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SYNFOS

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An expression for the amplitude of a pulse of synchrotron radiation coherently scattered in the forward direction by a Mössbauer absorber consisting of randomly oriented paramagnetic iron-containing molecules (for example, a frozen solution of a ^{57}Fe protein) in an applied magnetic field is derived from the theory of γ optics. It is assumed that the hyperfine splittings present in the Mössbauer nuclei can be described in the framework of the spin-Hamiltonian formalism. In the general case of a thick Mössbauer sample of this kind the response on an incident monochromatic and fully polarized beam cannot be given analytically because of the integrations involved. How nuclear forward-scattering for this general case is evaluated in the program package called SYNFOS is outlined.

Keywords: randomly oriented scatterer, nuclear resonant forward scattering, synchrotron radiation

1. Basic formulas

1.1. Randomly oriented Mössbauer scatterer

The SYNFOS program is written for a scatterer consisting of randomly oriented paramagnetic iron complexes, which are characterized by an effective electron spin S and placed in an external field $\vec{B}$ [1]. The complexes contain Mössbauer nuclei, which are assumed to be homogeneously distributed. The electronic ground states of such iron ions form an energetically isolated spin multiplet, described by a Hamiltonian of the following form [2]:

$$H_{\mathrm{el}} = \widehat{\vec{S}} \cdot \widetilde{D} \cdot \widehat{\vec{S}} + \beta_{\mathrm{e}} \widehat{\vec{S}} \cdot \widetilde{g} \cdot \vec{B} \tag{1.1}$$

with eigenfunctions and eigenvalues $\Phi_l^{(\mathrm{el})}$ and ε_l $(l = 1, \dots, 2S{+}1)$. In eq. (1.1), $\widetilde{D}$ and $\widetilde{g}$ are tensors describing electronic spin–orbit and Zeeman interactions, respectively. $\widehat{\vec{S}}$ is the effective spin operator and β_{e} is the Bohr magneton.

Mössbauer nuclei are characterized by the spin I_0 of the ground state and I_{e} of the excited state, by the width Γ of single zero-phonon absorption lines and by the frequency ω_{r} of the Mössbauer transition in the absence of hyperfine interactions. The following treatment assumes that the splitting of the electronic levels is considerably larger than the hyperfine energies. Under this assumption the hyperfine splitting of the ground level (0) and the excited level (e) of a Mössbauer nucleus is given by the Hamiltonians $H^{(0)}$ and $H^{(\mathrm{e})}$, respectively:

$$H^{(0)(\mathrm{e})} = \vec{s}\cdot \widetilde{A}^{(0)(\mathrm{e})} \cdot \widehat{\vec{I}} - \beta_{\mathrm{n}} g_{\mathrm{n}}^{(0)(\mathrm{e})} \widehat{\vec{I}} \cdot \vec{B} + \widehat{\vec{I}} \cdot \widetilde{V}^{(0)(\mathrm{e})} \cdot \widehat{\vec{I}}. \tag{1.2}$$

Here $\widehat{\vec{I}}$ is the nuclear spin operator and the tensors $\widetilde{A}$ and $\widetilde{V}$ describe the magnetic hyperfine interaction and the nuclear quadrupole interaction. The second term in eq. (1.2) is the nuclear Zeeman interaction term, where g_{n} is the nuclear g-factor and β_{n} the nuclear magneton. When the transitions between the electronic multiplet substates are slow compared to the nuclear precession frequencies (slow relaxation limit), the vectors $\vec{s}_l$ are determined by

$$\vec{s}_l = \langle \Phi_l^{(\mathrm{el})} | \widehat{\vec{S}} | \Phi_l^{(\mathrm{el})} \rangle. \tag{1.3}$$

In the case of fast relaxation only the thermal average

$$\vec{s} = \sum_l w_l \vec{s}_l \tag{1.4}$$

is observable, where the weight of the lth electronic state is

$$w_l = \frac{\mathrm{e}^{-\varepsilon_l/(k_{\mathrm{B}}T)}}{\sum_{l'} \mathrm{e}^{-\varepsilon_{l'}/(k_{\mathrm{B}}T)}}, \tag{1.5}$$

T is the temperature of the sample and k_{B} is the Boltzmann constant.

The form of the eigenfunctions of the Hamiltonians (eqs. (1.1) and (1.2)) is especially simple in the molecular frame of reference. In this frame the eigenfunctions $\Phi_l^{(\mathrm{el})}$ as well as the energies ε_l depend on the polar and azimuthal angle θ and φ, respectively, of the external field $\vec{B}$ ($\Phi_l^{(\mathrm{el})} \equiv \Phi_l^{(\mathrm{el})}(\theta,\varphi)$, $\varepsilon_l \equiv \varepsilon_l(\theta,\varphi)$). In the slow relaxation case, the nuclear multiplet wave functions ($\Phi_i^{(0)}$ and $\Phi_f^{(\mathrm{e})}$) and the corresponding energies ($\hbar\omega_i$ and $\hbar\omega_f$) also depend on the electronic state of the iron ($\hbar\omega_{i(f)} \equiv \hbar\omega_{i(f)}(l;\theta,\varphi)$). Further we consider mostly the case of significant hyperfine splitting of the nuclear levels, when the sample of randomly oriented complexes is characterized by a band of resonant absorptions of a width Δ with $\Delta \gg \Gamma$ [3]. This band has a complicated structure and cannot be described by any inhomogeneously broadened single line.

1.2. Synchrotron radiation pulses in a Mössbauer scatterer

The pulse of synchrotron radiation (SR) incident on the scatterer as defined in the previous section is described by the electric field of the radiation:

$$\vec{E}_0(z,t) = \vec{e}_0\left(t - \frac{z}{c_0}\right)\mathrm{e}^{-\mathrm{i}\omega_0(t - z/c_0)}, \quad z \leqslant 0, \tag{1.6}$$

where c_0 is the speed of light in vacuum. The γ-quanta propagate in the direction of the z-axis, normal to the surface of the Mössbauer sample. It is assumed that the radiation is fully linearly polarized along the x-axis ($\vec{e}_0 = (e_0, 0, 0)$). This direction is also labeled by $\vec{\sigma}$ in the following.

Transient processes in the scatterer modify the incident SR pulse. We are interested in the time range after t_0, when the short incident pulse is terminated ($E_0(d,t) \rightarrow 0,\ t \gg t_0$) and beyond which the evolution of the transmitted pulse is determined by forward scattered radiation only. In this time range the transmitted radiation field can be represented as

$$E_\alpha(z,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \cdot \mathrm{e}^{-\mathrm{i}\omega(t-z/c_0)} \cdot \big(\widetilde{R}_{\alpha x}(\omega, d) - \tilde{\delta}_{\alpha x}\big)\chi_0, \tag{1.7}$$

where $\alpha = x, y$ and d is the thickness of the sample with $z \geqslant d$. In eq. (1.7) the components of the tensor $\underset{\sim}{\widetilde{R}}(\omega, d)$ represent the response of the scatterer on a stationary beam of monochromatic Mössbauer radiation, $\underset{\sim}{\tilde{\delta}}$ is the unit tensor. Also the approximate relation

$$e_0(\tau) \approx \delta(\tau)\int_{-\infty}^{\infty} e_0(t)\,\mathrm{d}t = \chi_0\delta(\tau)$$

has been used [4]. It should be noted that Bragg diffraction is neglected in randomly oriented samples.

A semiclassical optical theory, describing the transformation of a monochromatic beam of Mössbauer radiation in resonant media, has been developed in [5–7]. This theory can be modified to derive the explicit form of $\widetilde{R}_{\alpha\beta}$ for the cases of randomly oriented samples:

$$\widetilde{R}_{\alpha\beta}(\omega, d) = \sum_{j=1,2} \tilde{\rho}^{(j)}_{\alpha\beta} \cdot \mathrm{e}^{(\mathrm{i}\omega d/c_0)\cdot(n^{(j)}(\omega)-1)}. \tag{1.8}$$

In eq. (1.8) j indicates the two elliptically polarized plane waves arising in the medium due to the birefringence phenomenon. The refractive indices $n^{(j)}(\omega)$ of these waves are expressed as

$$n^{(j)}(\omega) = n_{(\mathrm{el})}(\omega) + \frac{c_0}{\omega d} \cdot U^{(j)}(\omega, d), \tag{1.9}$$

where $n_{(\mathrm{el})}(\omega)$ accounts for the polarization of the electronic subsystem. The contribution of the resonant Mössbauer nuclei $U^{(j)}(\omega, d)$ is determined by the average elastic forward-scattering amplitudes $\bar{f}_{\alpha\beta} \equiv \bar{f}_{\alpha\beta}(\omega)$ of a single nucleus:

$$U^{(j)}(\omega, d) = \frac{d}{2}\big\{\bar{f}_{xx} + \bar{f}_{yy} + (-1)^j\big[\big(\bar{f}_{xx} - \bar{f}_{yy}\big)^2 + 4\bar{f}_{xy}\bar{f}_{yx}\big]^{1/2}\big\}. \tag{1.10}$$

The subscripts α, β indicate the polarization of the absorbed and the emitted photons ($\alpha, \beta = x, y$). Also the non-zero components of the tensor $\tilde{\rho}^{(j)}$ in eq. (1.8) are determined by the scattering amplitudes $\bar{f}_{\alpha\beta}$:

$$\tilde{\rho}^{(j)}_{\alpha\beta} = (-1)^j \cdot \frac{c_0}{\omega} \cdot \frac{\tilde{\delta}_{\alpha\beta}[n^{(j)} - n_{\mathrm{el}}](\omega/c_0) - 2\bar{f}_{\alpha\beta}}{n^{(1)} - n^{(2)}}. \tag{1.11}$$

To arrive at an explicit form for $U^{(j)}(\omega)$ and $\tilde{\rho}^{(j)}_{\alpha\beta}$, the averaged forward-scattering amplitudes $\bar{f}_{\alpha\beta}$ are expressed as

$$\begin{aligned}\bar{f}_{\alpha\beta}(\omega) = {} & \frac{1}{8\pi^2}\cdot\frac{b}{d}\int_0^{\pi}\sin\theta'\,\mathrm{d}\theta'\int_0^{2\pi}\int_0^{2\pi}\mathrm{d}\varphi'\,\mathrm{d}\psi\cdot\sum_l w_l \\ & \times\sum_{\mu,\mu'=\pm1,0}(-1)^{\mu}\Pi_{\alpha-\mu}\big(\psi,\theta',\varphi'\big)\Pi_{\beta\mu'}\big(\psi,\theta',\varphi'\big) \\ & \times\sum_n\frac{A^{(n)}_{\mu\mu'}}{\omega_{\mathrm{r}}-\omega+\omega_n-\imath\Gamma/(2\hbar)}.\end{aligned} \tag{1.12}$$

In eq. (1.12) n represents the $(2I_0+1)\times(2I_{\mathrm{e}}+1)$ Mössbauer transitions in the nucleus, i.e., $n=(i,f)$, $\omega_n=\omega_f-\omega_i$, and the short-hand notation b is defined as (see [5–8])

$$b=\frac{\pi}{\hbar}\,\frac{c_0^2 d\Gamma e^{-2W_{\mathrm{D}}}}{(1+\alpha)V_0\omega^2}\cdot\frac{2I_{\mathrm{e}}+1}{2(2I_0+1)}, \tag{1.13}$$

where V_0^{-1} is the density of Mössbauer nuclei, $\mathrm{e}^{-2W_{\mathrm{D}}}$ is the Debye–Waller factor and α is the conversion coefficient. The tensors $A^{(n)}_{\mu\mu'}$ in eq. (1.12) are determined by the transition matrix elements and have in the case of M1-transitions, e.g., for ^{57}Fe, the following explicit form (see [5–8]):

$$\begin{aligned}A^{(n)}_{\mu\mu'} = {} & \frac{3}{(2I_{\mathrm{e}}+1)}\sum_{m_{\mathrm{e}},m'_{\mathrm{e}}}\sum_{m_0,m'_0}(I_0m_0;1,\mu\mid I_{\mathrm{e}}m_{\mathrm{e}})\big(I_0m'_0;1,\mu'\mid I_{\mathrm{e}}m'_{\mathrm{e}}\big) \\ & \times C^*_{im_0}C_{im'_0}C^*_{fm'_{\mathrm{e}}}C_{fm_{\mathrm{e}}},\end{aligned} \tag{1.14}$$

where C_{im_0} and $C_{fm_{\mathrm{e}}}$ are coefficients of expansion of the nuclear multiplet wave functions $\Phi_i^{(0)}$ and $\Phi_f^{(\mathrm{e})}$ in the series of the eigenfunctions of the $\hat{I}_z$ operator. Finally, the matrices $\Pi_{\alpha\mu}(\psi,\theta',\varphi')$ in eq. (1.14) have the following components:

$$\Pi_{x\mu}=\frac{1}{\sqrt{2}}\big(D^1_{1\mu}-D^1_{-1\mu}\big)\quad\text{and}\quad\Pi_{y\mu}=\frac{\mathrm{i}}{\sqrt{2}}\big(D^1_{1\mu}-D^1_{-1\mu}\big). \tag{1.15}$$

Here $D^1_{\mu\mu'}\equiv D^1_{\mu\mu'}(\psi,\theta',\varphi')$ are the Wigner functions which couple the transition matrix elements calculated in the laboratory and molecular reference systems, respectively, and (ψ,θ',φ') are the corresponding Euler angles for different molecules [9].

Furthermore, it is convenient to consider the rotations (ψ,θ',φ') in two stages, where the intermediate orientation of the coordinate frame is characterized by the z-axis, parallel to the external field $\vec{B}$, i.e.,

$$D^1_{\mu\mu'}\big(\psi,\theta',\varphi'\big)=\sum_{\mu_0}D^1_{\mu\mu_0}(\varphi_0,\theta_0,0)D^1_{\mu_0\mu'}(\psi,-\theta,-\varphi), \tag{1.16}$$

with the polar and azimuthal angles θ_0,φ_0 and θ,φ of the vector $\vec{B}$ in the laboratory and in the molecular frame, respectively. An explicit integration over the angle ψ can be carried out in eq. (1.12) as both the transition frequencies ω_n and the coefficients C_{im_0}, C_{fm_e} depend on the angles θ and φ only ($\omega_n = \omega_f(l,\theta,\varphi) - \omega_i(l,\theta,\varphi)$, $C_{im_0} \equiv C_{im_0}(l,\theta,\varphi)$, $C_{fm_\mathrm{e}} \equiv C_{fm_\mathrm{e}}(l,\theta,\varphi)$).

Equation (1.12) involves an averaging procedure over the electronic spin multiplet states by summation over l, where the weight w_l is determined by eq. (1.5) and thus accounts for slow relaxation of this multiplet. In the case of fast relaxation ($w_l = (2S+1)^{-1}$) the summation over l in eq. (1.12) may be omitted as according to eqs. (1.4) and (1.5) the transition frequencies ω_n and the transition matrix elements no longer depend on this index.

Summarizing eqs. (1.12)–(1.16) the following relations are derived:

$$\begin{aligned} U^{(j)}(\omega,d) &\equiv U^{(j)}(\omega,d,\theta_0) \\ &= \overline{U} + U_{01}\sin^2\theta_0 + (-1)^j\left(U_{01}^2\sin^4\theta_0 + U_{02}^2\cos^2\theta_0\right)^{1/2}, \end{aligned} \tag{1.17}$$

$$\tilde{\rho}_{xx}^{(j)} = \frac{1}{2}\left[1 - (-1)^j\frac{U_{01}\cos 2\varphi_0\sin^2\theta_0}{(U_{01}^2\sin^4\theta_0 + U_{02}^2\cos^2\theta_0)^{1/2}}\right]$$

and

$$\tilde{\rho}_{yx}^{(j)}(\omega) = \frac{(-1)^j}{2}\,\frac{U_{01}\sin 2\varphi_0\sin^2\theta_0 - \mathrm{i}U_{02}\cos\theta_0}{(U_{01}^2\sin^4\theta_0 + U_{02}^2\cos^2\theta_0)^{1/2}} \tag{1.18}$$

with $\overline{U} = U_1 + U_{-1}$, $U_{01} = U_0 - \overline{U}/2$, $U_{02} = U_1 - U_{-1}$,

$$\begin{aligned} U_\mu(\omega,d) &= \frac{b}{4\pi}\int_0^\pi \sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\varphi\sum_l w_l(\theta,\varphi) \\ &\quad\times\sum_{i,f}\frac{w_{if;\mu}^{(l)}(\theta,\varphi)}{\omega_\mathrm{r} - \omega + \omega_f(\theta,\varphi;l) - \omega_i(\theta,\varphi;l) - \imath\Gamma/(2\hbar)} \end{aligned} \tag{1.19}$$

and

$$w_{if;\mu}^{(l)}(\theta,\varphi) = \sum_{\bar{\mu}\bar{\mu}'}\left[D^1_{\bar{\mu}'\mu}(\varphi,\theta,0)\right]^* D^1_{\bar{\mu}\mu}(\varphi,\theta,0)A^{(if)}_{\bar{\mu}\bar{\mu}'}(\theta,\varphi;l). \tag{1.20}$$

If eqs. (1.8) and (1.9) are inserted into eq. (1.7) it follows that the amplitudes of forward scattered SR can be expressed as

$$E_\alpha(0,\tau) = \mathrm{e}^{\mathrm{i}(\omega d/c_0)n_\mathrm{el}(\omega_\mathrm{r})}\sum_{j=1,2}\tilde{\rho}_{\alpha x}^{(j)}(\varphi_0)\chi_0\cdot\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\,\mathrm{e}^{-\mathrm{i}\omega\tau}\cdot\left(\mathrm{e}^{\mathrm{i}U^{(j)}(\omega,d,\theta_0)} - 1\right), \tag{1.21}$$

with $\tau = t - d/c_0$. It has been assumed that the transient processes in the fast electronic subsystem have been terminated and a stationary polarization has been put in for all actual values of τ. Therefore, $n_\mathrm{el}(\omega)$ has been considered constant in eq. (1.21).

2. Numerical calculations: ^{57}Fe Mössbauer absorbers

Equation (1.21) together with eqs. (1.14), (1.17)–(1.20) form a complete basis for simulations of the time-domain spectra of forward scattered SR if the eigenfunctions and the eigenvalues of the Hamiltonians (1.1) and (1.2) are known. The FORTRAN program SYNFOS, which has been written in order to verify the correct formulation of the theory, diagonalizes the Hamiltonians (1.1) and (1.2) for each set of angles θ, φ and carries out the numerical integrations over frequency parameter ω and angles θ, φ in eqs. (1.17) and (1.21), respectively. The output of the program presents the time-dependent intensity of the modified forward-scattered pulse:

$$i(t) = \left|\vec{E}(0,t)\right|^2 \cdot \frac{\mathrm{e}^{2\mu d}}{|\chi_0|^2}, \tag{2.1}$$

where 2μ is the coefficient of non-resonant absorption with $\mu = \mathrm{Im}[n_{\mathrm{el}}(\omega_{\mathrm{r}})]\ \omega_{\mathrm{r}}/c_0$.

The integration over Euler angles θ and φ is performed using a set of grid points which are to a high degree of approximation homogeneously distributed over an octant of the unit sphere [10]. The number of grid points per octant is $6 \cdot 2^n$, where n can be chosen from 2 to 7, while the number of octants to be evaluated is determined by the symmetry of the actual system. The field potentials $\vec{E}(0,t)$ are the sum of two parts:

$$\vec{E}(0,t) = \vec{E}'(0,t) + \vec{E}''(0,t), \tag{2.2}$$

where

$$E'_\alpha(0,t) = \chi_0 \Theta(t) \sum_{\mu=\pm 1} \zeta_{\alpha\mu}(\theta_0,\varphi_0) U_\mu(t,d), \tag{2.3}$$

$$\begin{aligned} U_\mu(t,d) = {} & -\frac{b}{4\pi}\, \mathrm{e}^{(\mathrm{i}n_{\mathrm{el}}\omega d/c_0 - \Gamma t/2\hbar)} \int_0^\pi \sin\theta\, \mathrm{d}\theta \int_0^\pi \mathrm{d}\varphi \sum_l w_l \\ & \times \sum_{i,f} \sum_{j=1,2} \tilde{\rho}^{(j)}_{\alpha x}(\varphi_0) w^{(l)}_{if;\mu}\, \mathrm{e}^{-\mathrm{i}(\omega_{\mathrm{r}}+\omega_f-\omega_i)t}, \end{aligned} \tag{2.4}$$

the coefficients $\zeta_{\alpha\mu}$ depend on angular variables and

$$\begin{aligned} E''_\alpha(0,t) = {} & \chi_0 \cdot \mathrm{e}^{\mathrm{i}n_{\mathrm{el}}\omega d/c_0} \sum_{j=1,2} \tilde{\rho}^{(j)}_{\alpha x}(\varphi_0) \cdot \frac{1}{2\pi} \int_{-\omega_M+\omega_{\mathrm{r}}}^{\omega_M+\omega_{\mathrm{r}}} \mathrm{d}\omega\, \mathrm{e}^{-\mathrm{i}\omega t} \\ & \times \left[\mathrm{e}^{\mathrm{i}U^{(j)}(\omega,d,\theta_0)} - 1 - \mathrm{i}U^{(j)}(\omega,d,\theta_0)\right]. \end{aligned} \tag{2.5}$$

The integrand in eq. (2.5) decreases as $|\omega - \omega_{\mathrm{r}}|^{-2}$ if $|\omega - \omega_{\mathrm{r}}| \to \infty$. Therefore, a frequency interval of reasonable length should be chosen to achieve sufficient precision of the approximate value of the original infinite integral, calculated as a fast Fourier transform.

Successful applications of the program SYNFOS are described in section IV-2.4 of this issue.

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