PHYSICAL REVIEW B VOLUME 25, NUMBER 1 1 JANUARY 1982

Mössbauer spectra in the presence of spin-phonon relaxation effects: Symmetry restrictions

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(Received 4 November 1980; revised manuscript received 22 May 1981)

The problem of evaluating the Mössbauer line shape in the presence of ion-phonon interactions has been considered. By means of a perturbation procedure it is shown how a limited number of matrix elements of the relaxation operator are relevant. Moreover, the restrictions imposed by the symmetry are also taken into account. In the case of Fe^{3+} in C_3 symmetry one has to diagonalize a 288×288 matrix. By taking into account the results obtained in this paper we have reduced the problem of deriving the line shape of the Mössbauer spectrum to that of diagonalizing three matrices of dimensions 16, 16, and 15.

I. INTRODUCTION

In recent years the theory of Mössbauer resonance spectra in relaxing systems has been considered by a number of authors.[1-12] In the case of ion-phonon interactions, which cannot be studied by means of simple stochastical models,[13] extremely complex computations can be required. In this paper we present a contribution to the theory which has the following advantages:

(1) It is shown how a limited number of matrix elements of the relaxation operator are relevant.

(2) The restrictions imposed by the symmetry of the complex consisting of the Mössbauer atom plus its nearest neighbors are taken explicitly into account.

In this way one can greatly reduce the dimension of the matrix of the relaxation operator so that the computations can be performed more quickly. As an application we consider the case of Fe^{3+} in C_3 symmetry.

II. SUMMARY OF THE GENERAL THEORY

The starting point of our analysis is the formal expression for the emission spectrum. By assuming that the statistical operator can be written as a product of an atomic operator ρ_A and a lattice operator ρ_L, one finds[6]

$$I(\omega,\vec{k})=\frac{2}{\Gamma}\mathrm{Re}\ \mathrm{Tr}_A[\rho_A H G(p) H^\dagger]\ , \tag{1}$$

where $p=\Gamma/2-i\omega$ (Γ is the Mössbauer linewidth and ω is the energy of the γ quantum), H is the multipole operator associated with the Mössbauer transition, and $G(p)$ is the Liouville operator

$$G(p)=[p-iL_A+R(p)]^{-1}\ , \tag{2}$$

where L_A is the Liouville operator corresponding to the atomic Hamiltonian and $R(p)$ is the relaxation operator. Its explicit form can be obtained by making use of the procedure outlined in Ref. 14:

$$\begin{aligned}R(p)= & \,PL_1(1-P)[p-i(1-P)L]^{-1}\\ & \times(1-P)L_1P\ ,\end{aligned} \tag{3}$$

where P is a projection operator which denotes the taking of the trace over the variables of the lattice, $P=\mathrm{Tr}_L(\rho_L\cdots)$, and L and L_1 are the Liouville operators corresponding to the total and ion-phonon interaction Hamiltonians, respectively.

For our purposes it is convenient to assume basis states of the form $|\Gamma_1^\sigma\rangle\,|\mathrm{Im}\rangle$, where $|\Gamma_i^\sigma\rangle$ denote the eigenstates of the spin Hamiltonian which transform as the irreducible representation Γ_i of the symmetry point group of the Mössbauer atom and $|\mathrm{Im}\rangle$ are eigenstates of the nucleus. By assuming that the hyperfine states arising from a given electronic level Γ_i and a nuclear one I are equally populated, Eq. (1) can be rewritten as

$$I(\omega,\vec{\mathrm{k}})=\frac{2}{\Gamma}\frac{1}{2I_1+1}\mathrm{Re}\sum_{\substack{m_0,m_0'\\ m_1,m_1'}}\langle m_1\,|\,H\,|\,m_0\rangle\langle m_0'\,|\,H^\dagger\,|\,m_1'\rangle\sum_{\substack{i,\alpha\\ j,\beta}}p_i\langle\Gamma_i^\alpha m_0,\Gamma_i^\alpha m_1\,|\,(p-iL_A+R)^{-1}\,|\,\Gamma_j^\beta m_0',\Gamma_j^\beta m_1'\rangle\,, \tag{4}$$

where the p_i's denote the occupation probability for the electronic states Γ_i. Therefore, it is seen that in order to derive the shape of the Mössbauer spectra one must compute the matrix of the operator $p-iL_A+R(p)$ and invert it. The dimension of this matrix is $(2S+1)^2(2I_e+1)(2I_g+1)$, where S denotes the electronic spin of the Mössbauer atom and I_e and I_g denote the spin of the nucleus in the excited state and in the ground state, respectively. In the case of Fe^{3+} the dimension of the matrix is 288×288.

We will show that a limited number of matrix elements are relevant for the calculation of the line shape, so that one can consider only a submatrix of the entire matrix of the operator $p-iL_A+R(p)$. This is a consequence of the fact that hyperfine and ion-phonon interaction energies are, in general, much smaller than the energy differences between electronic levels.

In order to prove this statement let us start from the power-series expansion (with the position $L_A=L_0+L_{\mathrm{hp}}$, where L_{hp} is the Liouville operator corresponding to the hyperfine Hamiltonian):

$$(p-iL_0-IL_{\mathrm{hp}}+R)^{-1}=(p-iL_0)^{-1}+(p-iL_0)^{-1}[\,-(-iL_A+R)+(-iL_A+R)(p-iL_0)^{-1}(-iL_A+R)+\cdots\,](p-iL_0)^{-1}\,. \tag{5}$$

The operator $(p-iL_0)^{-1}$ possesses only diagonal matrix elements:

$$\langle\Gamma_i^\alpha m_0,\Gamma_j^\beta m_1\,|\,(p-iL_0)^{-1}\,|\,I_i^\alpha m_0,\Gamma_j^\beta m_1\rangle=\left[i(\omega_0-\omega)+\frac{\Gamma}{2}+i(\omega_i-\omega_j)\right]^{-1}, \tag{6}$$

where ω_0 is the energy difference between the excited and ground levels of the nucleus and ω_i and ω_j are the energies of the electronic levels Γ_i and Γ_j, respectively. Since $\omega_0-\omega$ is of the order of magnitude of hyperfine energies $\omega_{\mathrm{hp}}<<|\omega_i-\omega_j|$, the matrix elements in Eq. (6) with $i=j$ are much greater than those corresponding to $i\neq j$. By taking into account this result it is seen that only the matrix elements of $R-iL_{\mathrm{hp}}$ of the form

$$\langle\Gamma_i^\alpha m_0,\Gamma_i^\beta m_1\,|\,R-iL_{\mathrm{hp}}\,|\,\Gamma_j^\gamma m_0\Gamma_j^\delta m_1\rangle$$

are relevant in calculating the line shape. Indeed, as a result of (5), these matrix elements are of the order of magnitude of $\omega_{\mathrm{hp}}^{-1}$ whereas the remaining ones are of the order of $(\omega_{\mathrm{hp}}+\omega_R)/|\omega_j-\omega_i|^2$. In other words, one can conceive the Mössbauer atom as a set of oscillators of frequency $\omega_0=\omega(\Gamma_i m_1)-\omega(\Gamma_i m_0)$ coupled by hyperfine and ion-phonon interactions. This is justified by the consideration that the coupling between these oscillators and all others of frequencies $\omega(\Gamma_i m_1)-\omega(\Gamma_j m_0)=\omega_0+\omega_{ij}$ is negligible (Fig. 1).

III. THE ROLE OF SYMMETRY

In the *ab initio* theories reported in the literature the expressions for the matrix elements of the relaxation superoperator are quite involved.[8] We will now show that by using a "dynamical spin Hamiltonian" to describe the ion-lattice interaction,[15–17] the complexity of the problem is greatly reduced. The dynamical spin Hamiltonian can be derived by using only the symmetry properties of the vibrations of the particles surrounding the paramagnetic ion and the symmetry properties of the wave functions of the paramagnetic ion, which are assumed to be known. The dynamical spin Hamiltonian has

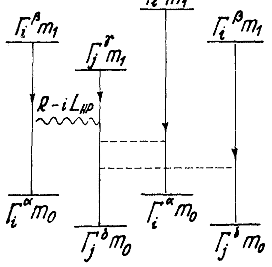

FIG. 1. Schematic representation of the transitions of the coupled system. Downward lines denote the gamma transitions between pairs of individual levels. The wavy line denotes significant coupling term. The dotted lines denote negligible coupling terms.

the characteristic of incorporating all kinds of relaxation mechanisms and leads to expressions for the transition probabilities containing some parameters whose determination is the central problem of the experimental work. The task of theory consists evidently in predicting the correct values for the parameters.

The dynamical spin Hamiltonian can be written as

$$\mathscr{H}_1=\sum_{l}\sum_{\sigma}A_1^{\sigma}F_1^{\sigma}\ , \tag{7}$$

where A_l^σ and F_l^σ are electron and lattice operators, respectively, transforming as the σ component of the irreducible representation Γ_1 of the point group of the Mössbauer atom. We consider the case without externally applied magnetic field; in fact, in the presence of the magnetic field the electronic degeneracy would be completely removed and the problem could be dealt with by simple stochastical models.[2] In the present case the operators A_l^σ are functions only of the components S_x, S_y, and S_z of the spin. One can always take the operator A_l^σ to be dimensionless with matrix elements of the order of unity. The quantities F_l^σ then have the dimensions of an energy and are of the same order of magnitude as the single contributions of the dynamical spin Hamiltonian.

In what follows we will make use of the correlation functions of lattice operators defined as

$$\langle F_l^{\sigma\dagger}(o)F_{l'}^{\sigma'}(t)\rangle=\mathrm{Tr}_L[\rho_L F_l^{\sigma\dagger}(o)F_{l'}^{\sigma'}(t)]\ , \tag{8}$$

where the trace is performed over a complete set of lattice states and

$$F_l^{\sigma\dagger}(t)=e^{iL_Lt}F_l^{\sigma}(o)\ . \tag{9}$$

It is easy to show that the correlation function satisfies the relation

$$\langle F_l^{\sigma\dagger}(o)F_{l'}^{\sigma'}(t)\rangle=\delta_{ll'}\delta_{\sigma\sigma'}J_l(t,T)\ , \tag{10}$$

where $J_l(t,T)$ is a function of temperature and time. In order to prove (10), note that the correlation function (8) is invariant under all the symmetry operators of the point group. On the other hand, the statistical operator ρ_L which is a function of the lattice Hamiltonian, is invariant under the same symmetry operations. Therefore, Eq. (10) directly follows from the orthogonality theorem for the representations of a group.[18] Moreover, we will assume that the correlation function for two lattice operators transforming as the same irreducible representation, but describing different physical processes, is equal to zero. This is not a result of group theory but arises only from plausibility arguments.

Here we will make the hypothesis that the lifetime of the lattice states involved in the relaxation processes is much shorter than the relaxation time and the Larmor period. These conditions are, in general, satisfied in the case of ion-phonon interactions which are the object of the present work.[19] Under these conditions the WNA is also valid.[20,21] We can thus substitute L for L_0 and ω for ω_0 (p for p_0) in Eq. (3).

By a straightforward procedure one obtains

$$\langle\Gamma_i^\alpha m_0,\Gamma_i^\beta m_1\,|\,R(P_0)\,|\,\Gamma_j^\gamma m_0',\Gamma_j^\delta m_1'\rangle=\delta_{m_0m_0'}\delta_{m_1m_1'}\sum_{l,\sigma}\left[\sum_{k,\epsilon}|\langle\Gamma_i^\alpha|A_l^\sigma|\Gamma_k^\epsilon\rangle|^2J_l(\omega_{ik},T)\delta_{ij}\delta_{\alpha\gamma}\delta_{\beta\delta}\right.$$
$$\left.-\langle\Gamma_i^\alpha|A_l^\sigma|\Gamma_j^\gamma\rangle\langle\Gamma_j^\delta|A_l^{\sigma\dagger}|\Gamma_i^\beta\rangle J_l(\omega_{ij},T)\right]\ , \tag{11}$$

where we have used the relation

$$\sum_{\sigma,\epsilon}\langle\Gamma_i^\alpha|A_j^{\sigma\dagger}|\Gamma_k^\epsilon\rangle\langle\Gamma_k^\epsilon|A_j^\sigma|\Gamma_i^\gamma\rangle=\delta_{\alpha\gamma}\sum_{\sigma,\epsilon}|\langle\Gamma_i^\alpha|A_j^{\sigma\dagger}|\Gamma_k^\epsilon\rangle|^2 \tag{12}$$

and where

$$J_l(\omega_{ij},T)=\int_0^\infty dt\ e^{-i(\omega_i-\omega_j)t}J_l(t,T)\ . \tag{13}$$

Equation (11) contains temperature-dependent terms of the form

$$W_{i\alpha,i\beta}^{j\gamma,j\delta}=\sum_{l,\sigma}\langle\Gamma_i^\alpha|A_l^\sigma|\Gamma_j^\gamma\rangle\langle\Gamma_j^\delta|A_l^{\sigma\dagger}|\Gamma_i^\beta\rangle J_l(\omega_{ij},T)\ , \tag{14}$$

which can be determined by experiments. Their temperature dependence allows us to establish the kind of relaxation. When $\beta=\alpha$ and $\delta=\gamma$ the quantities $W_{i\alpha,i\beta}^{j\gamma,j\delta}$ coincide with the transition probabilities $W(\Gamma_i^\alpha\rightarrow\Gamma_j^\gamma)$ between the electronic states Γ_i^α and Γ_j^γ. We observe that, in general, the relaxation operator cannot be written only as a function of the transition probabilities. An important exception is offered by the case of Kramers doublets. Let us denote with $|\Gamma_i^\alpha\rangle$ and $|\Gamma_i^{\alpha *}\rangle$ a pair of Kramers conjugate states. Invariance with respect to time reversal gives the relation

$$\langle\Gamma_i^\alpha|A_l^\sigma|\Gamma_k^\epsilon\rangle=-\langle\Gamma_k^{\epsilon *}|A_l^\sigma|\Gamma_i^{\alpha *}\rangle\ . \qquad (15)$$

By taking Eq. (15) into account, the diagonal matrix elements of the relaxation operator can be written in the form

$$\langle\Gamma_i^\alpha m_0,\Gamma_i^\beta m_1|R(P_0)|\Gamma_i^\alpha m_0,\Gamma_i^\beta m_1\rangle = \sum_{k,\epsilon(\neq i,\alpha)} W(\Gamma_i^\alpha\to\Gamma_k^\epsilon) +2(1-\delta_{\alpha\beta})W(\Gamma_i^\alpha\to\Gamma_i^\alpha)\ . \qquad (16)$$

Moreover, the only off-diagonal matrix elements different from zero have the form

$$\langle\Gamma_i^\alpha m_0,\Gamma_i^\alpha m_1|R(P_0)|\Gamma_j^\gamma m_0,\Gamma_j^\gamma m_1\rangle =-W(\Gamma_i^\alpha\to\Gamma_j^\gamma)\ . \qquad (17)$$

Therefore, when the hyperfine Hamiltonian is diagonal with respect to the electronic states, the matrix of the operator $p-iL_A+R$ factors into submatrices of lower dimensions. Contributions to the line shape arise only from the submatrix whose elements are of the form $\langle\Gamma_i^\alpha\Gamma_i^\alpha||\Gamma_j^\beta\Gamma_j^\beta\rangle$. In this case the expression for the line shape is in agreement with the results of Ref. 2.

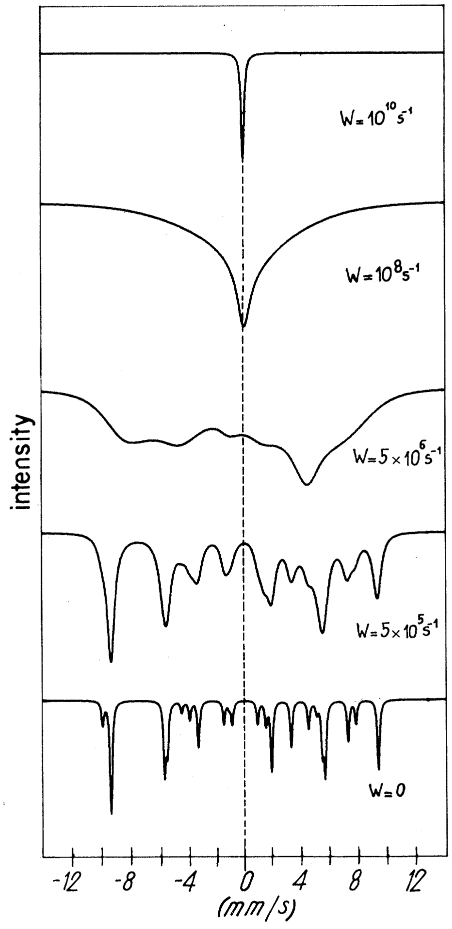

FIG. 2. Theoretical relaxation spectra of Fe^{3+} in a crystal field of C_3 symmetry evaluated for different values of the parameters. For simplicity reasons W_1 has been assumed to be equal to W_2 ($W_1=W_2=W$).

IV. AN EXAMPLE: THE CASE OF Fe^{3+} IN C_3 SYMMETRY

As a specific example let us consider the case of the Fe^{3+} ion in a crystal field of C_3 symmetry. The ground state $^6S_{5/2}$ of the ion splits into three Kramers doublets, transforming as (Γ_4, Γ_5) and Γ_6. In the case of methylamine sulphate[22] the three doublets have the simple form

$$|\Gamma_4\rangle=|\tfrac{1}{2}\rangle\ ,\quad |\Gamma_4'\rangle=|-\tfrac{5}{2}\rangle\ ,\quad |\Gamma_6\rangle=|\pm\tfrac{3}{2}\rangle\ ,$$
$$|\Gamma_5\rangle\,|-\tfrac{1}{2}\rangle\quad ,\quad |\Gamma_5'\rangle=|+\tfrac{5}{2}\rangle\ . \qquad (18)$$

From the multiplication table for the group[23] C_3 it is seen that the three Kramers doublets are coupled by spin operators transforming as (Γ_2, Γ_3). Here we consider only the quadrupolar relaxation.[17] It is seen that the spin operators having the required symmetry properties are of the form

$$A(\Gamma_2)=S_+^2,\quad A(\Gamma_2')=\tfrac{1}{2}(S_zS_-+S_-S_z)\ ,$$
$$A(\Gamma_3)=S_-^2,\quad A(\Gamma_3')=\tfrac{1}{2}(S_zS_++S_+S_z)\ .$$

Transition for which $\Delta m_s=\pm 2$, $\Delta m_s=\pm 1$ arise from operators of first and second kind, respectively. At the temperatures of interest the energy differences between the ground doublets ($\sim 1\ \text{cm}^{-1}$) are much smaller than the thermal energy kT. Therefore, the three doublets may be assumed to be equally populated. Moreover, since the density of phonon states does not change significantly for a frequency change of the order of $1\ \text{cm}^{-1}$, we can assume that the quantities $J(\omega_{ij},T)$ do not depend on ω_{ij}.

In order to calculate the line shape we have used the eigenvalue-eigenvector method described in Refs. 24 and 25 which largely reduces the compu-

TABLE I. Matrix of the tetradics $\langle \Gamma_i^\alpha m_0, \Gamma_i^\beta m_1 | R(P_0) | \Gamma_j^\gamma m_0, \Gamma_j^\delta m_1 \rangle$. The case of Fe^{3+} in C_3 symmetry.*

	$\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},-\frac{1}{2}$	$-\frac{1}{2},\frac{1}{2}$	$-\frac{1}{2},-\frac{1}{2}$	$\frac{3}{2},\frac{3}{2}$	$\frac{3}{2},-\frac{3}{2}$	$-\frac{3}{2},\frac{3}{2}$	$-\frac{3}{2},-\frac{3}{2}$	$-\frac{5}{2},-\frac{5}{2}$	$-\frac{5}{2},\frac{5}{2}$	$\frac{5}{2},-\frac{5}{2}$	$\frac{5}{2},\frac{5}{2}$
$\frac{1}{2},\frac{1}{2}$	W_1+W_1' $+W_2$				$-W_2$			$-W_1$				$-W_1'$
$\frac{1}{2},-\frac{1}{2}$		W_1+W_1' $+W_2$										
$-\frac{1}{2},\frac{1}{2}$			W_1+W_1' $+W_2$									
$-\frac{1}{2},-\frac{1}{2}$				W_1+W_1' $+W_2$	$-W_1$			$-W_2$	$-W_1'$			
$\frac{3}{2},\frac{3}{2}$	$-W_2$			$-W_1$	W_1+W_2 $+W_2'$							$-W_2'$
$\frac{3}{2},-\frac{3}{2}$						W_1+W_2+ $+W_2'$						
$-\frac{3}{2},\frac{3}{2}$							W_1+W_2 $+W_2'$					
$-\frac{3}{2},-\frac{3}{2}$	$-W_1$			$-W_2$				W_1+W_2 $+W_2'$	$-W_2'$			
$-\frac{5}{2},-\frac{5}{2}$				$-W_1'$				$-W_2'$	$W_1'+W_2'$			
$-\frac{5}{2},\frac{5}{2}$										$W_1'+W_2'$		
$\frac{5}{2},-\frac{5}{2}$											$W_1'+W_2'$	
$\frac{5}{2},\frac{5}{2}$	$-W_1'$				$-W_2'$							$W_1'+W_2'$

*$W_1 = |\langle \Gamma_6^* | A(\Gamma_3) | \Gamma_4 \rangle|^2 J_3(\omega_{46}, T)$, $W_1' = \frac{5}{9} W_1$

$W_2 = |\langle \Gamma_6 | A(\Gamma_3') | \Gamma_4 \rangle|^2 J_3'(\omega_{46}, T)$, $W_2' = \frac{5}{2} W_2$

tational time. In our case one should diagonalize a complex matrix of dimension 288×288. According to the results of Sec. II the dimension of this matrix can be reduced by a factor of 3. Finally, by taking into account the selection rules due to symmetry, one obtains three matrices of dimensions 16, 16, and 15.

The relaxation matrix is reported in Table I. Figure 2 shows the calculated Mössbauer line shapes for different values of the transition probabilities. On a Data General Eclipse S200 computer the spectrum was simulated in about 60 sec.

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