Nuclear resonant scattering of synchrotron radiation: a novel approach to the Mössbauer effect

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Introduction

The scientific and technological interest is ever more directed towards samples with small dimensions. Ultrathin layered magnetic structures display various interesting properties, some of them which are already implemented in technological applications. The study of complex hetogeneous nanostructures actualized the need for sensitive techniques that can probe the magnetic properties very locally. Hyperfine interaction techniques, which probe the electric and magnetic properties of the sample on a quasi-atomic level, are very suited to accommodate this need.

A nucleus embedded in a material will be submitted to an electromagnetic interaction with the surrounding electrons, called the hyperfine interaction [1]. In this context, the electrical quadrupole interaction and the magnetic dipole interaction are the most important. The electrical quadrupole interaction describes the interaction of the nuclear quadrupole moment (a measure for the deformation from sphericity of the nuclear charge distribution) with the electric field gradient (originating from a non-cubic charge distribution, as in the case of a tetragonal or hexagonal crystal structure). The magnetic dipole interaction describes the interaction between the nuclear magnetic moment and the magnetic fields.

The hyperfine interaction between the nucleus and its surrounding will cause a shift and a splitting of the nuclear energy levels. By measuring this shift and splitting very accurately, one can extract valuable properties of the material. For example, the magnetic hyperfine field is a measure for the magnetization vector in the material. The electric field gradient, on the other hand, depends on the local crystalline structure, and thus yields information on the local atomic configuration, epitaxial strain, defects etc. The subject of nuclear condensed matter physics is to study material properties by measuring the hyperfine interactions. This is normally done via various experimental methods like muon spin resonance (μSR), nuclear magnetic resonance (NMR), perturbed angular correlation (PAC) and Mössbauer spectroscopy. Recently, a new method was developed that probes the hyperfine interactions of nuclei via nuclear resonant scattering of synchrotron radiation [2]. This is a time-based extension of the Mössbauer effect that became feasable with the availability of very brilliant synchrotron radiation sources. The fact that the synchrotron radiation is polarized to a high degree and that the method relies on coherent scattering rather than incoherent absorption opens new experimental possibilities compared to conventional Mössbauer spectroscopy. In this contribution, an introduction will be given to the techniques of Mössbauer spectroscopy and nuclear resonant scattering of synchrotron radiation, and some applications in the field of magnetic multilayers will be discussed.

The most frequently used nucleus for Mössbauer spectroscopy and nuclear resonant scattering of synchrotron radiation is ^{57}Fe. The nuclear levels of interest are the ground state (defined as energy equal to zero) and an excited level at an energy of 14.413 keV. These levels are populated when a radioactive source of ^{57}Co decays. The nuclear level at 14.413 keV has a natural lifetime of 141 ns. As will be explained below, the nuclear level also can be populated via excitation from the ground state by 14.413 keV photons coming from an external source, be it a radioactive source or a synchrotron radiation source.

Hyperfine interactions

The m-substates of an isolated nucleus are degenerate (the m-states are the projection of the spin on a chosen z-axis). The electromagnetic interaction of the nuclear spin with the environment will lead to the shifting or splitting of the nuclear levels. In this course, we will mainly deal with the magnetic dipole interaction.

The interaction between the magnetic moment of the nucleus **μ** and a magnetic field **B** will lead to a Zeeman splitting of the nuclear levels. The Hamiltonian describing this interaction, is given as

$$H_B = -\frac{\mu}{\hbar I}\mathbf{I}\cdot\mathbf{B}$$

The eigenstates and energy eigenvalues E_M are easily determined when the z-axis is chosen along the field direction, yielding $E_M = -\frac{\mu B}{I}m$. A nuclear level with spin **I** is thus split into (2I+1) equidistant magnetic hyperfine levels, see Figure 1. In the case of ^{57}Fe, the ground and excited nuclear level have I = 1/2 and I = 3/2 respectively. The magnetic hyperfine interaction thus creates the sublevels m = +1/2 and -1/2 in the ground state, and m = +3/2, +1/2, -1/2 and –3/2 for the excited state.

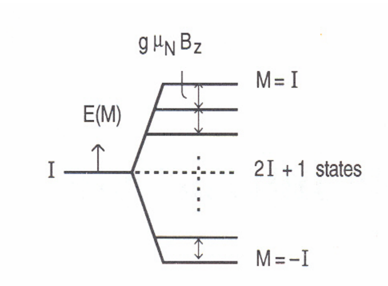

Figure 1 From [1] : Nuclear level splitting in a **B** field (nuclear

Mössbauer spectroscopy

Mössbauer spectroscopy dates back to 1958 when R. Mössbauer discovered the possibility of recoilless emission and absorption of γ-rays by nuclei [3]. Classically, when nuclei absorb or emit radiation, they undergo a recoil. However, if the absorbing and emitting nuclei are bound in a solid, the recoil energy is transferred to vibrational modes of the solid, known as phonons. Under certain conditions (heavy nuclei, low temperature, low γ-ray energy) the probability for zero-phonon transitions becomes appreciably high. In the case of a zero-phonon transition, the γ-ray will be absorbed and emitted without recoil, and thus the γ-ray energy exactly matches the energy difference of the nuclear decay. This phenomenon is known as the Mössbauer effect.

Mössbauer spectroscopy [4,5] relies on this effect. γ-rays emitted without recoil in a radioactive source can be resonantly absorbed by nuclei in the sample. Performing a Mössbauer experiment essentially means the recording of reduced transmission through the sample as a result of the nuclearly resonant absorption of photons. Due to the hyperfine interactions the nuclear energy levels in the sample may have slightly shifted or split into several sublevels with respect to the energy levels in the radioactive source. In order to record these minute changes, the source is moved with a variable velocity v, typically in the order of a few mm/s. The velocity causes a Doppler shift for the emitted γ-ray energy $E_\gamma = E_0 (1 + v/c)$ where E_0 is the nuclear transition energy in the source and c is the speed of light. For those velocities where E_γ matches one of the nuclear transitions in the sample **a resonant absorption is seen in the velocity spectrum**. Figure 2 shows the traditional setup for Mössbauer spectroscopy.

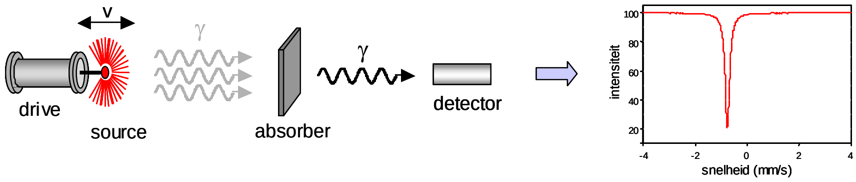

Figure 2: Schematic Mössbauer setup in a standard transmission experiment.

In the case of the Mössbauer probe ^{57}Fe, the magnetic hyperfine interaction creates the sublevels m = +1/2 and -1/2 in the ground state, and m = +3/2, +1/2, -1/2 and –3/2 for the excited state. This yields in principle eight possible transitions between the ground state and the excited state. However, a quantum mechanical selection rule further imposes $\Delta m = 0, \pm 1$, which limits the number of possible transitions to six. Therefore, six possible resonances are observed in the Mössbauer spectrum when ^{57}Fe nuclei are submitted to a magnetic hyperfine field. This is illustrated in the left panel of figure 3. Thus, as a function of the energy of the incoming photons (or velocity of the source), six absorption resonances are expected when the sample is magnetic.

From the positions of the absorption lines, the hyperfine interaction can be deduced, and thus, the strength of the electric and magnetic properties (magnetization) of the material can be extracted. The direction of the hyperfine field can be determined from the relative intensities of the resonances. This is illustrated in the right panel of figure figure 3.

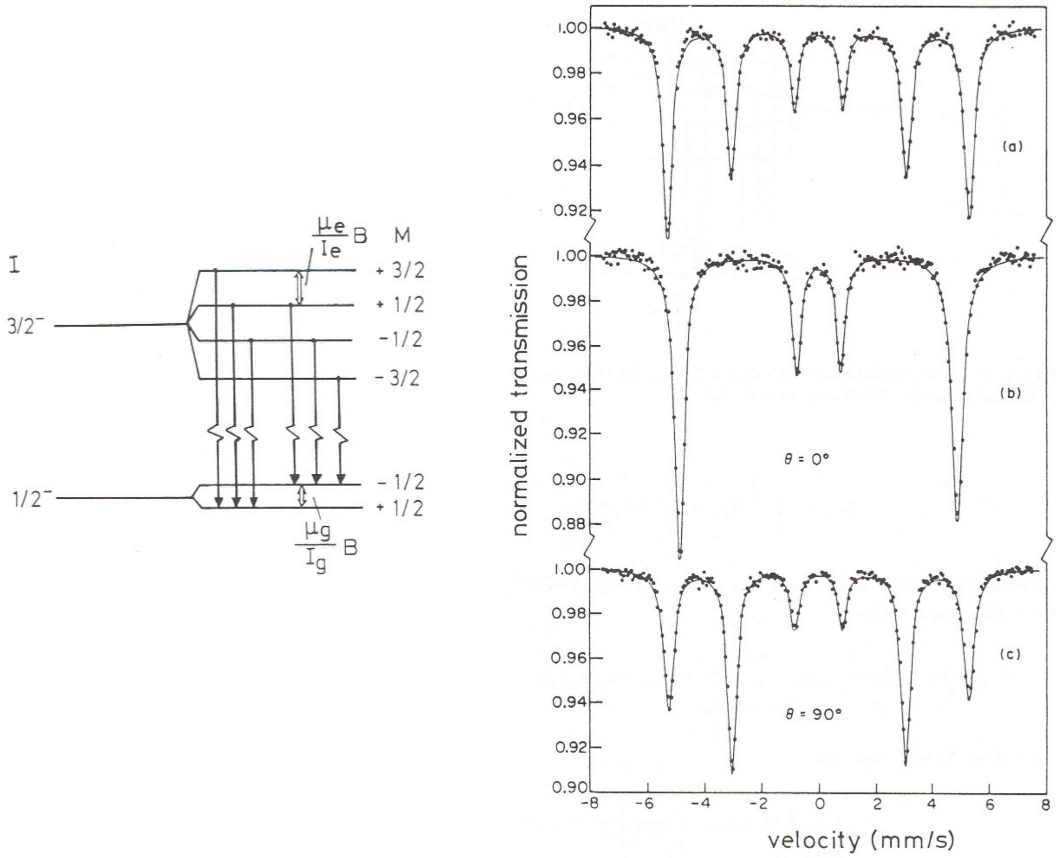

Figure 3 From [1]. Left: Splitting of the nuclear levels of ^{57}Fe in a B field. The γ-ray transitions shown obey the M1 radiation selction rules. Right: Mössbauer absoption spectra for iron metal. Right: (a) Unmagnetized iron absorber, (b) magnetized iron absorber with the magnetization along the photon direction (c) magnetized iron absorber with the magnetization perpendicular to the photon direction.

The above technique of transmission Mössbauer spectroscopy is very efficient if the sample can be made several μm thick, but becomes inefficient for ultrathin films, eventually deposited on a milimeter thick substrate. When dealing with ultrathin films and multilayers, the approach is slightly changed, and a method called Conversion Electron Mössbauer spectroscopy (CEMS) is applied. Instead of detecting the transmitted radiation, one will record conversion electrons. Indeed, there is a very high probability that the ^{57}Fe nuclei in the sample, after they had been excited through a 14.413 keV coming from the radioactive source, decay from the excited level to the ground state via the excitation of an electron from the electron shell. The excess energy of the electron is subsequently released via the emission of a characteristic X-ray, and/or via the emission of an electron from the electron shell. The detection of the electrons can be made very efficient. Furthermore, the electrons escape from the near-surface region only (up to at most 100 nm). Therefore, Conversion Electron Mössbauer spectroscopy is very well suited to study surfaces and ultrathin films.

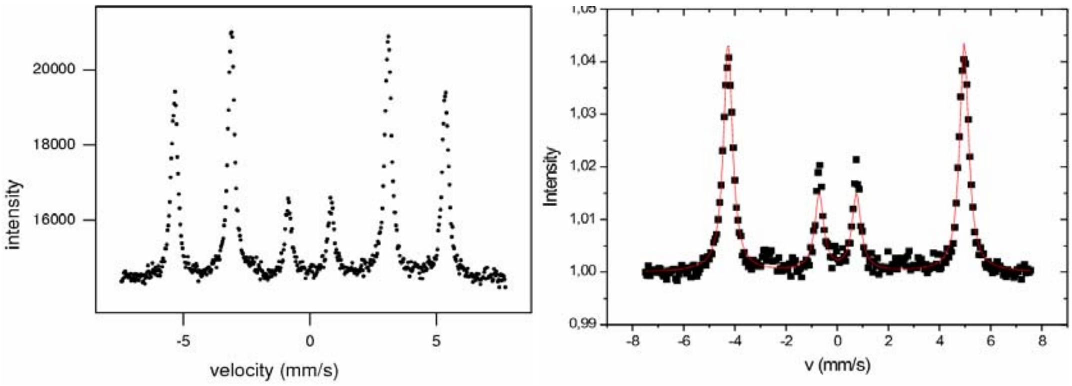

Figure 4. Left: Conversion electron Mössbauer spectrum recorded on an epitaxially grown iron thin film. Right: Conversion electron Mössbauer spectrum recorded on an epitaxially grown FePt thin film stabilized in the $L1_0$ crystalline phase. The photon direction was perpendicular to the plane of the thin film.

In figure 4, the CEMS spectrum on a thin epitaxially grown ^{57}Fe film is compared to the CEMS spectrum on a thin epitaxially grown ^{57}FePt film stabilized in the $L1_0$ crystalline phase. Both samples were oriented perpendicular to the photon direction. Comparison of the intensities of the resonances in the spectra in figure 3 and figure 4 immediately indicates that the magnetization in the epitaxially grown Fe thin film is oriented in the plane of the film (to minimize dipolar energy), whereas in the case of the epitaxially grown FePt $L1_0$ thin film, the magnetization is oriented out of the plane of the thin film (due to the very strong crystalline anisotropy). Further, the spectrum on the FePt $L1_0$ thin film is slightly asymmetric due to the electric quadrupole interaction, a signature of the tetragonal crystalline environment.

Generally, Mössbauer spectroscopy and its variant Conversion Electron Mössbauer Spectroscopy (CEMS) are easy and efficient methods to probe the local magnetization. In thin films, CEMS readily determines the angle that the magnetization makes with the normal to the sample. However, in some cases Mössbauer spectroscopy with a radioactive source becomes unpractically inefficient, for example if one is interested in the direction of the magnetization in the plane of an ultrathin film, especially when external magnetic fields are applied and if the sample has to be cooled to low temperatures. In such cases, it is advantages to make use of the well-directed synchrotron radiation.

Nuclear resonant scattering of synchrotron radiation

Synchrotron radiation has unique features which make nuclear resonant scattering with synchrotron radiation very attractive:

1. *Tunable energy spectrum* up to hundred keV.
2. Synchrotron radiation is highly *linearly polarized* in the plane of the storage ring.
3. *Pulsed time structure of the radiation:* pulses of 100 ps separated by intervals between 2 ns and 4 μs.
4. *High brilliance*: high intensity, small beam size and small beam divergence. The unfocussed beam spot at 30 m from the undulator is typically 1.0 x 0.8 mm^2 (FWHM).

Table 1 compares the properties of synchrotron radiation with the radiation from a radioactive source. Because the angular flux density of the generated resonant radiation exceeds that of a Mössbauer source, nuclear resonant scattering of synchrotron radiation is ideally suited for the study of hyperfine interactions in small samples. It is to be considered, however, that the properties of synchrotron radiation remain substantially different from the radiation from a radioactive source. The main differences are the broad energy bandwidth and pulsed time structure of synchrotron radiation. Indeed, even extreme efforts allow to monochromatize the radiation to the meV regime only. This imposes an alternative design of the experiment and the detection of the nuclear resonances.

Table 1: Comparison between synchrotron radiation and a radioactive source

Properties	**Synchrotron source**	**Mössbauer source**
Energy bandwidth	Very broad (meV)	Monochromatic (neV)
Polarization	Linear	Unpolarized
Time structure	Pulsed	Continuous
Directionality	Emission in very small cone	Isotropic emission
Setup	At large facility	Compact lab experiment

Contrary to Mössbauer spectroscopy, nuclear resonant scattering with synchrotron radiation is generally performed in time domain, where the nuclear decay is studied as a function of time after excitation by the synchrotron pulse. If one considers resonant scattering by an individual nucleus, the scattered intensity as a function of time will show an exponential decay, determined by the lifetime of the nuclear excited state. When the nuclei are embedded in a material, the energy levels will split due to the hyperfine interaction. Since the incident radiation has a broadband energy spectrum, all hyperfine levels can be excited simultaneously, giving rise to interferences between the different nuclear transitions. The interference shows up as fast quantum beats in the time spectrum, which are superposed on the exponential decay [6]. These quantum beats in the time spectrum are the fingerprints of the hyperfine splittings since the oscillation frequency depends on the energy difference between the possible nuclear transitions [7, 8]. In addition, for thick samples, the time spectrum will be modulated by multiple scattering of the radiation. This is a direct consequence of the spatial coherence of the scattered wavefield. This will cause the initial decay to be enhanced, called the ‘speedup’, and the spectrum will be modulated by a slowly varying dynamical beat. The period between subsequent dynamical beat minima is non-equidistant and decreases as the sample thickness increases. Figure 5 shows a typical nuclear resonant scattering spectrum for Fe. The three characteristics are easily recognized. For a general overview on nuclear resonant scattering of synchrotron radiation we refer to Ref. [9, 2].

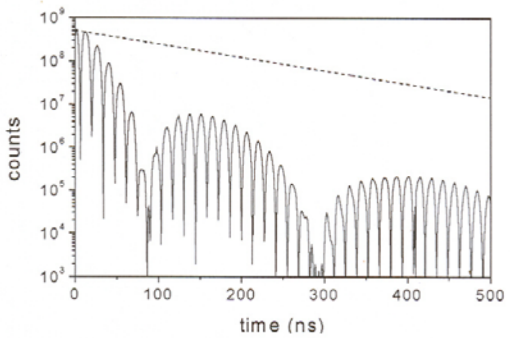

Figure 5: A typical nuclear resonant scattering spectrum from a thick ^{57}Fe absorber (effective thickness of 24), submitted to a hyperfine magnetic field of -33 T perpendicular to the synchrotron plane. Note that the ordinate is logarithmic. The dashed line gives a pure exponential decay.

Nuclear resonant scattering of synchrotron radiation is sensitive to the magnitude of the magnetization through the observed frequency. But, in addition, the technique is also ideally suited to determine the direction of the magnetization. Because synchrotron radiation is linearly polarized, one is able to determine the angle that the magnetization makes with the polarization as well as the angle that the magnetization makes with the photon. This is especially useful for the determination of the direction of the magnetization in thin films, and is illustrated in the following two examples. From the time spectra obtained with nuclear resonant scattering in different external field strengths, one can deduce an isotope-selective magnetization curve that reflects the magnetic properties of the *isotopically enriched parts* of the sample only.

Imaging the Magnetic Spin Structure of Exchange-Coupled Thin Films [10]

This work involves the study of the magnetic spin structure of a soft-magnetic film that is exchange-coupled to a hard-magnetic layer. The magnetization of the soft-magnetic film at the interface is pinned to the hard-magnetic film as a result of the exchange interaction. With increasing distance from the interface, the exchange coupling becomes weaker and the magnetization may rotate under the action of an external field. If, for example, the external field is applied orthogonal to the magnetization direction of the hard layer, the magnetic moments in the soft layer arrange in a spiral structure along the normal. Because of the reversible nature of this rotation, this is called the exchange spring effect.

The system studied is a bilayer system consisting of a hard-magnetic FePt layer and a soft-magnetic Fe layer. The depth dependence of the magnetization direction in the Fe layer could be determined by nuclear resonant scattering of synchrotron radiation from ultrathin ^{57}Fe probe layers.

The time spectra are theoretically well-described, and the contribution from various frequencies is closely related to the energy-dependent resonant strengths also encountered in Mössbauer spectroscopy and Conversion Electron Mössbauer spectroscopy. From the fit of the measured data, the

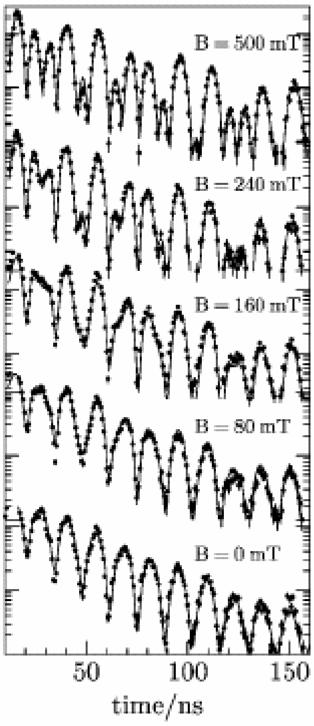

Figure 6: Nuclear resonant scattering of synchrotron radiation applied to an exchange spring [10]. Time spectra are recorded as a function of externally applied magnetic field. The line through the data points is a theoretical fit.

planar rotation angle of the magnetization at a specific depth of the Fe layer is derived.
In an external magnetic field a magnetic spiral structure was observed. The magnetic spiral structure as observed with nuclear resonant scattering of synchrotron radiation could be described within a one-dimensional micromagnetic model. This work demonstrates that nuclear resonant scattering of synchrotron radiation allows one to image vertical spin structures in stratified media with unprecedented accuracy.

Nuclear Resonant Magnetometry [11]

As shown in the previous example, nuclear resonant scattering of synchrotron radiation is extremely suitable for depth-resolved or layer-resolved magnetization measurements. However, because the incident synchrotron radiation is linearly polarized, the nuclear resonant scattering process is not sensitive to the sign of the hyperfine interaction. As a result, only the magnitude and ‘absolute’ orientation of the magnetization vector can be extracted. The sign of the magnetization vector cannot be measured. To overcome this limitation, the use of circularly polarized x-rays in nuclear resonant scattering of synchrotron radiation was introduced [11]. This way, the scattering process is sensitive to the sign of the hyperfine interaction, and the full magnetization information can be retrieved. This is illustrated in figure 7, showing the time spectra of a thin ^{57}Fe film under saturation conditions. The two opposite field directions give rise to clearly distinct time spectra.

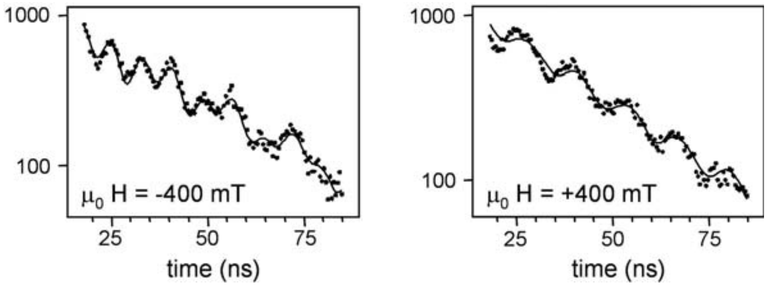

Figure 7: Saturation spectra of a 50 Å ^{57}Fe thin film measured with circularly polarized radiation. An external magnetic field of 400 mT was applied anti-parallel (left) or parallel (right) to the photon direction.

In this work, interlayer-coupled Fe/Cr(100) multilayers were studied. Fe/Cr multilayers are known to exhibit bilinear and biquadratic interlayer coupling, which leads to the ordering of the magnetic moments in subsequent Fe layers under 0º, 90º or 180º. Also the existence of non-collinear interlayer coupling was reported, where the subsequent Fe layers couple under an angle of 50º. This coupling angle cannot be explained by the simple models of bilinear and biquadratic interlayer coupling and would imply that also higher-order terms play a role in the interlayer exchange interaction. However, one has to be very careful in interpreting the result, since boundary effects at the edge of the multilayer stack may have influenced the results. To avoid boundary effects, **a symmetric Fe/Cr(100) quintalayer consisting of three evenly thick Fe layers was studied, in which the central Fe-layer was enriched in the resonant isotope**. This way, one could selectively probe the central Fe layer with nuclear resonant magnetometry.

The investigated sample is an epitaxial ^{56}Fe(50Å)/Cr(11Å)/^{57}Fe(50Å)/Cr(11Å)/^{56}Fe(50Å) quintalayer grown on MgO(100). For this sample a strong antiferromagnetic interlayer coupling is expected. When placed in a large external field applied along the easy axis, the magnetic moments in all three Fe layers will be aligned with the field. With decreasing fields, the outer moments will remain close to the field direction, while the moments in the central Fe layer are expected to rotate to the opposite direction. The magnetic response of the central ^{57}Fe layer was measured selectively with nuclear resonant magnetometry. This way an isotope-selective magnetization curve of the central Fe layer could be measured, see figure 8. The isotope-selective magnetization curve can be combined with the magnetization curve of the whole quintalayer, from which the angle $|\theta-\varphi|$ between the magnetization vectors in the subsequent Fe layers as a function of the external field strength could be determined. We found that the central magnetization at zero field is not completely opposite to the field direction. Consequently, the coupling cannot be purely antiferromagnetic. Instead, the nuclear resonant magnetization data show in a very direct way the presence of non-collinear coupling in the Fe/Cr quintalayer, with an interlayer coupling angle of 162º.

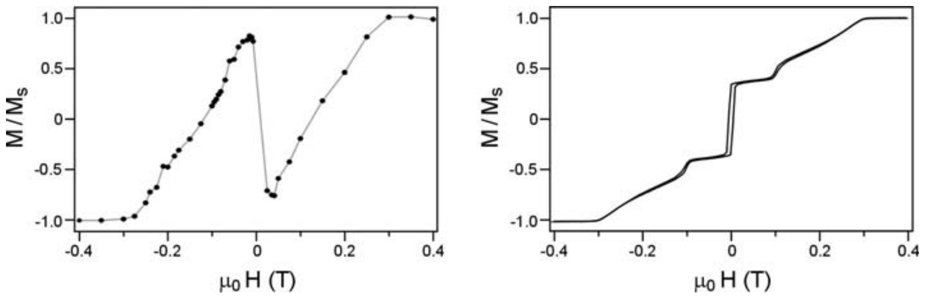

Figure 6: Measurements on ^{56}Fe(50Å)/Cr(11Å)/^{57}Fe(50Å)/Cr(11Å)/^{56}Fe(50Å) with the magnetic field applied along the easy axis. Left: isotope-selective magnetization curve of the central Fe layer. Right: macroscopic magnetization curve as a function of the external field strength

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