EFFINO

H. Spiering[1], L. Deák,[2] and L. Bottyán[2]
[1]Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität Mainz, Staudinger Weg 9, D-55099 Mainz, Germany
[2]KFKI Research Institute for Particle and Nuclear Physics, P.O.B. 49, H-1525 Budapest, Hungary

Abstract

The program EFFINO (Environment For FItting Nuclear Optics) evaluates Mössbauer absorption and time spectra both in nuclear forward scattering and in grazing incidence reflection geometry. Time-integral prompt and delayed angular scan spectra are also treated. The time spectra are calculated by Fourier transformation from frequency to time domain. The electric quadrupole and magnetic dipole fields at the nuclear sites are considered static at present. The specimen in both forward scattering and grazing incidence is assumed to be a multilayer, with individual thickness and interface roughness (the latter only for the grazing incidence case at present) and electronic index of refraction. Up to eight different layers plus eight repetition periods of those layers are treated. Each layer may contain zero to eight nuclear sites (zero in all layers being prompt x-ray reflectivity case), having their own effective thickness or (for grazing incidence) their own complex nuclear index of refraction. From the forward scattering amplitude, a differential 4x4 propagation matrix is constructed for each layer. Several experimental spectra of the same or different type(s) can be fitted simultaneously. Correlations between parameters of the same or of different spectra can be introduced.

1 Introduction

The theory of the Mössbauer absorption of γ radiation in the forward scattering geometry was described by Blume and Kistner [1] and successfully applied for the calculation of absorption spectra of single crystals [2] as well as for powder samples polarized in external magnetic fields [3]. They used a complex 2x2 index of refraction matrix n, corresponding to the two independent states of polarization. n was expressed by the coherent forward scattering amplitude f. Grazing incidence Mössbauer spectra were calculated by Andreeva et al. in several papers [4, 5, 6, 7, 8]. They started from the nuclear current density expression of the susceptibility tensor χ given by Afanas'ev and Kagan [9] and used the covariant formalism of anisotropic optics introduced by Federov [11] and applied for stratified media by Borzdov *et. al.* [10]. Deák *et al.* clarified the conditions under which the nuclear susceptibility tensor can be expressed in terms of the forward scattering amplitude and brought Andreeva's results into a closed reflectivity formula[18]. As recently shown [14], the general description of specular reflection of grazing incidence Mössbauer radiation by the dynamical theory of Mössbauer optics of Hannon and Trammell [12, 13] leads, after a unitary transformation, to the same 4x4 differential propagation matrix M as that of Deák *et al.*[18]. The calculation of the amplitudes of the reflected radiation in the energy domain has been reduced to the 2x2 block-matrix exponential expression such that the analytical solutions of Blume and Kistner could be used for time-effective numerical calculations [18]. Such mathematical expressions are implemented in the code of EFFINO.

The program EFFI has developed over the years in several steps from the Mössbauer fit program MOSFUN [19] which already used [3] the formalism of Blume and Kistner for the calculation of Mössbauer absorption spectra. The main concern was to make possible handling and fitting several data sets simultaneously whereby each data set (not necessarily a Mössbauer spectrum) may have its own 'theory', so that the program becomes an "environment" for parameter fitting. EFFINO (=*E*nvironment *F*or *FI*tting *N*uclear *O*ptics) is the implementation of *EFFI* for fitting energy and time-domain resonant nuclear (and electronic) scattering spectra in the two *N*uclear *O*ptical limits, i.e. in the forward scattering and in the grazing incidence geometry[24].

The spectrum parameters in EFFINO are determined by least squares fitting (Newton or gradient). Up to 16 spectra can be evaluated simultaneously. The matrix used for (linearly) correlating parameters and variables of a fit as first introduced by Kulcsár *et. al.*[20] has been generalized to products of parameters and can now be more flexibly used. The physical theories and the main part of organization are Fortran 77 code whereas the X-window subroutines are written in C-code [21]. The program was developed on PC's running LINUX system.

2 Theoretical aspects

Both in forward direction and in scattering geometry the sample is considered to consist of layers. Each layer is described by three parameters, the thickness and the real and imaginary part of the scalar electronic susceptibility χ at the nuclear transition energy. A layer may contain 0 to 8 inequivalent nuclear sites (zero in all layers being the prompt x-ray reflectivity case). If the hyperfine fields of sites are related to each other by symmetry operations (equivalent sites) an $n-$fold rotation axis normal to the layer, a twofold axis in the layer and the time inversion operator are provided for calculating the forward scattering amplitudes of the set of equivalent sites. (The time inversion operator is useful for magnetically ordered structures or samples in applied magnetic fields where the energy spectrum of the nuclear states at different sites is the same but the polarization of the states differs due to opposite hyperfine magnetic field directions.)

The minimum number of layers is one for synchrotron radiation and two for energy domain Mössbauer measurements, the first layer in the latter case representing a thin Mössbauer source (not taking self absorption into account). In grazing incidence scattering geometry, a single cover layer, n different 'sandwich' layers and a substrate layer is considered. A number of (or all) sandwich layers may repeat n_{repeat} times (periodic multilayer case). Typically the cover and substrate layers do not contain nuclear scatterers, but the program treats all types of layers the same way, except for the repetition period of the sandwich layers.

The Hamiltonian describing the physics at each site is the nuclear spin Hamiltonian of the nuclear ground and excited states with half integer spin (even spins have not been implemented yet) and a (presently) static magnetic dipole, electric monopole, and quadrupole field at the nucleus. Only magnetic dipole radiation is implemented at present.

In addition to the internal hyperfine field at the nuclei, an external magnetic field can be defined which is simply added to the internal fields. For conventional Mössbauer absorption, the external field at the source is independent of the field at the absorber.

The basic equation of the dynamical theory[16] describing scattering by a stratified specimen in the grazing incidence limit is Eq. A3 of Ref. [16]. With the following notations, $g_0 = k \sin\theta$ the component of the wave vector k normal to the surface, θ the angle of grazing incidence in the vacuum, $G = 4\pi N f/(2k\sin\theta)$, N the density of the scattering centers and f the 2×2 coherent forward scattering amplitude. The differential propagation[10, 18] (or scattering[16, 22]) matrix of layer l is given by a 4×4 complex matrix

$$M_l = \begin{pmatrix} I\sin\theta + \frac{\chi_l}{2\sin\theta} & \frac{\chi_l}{2\sin\theta} \\ -\frac{\chi_l}{2\sin\theta} & -I\sin\theta - \frac{\chi_l}{2\sin\theta} \end{pmatrix}, \tag{1}$$

where the complex susceptibility tensor $\chi_l = \frac{4\pi N_l}{k^2} f_l$ and the 2×2 unity matrix I were introduced.

Solely for computational efficiency reasons, now we apply to Eq. (1) a unitary transformation $M_l^{'} = C M_l C^{-1}$ with

$$C = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \tag{2}$$

to get the differential propagation matrix in the form

$$M_l^{'} = \begin{pmatrix} 0 & I\sin\theta + \frac{\chi_l}{\sin\theta} \\ I\sin\theta & 0 \end{pmatrix}. \tag{3}$$

from which for homogenous thin layer l of thickness d_l the characteristic matrix $L_l = \exp\left(ikd_l M_l^{'}\right)$ can be calculated in a closed form

$$L_l = \begin{pmatrix} \cosh(F_l) & \frac{1}{x_l} F_l \sinh(F_l) \\ x_l F_l^{-1} \sinh(F_l) & \cosh(F_l) \end{pmatrix}, \tag{4}$$

where $F_l = kd_l\sqrt{-\sin^2\theta - \chi_l}$ and $x_l = ikd_l\sin\theta$ [18]. For multilayers the total characteristic matrix is simply the matrix product of the layer characteristic matrices L_l, i.e. with $L = L_N \cdot \ldots \cdot L_2 L_1$ the reflectivity matrix reads

$$r = \left(L_{[11]} - L_{[12]} - L_{[21]} + L_{[22]}\right)^{-1} \left(L_{[11]} + L_{[12]} - L_{[21]} - L_{[22]}\right), \tag{5}$$

where $L_{[ij]}$ $(i,j = 1,2)$ are the 2×2 submatrices of the total characteristic matrix L [18].

To calculate L in Eq. (4), first we have to calculate the 2×2 square root matrix F. This can be made by using the identity

$$G^{1/2} = \frac{G + I\sqrt{\det G}}{\sqrt{Tr(G) + 2\sqrt{\det G}}}, \tag{6}$$

where G is 2×2 matrix. The sinh and cosh functions are calculated from their exp forms. The exponential of the 2×2 matrix G can be expressed by the scalar invariants of G [1], hence

$$\exp G = \exp(\frac{1}{2}Tr(G)) \left[\cos\sqrt{\det \bar{G}}I + \frac{\sin\sqrt{\det \bar{G}}}{\sqrt{\det \bar{G}}}\bar{G}\right], \qquad (7)$$

where $\bar{G} = G - 12ITr(G)$.

To calculate the characteristic matrix of a substrate layer, we have to find the $d \to \infty$ limit of L. From Eqs. (5) and (7) follows , that the corresponding limes is given by

$$L^{\infty} = \begin{pmatrix} I & s\sqrt{I + \frac{X}{\sin^2\theta}} \\ s\left(\sqrt{I + \frac{X}{\sin^2\theta}}\right)^{-1} & I \end{pmatrix} \qquad (8)$$

where $s = sgn\left([real((Tr(F)))]\right)$ is the sign of the real part of the trace of F.

This algebra turns out to be numerically very stable. In a single precision implementation of the optics routine the product up to 16 matrices (corresponding to 16 *different* layers) can be handled without serious numerical instabilities. In double precision this number doubles too. The double precision algorithm for a 1024 channel spectrum needs 0.92 sec calculation time on a 166 MHz pentium computer 512k cache and 32 Mbyte RAM. The majority (80%) of the time is taken by the optics routine.

For grazing incidence, the reflectivity matrix is calculated as function of two variables (*vs.* time and angle and *vs.* velocity and angle, for time domain and energy domain spectra, respectively. By adding the corresponding time or energy channels, an option is provided for fitting time-integral or energy-integral reflectivity curves (angular scans). In this routine, in the event of no defined resonant scatterers in the multilayer, the hyperfine algorithm is skipped in which special case the electronic scattering, the non-resonant x-ray reflectivity curve is fitted.

Each layer has its own interface roughness which is treated in a rather general way, using a characteristic matrix technique (similar to the treatment of the layer structure) allowing for roughness at interfaces of anisotropic layers[23].

3 Program description

The structure of EFFINO is designed to accomplish a simultaneous fit of theoretical curves to data sets of different type requiring different physical model functions ('theories') like synchrotron scattering spectra and Mössbauer absorption spectra. Moreover to each nuclear site an adequate theory is attached so that one site may have static hyperfine fields and another fluctuating fields (relaxation theory not yet implemented).

Simultaneous fitting requires the restriction of parameters to those common to different subsets of theories. This essential feature of EFFINO is implemented by a matrix called 'transformation matrix' in the Mössbauer program SIRIUS [20] or 'correlation matrix' in MOSFUN [19] The first notation will be used here. The transformation matrix T maps the parameters p_i, $i = 1...n_p$ to be fitted to the variables v_k, $k = 1...m_v$ defined by the theories: $v_k = \sum_i^{\nu} T_{ki} p_i$. If T is diagonal ($n_p = \nu_v$) then there are no correlations and the number of parameters is equal to the number of variables. For a large number of variables the matrix T becomes tortuous. Therefore small subsets of variables are selected with their own transformation matrix T^τ:

$$v_k^\tau = \sum_i^{\nu^\tau} T_{ki}^\tau p_i^\tau \tag{9}$$

EFFINO allows for free handling of the matrices, in order to combine and split subsets and the corresponding matrices (τ is free), and to rearrange parameters and/or variables inside subsets. In addition new parameters p_j^τ may be defined which are products of the original parameters: $p_l^\tau = p_i^\tau p_j^\tau$ such that the number of columns n_p^τ is larger than the number of rows ν_v^τ (number of variables) of the matrix. These products make possible to fit (or to fix) ratios of parameters which is often desired for intensity parameters of subspectra or between spectra.

Parameters generally can be fitted and belong to a transformation matrix whereas constants are listed and handled separately. As an example, the variables and constants of the grazing incidence time spectrum of a layer structure are listed and described in this section.

Table 1: Variables of the theory for grazing incidence time spectrum. Angles of global variables are defined with respect to the laboratory coordinate system.

Level	variable	comment
GLOBAL	counts	total number of counts
	background	avarage number of background counts
	t_{shift}	zero-time shift
	(P_ξ, P_η, P_ζ)	Poincaré vector of the synchrotron beam
	$H(\vartheta, \varphi)$	external magnetic field
	φ, ϑ, ψ	orientation of the scatterer
LAYER	thickness	thickness of the layer
	$\chi = (\chi_r, \chi_i)$	electronic sustceptibility of the layer
	roughness	
SITE	thickness	effective thickness of nuclear scatterers
	broadening	Gaussian and/or Lorentzian broadening
	isomer shift	
	$H(\vartheta, \varphi)$	hyperfine magnetic field defined in the principal axes system of the EFG
	$\pm\Delta E_Q, \eta$	Quadrupole splitting and asymmetry parameter of the EFG with the sign of V_{zz}
	$(\varphi, \vartheta, \psi)$	orientation of the EFG defined in the principal axes system of the scatterer

The default values of the matrices T^τ are unity matrices such that the parameters of the theory are identical with the fit variables. The structure of the theory is such that several levels can be defined. There are global variables and constants which do not depend on the nuclear site or the individual layers. For some quantities, the user has the choice to define them as constants or as parameters. Typical such quantities are the Poincaré vector (P_ξ, P_η, P_ζ)

of the synchrotron beam, the time-zero shift t_{shift}, the external magnetic field, the Eulerian angles φ, ϑ, ψ of the orientation of the specimen in the laboratory system, etc., these values are often known from external measurements but can be included in the fit parameter list.

Table 2: Constants of the theory for grazing incidence time spectrum.

GLOBAL	flag (sampling)	mode of calculation (see text)
	flag (Voigt)	Voigt/Gaussian profile
	v_{max}	max velocity in energy domain
	i_{T-max}	number of previous bunches
	$k(extension)$	2^k times the number of channels for the Fourier transformation
	$\Gamma, I_g, I_e, \mu_g, \mu_e, Q_g/Q_e, \lambda$	nuclear constants
	$kGauss \cdot \mu_n/mms^{-1}$	energy to velocity conversion
	unit thickness, unit χ	
LAYER	n_{repeat}	repetitions in the sandwich layer
SITE	$\pm n_z, n_y$	n_z, n_y-fold symmetry axis, sign: time inversion

EFFINO, like MOSFUN, is command-driven. An EFFINO command consists of two letters and optional command line inputs (e.g. RD {*file.dat*} = "read data from *file.dat*"). There belongs a command/option buffer to each command. Up to 6 buffers are handled. Command/option buffers can be created at any time during the fit session. They should at least contain one command to be executed and can be recursively called. An empty command 'CD' executes the content of the default (first) buffer *b1*, CD *b3,* for example executes the command string in *b3*, etc. EFFINO commands can be concatenated by a double ampersand '&&' : CD {*option*} && CD' {*option'*}, etc. An option may consist of concatenated commands and be stored in a buffer, so that a long chain of commands can be constructed in order to avoid excessive typing during fitting sessions.

A set of parameters can be excluded from variation during fitting by a versatile command FI (fix parameter) with options like FI {*t1-3 4 10 80-400 t5*} ("exclude parameters belonging to transformation matrices T^1, T^2, T^3, T^5 and parameters no. 4,10,80 to 400 from the fit"). Command FR ('free a parameter for fit') is the opposite of FI and it removes the fixed flag on the parameter list and allows variation during fitting. Although the parameter space is presently restricted to maximum 32 free parameters at a time, much higher dimensional fits can be automatically made by FIxing and FReeing parameter subsets even by a single or recursively called command string.

Besides data input, parameter input/output files and the fit result output files, which contain the theoretical curves and errors and the χ^2 fit results, there are two further files to mention. The history file lists all commands given to the program and the error messages during session, which may be used later for error analysis. The session file stores the command buffers. It is especially useful for the RD (read) commands of the data sets and of the parameter files (the latter describing the structure of the model, the 'theory'). The session file is typically used to start a session and read automatically all spectra and theories such that the last session is easily continued.

4 Acknowledgment

This work was partially supported by the Hungarian Scientific Research Fund (OTKA) under Contract Nos. T16667 and F022150.

References

[1] M. Blume and O. C. Kistner, Phys. Rev. **171** (1968) 417.

[2] R.W. Grant, R.M. Housley and U. Gonser, Phys. Rev **171** (1968) 417.

[3] H. Spiering and R. Witzgall, Hyperfine Interactions 120 (1978) 265-269.

[4] M. A. Andreeva and K. Rosete, Poverkhnost' **9** (1986) 145;
Vestnik Mosk. Univ., Ser. 3. Fiz. Astron. **27** (1986) 57.

[5] M. A. Andreeva and K. Rosete, Vestnik Mosk. Univ., Ser. 3. Fiz. Astron. **27** (1986) 57.

[6] S. M. Irkaev, M. A. Andreeva, V. G. Semenov, G. N. Beloserskii,
and O. V. Grishin, Nucl. Instrum. Methods **B74** (1993) 545.

[7] S. M. Irkaev, M. A. Andreeva, V. G. Semenov, G. N. Beloserskii,
and O. V. Grishin, Nucl. Instrum. Methods **B74** (1993) 554.

[8] M. A. Andreeva, S. M. Irkaev, and V. G. Semenov,
Sov. Phys.–JETP **78** (1994) 965.

[9] A. M. Afanas'ev and Yu. Kagan, Sov. Phys.–JETP **21** (1965) 215.

[10] G. M. Borzdov, L. M. Barskovskii, and V. I. Lavrukovich,
Zh. Prikl. Spektrosk. **25** (1976) 526.

[11] F. I. Fedorov, *Teoria Girotropii*, Nauka i Technika, Minsk, 1976.

[12] J. P. Hannon and G. T. Trammell, Phys. Rev. **169** (1968) 315.

[13] J. P. Hannon and G. T. Trammell, Phys. Rev. **186** (1969) 306.

[14] L. Deák, L. Bottyán, D.L. Nagy, and H. Spiering, "On the grazing incidence limit in Mössbauer Optics", submitted to Phys. Rev. B.

[15] M. A. Andreeva and R. N. Kuz'min, *Messbauerovskaya Gamma-Optika,*
Internal report, Moscow University, 1982.

[16] J. P. Hannon, N. V. Hung, G. T. Trammell, E. Gerdau, M. Mueller, R. Rüffer,
and H. Winkler, Phys. Rev. B **32** (1984) 5068.

[17] J. P. Hannon, G. T. Trammell, M. Mueller, E. Gerdau,
R. Rüffer, and H. Winkler, Phys. Rev. B **32** (1985) 6363.

[18] L. Deák, L. Bottyán, D. L. Nagy, and H. Spiering, Phys. Rev. B. **53** (1996) 6158.

[19] E.W. Müller, MOSFUN, Internal report, Anorganische Chemie und Analitische Chemie, Johannes Gutenberg-Universität, Mainz, 1982.

[20] K. Kulcsár, D.L. Nagy and L. Pócs, Proc. Conf. Mössbauer Spectrometry, Dresden, 1971, p. 594

[21] A. Vef, MOSFUN and several plot programs were extended for X-Window applications, Internal report, Anorganische Chemie und Analitische Chemie, Johannes Gutenberg-Universität, Mainz, 1982.

[22] R. Röhlsberger. *Grazing Incidence Optics for Nuclear Resonant Filtering of Synchrotron Radiation*, Ph.D. thesis, University Hamburg, 1994.

[23] L. Deák, L. Bottyán, D.L. Nagy, "An anisotropic treatment of interface roughness in neutron and Mössbauer-reflectometry" to be published

[24] In another implementation of EFFINO fitting of spin-polarized neutron reflectivity data of anisotropic (magnetic) multilayers is provided in a very similar scheme, making use of the transformation between the anisotropic optics of γ-rays and neutrons, respectively, as described in Ref. [25]

[25] L. Deák, L. Bottyán, D.L. Nagy, "A common anisotropic optical approach to synchrotron Mössbauer and neutron reflectometry" to be published.