche H., Gradmann U., Bethge H., Heuer D., Kohler U., Phys. Rev. Lett. 73 (1994), 898.
[3] Lu L., Bansmann J., Meiws-Broer K. H. J. Phys. Cond. Matter 10 (1998), 2873
[4] Ślęzak T., Karaś W., Krop K., Kubik M., Wilgocka–Ślęzak D., Spiridis N., Korecki J., J. Magn. Magn. Mat. 240 (2002), 362
[5] Elmers H. J., Hauschild J., Gradmann U., Phys. Rev. B 59 (1999), 3688
[6] Przybylski M., Korecki J., Gradmann U., Appl. Phys. A 52 (1991), 33
[7] Gerdau E., and de Waard H. (eds), Hyperfine Interact. 123/124 (1999), Baltzer Science Publishers; Rüffer R., Hyperfine Interact. 141/142 (2002), 83
[8] Röhlsberger R., Nuclear Condensed Matter Physics with Synchrotron Radiation, STMP 208, Springer-Verlag, Berlin, Heidelberg 2004.
[9] Stankov S., Rueffèr R., Sladecek M., Rennhofer M., Sepiol B., Vogl B., Spiridis N., Ślęzak T., Korecki J. Review of Scientific Instruments, 79 (2008), 045108
[10] Rüffer R., Chumakov A. I., Hyperfine Interact. 97-98 (1996), 589 http://www.esrf.fr/exp_facilities/ID18/
[11] Stankov S., Röhlsberger R., Ślęzak T., Sladecek M., Sepiol B., Vogl G., Chumakov A.I., Rüffer R., Spiridis N., Łażewski J., Parliński K., Korecki J., Phys.l Rev. Lett. 99, (2007) 185501
[12] Gradmann U., Korecki J., Waller C., Appl. Phys. A 39 (1986), 101
[13] Sturhahn W., Hyperfine Interact. 125 (2000), 149
[14] Elmers H. J. and Gradmann U., Appl. Phys. A 51 (1990), 255
[15] Baek I.-G., Lee H. G., Kim H.-J., Vescovo E., Phys. Rev. B 67 (2003) 075401