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Synchrotron Mössbauer reflectometry

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Grazing incidence nuclear resonant scattering of synchrotron radiation can be applied to perform depth-selective phase analysis and to determine the isotopic and magnetic structure of thin films and multilayers. Principles and recent experiments of this new kind of reflectometry are briefly reviewed. Methodological aspects are discussed. Model calculations demonstrate how the orientations of the sublattice magnetisation in ferro- and antiferromagnetic multilayers affect time-integral and time-differential spectra. Experimental examples show the efficiency of the method in investigating finite-stacking, in-plane and out-of-plane anisotropy and spin-flop effects in magnetic multilayers.

1. Introduction

Total external reflection (TER) of X-rays [1] and neutrons [2] from flat surfaces are phenomena dating back to the first half of the twentieth century. The real part of the index of refraction, n, of most materials for thermal neutrons and of all materials for X-rays is by about 10^{-5} less than unity. At low enough angles of grazing incidence $\Theta < \Theta_c = \sqrt{2(1-n)}$ the waves are totally reflected from a flat surface. The intensity of the reflected specular beam for $\Theta > \Theta_c$ rapidly decreases with increasing wave vector transfer $Q = 2k \sin\Theta$, where k is the wave vector of the incident radiation. In a stratified medium, reflected and refracted beams appear at each interface. The interference of the reflected beams leads to patterns of the reflectivity vs. wave vector transfer spectrum $R(Q)$ that bear information on the depth profile of the index of refraction $n(z)$, the argument z being the coordinate perpendicular to the sample surface. $R(Q)$ can be calculated from $n(z)$, e.g., using the method of *characteristic matrices* [3]. Therefore, in frames of a given model for the stratified system, $n(z)$ can be reconstructed (the parameters of the model can be fitted) from $R(Q) = |r(Q)|^2$, where $r(Q)$ is the reflectivity amplitude. This latter approach is the basic idea of *X-ray* and *neutron reflectometry*, two methods that can be used for mapping the electron density and the isotopic/magnetic structure of thin films, respectively. In fact, the coherent forward scattering of a scalar wave of momentum much higher than

that of the scatterers can be described [4] by the index of refraction close to unity

$$n = 1 + \frac{2\pi N}{k^2} f, \tag{1}$$

where N is the density of scatterers and f is the scattering amplitude. The electron density for X-rays or nuclear and magnetic scattering length density for neutrons is implied in the latter quantity. Throughout this paper we shall use the term "reflectometry" not just as a mere substitute for "grazing incidence scattering" but as the *application* of this phenomenon to *analyse the structure* of thin films and multilayers.

Soon after the discovery of the Mössbauer effect, TER of nuclear resonant photons was demonstrated [5]. Nevertheless, only three decades later the need for Mössbauer reflectometry was formulated [6] and its feasibility using strong ^{57}Co sources was demonstrated [7]. A serious limitation of Mössbauer reflectometry with conventional sources is the small ($\sim 10^{-5}$) solid angle involved. Due to its high collimation, synchrotron radiation (SR) is much better suited for reflectometric experiments than radioactive sources. Synchrotron Mössbauer reflectometry (SMR) is the application of grazing incidence nuclear resonant scattering of SR to thin film and multilayer structure analysis.

The first successful grazing incidence nuclear resonant specular reflection experiment with SR was performed by Grote et al. [8]. Chumakov et al. observed a pure nuclear reflection of SR from an isotopically periodic ^{57}Fe/Sc/^{56}Fe/Sc multilayer [9]. Alp et al. reported on the observation of nuclear resonant specular reflection with ^{119}Sn resonance [10]. An important step towards the realisation of SMR was the observation [11] of the *total reflection peak* [11,12], i.e., the high number of *delayed* photons appearing close to the critical angle of the *electronic* TER. The first SMR experiment aiming to study the magnetic structure of an antiferromagnetic (AF) ^{57}Fe/Cr multilayer was done in 1995 by Toellner et al. [13]. The last four years saw an increasing number of SMR experiments. In this paper we shall briefly review the principles and some methodological aspects of this technique. Main emphasis will be given to magnetic structure analysis of thin films and multilayers. More detailed reviews can be found in recent papers [14,15]. It will be shown that, using SMR, it is possible to study finite-stacking, in-plane and out-of-plane anisotropy and spin-flop effects. If not specified we shall always refer to the 14.413 keV transition of ^{57}Fe.

2. Principles of SMR, methodological aspects

Close to a Mössbauer resonance E_0, the photon's coherent scattering amplitude f in eq. (1) is a sum of the electronic and the nuclear coherent scattering amplitudes f_{e} and $f_{\mathrm{n}}(E)$ the latter being a rapidly varying function of the energy around E_0. The

nuclear scattering amplitude $f_{\mathrm{n}}(E)$ depends on the matrix elements $a_{\alpha\beta}$ of the hyperfine Hamiltonian [16]:

$$f_{\mathrm{n}} = \frac{kV}{hc} f_{\mathrm{LM}} \frac{1}{2I_{\mathrm{g}}+1} \sum_{\alpha,\beta} \frac{|a_{\alpha\beta}|^2}{E-(E_\alpha - E_\beta)+\mathrm{i}\Gamma/2}, \tag{2}$$

where k is the wave number, V the normalisation volume, f_{LM} the recoilless (Lamb–Mössbauer) fraction, I_{g} the ground state nuclear spin, E_α and E_β are the nuclear excited and ground state energies, respectively ($E_\alpha - E_\beta = E_0$) and Γ is the natural linewidth. For nuclear resonant scattering, f and n are 2×2 matrices rather than scalars since the two polarisation states of photons should be accounted for [16]. The optical approach based on eq. (1) is exactly valid for the coherent forward scattering of resonant photons and it is also a good approximation for specularly reflected grazing incident photons [17].

An SMR measurement is performed in Θ–2Θ geometry in either time integral or time differential regime. Time integral SMR means recording the total number of delayed photons from t_1 to t_2 as a function of Θ, where t_1 is a few nanoseconds determined by the bunch quality of the radiation source and by the dead time of the detector and the electronics while t_2 is a value somewhat below the bunch repetition time of the storage ring. As a rule, a Θ–2Θ scan of the *prompt* photons (conventionally called X-ray reflectometry) is recorded along with a delayed time integral SMR scan. Time differential SMR is a time response measurement in a fixed Θ–2Θ geometry performed at different values of Θ. Like in the forward scattering case, hyperfine interaction results in quantum beats of the time response. The first step of an SMR measurement is usually to take a time integral scan to select Θ values of high enough delayed count rate where time differential measurements can be performed. These can be found in the region of the total reflection peak and, in case of electronic or nuclear periodicity, in the region of electronic or nuclear Bragg reflections. A full SMR measurement consists of a prompt and a delayed time integral specular reflectivity scan and a set of time response reflectivity measurements of the delayed photons $R_t(t,\Theta) = |r_t(t,\Theta)|^2$, r_t being the Fourier transform of the energy domain reflectivity amplitude $r(E,\Theta)$. To extract the depth profile of hyperfine interactions with confidence, all these data should be evaluated *simultaneously*. If a full SMR measurement is not feasible for intensity reasons, a time integral scan may still contain valuable information for the structure of the thin film.

The grazing incidence specular reflectivity amplitude matrix r of a stratified thin film can be calculated both from the dynamical theory of Mössbauer optics [18] and from the susceptibility tensor deduced from the nuclear current density expression [19]. The two approaches are equivalent [20,21]. The reflectivity amplitude is given in terms of certain elements of a 4×4 characteristic matrix L which is the product of the exponentials of the differential propagation matrices M_i of the individual layers [17,22]. An appropriate choice of the basis leads to a shape of M_i the exponential of which can be computed solely by calculating 2×2 matrix exponentials [20,21]. Such a fast

algorithm is necessary to simultaneously fit several time response reflectivity curves depending on a common set of physical variables. However, due to the possibly high number of layers and the sites of inequivalent hyperfine interactions, the evaluation of an SMR measurement is not only a computational but also an organisational problem. Model functions and data fits presented in this paper have been calculated by the EFFINO program [21]. EFFINO solves this problem by implementing the technique of transformation matrices [23].

3. Depth selectivity

Although reflectometric methods clearly obey an inherent depth selectivity by directly yielding the depth profile $n(z)$ of the index of refraction, the main reason for the depth selectivity of SMR is the fact that close to Θ_c, the penetration depth of X-rays is rapidly decreasing with decreasing Θ down to a few nanometers. Therefore, by changing Θ around Θ_c (for $E = 14.413$ keV and an α-Fe sample $\Theta_c = 3.86$ mrad) and performing at each angle a time response measurement, one can, roughly speaking, adjust the depth at which the thin film is "sampled". Due to the existence of the "total reflection peak" [11,12], depth-selective hyperfine field analysis (i.e., phase analysis) is always possible on thin films containing the resonant isotope. Close to the surface ($\Theta \to 0$), the depth resolution is 1–2 nm but this figure becomes worse with increasing penetration depth at increasing Θ. The feasibility of depth-selective phase analysis by SMR was shown on the example of oxidised ^{57}Fe films and of an Al/^{57}Fe bilayer before and after ion beam mixing with 120 keV Xe ions [24]. Andreeva et al. have recently studied the depth profile of the electron density and of the hyperfine field in a Zr/[^{57}Fe/Cr]$_{26}$/Cr multilayer [25].

The ultimate depth selectivity of one monolayer can be reached by fabricating samples containing marker layers of the resonant isotope. The monolayer sensitivity of SMR was demonstrated by Niesen et al. in Au/^{57}Fe films on Ge substrate [26].

4. Magnetic structure of thin films and multilayers

Due to the full linear polarisation, nuclear resonant scattering of SR is extremely sensitive to the direction of the hyperfine magnetic field [27]. The same holds true for the grazing incidence geometry. Figures 1 and 2 show calculated Θ–2Θ scans and time response curves of an AF-coupled [^{57}Fe(2.00 nm)/Cr(2.62 nm)]$_{20}$ multilayer (the scattering plane is perpendicular to the electric field vector of the SR). The magnetic structure of the multilayer is supposed to be collinear so that the directions of the hyperfine field **B** alternate across consecutive Cr layers. The total reflection peak (0th order Bragg reflection) and the structural Bragg peak (1st order Bragg reflection) show up in the time integral scans at the same value of Θ as in the prompt scan. If **B** is parallel or antiparallel to the wave vector **k** of the SR, AF superreflections ($1/2$th and $3/2$th order Bragg reflections) can be observed which are missing if **B** is perpendicular

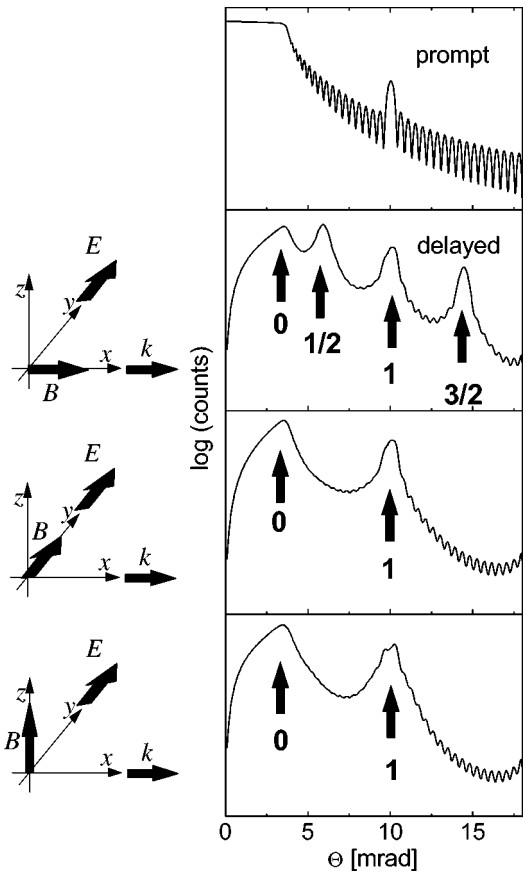

Figure 1. Calculated Θ–2Θ scans of an AF-coupled $[^{57}Fe(2.00\ nm)/Cr(2.62\ nm)]_{20}$ multilayer for three different directions of the hyperfine field **B** (the hyperfine field of the other sublattice is not shown). The scattering plane is perpendicular to the electric field vector E of the SR. The arrows indicate the Bragg reflections of different order.

to **k**. In fact, f only depends on the angle of **k** and **B** and so no AF cell doubling for f is possible if $\mathbf{k} \perp \mathbf{B}$. This is how time integral SMR can characterise the orientation of the AF sublattice magnetisation. The shape of the time response curves strongly depends on Θ. This is due to the fact that the phases of the waves scattered at different depth are shifted with respect to each other depending on Θ. The shape of the time response curves is most sensitive to the direction of **B** at electronically forbidden (half integer order) reflexes. If no anisotropy or finite stacking effects are present, the sublattice magnetisation of a collinear AF multilayer is expected to be aligned perpendicular to the magnetic field in low external fields. Therefore, in the above geometry strong AF reflections are expected in low fields which gradually disappear in increasing field when the sublattice magnetisations become parallel.

The way to thin film magnetic structure analysis with SMR has been opened by Toellner et al. who demonstrated the existence of pure nuclear reflections in an Fe/Cr

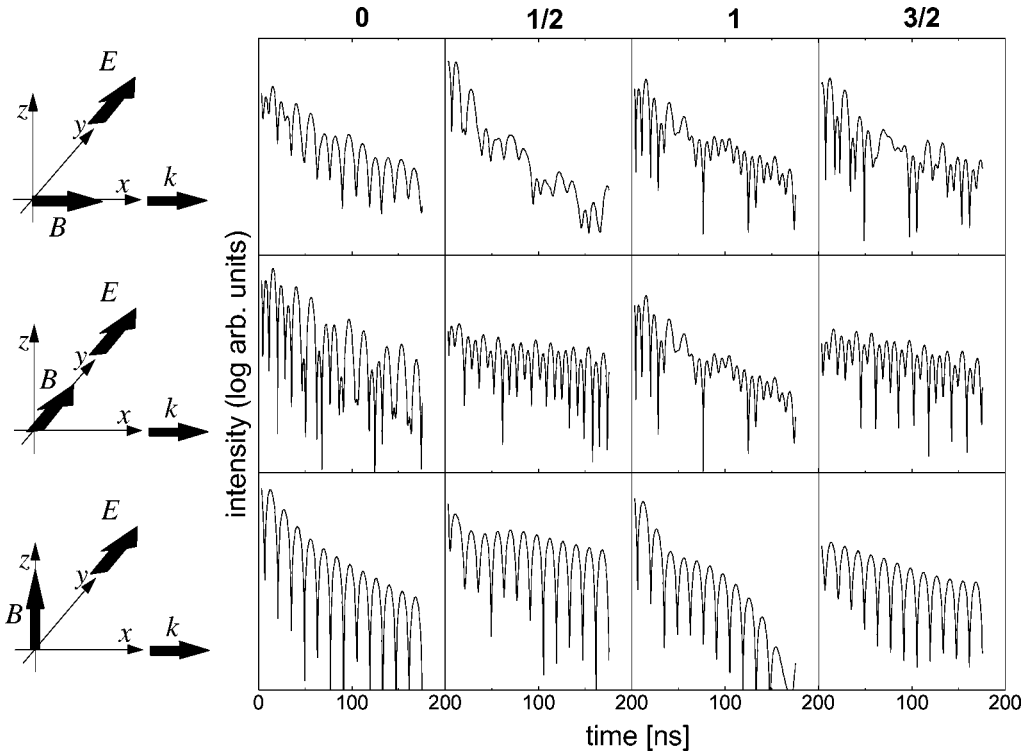

Figure 2. Calculated time response curves of an AF-coupled $[^{57}\mathrm{Fe}(2.00\ \mathrm{nm})/\mathrm{Cr}(2.62\ \mathrm{nm})]_{20}$ multilayer for three different directions of the hyperfine field **B** (the hyperfine field of the other sublattice is not shown). The scattering plane is perpendicular to the electric field vector E of the SR. The numbers indicate the order of the Bragg reflections.

multilayer [13]. The suppression of the AF reflection in increasing external magnetic field was first demonstrated on a Zerodur/$[^{57}\mathrm{Fe}(2.55\ \mathrm{nm})/^{\mathrm{nat}}\mathrm{FeSi}(1.5\ \mathrm{nm})]_{10}$ multilayer [28]. Similar behaviour is shown for a MgO(100)/$[^{57}\mathrm{Fe}(1.43\ \mathrm{nm})/\mathrm{Cr}(3.06\ \mathrm{nm})]_{16}$ superlattice in figure 3.

Time response curves of Zerodur/$[^{57}\mathrm{Fe}(2.55\ \mathrm{nm})/^{\mathrm{nat}}\mathrm{FeSi}(1.5\ \mathrm{nm})]_{10}$, especially those recorded at the AF reflection, are indicative of a 62° misalignment of the sublattice magnetisations with respect to the perpendicular-to-the-field alignment. This phenomenon was attributed to a depth-dependent bilinear coupling [28,29]. Having revisited the problem it was shown, that *finiteness* of the multilayer stacking [30] alone leads to a global twist of the sublattice magnetisations in small external fields so that an upper uncompensated finite AF-coupled block and a single uncoupled FM layer on the substrate can even better describe the measured time response curves [31].

SMR is very efficient in studying the effects of magnetocrystalline anisotropy. Step-induced canting of the Fe magnetisation in Fe/Ag superlattices has recently been observed [32]. Uniaxial in-plane anisotropy may lead to surface spin-flop [33] while an irreversible bulk spin-flop is expected in case of bi-axial in-plane anisotropy a phenom-

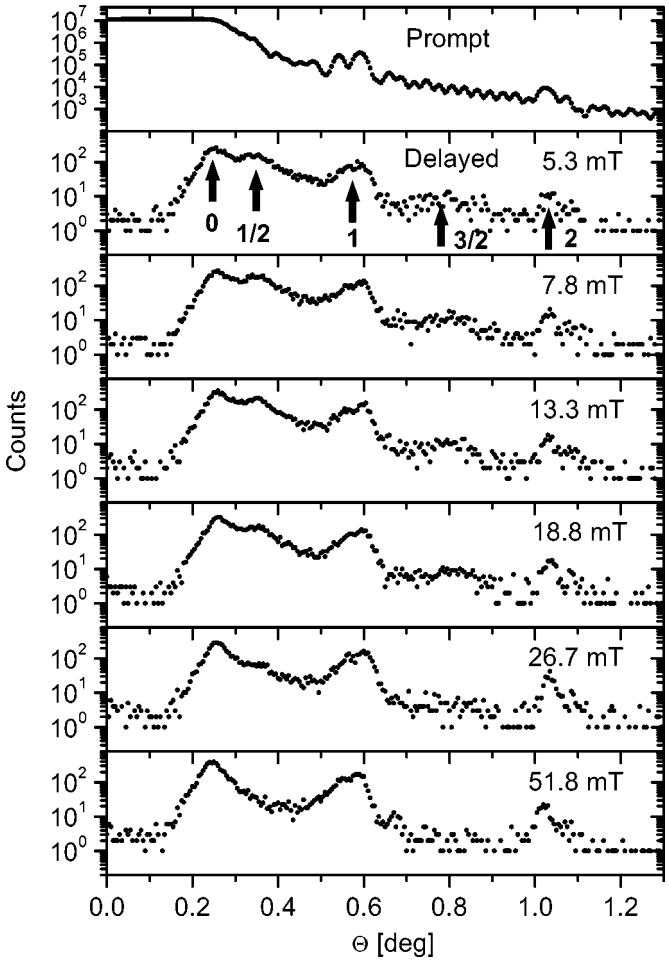

Figure 3. Θ–2Θ scans measured on a MgO(1 0 0)/[^{57}Fe(1.43 nm)/Cr(3.06 nm)]$_{16}$ superlattice in various external magnetic fields. The AF reflections are suppressed as the field increases. The arrows indicate the Bragg reflections of different order.

enon recently observed in a MgO(1 0 0)/[^{57}Fe(2.5 nm)/Cr(1.4 nm)]$_{10}$ superlattice [34]. An out-of-plane Fe magnetisation was observed using the ^{57}Fe marker layer technique in the inner region of 7 monolayers fcc Fe-sandwiched between FM fcc Co layers stabilised by Cu. The outer regions show an FM coupling to Co and an increased hyperfine magnetic field [35].

5. Conclusions

In conclusion we have summarised the principles and some recent applications of SMR, a method yielding both structural (chemical and magnetic) and depth infor-

mation. SMR is extremely suitable for studying details of the magnetic structure of thin films and multilayers.

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