Narrowing of γ-resonance lines in crystals by radio-frequency fields

Yu. A. Il'inskiĭ and R. V. Khokhlov

Moscow State University
(Submitted May 11, 1973)
Zh. Eksp. Teor. Fiz. **65**, 1619–1625 (October 1973)

Narrowing of γ-resonance lines in crystals is studied by methods employed in nuclear magnetic resonance. The resulting γ-radiation spectrum, linewidth, and line intensity distribution are analyzed.

The main difficulty in the development of a γ-ray laser using long-lived isomers is caused by the broadening of the Mossbauer γ-resonance line in comparison with the natural width. To obtain stimulated γ radiation, the line width must not exceed the natural width $1/T_1$ (T_1 is the lifetime of the excited state of the nucleus) by more than three or four orders[1]. At the same time, the line width at $T_1 > 10^{-5}$ sec is practically independent of the lifetime and is of the order of 10^4–10^5 Hz.[2]

The narrowing of the Mossbauer line is also of independent interest, since it uncovers new ways in γ spectroscopy and makes fundamental physical experiments feasible (see, e.g.,[3]).

There are several line-broadening mechanisms. Some of them can be eliminated by growing sufficiently perfect crystals of sufficiently pure substances. At the same time the magnetic dipole-dipole interaction of a nuclei, which leads to a broadening 10^4–10^5 Hz, is impossible to eliminate in practice, since the magnetic moments of the nuclei are different in the states between which the γ transition takes place. Since only a fraction of the nuclei is in the excited state, the crystal becomes inhomogeneous with respect to the values of the magnetic moment.

The dipole-dipole interaction of the nuclei usually determines the line width in nuclear magnetic resonance (NMR) in solids (line width on the order of 10^4–10^5 Hz). In the liquids, however, owing to the averaging that takes place in the course of motion, the corresponding line width is much smaller (down to 10^{-2} – 10^{-1} Hz). In solids, the NMR line width can be narrowed down by various methods, the most universal of which is the application of a series of $\pi/2$ radio pulses to the sample[4].

A corresponding procedure can be used also for γ resonance. This eliminates simultaneously the broadenings due to the electric quadrupole moments of the nuclei, to paramagnetic impurities, to inhomogeneities of the external magnetic fields, and to magnetic interactions with "foreign" nuclei and isotopes, provided that all these broadenings are small enough. We consider in this article the question of using such a procedure for γ resonance, and we estimate the width and intensity of the lines that can be obtained through this procedure.

1. INFLUENCE OF EXTERNAL RADIOFREQUENCY FIELD ON γ RESONANCE

The Hamiltonian of the nuclei and radiation in an external static magnetic field and a radiofrequency field is given by

$$\mathcal{H}=\mathcal{H}_n+\mathcal{H}_\gamma+\mathcal{H}', \tag{1}$$

where $\mathcal{H}_n$ is the Hamiltonian of the nuclei, $\mathcal{H}_\gamma$ is the Hamiltonian of the γ radiation, and

$$\mathcal{H}'=\sum_\lambda (a_\lambda \mathcal{H}_\lambda + a_\lambda^+ \mathcal{H}_\lambda^+)$$

is the interaction operator ($a\lambda$ is the γ-quantum annihilation operator in the mode with index λ), while the operator $\mathcal{H}_\lambda$ acts only on the variables of the nucleus. The nuclei are assumed to be fixed; only a recoilless emission (absorption) line is considered. The action of the recoil is considered in the theory of the Mossbauer effect. If no account is taken of the interaction between the nuclei, this line has an infinitesimally small width in lowest-order perturbation theory, and when the next higher approximations are considered it has the natural line width $1/T_1$.

The operator $\mathcal{H}_n$, owing to the presence of external alternating fields, depends on the time. We introduce unitary evolution operators of the subsystems $U_n(t)$ and $U_\gamma(t) = \exp\{-i\hbar^{-1}\mathcal{H}_\gamma(t)\}$ ($U_n(0) = 1$, $U_\gamma(0) = 1$), which satisfy the Schrödinger equation with Hamiltonians $\mathcal{H}_n$ and $\mathcal{H}_\gamma$, and commute with each other.

In the interaction representation, we obtain equations for the density matrix ρ:

$$i\hbar\partial\rho/\partial t=[\mathcal{H}'(t), \rho], \tag{2}$$

where $\mathcal{H}'(t) = U_n^{-1}(t)U_\gamma^{-1}(t)\mathcal{H}'U_\gamma(t)U_n(t)$.

In the second perturbation-theory approximation, that part of the operator ρ which is of interest in our problem is given by

$$\rho^{(2)}(t)=\frac{1}{\hbar^2}\int_0^t\int_0^t \mathcal{H}'(t')\rho_0\mathcal{H}'(t'')\,dt'\,dt''. \tag{3}$$

Assuming that the density matrix at the instant $t = 0$ is given by $\rho_0 = \rho_{0n}\rho_{0\gamma}$, where $\rho_{0\gamma} = |0\rangle\langle 0|$, and ρ_{0n} is the density matrix of the nuclei (i.e., there are no γ quanta at the instant $t = 0$), we obtain the probability of emission of a γ quantum in the mode λ with frequency $\omega\lambda$ by the instant of time t:

$$P_\lambda(t)=\int_0^t\int_0^t B_\lambda(t',t'')\exp\{i\omega_\lambda(t'-t'')\}dt'\,dt'', \tag{4}$$

where

$$B_\lambda(t',t'')=\frac{1}{\hbar^2}\mathrm{Sp}_n\{U_n^{-1}(t')\mathcal{H}_\lambda^+U_n(t')\rho_{0n}U_n^{-1}(t'')\mathcal{H}_\lambda U_n(t'')\}.$$

We express the Hamiltonian of the nuclei in the form $\mathcal{H}_n = \mathcal{H}_{n0} + \mathcal{H}_{nr} + \mathcal{H}_{ni}$, where $\mathcal{H}_{n0}$ is the Hamiltonian of the nuclei with allowance for the interaction of the nuclei with one another (including also the Zeeman energy in an external static magnetic field), $\mathcal{H}_{ni}$ is the nuclear-interaction operator (dipole-dipole interaction as well as the interaction of the quadrupole moments of the nuclei with the electric-field gradient in the crystal and the magnetic interaction with the inhomogeneities

of the magnetic field and with the magnetic fields of the impurities, "foreign" nuclei, and isotopes), and $\mathscr{H}_{nr}$ is the operator of the (magnetic dipole) interaction with the external magnetic field. It is assumed that $\mathscr{H}_{ni}$ is much smaller than the Zeeman splitting in the external field.

We use plane waves for the field modes; then

$$\mathscr{H}_\lambda = \sum_j \exp(i\mathbf{k}_\lambda \mathbf{r}_j)\mathscr{H}_{\lambda j},$$

where $\mathbf{r}_j$ is the radius vector of the j-th nucleus, and the operator $\mathscr{H}_{\lambda j}$ acts on the variables of only the j-th nucleus. Taking into account only two states of the nuclei, upper and lower, we can write

$$\mathscr{H}_{\lambda j} = \sum_{m_2 m_1} h_{\lambda m_2 m_1} |m_2^{(j)}\rangle\langle m_1^{(j)}|,$$

where $h_{\lambda m_2 m_1}$ are the matrix elements of the operator $\mathscr{H}_{\lambda j}$, and $|m_1^{(j)}\rangle$ and $|m_2^{(j)}\rangle$ are the state vectors of the j-th nucleus and correspond to the sublevel of the lower state with magnetic quantum number m_1 and of the upper one with m_2. The matrix elements $h_{\lambda m_2 m_1}$ depend on the type of the γ quantum.

The density matrix ρ_{0n} is chosen in the form of the product of the density matrices of the individual nuclei, $\rho_{0n} = \Pi\rho_j$, where ρ_j corresponds to equally-probable sublevels of the upper or lower states. The Zeeman splitting is always much less than kT even at low temperatures, and furthermore the "mixing" of the sublevels by the rf field leads to additional equalization of the populations. Small corrections to ρ_{0n} to account for the sublevel population difference and for the presence of interaction between the nuclei lead to very small corrections to the emission probabilities P_λ. Eliminating the operator $\mathscr{H}_{n0}$ by the unitary transformation

$$U_n(t) = \exp(-i\hbar^{-1}\mathscr{H}_{0n}t)V(t),$$

where V(t) satisfies the Schrödinger equation with Hamiltonian

$$\mathscr{H}_V = \mathscr{H}'_{nr} + \mathscr{H}'_{ni} = e^{i\mathscr{H}_{0n}t/\hbar}\mathscr{H}_{nr}e^{-i\mathscr{H}_{0n}t/\hbar} + e^{i\mathscr{H}_{0n}t/\hbar}\mathscr{H}_{ni}e^{-i\mathscr{H}_{0n}t/\hbar},$$

we can write down an expression for the correlation function $B_\lambda(t', t'')$ in the form

$$B_\lambda(t', t'') = \frac{1}{\hbar^2}\sum h^*_{\lambda m_2' m_1'} h_{\lambda m_2'' m_1''} \times \exp\{-i(\omega_{m_2' m_1'}t' - \omega_{m_2'' m_1''}t'')\}\mathrm{Sp}\{V^{-1}(t') \times |m_1'^{(s)}\rangle\langle m_2'^{(s)}| V(t')\rho_{0n}V^{-1}(t'')|m_2''^{(s)}\rangle\langle m_1''^{(s)}| V(t'')\}. \quad (5)$$

Here $\omega_{m_2 m_1}$ is the frequency of the γ transition between the corresponding sublevels. The sum is taken over m_2', m_1', m_2'', m_1'', and s, with the summation with respect to s carried out only over the nuclei in the upper excited state.

The nuclear interaction operator $\mathscr{H}_{ni}$ can be regarded as acting only in the subspaces of the magnetic substates of the nuclei, since the effects of the transfer of nuclear interaction from nucleus to nucleus cannot play a noticeable role in the line broadening in the crystal[3]. In analogy with the NMR theory[5], we can take into account in the operator $\mathscr{H}_{ni}$ only the part that commutes with $\mathscr{H}_{n0}$. The operator $\mathscr{H}'_{ni}$ can therefore be regarded as independent of the time.

The operator $\mathscr{H}'_{nr}$, which describes the influence of the rf fields, is chosen in analogy with the procedure in NMR[4] to be periodic with a period T, and such that the evolution operator $V_0(t)$ corresponding to this operator is also periodic, i.e., we stipulate $V_0(T) = 1$. We can then write $V(t) = V_0(t)W(t)$, where W(t) satisfies the equation

$$i\hbar\partial W/\partial t = V_0^{-1}(t)\mathscr{H}'_{ni}V_0(t)W. \quad (6)$$

In view of the periodicity of $V_0(t)$, we express W(t) in the form

$$W(t) = V_1(t)\exp(-i\hbar^{-1}\mathscr{H}_e t),$$

where $V_1(t)$ is periodic with period T, and $\mathscr{H}_e = i\hbar T^{-1}\ln W(T)$. The operator $\mathscr{H}_e$ is the operator of effective interaction in the presence of a radiofrequency field.

Expanding the periodic operator

$$\Omega^{(s)}_{m_2 m_1}(t) = V_1^{-1}(t)V_0^{-1}(t)|m_2^{(s)}\rangle\langle m_1^{(s)}|V_0(t)V_1(t)$$

in a Fourier series

$$\Omega^{(s)}_{m_2 m_1}(t) = \sum_\nu \Omega^{(s)}_{m_2 m_1 \nu} e^{i\omega_0 \nu t},$$

where $\omega_0 = 2\pi/T$, substituting this expansion in (5), and retaining the terms that depend only on $\tau = t' - t''$ (since the periodic nonstationary parts $B_\lambda(t', t'')$ make a negligibly small contribution to $P_\lambda(t)$ at large t), we obtain

$$B_\lambda(\tau) = \sum_{m_2 m_1 \nu} B_{\lambda m_2 m_1 \nu}(\tau),$$

$$B_{\lambda m_2 m_1 \nu}(\tau) = \hbar^{-2}|h_{\lambda m_2 m_1}|^2 \sum_s \mathrm{Sp}\{\Omega^{(s)}_{m_2 m_1 \nu} e^{i\mathscr{H}_e\tau/\hbar}\Omega^{*(s)}_{m_2 m_1 \nu}e^{-i\mathscr{H}_e\tau/\hbar}\rho_{0n}\} \times \exp\{-i(\omega_{m_2 m_1} + \nu\omega_0)\tau\}. \quad (7)$$

In the derivation of (7) we used the fact that the density matrix ρ_{0n} defined above commutes with $\mathscr{H}'_{nr}$ and with $\mathscr{H}'_{ni}$, and hence also with $\mathscr{H}_e$.

According to (4) we have at large t

$$P_\lambda(t) = t\int_{-\infty}^{\infty} B_\lambda(\tau)e^{i\omega_\lambda\tau}d\tau$$

and the decay probability $P_\lambda(t)/t$ per unit time is connected with $B_\lambda(\tau)$ by a Fourier transformation. The coefficients $h_{\lambda m_2 m_1}$ can be regarded as constant, and the spectrum consists of a series of lines at the frequencies $\omega_{m_2 m_1} + \nu\omega_0$, each of which is determined by a term $B_{\lambda m_2 m_1 \nu}(\tau)$. As seen from (7), the width of the individual line is given by the averaged Hamiltonian $\mathscr{H}_e$.

Thus, when an alternating field is applied, each Zeeman line $\omega_{m_2 m_1}$ is split into a "comb" $\omega_{m_2 m_1} + \nu\omega_0$ ($\nu = 0, \pm 1, \pm 2, \ldots$), the individual components of which can be resolved, since it is assumed that $\mathscr{H}_{ni}$, $\mathscr{H}_e \ll \hbar\omega_0$. The total integral intensity of the group of lines $\omega_{m_2 m_1} + \nu\omega_0$ is determined by the sum $\sum_\nu B_{\lambda m_2 m_1 \nu}(0)$. Using the definition (7), we can show that this sum is equal to

$$N_2|h_{\lambda m_2 m_1}|^2\hbar^{-2}(2I_2+1)^{-1},$$

where N_2 is the number of nuclei in the upper state, and I_2 is the spin of the upper state ($|m_2| \le I_2$). Consequently, the total integral intensity in the "comb" coincides with the intensity of the unsplit Zeeman line. Allowance for the recoil reduces to multiplication of all the intensities by the probability f of the recoilless Mossbauer radiation.

2. LINE WIDTHS AND COMPONENT INTENSITIES IN THE SPECTRUM

The line widths are determined by the averaged Hamiltonian $\mathscr{H}_e$. The Hamiltonian $\mathscr{H}_e = i\hbar T^{-1} \ln W(T)$ can be written in the form of an expansion in powers of $\tilde{\mathscr{H}}(t) = V_0^{-1}(t)\mathscr{H}'_{ni}V_0(t)$:

$$\mathscr{H}_e = \mathscr{H}_{e_1} + \mathscr{H}_{e_2} + \ldots;$$

$$\mathscr{H}_{e_1} = \frac{1}{T}\int_0^T \tilde{\mathscr{H}}(t)\,dt, \tag{8}$$

$$\mathscr{H}_{e_2} = -\frac{i}{2\hbar T}\int_0^T dt_2 \int_0^{t_2} [\tilde{\mathscr{H}}(t_2), \tilde{\mathscr{H}}(t_1)]\,dt_1 \tag{9}$$

and analogous expansion terms of higher order (see, e.g.,[4]).

Following the NMR methods, we choose the rf fields in the form of a periodic series of $\pi/2$ and π pulses with period T. Since the gyromagnetic ratios for the upper and lower states are different, this should be a sequence of pulses with a frequency that is resonant for the upper states, accompanied simultaneously by a sequence of pulses that are resonant for the lower state of the nuclei. The pulse sequences are chosen such to make at least $\mathscr{H}_{e1} = 0$, and if possible to equate to zero the higher order terms, $\mathscr{H}_{e2}$ etc.

That part of the magnetic dipole-dipole interaction operator which commutes with $\mathscr{H}_{n0}$ in the presence of a strong constant magnetic field along the z axis is given by

$$\mathscr{H}_{ni}^{d} = \sum_{i<j} b_{ij}(\mathbf{I}_i\mathbf{I}_j - 3I_{iz}I_{jz}) + \sum_{i'<j'} b_{i'j'}(\mathbf{I}_{i'}\mathbf{I}_{j'} - 3I_{i'z}I_{j'z}) - 2\sum_{i'j} b_{i'j}I_{i'z}I_{jz}, \tag{10}$$

where the indices i and j number the nuclei in the lower state, and i' and j' label the upper state. $\mathbf{I}_i$ denotes the nuclear spin operators, and the constants b_{ij} depend on the relative placement of the interacting nuclei, on the direction of the constant magnetic field, and on the values of the magnetic moments of the nuclei in the upper and lower states.

The $\pi/2$ radio pulses transform the operator $\mathscr{H}^{d}_{ni}$ into $V_0^{-1}(t)\mathscr{H}^{d}_{ni}V_0(t)$; the terms of the type I_jI_j remain unchanged, while I_{iz} goes over into I_{ix} or $-I_{iy}$ if the $\pi/2$ pulse rotates the spins about the y or x axis, respectively.

If the intervals between pulses are set at T/6 and T/12, and if the pulse that rotates the spins through $\pi/2$ about the x axis is designated 90°_x, then, for example, the series

$$\left(\frac{T}{12}, 90_x^\circ, \frac{T}{6}, -90_x^\circ, \frac{T}{12}, 90_y^\circ, \frac{T}{6}, -90_y^\circ, \frac{T}{12}, -90_x^\circ, \frac{T}{6}, 90_x^\circ, \frac{T}{12}, 90_y^\circ, \frac{T}{6}, -90_y^\circ\right) \tag{A_1}$$

for the upper state and the series in synchronism with the first series

$$\left(\frac{T}{12}, 90_x^\circ, \frac{T}{6}, 90_x^\circ \frac{T}{12}, 90_y^\circ, \frac{T}{6}, -90_y^\circ, \frac{T}{12}, -90_x^\circ, \frac{T}{6}, -90_x^\circ, \frac{T}{12}, 90_y^\circ, \frac{T}{6}, -90_y^\circ\right) \tag{A_2}$$

yield for the lower state $\mathscr{H}^{d}_{e_1} = 0$, where $\mathscr{H}^{d}_{e_1}$ is defined in accord with (8). The series (A_1) and (A_2) are modifications of the series

$$\left(\frac{T}{6}, 90_x^\circ, \frac{T}{3}, -90_x^\circ, \frac{T}{6}, 90_y^\circ, \frac{T}{3}, -90_y^\circ\right),$$

used in NMR[3]. For the series (A), the terms of second order in $\mathscr{H}^{d}_{e_2}$, which are connected with the first term in the operator $\mathscr{H}^{d}_{ni}$ defined by (10), also vanish, as do all the second-order crossing terms. The only non-vanishing second-order term is the one connected with the third term in (10).

Exact calculation of the resultant width of each of the lines of the "comb" is difficult, but as an estimate the line width decreases in the ratio $\mathscr{H}_{e2}/\mathscr{H}_{ni} \sim T/2T_2$ at $\mathscr{H}_{e2} = 0$ and $\mathscr{H}_{e3}/\mathscr{H}_{ni} \sim \frac{1}{6}(T/T_2)^2$ at $\mathscr{H}_{e2} = 0$, where $1/T_2$ is the line width prior to the narrowing and is specified by the interactions $\mathscr{H}_{ni}$.

Simultaneously with the broadening decrease due to the magnetic dipole interaction, the broadening due to the quadrupole interaction of the nuclei with the random electric-field gradients in the crystal will also decrease if the quadrupole interaction is small in comparison with the Zeeman interaction (e.g., in a cubic crystal). In a strong magnetic field, the corresponding term of the Hamiltonian is given by

$$\mathscr{H}_{ni}^{q} = -\frac{eqV_{zz}}{4I(2I-1)}(\mathbf{I}_z - 3I_z^2), \tag{11}$$

where V_{ZZ} is the second derivative of the potential the electric field in the direction of the magnetic field, q is the quadrupole moment, and I is the nuclear spin operator. The operator (11) has the same dependence on I as the first two terms in (10), and will become averaged together with the dipole-dipole interaction operator. At $T \ll T_2$ it is possible to reduce the line width appreciably.

Other series can also be used. Thus, the series

$$\left(\frac{T}{12}, 90_x^\circ, \frac{T}{6}, 90_x^\circ, \frac{T}{12}, 90_y^\circ, \frac{T}{6}, -90_y^\circ\right), \tag{B}$$

used for one of the states, and a similar series with a multiple period for the second state, will cause the vanishing of the dipole-dipole and quadrupole interactions in first order, and will also eliminate the broadenings due to local inhomogeneities of the external magnetic field, to the paramagnetic impurities, and to the magnetic interactions with "foreign" nuclei and isotopes. The series (B) must be periodically replaced by a similar series but with a rotation -90°_x, to prevent the deviations of the pulses from ideal $\pi/2$ pulses from playing an important role.

If the concentration of the working nuclei is small and the principal role is played by interaction with "foreign" nuclei and isotopes, then a simple series such as

$$\left(\frac{T}{2}, 180_x^\circ, \frac{T}{2}, -180_x^\circ\right) \tag{C}$$

can be useful for both states.

Interest attaches also to the distribution of the intensities in the "comb." The integral intensity of an individual line is proportional to $B_{\lambda m_2 m_1 \nu}(0)$. To find the intensities it is necessary to determine the operators $\Omega^{(S)}_{m_2 m_1}(t)$ and their Fourier components. Taking into account the smallness of the interaction $\mathscr{H}_{ni}$, we can assume, for the purpose of determining the intensities, that $V_1(t) = 1$; then the relative component intensities normalized to the total intensity of the Zeeman line can be shown to be equal to

$$J_{m_2 m_1 \nu} = \sum_{m_2' m_1'} |V^{m_2' m_1'}_{m_2 m_1 \nu}|^2,$$

$$V_{m_2m_1\nu}^{m_2'm_1'}=\frac{1}{T}\int_0^T\langle m_2'|V_0^{-1}(t)|m_2\rangle\langle m_1|V_0(t)|m_1'\rangle e^{-i\omega_\nu t}dt. \qquad (12)$$

For the series of the $\pi/2$ and π pulses, the operator $V_0(t)$ is a piecewise-constant rotation operator, and its matrix elements can be obtained from the formulas for the representations of the rotation groups corresponding to the spins of the nucleus in the upper and lower states. The corresponding calculations yield, say for spin $^3/_2$ in the upper state and $^1/_2$ in the lower, the following relative intensities of the unshifted Zeeman line ($\nu = 0$) for the series (A_1) and (A_2): $J_{-1/2\ 1/2\ 0} = J_{1/2\ -1/2\ 0} = J_{1/2\ 1/2\ 0} = J_{-1/2\ -1/2\ 0} = {}^1/_{18}$, $J_{3/2\ 1/2\ 0} = J_{-3/2\ 1/2\ 0} = {}^2/_9 = 0.222$.

The relative intensities in the "comb" $J_{3/2\ 1/2\nu}$ ($m_2 = {}^3/_2$, $m_1 = {}^1/_2$, $\nu = 0, \pm1, \ldots$) are as follows: $J_{3/2\ 1/2\ 0} = 0.222$; $J_{3/2\ 1/2\pm1} = 0.147$; $J_{3/2\ 1/2\pm2} = 0.095$; $J_{3/2\ 1/2\pm3} = 0.056$; $J_{3/2\ 1/2\pm4} = 0.029$; $J_{3/2\ 1/2\pm5} = 0.016$; $J_{3/2\ 1/2\pm6} = 0$.

It is seen from these values that an individual line may contain about 0.1 of the integral intensity of the total Zeeman line. In many experiments in which a narrow γ-resonance line is used one can use also the whole "comb". The width of the resonance can then be decreased by two orders or more by using rf pulses.

Thus, application of specially selected rf pulses to the crystal makes it possible to average out the magnetic dipole-dipole interaction of the nuclei, as well as their quadrupole interactions with the random electric-field gradients. This makes it possible to weaken appreciably the most important mechanisms that broaden the Mossbauer lines in comparison with their natural width.

[1] R. V. Khokhlov, ZhETF Pis. Red. 15, 580 (1972) [JETP Lett. 15, 414 (1972)].
[2] G. E. Bizina, A. G. Beda, N. A. Burgov, and A. V. Davydov, Zh. Eksp. Teor. Fiz. 45, 1408 (1963) [Sov. Phys.-JETP 18, 973 (1964)].
[3] C. A. Mead, Phys. Rev., 143, 990 (1966).
[4] U. Hacberton and J. S. Wangh, Phys. Rev., 175, 453 (1968).
[5] A. A. Abragam, The Principles of Nuclear Magnetism, Oxford, 1961.

Translated by J. G. Adashko
168