Angular dependence, blackness and polarization effects in integral conversion electron Mössbauer spectroscopy

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General expressions of the electron yield in $^{57}$Fe integral conversion electron Mössbauer spectroscopy were derived depending on the angle of incidence of the $\gamma$-rays, on the source polarization and on the isotopic abundance of the source and the absorber (blackness effects) using an exponential escape function of the electrons originating from all Mössbauer-resonance-related processes. The present approach provides a firm theoretical basis to determine the alignment and direction of magnetization in the absorber. The intensity formulae were justified by least squares fits of $\alpha$–$^{57}$Fe spectral intensities measured in linearly and elliptically polarized source and absorber geometries. The fits reproduce the experimentally set angles with high accuracy. Limits of the current approach and its relation to other, less complete treatments in the literature are discussed.

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I. INTRODUCTION

Mössbauer spectroscopy has been very successful in determination of the alignment and direction of magnetization of buried layers of Fe, the line intensities being dependent on the angle between the propagation direction of the X-ray beam from the source and the hyperfine field. Using linearly polarized source we may determine alignment, and, using circularly polarized radiation, also the sign of the magnetization component parallel to the propagation direction. For this reason polarized Mössbauer sources were prepared. The so called filter technique provide almost single line circularly polarized radiation, resulting in relatively simple spectra, but uses only a small part of the source intensity, application of a split multi-line source, however, results in more complex spectra, but provides higher intensity.

Due to the relatively shallow escape depth of the electrons, conversion electron Mössbauer spectroscopy (CEMS) is used for surface and thin film investigations. Not even in the case of homogeneous magnetization are conventional CEMS experiments (in which the $\gamma$-rays are perpendicularly incident on the sample plane) are appropriate to determine an arbitrary direction of magnetization. The relative intensities do not depend on the alignment of the magnetization within the sample plane, a frequent case with thin films, in which the shape anisotropy constraints the magnetization in the sample plane.

The theoretical description of transmission Mössbauer spectroscopy is available for quite general cases. However, in a CEMS experiment, the electron transport from the Mössbauer nucleus to the sample surface is rather complex which renders the calculation of the electron yield difficult. There exist semi-empirical formulae (based on Monte-Carlo simulations) providing the probability of the escape of an electron emitted with a given energy at a given depth below the surface, which can be built into the numerical algorithms, but seemingly do not allow analytical solutions, which would provide more thorough insight. As a result, most spectroscopists, when evaluating CEM spectra, neglect the use of such escape functions and assume that the sample is very thin. In case of perpendicular incidence and non-enriched samples, this may be justified, unlike for slanted incidence and for absorbers enriched in the Mössbauer-active isotope, when polarization- and angle-dependent blackness effects are appreciable. Even from otherwise quite general treatments of multilayer structures, e.g. discussion of polarization and blackness effects are missing. Papers that qualitatively elaborate such effects e.g. leave room for improvement in regard of generality and mathematical thoroughness. The opposite extreme is the grazing incidence (below 1°) CEMS spectroscopy, for which the theory is well established, but, as we shall see, at such angles, a different approximation of the theory applies. Moreover, experimental feasibility of grazing incidence CEMS using radioactive sources is quite limited due to solid angle reasons, which enables the use of less than a fraction of $\approx 10^{-5}$ of the source intensity.

In the last decade several instruments and methods were devised in our laboratory for CEM polarimetry at arbitrary (except grazing) angle of incidence and linear as well as elliptical polarization. The analysis of the measured spectra with these setups lead us to recognize, that treatment of the blackness effect and polarization of the radiation
in the literature for conversion electron Mössbauer spectroscopy at low angle of incidence and of enriched samples in the resonant isotope is not satisfactory. The present paper tries to fill this gap. Here we derive the CEM spectral intensity in case of polarized (Mössbauer) sources, when the γ-rays fall on a homogeneously magnetized sample at arbitrary (except for grazing) angle of incidence. We will show under what circumstances the escape function should be used and be neglected and the absorber consequently be considered thick and thin, respectively.

II. CEM SPECTRA WITH THE POLARIZED \( \gamma \)-RAY INCIDENT ON THE ABSORBER AT AN ARBITRARY ANGLE

In the following, concerning nuclear resonance we will follow the theoretical considerations and formalism used in\(^\text{12}\). Here the case of a single, homogeneous layer will be considered. Generalization for multilayers is straightforward.

The number of detected electrons created by a photon beam of energy \( E \) may be written as:

\[
N_{\text{CE}}(D, E) \propto \int_0^D \text{Tr} \left( \overline{\rho}(z, E)\overline{N}(z)\overline{\sigma}^{M}(z, E) \right) W(z) \, dz, \tag{1}
\]

where \( D \) is the sample thickness, \( \overline{\rho}(z) \) is the density matrix of the photons at a depth of \( z \), \( N \) is the density of the scattering centres, \( \overline{\sigma}^{M} \) is the part of the absorption cross section tensor belonging to Mössbauer effect, \( W(z) \) is the probability of a conversion electron be emitted following the absorption of an incoming photon at depth \( z \) and that it reaches the surface of the sample. In the case of differential CEMS (DCEMS) one should write \( W(z, E_e) \), where \( E_e \) is the energy of the emitted electron, and \( W(z, E_e) \) gives the escape probability of an electron being emitted with energy \( E_e \). For brevity, unless it may lead to misunderstanding, we will omit the energy dependence in the formulae.

The transfer operator \( \overline{T}(z) \) defined by

\[
|\psi(z)\rangle = \overline{T}(z) |\psi(0)\rangle \tag{2}
\]

determines the wave at depth \( z \) from the wave \( |\psi(z = 0)\rangle \) at the surface. Accordingly, for the density matrix we get

\[
\overline{\rho}(z) = \overline{T}(z)\overline{\rho}(0)\overline{T}^\dagger(z), \tag{3}
\]

where \( \overline{T}^\dagger \) denotes the hermitian adjoint operator. After some permutation and substitution we may write

\[
N_{\text{CE}}(D, E) \propto \text{Tr} \left( \overline{T}(0, E)\overline{T}(D, E) \right), \quad \text{where}
\]

\[
\overline{J}(D, E) = \int_0^D \overline{T}(z, E)\overline{\sigma}^{M}(z, E)\overline{T}(z, E)\overline{N}(z)W(z) \, dz. \tag{4}
\]

For a single homogeneous layer \( \overline{T}(z) \) has the following form\(^\text{12}\):

\[
\overline{T}(z) = \sinh \left( ik_0\overline{m}z \sin \vartheta \right) \overline{m}^{-1} (I - \overline{R}) + \cosh \left( ik_0\overline{m}z \sin \vartheta \right) (I + \overline{R}), \tag{5}
\]

where \( k_0 \) is the wave number in vacuum, \( \vartheta \) is the glancing angle of the incoming X-ray beam, \( I \) denotes the unity matrix, \( |\psi_{\text{Reflected}}(0)\rangle = \overline{R}|\psi(0)\rangle \) is the reflected wave (with \( \overline{R} \) being the reflectivity tensor) at the surface of the sample and we introduced the tensor quantity \( \overline{m} \) with the definition

\[
\overline{m} = \sqrt{I + \frac{1}{\sin^2 \vartheta} \overline{X}}, \tag{6}
\]

where \( \overline{X} \) is the dielectric susceptibility tensor. For multilayers the resulting transfer matrix is the product of single layer \( \overline{T} \) matrices of form \(^\text{13}\). For large angles of incidence, \( \vartheta \) the reflected beam for X-rays is weak, i.e. \( \overline{R} \) is small as compared to the unity matrix. Consequently

\[
\overline{T}(z) = \sinh \left( ik_0\overline{m}z \sin \vartheta \right) \overline{m}^{-1} + \cosh \left( ik_0\overline{m}z \sin \vartheta \right). \tag{7}
\]
For nearly perpendicular incidence (θ ≈ π/2) the matrix \( \overline{m} \) will be the index of refraction matrix \( \overline{r} = \sqrt{1 + \chi} \approx 1 + \frac{1}{2} \chi \). Since the dielectric susceptibility for X-rays is always small, the inverse of the index of refraction matrix is also close to the unity matrix, \( \overline{m}^{-1} \approx \overline{r} \), which leads to the approximation given in (8), namely:

\[
\overline{r}(z) = e^{i k_0 m z} \approx e^{i k_0 z} e^{\frac{i}{2} k_0 \chi z}.
\]  

(8)

For small angles of incidence approximation \( \chi \) is not valid. We may expand, however, \( \overline{m} \) and \( \overline{m}^{-1} \) into Taylor-series

\[
\overline{m} = \overline{r} + \frac{1}{2} \sin^2 \theta \chi - \frac{1}{8} \sin^4 \theta \chi^2 + \ldots
\]

\[
\overline{m}^{-1} = \overline{r} - \frac{1}{2} \sin^2 \theta \chi + \frac{3}{8} \sin^4 \theta \chi^2 + \ldots
\]

(9)

In first order we get

\[
\overline{r}(z) \approx e^{i k_0 \sin \theta} e^{\frac{i}{2} k_0 \sin^2 \theta} + \sinh \left( i k_0 \sin \theta \right) \left( \overline{m}^{-1} - \overline{r} \right).
\]

Higher order terms are negligible if the eigenvalues of \( \overline{r} \) fulfill the condition \( |\chi| < \sin^2 \theta \). For \( ^{57}\text{Fe} \) on resonance (\(|\chi| \lesssim 0.01\)), therefore the first order approximation is valid down to about \( \theta \approx 4 - 5^\circ \). Unless for very small angles, \( \overline{m} \approx \overline{r} \) and therefore \( \overline{m}^{-1} \approx \overline{r} \). Since in the following we will not consider grazing angles, we will neglect the second term \( \sinh(\ldots)(\overline{m}^{-1} - \overline{r}) \) on the right side of (10).

The absorption cross-section tensor for a single atom (molecule, etc.) can be defined as \( ^{8,15} \)

\[
\overline{\sigma}(z) = -\frac{i k_0}{N(z)} \left( \overline{r}(z) - \overline{r}^t(z) \right) \approx -\frac{i k_0}{2N(z)} \left( \chi(z) - \overline{\chi}^t(z) \right).
\]

(11)

Near the nuclear resonance, the electronic contribution to the susceptibility is negligible compared to the nuclear one, therefore we may write:

\[
\overline{\sigma}^M(z) \approx -\frac{i k_0}{2N(z)} \left( \chi(z) - \overline{\chi}^t(z) \right).
\]

(12)

Substituting (12) and the first term of (10) into (4), the CEMS intensity matrix \( J \) for a homogeneous layer becomes:

\[
J(D) = - \int_0^D e^{-i \frac{1}{2} k_0 \chi z} \sin \theta \frac{i k_0}{2} \left( \chi(z) - \overline{\chi}^t(z) \right) e^{i \frac{1}{2} k_0 \chi z} W(z) dz
\]

\[
= -\sin \theta \int_0^D W(z) \partial \partial z \left( e^{-i \frac{1}{2} k_0 \chi z} \right) e^{i \frac{1}{2} k_0 \chi z} dz.
\]

(13)

Introducing the \( s = i \frac{1}{2} k_0 z \) notation and using the Baker- Campbell- Hausdorff formula, the product of the two matrix exponentials can be written as

\[
e^{-s \overline{\chi}^t} e^{\overline{s} \overline{\chi}} = e^{\overline{s}(\overline{\chi} - \overline{\chi}^t) - \frac{s}{2} \overline{\chi}^t \cdot \overline{\chi} + \frac{1}{2!} s^2 \overline{[\overline{\chi}, \overline{\chi}^t]} + \frac{1}{3!} s^3 \overline{[\overline{\chi}, \overline{\chi}^t], \overline{[\overline{\chi}, \overline{\chi}]}] + \ldots}.
\]

(14)

For the M1 nuclear transitions, like in \( ^{57}\text{Fe} \), for almost all practical cases the \( \overline{[\overline{\chi}, \overline{\chi}^t]} = 0 \) condition is fulfilled with a good approximation. Otherwise one has to estimate the contribution of higher order commutator terms in (14). In the following we will assume that \( \overline{[\overline{\chi}, \overline{\chi}^t]} = 0 \) is fulfilled, therefore we have

\[
J(D, E) = -\sin \theta \int_0^D W(z) \partial \partial z \left( e^{-N \overline{\sigma}^M(z) \sin \theta \overline{\overline{s}}} \right) dz.
\]

(15)

Not regarding the number of approximations we had to make in order to obtain eq. (15), the result may seem to be commonsensical: the \( \sin \theta \) term in front of the integral simply takes the reduced cross section of a slanted sample into account. The number of resonantly absorbed photons at depth \( z \) is given by the derivative term inside the integral. For small angles the photons travel a longer path \( z / \sin \theta \) to reach depth \( z \) and therefore they get absorbed more likely near the surface as compared to the case of perpendicular incidence. However, one should keep in mind, that eq. (15) is only valid for not too small angles, when the linear approximation in eq. (19) is valid.
Until now we did not take an essential feature of the Mössbauer effect into account, namely the moving source. The density matrix of the γ-ray beam emitted by the Mössbauer source that moves with velocity \( v \) can be written as

\[
\overline{\rho}(z = 0, E, v) = \sum_i \overline{\rho}_i^{\text{sol}} \mathcal{L}_i(E, v) = \sum_i \overline{\rho}_i^{\text{sol}} \frac{\Gamma}{2\pi} \frac{1}{(E - E_i + \frac{\Gamma}{2})^2 + \frac{\Gamma^2}{4}},
\]

where \( \overline{\rho}_i^{\text{sol}} \) characterizes the intensity ratio and polarization of the \( i \)-th line at position \( E_i \) in the energy spectrum, \( \mathcal{L}_i(E, v) \) is the (Lorentzian) shape function of the \( i \)-th line, \( \Gamma \) is the line width and \( c \) is the speed of light. As a function of the Mössbauer drive velocity the measured CEMS intensity is

\[
I_{\text{CEMS}}(D, v) = f_S \mathcal{I} \sum_i \text{Tr} \left( \overline{\rho}_i^{\text{sol}} \int \mathcal{L}_i(E, v) \overline{\rho}(D, E) \, dE \right),
\]

where \( f_S \) is Mössbauer-Lamb factor of the source and \( \mathcal{I} \) is the total intensity of the source incident on the sample.

In order to calculate the CEMS spectra the knowledge of the electron escape function \( W(z) \) is necessary. Liljequist derived semi-empirical formulae based on his Monte-Carlo simulations\(^{10,11}\). Instead of depth, he uses the equivalent depth in iron defined as

\[
t = \frac{\rho}{\rho_{Fe}} z,
\]

where \( \rho \) is the density of the sample and \( \rho_{Fe} \) the density of natural iron at ambient conditions. For a homogeneous layer, the escape function can be well approximated with an exponential,

\[
W(z) = W_0 e^{-\frac{t(z)}{\tau}} = W_0 e^{-z \frac{\rho}{\rho_{Fe}} \tau} = W_0 e^{-\frac{z}{\tau_{Fe}}},
\]

where \( W_0 \) expressing the probability of emission of a conversion electron after photon absorption at an iron-equivalent depth of \( \tau \approx 540 \text{ FeÅ} \) to reach the surface of the sample. The more general escape function are derived in appendix \( A \). The exponential approximation is advantageous in the parameter fitting routines, since the code based on this is by two orders of magnitude faster than the one based on exact formulae, while providing a good approximation. Moreover, the exponential approximation is easier to handle analytically in some special cases. Indeed, with \( [15] \) we have

\[
I_{\text{CEMS}}(D, v) = a \sum_i \text{Tr} \left[ \overline{\rho}_i^{\text{sol}} \int \mathcal{L}_i(E, v) \zeta N \overline{\sigma}^M(E) \sin \vartheta \right.
\]

\[
\cdot \left( \zeta N \overline{\sigma}^M(E) + \overline{I} \sin \vartheta \right)^{-1} \left( I - e^{-D \left( \frac{N \sigma(E)}{\sin \vartheta} + \frac{1}{\zeta} \right)} \right) \, dE \left],
\]

where \( a = W_0 f_S \mathcal{I} \).

First let us consider the unpolarized case. Applying the formula of effective thickness as \( t = \frac{\rho}{\rho_{Fe}} D = \frac{N}{\rho_{Fe}} D \), and similarly \( \tau = \frac{N}{\rho_{Fe}} \zeta \) and the absorption coefficient (for natural iron at ambient conditions) as \( \alpha = \frac{N}{\rho_{Fe}} \sigma \), the exponent in eq. \( [20] \) can be transformed as follows:

\[
-D \left( \frac{N \sigma(E)}{\sin \vartheta} + \frac{1}{\zeta} \right) = -\alpha t \tau \alpha + \sin \vartheta
\]

\[
= -\alpha t \frac{\tau \alpha + \sin \vartheta}{\tau \alpha \sin \vartheta}.
\]

It may be convenient to interpret the quantity

\[
t'(E, \vartheta) = t \frac{\tau \alpha(E) + \sin \vartheta}{\tau \alpha(E) \sin \vartheta}
\]

as a corrected effective thickness\(^{10}\).

In the polarized case for small angles (\( \sin \vartheta \approx 0 \)) we have \( \zeta N \overline{\sigma}^M(E) \left( \zeta N \overline{\sigma}^M(E) + \overline{I} \sin \vartheta \right)^{-1} \approx \overline{I} \) and therefore

\[
I_{\text{CEMS}}(D, v) = a \sin \vartheta \left[ \overline{I} - \sum_i \text{Tr} \left( \overline{\rho}_i^{\text{sol}} \int \mathcal{L}_i(E, v) e^{-N \overline{\sigma}^M(E) \overline{I} \sin \vartheta} \, dE \right) \right],
\]
which formally corresponds to the thick sample case in absorption Mössbauer spectroscopy, as it was conjectured in. We should not forget, however, that beside the above mentioned constraints in deriving (15) and (20), this approximation is not valid for grazing angles, when the reflections due to the electronic contribution to the susceptibility are not negligible.

At nearly perpendicular incidence, when \( \sin \vartheta \approx 1 \) we expand the exponent in Taylor series up to second order:

\[
\left( I - e^{-D(N \sigma^M(E) + \frac{1}{\zeta})} \right) \approx D \left( N \sigma^M(E) + \frac{1}{\zeta} \right) + \frac{1}{2} D^2 \left( N \sigma^M_i(E) + \frac{1}{\zeta} \right)^2 + \ldots
\]  

(24)

In case the second term is negligible compared to the first one, i.e.

\[
\frac{1}{2} D^2 \left( N \sigma^M_i(E) + \frac{1}{\zeta} \right)^2 \ll D \left( N \sigma^M_i(E) + \frac{1}{\zeta} \right),
\]

(25)

where \( \sigma_i \) is the \( i \)-th eigenvalue of \( \sigma \), the intensity expression

\[
I_{CEMS}(D, v) = a D \sum_i \text{Tr} \left( \rho\text{pol}_i \int N \sigma^M_i(E) \mathcal{L}_i(E, v) dE \right),
\]

(26)

formally corresponds to the thin sample case in Mössbauer spectroscopy, as discussed by.

From the above, the condition of the thin absorber limit in perpendicular incidence is

\[
D \ll \frac{2}{N \sigma^M_{\text{max}} + \frac{1}{\zeta}}.
\]

(27)

where \( \sigma^M_{\text{max}} \) is the maximal eigenvalue of the absorption cross section tensor.

This condition means, that \( D \) is the characteristic information depth of the surface of the sample for CEM spectroscopy; no significant number of electrons will reach the sample surface from deeper layers of the sample and/or the photons will not reach a larger perpendicular depth in the sample.

For multilayers we may follow the same steps, the main difference and question will be the electron escape function, which may become quite complex. The conversion electrons emitted from atoms in different layers should be summed up, taking into account the proper escape function(s), which probably may be determined as some good examples of show, but this is out of the scope of this paper.

### III. THICK SOURCE

Blackness effects in Mössbauer spectroscopy are not limited to the absorber. Due to the possible self-absorption of the emitted photons, additional broadening may arise or, in case of a split multi-line source, the relative line intensities of the emitted lines of the Mössbauer source may considerably be modified, provided that \( \gamma \)-emission occurs relatively deep below the surface of the source and the substrate of the source contains large amount of the resonant isotope. In the commonly used single line sources these effects are avoided by letting the resonant isotope diffuse only into a shallow surface layer of the substrate. When using such sources in perpendicular emission geometry, blackness effect rarely occurs. However, the relative intensities of a split multiline source of \( \alpha \)-Fe substrate at slanted exit of the \( \gamma \)-rays, which is studied experimentally and discussed below are considerably modified by the blackness effects. In the following we discuss the case of the thick source.

Following the same logic as in deriving (3) the density matrix of the photons emitted by the Mössbauer source may be written as

\[
\bar{\rho}(E) \propto \int_0^{D_s} \mathcal{P}^D(D_s - z, E) \rho^M(E) \mathcal{P}^D(D_s - z, E) N_s(z) dz,
\]

(28)

where \( D_s \) is the physical thickness of the substrate of the source and \( N_s(z) \) is the number of the nuclei emitting the resonant photons at depth \( z \). The Mössbauer sources are commonly prepared by introducing the radioactive atoms into the host material by diffusion. Therefore it is correct to assume that \( N_s(z) \) follows a diffusion profile, i.e. an expression containing an error function.
IV. EXPERIMENTS AND THEORY

CEM polarimetric measurements were performed using α-iron foils, a natural Fe foil of 15 μm thickness as the substrate of the $^{57}$Co(α-Fe) source and a $^{57}$Fe foil of 20 μm thickness as the sample. A detailed description of these experiments was published in $^{10}$. The experimental spectra are the same here as in $^{10}$, but the spectra are evaluated using a different model function. The emphasis here is being on the verification of the theory derived in the present paper.

Linear polarimetric measurements were performed in perpendicular incidence geometry, both the source and sample was magnetized perpendicular to the propagation direction. The results of such two measurements are shown in Fig. 1 where the magnetic fields on the source and sample are parallel and perpendicular to each other.

Elliptical (close to circular) polarimetric measurements were performed with a slanted source and a slanted sample, both magnetized in their planes the magnetization vectors and the wave vector laying in the same plane. The sample planes enclosed $\vartheta = 10^\circ$ (source) and $\vartheta = 5^\circ$ (sample) with the propagation direction. The results of such two CEM experiments are shown in Fig. 2 where the external magnetic fields (230 mT) on the source and sample are parallel and antiparallel to each other.

Having implemented the theory outlined in the former sections, measured spectra were fitted using the general fitting program FitSuite developed earlier $^{20}$. The positions and intensities of the Mössbauer lines (i.e. the contribution of the resonant absorption to $\mathbf{\sigma}(E)$) were calculated solving the eigenvalue problem belonging to the corresponding hyperfine Hamiltonian. The theory described in $^{21}$ and implemented in EFFI $^{22}$ were adopted and modified to include
the theoretical considerations presented above, namely eq. (20).

TABLE I: Essential fitted parameters, linear polarimetry. \( \vartheta \) and \( \varphi \) are the angles enclosed by the hyperfine field and the \( z \) axis (propagation direction of the X-rays). \( \varphi \) are the angles are the azimuthal angles measured around the \( z \) axis from the \( x \) axis being in plane of incidence.

| Parameter      | Fitted    | Expected |
|----------------|-----------|----------|
| \( |B| \)          | 33.04 T ± 0.02 T | –        |
| \( \vartheta_{\text{source}} \) | 86.0° ± 0.9° | 90°      |
| \( \varphi_{\text{source}} \) | 0° (fixed) |          |
| Parallel case: |           |          |
| \( \vartheta_{\text{sample}} \) | 108.9° ± 0.7° | 90°      |
| \( \varphi_{\text{sample}} \) | 4.2° ± 1.7° | 0°       |
| Perpendicular case: | | |
| \( \vartheta_{\text{sample}} \) | 90.1° ± 4.1° | 90°      |
| \( \varphi_{\text{sample}} \) | 91.2° ± 4.8° | 90°      |

In linear polarimetric case the X-ray beam is nearly perpendicular to the source and sample planes, therefore no thickness and angle dependence is expected according to (26). The magnitude and orientations of the hyperfine fields (see Table I) were found to agree quite well with the experimental values, set by the direction of the external magnetic fields. The fits and their \( \chi^2 \) statistics are acceptable. In agreement with this according to our simulations change of the thickness give rise to intensity change, but the shape of the spectra remains unchanged.

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TABLE II: Essential fitted parameters, circular polarimetry. \( \vartheta \)... are defined in the same way as in Table I.

| Parameter            | Fitted      | Expected |
|----------------------|-------------|----------|
| Source slant angle   | 6.53° ± 0.03° | 10°      |
| Sample slant angle   | 4.936° ± 0.003° | 5°       |
| \( |B| \)                | 32.966 T ± 0.0004 T | –        |
| \( \vartheta_{\text{source}} \) | 8.2° ± 0.6° | 10°      |
| \( \varphi_{\text{source}} \) | 0.3° ± 0.08° | 0°       |
| Parallel case:       |             |          |
| \( \vartheta_{\text{sample}} \) | 13.8° ± 0.3° | 5°       |
| \( \varphi_{\text{sample}} \) | 0.16° ± 0.09° | 0°       |
| Antiparallel case:   |             |          |
| \( \vartheta_{\text{sample}} \) | 193.9° ± 0.2° | 185°     |
| \( \varphi_{\text{sample}} \) | 0.2° ± 0.36° | 0°       |

This is not the case for circular polarimetric experiments, where the blackness effect has an important role and therefore the intensity ratios strongly depend on the thickness and slant angle, as it can be seen in Figs. 3A. Without this effect, the intensity ratios of the spectra of Fig. 2 could not be explained either. Although the features of the measured spectra are reproduced relatively well in this case, in the antiparallel case the figure of merit of the fit worse, and the fitted hyperfine field orientations (Table II) slightly differ from the actual experimental values. These discrepancies are probably due to fact, that the reorientation by the small external field was not completely successfull.

In fitting the circular polarimetric spectra at an angle of incidence of \( \vartheta = 5° \), when the perpendicular information depth \( D \) is much lower, we had to take into account an additional singlet site with isomer shift \( (0.11 ± 0.02) \text{ mm·s}^{-1} \), effective thickness \( (3000 ± 100) \text{ Fe}^{57} \text{Å} \) with Lorentzian broadening of \( (5.8 ± 0.6) \text{Γ}_{\text{nat}} \) (%nat = 0.097 mm·s\(^{-1}\)) is the width of the natural line broadening) which is most probably due to the iron oxide on the surface of the absorber. In case of linear polarimetric measurements this component did not appear, since in pendicular incidence its contribution to the measured spectrum was much weaker.

V. SUMMARY

We have found that the CEM spectra may be regarded, as Mössbauer spectra:
FIG. 3: Demonstration of blackness effect because of thickness dependence. Results of circular polarimetric simulations with antiparallel source and sample magnetizations for different sample thicknesses. Other parameters are the same as in the corresponding fitted spectrum plotted in Fig. 2.

- of a thick sample, if the X-rays coming from the source fall on the sample under small angle, which is still greater than what we usually call grazing incidence;
- of a thin sample, if the X-rays coming from the source fall on the sample perpendicularly and the condition (27) is fulfilled.

These statements were verified for electron escape functions of a single exponential function, in cases where this approximation is inappropriate these statements may not be valid either. Furthermore, we may not regard the CEM spectra neither as a thin nor a thick Mössbauer spectrum for angles between the two limiting cases.

We fitted the experimental results according to the model based on considerations of this paper using the program FitSuite.

APPENDIX A: ELECTRON ESCAPE FUNCTION

The electrons are emitted because of several processes after irradiation by X-ray, which all should be taken into account in the escape functions. According to the electron escape probability from depth $z$ can be written as:

$$W(z) = \sum_i c_i W_i(z), \quad (A1)$$

where $c_i$ gives the contribution of the $i$-th process, for which the escape function is $W_i(z)$. The escape function, using as argument the equivalent iron depth $t$ instead of $z$ (definition is given in (18) ) for K, L-M and Auger electrons, has the form:

$$W_i \left( x = \frac{t}{t_{Bethe}} \right) = \begin{cases} 0.74 - 2.7x + 2.5x^2 & \text{if } 0 \leq x \leq 0.55 \\ 0 & \text{otherwise} \end{cases}, \quad (A2)$$
FIG. 4: Demonstration of blackness effect because of angular dependence. Results of circular polarimetric simulations with antiparallel source and sample magnetizations for 40 nm thick samples slanted in different angles. Other parameters are the same as in the corresponding fitted spectrum plotted in Fig. 2.

where $r_{\text{Bethe}}^i$ is the Bethe range (which is on average the total distance, which an electron travels until it is stopped down). Alternative formulae for K, L-M and Auger electrons based on Gaussian functions are available in\textsuperscript{18,23}:

$$W(t, E_e) = A(Z, E_e) e^{-\frac{t}{r(Z, E_e)}} e^{-\left(\frac{1.9 R(Z, E_e)}{t}\right)^2},$$

(A3)

where $Z$ is the atomic number and $E_e$ the energy with which the electron was emitted from the atom. For further details regarding the functions $A(Z, E_e)$ and $R(Z, E_e)$ see\textsuperscript{18}. To get the alternative $W_i(t)$ functions of (A2) we have to integrate $W(t, E_e)$ according to the electron energies in the corresponding ranges too. Therefore (A3) is more appropriate for DCEMS problems, for which (A2) is completely inappropriate.

For photo-electrons the escape function has the form:

$$W_i(t) = \frac{U_{\infty i}}{r_i^{\text{eff}}} \left\{ \begin{array}{ll}
1 - 0.5 \left[ E_2(\mu_i t) - E_2(\mu_i (r_i^{\text{eff}} - t)) \right] & \text{if } 0 \leq t \leq r_i^{\text{eff}} \\
0.5 \left[ E_2(\mu_i (t - r_i^{\text{eff}})) - E_2(\mu_i t) \right] & \text{if } r_i^{\text{eff}} < t
\end{array} \right.,$$

(A4)

where $E_2(x)$ is the second order exponential integral function defined by $E_2(x) = \int_1^\infty \frac{e^{-xh}}{h^2} dh = \int_0^1 e^{-\frac{x}{1+y^2}} dy$, $r_i^{\text{eff}}$ is the so called effective range, $\mu_i$ is absorption coefficient for the conversion photons, $U_{\infty i}$ is a normalization constant.

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