

Ambiguity Problem in Analyzing Mössbauer Spectra

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Abstract

The Mössbauer parameters, H_{hf} , $eV_{z'z'}Q$, η , θ_H and ϕ_H defined in the text are related to the eigen values of an Fe^{57} nucleus in analytical forms. The ambiguity problem arising in analyses of powder spectra is discussed. It is also shown that intensities of powder spectra do not give any information to reduce the ambiguity.

§ 1. Introduction.

For the case of Fe^{57} nuclei exposed to simultaneously magnetic fields and electric field gradients, a unique set of parameters can not be determined from a Mössbauer spectrum obtained for a powder sample. In general, an infinite number of sets of parameters appearing in the restricted range of values gives the same line positions. In addition, those sets give the same line intensities for powder spectra. This ambiguity problem was pointed out first by Karyagin in 1966¹⁾ and by Dabrowski in 1971²⁾. However, parameter fitting procedures by numerical calculation with the aid of computers have widely been used, and the attention to the problem has been turned aside and the problem has been not widely recognized for a long time. Recently, van Dongen Torman et al. have emphasized the importance of this problem and have given the detail in another analytical expression than the others³⁾. Independently, we have also tried to solve the problem by an analytical treatment and have got different and more convenient expressions for analyses of powder spectra.

§ 2. Interaction Hamiltonian and coordinate system.

The Hamiltonians of the magnetic dipole and the electric quadrupole interaction for a nucleus with spin I in magnetic fields (H_{hf}) and electric field gradients (EFG) are expressed in conventional notations as follows,

$$H_g = -g_g \mu_N H_{hf} I_{gz} \quad \text{for } I_g = \frac{1}{2}, \quad (1)$$

$$H_e = -g_e \mu_N H_{hf} I_{ez} + \frac{eV_{z'z'}Q}{4I(2I-1)} [3I_{ez}^2 - I_e(I_e+1) + \eta(I_{ez'}^2 - I_{ey'}^2)]$$

$$\text{for } I_e = \frac{3}{2}, \quad (2)$$

where

$$\eta = \frac{V_{x'x'} - V_{y'y'}}{V_{z'z'}}, \quad |V_{z'z'}| \geq |V_{y'y'}| \geq |V_{x'x'}|,$$

and the quantities corresponding to the ground state are indexed by g and those corresponding to the excited state by e . x' , y' and z' are the principal axes of the EFG tensor and z is chosen as being parallel to H_{hf} . The direction of H_{hf} and that of the principal axes of the EFG tensor are related by polar angles θ_H and ϕ_H as shown in Fig. 1. The eigen values obtained from the Hamiltonian (2) depend on the five parameters of H_{hf} , $eV_{z'z'}$, Q , η , θ_H and ϕ_H , but those from the Hamiltonian (1) on only H_{hf} . Energy levels in a general case are shown in Fig. 2.

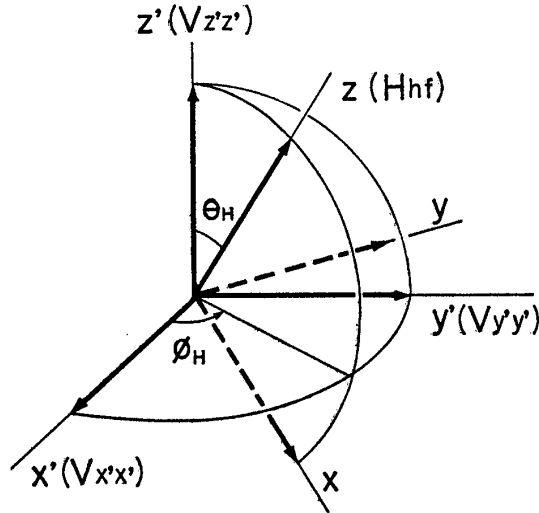


Fig. 1. The relation between the direction of H_{hf} and the principal axes of the EFG tensor. The x, y, z magnetic field coordinate system is also defined.

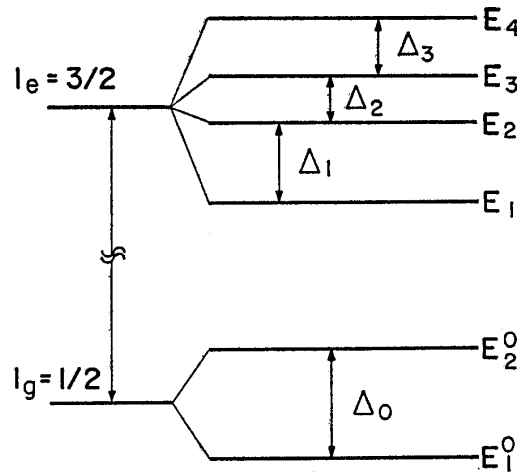


Fig. 2. Energy levels of the ground state with $I_g=1/2$ and the excited state with $I_e=3/2$ lifted by magnetic fields and electric field gradients.

From the line positions of an observed spectrum four independent values of Δ_0 , Δ_1 , Δ_2 and Δ_3 are determined. It is clear that using these four values a unique set of five parameters, H_{hf} , $eV_{z'z'Q}$, η , θ_H and ϕ_H can not generally be determined. The ambiguity problem results from this fact.

For an analytical treatment of the problem the same coordinate system must be used for H_{hf} and the EFG tensor. In many cases has been used the coordinate system coinciding with the principal axes of the EFG tensor which makes the matrix elements for the state with $I_e=3/2$ simple. In the present case, however, the magnetic field coordinate system has much advantage in calculation of the line intensities as shown later. The x axis can be arbitrary in the plane perpendicular to the z axis. Here, it is chosen to be perpendicular to the z axis in a zz' plane and the y axis is settled automatically. The x, y, z system is shown in Fig. 1.

§ 3. Analytical treatment.

For the ground state with $I_g=1/2$, the eigen values are easily calculated from the Hamiltonian (1) and the well known value of the splitting Δ_0 is obtained:

$$\Delta_0 = g_g \mu_N H_{hf}.$$

The value of H_{hf} is separately determined from this ground state splitting Δ_0 , since the value of g_g has already been known from other experiments. Thus, the ambiguity problem is reduced to that among the four parameters, $eV_{z'z'Q}$, η , θ_H , ϕ_H , the relation among which is obtained from the excited state splittings, Δ_1 , Δ_2 , Δ_3 , or the eigen values E_1 , E_2 , E_3 , E_4 . For the excited state with $I_e=3/2$, the matrix of the Hamiltonian (2) is written on the basis of $|I_e=3/2, m\rangle$ and in a unit of $g_e \mu_N H_{hf}$.

$$\left\langle I_e = \frac{3}{2}, m \left| H_e \right| I_e = \frac{3}{2}, m \right\rangle = \begin{bmatrix} \alpha + \frac{3}{2} & \beta & \gamma & 0 \\ \bar{\beta} & -\alpha + \frac{1}{2} & 0 & \gamma \\ \bar{\gamma} & 0 & -\alpha - \frac{1}{2} & -\beta \\ 0 & \bar{\gamma} & -\bar{\beta} & \alpha - \frac{3}{2} \end{bmatrix} \quad (3)$$

where

$$\alpha \equiv \frac{3}{4} \lambda (2 - 3 \sin^2 \theta_H + \eta \sin^2 \theta_H \cos 2\phi_H), \quad (4)$$

$$\beta \equiv \frac{\sqrt{3}}{2} \lambda (-3 + \eta \cos 2\phi_H) \sin \theta_H \cos \theta_H - i \frac{\sqrt{3}}{2} \lambda \eta \sin \theta_H \sin 2\phi_H, \quad (5)$$

$$\gamma \equiv \frac{\sqrt{3}}{4} \lambda \{3 \sin^2 \theta_H + \eta \cos 2\phi_H (2 - \sin^2 \theta_H)\} - i \frac{\sqrt{3}}{2} \lambda \eta \cos \theta_H \sin 2\phi_H, \quad (6)$$

and

$$\lambda \equiv \frac{\frac{1}{2}eV_{z'z'}Q}{3g_e\mu_N H_{hf}}.$$

Hereafter, λ is used instead of $eV_{z'z'}Q$. From the secular equation formed from the matrix (3) the following equation is obtained:

$$E^4 - 2\left(\alpha^2 + |\beta|^2 + |\gamma|^2 + \frac{5}{4}\right)E^2 - 4\alpha E + \alpha^4 + 2\alpha^2(|\beta|^2 + |\gamma|^2) + (|\beta|^2 + |\gamma|^2)^2 - \frac{5}{2}\alpha^2 - \frac{3}{2}(|\beta|^2 - |\gamma|^2) + \frac{9}{16} = 0. \quad (7)$$

Although the four roots of the above equation can not be obtained in analytical forms, there are the following relations between the set of eigen values (the roots) and that of absolute values of the matrix elements, namely between (E_1, E_2, E_3, E_4) and $(\alpha, |\beta|^2, |\gamma|^2)$.

$$\left. \begin{aligned} \alpha &= \frac{1}{4} \sum_{\langle ijk \rangle} E_i E_j E_k, \\ \alpha^2 + |\beta|^2 + |\gamma|^2 &= \frac{1}{4} \left(\sum_{i=1}^4 E_i^2 - 5 \right), \\ \alpha^4 + 2\alpha^2(|\beta|^2 + |\gamma|^2) + (|\beta|^2 + |\gamma|^2)^2 - \frac{5}{2}\alpha^2 - \frac{3}{2}(|\beta|^2 - |\gamma|^2) + \frac{9}{16} &= E_1 E_2 E_3 E_4 \end{aligned} \right\}. \quad (8)$$

These relations are very useful to get the absolute values of the matrix elements from the observed spectra and to gain an insight into the ambiguity problem. From the analysis of an observed spectrum, E_1, E_2, E_3 and E_4 are obtained using the values of A_1, A_2 and A_3 and a traceless condition of $E_1 + E_2 + E_3 + E_4 = 0$. Therefore, $\alpha, |\beta|^2$ and $|\gamma|^2$ can be obtained as solutions of the simultaneous equations (8). The values of $\alpha, |\beta|^2$ and $|\gamma|^2$ thus obtained from the observed spectra are realized generally by an infinite number of sets of parameters, $(\lambda, \eta, \theta_H, \phi_H)$. Fortunately, the relations between a set of given values of $(\alpha, |\beta|^2, |\gamma|^2)$ and the values of λ, η, θ_H and ϕ_H are found in rather simple forms:

$$\frac{9}{4}\lambda^2\left(1 + \frac{\eta^2}{3}\right) = \alpha^2 + |\beta|^2 + |\gamma|^2, \quad (9)$$

$$\sin^2 \theta_H = \frac{1}{\eta^2 - 9} \left(\frac{16\alpha^2}{9\lambda^2} + \frac{4|\beta|^2}{3\lambda^2} + \frac{8\alpha}{3\lambda} - 8 \right), \quad (10)$$

$$\cos 2\phi_H = \frac{1}{\eta \sin^2 \theta_H} \left(\frac{4\alpha}{3\lambda} + 3 \sin^2 \theta_H - 2 \right). \quad (11)$$

A value of λ can be calculated easily if a value of η is fixed in the equation (9), and vice versa. Successively, the corresponding values of θ_H and ϕ_H are obtained from the equations (10) and (11). Values of an asymmetry parameter η can be restricted to a range of $0 \leq \eta \leq 1$ without any loss of generality. When η changes from 0 to 1 in the equation (9), the corresponding value of λ changes only about 15%. Therefore, λ is restricted to a small range of values from line positions of observed

spectra through the equation (9). In order to get allowed sets of the parameters for the given values of $(\alpha, |\beta|^2, |\gamma|^2)$, a practical way is to calculate the values of λ , θ_H and ϕ_H as functions of η under the conditions of $0 \leq \eta \leq 1$, $0 \leq \sin \theta_H \leq 1$ and $|\cos 2\phi_H| \leq 1$. For some spectra the values of the parameters explaining them appear in a very narrow range. Exceptionally, there are four spectra for each of which a unique set of parameters can be determined from the line positions. Conversely speaking, if an observed spectrum can be fitted with one of the following sets of parameters, that is the unique solution for it.

- I. $\theta_H = 0^\circ$, λ and η have no restriction.
- II. $\theta_H = 90^\circ$, $\phi_H = 0^\circ$, λ and η have no restriction.
- III. $\theta_H = 90^\circ$, $\phi_H = 90^\circ$, λ and η have no restriction.
- IV. $\theta_H = 90^\circ$, $\eta = 0$ λ has no restriction.

Each of the four cases is derived under the condition that one of the matrix elements, $|\beta|^2$, vanishes. The cases I, II and III correspond to situations that the direction of H_{hf} is parallel to one of the principal axes of the EFG tensor. The case IV corresponds to situations that the field gradient is axially symmetric and the direction of H_{hf} is in a plane perpendicular to the symmetric axis. In this case x' and y' axes can be chosen arbitrary in the plane and ϕ_H is meaningless.

§ 4. Line intensities.

In the magnetic field coordinate system used here, the eigen functions of the ground state with $I_g = 1/2$ are always $|I_g = 1/2, -1/2\rangle$ and $|I_g = 1/2, 1/2\rangle$ independently of the values of parameters H_{hf} , $eV_{zz'}/Q$, η , θ_H and ϕ_H . Therefore only eigen functions for the excited state with $I_e = 3/2$ come into question. The eigen function ϕ_i of the sub-level with the eigen value E_i is

$$\phi_i = \sum_{m=-3/2}^{3/2} a_i^m |I_e = \frac{3}{2}, m\rangle.$$

Coefficients a_i^m are functions of the matrix elements and the eigen value E_i , and usually complex numbers:

$$a_i^m = f^m(\alpha, \beta, \bar{\beta}, \gamma, \bar{\gamma}, E_i). \quad (12)$$

For powder samples incident γ -rays are averaged over all directions, so transition probabilities are determined by absolute values of coefficients, $|a_i^m|^2$. It is known from the equation (12) that $|a_i^m|^2$ depends only on α , $|\beta|^2$, $|\gamma|^2$ and E_i , namely on the absolute values of the matrix elements and the eigen value. This fact means that the sets of parameters resulting in the same values of α , $|\beta|^2$ and $|\gamma|^2$ give the same powder spectra including intensities. Therefore the ambiguity can not be removed even though the intensities of powder spectra are taken into consider-

ation.

To determine a unique set of parameters explaining the situation realized in the material in question, the intensity ratio of Mössbauer spectra must be observed for single crystal samples as the function of the direction of incident γ -rays, except for the special cases I~IV mentioned in § 3. We would like to point out that there is one special direction of incident γ -rays not to reduce the ambiguity problem. When the direction of incident γ -rays is chosen to be parallel to that of H_{hf} ($\theta_\gamma = \theta_H$, $\phi_\gamma = \phi_H$)*, the transition probability depends on only $|a_i^m|^2$, namely on the absolute value of the matrix elements, α , $|\beta|^2$, $|\gamma|^2$. Therefore, to determine a unique set of parameters from intensity measurements using single crystals must be used other directions of incident γ -rays than that specified by $\theta_\gamma = \theta_H$ and $\phi_\gamma = \phi_H$.

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* A direction of incident γ -rays is defined by polar angles θ_γ and ϕ_γ relative to the principal axes of the EFG tensor.