Separation of hyperfine interactions in Mössbauer spectroscopy

Krzysztof R. Szymański¹

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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

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✉ Krzysztof R. Szymański
k.szymanski@uwb.edu.pl

¹ Faculty of Physics, University of Białystok, Ciołkowskiego 1L, 15-245 Białystok, Poland

2 Separation of the hyperfine interactions

$$W_{\zeta}^n = p \sum_{\alpha\beta} v_{\alpha\beta}^n A_{\alpha\beta\zeta}, \quad p^{-1} = \sum_{\alpha\beta} A_{\alpha\beta\zeta}. \quad (1)$$
$$W^1 = \delta + \frac{1}{8} a \kappa \cdot V \cdot \kappa, \quad (2)$$

$$W^2 = \frac{1}{4} \left(\gamma_{1/2}^2 - 3\gamma_{1/2}\gamma_{3/2} + 4\gamma_{3/2}^2 \right) B^2 - \frac{1}{4} \gamma_{3/2} \left(\gamma_{1/2} - 3\gamma_{3/2} \right) B^2 + \frac{1}{4} a \delta \boldsymbol{\kappa} \cdot \mathbf{V} \cdot \boldsymbol{\kappa} + \delta^2 + \frac{1}{24} a \text{Tr} \mathbf{V}^2. \quad (3)$$

We will show that by arranging relatively small number measurements with different orientation of κ , all components of $hmf \mathbf{B}$, $efg \mathbf{V}$, and the isomer shift δ 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 suw frame. For measurement with wave vector of photon $\mathbf{k}$ parallel to the (hkl) direction in the suw frame the moments (1) will be abbreviated explicitly by W_{hkl}^1 and W_{hkl}^2 .

$$W_{if}^n = \frac{1}{3} (W_{100}^n + W_{010}^n + W_{001}^n). \quad (4)$$
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Fig. 1 (a) Principal axes system of an electric field gradient (V_x , V_y , V_z) and an absorber frame axes (s , u , w); wave vector of photon (k) and hmf (B) are shown. Absorber is rigidly connected with both frames. Different orientations of k vector are controlled during experiments by angles Θ and ϕ , and its direction is abbreviated by hkl Miller indices with respect to the suw frame

$$W_{if}^1 = \delta. \quad (5)$$

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:

$$\begin{aligned} V_{ss} &= \frac{8}{a} (W_{100}^1 - W_{if}^1), \\ V_{uu} &= \frac{8}{a} (W_{010}^1 - W_{if}^1), \\ V_{ww} &= \frac{8}{a} (W_{001}^1 - W_{if}^1). \end{aligned} \quad (6)$$

Off-diagonal components of V_{ij} are:

$$\begin{aligned} V_{su} &= \frac{4}{a} (2W_{110}^1 - W_{100}^1 - W_{010}^1), \\ V_{sw} &= \frac{4}{a} (2W_{101}^1 - W_{100}^1 - W_{001}^1), \\ V_{uw} &= \frac{4}{a} (2W_{011}^1 - W_{010}^1 - W_{001}^1). \end{aligned} \quad (7)$$

Fig. 2 Line positions and intensities shown schematically by bar diagrams for the Mössbauer spectra generated for various orientation of the $\mathbf{k}$ vector. Directions of $\mathbf{k}$ in the suw frame are shown by integers. Abbreviation tf (texture free) indicates bar diagram resulting from averaging of spectra simulated with $\mathbf{k}$ along (100), (010), and (001) directions

Eqs (6) and (7) allows calculation of any property of the efg tensor $\mathbf{V}$ since all its components V_{ij} in suw frame are known. In particular by estimating $\text{Tr}\mathbf{V}^2$ from (6) and (7) and averaging (3) for texture-free absorber one get explicit form for the hmf $\mathbf{B}$:

$$B^2 = \frac{24W_{tf}^2 - 24(W_{tf}^1)^2 - a^2 \text{Tr}\mathbf{V}^2}{6\gamma_{1/2}^2 - 20\gamma_{1/2}\gamma_{3/2} + 30\gamma_{3/2}^2}. \quad (8)$$

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

$$(\mathbf{m} \cdot \boldsymbol{\kappa})^2 = \frac{1}{3} - \frac{4}{\gamma_{3/2}(\gamma_{1/2} - 3\gamma_{3/2})B^2} \left(W^2 - W_{tf}^2 - 2W_{tf}^1(W^1 - W_{tf}^1) \right). \quad (9)$$

Fig. 3 Sample holder for measurements of flat samples under directions considered in the text. Holder is a cube (a) divided by two halves (b). A flat absorber is mounted between the halves at the center of the cube. Radiation passes through the holes on the edges or faces. Three edges of the cube can be considered as suw frame (see text and fig. 1)

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

$$\begin{aligned} m_s m_s &= w_{100}, m_u m_u = w_{010}, m_w m_w = w_{001}, \\ m_s m_u &= \frac{1}{2}(w_{110} - w_{100} - w_{010}), \\ m_s m_w &= \frac{1}{2}(w_{101} - w_{100} - w_{001}), \\ m_u m_w &= \frac{1}{2}(w_{011} - w_{010} - w_{001}). \end{aligned} \quad (10)$$

By standard diagonalization of (10) one can get direction of axis to which $hmf \mathbf{B}$ is parallel. Slightly different, equivalent treatment is presented in [6] Sign of the $\mathbf{B}$ 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 $\mathbf{k}$ 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 γ radiation used in Mössbauer spectroscopy.

A holder suitable for measurements with required orientation is presented.

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