Nonlinear rf spectroscopy of Mössbauer nuclei under conditions of inhomogeneous line broadening

A. V. Mitin, E. F. Makarov,[1)] and N. V. Polyakov

Kazan' Physicotechnical Institute, USSR Academy of Sciences

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Gamma magnetic resonance is considered in media with inhomogeneous magnetic hyperfine line broadening. The possibility is demonstrated of using radio-frequency methods to resolve the quasienergetic and hyperfine structures upon appreciable inhomogeneous broadening of the Mössbauer line. The radio-frequency spectra are analyzed for the ^{57}Fe isotope.

INTRODUCTION

It is known that gamma magnetic resonance (GMR)[1,2] constitutes simultaneous excitation of a nucleus by a gamma quantum (the Mössbauer effect) and by a quantum of a radio-frequency (rf) field, which induces NMR transitions within the hyperfine (hf) structure of the levels. The GMR effect was experimentally investigated both in ferromagnets[3–5] and paramagnets.[6–9] However, the quasienergetic (QE) splitting, predicted in Ref. 10, of a Mössbauer line into $(2I_{e,g}+1)$ components ($I_{e,g}$ are respectively the spins of the excited and ground states of the nucleus) has not yet been observed. To observe this splitting it is necessary that the rf field strength be of the order of the natural line width, or 14 kOe in the case of ^{57}Fe. Such strong fields can be produced only by strengthening the rf field at the nucleus by hf interaction. One of the factors that hinder the observation of the QE splitting of a Mössbauer line is the inhomogeneous broadening of the latter.

Methods of suppressing the inhomogeneous broadening were discussed in a number of papers dealing with development of a gamma-ray laser using long-lived isotopes.[11–14] The authors of these papers were interested in inhomogeneous line broadening mechanisms connected with fluctuations of the isomer shift, the electric field gradient, or magnetic dipole-dipole interaction. The question of eliminating the inhomogeneous Mössbauer-line broadening due to the magnetic hf interaction was not sufficiently well studied. In many materials, however, magnetic disorder leads precisely to this Mössbauer-line broadening.[15,16] We investigate here the possibility of using the GMR method to study such substances.

§1. EQUATION FOR THE DENSITY MATRIX AND ITS SOLUTION IN THE GMR CASE

The propagation of gamma radiation through a sample containing Mössbauer nuclei excited by an rf field can be described by a Maxwell equation supplemented by the equation for the density matrix:

$$(\partial\hat{\rho}/\partial t)_{eg} = -i\hbar^{-1}([\hat{\mathcal{H}},\hat{\rho}]_{eg} + i\hbar^{-1}(\hat{\mathbf{H}}^{\gamma}\hat{\mu}_{eg})\rho_g^{(0)} + \Gamma\rho_{eg}/2. \quad (1)$$

The Hamiltonian of the system is of the form

$$\hat{\mathcal{H}}=\hat{\mathcal{H}}_e+\hat{\mathcal{H}}_g+\hat{\mathcal{H}}_1(t), \quad \hat{\mathcal{H}}_e=\hbar\omega_e\hat{I}_{ez}+\hbar\omega_0,$$
$$\hat{\mathcal{H}}_g=\hbar\omega_g\hat{I}_{gz}, \quad \hat{\mathcal{H}}_1(t)=\hbar\omega_1(\hat{I}_{ex}\cos\omega t+\hat{I}_{ey}\sin\omega t), \quad (2)$$

where $\hat{I}_{kx}, \hat{I}_{ky}, \hat{I}_{kz}$ are the nuclear-spin components.

Here $|g\rangle$ and $|e\rangle$ are respectively the eigenfunctions of the ground and excited states of the nucleus; $\rho_g^{(0)}$ are the equilibrium populations of the sublevels of the ground state of the nucleus, γ is the natural line width, $\hbar\omega$ is the energy of the gamma transition between the unsplit g- and e-states, $\omega_k = -g_k\beta_N H_{\text{hf}}$, H_{hf} is the intensity of the hf field at the nucleus; μ is the magnetic dipole-moment operator; β_N and g_k are the nuclear magneton and the g factor of the k th state $(k=e,g)$; $\hbar\omega_1$ is the rf field amplitude.

To solve Eq. (1) we change to a coordinate frame that rotates at a frequency ω around the Z axis; in this frame, the Hamiltonian $\hat{\mathcal{H}}_1(t)$ is independent of time. After the usual transformations we obtain an expression for the form of the Mössbauer absorption spectrum under GMR conditions[17]:

$$P = -b\sum_{m_{g1},m_{e_1}}\sum_{M}\sum_{p}\frac{F^2(I_g,L,I_e;m_{g1},M,m_{e1})[d^L_{p,m}(\theta)]^2}{(\Gamma/2)^2+(r_e m_{e1}-r_g m_{g1}+M\omega+\omega_d)^2},$$
$$p=\pm 1,$$

where

$$F(I_g,L,I_e;m_{g1},M,m_{e1}) = \sum_{m_g,m_e} d^{(I_g)}_{m_{g1}m_g}(\beta_g)C(I_g,L,I_e;m_g,M,m_e)d^{(I_e)}_{m_e m_{e_1}}(-\beta_e),$$

$$b=\pi nff'(2L+1)\Gamma^2/2k^2(2I_g+1)(1+\alpha), \quad (3)$$

and n is the number of resonant nuclei per cm^2 of the sample.

Here $d_{mm'}(\beta)$ is the Wigner d-function, $\omega_d=\omega_\gamma-\omega_0$ is the Doppler shift; $r_k=[(\omega_k-\omega)^2+\omega_1^2]^{1/2}$ is the amplitude of the effective field at the nucleus; $\beta_k=\arcsin(\omega_1/r_k)$ is the angle between the effective field and the Z axis; $C(I_g,L,I_e;m_g,M,m_e)$ is a Clebsch-Gordan coefficient; α is the internal-conversion coefficient.

Note that in contrast to the expression obtained by Gabriel,[2] Eq. (3) takes into account the interference between the ground and excited states of the nucleus; this is particularly important for weak hf fields at the nucleus and if the homogeneous line broadening is appreciable.

We consider in this connection the case when the Mössbauer spectrum is broadened as a result of the scatter of the magnetic hf interaction. We specify a normal distribution of the hf fields at the nucleus

$$g(H_{\text{hf}}) = (2\pi\sigma^2)^{-1/2}\exp[-(H_{\text{hf}}-H_{\text{hf}}^0)^2/2\sigma^2],$$

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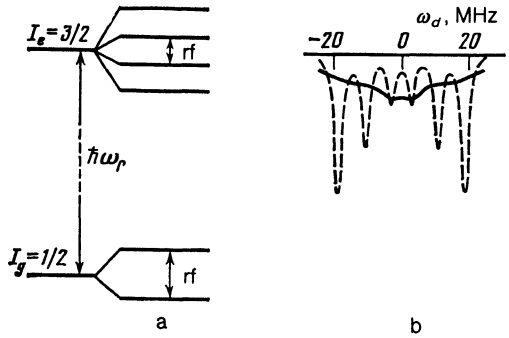

FIG. 1. a) Energy-level scheme of the isotope ^{57}Fe. The arrows show the transitions excited by the gamma radiation and by the rf-field quanta. b) Mössbauer spectrum of ^{57}Fe for the case *a* (i.e., in the absence of isomer shift and quadrupole splitting). The spectrum was calculated for $H_{hf}^0 = 100$ kOe in the absence of inhomogeneous broadening ($\sigma = 0$, dashed curve) and in its presence ($\sigma = 6.6$ MHz, solid curve).

where H_{hf}^0 is the mean value of the hf field at the nucleus and σ^2 is the variance of the distribution.

With allowance for the inhomogeneous broadening, the γ-ray absorption is given by

$$P = \int_{-\infty}^{\infty} P(H_{hf})\, g(H_{hf})\, d.H_{hf} \quad . \tag{4}$$

We use Eq. (4) for calculations for the isotope ^{57}Fe (see Fig. 1). Figure 1b shows the Mössbauer spectrum for $H_{hf}^0 = 100$ kOe in the absence of inhomogeneous broadening (dashed curve). The solid curve of Fig 1b shows the same spectrum, but in the presence of inhomogeneous broadening ($\sigma = 6\Gamma$). It is clearly seen that the hf structure becomes completely smeared out even for a relatively small broadening.

We consider now the case when the gamma radiation is at resonance with one of the allowed gamma transitions. We have carried out the numerical calculations for the transition $(1/2)_g \rightarrow (1/2)_e$, at a Doppler broadening[2)] 10.79 MHz. Figure 2 (curve 1) shows the dependence of the gamma-ray absorption P on the frequency ω of the rf field H_1 for different values of the inhomogeneous line broadening. The increase of the absorption at frequencies, equal to the hf splitting of the excited (7.88 MHz) and ground (− 13.4 MHz) states of the nucleus, is due to the QE splitting of the Mössbauer line.

Since the inhomogeneous line broadening causes the gains of the rf field at the nucleus to have a scatter, we have replaced ω_1 in the calculations by $\omega_1 H_{hf}/H_{hf}$. The rf spectra for the case of an inhomogeneously broadened line are represented in Fig. 2 by curves 2 and 3 at $\sigma = 3\Gamma$ and 6Γ, respectively. It can be seen from this figure that the form of the rf spectra in the presence of broadening is substantially altered, and the line intensities decrease by approximately σ/Γ times. The greatest change in the intensity and form of the rf spectrum occurs at frequencies close to the hf splitting of the excited state of the nucleus (7.88 MHz).

Interference between magnetic excitations of the ground and excited states of a nucleus under GMR conditions was demonstrated theoretically in Ref. 17 and observed experimentally in Ref. 9.

We consider next the manifestation of interference in the case of inhomogeneous broadening. Figure 3 shows the rf spectra with (solid curves) and without (dashed) allowance for interference (Ref. 2) for different values of the inhomogeneous line broadening. It is clearly seen that even in sufficiently strong hf fields ($H_{rf}^0 = 100$ kOe) allowance for the interference is quite vital for the interpretation of the experimental data. We note also that the position of the maxima of the curve of Fig. 3 makes it possible to determine the mean value of the hf field at the nucleus.

Rf detection of the hf structure is most effective if the g-factors of the ground and excited states of the nucleus have opposite signs, since the line spacing in the rf spectrum is proportional to $|g_e - g_g|$, whereas in the usual Mössbauer spectrum the rf splitting is proportional to $|g_e(m_e - m_e') - g_g(m_g - m_g')|$ at $|\Delta m_{e,g}| = 0.1$. It can be easily shown that for ^{57}Fe the spacing between the rf-spectrum lines is approximately three times larger than in the Mössbauer spectrum. This is precisely the advantage of rf detection of the hf structure for weak hf fields and for large inhomogeneous line broadening.

It is more convenient to determine the hf field at a nucleus from the rf spectra if the Doppler shift is zero. The reasons are: a) the gamma-ray spectrum for high inhomogeneous broadening is more intense at a zero Doppler shift

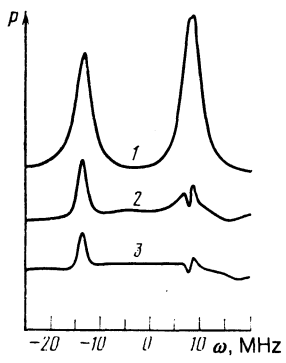

FIG. 2. Gamma-quantum absorption P vs frequency ω at $\omega_d = 10.79$ MHz and $\omega_1 = 1.1$ MHz: 1—$\sigma = 0$, 2—3.3, 3—6.8 MHz.

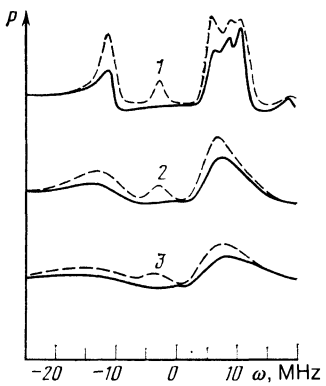

FIG. 3. Gamma-quantum absorption P vs frequency ω at $\omega_d = 0$ and $\omega_1 = 1.1$. MHz: 1—$\sigma = 0$, 2—3.3, 3—6.6 MHz.

than on the wings of the spectrum (see Fig. 1b); it is easier to set up experiments for the observation of the rf spectra at $\omega_d = 0$.

§2. TWO-FREQUENCY ANALYSIS OF MÖSSBAUER LINES

The resonant rf field H_1, as already noted, splits the Mössbauer line and forms thereby a QE structure. However, even a small inhomogeneous broadening can smear out the QE structure completely, whereas the hf structure of the spectrum is preserved. This is understandable, since the value of the QE splitting is determined by the amplitude of the field H_1, while the hf splitting is determined by the field H_{nf}. To detect the QE structure in the presence of strong inhomogeneous broadening it is therefore necessary to use the two-frequency method. To this end we apply to the sample, besides the strong rf field H_1, a frequency-scanned test field H_2 which, just as the field that produces the QE structure, is transverse. Scanning electromagnetic fields are extensively used in spectroscopy to resolve inhomogeneously broadened spectra (see, e.g., Refs. 18–20).

The feasibility of detecting a QE structure by a transverse test field H_2 can be understood from the following considerations.

The gamma radiation incident on the absorber from a source having a natural width $\sigma \gg \Gamma$ interacts with the Mössbauer nucleus whose QE structure is produced by the strong field H_1. It must be emphasized that the field H_1 is at resonance only with a definite nuclear spin packet and produces therefore a QE structure only for this packet, so that the field H_2 will detect the QE structure of just this packet. Clearly, the larger the inhomogeneous linewidth, fewer spin packets are at resonance with the frequency ω, and the intensity of absorption of the "burned" lines is lower. Therefore this method, while increasing the resolving power of gamma-resonance spectroscopy by a factor σ/Γ, decreases by the same factor the line intensity. For very broad lines it is therefore necessary to use more powerful gamma-ray sources.

To take the scanning field into account we add to the Hamiltonian (2) the term

$$\mathcal{H}_2(t) = \hbar\omega_2(\hat{I}_{ex}\cos\Omega t + \hat{I}_{ey}\sin\Omega t), \tag{5}$$

where $\hbar\omega_2$ is the amplitude and Ω the frequency of the field H_2.

We obtain the solution of Eq. (1) with the term (5) in exactly the same manner as in §1. We assume here that the amplitude of the field H_2 is much less than that of the field H_1 and is less than the natural line width. Under these assumptions we obtain the following expression for the gamma-ray absorption:

$$P(t) = \operatorname{Re}[P_0(t) + P_1(t) + P_2(t)], \tag{6}$$

where

$$P_0(t) = \sum_{\text{all } m} B^{m_{e1}}_{m_e m_{e2}} C^{-1}_{m_{e1} m_{e2}} \mu_{m_g m_e} \mu^*_{m_{e2} m_g} \exp[i\omega t\,(m_{e2} - m_e)],$$

$$P_1(t) = i\omega_2 \sum_{\text{all } m} B^{m_{e1}}_{m_e m_{e2}} \langle m_{e2}|I_x|m_{e3}\rangle B^{m_{e4}}_{m_{e3} m_{e5}} \mu_{m_g m_e} \mu^*_{m_{e5} m_g}$$

$$\times [C_{m_{e1}+m_{e4},\, m_{e5}} + i(\Omega - \omega)(m_{e2} - m_{e3}) - i r_g m_g]^{-1} C^{-1}_{m_{e4} m_{e5}}$$

$$\times \exp[i\omega t\,(m_{e5} - m_e) + i(\Omega - \omega)\, t\,(m_{e2} - m_{e3})],$$

$$P_2(t) = -i\hbar^{-1}\omega_2^2 \sum_{\text{all } m} B^{m_{e1}}_{m_e m_{e2}} \langle m_{e2}|I_x|m_{e3}\rangle B^{m_{e4}}_{m_{e3} m_{e5}}$$

$$\times \langle m_{e5}|I_x|m_{e6}\rangle B^{m_{e7}}_{m_{e6} m_{e8}} \mu_{m_g m_e} \mu^*_{m_{e8} m_g} C^{-1}_{m_{e7} m_{e8}}$$

$$\times [C_{m_{e4} m_{e8}} + i(\Omega - \omega)(m_{e5} - m_{e6})]^{-1}$$

$$\times [C_{m_{e1} m_{e8}} + i(\Omega - \omega)(m_{e2} - m_{e3} + m_{e5} - m_{e6})]^{-1}$$

$$\times \exp[i\omega t\,(m_{e8} - m_e)$$

$$+ i(\Omega - \omega)\, t\,(m_{e2} - m_{e3} + m_{e5} - m_{e6})]$$

and

$$B^{m'm''}_{mm'} = d^{(I)}_{mm'}(-\beta)\, d^{(I)}_{m'm''}(\beta),$$

$$C_{m_e m_{e'}} = \Gamma/2 + i(r_e m_e - \omega_g m_g - \omega m_{e'} + \omega_d).$$

Here P_1 and P_2 are the small terms of first and second order in H_2.

We seek now the stationary solution. The term P_1 is nonzero only in the case of coherent detection. For the noncoherent detection considered here it vanishes, since P_2 makes a noncoherent contribution under the conditions

$$m_{e2} - m_{e3} + m_{e5} - m_{e6} = 0, \quad m_{e8} - m_e = 0. \tag{7}$$

In view of (7), we can express P in the form

$$P_{\text{stat}} = \operatorname{Re}\Big\{ \sum_{\text{all } m} B^{m_{e1}}_{m_e m_{e2}} C^{-1}_{m_{e1} m_{e2}} |\mu_{m_g m_e}|^2 - i\hbar^{-1}\omega_2^2$$

$$\times \sum_{\text{all } m} B^{m_{e1}}_{m_e m_{e2}} \langle m_{e2}|I_x|m_{e2} \pm 1\rangle B^{m_{e3}}_{m_{e2}\pm 1,\, m_{e4}\pm 1}$$

$$\times \langle m_{e4} \pm 1|I_x|m_{e4}\rangle B^{m_{e5}}_{m_{e4} m_e} |\mu_{m_g m_e}|^2 C^{-1}_{m_{e5} m_e}$$

$$\times [C_{m_{e3} m_e} \pm i(\Omega - \omega)]^{-1} C^{-1}_{m_{e1} m_e} \Big\}. \tag{8}$$

We have assumed here that the frequency ω is close to the hf splitting of the excited state of the nucleus, and have neglect-

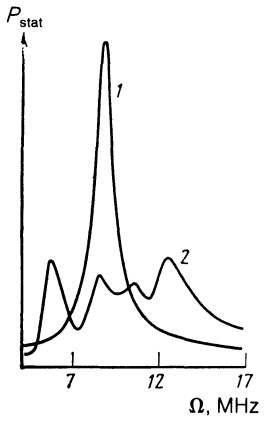

FIG. 4. Static component of gamma-quantum absorption P vs the frequency of the scanning field H_2 at $\omega_d = 12.88$ MHz ($H^0_{\text{hf}} = 150$ kOe) and amplitude the pump-field ω_1, $\sigma = 2.2$ MHz; 1—$\omega_1 = 0$; 2—$\omega_1 = 2.2$ MHz.

ed the influence of the ground state; this is valid for sufficiently strong hf fields. This assumption was made to simplify the numerical calculations.

In analogy with the preceding section, we average P_{stat} over a normal distribution.

We calculate the dependence of P_{stat} on the frequency Ω of the scanning field H_2 numerically for $H_{hf}^0 = 150$ kOe and $\omega_d = 12.88$ MHz at various values of H_1. The calculation results are shown in Fig. 4. One can readily see the QE levels (Fig. 4, curve 2) produced in a nuclear system by a field H_1 of amplitude $\omega_1 = 2$ (to produce quasilevels with well-resolved structure it is necessary that the rf field amplitude exceed the natural line width). In the absence of the rf field H_1, as expected, the quasilevels collapse to form a single line (Fig. 4, curve 1). It is important to note that all the lines detected by the field H_2 are of natural width. The spectra obtained are highly sensitive to the Doppler shift of the frequency of the gamma radiation incident on the absorber. The amplitudes of the burned lines is proportional to ω_2^2.

CONCLUSION

The method proposed in the present paper to investigate the hf and QE structures can be useful for the study of electron-nuclear characteristic of various substances with inhomogeneous broadening and of hf origin.

As already mentioned in the Introduction, the method proposed can be used to investigate metallic glasses, say of the $Fe_m M_n$ type (with the metalloids $M = C$, P, or B and $m \gtrsim n$), in which the hf fields at the iron nuclei are determined for the most part by charge transport from the metalloid to the $3d$ shell of the iron.[21] The transfer of the electron density from, say, phosphorus atoms decreases the hf field at the iron nuclei, making the hf field dependent on the number of nearest neighbors.[15] Radio-frequency analysis of a Mössbauer line is made possible by the magnetically soft character of metallic glasses.[22]

Other objects for research can be frozen solutions of paramagnetic complexes.[23] The main cause of the inhomogeneous broadening is here the random orientation of the crystal-field axes of the complex relative to the applied magnetic fields. However, the principle underlying the method, that of separating a spin packet with a definite hf field does not change, and the rf method can be used to analyze the magnetic structure of amorphous paramagnets (see, e.g., Ref. 8).

A shortcoming of this method is the smallness of the considered effects. Thus, when the hf structure of an inhomogeneously broadened spectrum is observed, the GMR effect is decreased by an approximate factor σ/Γ, and when the QE structure is detected by the two-frequency GMR method the decrease is by a factor $\sigma(\omega_1/\omega_2)^2/\Gamma$. The smallness of the effects considered here, however, is not a fundamental difficulty, since high power gamma-ray sources (up to 1 Ci) are already available.

[1)]Institute of Chemical Physics, USSR Academy of Sciences (Moscow).
[2)]We assume here and elsewhere that the isomer shift of the source relative to the absorber is zero.

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