Eq. (A6) reduces to

$$Y_{ij}(\tau_1\cdots\tau_m;\tau_1'\cdots\tau_n';\tau_1''\cdots\tau_p'')=(j\mid Y'Y''Y'''\mid i),\tag{A7}$$

with

$$\begin{aligned}Y'&=P(t-\tau_1)F\cdots FP(\tau_m-t_1),\\ Y''&=P(t_1-\tau_1')F\cdots FP(\tau_n'-t_2),\\ Y'''&=P(t_2-\tau_1'')F\cdots FP(\tau_p'').\end{aligned}\tag{A8}$$

On substituting (A7) into (A4) we see that the equality (A1) indeed holds. In a similar way it can be shown that the general term in Eq. (3.17) is correct.

APPENDIX B

The expression (3.21) only involves an inversion of a 2×2 matrix and hence can easily be reduced to an algebraic expression. First we note that Eq. (3.21) can be rewritten as

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\sum_{m_0m_1}\tfrac{1}{4}\mid\langle I_0m_0\mid\mathcal{K}^{(+)}\mid I_1m_1\rangle\mid^2\sum_{ij}p_i(j\mid[\tilde{A}^{-1}(p)+3Q^2\eta^2\tilde{B}(p)]^{-1}\mid i).\tag{B1}$$

Then on substituting the explicit expression for $\tilde{A}$ and $\tilde{B}$ into (B1) and performing the matrix inversions we obtain

$$\sum_{ij}p_i(j\mid[\tilde{A}^{-1}(p)+3Q^2\eta^2\tilde{B}(p)]^{-1}\mid i)=N/D,\tag{B2}$$

where

$$\begin{aligned}N&=d(p+i\beta+2W)+3Q^2\eta^2(p-i\beta)\\ D&=d[(p+i(\beta-C_1+C_0)+W)(p+i(\beta+C_1-C_0)+W)-W^2]\\ &\quad+3Q^2\eta^2[(p+i(\beta+C_1-C_0)+W)(p-i(\beta-C_1'+C_0)+W)\\ &\quad+(p+i(\beta-C_1+C_0)+W)(p-i(\beta+C_1'-C_0)+W)+2W^2+3Q^2\eta^2],\end{aligned}$$

with

$$d=(p-i\beta)^2+(C_1'-C_0)^2+2W(p-i\beta).$$

We have used here the fact that $p_i=\frac{1}{2}$, and we have taken $W_{+-}=W_{-+}=W$.

PHYSICAL REVIEW VOLUME 165, NUMBER 2 10 JANUARY 1968

Mössbauer Spectra in a Fluctuating Environment II. Randomly Varying Electric Field Gradients*

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(Received 4 August 1967)

We derive an expression for the Mössbauer line shape in the presence of an electric field gradient which jumps at random between the x, y, and z axes. This Hamiltonian represents an idealized model for the effects on a nucleus of Jahn-Teller distortions, jump diffusion of vacancies, or electronic relaxation. A simplified calculation based on a model in which the field gradient jumps between positive and negative values along the z axis is also given. In certain limiting circumstances the two calculations give similar results: The Mössbauer line shape consists of a single unsplit line for fast jumping, and of a quadrupole doublet for slow transitions. The results of the calculation agree with experiments of Pipkorn and Leider and of Chappert, Frankel, and Blum, as interpreted by Ham.

I. INTRODUCTION

SEVERAL recent Mössbauer-effect experiments on Fe^{2+} in cubic materials have yielded spectra which are interpreted as being produced by a fluctuating electric field gradient at the nucleus.[1–3] Such fluctuations have been attributed to Jahn-Teller effects, jump diffusion of vacancies, or electronic relaxation. Ham[4]

* Work perfurmed under the auspices of the U.S. Atomic Energy Commission.

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[1] H. R. Leider and D. N. Pipkorn, Bull. Am. Phys. Soc. **11**, 49 (1966); Phys. Rev. **165**, 494 (1968).

[2] R. B. Frankel and N. A. Blum, Bull. Am. Phys. Soc. **12**, 24 (1967); J. Chappert, R. B. Frankel, and N. A. Blum, *ibid.* **12**, 352 (1967); Phys. Letters **25A**, 149 (1967).

[3] D. H. Lindley and P. G. Debrunner, Phys. Rev. **146**, 199 (1966).

[4] F. S. Ham Phys. Rev. **155**, 170 (1967).

has given a persuasive explanation for these experiments on the basis of electronic relaxation in the presence of a random strain. In this paper, we will give a time-dependent Hamiltonian which represents a reasonable physical model for all of the above effects, and, with the use of this Hamiltonian, we calculate the Mössbauer line shape and compare with experiments.

If an ion with a degenerate ground state is in a cubic environment, the surroundings are expected, according to the Jahn-Teller theorem, to distort in such a way that the electronic degeneracy is removed. The distorted surroundings would then produce an electric field gradient at the nulceus. There are, however, several equivalent directions at a cubic site along which these distortions can occur, and, as a result of thermal excitations, the surroundings would jump from one to another of these equivalent distortions. A nucleus in the center of the ion would see, as a result of these effects, an electric field gradient which jumped at random from one axis to another. The jump rate would be determined by the temperature, and in turn this rate determines the nature of the Mössbauer spectrum. It is clear that an identical physical picture, from the point of view of the nucleus, would be produced by a vacancy in one of the neighboring sites of the ion. The vacancy would jump, as a result of thermal excitation, from one equivalent position to another, producing again a fluctuating field gradient at the nucleus.

In Ham's[4] picture of the Mössbauer spectrum of Fe^{2+} in MgO,[1,2] the three-fold degenerate Γ_5 ground state is split by random strains into three singlets. None of these singlets can produce a magnetic hyperfine field at the nucleus, but when the ion is in one of the levels, it will produce a field gradient at the nucleus. The sublevels of Γ_5 transform like xy, xz, and yz. (We suppose that these levels are eigenstates. In general, the eigenstates will be a linear combination of these levels, but as Ham has shown, the magnitude of the field gradient at the nucleus is independent of the particular combination used.) As a result of electronic relaxation, the ion will jump between the three states. When the ion is in $|xy\rangle$, a field gradient along z is produced at the nucleus, etc. The physical picture is therefore as in the preceding cases.

Our approach will be to construct a Hamiltonian which is a random function of the time, and which consists of an electric field gradient fixed in magnitude, but which jumps between the x, y, and z axes. We then use the formalism given in an accompanying paper[5] to calculate the Mössbauer line shape. The problem considered here is complicated because the Hamiltonian does not commute with itself at separate instants of time. We nevertheless are able to solve this problem, and we compare the solution with that for a simpler problem, in which the field gradient fluctuates from + to − only along the z axis (for which the Hamiltonian commutes with itself at all times). We find that the solutions for these two cases are identical in form with slight numerical differences in the limit where each field gradient is equally probable, but they differ when the time-average gradient is not zero.

The mathematical results for the line shape for our model agree with intuitive arguments based on the concept of motional narrowing. When the jump rate is rapid compared to the precession rate of the nucleus in the field gradient, the line is unsplit and has the natural width, while when the jump rate is slow compared to the precession rate a quadrupole splitting appears.

In the next section, we construct the Hamiltonian for the system and derive an expression for the line shape. We then compare the results of this calculation with those for a simplified Hamiltonian. There is very good agreement with the experimental results of Pipkorn and Leider.[1]

II. HAMILTONIAN AND LINE SHAPE FOR A FLUCTUATING ELECTRIC FIELD GRADIENT

We wish to give the Hamiltonian for a nucleus in an electric field gradient which jumps at random between the x, y, and z axes. To do this we introduce a random function of time $f(t)$ which takes on the three possible values, ± 1 and 0. Stochastic functions such as this have been thoroughly discussed previously (see Refs. 15, 16, 20, and 21 of I). The Hamiltonian may be written

$$\begin{aligned}\mathcal{H}(t)=\mathcal{H}_0&+[1-f^2(t)]Q(3I_z^2-I^2)\\&+\tfrac{1}{2}f(t)[1+f(t)]Q(3I_x^2-I^2)\\&+\tfrac{1}{2}f(t)[1-f(t)]Q(3I_y^2-I^2),\end{aligned}\quad(1)$$

where $\mathcal{H}_0$ is the Hamiltonian for the nucleus in the absence of any perturbations and Q is a constant proportional to the product of the electric field gradient and the quadrupole moment of the nucleus. When $f(t)=0$, (1) reduces to $\mathcal{H}_0+Q(3I_z^2-I^2)$, while for $f(t)=1$, $\mathcal{H}(t)\to\mathcal{H}_0+Q(3I_x^2-I^2)$, and $f(t)=-1$ yields $\mathcal{H}(t)\to\mathcal{H}_0+Q(3I_y^2-I^2)$. Hence, as the random function $f(t)$ jumps between its three permissible values, the field gradient jumps between the three axes. Specification of the matrix W of transition probabilities per unit time between the three values of $f(t)$ then completes the construction of the model for the processes discussed in the introduction. Before proceeding with the calculation, we rearrange some of the terms in (1). Since

$$\begin{aligned}\tfrac{1}{2}f(1+f)Q(3I_x^2-I^2)+\tfrac{1}{2}f(1-f)Q(3I_y^2-I^2)\\=\tfrac{3}{2}fQ(I_x^2-I_y^2)-\tfrac{1}{2}f^2Q(3I_z^2-I^2),\end{aligned}\quad(2)$$

we may write

$$\mathcal{H}(t)=\mathcal{H}_0+[1-\tfrac{3}{2}f^2(t)]Q(3I_z^2-I^2)+\tfrac{3}{4}f(t)Q(I_+^2+I_-^2),\quad(3)$$

where $I_\pm=I_x\pm iI_y$, and $I_x^2-I_y^2=\frac{1}{2}(I_+^2+I_-^2)$. We note that if the transition probabilities per unit time between

[5] M. Blume and J. A. Tjon, preceeding paper, Phys. Rev. 165, 446 (1968). Referred to as I.

the various values of $f(t)$ are all equal, i.e., $W_{+-}=W_{+0}=W_{-0}=\cdots=W$, then the average of $f(t)$ will equal zero. Also, the average of $f^2(t)$ will be $\frac{2}{3}$, so that, in this case, $\bar{\mathcal{H}}(t)=\mathcal{H}_0$.

To calculate the line shape, we must evaluate Eq. (2.8) of I for the probability $W(\mathbf{k})$ of emission of a photon $\mathbf{k}\omega$:

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\int_0^\infty dt\ \exp(i\omega t-\tfrac{1}{2}\Gamma t)\times(\langle\mathcal{H}^{(-)}\mathcal{H}^{(+)}(t)\rangle)_{\mathrm{av}}. \quad (4)$$

Here Γ is the natural linewidth and $\mathcal{H}^{(+)}$ is the Hamiltonian for emission of a photon $\mathbf{k}$ by the nucleus,

$$\mathcal{H}^{(-)}=\mathcal{H}^{(+)\dagger},$$

and

$$\mathcal{H}^{(+)}(t)=\exp\left(i\int_0^t\mathcal{H}(t')\,dt'\right)\mathcal{H}^{(+)}\exp\left(-i\int_0^t\mathcal{H}(t')\,dt'\right),$$

with, in the present problem, $\mathcal{H}(t)$ given by (3). The notation $(\ )_{\mathrm{av}}$ in the correlation function in (4) indicates that a stochastic average over all functions $f(t)$ is to be performed. We calculate the correlation function for a nuclear transition from an excited level with spin $I_1=\frac{3}{2}$ to a ground level with spin $I_0=\frac{1}{2}$. We have

$$\langle\mathcal{H}^{(-)}\mathcal{H}^{(+)}(t)\rangle=(1/2I_1+1)\sum_{m_1m_0,m_1'm_0'}\langle I_1m_1\mid\mathcal{H}^{(-)}\mid I_0m_0\rangle\times\langle I_0m_0\mid\exp\left(i\int_0^t\mathcal{H}(t')\,dt'\right)\mid I_0m_0'\rangle\langle I_0m_0'\mid\mathcal{H}^{(+)}\mid I_1m_1'\rangle\langle I_1m_1'\mid\exp\left(-i\int_0^t\mathcal{H}(t')\,dt'\right)\mid I_1m_1\rangle. \quad (5)$$

Because $I_0=\frac{1}{2}$ the quadrupole terms in (3) have no effect in the I_0 matrix element, and we obtain

$$\langle I_0m_0\mid\exp\left(i\int_0^t\mathcal{H}(t')\,dt'\right)\mid I_0m_0'\rangle=\exp(iE_0t)\delta_{m_0m_0'}. \quad (6)$$

The central part of the calculation is then the evaluation of

$$\left(\langle I_1m_1'\mid\exp\left[-i\int_0^t\mathcal{H}(t')\,dt'\right]\mid I_1m_1\rangle\right)_{\mathrm{av}}=\exp(-iE_1t)\left(\langle I_1m_1'\mid\exp\left[-i\int_0^t(\mathcal{H}_1(t')+V(t'))dt'\right]\mid I_1m_1\rangle\right)_{\mathrm{av}}, \quad (7)$$

where

$$\mathcal{H}_1(t)=[1-\tfrac{3}{2}f^2(t)]Q(3I_z^2-I^2)$$

and

$$V(t)=\tfrac{3}{4}f(t)Q(I_+^2+I_-^2).$$

Using reasoning identical to that following Eq. (3.11) of I, it follows that if we consider the probability of emission from a powder we need only the diagonal element of (7). Also, even for a single crystal, the nondiagonal elements of (7) vanish if the three values of $f(t)$ are equally probable. In the general case, it is possible to calculate the off-diagonal elements by a procedure identical to that used in the following for the diagonal elements. Under the above restrictions, then, we have, on substituting (7), (6), and (5) in (4),

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\int_0^\infty dt\ \exp[i(\omega-\omega_0)t-\tfrac{1}{2}\Gamma t](1/2I_1+1)\sum_{m_1m_0}\mid\langle I_0m_0\mid\mathcal{H}^{(+)}\mid I_1m_1\rangle\mid^2\times\left(\langle I_1m_1\mid\exp\left[-i\int_0^t(\mathcal{H}_1(t')+V(t'))dt'\right]\mid I_1m_1\rangle\right)_{\mathrm{av}}, \quad (8)$$

where $\omega_0=E_1-E_0$ is the frequency of the unperturbed transition. We consider now the calculation of

$$G_{m_1}(t)=\left(\langle I_1m_1\mid\exp\left[-i\int_0^t(\mathcal{H}_1(t')+V(t'))dt'\right]\mid I_1m_1\rangle\right)_{\mathrm{av}}. \quad (9)$$

Writing

$$\exp\left(-i\int_0^t(\mathcal{H}_1(t')+V(t'))dt'\right)=\exp\left(-i\int_0^t\mathcal{H}_1(t')\,dt'\right)\exp\left(-i\int_0^t\bar{V}(t')\,dt'\right),$$

with

$$\bar{V}(t)=\exp\left(i\int_0^t\mathcal{H}_1(t')\,dt'\right)V(t)\exp\left(-i\int_0^t\mathcal{H}_1(t')\,dt'\right),$$

and expanding

$$\exp\left(-i\int_0^t \bar{V}(t')\,dt'\right)$$

in a time-ordered series, we find

$$G_{m_1}(t)=\sum_n(-i)^n\int_0^t dt_1\cdots\int_0^{t_{n-1}}dt_n\left(\langle I_1m_1\mid\exp\left[-i\int_0^t\mathcal{H}_1(t')\,dt'\right]\bar{V}(t_1)\cdots\bar{V}(t_n)\mid I_1m_1\rangle\right)_{\text{av}}. \tag{10}$$

Since $\bar{V}(t)$ has the selection rule $\Delta m=\pm2$, only terms with even n occur for the diagonal elements. Because of this rule, and since $I_1=\frac{3}{2}$, we have

$$\langle I_1m_1\mid\exp\left(-i\int_0^t\mathcal{H}_1(t')\,dt'\right)\bar{V}(t_1)\cdots\bar{V}(t_{2n})\mid I_1m_1\rangle=\Psi_{2n}$$

$$=\exp\left(i\alpha\int_0^t f_1(t')\,dt'\right)\langle I_1m_1\mid\bar{V}(t_1)\bar{V}(t_2)\mid I_1m_1\rangle\cdots\langle I_1m_1\mid\bar{V}(t_{2n-1})\bar{V}(t_{2n})\mid I_1m_1\rangle, \tag{11}$$

where

$$\alpha=\alpha(m_1)=-\tfrac{1}{2}Q(3m_1^2-15/4)\quad\text{and}\quad f_1(t)=2[1-\tfrac{3}{2}f^2(t)].$$

Further,

$$\langle I_1m_1\mid\bar{V}(t_1)\bar{V}(t_2)\mid I_1m_1\rangle$$

$$=\exp\left(-i\alpha\int_0^{t_1}f_1(t')\,dt'\right)f(t_1)\exp\left(-i\alpha\int_0^{t_1}f_1(t')\,dt'\right)\exp\left(i\alpha\int_0^{t_2}f_1(t')\,dt'\right)f(t_2)\exp\left(i\alpha\int_0^{t_2}f_1(t')\,dt'\right)$$

$$\times(\tfrac{3}{4}Q)^2\mid\langle I_1m_1\mid I_+^2\mid I_1m_1-2\rangle\mid^2,$$

where we have used the fact that

$$-\tfrac{1}{2}Q[3(m_1\pm2)^2-15/4]=-\alpha(m_1).$$

Then, since $\mid\langle I_1m_1\mid I_\pm^2\mid I_1m_1\pm2\rangle\mid^2=12$, Eq. (11) becomes

$$\Psi_{2n}=[(27/4)Q^2]^n\exp\left(i\alpha\int_{t_1}^t f_1(t')\,dt'\right)f(t_1)\exp\left(-i\alpha\int_{t_2}^{t_1}f_1(t')\,dt'\right)f(t_2)\cdots f(t_{2n})\exp\left(i\alpha\int_0^{t_{2n}}f_1(t')\,dt'\right).$$

To take the stochastic average of Ψ_{2n}, we introduce the restricted average, subject to the condition $f(t)=i$ at $t=0$ and $f(t)=j$ at t. We denote this average by $(j\mid\Psi_{2n}\mid i)$. Since $i,j=\pm1,0$, this restricted average is a 3×3 matrix. The full average which we require is then given bya veraging over initial values i and summing over final values j:

$$\bar{\Psi}_{2n}=\sum_{ij}p_i(j\mid\Psi_{2n}\mid i),$$

where p_i is the *a priori* probability of the value i at $t=0$. If each of the values ±1, 0 is equally probable, $p_i=\frac{1}{3}$. To obtain this restricted average of Ψ_{2n} we introduce $(j\mid A(t_n-t_{n'})\mid i)$, the restricted average of

$$\exp\left(i\alpha\int_{t_{n'}}^{t_n}f_1(t')\,dt'\right),$$

subject to $f(t_{n'})=i$ and $f(t_n)=j$. Similarly, $(j\mid B(t_n-t_{n'})\mid i)$ is the average of

$$f(t_n)\exp\left(-i\alpha\int_{t_{n'}}^{t_n}f_1(t')\,dt'\right)f(t_{n'}),$$

subject to the same conditions. Then

$$\bar{\Psi}_{2n}=\sum_{ij}p_i(j\mid(3\alpha^2)^nA(t-t_1)B(t_1-t_2)\cdots B(t_{2n-1}-t_{2n})A(t_{2n})\mid i), \tag{12}$$

where we have written $(27/4)Q^2=3\alpha^2$. From (10) and (12),

$$G_{m_1}(t)=\sum_{ij}p_i\left(j\left|\sum_n(-3\alpha^2)^n\int_0^t dt_1\cdots\int_0^{t_{2n-1}}dt_{2n}A(t-t_1)B(t_1-t_2)\cdots B(t_{2n-1}-t_{2n})A(t_{2n})\right|i\right),$$

and, taking the Laplace transform of $G_{m_1}(t)$,

$$\tilde{G}_{m_1}(p)=\int_0^\infty dt\,\exp(-pt)G_{m_1}(t)$$
$$=\sum_{ij}p_i\langle j\,|\,\sum_n(-3\alpha^2)^n\tilde{A}(p)[\tilde{B}(p)\tilde{A}(p)]^n\,|\,i\rangle, \tag{13}$$

where

$$\tilde{A}(p)=\int_0^\infty dt\,\exp(-pt)A(t),$$

and

$$\tilde{B}(p)=\int_0^\infty dt\,\exp(-pt)B(t),$$

are both 3×3 matrices. Performing the summation in (13) yields

$$\tilde{G}_{m_1}(p)=\sum_{ij}p_i\langle j\,|\,\tilde{A}(p)[1+3\alpha^2\tilde{B}(p)\tilde{A}(p)]^{-1}\,|\,i\rangle \tag{14}$$

and, on substituting in (8),

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}(1/2I_1+1)\sum_{m_0m_1}|\langle I_0m_0\,|\,\mathcal{H}^{(+)}\,|\,I_1m_1\rangle|^2$$
$$\times\sum_{ij}p_i\langle j\,|\,\tilde{A}(p)[1+3\alpha^2\tilde{B}(p)\tilde{A}(p)]^{-1}\,|\,i\rangle, \tag{15}$$

with $p=-i(\omega-\omega_0)+\frac{1}{2}\Gamma$. The problem reduces to the evaluation of the 3×3 matrices $\tilde{A}(p)$ and $\tilde{B}(p)$ and to the calculation of the elements of $[1+3\alpha^2\tilde{B}(p)\tilde{A}(p)]^{-1}$. The matrices $\tilde{A}(p)$ and $\tilde{B}(p)$ can be found by following the procedures of Anderson, Kubo, and Sack (see Refs. of I, as well as Appendix A of that paper). We obtain

$$\tilde{A}(p)=(p-i\alpha F_1-\mathcal{W})^{-1},$$
$$\tilde{B}(p)=F(p+i\alpha F_1-\mathcal{W})^{-1}F,$$

where

$$F=\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}$$

is the matrix whose diagonal elements are the permissible values of $f(t)$,

$$F_1=\begin{pmatrix}-1&0&0\\0&2&0\\0&0&-1\end{pmatrix}$$

is the diagonal matrix of values of $f_1(t)=2-3f^2(t)$, and $\mathcal{W}$ is the matrix of transition probabilities per unit time between the three values of $f(t)$. If these probabilities are all equal, we have $p_i=\frac{1}{3}$ and

$$\mathcal{W}=\begin{pmatrix}-2W&W&W\\W&-2W&W\\W&W&-2W\end{pmatrix}.$$

This condition should be satisfied in the three physical situations discussed in the introduction. In the case of electronic relaxation, we must add the proviso that the temperature be high compared to the splitting of the three levels $|xy\rangle$, $|xz\rangle$, and $|yz\rangle$ by the local strain, but this is the case for all of the experiments so far performed. Using this expression for $\mathcal{W}$ and taking $p_i=\frac{1}{3}$, it is possible by straightforward but tedious algebra to evaluate (14). We simply quote the result here,

$$\tilde{G}_{m_1}(p)=\frac{p+3W}{p^2+3Wp+4\alpha^2}$$
$$=\frac{1}{2}\frac{1-3W/(9W^2-16\alpha^2)^{1/2}}{p+\frac{3}{2}W+\frac{1}{2}(9W^2-16\alpha^2)^{1/2}}$$
$$+\frac{1}{2}\frac{1+3W/(9W^2-16\alpha^2)^{1/2}}{p+\frac{3}{2}W-\frac{1}{2}(9W^2-16\alpha^2)^{1/2}}. \tag{16}$$

The nature of the spectrum depends on whether $9W^2>$ or $<16\alpha^2$. When $W>\frac{4}{3}\alpha$, the radical is real and contributes to the width, while for $W<\frac{4}{3}\alpha$ a splitting into two lines is found. In Fig. 1, we show a series of spectra calculated from (15). We have taken

$$W=W_0\frac{\exp(-\Delta/2T)}{\sinh(\Delta/2T)}, \tag{17}$$

the temperature dependence of an Orbach-type relaxation process.[4] Choosing $\Delta\approx100$ cm^{-1} and W_0 so that $W(14°\mathrm{K})=\frac{4}{3}\alpha$, the results in Fig. 1 give excellent agreement with the experimental results of Pipkorn and Leider.

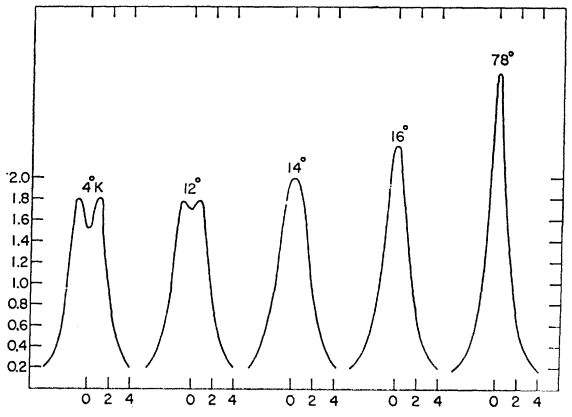

FIG. 1. Mössbauer line shape as calculated from Eqs. (15) and (17), for different values of T.

III. SOLUTION FOR A SIMPLIFIED HAMILTONIAN

The calculation of the line shape in II was complicated by the noncommutativity of the Hamiltonian at different times. This noncommutativity has physical consequences in the polarization and intensity of the radiation emitted from a single-crystal source in which one of the axes is singled out. As we pointed out in the preceding section, however, these effects do not appear in polycrystalline materials for which there is no specific orientation. It is of some interest to compare the results of the model used in the preceding section with one that does not have these complications. We consider the Hamiltonian

$$\mathcal{H}(t)=\mathcal{H}_0+Qf(t)\,(3I_z^2-I^2), \tag{18}$$

where here $f(t)$ takes on the values ± 1 (but *not* 0). The electric field gradient then jumps from positive to negative, but always along the z axis. We clearly have $[\mathcal{H}(t),\ \mathcal{H}(t')]=0$ for Eq. (18). This enables us to consider the stochastic and quantum-mechanical aspects of the problem separately, for we may diagonalize $\mathcal{H}(t)$ at one instant and be assured that it will always be diagonal. This was not possible with (1), since the appropriate quantization axis there depends on the nature of the transition matrix W, i.e., it is not possible to disentangle the stochastic and quantum-mechanical parts of the problem.

We reevaluate (5) using the Hamiltonian (18). Equation (6) for the matrix element in the spin $I_0=\frac{1}{2}$ ground state is unchanged, but (7) can now be written down directly:

$$\langle I_1m_1' \mid \exp\left(-i\int_0^t \mathcal{H}(t')\,dt'\right) \mid I_1m_1\rangle$$

$$=\exp(-iE_1t)\,\exp\left(2i\alpha\int_0^t f(t')\,dt'\right)\delta_{m_1m_1'}, \tag{19}$$

where α is as defined following (11). Using (19) and (5) in (4),

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}(2I_1+1)^{-1}\int_0^\infty dt\,\exp[i(\omega-\omega_0)t-\tfrac{1}{2}\Gamma t]$$
$$\times\sum_{m_0m_1}\mid\langle I_0m_0\mid\mathcal{H}^{(+)}\mid I_1m_1\rangle\mid^2$$
$$\times\left(\exp\left[2i\alpha\int_0^t f(t')\,dt'\right]\right)_{\mathrm{av}}. \tag{20}$$

The stochastic average in (20) is given in Eq. (3.3) of I, provided α in that equation is replaced by 2α. Substituting that result in (20) gives

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}(2I_1+1)^{-1}\sum_{m_0m_1}\mid\langle I_0m_0\mid\mathcal{H}^{(+)}\mid I_1m_1\rangle\mid^2$$
$$\times\sum_{ij=\pm1}p_i(j\mid p-2i\alpha F-\mathcal{W}]^{-1}\mid i), \tag{21}$$

where now

$$F=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\qquad \mathcal{W}=\begin{pmatrix}-W_{+-} & W_{+-}\\ W_{-+} & -W_{-+}\end{pmatrix},$$

and where $p=-i(\omega-\omega_0)+\frac{1}{2}\Gamma$. For $W_{+-}=W_{-+}=W$, and for $p_i=\frac{1}{2}$, inversion of the matrix yields

$$\tfrac{1}{2}\sum_{ij=\pm1}(j\mid(p-2i\alpha F-\mathcal{W})^{-1}\mid i)$$
$$=[(p+2W)/(p^2+2Wp+4\alpha^2)]$$
$$=\frac{1}{2}\,\frac{1-W/(W^2-4\alpha^2)^{1/2}}{p+W+(W^2-4\alpha^2)^{1/2}}$$
$$+\frac{1}{2}\,\frac{1+W/(W^2-4\alpha^2)^{1/2}}{p+W-(W^2-4\alpha^2)^{1/2}}. \tag{22}$$

If in (22) we let $W\to\frac{3}{2}W$, this equation is identical to (17). The factor $\frac{3}{2}$ is reasonable, because there are three possible values of the Hamiltonian (1), but only two of (18).

The line shapes produced by (18) and (1) agree, it should be emphasized, only in the limiting conditions discussed above. For example, it is possible to obtain, for certain relaxation matrices $\mathcal{W}$, a four-line pattern or a three-line pattern from (1), while (18) can yield only the standard two-line pattern in addition to an unsplit line. To calculate these effects numerical evaluation of (14) and (15) is the most economical procedure.

ACKNOWLEDGMENTS

We are indebted to D. Pipkorn, H. Leider, R. Frankel, and F. S. Ham for helpful discussions and for conveying their results prior to publication. After this work was completed we received a preprint from F. Hartmann-Boutron which contains the results of Sec. III. In addition, she treats the line shape in the presence of coherent tunneling between two equivalent Jahn-Teller distortions, a process which we have not considered. We thank Mme. Hartmann-Boutron for communicating these results prior to publication.