

# Nonlinear effects in magnetically dilute paramagnets in parallel magnetic fields

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The nonlinear response in magnetically dilute paramagnets in parallel constant and alternating magnetic fields is considered. The nonlinearity of the response is due to nonlinear relaxation effects and to resonant transitions in parallel fields. Relaxation effects are considered for particles with spin  $1/2$  and  $1$  in a strong alternating field. These effects are appreciable also in cases when EPR is not observable. Resonance effects are considered in the presence of relaxation effects for paramagnetic particles with spin  $1/2$  and with nuclear spins  $1/2$  and  $1$ . The contributions of effects of various type are substantial at different values of the field  $H_0$ , so that the relaxation effects can be described on the basis of a simple model of a two-level system even in the case of nonzero nuclear spin.

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Isaev-Ivanov<sup>1-3</sup> and the authors have experimentally observed and investigated, in a number of paramagnetic substances, nonlinear effects of a new type in constant and harmonic magnetic fields. The physical nature of the observed effects has been qualitatively described. A more rigorous quantum-mechanical analysis is presented in Ref. 4.

The study of nonlinear effects in parallel fields is of undisputed interest, since their use under appropriate experimental conditions makes it possible to investigate paramagnets in which an EPR signal is unobservable because of the large broadening of the resonance lines. It makes it also possible to obtain information (e.g., on the spin-lattice relaxation mechanisms) different from that obtained by EPR, in cases when the latter is observable. The presence of nonlinear effects leads to the appearance of higher harmonics in the magnetization. Experiment yields the amplitude and the phase, or the phase components, of one or several harmonics as functions of the constant field  $H_0$ .

In Refs. 1–3 was investigated, at an ac field frequency  $\nu=50$  Mhz, the dependence of the amplitudes of the second harmonic of the magnetization,  $|M_2|$ , on the value of the constant field  $H_0$  at temperatures near 300 K and at 77 K. A maximum of  $|M_2|$  was observed as a rule in a weak constant field  $H_0$ . Investigation of the concentration dependence of the effect in solutions has shown that its relative magnitude  $M_{2\max}(\chi_0 H_1)^{-1}$  decreases upon dilution. Greatest interest attaches therefore to the case of dilute paramagnets, when the interaction of the paramagnetic particles can be neglected, and the processes due to spin-spin interaction are much slower than the relaxation processes due to the spin-lattice interaction. It suffices in this case to consider an individual paramagnetic particle coupled with the lattice to which all the non-spin degrees of freedom pertain. Such a model corresponds to the case of concentrated solutions, if the interaction of the paramagnetic particles is greatly weakened by thermal motion. As noted in Refs. 1–4, nonlinear effects of two types are possible in such systems.

1. Relaxation nonlinear effects due to the influence of the alternating field on the relaxation processes. This

influence manifests itself either in a modulation of the energy levels between which the relaxation processes occur, or else in modulation of the interaction with the lattice. The latter takes place, for example, in a liquid in which relaxation is caused by anisotropy of the  $g$  factor. As a result, the stationary values of the probabilities of the relaxation transitions become functions of the instantaneous values of the external field, and this leads to nonlinearity of the response.

2. Resonant nonlinear effects that arise in the presence of resonance transitions in parallel fields. Such transitions are possible in the presence of hyperfine or fine electron-spin interaction, not averaged by thermal motion, with energy of the order of the Zeeman interaction. In this case there are no “pure” magnetic-quantum number states; they are mixed so that resonance transitions in parallel fields are possible. The magnetization second-harmonic amplitude has resonances at the frequencies  $\omega=\omega_i$  and  $2\omega=\omega_i$ , where  $\omega_i$  is the  $i$ -th resonant frequency of the spin system. The effect is proportional to the saturation factor. Resonant nonlinear effects for perpendicular orientation of the fields are described in Ref. 5. In this case there are no nonlinear effects if the alternating field is rotating.

We consider in this paper nonlinear relaxation effects for the case of relaxation of a paramagnetic particle with spin  $S=\frac{1}{2}$  (two-level system) and  $S=1$  (three-level system) in a liquid at a large alternating-field amplitude. We consider also nonlinear resonance effects with allowance for relaxation, for a system with spin  $S=\frac{1}{2}$  and nuclear spins  $I=\frac{1}{2}$  and  $I=1$ . Some of the results are valid for a system of paramagnetic particles in a solid matrix. In fields  $H_0$  such that  $\gamma H_0 \geq 5\omega_m$ , where  $\omega_m$  is the maximum resonant frequency of the spin system, the resonant nonlinear effects can be compared with the relaxation effects, so that their analysis is much simpler. The frequency dependence of the effects is obtained.

## 1. NONLINEAR RESONANCE EFFECTS

The Hamiltonian of the spin system interacting with the external field and with the lattice will be written in the usual form

$$\mathcal{H}(t) = \mathcal{H}_s(t) + \mathcal{H}_{sr}(t) + \mathcal{H}_l(t), \quad (1)$$

where  $\mathcal{H}_s(t)$  is the Hamiltonian of the spin system;  $\mathcal{H}_{sr}(t)$  is the Hamiltonian of the spin-lattice interaction and ensures the relaxation;  $\mathcal{H}_l(t)$  is the lattice Hamiltonian.

The methods for deriving the kinetic equation for a spin density matrix are well known.<sup>6-10</sup> We are interested in the high-temperature region. In addition, full account must be taken of the interaction with the alternating magnetic field. We use therefore the kinetic equation obtained in Ref. 6, and neglect the memory effects (the non-Markov character of the motion), and assume the spin-lattice interaction energy to be small:

$$\begin{aligned} d\sigma_s(t)/dt = & -i\hbar^{-1}[\mathcal{H}_s(t), \sigma_s(t)] \\ & -\hbar^{-2} \sum_{\lambda, \lambda'} \int_0^{\infty} d\tau \{ C_{\lambda\lambda'}(\tau) [v_\lambda, [V_\lambda, \sigma_s(t)]] \\ & + C_{\lambda\lambda'}(\tau) [v_\lambda, [V_\lambda, \sigma_s(t)]]_+ \}, \end{aligned} \quad (2)$$

where  $[a, b]_+ = a \cdot b + b \cdot a$  is the anticommutator,  $E_{sr} \ll E_s$ ,  $E_{sr} \ll E_l$ , and  $\hbar^{-1} E_{sr} \tau_c < 1$ . We use the usual form of the spin-lattice interaction Hamiltonian, in the form of the spin ( $v$ ) and lattice ( $u$ ) operators:

$$\mathcal{H}_{sr} = \sum_i v_i u_i, \quad (3)$$

$C_{\lambda\lambda'}^\pm(\tau)$  stands for the symmetrical and antisymmetrical correlation functions of the lattice operators

$$\begin{aligned} C_{\lambda\lambda'}^\pm(\tau) = & \frac{1}{2} [C_{\lambda\lambda'}(\tau) \pm C_{\lambda\lambda'}(-\tau)], \\ C_{\lambda\lambda'}(\tau) = & \text{Sp}_r [f(\mathcal{H}_l) u_\lambda(t+\tau) u_{\lambda'}(t)], \end{aligned} \quad (4)$$

where  $\text{Sp}_r$  is the trace over the lattice variables,  $f(\mathcal{H}_l)$  is the equilibrium density matrix of the lattice,

$$v_\lambda = \exp \left[ (i\hbar)^{-1} \int_{t-\tau}^t dt' \mathcal{H}_s(t') \right] v_\lambda \exp \left[ -(i\hbar)^{-1} \int_{t-\tau}^t dt' \mathcal{H}_s(t') \right]. \quad (5)$$

We assume that the lattice can be characterized mathematically by a correlation time  $\tau_c$  such that all the thermodynamic correlation functions  $C_{\lambda\lambda'}(\tau)$  satisfy in the high-temperature region the condition  $C_{\lambda\lambda'}(\tau) = 0$  at  $|\tau| > \tau_c$ .

We confine ourselves to the case of axial symmetry. The Hamiltonian of the spin system, in the presence of hyperfine interaction between the electron spin  $S$  and the nuclear spin  $I$  in a magnetic field parallel to the  $z$  axis, is given by<sup>11,12</sup>

$$\begin{aligned} \mathcal{H}_s(t) = & \mathcal{H}_0 + \mathcal{H}_1(t) = \hbar\gamma H_0 S_z + aIS + \hbar\gamma H_1 S_z \sin \omega t, \\ \mathcal{H}_{sr}(t) = & \frac{1}{2} \hbar [(\Delta\gamma H(t) + bI_z) S_x - \frac{1}{2} b(I_+ S_- \\ & + I_- S_+)] (3 \cos^2 \theta - 1) + \frac{1}{2} \hbar [(\Delta\gamma H(t) + bI_z) \\ & \times (S_+ e^{-i\omega t} + S_- e^{i\omega t}) + b(I_+ e^{-i\omega t} + I_- e^{i\omega t}) S_z] \sin \theta \cos \theta \\ & + \frac{1}{2} b(I_+ S_+ e^{-2i\omega t} + I_- S_- e^{2i\omega t}) \sin^2 \theta. \end{aligned} \quad (6)$$

Here

$$\begin{aligned} \gamma = & \frac{1}{2} \gamma_{\parallel} + \frac{1}{2} \gamma_{\perp}, \quad \Delta\gamma = \gamma_{\parallel} - \gamma_{\perp}, \\ a = & \frac{1}{2} A_{\parallel} + \frac{1}{2} A_{\perp}, \quad b = A_{\parallel} - A_{\perp}, \quad H(t) = H_0 + H_1 \sin \omega t, \end{aligned}$$

where  $A$  is the hyperfine-interaction constant.

We have neglected the nuclear Zeeman interaction compared with the hyperfine interaction. The magnetization of the system is determined by the value of  $\langle S_x \rangle$  and depends on the time. This is due both to resonant

transitions in parallel fields and to the time dependence of the stationary values of the relaxation-transition probabilities. As a result, the response will be nonlinear. This response will be considered for the system  $S = \frac{1}{2}, I = \frac{1}{2}$ .

The eigenfunctions of the Hamiltonian  $\mathcal{H}_0$  take in this case the form

$$\begin{aligned} |\varphi_1\rangle = & |\alpha_s \alpha_l\rangle, \quad |\varphi_2\rangle = C[|\alpha_s \beta_l\rangle - d|\beta_s \alpha_l\rangle], \\ |\varphi_3\rangle = & C[|\beta_s \alpha_l\rangle + d|\alpha_s \beta_l\rangle], \quad |\varphi_4\rangle = |\beta_s \beta_l\rangle, \end{aligned}$$

where

$$d = a^{-1} [\gamma H_0 - (\gamma^2 H_0^2 + a^2)^{1/2}],$$

$C = (1 + d^2)^{-1/2}$ ;  $\alpha_s, \beta_s, \alpha_l, \beta_l$  are the eigenfunctions of the operators  $S_x$  and  $I_x$ , respectively. One resonant transition will be observed for this system in parallel fields between the second and third levels, with a frequency

$$\omega_{23} = (\gamma^2 H_0^2 + a^2)^{1/2}.$$

We obtain next equations in the  $\mathcal{H}_0$  representation for those spin density-matrix components which contribute to  $\langle M_x \rangle$ . Since a contribution to the integral of the relaxation part of Eq. (2) is made only by the time region  $\tau \leq \tau_c$ , the external field  $H(t)$  acting on the spin system can be regarded as constant if the frequency of the alternating field is low compared with the characteristic lattice-motion frequencies, so that the relation  $\omega \tau_c \ll 1$  holds. The spin operators  $V_\lambda$  of the operator  $\mathcal{H}_{sr}$  in the interaction representation, which enter in the integrand of (2), can then be written in the form

$$V_\lambda = \exp[(i\hbar)^{-1}(\mathcal{H}_0 + \mathcal{H}_1(t))\tau] v_\lambda \exp[-(i\hbar)^{-1}(\mathcal{H}_0 + \mathcal{H}_1(t))\tau]. \quad (7)$$

Since  $\mathcal{H}_0$  does not commute with  $\mathcal{H}_1(t)$ , the matrix elements of the operators  $V_\lambda$  were calculated with the aid of the operator identity<sup>13</sup>

$$\exp[(A+B)t] = \exp(At) + \int_0^t \exp[(A+B)u] B \exp[A(t-u)] du. \quad (8)$$

In the derivation of the equations we used the smallness of  $\beta\omega$ , where  $\beta = \hbar(kT)^{-1}$ , and also the relation for the spectral densities of the symmetrical and antisymmetrical correlation functions:

$$J_{\lambda\lambda'}^-(\omega) = J_{\lambda\lambda'}^+(\omega) \text{th} \left( \frac{\beta\omega}{2} \right), \quad (9)$$

$$J_{\lambda\lambda'}^\pm(\omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} d\tau C_{\lambda\lambda'}^\pm(\tau) \exp(i\omega\tau).$$

The frequencies of the transitions between the levels of the Hamiltonian  $\mathcal{H}_0$  will be low compared with the characteristic lattice-motion frequencies  $\tau_c^{-1}$  in the considered field range. Therefore the spectral densities will be assumed to be independent of frequency.

In these approximations the system of equations for the components of the spin density matrix in the  $\mathcal{H}_0$  representation will take the form

$$\begin{aligned} dX_1/dt = & -i\omega_{23} X_2 - i\hbar^{-1}(\mathcal{H}_{22} - \mathcal{H}_{33}) X_2 - 2i\hbar^{-1} \mathcal{H}_{32} X_3 - \Gamma_{11} X_1, \\ dX_2/dt = & -i\omega_{23} X_1 - i\hbar^{-1}(\mathcal{H}_{22} - \mathcal{H}_{33}) X_1 \\ & - \Gamma_{22} X_2 - \Gamma_{23} (X_3 - X_3^0) - \Gamma_{24} (X_4 - X_4^0) - \Gamma_{25} (X_5 - X_5^0) \\ & - \frac{1}{2} b \gamma H_1(t) C^2 [{}^1 J_{33} J_1^+(0) b a_+ + J_2^+(0) (\Delta\gamma H(t) b_1 + \frac{1}{2} db^2)], \\ dX_3/dt = & -2i\hbar^{-1} \mathcal{H}_{32} X_1 - \Gamma_{33} X_3 - \Gamma_{35} (X_5 - X_5^0) \end{aligned}$$

$$\begin{aligned}
& +\Gamma_{31}(X_1-X_1^0)+\Gamma_{33}(X_3-X_3^0)-\frac{1}{2}\beta\gamma H_1(t)C^2[\frac{1}{2}J_1^+(0)bb_1 \\
& \quad +\frac{1}{2}J_2^+(0)(4\Delta\gamma H(t)a_1+(1-d^2)b^2)], \\
& \frac{1}{2}dX_1/dt=-\Gamma_{12}X_2+\Gamma_{13}(X_3-X_3^0)-\Gamma_{14}(X_4-X_4^0) \\
& \quad -\Gamma_{15}(X_5-X_5^0)-\frac{1}{2}\beta\gamma H_1(t)J_2^+(0)b\Delta\gamma H(t), \\
& dX_2/dt=-\Gamma_{22}X_2+\Gamma_{23}(X_3-X_3^0)-\Gamma_{24}(X_4-X_4^0) \\
& \quad -\Gamma_{25}(X_5-X_5^0)-\frac{1}{2}\beta\gamma H_1(t)[J_2^+(0)b_0+\frac{1}{2}J_2^+(0)b^2].
\end{aligned} \quad (10)$$

The terms proportional to  $\beta$  are responsible for the relaxation to the instantaneous value of the magnetic field. The following notation is used here:  $X_1=\sigma_{23}-\sigma_{32}$ ,  $X_2=\sigma_{23}+\sigma_{32}$ ,  $X_3=\sigma_{33}-\sigma_{22}$ ,  $X_4=(\sigma_{33}-\sigma_{44})-(\sigma_{11}-\sigma_{22})$ ,  $X_5=\sigma_{11}-\sigma_{44}$ ,  $X_k^0$  are the equilibrium values of the corresponding density-matrix components, and  $\mathcal{H}_{ik}^0=\langle\varphi_i|\mathcal{H}_k(t)|\varphi_k\rangle$ . The relaxation coefficients  $\Gamma_{ik}$ , with  $\Gamma_{ik}=\Gamma_{ki}$ , are defined by the expressions

$$\begin{aligned}
\Gamma_{11}&=\frac{1}{2}\beta J_1 b_0+\frac{1}{2}\beta J_2 a_0, & \Gamma_{33}&=\frac{1}{2}\beta J_1 C^2 a_1^2+\frac{1}{2}\beta J_2 a_0, \\
\Gamma_{22}&=\frac{1}{2}\beta J_1 C^2 a_1 b_1, & \Gamma_{24}&=\frac{1}{2}\beta J_2 C^2 b b_1, \\
\Gamma_{25}&=\frac{1}{2}\beta J_2 C^2 \Delta\gamma H(t)[b_1-\frac{1}{2}(1-d^2)b], \\
\Gamma_{32}&=\frac{1}{2}\beta J_1 C^2 b_1^2+\frac{1}{2}\beta J_2 a_0, & \Gamma_{34}&=\frac{1}{2}\beta C^2 a_1 b, \\
\Gamma_{35}&=\frac{1}{2}\beta J_2 C^2 \Delta\gamma H(t)(a_1+bb_1), & \Gamma_{44}&=\frac{1}{2}\beta J_2 a_0, \\
\Gamma_{45}&=\frac{1}{2}\beta J_2 \Delta\gamma H(t)b, & \Gamma_{55}&=\frac{1}{2}\beta(J_2 a_0+J_2 b^2),
\end{aligned} \quad (11)$$

where

$$\begin{aligned}
a_0&=b^2+2\Delta\gamma H_0^2, & b_0&=\Delta\gamma^2 H_0^2+\frac{1}{2}b^2, \\
a_1&=bd+\Delta\gamma H_0(1-d^2), & b_1&=d\Delta\gamma H_0-\frac{1}{2}b(1-d^2), \\
J_2&=J_2^+(0)=\frac{1}{2}\tau_0, & J_1&=J_1^+(0)=\frac{2d}{2\tau_0}, & J_3&=J_3^+(0)=\frac{1}{2}\tau_0.
\end{aligned} \quad (12)$$

We are interested in a stationary solution. Therefore the components of the spin density matrix can be represented as series in the harmonics of the external alternating field. The coefficients of the series are independent of time:

$$X_n=\sum_k X_{nk} \exp(ik\omega t), \quad dX_n/dt=0. \quad (13)$$

The expansion coefficients are functions of the amplitude of the alternating field. Under the condition  $\gamma H_1 \omega^{-1} < 1$  the main contribution to the coefficients  $X_{ik}$  is obviously made by the term  $\sim H_1^k$ . We neglect the terms of higher order in  $H_1$ . Then if one of the unaccounted-for relaxation mechanisms predominates, it is possible to obtain an analytic solution. Leaving out the intermediate results, we present directly the expressions for the second harmonic of the magnetization

$$\langle M_x \rangle = \frac{1}{2} \hbar \gamma N [X_1 - (1-d^2)C^2 X_2 + 2dC^2 X_3]$$

1) in the case  $b \gg \Delta\gamma H_0$

$$\begin{aligned}
\langle M_x(2\omega) \rangle &= \frac{1}{2} \text{Re} \{ \exp(-i2\omega t) \frac{1}{2} \chi_0 H_1^2 H_0 \gamma^2 a^2 \omega \Delta_1^{-1} \Delta_2^{-1} \\
& \quad \times [ \omega(\omega+3i\Gamma_{11})(2\omega+2i\Gamma_{11})+2\omega(2\omega+3i\Gamma_{11})(\omega+2i\Gamma_{11}) ] \}, \\
\Delta_1 &= \omega [ (\omega+i\Gamma_{11})^2 - a^2 ] (\omega+3i\Gamma_{11}) - \gamma^2 H_0^2 (\omega+i\Gamma_{11})(\omega+2i\Gamma_{11}), \\
\Delta_2 &= 2\omega [ (2\omega+i\Gamma_{11})^2 - a^2 ] (2\omega+3i\Gamma_{11}) - \gamma^2 H_0^2 (2\omega+i\Gamma_{11})(2\omega+2i\Gamma_{11});
\end{aligned} \quad (14)$$

2) in the case  $\Delta\gamma H_0 \gg b$

$$\begin{aligned}
\langle M_x(2\omega) \rangle &= \frac{1}{2} \text{Re} \{ \exp(-i2\omega t) \frac{1}{2} \chi_0 \Delta_1^{-1} \Delta_2^{-1} \chi_0 H_1^2 a^2 \omega^3 \\
& \quad \times (\omega+2i\Gamma_{11})(2\omega+2i\Gamma_{11}) [ -\gamma^2 H_0 (3\omega+2i\Gamma_{11}) + i\Delta\gamma^2 H_0 \\
& \quad \times (\frac{1}{2}J_1^+ + \frac{1}{2}J_2^+) ((\omega+i\Gamma_{11})(2\omega+i\Gamma_{11}) - \gamma^2 H_0^2) ] \\
& \quad - \frac{1}{2} \chi_0 H_0^2 \omega \Delta\gamma^2 H_0 J_2^+ [ 2(\omega+2i\Gamma_{11})^{-1} + \omega a^2 \Delta_1^{-1} \\
& \quad \times (\omega+i\Gamma_{11}) ] [ 2(2\omega+2i\Gamma_{11})^{-1} + 2\omega a^2 \Delta_2^{-1} (2\omega+i\Gamma_{11}) ] \}, \\
\Delta_1 &= (\omega+2i\Gamma_{11}) \{ \omega [ (\omega+i\Gamma_{11})^2 - \gamma^2 H_0^2 ] (\omega+2i\Gamma_{11}) - a^2 (\omega+i\Gamma_{11})(\omega+i\Gamma_{11}) \}, \\
\Delta_2 &= (2\omega+2i\Gamma_{11}) \{ 2\omega [ (2\omega+i\Gamma_{11})^2 \\
& \quad - \gamma^2 H_0^2 ] (2\omega+2i\Gamma_{11}) - a^2 (2\omega+i\Gamma_{11})(2\omega+i\Gamma_{11}) \}.
\end{aligned} \quad (15)$$

In the latter case there are present besides the resonance effects also relaxation effects—the term of (15)—as well as interference effects due to superposition of the above two types. The relaxation effects are of the same magnitude and have the same singularities as in a two-level system when the relaxation is due to anisotropy of the  $g$  factor.<sup>1-4</sup>

The solution of the system (10) in the case when both relaxation mechanisms operate was obtained numerically with a computer. In the limiting cases the numerical solution agreed with the analytically obtained ones: with expression (15) for the case  $b \gg \gamma H_0$ , and with (15) at  $\gamma H_0 \gg b$ . In the case  $a \rightarrow 0$  and  $b \rightarrow 0$  it agrees with the analytic solution obtained in Refs. 2-4 for the relaxation effects, as well as with the solution obtained in the second part of the present paper for the limiting case of small alternating-field amplitudes.

The dependence of the relative magnitude of the phase components  $M_2(\chi_0 H_1)^{-1}$  on  $H_0$  is shown in Fig. 1 at alternating-field frequencies 15 and 150 MHz. For curve 2, the spin-system parameters correspond to the parameters of the nitroxyl radical. The second phase component is in this case very small, its maximum is  $\approx 0.7 \times 10^{-3}$ , and it is therefore not shown in the figure. If the anisotropy of the  $g$  factor is large, the anisotropic part  $b$  of the hyperfine interaction has very little effect on the form of the signal, especially in a strong field  $H_0$ . The reason is that the probabilities of the relaxation processes due to the  $g$ -factor anisotropy are proportional to  $H_0^2$ . The differences of the amplitudes and widths of the resonance lines, curves 3 of Fig. 1, are due precisely to this dependence. When the spin-system parameters correspond to the parameters of curve 2, i.e., the relaxation is due to the anisotropy of the hyperfine interaction, the amplitudes of the resonance lines at an alternating-field frequency  $\nu = 150$  MHz are approximately equal. Thus, knowing the amplitudes or widths of the resonance lines we can find the contribution made to the relaxation by the mechanism due to the

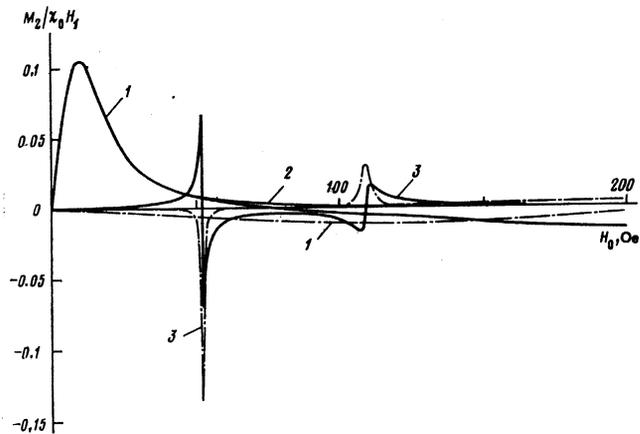


FIG. 1. Phase components  $M_2$  for the system  $S = 1/2$ ,  $I = 1/2$  in the region of a weak field  $H_0$ :  $a = 3.044 \times 10^8 \text{ sec}^{-1}$ ,  $\tau_0 = 10^{-10} \text{ sec}$ . Curve 1)  $b = 3.2 \times 10^7 \text{ sec}^{-1}$ ,  $\gamma^{-1} \Delta\gamma = 0.8$ ,  $\nu = 15 \text{ MHz}$ ; curve 2)  $b = 5.814 \times 10^8 \text{ sec}^{-1}$ ,  $\gamma^{-1} \Delta\gamma = 1.5 \times 10^{-4}$ ,  $\nu = 15 \text{ MHz}$ ; curve 3)  $b = 3.2 \times 10^7 \text{ sec}^{-1}$ ,  $\gamma^{-1} \Delta\gamma = 0.8$ ,  $\nu = 150 \text{ MHz}$ . Solid curves— $M_2^{CS}$ , dashed— $M_2^{sin}$ .

*g*-factor anisotropy, and determine this anisotropy. In addition, knowing the distances between the maxima of the resonance lines and the frequency of the alternating field it is possible to obtain the usual spectroscopic information, namely the magnitude of the isotropic part of the hyperfine interaction *a* and  $\gamma$ . Under the condition  $\omega \gg a$  the different phase components have dispersion and absorption forms. This makes it possible to use their forms to adjust the phase of the reference voltage during the experiment.

If the alternating-field frequency satisfies the condition  $2\omega < a$ , the resonance effects are also sizable (see curves 1 and 2 of Fig. 1). The maximum is then shifted towards a very weak field  $H_0$ . The presence of effects in this case is due to the absorption of the RF power on the resonance-line wings. Under our assumption that the spectral densities of the correlation functions are independent of frequency, curve 2 corresponds to resonance effects without admixture of relaxation effects. It is seen from a comparison of curves 1 and 2 that if  $2\omega < a$  the relaxation effects are comparable in magnitude with the resonance effects and are shifted towards stronger fields.

All the investigated objects have as a rule a nuclear spin larger than  $\frac{1}{2}$ . To assess the influence exerted on the character of the observed effects by the increase in the number of the resonant transitions in parallel fields at a fixed frequency of the alternating field  $H_1(t)$ , we examine nonlinear effects for the system  $S = \frac{1}{2}, I = 1$ .

The Hamiltonian of the system coincides with (6). The entire calculation process and the imposed restrictions are similar to those for the system  $S = \frac{1}{2}, I = \frac{1}{2}$ . The eigenfunctions and the eigenvalues of the operator  $\mathcal{H}_0$  are easily obtained in the usual manner, by solving the secular equation. In our case, two resonant transitions are possible in parallel fields. We do not present here the unwieldy system of equations for the density matrix elements that contribute to  $\langle M_x \rangle$ . It consists of nine equations. This system can be solved only numerically. The solution was obtained with a computer. In the limit

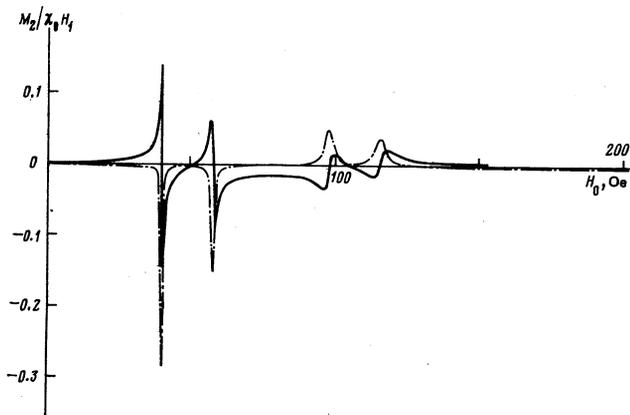


FIG. 2. Phase components  $M_2$  for the system  $S = 1/2, I = 1$  in a weak field  $H_0$  at  $\nu = 150$  MHz,  $a = 3.044 \times 10^8$  sec $^{-1}$ ,  $b = 3.2 \times 10^7$  sec $^{-1}$ ,  $\gamma^{-1}\Delta\gamma = 0.8$ ,  $\tau_c = 10^{-10}$  sec. Solid curves— $M_2^{\cos}$ , dashed— $M_2^{\sin}$ .

as  $a \rightarrow 0$  and  $b \rightarrow 0$ , when only relaxation effects remain, this solution agreed also with the solution for the two-level system  $I = 0, S = \frac{1}{2}$ . Plots of the phase components  $M_2/\chi_0 H_1$  ( $I = 1$ ) against the field  $H_0$  are shown in Figs. 2 and 3. Figure 2 shows four resonances that appear under the following conditions

$$\omega = \omega_{21} = [(\gamma H_0 + 1/2 a)^2 + 2a^2]^{1/2}, \quad 2\omega = \omega_{21};$$

$$\omega = \omega_{35} = [(\gamma H_0 - 1/2 a)^2 + 2a^2]^{1/2}, \quad 2\omega = \omega_{35}.$$

The curves have the same singularities as in the system  $S = \frac{1}{2}, I = \frac{1}{2}$ . The sign of the effect at  $\omega = \omega_i$  is opposite to that at  $2\omega = \omega_i$ . The reason is that in the first case, under saturation conditions, the relaxation cannot cope with the reduction to thermal equilibrium, and part of the energy is emitted in the form of higher-harmonic photons, while the second case a two-photon transition takes place and the effect has the same sign as ordinary saturation.

Figure 3 shows the phase components  $M_2/\chi_0 H_1$  for 15 MHz, when  $2\omega < a$ . For curves 2, the spin-system parameters correspond to the parameters of the nitroxyl radical, and pure resonance effects are then realized. The phase component  $M_2^{\sin}$  coincides in this case with  $M_2^{\sin}$  of curve 1, i.e., the contribution of the resonance effects to this component is very small if  $2\omega < a$ . The resonance effects on the second phase component  $M_2$  (curves 1 and 3) can be neglected already in fields  $H_0 \approx 60$  Oe. At an alternating field frequency  $\nu = 15$  MHz in the three-level system  $S = \frac{1}{2}, I = 1$  (see Fig. 3), compared with the four level system  $S = \frac{1}{2}, I = \frac{1}{2}$  (see Fig. 1), in the case of identical hyperfine interaction constants of value such that  $2\omega < a$  is satisfied, the maximum of the resonance effects shifts slightly towards stronger fields, and the ratio of the amplitudes of the phase components is also changed somewhat. Taking this circumstance into account, the experimental results for higher values of the nuclear spin  $I > 1$ , under the condition  $2\omega < a$ , can be qualitatively analyzed on the basis of the equations of motion for the system  $S = \frac{1}{2}, I = 1$ . If the frequency  $\omega \lesssim a$ , then it suffices to obtain the eigenfunctions and eigenvalues of the system to determine the positions of the resonance transitions, and hence also the form of the phase components of the response at the second harmonic.

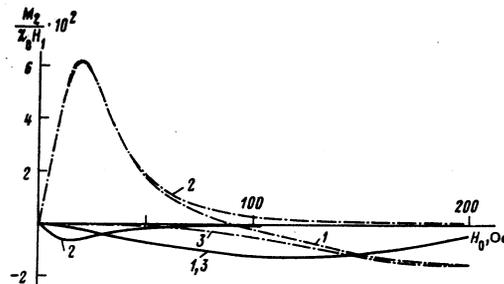


FIG. 3. Phase components  $M_2$  for the system  $S = 1/2, I = 1$  in a weak field  $H_0$  at  $\nu = 15$  MHz,  $\nu_c = 10^{-10}$  sec. Curve 1)  $a = 3.044 \times 10^8$  sec $^{-1}$ ,  $\gamma^{-1}\Delta\gamma = 0.8$ ; curve 2)  $a = 3.044 \times 10^8$  sec $^{-1}$ ,  $b = 5.814 \times 10^8$  sec $^{-1}$ ,  $\gamma^{-1}\Delta\gamma = 1.5 \times 10^{-3}$ ; curve 3)  $a = 0$ ,  $b = 3.2 \times 10^7$  sec $^{-1}$ ,  $\gamma^{-1}\Delta\gamma = 0.8$ . Dashed curves— $M_2^{\cos}$ , solid— $M_2^{\sin}$ .

The dependence of the phase components  $M_2/\chi_0 H_1$  on  $H_0$  at the frequency  $\nu=150$  MHz and at hyperfine-interaction constant values such that  $\omega > a$ , in fields  $H_0 \geq 150$  Oe, shows that at a field value  $H_0 \geq 5\omega_m/\gamma$ , where  $\omega_m$  is the maximum resonance frequency of the system (in the region of the relaxation effects), and for the nuclear spins  $I = \frac{1}{2}$  and  $I=1$ , the phase components coincide with those for the two-level system. This confirms the earlier conclusion that in the case of nonzero nuclear spin the relaxation effects in strong fields can be analyzed by using much simpler equations for the two level system and for frequencies  $\omega \gg a$ , since they contribute to much stronger fields than the resonance effects. We now proceed to consider them.

## 2. NONLINEAR RELAXATION EFFECTS

We consider here relaxation effects not only for the case  $S = \frac{1}{2}$ , but also for triplet states. The possibility of studying the latter with the aid of nonlinear effects can be of great interest, inasmuch as no EPR signal is observable for them in solution because of the relaxation-line broadening.

For a paramagnetic particle with spin  $S = \frac{1}{2}$  in a magnetic field parallel to the  $z$  axis, the spin Hamiltonian is of the form<sup>12</sup>

$$\mathcal{H}_s(t) = \mathcal{H}_0 + \mathcal{H}_1(t) = \hbar\gamma H_0 S_z + \hbar\gamma H_1 S_x \sin \omega t,$$

$$\mathcal{H}_{sr}(t) = \hbar\Delta\gamma H(t) (3 \cos^2 \theta - 1) S_z + \hbar\Delta\gamma H(t) \sin \theta \cos \theta (S_+ e^{-i\omega t} + S_- e^{i\omega t}).$$

The behavior of the spin system is described by Eq. (2) for the spin density matrix. The conditions under which this equation is valid were described above. If the alternating-field frequency is low compared with the characteristic frequencies  $\omega \ll \omega_c^{-1}$  of the lattice motion then, recognizing that a contribution to the integral of the relaxation part is made only by the time region  $\tau \leq \tau_c$ , we can regard the external field as constant. The spin operators  $V_\lambda$  are then described by Eq. (7). For a particle with nuclear spin  $I=0$ , the Hamiltonian  $\mathcal{H}_0$  commutes with  $\mathcal{H}_1(t)$ , i.e., the spin density matrix is diagonal in the  $\mathcal{H}_0$  representation, and the commutator  $[\mathcal{H}_0, \sigma_s] = 0$ . Then expression (7) for  $V_\lambda$  can be reduced to another representation with the aid of the expansion<sup>9</sup>

$$\exp[(i\hbar)^{-1} \mathcal{H}_1 \tau] v_\lambda \exp[-(i\hbar)^{-1} \mathcal{H}_0 \tau] = \sum_p v_\lambda^{(p)} \exp(-i\omega_\lambda^{(p)} \tau).$$

In our case the frequencies  $\omega_\lambda^{(p)}$  are slow functions of the time. Next, multiplying both sides of (2) by the operator  $M_x$ , taking the trace over the spin variables, and using the commutation and permutation relations for the spin operators<sup>10</sup> we can easily change over in the high-temperature approximation to the equation for the macroscopic magnetization. Following transformations with account taken of (9), the equation reduces to the Bloch equation with a relaxation time that depends on the instantaneous value of the external magnetic field:

$$dM_x/dt = -(M_x(t) - \chi_0 H(t)) T_1^{-1}(H(t)).$$

At not too large an alternating-field amplitude, when  $\gamma H_1 \omega^{-1} < 1$  and  $\gamma H_1 \tau_c < 1$ , the maximum of the second-harmonic amplitude 1, 2, 4 takes place at  $\omega T_0 \sim 1$ , where  $T_0$  is the time-independent part of the spin-lattice relaxation time. We are interested in the second harmon-

ic of the magnetization at magnetic-field amplitudes and frequencies such that  $\gamma H_1 \omega^{-1}$  can be arbitrary, and  $\gamma H_1 \tau_c < 1$ .

The relaxation due to the spin-spin interactions, to the spin-rotational interaction, as well as other mechanisms independent of the external magnetic field, can be additively included in  $T_1^{-1}$  (Refs. 10, 12, 14):

$$T_1^{-1} = \frac{1}{15} \Delta\gamma^2 H^2(t) \tau_c (1 + \gamma^2 H^2(t) \tau_c^2)^{-1} + T_{01}^{-1},$$

$$T_{01}^{-1} = \frac{1}{15} \pi N S(S+1) \gamma^4 \hbar^2 \tau_p d_c^{-2} + \text{Sp} \{ \Delta g \cdot \Delta g \} / 9 \tau_c + T_0^{-1};$$

$T_0$  is the relaxation time due to other mechanisms not mentioned here and independent of the external field,  $\tau_c$  and  $\tau_p$  are the correlation times of the rotational and translational diffusion,  $N$  is the number of particles per  $\text{cm}^3$ , and  $d_c$  is the closest-approach distance between the particles.

The nonlinear response is given in this case by

$$\langle M_x \rangle = \chi_0 H(t) - \chi_0 H_1 \omega T_1^0 \sum_{\substack{h, l, p, q \\ n, r, q=0}} (-1)^{h+p} [1 + (n-2m+3r-4q+1)^2 \omega^2 T_1^{02}]^{-1} \\ \times I_n(a_1) I_l(a_2) I_p(a_3) I_r(a_4) I_n(a_1) I_m(a_2) I_r(a_3) I_q(a_4) \\ \times \left\{ \left[ \cos \frac{\pi}{2} (l+s+m+q) + (n-2m+3r-4q+1) \omega T_1^0 \sin \frac{\pi}{2} (l+s+m+q) \right] \right. \\ \times \cos (k+2l+3p+4s+n-2m+3r-4q+1) \omega t - \left[ \sin \frac{\pi}{2} (l+s+m+q) \right. \\ \left. - (n-2m+3r-4q+1) \omega T_1^0 \cos \frac{\pi}{2} (l+s+m+q) \right] \\ \left. \times \sin (k+2l+3p+4s+n-2m+3r-4q+1) \omega t \right\}. \quad (16)$$

Here  $I_n(a_i)$  are modified Bessel functions,

$$(T_1^0)^{-1} = T_{01}^{-1} + \frac{1}{15} \tau_c^{-1} (\gamma^{-1} \Delta\gamma)^2 \omega_0^2 \tau_c^2 (1 + \omega_0^2 \tau_c^2)^{-1} + a_0,$$

$$a_0 = \frac{1}{15} \tau_c^{-1} (\gamma^{-1} \Delta\gamma)^2 \gamma^2 H_1^2 \tau_c^2 (1 + \omega_0^2 \tau_c^2)^{-1} (1 + 3\omega_0^2 \tau_c^2 - \frac{3}{4} \gamma^2 H_1^2 \tau_c^2),$$

$$a_1 = -\frac{2}{15} (\gamma H_1 \omega^{-1}) (\gamma^{-1} \Delta\gamma)^2 \omega_0 \tau_c (1 + \omega_0^2 \tau_c^2)^{-2} [2 - 3\gamma^2 H_1^2 \tau_c^2 (1 + \omega_0^2 \tau_c^2)^{-1}],$$

$$a_2 = -\frac{1}{30} (\gamma H_1 \omega^{-1})^2 (\gamma^{-1} \Delta\gamma)^2 \omega_0 \tau_c (1 + \omega_0^2 \tau_c^2)^{-3} (1 - 3\omega_0^2 \tau_c^2 - \gamma^2 H_1^2 \tau_c^2),$$

$$a_3 = -\frac{1}{15} (\gamma H_1 \omega^{-1})^3 (\gamma^{-1} \Delta\gamma)^2 \omega_0 \tau_c \omega^2 \tau_c^2 (1 + \omega_0^2 \tau_c^2)^{-2},$$

$$a_4 = -\frac{1}{150} (\gamma H_1 \omega^{-1})^4 (\gamma^{-1} \Delta\gamma)^2 \omega^3 \tau_c^2 (1 + \omega_0^2 \tau_c^2)^{-2}, \quad \omega_0 = \gamma H_0.$$

It is easy to separate from the response (16) the second harmonic  $M_2$  of interest to us. Figure 4 shows the phase components  $M_2$  corresponding to the solution (16) as functions of  $H_0$ . The amplitudes of the phase compo-

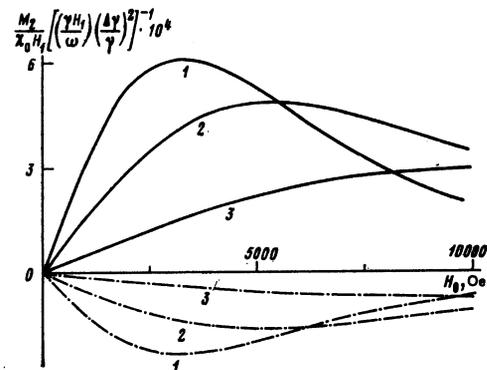


FIG. 4. Relaxation effects in two-level system;  $\nu = 500$  MHz,  $\gamma^{-1} \Delta\gamma = 0.4$ ,  $H_1 = 100$  Oe,  $C = 10^{-2}$  mol/l. Curves: 1)  $\tau_c = 10^{-11}$  sec, 2)  $6 \times 10^{-12}$  sec, 3)  $3 \times 10^{-12}$  sec. Solid curves— $M_2^{\sin}$ , dashed— $M_2^{\cos}$ .

nents were calculated for convenience relative to  $\chi_0 H_1$  and  $\gamma H_1 \omega^{-1}$ ,  $(\gamma^{-1} \Delta \gamma)^2$ . The parameter is  $\tau_c$ . At the employed values of  $T_0$  and  $\gamma^{-1} \Delta \gamma$  the EPR signal cannot be observed because of the very large line width, while the nonlinear effects are appreciable. It is seen from the figure that the position of the maximum depends very strongly on  $\tau_c$  from the experimental curves. The relation between the values of the phase components remains practically unchanged.

To describe the obtained phase curves we can introduce as parameters the positions of the maxima  $H_{\max}^{\sin}$  and  $H_{\max}^{\cos}$  and the maximum relative magnitude of the effects

$$M_{2mo}^{\sin} = M_{2mo}^{\sin} / \chi_0 H_1, \quad M_{2mo}^{\cos} = M_{2mo}^{\cos} / \chi_0 H_1.$$

If the parameter is  $T_0$ , then the positions of the maxima hardly change with  $T_0$ , and only the magnitude of the effect and the ratio of the amplitudes of the phase components change.  $T_0$  and  $\tau_c$  thus manifest themselves differently in the effects, so that they can be determined by in the inverse problem. The effect is  $\propto \nu$  for  $M_{2mo}^{\sin}$  and  $\propto \nu^2$  for  $M_{2mo}^{\cos}$  up to values of such that the value of  $\omega T_0$  becomes noticeable under the condition  $\gamma H_1 \omega^{-1} = \text{const}$ . The effect retains its maximum at  $\omega \propto T_0^{-1}$  and at large  $H_1$ . The amplitude of the phase curves referred to  $H_1^2$ , depends very little on  $H_1$  up to  $H_1 \sim 100$  Oe. It is difficult in practice to obtain an alternating field of larger amplitude, and large values of  $H_1$  were therefore not considered. The effects are proportional to  $(\gamma^{-1} \Delta \gamma)^n$ , where  $1 \leq n \leq 2$ , depending on the values of  $\tau_c$  and  $T_0$ . From among the distinguishing features of the effect we note also that the under definite relations between  $T_0$ ,  $\tau_c$ , and  $\omega$  the component  $M_{2mo}^{\sin}$  becomes an alternating-sign function, and this apparently simplifies the determination of the parameters. By varying the temperature and the viscosity of the solutions and by comparing the experimental and calculated curves we can obtain data on the contributions of the various mechanisms to the spin-lattice relaxation.

For a system of ions in a lattice, the role of the time  $c$  is assumed in the relaxation processes by the characteristic time of the relaxation interaction.<sup>15</sup>

We consider now a case of practical interest, that of relaxation of triplet states in a liquid in parallel fields. For simplicity we assume that the exchange interaction is isotropic. The Hamiltonian of the system takes in the case of axial symmetry the form<sup>11</sup>

$$\begin{aligned} \mathcal{H}_e &= \hbar \gamma H(t) \bar{S}_z, \\ \mathcal{H}_{es} &= \frac{1}{2} D (3 \cos^2 \theta - 1) S_z^2 + \frac{1}{2} D \sin \theta \cos \theta [(S_+ S_z + S_z S_+) e^{-i\omega t} \\ &+ (S_z S_- + S_- S_z) e^{i\omega t}] + \frac{1}{2} (3 \cos^2 \theta - 1) \hbar \Delta \gamma H(t) S_z \\ &+ \frac{1}{2} \hbar \Delta \gamma H(t) \sin \theta \cos \theta (S_+ e^{-i\omega t} + S_- e^{i\omega t}). \end{aligned}$$

Since the exchange interaction commutes with the Zeeman interaction, the magnitude of the latter is linearly connected with the field  $H_0$ , and the levels are equidistant. In this case one can introduce a single spin-lattice relaxation time.<sup>15,16</sup> In fact, on going from the kinetic equation for the spin density matrix (2) to the equation for the  $z$  component of the macroscopic magnetic moment, under conditions of not too high alternating-field frequencies  $\omega \tau_c \ll 1$  and not too large a fine-interaction constant  $\hbar^{-1} D \tau_c < 1$ , we obtain, just as for a two-level

system, a Bloch equation with a relaxation time that depends on the instantaneous value of the external magnetic field:

$$T_1^{-1} = \frac{1}{2} (D_1^2 + \Delta \gamma^2 H^2(t)) \tau_c (1 + \gamma^2 H^2(t) \tau_c^2)^{-1} + T_{01}^{-1}, \quad D_1 = \hbar^{-1} D.$$

The solution for the nonlinear response will agree with expression (16) for a two-level system, subject to some modification of  $T_1^0$ ;

$$(T_1^0)^{-1} = T_{01}^{-1} + \frac{1}{2} (D_1^2 + \Delta \gamma^2 H^2) \tau_c (1 + \omega_0^2 \tau_c^2)^{-1} + a_0,$$

and to replacement of  $(\gamma^{-1} \Delta \gamma)^2$  by  $(\gamma^{-1} \Delta \gamma)^2 - D_1^2 \tau_c^2$  in the expressions for  $a_i$  ( $i=0, \dots, 4$ ). Everything said above is in fact valid also for particles with  $S > 1$  when other interactions are neglected.

The dependence of the phase components  $M_2$  on the value of  $H_0$  for a three-level system is of the same type as for two levels. The signs in this case are opposite to the signs of the curves for the two-level system, inasmuch as the decisive contribution to the relaxation is made by the mechanism due to the fine interaction and not by the  $g$ -factor anisotropy. Even at short  $T_0^{-1} = 5.55 \times 10^{10} \text{ sec}^{-1}$  and large  $D_1 = 5.13 \times 10^{10} \text{ sec}^{-1}$ , when the EPR signal is not observable, the linear effects at  $\tau_c = 10^{-11} \text{ sec}$  are appreciable,  $M_{2mo}^{\sin} = -3.2 \times 10^{-5}$  and  $M_{2mo}^{\cos} = 6 \times 10^{-6}$  at a frequency  $\nu = 500 \text{ MHz}$  and at  $\gamma H_1 \omega^{-1} = 1.84$ . When  $\tau_c$  is decreased by a factor of three, the maximum shifts noticeably from the field  $H_0 \approx 3.5 \text{ kOe}$  into the strong-field region (12.5 kOe), and the nonlinear effects remain appreciable:  $M_{2mo}^{\sin} = 4 \times 10^{-6}$ . In the case of longer relaxation times  $T_0^{-1} = 6 \times 10^7 \text{ sec}^{-1}$  and smaller fine-interaction constants  $D_1 = 8.6 \times 10^9 \text{ sec}^{-1}$ , an appreciable value of the effect ( $M_{2mo}^{\sin} = -1.7 \times 10^{-4}$ ,  $M_{2mo}^{\cos} = 4.5 \times 10^{-4}$ ) is obtained in relatively weak fields ( $H_{\max}^{\sin} = 1 \text{ kOe}$ ,  $H_{\max}^{\cos} = 2 \text{ kOe}$ ) and at a low frequency of the alternating field,  $\nu = 15 \text{ MHz}$  ( $\tau_c = 3 \times 10^{-11} \text{ sec}$ ). The sign of the phase component  $M_{2mo}^{\sin}$  remains alternating.

For a three-level system, the value of  $T_0$  influences the effects in approximately the same manner as in the case of a two-level system. The amplitude of the phase components in the region  $D_1 \tau_c < 1$  is proportional to  $D_1^2$ . The dependences on  $H_1$  and on the frequencies are the same as for  $S = \frac{1}{2}$ .

It follows from the foregoing that by choosing appropriate experimental conditions (frequency and amplitude of the alternating field, the scanning of  $H_0$ ) it is possible to obtain nonlinear effects of large magnitude and use them to investigate paramagnetic substances. This is done by determining from an analysis of the experimental curves the parameters of the spin system and of the molecular motion. If the concentration, viscosity and temperature are varied it is possible to obtain also the contributions of the different relaxation mechanisms even in paramagnets in which the EPR signal is not observable.

### 3. DISCUSSION OF EXPERIMENTAL RESULTS

Let us discuss briefly the experimental results reported in Refs. 1 and 2. At an alternating-field frequency  $\nu = 50 \text{ MHz}$  the nonlinear effects were registered in solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in glycerine at temperatures 275–345 K and at solution concen-

trations 2 and 1 mol/l, respectively. The spin Hamiltonian for the  $\text{Cu}^{2+}$  ion is described by expressions (6), where  $S = \frac{1}{2}$  and  $I = \frac{3}{2}$ . In this case, three resonant transitions are possible in parallel fields, with frequencies

$$\omega_1 = [(\gamma H_0 - a)^2 + 3a^2]^{\frac{1}{2}}, \quad \omega_2 = [(\gamma H_0 + a)^2 + 3a^2]^{\frac{1}{2}}, \\ \omega_3 = [\gamma^2 H_0^2 + 16a^2]^{\frac{1}{2}}.$$

At  $\nu = 50$  MHz, the conditions  $2\omega < \omega_m$  and  $2\omega < a$  are satisfied, and the results can be analyzed on the basis of the equations of motion for the system  $S = \frac{1}{2}, I = 1$ . Estimates of the correlation time yield  $\tau_c = 4.5 \times 10^{-10}$  sec at  $T = 325$  K and  $\tau_c = 1.5 \times 10^{-9}$  sec at 245 K. For a qualitative analysis it is still possible to use here the rapid-motion model, when  $\hbar^{-1} E_{sr} \tau_c < 1$ . The local field due to the neighboring spin at concentrations 1–2 mol/l is of the order of 10–20 Oe, and the correlation times of the translational motion are  $\tau_p \sim \tau_c$ . Therefore the contribution made to the relaxation by the spin-spin interaction can be neglected. The maximum of  $|M_2|$  in the calculated curves occurred in a field  $H_0 \approx 60$  Oe for  $\tau_c = 4.6 \times 10^{-10}$  and in a field  $H_0 \approx 90$  Oe at  $\tau_c = 1.5 \times 10^{-9}$  sec. The parameters used in the calculations were  $g = 2.16$ ,  $\Delta g = 0.3$ ,  $a = 0.94 \times 10^9$  sec $^{-1}$ , and  $b = 1.71 \times 10^9$  sec $^{-1}$  (Ref. 14). The experimental curves had maxima in the fields  $H_0 \approx 133$  Oe and  $H_0 \approx 114$  Oe, respectively. The difference between the positions of the maxima of the theoretical and experimental curves is due to the fact that at these concentrations the relaxation is determined by spin exchange.<sup>17</sup> Since the resonant transition take place in parallel fields, the presence of exchange interaction leads only to a broadening of the resonance lines.<sup>18</sup> When the viscosity of the solution is decreased, the rate constant of exchange-pair production increases and the effectiveness of the exchange relaxation increases, so that the resonance lines are broadened. Since the effects are connected with resonant absorption on the wings of the resonance lines, their broadening leads to a shift of the maxima of the effects towards stronger fields  $H_0$ , and to a decrease of their values, as is indeed observed in experiment. In the absence of exchange relaxation, a decrease of the correlation time leads to the opposite effect. One other cause of the shift of the maxima of the effects towards stronger fields with decreasing viscosity is, as already mentioned,<sup>1,2</sup> the contribution of the relaxation effects. Calculations show that their maximum at  $\tau_c \approx 3 \times 10^{-10}$  will occur in fields  $H_0 \leq 110$  Oe.

In Refs. 1 and 2 were investigated also solutions of DPPH in benzene at 300 K and solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

and of  $\text{FeCl}_3$  in alcohol at 77K, as well as a ruby crystal with 0.03% Cr. As indicated in Ref. 4, in these cases the effects are apparently governed also by resonant transitions. The hyperfine interaction constants with the nuclear spins of nitrogen for DPPH are  $a\gamma^{-1} \approx 12$ –14 Oe (Ref. 19), with the  $\text{Cr}^{53}$  nucleus in ruby  $a\gamma^{-1} \approx 17$  Oe (Ref. 14), and with nuclei of chlorine ligands in the case of  $\text{FeCl}_3$  apparently of the same order. Since  $a \sim \omega$ , the contribution of the resonance effects exceeds the contribution of the effects of other type.

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