Separation of hyperfine interactions in Mössbauer spectroscopy

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Abstract
Problem of determination of isomer shift, all components of the electric field gradient and hyperfine magnetic field in case of mixed hyperfine interactions is presented. Orientation of hyperfine fields in the absorber Cartesian frame can be determined by few measurements with use of unpolarized radiation under different directions of wave vector with respect to the absorber. The method can be applied for absorbers with well separated absorption lines in their spectra. Explicit formulas for tensor components of hyperfine interactions derived from velocity moments formalism are presented.

Keywords  Hyperfine magnetic field · Electric field gradient · The intensity tensor · Hyperfine interactions · Mössbauer spectroscopy

1 Introduction

Determining the hyperfine parameters from the Mössbauer spectrum has been widely discussed in the literature, and it is known that all parameters cannot be determined from a spectra of texture-free samples [1]. Only three independent invariants and the hyperfine magnetic field (hmf) can be determined. How to determine all parameters from the spectrum of a single crystal by using polarized radiation [2, 3] or application of external magnetic field [4, 5] has been already presented; use of unpolarized radiation has been discussed fully quite recently [6].

We show how to separate isomer shift, components of the electric field gradient (efg) tensor and components of the hmf pseudovector by measurements on a single site absorber with a few different directions of the wave vector of the photon with respect to the absorber frame. Explicit form of hyperfine interactions is performed within the intensity tensor formalism [7–9] and the concept of the
velocity moments [10]. Presented considerations are valid for nuclear transitions between nuclear levels with spin 3/2 and 1/2.

2 Separation of the hyperfine interactions

In the thin-absorber approximation, single site spectrum can be considered as set of absorption lines with amplitudes $A_{\alpha\beta}$ located at velocities $v_{\alpha\beta}$. Index $\alpha$ corresponds to four excited states while $\beta$ to the two nuclear ground states. The $n$th velocity moment of the spectrum, having dimension of velocity to the power of $n$ is defined as:

$$W^n_\zeta = p\sum_{\alpha\beta} v^n_{\alpha\beta} A_{\alpha\beta} \zeta,$$

$$p^{-1} = \frac{\sum_{\alpha\beta} A_{\alpha\beta} \zeta}{C_1} \left( \frac{1}{C_1} \right).$$

The explicit form of the moments of the spectra were given in [10] and for the purposes of our analysis we need only:

$$W^1 = \delta + \frac{1}{8} a \kappa \cdot V \cdot \kappa,$$

$$W^2 = \frac{1}{4} \left( \gamma^2_{1/2} - 3\gamma_{1/2} \gamma_{3/2} + 4\gamma^2_{3/2} \right) B^2 - \frac{1}{4} \gamma_{3/2} \left( \gamma_{1/2} - 3\gamma_{3/2} \right)$$

$$B^2 (m \cdot \kappa)^2 + \frac{1}{4} a \delta \kappa \cdot V \cdot \kappa + \delta^2 + \frac{1}{24} a \text{Tr} V^2.$$

where $a = e Q c / E$ is a proportionality constant between the efg components (in $[\text{V/m}^2\text{SI units}]$) and the velocity (in $[\text{mm/s}]$). $Q$ is the nuclear quadrupole moment of the excited state, and $e$ is the elementary charge (positive value). Numerical value $a = 3.4\cdot10^{-22}$ mm/s-m$^2$/V, $\gamma_{1/2} = 0.118821$ mm/s/T, $\gamma_{3/2} = -0.1035441$ mm/s/T [10]. $V$ is the electric field gradient (efg) and $\delta$ the isomers shift. Unit vectors $m$ and $\kappa$ are parallel to the hyperfine magnetic field ($hmf$) pseudovector $B$ and the wave vector of photon $k$, respectively.

The $n$th moment depend of the $hmf B$, efg $V$, and the isomer shift $\delta$ - the microscopic values which we would like to determine, and on the orientation of the beam with respect to the absorber $\kappa$. The last value depend on the experimental condition and in principle may have any orientation.

We will show that by arranging relatively small number measurements with different orientation of $\kappa$, all components of $hmf B$, efg $V$, and the isomer shift $\delta$ can be extracted from eqs. (2), (3). To do so let us introduce the absorber frame, which is a Cartesian frame fixed to the axes of a holder of our single site crystal, see Fig. 1. We will call it $suvw$ frame. For measurement with wave vector of photon $k$ parallel to the $(hkl)$ direction in the $suvw$ frame the moments (1) will be abbreviated explicitly by $W^1_{hkl}$ and $W^2_{hkl}$.

So called texture free spectra can be obtained by averaging of three measurements performed with $k$ vector parallel to (100), (010) and (001) directions. Moments corresponding to these averages will be abbreviated by index $tf$ (texture free):

$$W^n_{tf} = \frac{1}{3} (W^n_{100} + W^n_{010} + W^n_{001}).$$

Because efg tensor $V$ is traceless, the first velocity moment (1) for texture free spectrum is equal to the isomer shift.
Diagonal components of \( efg \) tensor \( V_{ij} \) in the absorber frame \( suw \) (Fig. 1) can be obtained by combination of (2) and (4) in with \( k \) vector parallel to (100), (010) and (001) directions:

\[
\begin{align*}
V_{ss} &= \frac{8}{a} \left( W_{100}^{l} - W_{100}^{g} \right), \\
V_{uu} &= \frac{8}{a} \left( W_{010}^{l} - W_{010}^{g} \right), \\
V_{ww} &= \frac{8}{a} \left( W_{001}^{l} - W_{001}^{g} \right). \\
\end{align*}
\]

Off-diagonal components of \( V_{ij} \) are:

\[
\begin{align*}
V_{su} &= \frac{4}{a} \left( 2W_{110}^{l} - W_{100}^{l} - W_{010}^{l} \right), \\
V_{sw} &= \frac{4}{a} \left( 2W_{101}^{l} - W_{100}^{l} - W_{001}^{l} \right), \\
V_{uw} &= \frac{4}{a} \left( 2W_{011}^{l} - W_{010}^{l} - W_{001}^{l} \right). \\
\end{align*}
\]
Eqs (6) and (7) allows calculation of any property of the efg tensor $V$ since all its components $V_{ij}$ in $suw$ frame are known. In particular by estimating $\text{Tr}V^2$ from (6) and (7) and averaging (3) for texture-free absorber one get explicit form for the $hmf B$:

$$
B^2 = \frac{24W_{t}^2-24\left(W_{t}^1\right)^2-a^2\text{Tr}V^2}{6\gamma_1^2-20\gamma_1^2\gamma_3^2/2 + 30\gamma_3^2}.
$$

(8)

To have all hyperfine interactions separated, we need to find orientation of the $hmf B$: in the $suw$ frame. In [6] we have shown, that

$$
(m . \kappa)^2 = \frac{1}{3} \frac{4}{\gamma_3^2/2 \left(\gamma_1/2 - 3\gamma_3/2\right)} \left(\frac{W^2-W_{t}^2-2W_{t}^1\left(W^1-W_{t}^1\right)}{B^2}\right).
$$

(9)
Let us abbreviate right hand side of eq. (9) by $w_{hkl}$, where $\kappa$ is parallel to $(hkl)$ direction. Thus $(m \cdot \kappa)^2 = w_{hkl}$ and $\kappa \parallel (hkl)$. Combining (9) for $\kappa$ vector parallel to (100), (010), (001), (110), (101) and (011) directions in $suw$ frame, we get all components $m_i m_j$ of the $m \otimes m$ tensor:

$$
\begin{align*}
    m_x m_y &= w_{100},
    m_u m_u = w_{010},
    m_w m_w = w_{001},
    \\
    m_x m_u &= \frac{1}{2} (w_{110} - w_{100} - w_{010}),
    \\
    m_x m_w &= \frac{1}{2} (w_{101} - w_{100} - w_{001}),
    \\
    m_u m_w &= \frac{1}{2} (w_{011} - w_{010} - w_{001}).
\end{align*}
$$

By standard diagonalization of (10) one can get direction of axis to which $hmf$ $B$ is parallel. Slightly different, equivalent treatment is presented in [6] Sign of the $B$ pseudovector cannot be determined by these type of measurement, unless circularly polarized radiation is used.

### 3 Toward experiments

Experiments demonstrating separation of hyperfine interactions have not been performed yet. In Fig. 2 We show results of simulations of the lines positions and intensities under orientations of $k$ vector considered in the text. Since measurements needs to performed in six directions, (100), (010), (001), (110), (101) and (011), we propose dedicated for this type of experiment sample holder (Fig. 3).

### 4 Summary

We have shown, that by measurement of the velocity moments under at least six orientations of the photon beam, one is able to separate hyperfine interactions and obtain isomer shift, all components of the $efg$ and $hmf$ in the arbitrary chosen reference frame. Explicit forms are given in eqs. (5–8) and (10).

The characteristic feature and advantage of the method discussed here is that one does not need perform any orientation of the single-crystal absorber. The absorber plate should be thin enough to be partially transparent for $\gamma$ radiation used in Mössbauer spectroscopy.

A holder suitable for measurements with required orientation is presented.
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