

Shapes of Mössbauer spectra in the rapid-relaxation limit

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It is shown that in the rapid-relaxation limit, when the electron-spin relaxation time is small but finite, and the relaxation process is manifest in an asymmetry of the quadrupole doublet or in an abrupt broadening of the line, it is possible to determine from an analysis of the Mössbauer spectrum the Fourier components of the correlation functions $\langle\langle S^i(t)S^j(0)\rangle\rangle$ at zero frequency, where S^i is the i th component of the spin of the electron shell of the Mössbauer atom. The derived formulas make it possible to describe a great variety of spectrum shapes with a small number of parameters, and inasmuch as these formulas have been derived from first principles and are in this sense exact, they make it possible to extract strictly defined information on the relaxation process from the Mössbauer data.

1. INTRODUCTION

A large number of theoretical papers have by now been published (see^[1-15] and the reference therein) on the analysis of the hyperfine structure (hfs) of Mössbauer spectra under conditions of relaxation of the electron spin that produces a magnetic field at a resonant nucleus. These investigations were aimed mainly at the derivation of general equations describing the hfs spectra under the relaxation conditions, and also at determining qualitatively various forms of these spectra, so that by now we know fairly well theoretically what the relaxation equations and the regions of their applicability should be. In fact, relaxation equations have been obtained for all the known relaxation mechanisms, the only exception being spin-spin relaxation in paramagnets.

Nonetheless, even if we exclude this special case of spin-spin relaxation, the problem of the reduction of the experimental spectra still remains quite complicated. This is due, first, to the need for considering the relaxation processes in a system having a relatively large number of degrees of freedom. Thus, in the most typical case of the isotope Fe^{57} ($I_g = 1/2$, $I_e = 3/2$), in the most general case a total of $(2I_g + 1)(2I_e + 1)(2S + 1)^2 = 288$ transitions between the states of the combined system consisting of the nucleus and the electron shell exert an influence on the formation of the spectrum of the iron ion Fe^{3+} ($S = 5/2$). The obtained data must therefore be analyzed as a rule within the framework of some simplified model, which only takes approximate account of the influence of relaxation on the hyperfine structure of the Mössbauer spectrum. In addition, it is usually necessary to resort to additional assumptions concerning the relaxation itself, and this simplifies the problem greatly.

The theoretical problem raised in this connection is to find the situations in which the relaxation processes can be described in terms of quantities that are fully defined and have a clear cut physical meaning. In the present paper we analyze the limiting case of rapid relaxation. As will be shown below, it becomes possible to obtain here a relatively simple description of the relaxation spectra with the aid of a small number of parameters that have fully defined physical meanings. The most convenient for the analysis is the method used by Gabriel et al.^[9] and also by Schwegler^[13].

The relaxation spectrum is expressed in terms of the Fourier component, at zero frequency, of the relax-

tion functions $\langle\langle S^i(t)S^k(0)\rangle\rangle$, which describe the motion of the spin of the Mössbauer atom in time. As a function of these parameters, the summary spectrum can be realized in a large number of forms that differ noticeably from one another. This occurs both in the absence and in the presence of quadrupole interaction. In the former case the spectrum, outwardly constituting a single line, is actually the sum of unresolved lines with different widths and intensities, and the summary spectrum, depending on the form of the tensor $\langle\langle S^i(t)S^k(0)\rangle\rangle_{\omega=0}$, can experience even visually noticeable changes in the form. In the presence of quadrupole splitting, the character of the relaxation-induced asymmetry of the quadrupole spectra, as well as other more detailed characteristics of the shapes of the individual components are also functions of these parameters. All this gives grounds for assuming that in the case of rapid relaxation it is possible not only to predict the behavior of the relaxation spectrum, but also to extract from experiment the set of parameters that have a clearly defined physical meaning and are not connected with any model representations. The calculation of these correlation functions, by starting from certain theoretical representations, is already a special problem, and in many cases it can be carried out by numerical means.

The determination of the form of the spectrum in the limit of rapid relaxation was the subject of studies by Wegener^[5] and by Bradford and Marshall^[6], but they used simplifying models either with respect to the character of the hyperfine interaction^[5] or with respect to the relaxation process^[6] (see also^[15]).

In Sec. 2 below we derive and analyze general expressions describing the Mössbauer spectrum in the rapid-relaxation limit, and in Secs. 3–5 we consider a number of particular examples.

2. FORMULATION OF PROBLEM AND DERIVATION OF GENERAL FORMULAS

We consider a Mössbauer atom with nonzero total angular momentum of the electron shell (which for brevity will be designated by the letter S); let I_g and I_e be the nuclear spins in the ground and excited states. Owing to the hyperfine interaction between the nuclear and electron spins, for which we assume a Hamiltonian in the form

$$H_{hf} = A_n A_e S I_e \quad (1)$$

($\kappa = e, g; i, j = x, y, z$), a magnetic hyperfine structure appears in the Mössbauer spectra. (Summation over repeated indices is implied throughout.) The character of the manifestation of the hfs depends significantly on the interaction of the electron spin with the phonons, with the neighboring paramagnetic ions, and with the conduction electrons in the metals; in one word, on all the interactions that cause relaxation of the electron spin.

We represent the total Hamiltonian of the system in the form

$$H_{\kappa} = H_{\kappa}^* + H_{\kappa}^{*+} + H_{e\kappa}, \quad (2)$$

where H_{κ}^* is the nuclear quadrupole interaction (which does not depend on the spin of the electron shell) at $H_{e\kappa}$ is a Hamiltonian that includes the interaction of the electron shell with the crystal field and with the external magnetic field, the interaction responsible for the relaxation, and also the Hamiltonian corresponding to the rest of the system. The concrete form of these interactions is of no importance for the time being.

An exact expression for the shape of the absorption spectrum of a γ quantum with wave vector \mathbf{k} and polarization η_{α} ($\alpha = 1, 2$), in the case of a thin absorber, is given by

$$\varphi(\omega) = \text{Re} \int_0^{\infty} dt \exp\left(i\omega t - \frac{\Gamma}{2} t\right) \langle (\eta_{\alpha}^* \mathbf{j}(\mathbf{k}, t)) (\eta_{\alpha} \mathbf{j}^*(\mathbf{k})) \rangle, \quad (3)$$

where Γ is the total width of the source and absorber lines; $\mathbf{j}^*(\mathbf{k})$ is the Fourier component of the density operator of the conduction and spin currents of the nucleons in the nucleus, which is responsible for the transition of the nucleus from the ground state to the excited state, and

$$\mathbf{j}(\mathbf{k}, t) = \exp\left(\frac{i}{\hbar} H_{e\kappa} t\right) \mathbf{j}(\mathbf{k}) \exp\left(-\frac{i}{\hbar} H_{e\kappa} t\right).$$

The angle brackets denote statistical averaging over a canonical ensemble with Hamiltonian H_{κ} .

We now introduce the Liouville operator \hat{L} in accordance with the formula

$$\hat{L}A = \hbar^{-1}(H_{\kappa}A - AH_{\kappa}), \quad (4)$$

where A is the usual quantum mechanical operator. The correlation function in formula (3) can then be rewritten in the form

$$\langle (\eta_{\alpha}^* \mathbf{j}(\mathbf{k})) e^{-\hat{L}t} (\eta_{\alpha} \mathbf{j}^*(\mathbf{k})) \rangle. \quad (5)$$

It is seen from the definition (4) that the Liouville operator \hat{L} transforms one ordinary operator into another, and in this sense it can be called a superoperator. It can be represented in the form of a supermatrix (a matrix acting on the matrix) with four indices. Thus, formula (4) corresponds to the notation

$$\sum_{n'm'} \hat{L}_{nm, n'm'} A_{n'm'} = \frac{1}{\hbar} \sum_{\kappa} (H_{n\kappa} A_{\kappa m} - A_{n\kappa} H_{\kappa m}).$$

Substituting (5) in (3) and integration with respect to time, we obtain

$$\varphi(\omega) = -\text{Im} \left\langle (\eta_{\alpha}^* \mathbf{j}(\mathbf{k})) \frac{1}{\omega - \hat{L} + i\Gamma/2} (\eta_{\alpha} \mathbf{j}^*(\mathbf{k})) \right\rangle. \quad (6)$$

We now assume that the temperature T of the sample satisfies the condition

$$k_B T \gg \hbar \omega_{\text{hf}}, \quad (7)$$

where k_B is the Boltzmann constant and ω_{hf} is a cer-

tain characteristic frequency corresponding to the hyperfine interaction. In this case, after statistical averaging in (6), we can neglect in the expression for the density matrix ρ the interaction of the Mössbauer nucleus with the remaining crystal, and write approximately

$$\rho \approx \frac{1}{2I_{\kappa} + 1} \frac{\exp\{-H_{e\kappa}/k_B T\}}{Z_{e\kappa}} = \frac{1}{2I_{\kappa} + 1} \rho_{e\kappa}.$$

Here Z is the partition function. As a result we get for $\varphi(\omega)$

$$\varphi(\omega) = -\frac{1}{2I_{\kappa} + 1} \text{Im} \sum_{m_g} \langle m_g | (\eta_{\alpha}^* \mathbf{j}(\mathbf{k})) \hat{G}(\omega) (\eta_{\alpha} \mathbf{j}^*(\mathbf{k})) | m_g \rangle, \quad (8)$$

where $|m_g\rangle$ are the eigenfunctions of I_{κ}^z , and the superoperator

$$\hat{G}(\omega) = P \frac{1}{\omega - \hat{L} + i\Gamma/2} P \quad (9)$$

now acts only on the nuclear variables, inasmuch as

$$P = \text{Sp}_{e\kappa}(\rho_{e\kappa} \dots) \quad (10)$$

in (9) is a projecting operator with the following obvious properties: If A is an operator acting both on the nuclear and on the electron variables, then $PA = \text{Tr}_{e\kappa}(\rho_{e\kappa} A)$ acts only on the variables of the nucleus. On the other hand if B is an operator acting on the nuclear variables, then $PB = B$. In addition, $P^2 = P$. Expression (9) for $\hat{G}(\omega)$ is easily transformed into (see^[9,13])

$$\hat{G}(\omega) = \frac{1}{\omega - \hat{P}\hat{L}P - \hat{M}(\omega) + i\Gamma/2}, \quad (11)$$

where the superoperator

$$\hat{M}(\omega) = \hat{P}\hat{L}Q \frac{1}{\omega - \hat{Q}\hat{L}Q + i\Gamma/2} \hat{Q}\hat{L}P \quad (12)$$

determines precisely the renormalization, due to electron-spin relaxation, of the positions and widths of the remaining components of the spectrum. Here $Q = 1 - P$.

Let us proceed to analyze these expressions. In view of the definitions (4) and (10), it is easy to verify that $\hat{P}\hat{L}P \equiv \langle \hat{L} \rangle$ is a Liouville operator acting only in the space of the nuclear variables and corresponds to the average Hamiltonian

$$\langle H_{\kappa}^* \rangle = H_{\kappa}^* + A_{\kappa} A_{ij} \langle S^i \rangle_{e\kappa} I_{\kappa}^j, \quad (13)$$

where $\langle S^i \rangle_{e\kappa} = \text{PS}^i$. In other words,

$$\langle \hat{L} \rangle B = \hbar^{-1} (\langle H_{\kappa}^* \rangle B - B \langle H_{\kappa}^* \rangle). \quad (14)$$

As to the superoperator $\hat{M}(\omega)$, a simple analysis shows that it can be transformed into

$$\hat{M}(\omega) = P (\hat{L}_{n\kappa} - \langle \hat{L}_{n\kappa} \rangle) \frac{1}{\omega - \hat{Q}\hat{L}Q + i\Gamma/2} (\hat{L}_{n\kappa} - \langle \hat{L}_{n\kappa} \rangle) P, \quad (15)$$

where the Liouville operator $\langle \hat{L}_{\text{hf}} \rangle$ corresponds to $\langle H_{\text{hf}}^* \rangle = A_{\kappa} A_{ij} \langle S^i \rangle_{e\kappa} I_{\kappa}^j$. It is seen from (15) that $\hat{M}(\omega)$ is now proportional to the square of the hyperfine interaction. On the other hand, in the rapid-relaxation case considered by us, when

$$\omega_{\text{hf}} \tau_{\text{rel}} \ll 1 \quad (16)$$

(where τ_{rel} is a certain characteristic electron-spin relaxation time), the interaction of the electron spin with the remaining crystal is much stronger than the hyperfine interaction, so that formula (15) can be significantly simplified. Namely, the operator $\hat{Q}\hat{L}Q$ in the denominator of (15) can be replaced by the electron operator $\hat{L}_{e\kappa}$. In addition, at frequencies ω on the order

of ω_{hf} and less we can neglect the frequency dependence of $\hat{M}(\omega)$ and put $\omega = 0$ in (15). It is obvious here that we remain within the framework of the same accuracy with which we can retain in the denominator for (15) only the electron operator \hat{L}_{e1} . The dependence of \hat{M} on ω becomes significant when we go away far from the center of the resonance into the frequency region $\omega \gg \omega_{hf}$, but of the order of \hbar/τ_{rel} . Here, however, we are not interested in such high frequencies. We note only that the dependence of \hat{M} on ω may turn out to be significant also when it comes to determining the total intensity of the spectral lines. Neglect of this dependence means neglect of quantities on the order of $(\omega_{hf}\tau_{rel})^2$ in the total intensity. In spite of the relative smallness of this correction, it may nevertheless turn out to be noticeable in precision measurements of the Mössbauer-effect probability. In the present paper, however, we are not interested in these effects.

Using now the explicit form (1) of the Hamiltonian H_{hf} , we obtain within the framework of the approximations assumed above the following formula for \hat{M} :

$$\hat{M} = \frac{1}{2} \alpha_{ij} [A_e^2 (I_e^j I_e^i + I_e^i I_e^j) - A_g^2 (I_g^j I_g^i + I_g^i I_g^j)] - \frac{1}{2} \beta_{ij} e^{ijk} (A_e^2 I_e^k - A_g^2 I_g^k) - i \gamma_{ij} (A_e I_e^i - A_g I_g^i) (A_e I_e^j - A_g I_g^j), \quad (17)$$

where

$$\alpha_{ij} = \frac{1}{4} A_{ip} A_{jq} \sum_{\alpha, \beta} \frac{\rho_{\alpha} - \rho_{\beta}}{E_{\alpha} - E_{\beta}} (\mathcal{S}_{\alpha\beta}^p \mathcal{S}_{\beta\alpha}^q + \mathcal{S}_{\alpha\beta}^q \mathcal{S}_{\beta\alpha}^p), \quad (18)$$

$$\beta_{ij} = \frac{1}{2i} A_{ip} A_{jq} P \sum_{\alpha, \beta} \frac{\rho_{\alpha}}{E_{\alpha} - E_{\beta}} (\mathcal{S}_{\alpha\beta}^p \mathcal{S}_{\beta\alpha}^q - \mathcal{S}_{\alpha\beta}^q \mathcal{S}_{\beta\alpha}^p), \quad (19)$$

$$\gamma_{ij} = \pi A_{ip} A_{jq} \sum_{\alpha, \beta} \rho_{\alpha} \mathcal{S}_{\alpha\beta}^p \mathcal{S}_{\beta\alpha}^q \delta(E_{\alpha} - E_{\beta}). \quad (20)$$

Here $|\alpha\rangle$ and E_{α} are the eigenfunctions and eigenvalues of the Hamiltonian H_{e1} ; $\rho_{\alpha} = \langle \alpha | \rho_{e1} | \alpha \rangle$; $\mathcal{S}^i = \mathcal{S}^i - \langle \mathcal{S}^i \rangle_{e1}$; finally, P in formula (19) means the principal value. We note that α_{ij} , β_{ij} , and γ_{ij} are real quantities, with

$$\alpha_{ji} = \alpha_{ij}, \quad \beta_{ji} = -\beta_{ij}, \quad \gamma_{ji} = \gamma_{ij}. \quad (21)$$

Formulas (8), (11), and (17) provide us with a complete phenomenological description of the form of the spectrum in the limit of rapid relaxation, such, however, that all the parameters have a clearly defined physical meaning. An important circumstance is that these formulas are a rigorous result obtained under the assumptions (7) and (16), i.e., under the condition that the sample temperature is much higher than the hyperfine interaction and that the relaxation time of the electron spin is much less than ω_{hf}^{-1} . Formula (17) has then a simple physical meaning. The contributions with α_{ij} and β_{ij} describe simply a renormalization of the nuclear levels in second-order perturbation theory, wherein the term with α_{ij} is equivalent to a certain additional "quadrupole" interaction and to an additional "chemical" shift, while the term with β_{ij} is equivalent to a quasi-magnetic hyperfine interaction.

As to the terms with γ_{ij} , they are connected with the following processes. If an additional magnetic field h_z is produced at the nucleus as a result of the fluctuations, then the positions of the hyperfine-structure lines shift by an amount on the order of $(A_e m_e - A_g m_g) h_z$. But since h_z varies with time, the presence of a random field leads to a line broadening which is obviously of the order of

$$\tau_c \hbar^{-1} [(A_e m_e - A_g m_g) \hbar_z]^2, \quad (22)$$

where τ_c is the characteristic time during which the field h_z retains its value and direction, while \hbar_z is the field amplitude averaged over this time. It is clear that in the general case the fluctuations in the other directions (i.e., along the axes x and y) are on a par, and this is the reason for the form of the last term in (17).

We have expressed the superoperator \hat{M} in (17) in terms of components of the spin operators of the ground and excited states of the nucleus. In exactly the same manner as in the case of the Liouville operator L , the matrix elements \hat{M} are characterized by four indices m_e , m_g , m'_e , and m'_g , and are determined from the formulas

$$\begin{aligned} (I_e^i I_e^j)_{m_e m_g, m'_e m'_g} &= (I_e^i I_e^j)_{m_e m_g} \delta_{m_e m'_e, m_g m'_g}, \\ (I_g^i I_g^j)_{m_e m_g, m'_e m'_g} &= (I_g^i I_g^j)_{m'_e m'_g} \delta_{m_e m'_e, m_g m'_g}, \\ (I_e^i I_g^j)_{m_e m_g, m'_e m'_g} &= (I_e^i)_{m_e m'_e} (I_g^j)_{m_g m'_g}. \end{aligned}$$

In a number of physical situations, further significant simplification of the relaxation operator \hat{M} is possible. For example, if it is assumed that the sample temperature is not too low and the relaxation time is not too short, so that the following condition is satisfied

$$k_B T \tau_{rel} / \hbar \gg 1, \quad (23)$$

then it is easily seen that $\alpha_{ij} \ll \gamma_{ij}$, and consequently the contribution of the terms with α_{ij} to \hat{M} can be neglected. Indeed, from expression (18) for α_{ij} we see that the sum over α and β has no singularity as $E_{\alpha} \rightarrow E_{\beta}$, and at the small difference $E_{\alpha} - E_{\beta} \approx \hbar/\tau_{rel}$ we have $(\rho_{\alpha} - \rho_{\beta}) / (E_{\alpha} - E_{\beta}) \lesssim 1/k_B T$. We can therefore conclude immediately that the terms with α_{ij} are of the order of $(\hbar\omega_{hf})^2/k_B T$, whereas the contribution of the terms with γ_{ij} is of the order of $(\hbar\omega_{hf})^2/(\hbar/\tau_{rel})$. We shall henceforth assume that the condition (33) is satisfied.

As to the tensor β_{ij} , it is clear even from symmetry considerations that in the absence of an external magnetic field or else of spontaneous magnetization of the sample, all the components of this tensor are rigorously equal to zero. Indeed, β_{ij} is an antisymmetrical tensor, and to construct it it is necessary to have a certain pseudovector, such as may be the magnetic field. If the latter differs from zero, then in the general case the tensor β_{ij} is also different from zero, and at a certain value of the field H the tensor β_{ij} may become comparable with γ_{ij} . The tensor β_{ij} reaches its maximum value at $H \approx \hbar/\mu_B \tau_{rel}$, where μ_B is the Bohr magneton. Further increase of the field, β_{ij} tends to zero like c/H , where the proportionality constant c no longer depends on the details of the relaxation process and is determined only by the character of the splitting of the ion levels by the crystal field. Indeed, it is easily seen from (19) that if $H > \hbar/\mu_B \tau_{rel}$ one can take $|\alpha\rangle$ and E_{α} in this formula to mean respectively the states and the energies of the individual ion in the crystal field, and neglect the interaction that causes the electron-spin relaxation. In the case of ferromagnetic substances, an expression valid at temperatures below the critical temperature Θ_c , where the spin-wave approximation is still applicable, was indeed obtained for β_{ij} in [2]. It turned out there that

$$\beta_{ij} = e^{ijz} \frac{H_e^2}{2\sqrt{2}\pi S \Theta_c \sqrt{\Theta_c \Delta}},$$

where the z axis was chosen along the direction of the spontaneous magnetization and the remaining notation is that of [2].

It is interesting to note that it is quite difficult to de-

rive the term with β_{ij} within the framework of a stochastic analysis, since it is connected not with real relaxation processes but with virtual processes that cause renormalization of the nuclear levels.

Summarizing the results obtained above, we arrive at the following general formulas that provide a complete description of the shape of the Mössbauer spectrum in the fast-relaxation limit:

$$\varphi(\omega) = -\frac{1}{2I_e + 1} \text{Im} \sum_{\substack{m_e m_g \\ m_e' m_g'}} (\eta_{\alpha'} j(k))_{m_e m_g} \times \left(\frac{1}{\omega - \langle \hat{L} \rangle - \hat{M} + i\Gamma/2} \right)_{m_e m_g, m_e' m_g'} (\eta_{\alpha} j^+(k))_{m_e' m_g'} \quad (24)$$

where in accordance with (13) and (14) we have

$$\langle \hat{L} \rangle = \frac{eQ_e V_{ij}}{4I_e(2I_e - 1)} \left[I_e^i I_e^j + I_e^i I_e^i - \frac{2}{3} \delta^{ij} I_e(I_e + 1) \right] - \frac{eQ_g V_{ij}}{4I_g(2I_g - 1)} \left[I_g^i I_g^j + I_g^i I_g^i - \frac{2}{3} \delta^{ij} I_g(I_g + 1) \right] + A_{ij} \langle S^i \rangle_{e1} (A_e I_e^j - A_g I_g^j), \quad (25)$$

and the superoperator \hat{M} is given by

$$\hat{M} = -\beta^k (A_e^2 I_e^k - A_g^2 I_g^k) - i\gamma_{ij} (A_e I_e^i - A_g I_g^i) (A_e I_e^j - A_g I_g^j). \quad (26)$$

Here $\beta^k = \beta_{ij} \epsilon^{ijk}/2$. The rules for finding the matrix elements of $\langle \hat{L} \rangle$ and \hat{M} were given above. (In (25) we used the explicit expression for H_Q .)

As seen from (24), in its most general formulation, the problem of finding the shape of the spectrum in the rapid-relaxation limit reduces to an inversion of a matrix of order $(2I_e + 1)(2I_g + 1)$, and the number of the parameters that determine the relaxation is relatively small. On the other hand, if the problem possesses a definite symmetry, the number of these parameters can be greatly decreased. It will be shown in the subsequent sections that formulas (24)–(26) make it possible to describe a great variety of forms of relaxation spectra.

3. ASYMMETRY OF QUADRUPOLE SPECTRA. THE BLUME EFFECT

We shall analyze concrete cases with the isotope Fe^{57} as an example. If the Mössbauer nucleus experiences in addition to the magnetic hyperfine interaction also a quadrupole interaction, then after the relaxation collapse of the magnetic hyperfine structure into a quadrupole doublet, the latter turns out to be highly asymmetrical. This is known as the Blume effect^[3] and was observed in experiment many times.

According to Blume's first investigations, where a simple relaxation model was used, the quadrupole-spectrum line corresponding to the transitions $(\pm 1/2 \rightarrow \pm 1/2)$ and $(\pm 1/2 \rightarrow \mp 1/2)$ turned out to be less broadened, and hence more intense than the second line $(\pm 1/2 \rightarrow \pm 3/2)$. Several experimentally measured spectra have revealed just this type of asymmetry. The inverse situation, however, is also possible where it is precisely the first of these two lines which is more broadened, and hence less intense. An example of such a behavior was given in^[10], where the authors had to complicate greatly the initial mathematical formalism in order to consider this case.

It will be shown below that within the framework of the general description presented by us we can obtain a great variety of quadrupole-doublet forms differing not only in the intensities of the individual peaks but also in the structure of each peak individually.

Thus, we turn to the general formulas (24)–(26), and in order not to complicate excessively the analysis that follows we make a number of assumptions. We assume first that the electrostatic field gradient at the nucleus has axial symmetry relative to the z axis, and that the quadrupole interaction itself is much larger than the relaxation terms as well as the line width Γ , so that the Mössbauer spectrum is visually a doublet. On the other hand, we assume that the relaxation terms themselves are of the same order as Γ . By the same token, they determine to a considerable degree the structures of the individual components of the doublet. Finally, we put $\langle S \rangle_{e1} = 0$. Recognizing that $I_g = 1/2$, we have

$$\langle \hat{L} \rangle + \hat{M} = Q[(I_e^2)^2 - 1/3 I_e(I_e + 1)] - \beta_e (A_e^2 I_e^i - A_g^2 I_g^i) - i\gamma_{ij} (A_e I_e^i - A_g I_g^i) (A_e I_e^j - A_g I_g^j)$$

We consider first the situation when there is no external magnetic field; then $\beta_i = 0$. From among the remaining possible cases we separate four cases in which all the tensor components γ_{ij} vanish with the exception of (a) $\gamma_{zz} = \gamma$ (longitudinal relaxation), (b) $\gamma_{xx} = \gamma$ (anisotropic transverse relaxation), (c) $\gamma_{xx} = \gamma_{yy} = \gamma/2$ (isotropic transverse relaxation), and (d) $\gamma_{xx} = \gamma_{yy} = \gamma_{zz} = \gamma/3$ (isotropic relaxation).

The case of longitudinal relaxation is simplest. The spectrum consists then of three lines with the parameters listed in the table (case a). The corresponding spectrum is shown in Fig. 1a, where we assume for the sake of argument $Q = 5\Gamma$, $\gamma A_g^2 = \Gamma$, and $A_e = -0.571 A_g$. As seen from this figure, the spectrum is a clearly-pronounced asymptotic doublet typical of the normal Blume effect^[3]. The same figure shows (dashed) the spectrum at $\gamma = 0$.

In cases b and c the character of the asymmetry changes (see Figs. 1b and 1c). The peak that becomes more intense corresponds to the transitions $(\pm 1/2 \rightarrow \pm 3/2)$. The parameters of the individual components of these spectra are also listed in the table (b-case of anisotropic transverse relaxation and c-case of isotropic transverse relaxation).

Although the spectra in Figs. 1b and 1c are similar, there is nevertheless a definite difference in the structure of the peak at $\omega = -Q$; this difference can be easily revealed by analyzing the form of the spectrum with the aid of a computer.

In the case of isotropic relaxation (see Fig. 1d), the

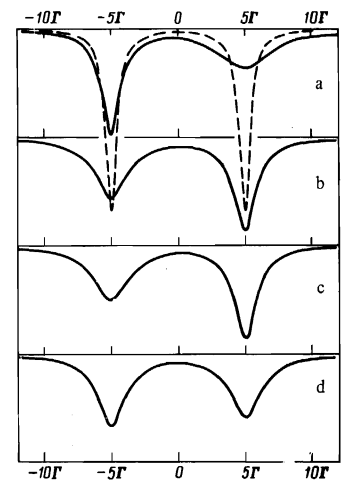


FIG. 1. Asymmetry of quadrupole spectra in the absence of an external magnetic field (see the explanation in the text).

	Position	Width	Intensity, rel. un.*
a	Q	$\Gamma + \frac{1}{2}\gamma(3A_e - A_g)^2$	$\frac{1}{2}$
	-Q	$\Gamma + \frac{1}{2}\gamma(A_e - A_g)^2$	$\frac{1}{3}$
b	Q	$\Gamma + \frac{1}{2}\gamma(3A_e + A_g)^2$	$\frac{1}{6}$
	-Q	$\Gamma + \frac{1}{2}\gamma(7A_e^2 - 4A_e A_g + A_g^2)$	$\frac{1}{2}$
c	Q	$\Gamma + \frac{1}{2}\gamma(7A_e^2 + 4A_e A_g + A_g^2)$	$\frac{1}{12}$
	-Q	$\Gamma + \frac{1}{2}\gamma(3A_e^2 + A_g^2)$	$\frac{1}{2}$
d	Q	$\Gamma + \frac{1}{2}\gamma(7A_e^2 - 4A_e A_g + A_g^2)$	$\frac{1}{6}$
	-Q	$\Gamma + \frac{1}{2}\gamma(5A_e^2 - 2A_e A_g + A_g^2)$	$\frac{1}{2}$
	Q	$\Gamma + \frac{1}{6}\gamma(15A_e^2 - 10A_e A_g + 3A_g^2)$	$\frac{1}{3}$
	-Q	$\Gamma + \frac{1}{6}\gamma(15A_e^2 + 2A_e A_g + 3A_g^2)$	$\frac{1}{6}$

*The intensities presented here are for polycrystalline samples.

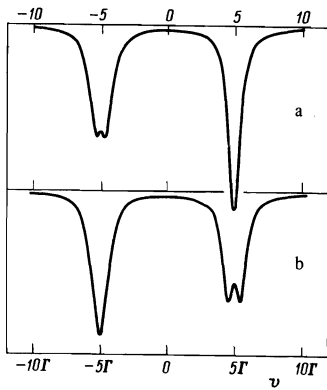


FIG. 2

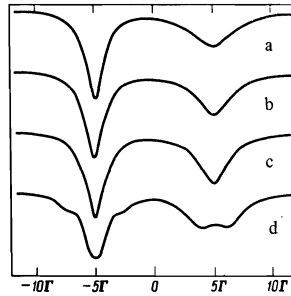


FIG. 4

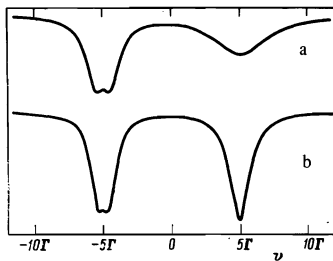


FIG. 3

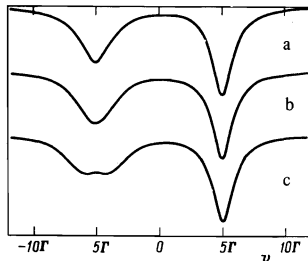


FIG. 5

FIG. 2. Influence of "pseudomagnetic" term on the character of the asymmetry of the quadrupole spectrum ($Q = 5\Gamma, \beta A_g^2 = \Gamma$): a) $\beta \parallel z$, b) $\beta \perp z$.

FIG. 3. Simultaneous effect of the terms with β and with γ ($Q = 5\Gamma, \beta A_g^2 = \Gamma$): a) $\beta = \gamma$; b) $\beta = 5\gamma$. The vector β is parallel to the z axis.

FIG. 4. Simultaneous effect of the terms with β and with γ . The vector β is perpendicular to the z axis ($Q = 5\Gamma, \gamma A_g^2 = \Gamma$): a) $\beta = 0.5\gamma$, b) $\beta = \gamma$, c) $\beta = 1.5\gamma$, d) $\beta = 3\gamma$.

FIG. 5. Case when β is parallel to the z axis, $\gamma_{xx} = \gamma$, and the remaining components of the tensor γ_{ij} are equal to zero ($Q = 5\Gamma, \gamma A_g^2 = \Gamma$): a) $\beta = \gamma$, b) $\beta = 2\gamma$, c) $\beta = 3\gamma$.

quadrupole doublet becomes visually symmetrical. Yet, as seen from the table (case d), the peaks have different structures.

Of great interest is the influence exerted on the shape of the spectrum by the term

$$-\beta(A_e^2 I_z - A_g^2 I_x), \quad (27)$$

which appears when an external magnetic field is applied to the sample. We shall dwell on this question in greater detail, since this type of manifestation of relaxation effects in Mössbauer spectra was not considered in detail before. We start with consideration of the idealized case when $\gamma_{ij} = 0$. It is obvious that the contribution (27) will cause a splitting of the individual

doublet components, since it is equivalent in structure to the interaction of the nucleus with some additional magnetic field, the value of which is, however, different for the ground and excited states of the nucleus. It is interesting that the character of the resultant splitting depends significantly on how the vector β is oriented relative to the z axis. In the case when β is directed along the z axis, owing to the specifics of the values of A_e and A_g for the Fe^{57} nucleus, the doublet line with energy $\omega = -Q$ is split much more strongly (see Fig. 2a). On the other hand, the situation is reversed if the vector β is perpendicular to the z axis (see Fig. 2b). This may be the cause of the very interesting influence of an external magnetic field on the Blume effect. The contribution (27) to \bar{M} from the external magnetic field can greatly influence the character of the asymmetry and even reverse its sign. This can be seen in Fig. 3, which shows the hyperfine structure spectra in the case when the vector β is directed along the z axis, $\gamma_{zz} = \gamma$, and all the remaining components of the tensor γ_{ij} are equal to zero. It is interesting that in this case the line with $\omega = Q$ is not sensitive to the presence of a term with β , whereas the line $\omega = -Q$ is split into four components.

On the other hand, if the pseudomagnetic vector β is perpendicular to the z axis and the tensor γ_{ij} has qualitatively the same form, then the addition of the term with β enhances the Blume effect (see Fig. 4). It is of interest to note here the structure of the doublet components, which consist, depending on the relation between β and γ , of one, two, three, or four lines. At other orientations of the vector β relative to the z axis, and at a different structure of the tensor γ_{ij} , no other qualitatively new situations arise (see, e.g., Fig. 5).

4. SPECTRA IN THE ABSENCE OF QUADRUPOLE INTERACTION

If there is no quadrupole interaction or spontaneous magnetization of the sample, then under rapid relaxation conditions the magnetic hyperfine structure spectrum collapses into a single line, the shape of which is described by Eqs. (24) and (26), in which $\langle \hat{L} \rangle$ and β_i should be set equal to zero. Depending on the structure of the tensor γ_{ij} , the line can acquire qualitatively different shapes.

The customarily employed models correspond in our case to longitudinal relaxation. The shape of the collapsed lines corresponds in this case to a peak that is sharply pointed at the center, and a line with this shape was actually observed in experiment. It is clear, however, that such cases are not general, and, in particular, Mörup has observed in $NH_4Fe(SO_4)_2 \cdot 12H_2O$ a line^[16] whose shape could not be described in any way by models with longitudinal relaxation. To explain the results, he had to resort to an additional nuclear-spin rather than the electronic relaxation mechanism.

We have reduced the experimental spectrum measured by Mörup by using the formulas cited above, in which we varied the tensor components γ_{ij} until best agreement was obtained (see Fig. 6, where the solid curve is the result of the theoretical calculations). The best agreement was obtained in the case $\gamma_{ij} = \gamma_{ij}^0$, i.e., in the case of isotropic relaxation. It is interesting to note that in spite of the strong relaxation the lines are in this case pure Lorentzians with width $\Gamma + \frac{1}{2}\gamma(15A_e^2$

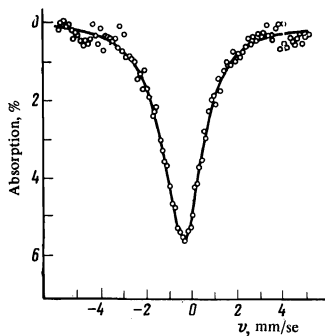


FIG. 6. Results of theoretical reduction of the experimental spectrum measured in [16] ($T = 200^\circ\text{K}$, $H = 0$).

$-10A_e A_g + 3A_g^2$). Calculations yield for γ a value $\gamma = 0.342 \text{ sec/cm}$ if A_e and A_g are determined using $H_{hf} = 590 \text{ kG}$ as the hyperfine field for the doublet with $S_z = \frac{5}{2}$ and it is assumed that $\Gamma = 0.35 \text{ mm/sec}$ [16, 17]. Actually the result obtained by us means that in the compound $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ the iron-ion spin fluctuations are isotropic in all directions. This is not at all surprising, since the nearest environment of the Fe^{3+} ions in iron-ammonium alums has a nearly cubic symmetry. Moreover, we succeeded in adequately describing the spectrum within the framework of phenomenological constants of unique nature, whereas in [16] it was necessary to introduce two qualitatively different relaxation mechanisms.

On applying a strong external magnetic field, Mørup [16] observed a noticeable narrowing of the line and a change in its shape in a direction called for by the predominance of the longitudinal relaxation. It is easy to understand this change of shape qualitatively even from formulas (19) and (20), but we emphasize the following circumstances. When an external magnetic field is applied, the superpropagator \hat{M} (see (26)) acquires a pseudomagnetic term that depends on the orientation of the external field relative to the crystal-symmetry axes. Consequently, in polycrystals the problem of reconstructing from the measured spectra the constants γ_{ij} and β_i , which determine the relaxation process, is very complicated in the presence of an external magnetic field. This problem calls for a special theoretical analysis. No such problem arises in single-crystal samples, and experiments with single crystals are exceedingly important for the determination of these fundamental relaxation constants. On the other hand, if there is no magnetic field, then experiments with polycrystals also give exactly defined information concerning the relaxation process.

5. "ANOMALOUS" SPECTRA

A number of presently known experimental relaxation spectra in magnetically-ordered substances [18-23] exhibit a so-called "anomalous" behavior when the Curie point is approached. The "anomaly" is manifest in the fact that the sextuplet of lines usually comprising the iron spectrum acquires abruptly a central peak as TC is approached, although the well-resolved structure corresponding to the magnetically ordered state still remains. In other words, an impression is gained that the magnet breaks up into magnetic and paramagnetic phases.

To explain this "anomalous" behavior of the spectrum, Levinson and Luban have suggested [12] that in addition to the rapid relaxation processes of spin-fluctuation "diffusion" there occurs in magnetically ordered

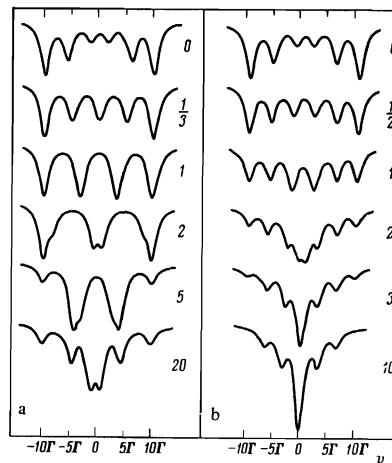


FIG. 7. Changes experienced by hfs spectra when the "magnetic" and "pseudomagnetic" terms compete: a) $\beta \parallel \alpha$, b) $\beta \perp \alpha$. The numbers at the curves stand for the ratio $-\beta A_g/\alpha$.

substances also a slower process wherein macroscopically large regions are remagnetized at once, i.e., a process analogous to the relaxation of supermagnetic particles. It can be assumed that as TC is approached the rate of such a magnetization reversal increases, and this can be manifest in the hfs spectra as a relaxation that is inherent in pure paramagnetic substances. Unfortunately, it is still impossible to carry out even approximate calculations within the framework of this model, so that the extent to which the model predicted in [12] is valid is still unclear.

We wish to point out in this connection that the general description proposed here for the hfs spectra covers in the limit of rapid relaxation a number of cases wherein the form of the spectrum recalls the form of the "anomalous" spectra. These spectra appear when the relaxation-rate decrease expected from general considerations as the Curie point is approached is manifest by the appearance of a large "pseudomagnetic" term comparable with the last term of $\langle \hat{L} \rangle$ (25), which determines the usual magnetic hyperfine splitting. Figure 7 shows the hfs spectra at various ratios of the parameters β_j and $\alpha_j = A_{ij} \langle S_i^z \rangle_{e1}$. In the left-hand side of Fig. 7 are shown the spectra for the case $\beta \parallel \alpha$, and in the right hand side for the case $\beta \perp \alpha$. It is seen from Fig. 7 that, especially in the case $\beta \perp \alpha$, the resultant spectra are very similar to the "anomalous" ones (cf., e.g., [20]). Thus, one can postulate the appearance of an appreciable "pseudomagnetic" term as an alternative explanation of the "anomalous" spectra, without going outside the framework of rapid relaxation processes.

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