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Explicit expression for the intensity tensor for 3/2–1/2 transitions and solution of the ambiguity problem in Mössbauer spectroscopy

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Abstract. Analytical expressions for the intensity tensor in the case of 3/2–1/2 nuclear transitions are obtained and the properties of the trace, symmetric and antisymmetric parts of the intensity tensor for a single transition are discussed. It is shown that in the principal axis system of the symmetric part of the intensity tensor the angular dependence of absorption of the circularly polarized resonant radiation depends essentially on only one parameter—the maximal degree of circular polarization. The latter parameter is directly connected with the antisymmetric part of the intensity tensor. It is shown that the so-called ambiguity problem, including the sign of the hyperfine magnetic field, can be solved by measuring the antisymmetric part using circularly polarized radiation. Some values typical in circular polarimetry can be measured in a standard experiment and vice versa. Explicit expressions for the line intensities of the powdered absorber are given in the general case of mixed transitions. The symmetry of the shape of the spectra with different signs of the electric field is explained. An experiment is proposed in which all parameters of the $I = 3/2$ spin Hamiltonian can be unambiguously determined.

1. Introduction

Development of EPR and MNR techniques in the 1950s resulted in an interest in the behaviour of a spin exposed to mixed magnetic and electric interactions [1–7]. A proper solution of the respective spin Hamiltonian also became needed after discovery of the Mössbauer effect, and the formulas for the probabilities of observed nuclear transitions under magnetic fields were given first in [8] and [9]. Then, the transition probabilities and absorption line shape were treated in a large number of works by perturbation or numerical methods. Examples, which certainly do not cover all the field, can be found in [10–19]. The parameters of the hyperfine fields in cases of mixed interactions were measured by Mössbauer spectroscopy, see some representative examples [20–25], and the results were compared with calculations based on the spin-3/2 Hamiltonian.

However, in 1966 it was pointed out [20] that the knowledge of nuclear levels resulting from combined interactions does not lead to a unique solution for all hyperfine parameters. The arising ambiguity, analysed e.g. in [23] and [25–28], cannot be lifted either by taking into account line intensities in a single measurement with an unpolarized source, or by changing the magnitude of the external magnetic field. However, it can be reduced when polarized radiation is used, see [25]. It is to be noted that the form of the eigenvalues and eigenfunctions of the $I = 3/2$ Hamiltonian, necessary for discussion of the 3/2–1/2 transitions observed in Mössbauer spectroscopy, is quite complicated [20, 29]. The secular equation, which is

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of fourth order, can in principle be solved analytically [29, 30]. Unfortunately, an analytical expression for the line intensity which was derived in [31] using the superoperator technique is too complicated for a detailed discussion. Certain activity was also devoted to derivation of the exact relationships between energy levels [6, 20, 30] or line intensities [23]. Some of them found wide applications [32].

The intensity tensor formalism, which is specially interesting for us, was introduced in [33–35] and used intensively [36–43]. In the cited papers, the intensely tensor components were constructed from the eigenstates of the excited and ground state Hamiltonians. Since the eigenstates of the 3/2 spin Hamiltonian are described by complicated expressions, the detailed discussion was performed in extremal cases only: either small magnetic or small quadrupole interactions. In principle, an analytical form of the intensity tensor can be obtained from analytical expressions for energies [29] and constructed eigenstates [20, 43] inserted into formulas for the intensity tensor components. However, results of such a procedure are useless because of their complexity. We should like to demonstrate that there is an alternative way to derive convenient expressions for the probabilities.

First we obtain a set of linear equations for the probabilities. Next, the probabilities will be obtained as functions of hyperfine parameters defining the hyperfine fields and the energies of the excited states, which define line positions in the spectrum. We will show that all hyperfine parameters can be measured by means of a monochromatic, circularly polarized Mössbauer source (MCPMS) [44–46]. Finally, explicit results for line intensities to be expected in some special experimental arrangements are given and some details are discussed, to the best of our knowledge, for the first time.

2. The Hamiltonian and the secular equation

The Hamiltonian of the nuclear system with spin $\hat{\boldsymbol{I}}$ in the principal axis system (PAS) of the electric field gradient (EFG) tensor was defined in [5] and [29] as:

$$H^I = -g_I \mu_N \hat{\boldsymbol{I}} \cdot \boldsymbol{B} + \frac{eQV_{zz}}{4I(2I-1)} \left(3\hat{\boldsymbol{I}}_z^2 - \hat{\boldsymbol{I}}^2 + \frac{\eta}{2}(\hat{\boldsymbol{I}}_+^2 + \hat{\boldsymbol{I}}_-^2) \right) \tag{2.1}$$

where g_I is a nuclear g-factor and μ_N denotes the nuclear magneton. Cartesian components of the EFG tensor are $V_{ij} = -\partial^2 V/\partial x_i \partial x_j$, where V denotes an electric potential at the nucleus. Q is the nuclear quadrupole moment and η denotes the so-called asymmetry parameter. The coordinate system can be chosen so that $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$ and then $\eta = (V_{xx} - V_{yy})/V_{zz}$. Let us accept as a basis states $|I_e, m_e\rangle$ and $|I_g, m_g\rangle$, which are the eigenstates of the $\hat{I}_z$, the z-component of the angular momentum operator in the PAS system of the EFG. The excited and the ground eigenstates of the Hamiltonian are $|e^\alpha\rangle = \sum_{m_e} e^\alpha_{m_e} |I_e, m_e\rangle$ and $|g^\beta\rangle = \sum_{m_g} g^\beta_{m_g} |I_g, m_g\rangle$, respectively. Then, the secular equation of the $H^{3/2}$ Hamiltonian is:

$$\lambda^4 + p\lambda^2 + q\lambda + r = 0 \tag{2.2}$$

where

$$\begin{aligned} p &= -10 - 2R^2 \left(1 + \frac{\eta^2}{3}\right) \\ q &= -16\boldsymbol{m} \cdot \hat{\boldsymbol{\Phi}} \cdot \boldsymbol{m} \\ r &= \tfrac{1}{4}(p+4)^2 - 16\boldsymbol{m} \cdot \hat{\boldsymbol{\Phi}} \cdot \boldsymbol{m} \end{aligned} \tag{2.3}$$

with $R = eQV_{zz}/(2g_{3/2}\mu_N B)$. The unit vector $\boldsymbol{m}$, defined by spherical angles θ and φ, is parallel to the direction of the hyperfine magnetic field $\boldsymbol{B}$. $\hat{\boldsymbol{\Phi}}$ is a tensor proportional to the

EFG tensor and in its PAS it reads:

$$\hat{\mathbf{\Phi}} = -\frac{R}{2}\begin{bmatrix} 1-\eta & 0 & 0 \\ 0 & 1+\eta & 0 \\ 0 & 0 & -2 \end{bmatrix} \tag{2.4}$$

The coefficient at the λ^3 term in equation (2.2) is zero, because the Hamiltonian $H^{3/2}$ is traceless. An analytic form for λ_α can be found in [29] and [30]. The values λ_α are proportional to the eigenenergies of E_α of the Hamiltonian $H^{3/2}$: $\lambda_\alpha = 2E_\alpha/(g_{3/2}\mu_N B)$.

3. Intensity tensor formalism

The transition probability between excited $|e^\alpha\rangle$ and ground $|g^\beta\rangle$ states can be obtained in the intensity tensor formalism. In the thin absorber approximation, the area under an absorption line for circular polarization is equal to [41]:

$$A_{\alpha\beta\zeta} = f_s t \frac{\Gamma\pi}{2}\frac{1}{2}(\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta} - \gamma\cdot\hat{\boldsymbol{I}}^{(s)}_{\alpha\beta}\cdot\gamma - 2\zeta\boldsymbol{G}_{\alpha\beta}\cdot\gamma) \tag{3.1}$$

where t is the effective thickness of the absorber, f_s the recoilless fraction of the source and Γ the natural width. Index $\zeta = \pm 1$ described two opposite circular polarizations of the photon. γ is a unit vector parallel to the direction of the photon. $\hat{\boldsymbol{I}}$ is the so-called intensity tensor of the transition between states α and β, and it is convenient to define its spherical components. Any vector $\boldsymbol{V} = \sum v_i \boldsymbol{e}_i$ can be expressed in the spherical basis: $\boldsymbol{V} = \sum b^i \boldsymbol{u}_i^*$, where spherical basis vectors are defined as: $\boldsymbol{u}_{\pm1} = 2^{-1}(\mp\boldsymbol{e}_x - \mathrm{i}\boldsymbol{e}_y)$, $\boldsymbol{u}_0 = \boldsymbol{e}_z$. Spherical components of the intensity tensor are thus constructed as:

$$I^{ij}_{\alpha\beta} = V_i^{\alpha\beta *} V_j^{\alpha\beta} \tag{3.2}$$

where $V_M^{\alpha\beta}$ are spherical components of the vector describing nuclear transition from the excited to the ground state:

$$V_M^{\alpha\beta} = \sqrt{2L+1}\sum_{m_e m_g} e_{m_e}^{\alpha *} g_{m_g}^{\beta} (-1)^{I_g - L + m_e}\begin{pmatrix} I_g & L & I_e \\ m_g & M & -m_e \end{pmatrix}. \tag{3.3}$$

The last expression in the parenthesis is Wigner's $3j$ symbol.

Further on, we will use Cartesian components of tensors. $\hat{\boldsymbol{I}}^{(s)}_{\alpha\beta}$ is the symmetric part of the intensity tensor defined as usually:

$$\hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} = (\hat{\boldsymbol{I}}_{\alpha\beta} + \hat{\boldsymbol{I}}^*_{\alpha\beta})/2. \tag{3.4}$$

The real $\boldsymbol{G}_{\alpha\beta}$ vector is constructed from the antisymmetric part of the intensity tensor and its components are given by:

$$G^k_{\alpha\beta} = \varepsilon_{kpr} I^{pr}_{\alpha\beta}/2\mathrm{i}. \tag{3.5}$$

The first two terms of equation (3.1) correspond to the measurements with an unpolarized source. The third term, containing the antisymmetric part of the intensity tensor, relates to the circular polarization of the radiation, and measurements with two opposite polarizations can deliver direct information about $\boldsymbol{G}_{\alpha\beta}$ vectors, whose properties are examined in the next section.

4. Some properties of the intensity tensor of pure transition

We shall drop indices α and β in this section because only one pair of indices will be considered. Let us diagonalize the symmetric part of $\hat{\boldsymbol{I}}$. Note that $\boldsymbol{G}$ is an eigenvector of $\hat{\boldsymbol{I}}$ with an eigenvalue $x_G = 0$, which follows from the construction of $\hat{\boldsymbol{I}}$:

$$I^{ij}G^j = b^i b^{j*}\varepsilon_{jkl} b^k b^{l*}/2\mathrm{i} = b^i \boldsymbol{b}\cdot(\boldsymbol{b}\times\boldsymbol{b}^*)/2\mathrm{i} = 0 \tag{4.1}$$

where b^i are Cartesian components of the $\boldsymbol{V}$ vector (3.3). The same property (4.1) holds for the symmetric part $\hat{\boldsymbol{I}}^{(s)}$ and is equivalent to the fact that invariant $\mathrm{Det}\,\hat{\boldsymbol{I}}^{(s)} = 0$. To find two other eigenvalues of $\hat{\boldsymbol{I}}^{(s)}$ it is convenient to use another invariant, namely the sum of minors $C_{xx} + C_{yy} + C_{zz}$, where

$$C_{zz} = \begin{vmatrix} I_{xx}^{(s)} & I_{xy}^{(s)} \\ I_{yx}^{(s)} & I_{yy}^{(s)} \end{vmatrix} \tag{4.2}$$

and C_{xx}, C_{yy} are defined analogously. The sum of minors can be shown to be equal $|\boldsymbol{G}|^2$. The secular equation of the intensity tensor is of the form:

$$x(x^2 - x\,\mathrm{Tr}\,\hat{\boldsymbol{I}} + |\boldsymbol{G}|^2) = 0 \tag{4.3}$$

so two other eigenvalues are:

$$x_{1,2} = \tfrac{1}{2}\left(\mathrm{Tr}\,\hat{\boldsymbol{I}} \pm \sqrt{(\mathrm{Tr}\,\hat{\boldsymbol{I}})^2 - 4|\boldsymbol{G}|^2}\right). \tag{4.4}$$

The intensity tensor is characterized by five independent components: three rotation angles which orient its PAS, and two invariants, $\mathrm{Tr}\,\hat{\boldsymbol{I}}$ and $|\boldsymbol{G}|^2$. These components correspond to the five parameters determining hyperfine structure, for example B_x, B_y, B_z, V_{zz} and η.

Having diagonalized $\hat{\boldsymbol{I}}^{(s)}$ we can easily examine the dependence of absorption of the circularly polarized radiation as given by equation (3.1). The trace of $\hat{\boldsymbol{I}}$ is proportional to the intensity averaged over all possible orientations of the γ vector. Solutions (4.4) indicate that absorption depends on one parameter only, namely the ratio $|\boldsymbol{G}|/\,\mathrm{Tr}\,\hat{\boldsymbol{I}}$. Indeed, equation (3.1) has a particularly simple form in the PAS of $\hat{\boldsymbol{I}}^{(s)}$:

$$\frac{A_\zeta^{PAS}}{\langle A_\zeta\rangle} = 1 - \frac{1}{4}\gamma\cdot\begin{bmatrix} 1+3\sqrt{1-P^2} & 0 & 0 \\ 0 & 1-3\sqrt{1-P^2} & 0 \\ 0 & 0 & -2 \end{bmatrix}\cdot\gamma - \zeta\frac{3P}{2}\frac{\boldsymbol{G}}{|\boldsymbol{G}|}\cdot\gamma \tag{4.5}$$

where

$$\langle A_\zeta\rangle = f_s t\frac{\Gamma\pi}{2}\frac{1}{3}\,\mathrm{Tr}\,\hat{\boldsymbol{I}} \tag{4.6}$$

and $P = 2|\boldsymbol{G}|/\,\mathrm{Tr}\,\hat{\boldsymbol{I}}$ (note that the PAS of the $\hat{\boldsymbol{I}}^{(s)}$ tensor in the general case is different from the PAS of the EFG tensor (2.4)). The maximum absorption occurs when the direction of γ coincides with the direction of $\boldsymbol{G}$ and is equal to

$$A_{\max} = f_s t\frac{\Gamma\pi}{2}\frac{1}{2}\,\mathrm{Tr}\,\hat{\boldsymbol{I}}(1+P). \tag{4.7}$$

It can be shown, see appendix A, that for a given transition, P is the maximum circular polarization degree which is achieved when γ is along $\boldsymbol{G}$. When $P = 1$, the angular distribution given by equation (4.5) has an axial symmetry along $\boldsymbol{G}$ (is pear shaped), while for $P = 0$ the distribution has axial symmetry along direction perpendicular to $\boldsymbol{G}$ (is pretzel shaped), see figure 1.

5. Explicit formulas for the intensity tensor components

Consider an operator $\hat{O}$ acting on the eigenstates $|e^\alpha\rangle$. For the eigenvalues of the Hamiltonian H, E_α, and any power n:

$$\sum_\alpha E_\alpha^n\langle e^\alpha|\hat{O}|e^\alpha\rangle = \sum_\alpha\langle e^\alpha|\hat{O}\hat{H}^n|e^\alpha\rangle = \mathrm{Tr}\,\hat{O}\hat{H}^n. \tag{5.1}$$

We see that evaluation of the left-hand sum requires summation of diagonal elements of the operator $\hat{O}\hat{H}^n$. Constructing appropriate operators $\hat{O}$ from two eigenstates of the ground

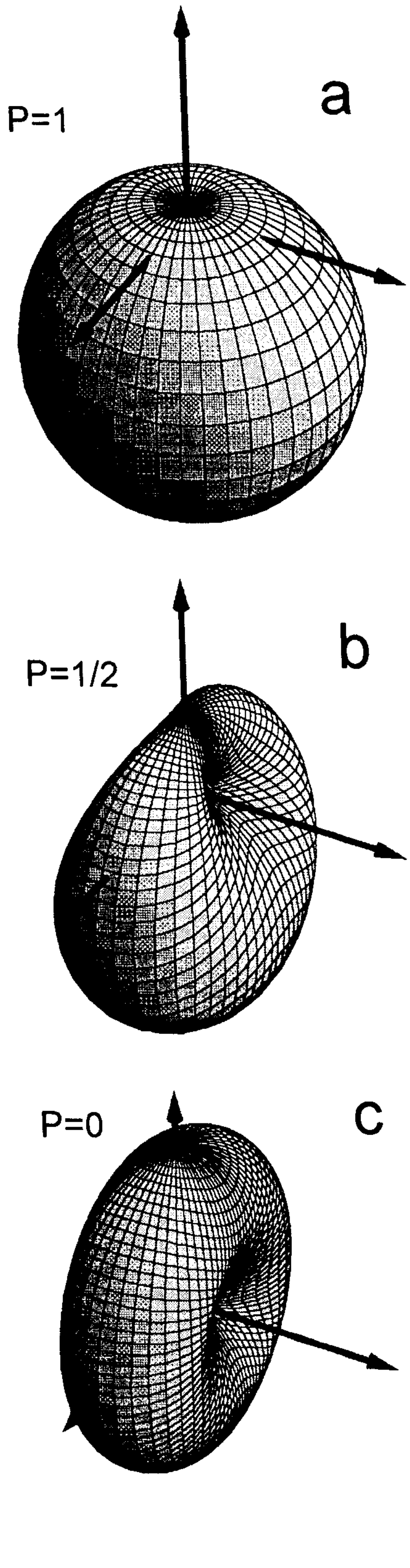

Figure 1. Angular distribution of the circularly polarized radiation in its PAS for three values of the P parameter. The length of any vector connecting axes origin and a point on the surface is proportional to the intensity given by equation (4.5). The $\boldsymbol{G}$ vector is parallel to the vertical axis.

state spin-1/2 Hamiltonian, see appendix B for details, we obtain the following results for the intensity tensor components:

$$\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta} = \frac{3}{8} + \beta\frac{40\lambda_\alpha^2 - 4q\lambda_\alpha + (p+4)(p+16) - 4r}{16w_\alpha} \tag{5.2}$$

$$\boldsymbol{G}_{\alpha\beta} = -\frac{1}{8w_\alpha}(16\hat{\boldsymbol{\Phi}}^2 + a_{1,\alpha\beta}\hat{\boldsymbol{\Phi}} + a_{0,\alpha\beta}\hat{\boldsymbol{1}})\cdot\boldsymbol{m} \tag{5.3}$$

$$\hat{\boldsymbol{I}}_{\alpha\beta}^{(s)} = \frac{1}{32w_\alpha}(-16\beta\boldsymbol{s}_{\alpha\beta}\otimes\boldsymbol{s}_{\alpha\beta} + 64\beta\hat{\boldsymbol{\Phi}}^2 - 8(2\lambda_\alpha^2 + p + 4 + 4\beta\lambda_\alpha)\hat{\boldsymbol{\Phi}} + c_{\alpha\beta}\cdot\hat{\boldsymbol{1}}) \tag{5.4}$$

where the following abbreviations are used:

$$\begin{aligned} w_\alpha &= 4\lambda_\alpha^3 + 2p\lambda_\alpha + q \\ a_{0,\alpha\beta} &= 10\lambda_\alpha^2 + 3(p+4) + \beta\lambda_\alpha(2\lambda_\alpha^2 + p + 16) \\ a_{1,\alpha\beta} &= 16\lambda_\alpha + 2\beta(2\lambda_\alpha^2 + p + 16) \\ c_{\alpha\beta} &= 8\lambda_\alpha(2\lambda_\alpha^2 + p + 4) + \beta(32\lambda_\alpha^2 - 4q\lambda_\alpha + p^2 + 32p - 4r + 256) \\ \boldsymbol{s}_{\alpha\beta} &= 2\hat{\boldsymbol{\Phi}}\cdot\boldsymbol{m} + (\lambda_\alpha + 3\beta)\boldsymbol{m}. \end{aligned} \tag{5.5}$$

Let us discuss briefly these results. The tensor components depend on the hyperfine fields and the energies of excited states. The sum of traces (5.2) over the β is equal to $(2L+1)/(2I_e+1) = 3/4$. This result was obtained in a different way in [23].

It follows from equation (B.9) that the sum of the $\boldsymbol{G}_{\alpha\beta}$ vectors over all excited states selected by β is proportional to the direction of the hyperfine magnetic field. This property offers a possibility of measuring the direction of the hyperfine magnetic field in the case of mixed interactions. From (5.3) we see that vector $\boldsymbol{G}_{\alpha\beta}$ is (i) proportional to $\boldsymbol{m}$ when magnetic interaction is dominating, (ii) proportional to $\boldsymbol{m}$ when the hyperfine magnetic field is acting along the PAS of the EFG tensor and (iii) a pseudovector, like $\boldsymbol{m}$.

The first term in (5.4) represents the nondiagonal contribution to the symmetric part of the intensity tensor, while the other three are diagonal in the PAS of the EFG. An expression for the trace of the matrix (5.4) should be the same as equation (5.2). Indeed, we notice that the trace of the tensor product in (5.4) is equal to the scalar product $\boldsymbol{s}_{\alpha\beta}\cdot\boldsymbol{s}_{\alpha\beta}$, the trace of $\hat{\boldsymbol{\Phi}}^2$ is equal to $-3/4(p+10)$ and the trace of the third term in (5.4) vanishes. As a result, the summation all of the contributions produces equation (5.2).

6. Applications

6.1. Solution of the ambiguity problem

Below we present theoretical considerations which show the possibility of measuring all parameters appearing in the Hamiltonian (2.1).

It follows from equation (3.1) that the intensities measured with opposite circular polarizations will differ by a value proportional to the product $\boldsymbol{G}_{\alpha\beta}\cdot\boldsymbol{\gamma}$. Further on it is clear that performing measurements in three perpendicular directions, say $\boldsymbol{e}_i$, in any Cartesian frame, one can measure three scalar products $\boldsymbol{G}_{\alpha\beta}\cdot\boldsymbol{e}_t$, $t = x, y, z$, in that system. In this way all components of the vector $\boldsymbol{G}_{\alpha\beta}$, thus also $|\boldsymbol{G}_{\alpha\beta}|$, can be measured. The latter cannot be expressed by p, q and r only, and contains the term proportional to the third power of R when expanded in R, see equation (B.13).

From measured excited energies λ_i from line positions the p, q and r parameters are obtained. Having additionally $|\boldsymbol{G}_{\alpha\beta}|$ one can find the invariant $R^3(1-\eta^2)$ from equation (B.13).

It is described by a rather complicated expression:

$$R^3(1-\eta^2) = \frac{1}{64}\left(1024w_\alpha^2|\boldsymbol{G}_{\alpha\beta}|^2 - \sum_{k=0}^{3} a_{k,\alpha\beta}\lambda_\alpha^k\right)[32\lambda_\alpha - q + 4\beta(2\lambda_\alpha^2 + p + 16)]^{-1} \tag{6.1}$$

where coefficients $a_{k,\alpha\beta}$ are given in appendix B. Another invariant, which is a function of R and η, equation (2.3), can be found from the line positions:

$$R^2\left(1+\frac{\eta^2}{3}\right) = -\frac{1}{2}(p+10). \tag{6.2}$$

Equations (6.1) and (6.2) can be solved with respect to the two variables, R and η, in a way analogous to the one presented in [35]. The explicit results reads:

$$\eta = \sqrt{3}\tan\frac{\arccos I_\eta}{3} \tag{6.3}$$

$$R = (\operatorname{sign} I_\eta)\sqrt{\frac{-p-10}{2}}\cos\frac{\arccos I_\eta}{3} \tag{6.4}$$

where

$$I_\eta = \frac{\sqrt{2}}{32(-p-10)^{3/2}}\left(1024w_\alpha^2|\boldsymbol{G}_{\alpha\beta}|^2 - \sum_{k=0}^{3} a_{k,\alpha\beta}\lambda_\alpha^k\right)[32\lambda_\alpha - q + 4\beta(2\lambda_\alpha^2 + p + 16)]^{-1}. \tag{6.5}$$

Having values of R and η, polar angles of the $\boldsymbol{m}$ vector in the PAS of the EFG can be found using explicit expressions for the coefficients of the secular equation (2.2)

$$\cos^2\theta = \frac{(p+16)^2 + 64R^2 - 4qR - 4r}{16R^2(9-\eta^2)} \tag{6.6}$$

$$\cos 2\varphi = \frac{1}{\eta}\frac{3p^2 + 72p - 12r + 2qR(3-\eta^2) + 528}{(p+4)^2 - 128R^2 - 4qR - 4r}. \tag{6.7}$$

Equations (6.3)–(6.7) present solutions to the ambiguity problem arising from the determination of four quantities (R, η, θ, φ) from four energy levels constrained by the condition that its sum is equal to zero. We see that it is crucial to carry out precise measurement of the length $|\boldsymbol{G}_{\alpha\beta}|$, or the maximal polarization degree, or the invariant $C_{xx}+C_{yy}+C_{zz}$, as discussed in section 4. It follows from equation (6.1) that such precise determination of $|\boldsymbol{G}_{\alpha\beta}|$ requires measurements with precision high enough to detect the terms which are of the order of R^3. It is interesting to note that the parameter P, characteristic for measurements with polarized radiation, can be obtained from the measurements of the symmetric part of the intensity tensor with an unpolarized beam.

Equations (6.6) and (6.7) still leave some ambiguity. Namely, there are eight possible orientations of vector $\boldsymbol{m}$ in the PAS of the EFG tensor, which are characterized by the same values of $\cos^2\theta$ and $\cos 2\varphi$. This ambiguity can only be removed by finding the orientation of the vector $\boldsymbol{m}$ and the orientation of the PAS of the EFG. As discussed in section 5, the orientation of the hyperfine magnetic field can be found in the MCPMS experiment [44] from the sum of $\boldsymbol{G}_{\alpha\beta}$ vectors over excited states. The orientation of PAS of the EFG can be found from equation (B.16). The weighted sum of the symmetric intensity tensor components over all states is proportional to the EFG. Thus using the procedure described already in [34], from the measured anisotropy of the line intensities weighted by their positions, the orientation of the EFG tensor can be found.

6.2. *Shape of the Mössbauer spectra*

6.2.1. Single site, arbitrary orientation. For magnetic interaction larger than the quadrupole one and energy order so that $\lambda_1 < \lambda_2 < \lambda_3 < \lambda_4$, one can introduce the frequently used absorption line abbreviation [18, 19, 21] by integers 1, 2, ..., 8. Lines 1 to 6 form a set known as a Zeeman sextet. Lines 7 and 8 correspond to the forbidden transitions in the case of pure magnetic interactions. The transition indices α and β for ^{57}Fe ascribed to subsequent lines are given in table 1. Absorption lines with indices i, $i = 1$–8 are located on the velocity scale at v_i:

$$v_i = \frac{B}{2}(\gamma_{3/2}\lambda_\alpha - \beta\gamma_{1/2}) + \delta \tag{6.8}$$

where $\gamma_{1/2} = g_{1/2}\mu_N c/E_\gamma = 0.118\,821$ mm s^{-1} T^{-1} and $\gamma_{3/2} = g_{3/2}\mu_N c/E_\gamma = -0.0678$ mm s^{-1} T^{-1} [47]. Parameter δ is the isomer shift and B the hyperfine magnetic field. Indices α and β have to be taken from the ith column of table 1. The line intensity for an arbitrary orientation of $\boldsymbol{\gamma}$ and $\boldsymbol{m}$ vectors with respect to the principal axes of the EFG is given by equation (3.1).

Table 1. Indices α and β ascribed to the consecutive absorption lines for the case of $\lambda_1 < \lambda_2 < \lambda_3 < \lambda_4$.

	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$	$i = 6$	$i = 7$	$i = 8$
α	4	3	2	3	2	1	1	4
β	+1	+1	+1	−1	−1	−1	+1	−1

6.2.2. Powdered absorber. In the case of powdered absorber, strictly speaking a randomly oriented sample, the line intensity is proportional to the trace of the intensity tensor.

$$A_{\alpha\beta} = f_s t \frac{\Gamma\pi}{2}\frac{1}{3}\,\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta}. \tag{6.9}$$

From the solution presented in [29] it follows that reduced energies can be expressed by p, q and r parameters. These three parameters are functions of five hyperfine field parameters of the $I = 3/2$ Hamiltonian (2.1). Thus from the line positions one can obtain no more than the parameters p, q and r. The intensities themselves observed on powdered absorber bring also nothing more since they depend explicitly on the energies, and p, q and r only.

6.2.3. In field measurements on a single crystal. Circularly polarized radiation is used frequently in a geometry in which external magnetic field is parallel or antiparallel to the radiation direction. In such a case, the expression for the line intensities consists of terms $\boldsymbol{m} \cdot \hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} \cdot \boldsymbol{m}$ and $\boldsymbol{G}_{\alpha\beta} \cdot \boldsymbol{m}$ which are equal to:

$$\boldsymbol{m} \cdot \hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} \cdot \boldsymbol{m} = \frac{1}{128 w_\alpha}[\beta(64\lambda_\alpha^2 + 8\lambda_\alpha q + 8(p+4)(p+16) - q^2 - 32r) + 64\lambda_\alpha^3 + 4\lambda_\alpha^2 q + 32\lambda_\alpha(p-8) + 2q(p+28)] \tag{6.10}$$

and

$$\boldsymbol{G}_{\alpha\beta} \cdot \boldsymbol{m} = \frac{1}{64 w_\alpha}[\beta(2\lambda_\alpha^2 + p + 16)(-8\lambda_\alpha + q) - 80\lambda_\alpha^2 + 8\lambda_\alpha q - 2p^2 - 40p + 8r - 128] \tag{6.11}$$

respectively. Because both expressions (6.10) and (6.11) are constructed from p, q and r parameters only, even in the case of a single crystal sample, where only a single site is present, neither the intensity analysis of a single measurement of unpolarized nor circularly polarized radiation emitted parallel/antiparallel to the hyperfine magnetic field can guarantee solution of the ambiguity problem.

Finally, for a typical case when the hyperfine magnetic field is parallel to the direction of the beam, i.e. $\gamma = m$, one obtains from equation (3.1) an explicit formula for the line intensity:

$$A_{\alpha\beta\zeta} = f_s t \frac{\Gamma\pi}{2}\frac{1}{256w_\alpha}[2(2\lambda_\alpha^2 + p + 4)(32\lambda_\alpha - q) + \beta(256\lambda_\alpha^2 - 40q\lambda_\alpha + q^2) \\ +8\zeta(40\lambda_\alpha^2 - 4q\lambda_\alpha + p^2 + 20p - 4r + 64) + 4\zeta\beta(2\lambda_\alpha^2 + p + 16)(8\lambda_a - q)]. \tag{6.12}$$

6.3. $R\zeta v$ symmetry of the Mössbauer spectra

Let us consider the spectra which were simulated in paper [43] for the case of mixed hyperfine interactions and the measurements by MCPMS. The spectra exhibit, see figures 1(a) and (b) in [43], a mirror symmetry with respect to the velocity scale in the case when polarization is changed from the left to the right handed and the sign of the EFG is changed as well. More formally, let us consider that the Mössbauer atoms reside at two sites. Assume that only the sign of the EFG is different at these sites. The spectral lines attributed to the sites are measured with two opposite polarizations and the Mössbauer spectra $A_\zeta(R, B, v)$ and $A_{-\zeta}(-R, B, v)$, respectively, where v is the Doppler velocity, are obtained. It was shown in [43] that when the hyperfine magnetic field B is reversed

$$A_\zeta(R, B, v) = A_{-\zeta}(R, -B, v) \tag{6.13}$$

which follows simply from the time invariance symmetry. A similar reason explains also another relationship, namely:

$$A_\zeta(R, B, v) = A_{-\zeta}(-R, B, -v). \tag{6.14}$$

Equation (6.14) requires detailed elucidation. First, let us examine the secular equation (2.2) and its roots, λ_α. We see that the change of sign of R in the Hamiltonian results in the change of sign of q in equation (2.2). Thus, from the known relations between the roots of the polynomial and its coefficients we conclude that change of R in the Hamiltonian results in a new set of eigenvalues $-\lambda_\alpha$. After that, having the explicit formulas for the intensity tensor components, one can easily examine that equations for the trace and for the $\hat{\boldsymbol{I}}^{(s)}_{\alpha\beta}$ remain unchanged and $\boldsymbol{G}_{\alpha\pm1}$ changes sign when both R, and β, change sign. Thus we have:

$$\begin{aligned} \hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} &= \hat{\boldsymbol{I}}^{(s)}_{\alpha^*-\beta} \\ \hat{\boldsymbol{G}}_{\alpha\beta} &= -\boldsymbol{G}_{\alpha^*-\beta} \end{aligned} \tag{6.15}$$

where the star superscript has the following meaning: $\lambda_{\alpha^*} = -\lambda_\alpha$. Inspection of equation (6.8) shows that $v_i - \delta$ will change its sign when the signs of λ_α and the index β are changed simultaneously. Thus, we see that equations (6.13) and (6.14) are generally valid. They may be applied in the investigations of amorphous materials in testing the hypothesis about symmetry of the distribution of the EFG tensor components. If the distribution of the V_{zz} is an even function, then under an applied external magnetic field one has to observe symmetries given by equations (6.13) and (6.14). To our knowledge such an experiment has not been performed so far.

7. Conclusions

The explicit form of the intensity tensor has been obtained, see equations (5.2) and (5.4). In the case of a single site and pure transition in the presence of mixed interactions, the measurements of the antisymmetric part of the intensity tensor—$\boldsymbol{G}_{\alpha\beta}$ vectors—can be realized with the aid of a circularly polarized source. The resultant vector of the sum of $\boldsymbol{G}_{\alpha\beta}$ over excited states is directed along the hyperfine magnetic field. Knowledge of the $\boldsymbol{G}_{\alpha\beta}$ vector and positions of the excited levels allows unique determination of R, η, θ and φ. The measurements of intensities require precision better than R^3 if the quadrupole interaction is small with respect to the magnetic one. The length of the $\boldsymbol{G}_{\alpha\beta}$ vector can be measured in two other ways: as a maximal circular polarization degree or as an invariant of the symmetric part of the intensity tensor in standard measurements. An analytical expression for the line intensity of the powdered absorber is given in equation (6.9) and the 'mirror symmetry' of the spectra present in MCPMS experiments has been explained as a consequence of the time invariance symmetry.

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Appendix A

Let us examine the physical meaning of P. The probability of absorption of the left/right-handed polarized photon is equal to the ζ component of the polarization vector:

$$P_\zeta = \mathrm{Tr}(\rho\sigma_\zeta) \qquad \text{where } \sigma_\zeta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{A.1}$$

and ρ is the density matrix of the photon for given transition [40, 42]. In the considered case the diagonal elements of the matrix ρ are equal to the diagonal elements of the matrix ρ given already in [43]. After simplifications we obtain for the photon direction along $\boldsymbol{\gamma}$

$$P_\zeta = \frac{2\boldsymbol{G}\cdot\boldsymbol{\gamma}}{\mathrm{Tr}\,\hat{\boldsymbol{I}} - \boldsymbol{\gamma}\boldsymbol{I}\boldsymbol{\gamma}^T}. \tag{A.2}$$

When $\boldsymbol{\gamma}$ and $\boldsymbol{G}$ directions coincide, P achieves an extremal value and is proportional to the ratio of the invariants $\boldsymbol{G}$ and $\mathrm{Tr}(I)$:

$$P = \frac{2|\boldsymbol{G}|}{\mathrm{Tr}\,\hat{\boldsymbol{I}}}. \tag{A.3}$$

Appendix B

From the construction of the intensity tensor, equation (3.2), its components are given by a bilinear form with respect to the excited state. Thus the trace can be written as:

$$\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta} = \langle e^\alpha|\hat{T}^\beta|e^\alpha\rangle \tag{B.1}$$

where $\hat{T}^\beta$ is a Hermitian operator acting in the four-dimensional space. Index β runs over two values: $\beta = +1$ corresponding to the higher energy ground state and $\beta = -1$ to the lower energy one. An explicit form of the $\hat{T}^\beta$ operator in the $|I_e, m_e\rangle$ basis is:

$$\hat{T}^\beta = \frac{1}{2}\hat{\mathbf{1}} + \frac{\beta}{4}\begin{bmatrix} -(3c^2-1) & -\sqrt{3}sc\,\mathrm{e}^{-\mathrm{i}\varphi} & 0 & 0 \\ -\sqrt{3}sc\,\mathrm{e}^{\mathrm{i}\varphi} & -c^2 & -2sc\,\mathrm{e}^{-\mathrm{i}\varphi} & 0 \\ 0 & -2sc\,\mathrm{e}^{\mathrm{i}\varphi} & -s^2 & -\sqrt{3}sc\,\mathrm{e}^{-\mathrm{i}\varphi} \\ 0 & 0 & -\sqrt{3}sc\,\mathrm{e}^{\mathrm{i}\varphi} & -(3s^2-1) \end{bmatrix}. \tag{B.2}$$

The symbols s and c are equal to $\sin\theta/2$ and $\cos\theta/2$, respectively, and (θ, φ) denote polar angles of $\boldsymbol{m}$, as in section 2. Using equation (5.1) for $\hat{O} = \hat{T}^\beta$ and $n = 0, 1, 2, 3$ and expressing functions of the angles θ and φ by coefficients of the secular equation (2.2), one arrives at the following linear problem for $\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta}$:

$$\sum_\alpha \mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta} = \frac{3}{2} \tag{B.3}$$

$$\sum_\alpha \lambda_\alpha \,\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta} = \beta\frac{5}{2} \tag{B.4}$$

$$\sum_\alpha \lambda_\alpha^2 \,\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta} = -\frac{1}{4}(3p + \beta q) \tag{B.5}$$

$$\sum_\alpha \lambda_\alpha^3 \,\mathrm{Tr}\,\hat{\boldsymbol{I}}_{\alpha\beta} = \frac{1}{16}(-18q + \beta(64 - 20p + p^2 - 4r)). \tag{B.6}$$

The solution of the above set contains powers of energies higher than three. Each value λ_α^n, $n > 3$ can be reduced to the polynomial of the $(n-2)$th order by applying the secular equation (2.2), namely

$$\lambda_\alpha^n = \lambda_\alpha^{n-4}(-p\lambda_\alpha^2 - q\lambda_\alpha - r) \tag{B.7}$$

which results in an explicit expression for the trace, given by equation (5.2).

Similarly, component G_{ab}^t of the vector $\boldsymbol{G}_{\alpha\beta}$, where $t = x, y, z$, is in bilinear form with respect to the both excited and ground states. Thus the component can be regarded as

$$G_{\alpha\beta}^t = \langle e^\alpha|\hat{G}_t^\beta|e^\alpha\rangle. \tag{B.8}$$

Replacing the $\hat{O}$ operator in (5.1) by $\hat{G}_t^\beta$ one arrives at another linear problem:

$$\sum_\alpha \boldsymbol{G}_{\alpha\beta} = -\frac{1}{4}\beta\boldsymbol{m} \tag{B.9}$$

$$\sum_\alpha \lambda_\alpha\boldsymbol{G}_{\alpha\beta} = -\frac{1}{4}[5\cdot\hat{\mathbf{1}} + 2\beta\hat{\boldsymbol{\Phi}}]\boldsymbol{m} \tag{B.10}$$

$$\sum_\alpha \lambda_\alpha^2\boldsymbol{G}_{\alpha\beta} = -\frac{1}{8}[\beta(16-p)\cdot\hat{\mathbf{1}} + 16\hat{\boldsymbol{\Phi}}]\boldsymbol{m} \tag{B.11}$$

$$\sum_\alpha \lambda_\alpha^3\boldsymbol{G}_{\alpha\beta} = \frac{1}{8}[(7p - 12 + 2\beta q)\cdot\hat{\mathbf{1}} - 2\beta(16-p)\hat{\boldsymbol{\Phi}} - 16\hat{\boldsymbol{\Phi}}\cdot\hat{\boldsymbol{\Phi}}]\boldsymbol{m}. \tag{B.12}$$

Solution of (B.9)–(B.12) results in equation (5.3). The explicit expression for the scalar $|\boldsymbol{G}_{\alpha\beta}|^2$ reads:

$$|\boldsymbol{G}_{\alpha\beta}|^2 = \frac{1}{1024w_\alpha^2}\left(\sum_{k=0}^{3} a_{k,\alpha\beta}\lambda_\alpha^k + 64(1-\eta^2)R^3(32\lambda_\alpha - q + 4\beta(2\lambda_\alpha^2 + p + 16))\right) \tag{B.13}$$

where

$$\begin{aligned} a_{0,\alpha\beta} &= (p^2 + 20p + 64)^2 - 8r(p^2 + 20p - 2r + 392) + 12\beta q(p^2 + 32p + 12r + 256) \\ a_{1,\alpha\beta} &= -8q(p^2 + 8p - 4r + 272) + 24\beta(p+4)(p+8)(p+16) + 16\beta(9q^2 - 6pr - 136r) \\ a_{2,\alpha\beta} &= 16(14p^2 + q^2 + 32p - 56r + 704) + 32\beta q(3p - 44) \\ a_{3,\alpha\beta} &= -640q + 16\beta(3p^2 + 16p - 12r + 416). \end{aligned} \tag{B.14}$$

Similar calculations for $\hat{\boldsymbol{I}}^{(s)}_{\alpha\beta}$ yield:

$$\sum_{\alpha} \hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} = \frac{1}{2} \cdot \hat{\mathbf{1}} \tag{B.15}$$

$$\sum_{\alpha} \hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} \lambda_\alpha = \beta \hat{\mathbf{1}} - \frac{1}{2}\hat{\boldsymbol{\Phi}} - \beta \frac{1}{2} \hat{\boldsymbol{F}}_0 \tag{B.16}$$

$$\sum_{\alpha} \hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} \lambda_\alpha^2 = \frac{1}{8}(8 - \beta q - 2p) \cdot \hat{\mathbf{1}} - \beta \hat{\boldsymbol{\Phi}} - 3\hat{\boldsymbol{F}}_0 - \beta \hat{\boldsymbol{F}}_1 \tag{B.17}$$

$$\sum_{\alpha} \hat{\boldsymbol{I}}^{(s)}_{\alpha\beta} \lambda_\alpha^3 = \frac{1}{32}(\beta(p^2 + 16^2 - 4r) - 16q) \cdot \hat{\mathbf{1}} + \frac{1}{4}(p-4)\hat{\boldsymbol{\Phi}} + 2\beta\hat{\boldsymbol{\Phi}}^2 \\ - \frac{1}{2}\beta(9-p)\hat{\boldsymbol{F}}_0 - 3\hat{\boldsymbol{F}}_1 - 2\beta\hat{\boldsymbol{F}}_2 \tag{B.18}$$

where $\hat{\boldsymbol{F}}_1$ are symmetric tensors defined as tensor products of vectors:

$$\begin{aligned} \hat{\boldsymbol{F}}_0 &= \boldsymbol{m} \otimes \boldsymbol{m} \\ \hat{\boldsymbol{F}}_1 &= \boldsymbol{m} \otimes \hat{\boldsymbol{\Phi}} \cdot \boldsymbol{m} + \hat{\boldsymbol{\Phi}} \cdot \boldsymbol{m} \otimes \boldsymbol{m} \\ \hat{\boldsymbol{F}}_2 &= \hat{\boldsymbol{\Phi}} \cdot \boldsymbol{m} \otimes \hat{\boldsymbol{\Phi}} \cdot \boldsymbol{m}. \end{aligned} \tag{B.19}$$

From equations (B.15)–(B.18) the symmetric part of the intensity tensor (5.4) is obtained.

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