

Publishable final activity report



Contract n°: NMP4-CT-2003-001516

**Title: DYNAMICS IN NANO-SCALE MATERIALS
STUDIED WITH SYNCHROTRON RADIATION
(DYNASYNC)**

<http://www.dynasync.kfki.hu/>

Summary description of project objectives

Dynamical properties of condensed matter are of paramount importance for the functionality of future nanoscale devices. The role of the interfaces between adjacent materials becomes increasingly relevant with decreasing size of the structural units, and novel dynamical phenomena are expected in these nanostructures. Since the properties of low-dimensional structures are significantly different from those of corresponding bulk materials, new methods have to be developed for the experimental characterization and the theoretical modelling. An efficient way to achieve it is to use the extremely brilliant x-rays from modern synchrotron radiation sources like the European Synchrotron Radiation Facility (ESRF) to study the dynamical properties under ultrahigh vacuum (UHV) conditions. We will show how powerful nuclear resonant scattering of synchrotron radiation is in studying vibrational properties, diffusion and growth, and magnetic processes especially concerning its high spatial and temporal resolution.

The overall objective of the Project is to increase the basic understanding of dynamic phenomena and in particular of their size dependence in nanostructures. The combination of nuclear resonant scattering experiments with advanced surface sensitive experimental and computational methods yields detailed insights into the following areas:

- The modification of collective excitations like phonons by interfaces and boundaries in thin films, multilayers, and nanoparticles.
- The role of diffusion in the kinetics of structural changes that occur during processing of materials or the growth of thin films.
- The dynamical magnetic properties of nanostructures, the evolution of magnetic properties during growth and the interlayer coupling of magnetic layers, as they determine the fast magnetization reversal and the ultimate magnetic storage density.

Contractors involved

Participant Role*	Participant no.	Participant name	Participant short name	Participant Country
CO	1	Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences	ICSC	Poland
CR	2	Institut für Materialphysik der Universität Wien	UW	Austria
CR	3	The European Synchrotron Radiation Facility	ESRF	France
CR	4	Stiftung Deutsches Elektronen-Synchrotron	DESY	Germany

CR	5	Instituut voor Kern- en Stralingsfysica, University of Leuven	K.U. LEUVEN	Belgium
CR	6	Institute of Nuclear Physics	INP	Poland
CR	7	KFKI Research Institute for Particle and Nuclear Physics	KFKI RMKI	Hungary

*CO – Coordinator

CR – Contractor

Co-ordinator contact details Institute of Catalysis and Surface Chemistry, Polish Academy of Science ul. Niezapominajek 8 30-239 Kraków, Poland	Contact person and Coordinator Leader: Prof. Józef Korecki e-mail: korecki@uci.agh.edu.pl phone: +48 12 63 95 165 fax: +48 12 425 19 23
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Work performed and results achieved

One of the central activities in the frame of the DYNASYNC project was the development of an extended UHV system for in-situ investigations of surface nano-structures using the method of nuclear resonant scattering (NRS) at the ESRF. Moreover, a portable UHV chamber was developed (UW) for in-situ grazing incidence small angle X-ray diffraction and photon correlation spectroscopy measurements. Another key activity within the project was the development of a multi-APD array for spatially resolved NRS measurements at the ESRF. After commissioning of this new detector system, a first successful study on diffuse scattering from magnetic domains in thin films could be performed.

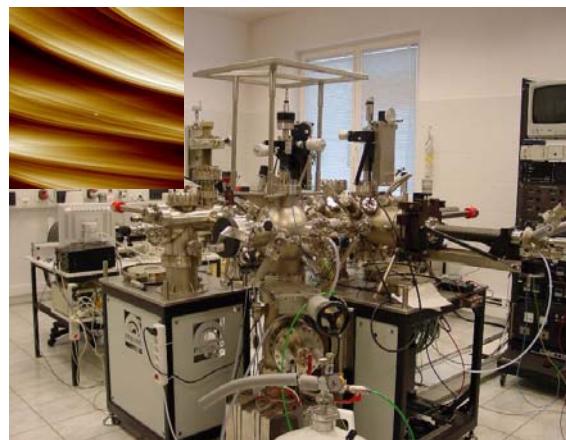


Fig. 1: Upgraded STM system at ICSC. The inset shows a $3 \times 3 \mu\text{m}^2$ topographic STM scan of a W(110) surface

Various characterization techniques were implemented in the partner laboratories in order to complement synchrotron radiation studies. For example, a UHV chamber for combined

ellipsometric and NRS experiments was developed at DESY, new MOKE spectrometers were installed at K.U.Leuven and ICSC, and an STM upgrade was completed at ICSC for characterization of surface nanostructures. This latter system is shown in Fig. 1. To facilitate portability and exchange between the partners' laboratories, the compatibility of UHV systems in several partner laboratories has been established.

Finally, the available and by the project extended capabilities for theory and computation in the consortium was decisive for the interpretation of the experimental results and the strategy of the experimental tasks.

Following the achievements in the workpackage **Instrumentation and Software (WP4)**, according to the project objectives, the scientific work focused on three major areas:

1. **Diffusion and the kinetics of structural changes (WP1: Diffusion and growth)**
2. **Collective excitations in nanostructures (WP2: Phonons)**
3. **Dynamical magnetic properties of nanostructures (WP3: Magnetization dynamics)**

In the following we summarize selected main results for each of these workpackages.

WP1: Diffusion and Growth

Major progress was made in the understanding of diffusion in isotopic $^{56}\text{FePt}/^{57}\text{FePt}$ multilayers. After growth, the isotopic multilayer showed the desired crystalline structure. As expected, no superstructure could be observed in the electronic reflectivity, however, a marked superstructure was observed in the NRS reflectivity curves. From the evolution of the superstructure as a function of annealing conditions, the diffusivity was deduced. The results suggest a change in the diffusion mechanism at those investigated low temperatures compared to the mechanism at high temperatures.

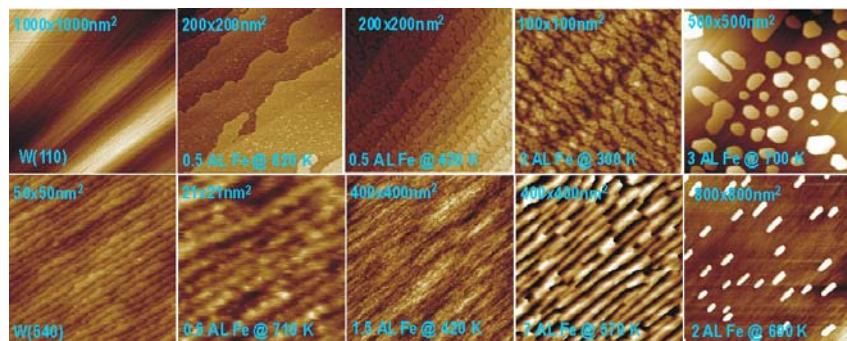
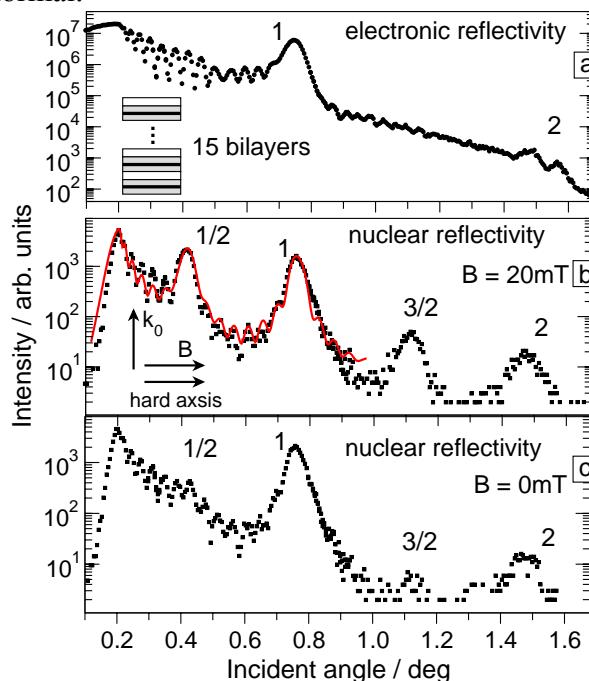


Fig. 2 STM images of tungsten substrates (first row) and Fe nano-structures on tungsten surfaces: W(110) – top, W(540) – bottom.

(540)-stepped one (bottom), at typical growth stages at given deposition temperature. The most striking feature is a periodic structure along the steps for the Fe monolayer on W(540) that reassembles misfit dislocations for thicker films on flat substrates, and a strong anisotropy in the Fe island growth. The last is due to diffusion limitation along the step normal.



A surprising discovery was made during the investigation of the growth of the native oxide on polycrystalline Fe layers. When stacking many of them in a Fe/Fe-oxide multilayer, it appeared that the moment orientation in adjacent Fe layers is almost perpendicular to each other. This leads to magnetic superstructure reflections in the NRS reflectivity (Fig. 3). The behaviour in external magnetic fields could be described within a model where the coupling between Fe layers is mediated by antiferromagnetic order in the Fe-oxide spacer.

Figure 3: Electronic and nuclear reflectivity of a Fe/Fe-oxide multilayer, showing superstructure reflections when an external field is applied along the hard axis (b). In remanence these reflections vanish.

WP2: Phonons

In the frame of WP2, pioneering experiments were performed under UHV conditions in the newly installed vacuum system at beam line ID18 of the ESRF. An impression of the complexity of the system is given in Fig.4. The main goal of this experiment was the investigation of the vibrational properties of iron monolayers on a tungsten surface. The very

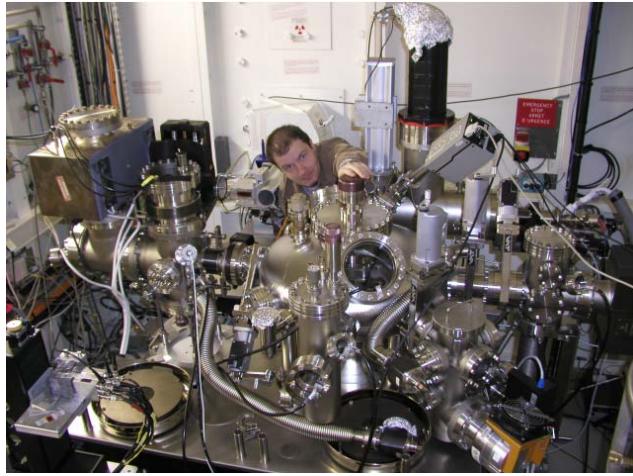


Figure 4 Overview of the UHV system installed at the beam line ID18 of the ESRF. Shown on the picture is S. Stankov (Uni Wien/ESRF) during the experiment

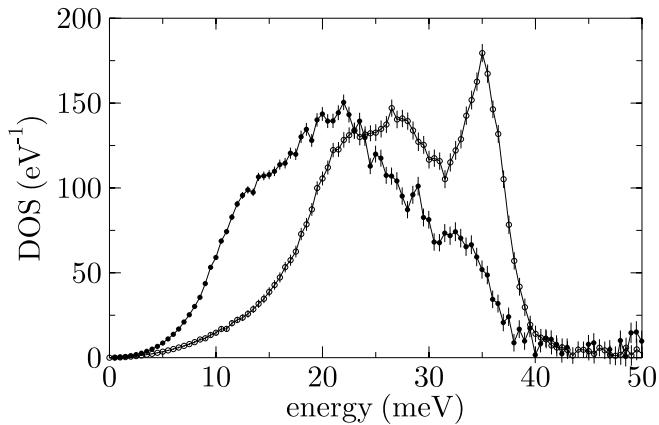


Figure 5 Vibrational density of states (VDOS) of one monolayer of iron (filled circles) in comparison with the VDOS of bulk Fe (open circles).

small amount of material – a single monolayer of atoms on a surface – represents a major challenge of the experiment. To the great surprise of all experimentalists, the measured signal was much larger than expected, so that instead of a test experiment, a systematic investigation of the vibrational properties could be performed as a function of coverage. One of the main experimental results is shown in Fig. 5, displaying the vibrational density of states (VDOS) of the Fe atoms in the monolayer, as compared to the VDOS of bulk Fe. A strong softening is observed that results from the lower dimensionality and the particular structure of the system. We interpret the softening as caused by the missing bindings in outward (vacuum) direction and the coupling of the iron vibrations to the vibrations of the tungsten substrate.

A series of VDOS measurements is shown in Fig. 6 for various coverages ranging from 1 monolayer up to 40 monolayers of Fe. For very thin films, i.e. one and two monolayers, the density of states show pronounced difference for the in-plane [1-10] and [001] directions. The origin of the anisotropy is the lattice mismatch between the substrate and the deposited iron layers that induce strains in the [1-10] direction of the iron film.

The experiments are interpreted using first-principle theory. Ab-initio vibrational calculations of the Fe monolayer on W(110), which take into account, the magnetic interactions among the Fe atoms, provide the phonon dispersion relations of a simulated slab. Figure 7 shows these curves as a relation between the phonon frequencies and wave vector. Red curves are representing mainly the surface Fe atom vibrations, while the blue lines illustrate the motion of W atoms in the substrate.

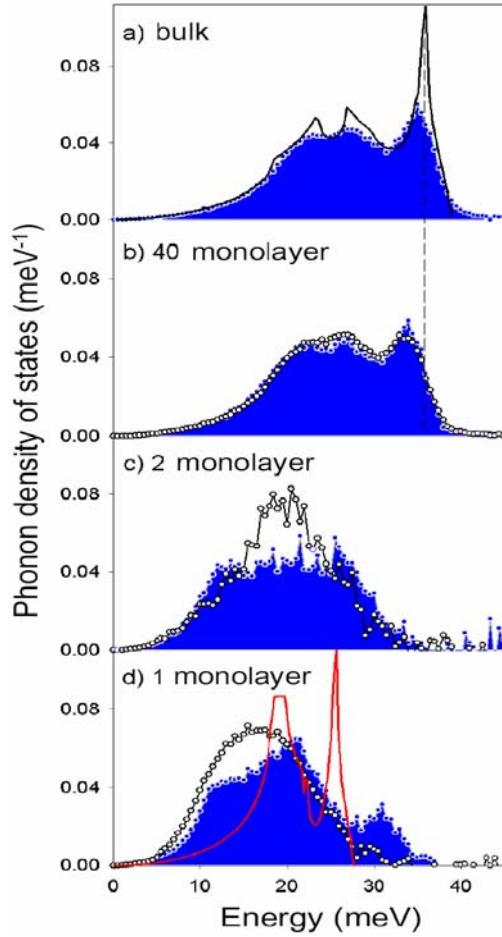
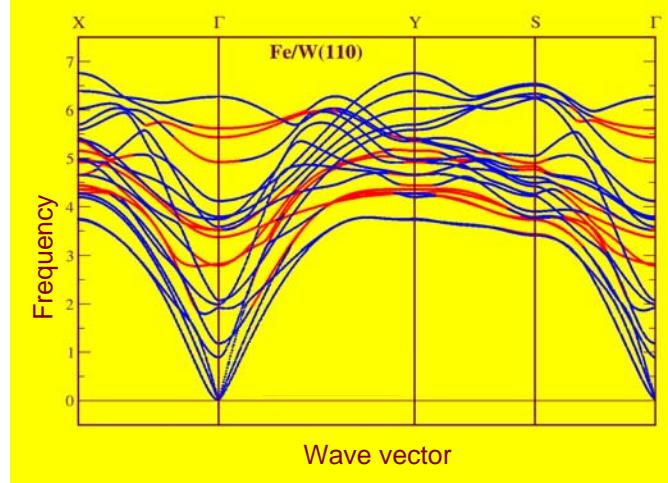


Figure 6 (left) Phonon density of states for bulk polycrystalline α -Fe and for single crystalline iron films consisting of 40, 2 and 1 monolayer deposited on a W(110) substrate. Layers with 40, 2 and 1 monolayer iron were measured with the incoming x-ray beam in two different in-plane directions, [001] (blue area plot and blue dots) and [-110] (black circles). The black and red lines in bulk and for a monolayer, respectively, show inelastic neutron scattering data for alpha-Fe and W.

Figure 7 (below) phonon dispersion curves for Fe on W(110).



From the measured vibrational spectra and the phonon density of states one is able to derive a number of elastic and thermodynamic quantities like mean displacement, average force constant k , heat capacity, vibrational entropy etc. As shown here, nuclear inelastic scattering is capable to determine such quantities for ultrasmall quantities of material. For the Fe films on W(110) investigated here, some of these quantities are shown in Fig. 8 as function of the inverse number of layers $1/N$. Quite remarkably, one finds a linear relationship between these quantities and $1/N$, valid down to thicknesses of 2 monolayers. This suggests that the vibrational properties significantly differ from the bulk only in the atomic layers at the very interfaces. This applies as well for the corresponding decomposition of the VDOS.

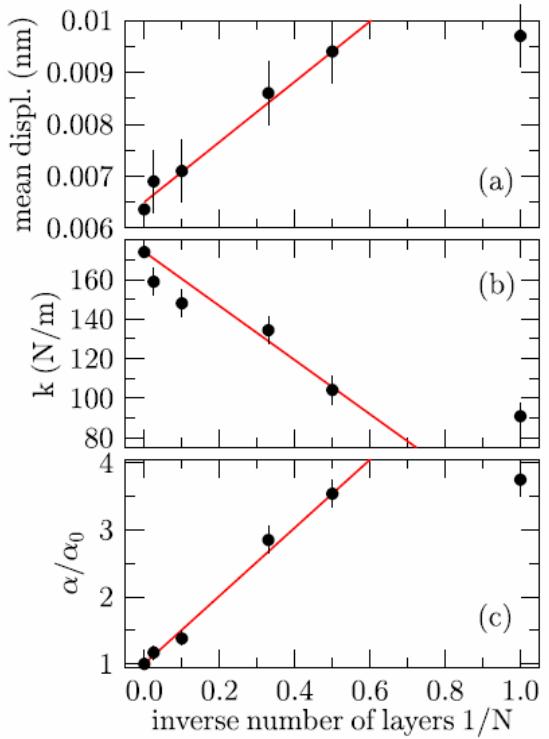


Figure 8: Mean displacement, average force constant, and Debye enhancement factor α , resulting from a parabolic fit of the low-energy VDOS $g(E) = \alpha E^2$

WP3: Magnetization dynamics

As a major advancement in WP3, a nuclear resonant scattering experiment on spin dynamics in Fe/FeSi/Fe trilayers should be mentioned here. A remarkable correlation between the spin dynamics in the spacer layer and the interlayer coupling was observed. The dynamical behaviour is temperature dependent, and it has serious repercussions on the temperature dependence of the biquadratic interlayer coupling. In order to access low temperatures and high external magnetic field in GINRS geometry a cryomagnet system (see Fig. 9) has been utilized on a two-circle element to allow for Θ - 2Θ scans.



Figure 9 Cryomagnet system in operation for GINRS measurements at ID22N. The system is top-loading (up to 48 mm sample diameter). Temperatures between 1.5 and 300 K and external magnetic fields between 0 and 6 Tesla in the horizontal plane, parallel and perpendicular to the synchrotron beam, are accessible. The system is mounted on a two-circle element to allow for Θ - 2Θ scans of thin films and multilayers.

In another experiment, magnetization dynamics during the growth of epitaxial Fe films on a tungsten W(110) single crystal was studied via NRS at the ESRF. The combination of UHV conditions and the high brilliance of the third generation synchrotron source provided us the unique possibility to probe the evolution of the Fe film spin structure during the film growth via the accumulation of the high quality time spectra during the ^{57}Fe deposition process, as shown schematically in Fig. 10a. There are two different thickness regimes where the most intriguing properties have been found: i) ultrathin films with the thickness in the range 0.5 - 4 ML when the onset of ferromagnetic behavior is expected, and ii) Fe films with thickness of few tens of ML, in the vicinity of the in plane spin reorientation transition (SRT). A complex morphology of the ultrathin Fe films, exemplified in Fig. 10b, results in a non-collinear magnetic structure derived from the numerical analysis of the GI-NRS data. The structure is related to the film morphology characterized by a deviation from a layer-by-layer growth mode beyond the first monolayer and periodic misfit dislocations. Competition of out-of-plane and in-plane magnetic anisotropy for double layer Fe patches and for thicker Fe areas, respectively, leads to spin structures at buried layers, which could not be solved using traditional methods. The layer resolved map of hyperfine magnetic fields could be obtained for the first time, as shown in Fig. 10c.

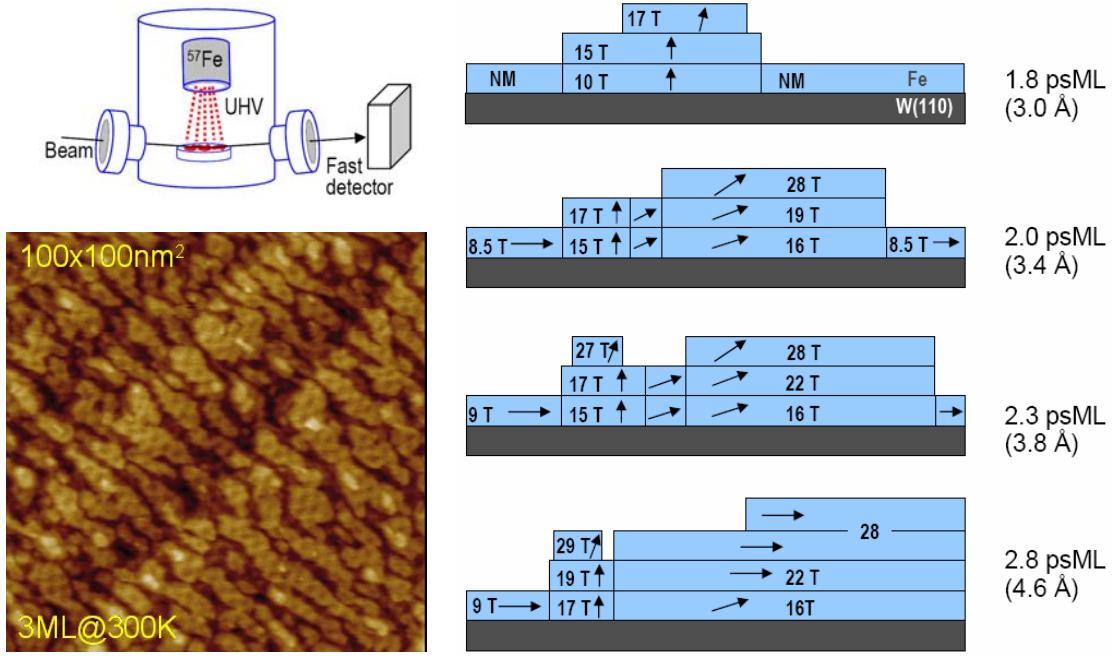


Figure 10. (top left) Geometry of the grazing incidence nuclear scattering (GI-NRS) UHV experiment at ID 18. (bottom left) STM image illustrating the growth mode for a 3 ML Fe film on W(110) (right) The spin structure derived from GI-NRS data shown for selected ^{57}Fe coverage (in equivalents of pseudomorphic monolayers (psML). The numbers indicate the layer values of the hyperfine magnetic fields. The layer resolved spin orientation is depicted by arrows.

Even more spectacular results were obtained for the dynamics of the in-plane SRT. Based on the NRS analysis, a new model of the transition has been proposed. The thickness induced transition of the magnetization from [1-10] to [001] direction originates at the Fe/W(110) interface and occurs through transient non-collinear magnetization structures, as shown in Fig. 11.

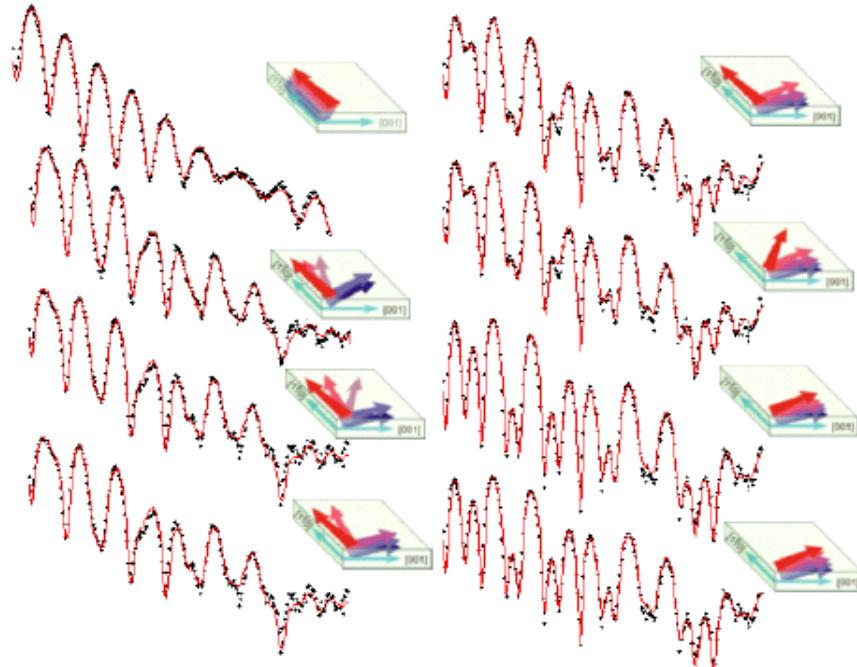


Figure 11. In-plane spin reorientation transition as seen by nuclear resonance scattering. The time spectra in the transition (from 23 ML, top left, to 25 ML, bottom right) are fitted using fan-like magnetization structures, as shown in the insets.

Formation and transformation of domains in antiferromagnetically coupled multilayers is a hot issue since the size of such domains determines the noise of magnetoresistive read heads in storage devices. Exciting new aspects of these transformations were revealed by off-specular synchrotron Mössbauer reflectometry (SMR) on Fe/Cr and Fe/FeSi multilayers. A spontaneous and irreversible growth of the domain size ('domain ripening') was found when demagnetizing the multilayer from saturation. In contrast to naïve expectation, ripening was found to be abrupt rather than continuous, a feature fully understood in terms of a Monte Carlo simulation. Systematic study of domain ripening and spin-flop-induced 'domain coarsening' resulted in the explanation of the mysterious 'supersaturation domain memory effect'. Off-specular SMR experiments have been performed in a very efficient way using the multi-APD array; domain transformations are clearly seen in the 2D detector maps as shown in Fig. 12.

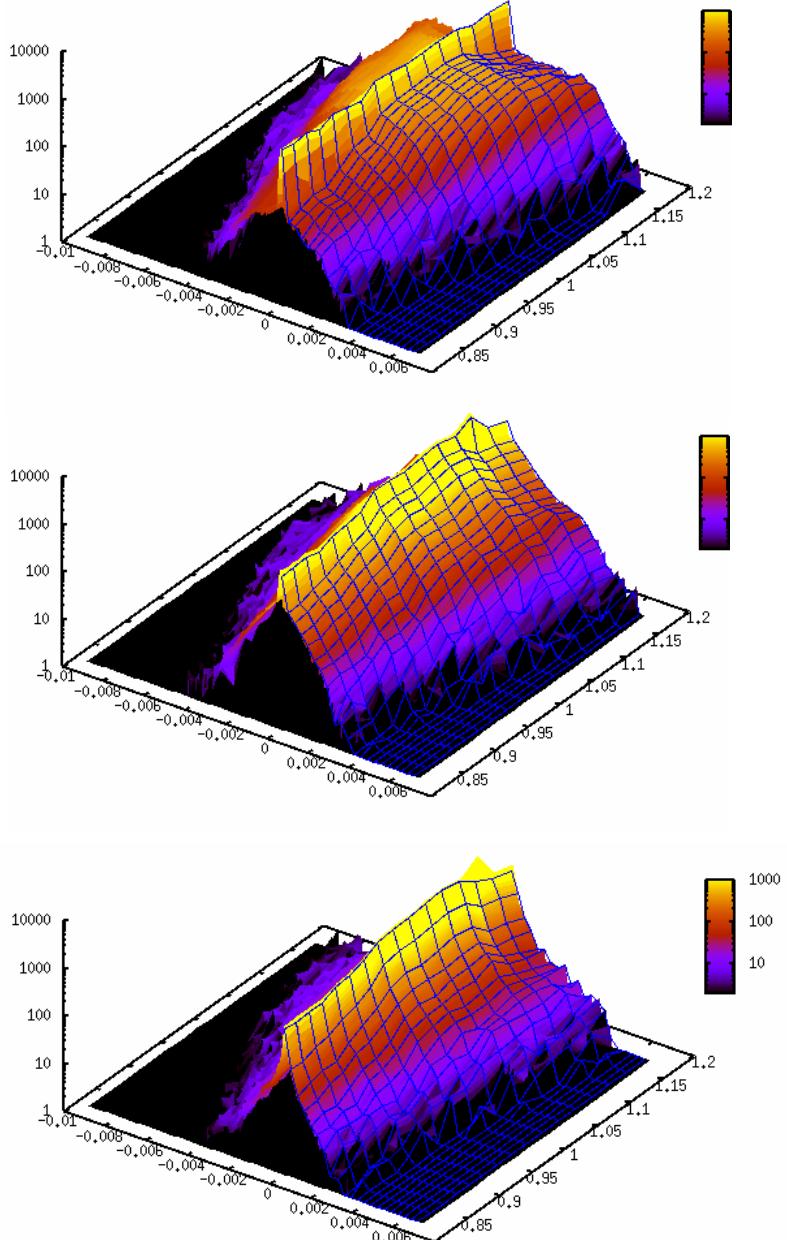


Figure 12. Off-specular 2D ($\omega-2\Theta$) SMR map, measured with the newly developed multi-APD array (time resolution 1 ns, pixel size 100 mm). The sample was an antiferromagnetically coupled Fe/Cr multilayer in the native domain state (top), after domain ripening (center) and after domain coarsening (bottom).

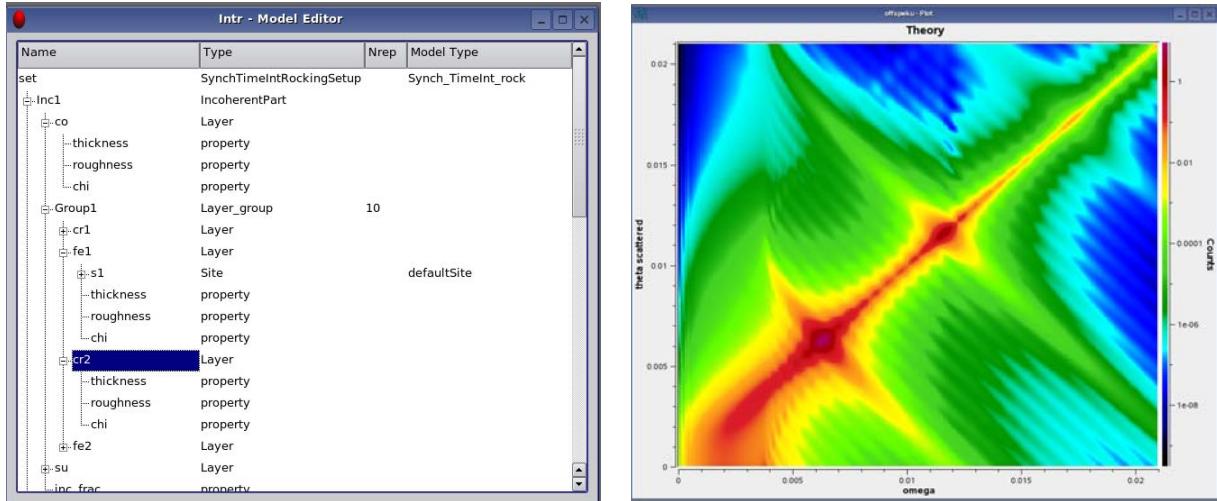


Figure 13. Parameter editor user interface (left side) and off-specular 2D SMR maps window (right side) of the user-friendly experimental data reduction surface EFFI2.

To evaluate off-specular 2D SMR maps, a new theory had to be developed since the so-called DWBA method widely used in neutron reflectometry results in extremely lengthy algorithms. The simplified 'DWA' method is by two or three orders of magnitude faster than the DWMA method without significantly decreasing the accuracy. A user-friendly graphical interface (EFFI2) was developed to host the DWA off-specular SMR code as well as a number of other algorithms used in thin film analysis. EFFI2 allows, for the first time, to simultaneously evaluate experimental data taken by very different experimental techniques on the same sample in a really user-friendly manner. The appearance of the graphical interface and the calculated off-specular 2D SMR map of an antiferromagnetic Fe/Cr multilayer in the ripened domain state is shown in Fig. 13.

End results with intentions for use and impact

The methods and instruments developed within the DYNASYNC project open unique possibilities to simultaneously investigate a multitude of dynamical properties. New prospects are on the horizon allowing one to investigate the intimate relationship between magnetism or diffusion and lattice dynamics, correlated with structure and morphology. This is particularly interesting in the field of functional magnetic structures. It is obvious that physical properties of new devices will depend not only on their structural, but also on their dynamical properties. Examples are nanoscale sensor/actuator systems that rely on the shape memory effect and nanoscale magnetostrictive devices. The performance of these systems will be strongly influenced by finite-size effects and the dimensionality of the system. The microscopic origin of these effects is by far not understood yet. A thorough understanding opens the way to tailor the development of future functional nanoscale systems. We expect the project to yield significant contributions to this field, stemming from the unique properties of the experimental method. A distinct advantage of the technique of nuclear resonant scattering is that it is isotope-specific. Compared to other methods, the signal is essentially free of contributions from surrounding materials. Moreover, probe layers can be selectively deposited to study the magnetic and dynamic properties with atomic resolution.

Nuclear resonant scattering of synchrotron radiation is practically only feasible at the specialized beam lines of modern 3rd generation sources like the ESRF, APS and Spring-8. A major aspect of the project is the development of new sample environments and on-line

characterization techniques. The new methodology developed here can be used to follow time dependent processes in real time. Nuclear resonant scattering experiments can be performed *in situ*, under UHV conditions, during the formation process of the system (deposition, oxidation, annealing). It gives the unique structural, chemical or magnetic information on the properties evolution while the nanostructures are grown and modified.

The experimental facilities developed within the project are available for the international community in the field of nanoscience and technology. This will strengthen the leading role of the European partners for the integration of nanoscience into large-scale research facilities.