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Nonlinear relaxation effects in paramagnetic substances

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An analysis is made of the possibility of using nonlinear effects in the magnetization of paramagnets for investigating paramagnetic centers. The existence of new nonlinear effects is postulated: these are due to the known dependence of the relaxation time on the external magnetic field. An analysis of the case of two parallel magnetic fields shows that the magnitude of the effect (ratio of the magnetizations at the doubled and fundamental frequencies) may reach 20% even in fields of the order of 100 Oe. A description is given of apparatus constructed for detection and measurement of these nonlinear effects. The experiments carried out using this apparatus demonstrated the existence of strong nonlinear effects in weak magnetic fields and confirmed the assumption of a high sensitivity of the nonlinear effect method in investigations of paramagnetic substances.

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INTRODUCTION

It is well known that there are quite a few experimental situations in which fundamental and technical difficulties make it impossible to realize fully the high sensitivity and information potential of the ESR method. Other methods for investigating paramagnetic substances such as measurements of the magnetic susceptibility[1] and the Gorter method[2] suffer from a low sensitivity and, therefore, their usefulness is limited.

It follows from this statement that it would be extremely useful to develop new methods for investigating paramagnetic substances, particularly those that would give information unattainable by the ESR method and would have a sensitivity comparable with that of ESR spectroscopy, at least in some situations. The solution may lie in the adoption of methods based on various nonlinear effects in paramagnetic substances. It can be shown[3] that if the nonlinearity coefficient in the magnetization of a paramagnet in a harmonic rf field of amplitude $H_1 = 50$–100 Oe reaches 10%, the sensitivity of the method of measuring higher harmonics of the magnetization becomes equal to the sensitivity of the ESR method in which the ESR absorption line width is ~10 Oe.

We shall now review briefly possible nonlinear effects.

1. The nonlinear effects due to the nonlinearity of the magnetization curve of paramagnets are strong only in high fields at low temperatures or if optical pumping is used.[4]

2. The nonlinear effects resulting from saturation of paramagnetic resonance transitions[5] appear when not only allowed but also forbidden transitions become saturated.[3]

3. There are also nonlinear adiabatic effects observed on adiabatic magnetization of substances with high concentrations of paramagnetic particles.[3,6]

4. The nonlinear relaxation effects[3] should exist if the well-known dependence of the relaxation times T_1 and T_2 on the intensity of an external static magnetic field applies also to the instantaneous amplitude of an external alternating field.

In the case of a paramagnetic particle of spin $S = \frac{1}{2}$ in a liquid whose Hamiltonian is

$$\hat{\mathscr{H}} = \beta H(t)\left[(\Delta g\cos^2\theta + g_\perp)\hat{S}_z + \Delta g\cos\theta\sin\theta\cdot{}^1/_2(\hat{S}_+ e^{-i\varphi} + \hat{S}_- e^{i\varphi})\right], \quad (1)$$

the application of nonstationary perturbation theory and the assumption that

$$\Delta g = g_\parallel - g_\perp \ll g_\perp, \quad H(t) = H_0 + H_1\sin\omega t,$$
$$g_\perp\beta/\hbar = \gamma, \quad \gamma H_1/\omega < 1$$

and that the stationary correlation function is $G(\tau) = G(0)\exp(-|\tau|/\tau_c)$, gives,[3] in the first order of smallness of $1/T_1$:

$$\frac{1}{T_1(t)} = \frac{4\beta^2\Delta g^2\tau_c G(0)}{\hbar^2}\left\{\frac{H_0{}^2}{1+(\gamma H_0\tau_c)^2}\right.$$

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$$+\;H_1\frac{1-(\gamma^2H_0^2-\omega^2)\tau_c^2}{[1+(\gamma H_0+\omega)^2\tau_c^2][1+(\gamma H_0-\omega)^2\tau_c^2]}+H_0H_1\left(\frac{1}{1+(\gamma H_0\tau_c)^2}\right.$$
$$\left.+\frac{1+(\gamma^2H_0^2+\omega^2)\tau_c^2}{[1+(\gamma H_0-\omega)^2\tau_c^2][1+(\gamma H_0+\omega)^2\tau_c^2]}\right)\sin\omega t\Big\}. \qquad (2)$$

In the case of rapid motion, i.e., when $(\gamma H+\omega)\tau_c \ll 1$, we obtain

$$\frac{1}{T_1(t)}=\frac{4\beta^2\Delta g^2\tau_c G(0)}{\hbar^2}(H_0+H_1\sin\omega t)^2. \qquad (3)$$

Thus, if we know the Hamiltonian and the spectrum of thermal fluctuations of a two-level system, we can find the dependence of the relaxation time on the intensities of external fields, frequency, and time. It is interesting to note that if $\omega\tau_c$ can assume any value and H_1 can be comparable with H_0, the relaxation time and, consequently, the magnetization depend reasonantly on H_0 or ω.

It is clear from Eq. (3) that in the case of rapid motion the dependence of the relaxation time on an external alternating magnetic field is identical with the familiar dependence of the relaxation time on a static magnetic field.[7] Therefore, if we assume

$$T=T_0+aH^2=T_0[1+\Delta T(H)/T_0],$$

where T_0 is the relaxation time in zero magnetic field, and if we use the Bloch equation

$$dM/dt=[\chi_0H(t)-M]/T_1(H), \qquad (4)$$

we can find solutions for higher harmonics of the magnetization. If $\Delta T(H)/T_0 \ll 1$, Eq. (4) is easily solved and, in the first order of smallness, the magnetization acquires higher harmonics. The following expressions are obtained for the second harmonic:

$$\begin{gathered} M_2=|M_2|\sin(2\omega t+\varphi_2),\\ \varphi_2=\mathrm{arctg}[3\omega T_0(2\omega^2T_0^2-1)^{-1}],\\ |M_2|/\chi_0H_1=aH_0H_1\omega[1+5(\omega T_0)^2+4(\omega T_0)^4]^{-1/2}. \end{gathered} \qquad (5)$$

It follows from the above expressions that the amplitude and phase of higher harmonics depend on the frequency; the nonlinear effect is strongest at $\omega T_0=1$ and it is then equal to $|M_2|/\chi_0H_1=\frac{1}{3}\Delta T(H)/T_0$, and the relaxation time T_0 can be determined by measuring the phase of the second harmonic.

Equation (4) was solved in the $\Delta T(H)/T_0 \gtrsim 1$ case by representing the magnetization as a Fourier series, whose coefficients were found by the harmonic balance method.[3] The resultant solution for the second harmonic of the magnetization is shown in Fig. 1. It is clear from this figure that the magnitude and position of the maximum of the second magnetization harmonic are governed, on the one hand, by the nature of the investigated paramagnet and, on the other, by the experimental conditions. Calculations[3] indicate that in sufficiently strong fields, i.e., when the modulation of the relaxation time is considerable, the nonlinear effects reach 25% ($\omega T_0=0.1$; $H_1^2=H_0^2=5T_0/a$). The magnetic fields needed for such modulation depend on the nature of the paramagnet and can be estimated from the theory of paramagnetic relaxation.

The theory of paramagnetic relaxation is based on the existence of fluctuating magnetic and electric fields in a relaxing spin. The spin–lattice relaxation time of a two-level system, considered in the first order of the theory of time-dependent perturbations, is of the form[8,9]

$$T_1^{-1}=\hbar^{-2}\overline{|V_{ab}(t)|^2}J(\omega_{ba}), \qquad (6)$$

where $V_{ab}(t)$ is the nondiagonal matrix element of the perturbation operator proportional to the amplitude of the fluctuating fields; $J(\omega_{ba})$ is the spectral density of fluctuations at the frequency ω_{ba}. The specific nature of the dependence of the relaxation time on the external magnetic field is governed by the nature of intermolecular and intramolecular interactions and by the spectrum of thermal motion modulating these interactions. It is clear from Eq. (6) that the relaxation time may depend on the intensity of an external magnetic field for two reasons: firstly, because of the field dependence of the nondiagonal matrix elements $V_{ab}(t)$, i.e., of the amplitudes of the fluctuating fields; secondly, because of the inhomogeneity of the spectral density of thermal fluctuations $J(\omega_{ba})$.

The theory of paramagnetic relaxation in liquids is developed more than other theories and it agrees well with the experimental results.[7,9] In the case of solutions the amplitude of a magnetic field needed for modulation of the relaxation time by a factor of two amounts to 10–1000 Oe, depending on the viscosity, molecular weight of paramagnetic particles, and actual relaxation mechanism.[3]

In solids at high temperatures, when the main contribution to the relaxation is due to multiphonon processes, the theory does not give the dependence of the relaxation time on the intensity of an external magnetic field although such a dependence has been observed experimentally, at least in the case of high concentrations of paramagnetic particles.[2]

The use of nonlinear relaxation effects is promising in the method of recording higher harmonics because these effects: a) may be strong in relatively weak magnetic fields; b) give new information, in contrast to the nonlinear effects which appear on saturation of

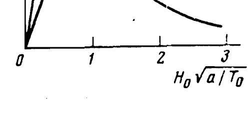

FIG. 1. Theoretical dependences of the amplitude of the second harmonic of the magnetization on the intensity of a static external magnetic field in nonlinear relaxation effects: a) $\omega T_0=0.5$, $H_1\sqrt{a/T_0}=0.32$; b) $\omega T_0=0.5$, $H_1\sqrt{a/T_0}=1$; c) $\omega T_0=0.1$, $H_1\sqrt{a/T_0}=1.73$.

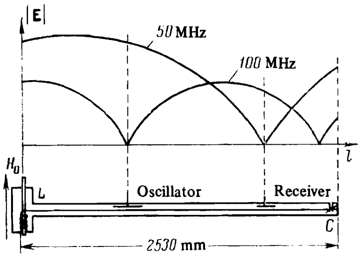

FIG. 2. Two-mode hybrid resonator.

resonance transitions; c) appear for low concentrations of paramagnetic substances, in contrast to the nonlinear adiabatic effects.

DESCRIPTION OF APPARATUS

The nonlinear effects in parallel fields were investigated using apparatus in which the main unit was a two-mode hybrid resonator. This resonator is shown schematically in Fig. 2. It represents a coaxial line closed at the ends by an inductance coil L and a variable capacitor C. The relationship between the wave impedance of the line and L, C was selected in such a way that the hybrid resonator could be excited at frequencies of 50 and 100 MHz. A special feature of this resonator was that the nodes of the 50 and 100 MHz electric fields occurred at different points in the resonator. This ensured 80 dB suppression of the second harmonic of an oscillator which excited the 50 MHz mode by a probe if the probe was located in the resonator in such a way that it coincided with a node of the 100 MHz mode. Similar 80 dB filtration of the exciting voltage was established at the input of a 100 MHz receiver.

An exciting oscillator (50 MHz, 8 W) was connected to the resonator via a band-pass filter which provided an additional 60 dB filtration of the second harmonic of the oscillator. When the power dissipated in the resonator was 5 W (the voltage across the exciting probe was ~ 20 V and the voltage across the coil was ~ 800 V), the intensity of the exciting magnetic field in the coil L was 25 Oe. A static magnetic field, applied parallel to the high-frequency field, was created by Helmholtz coils and its maximum value reached 250 Oe.

The resultant second harmonic signal was amplified with a receiver (pass band 100 kHz, noise factor 10 dB) and was passed through an amplitude detector to the Y input of a recording instrument. The X input received a voltage proportional to the current in the Helmholtz coils. The recording instrument was an $X-Y$ plotter or a cathode-ray oscillograph. The magnetic field in the Helmholtz coils was scanned in a sawtooth-manner at frequencies of 0.001–10 Hz.

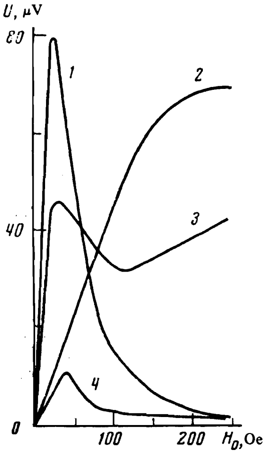

FIG. 3. Dependences of the signal on the intensity of an external magnetic field $\mathbf{H}_0 \parallel \mathbf{H}_1$ for compounds of Cr^{3+}: 1) Cr^{3+} in glycerine ($c = 2$ mole/liter), $T = 77$ °K; 2) $KCr(SO_4)_2 \cdot 12H_2O$, $T = 300$ °K; 3) $Cr_2(SO_4)_3 \cdot 18H_2O$, $T = 77$ °K; 4) 0.03% Cr^{3+} in Al_2O_3, $T = 300$ °K.

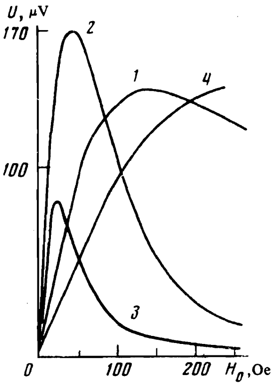

FIG. 4. Dependences of the signal on the intensity of an external magnetic field $\mathbf{H}_0 \parallel \mathbf{H}_1$ for compounds of Fe^{3+} at $T = 77$ °K: 1)–3) $FeCl_3$ in alcohol, $c = 1.5$, 0.4, and 0.05 mole/liter (curves 1, 2, and 3, respectively); 4) $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$.

Thus, we recorded experimentally the dependence of the second harmonic amplitude at the output of the two-mode resonator as a function of the intensity of a static magnetic field. Samples were placed inside the inductance coil L of the resonator (nine turns, internal diameter 10 mm) and they were located in ampoules (internal diameter 4 mm, height of the sample 40 mm). The space factor of the coil was $\eta = 0.15$.

In addition to recording the second harmonic signal, we were able also to determine the absorption spectra in parallel fields. This was done by the usual method in which the magnetic field was modulated. The two-mode hybrid resonator was used as a normal reflection resonator at 50 MHz. The signal from this reflection resonator was detected, amplified with a narrow-band amplifier at the modulation frequency, passed through a lock-in detector, and applied to the Y input of an $X-Y$ recorder. In this way we were able to record the first derivatives of the absorption spectra in parallel fields.

EXPERIMENTAL RESULTS

The apparatus described above enabled us to observe second harmonics of the magnetization in a number of substances. The experiments were carried out in the $\mathbf{H}_0 \parallel \mathbf{H}_1$ configuration. At temperatures of 77 and 300 °K we investigated paramagnetic salts: these were polycrystalline powders, their solutions in alcohol and glycerin, crystalline DPPH and its solutions in benzene, and also a ruby crystal with its c axis oriented parallel to the high-frequency magnetic field. In all cases and at all temperatures the amplitude of the second harmonic was proportional to $\mathbf{H}_1^2$.

The dependence of the second harmonic signal on the static magnetic field, applied parallel to the hf field, is reproduced in Figs. 3 and 4 for several compounds of Cr^{3+} and Fe^{3+}. The signal disappeared when paramagnetic salts of the hydrates $KCr(SO_4)_2 \cdot 12H_2O$, $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot 5H_2O$ were heated until they lost the water of

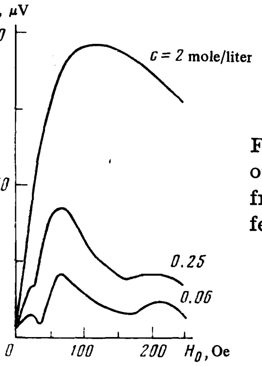

FIG. 5. Dependences of the signal on the magnetic field $\mathbf{H}_0 \parallel \mathbf{H}_1$ for CuCl frozen in alcohol, plotted for different concentrations of Cu^{2+}.

crystallization. In the case of $CuCl_2 \cdot 2H_2O$ the loss of the water of crystallization increased the signal by a factor of about 2.

The influence of the concentration of paramagnetic substances on the second harmonic signal was investigated employing solutions at various temperatures. Figures 4 and 5 show the dependences of the second harmonic signal on $\mathbf{H}_0 \parallel \mathbf{H}_1$ in frozen alcohol solutions of $CuCl_2 \cdot 2H_2O$ and $FeCl_3$ of various concentrations. We found that the signal was not proportional to the concentration.

In addition to paramagnetic ions, we observed the second harmonic signal for crystalline DPPH. This signal had one maximum in a field of ~ 20 Oe. The appearance of the second harmonic signal in parallel fields was also observed in solutions kept at room temperature (Fig. 6). When the concentration of DPPH in benzene was reduced, the signal maximum shifted toward higher fields. When the temperature of a solution of Cu^{2+} in glycerine was increased from 283 to 33 °K the signal decreased by a factor of almost 10 and the maximum shifted to stronger fields.

In parallel fields the absorption spectra of all the investigated substances were of nonresonant nature, with the exception of the salt $CuCl_2 \cdot 2H_2O$.

A more detailed description of the experimental results can be found in[3].

DISCUSSION OF EXPERIMENTAL RESULTS

The theory of nonlinear relaxation effects, nonlinear adiabatic effects, and nonlinear effects in the presence of resonance transitions in parallel fields[3] all predict the possibility of existence of strong nonlinear effects in the $\mathbf{H}_0 \parallel \mathbf{H}_1$ configuration but none of these theories even pretend to give a quantitative description. Therefore, our discussion of the experimental results has to be qualitative.

As mentioned earlier, most of the samples did not exhibit resonant absorption in parallel fields. Therefore, the appearance of the higher magnetization harmonics in these samples cannot be explained by the saturation of resonance transitions. Cooling from 300 to 77 °K is known[2] to increase T_1 by one or two orders of magnitude. The saturation factor and, consequently, the nonlinear effects should increase accordingly if they are due to the saturation of resonance transitions, but this is not observed experimentally. In that case when a resonance transition is found in parallel fields ($CuCl_2 \cdot 2H_2O$, when the maximum of the dependence of the second harmonic signal on the field occurs in the field corresponding to the resonance transition), the second harmonic signal can be explained by the saturation of resonance transitions.

Estimates of the adiabatic nonlinear effects[3] in high-concentration paramagnetic salts give values two orders of magnitude higher than those found experimentally even at temperatures of 77 °K when the adiabaticity condition is satisfied. According to[3], the dependence of M_2 on H_0 should have a maximum at H_0 equal to H_L (internal local field[2]). A comparison of the experimental results with the values of H_L given in[2,10,11] shows that the maximum of M_2 is always observed in fields lower than H_L. When concentrated paramagnets are diluted, the nonlinear adiabatic effects should disappear because under these conditions we cannot introduce the concept of a spin temperature for the whole spin system. However, the experimental evidence shows that all the nonlinear effects increase strongly on dilution. Moreover, the nonlinear effects are observed even for concentrations of $\sim 10^{-2}$ mole/liter (DPPH, Cu^{2+}) and of the order of $\sim 10^{-3}$ mole/liter (Fe^{3+}), i.e., at concentrations such that the method of parallel fields[2,10] is completely inappropriate. Moreover, according to the results of Gorter,[2] $H_L = \sqrt{b/c}$ is independent of temperature in the range from 300 to 4 °K, i.e., the change in temperature should not alter the position of the maximum of M_2. It is clear from Table 1 that such a shift does exist and can be considerable. The above discussion shows that the observed nonlinear effects are not adiabatic even for $\omega T_i > 1$ and $\omega T_2 < 1$.

The nonlinear relaxation effects should be propor-

TABLE 1.

Concentration, cm^{-3}	S	T, K	$\chi_0 H_1$	U_{max}, μV	H_L max	$\frac{M_{2\,max}}{\chi_0 H_1}$
$CuCl_2 \cdot H_2O$						
$3.4 \cdot 10^{21}$	1/2	300	$1.8 \cdot 10^{-4}$	15	20	$9.3 \cdot 10^{-5}$
		77	$6.9 \cdot 10^{-4}$	130	28	$2.1 \cdot 10^{-4}$
$CuCl_2 \cdot 2H_2O$ in glycerine						
$1.2 \cdot 10^{21}$	1/2	345	$5.4 \cdot 10^{-5}$	3	133	$6.0 \cdot 10^{-5}$
		325	$5.8 \cdot 10^{-5}$	6	114	$1.1 \cdot 10^{-4}$
		305	$6.1 \cdot 10^{-5}$	16	95	$2.8 \cdot 10^{-4}$
		275	$6.8 \cdot 10^{-5}$	21	85	$3.4 \cdot 10^{-4}$
$CuSO_4 \cdot 5H_2O$						
$3.1 \cdot 10^{21}$	1/2	300	$1.6 \cdot 10^{-4}$	23	240	$1.6 \cdot 10^{-4}$
		77	$6.3 \cdot 10^{-4}$	70	151	$1.6 \cdot 10^{-4}$
$CuSO_4 \cdot 5H_2O$ in glycerine						
$6.0 \cdot 10^{20}$	1/2	300	$3.1 \cdot 10^{-5}$	8	114	$3.0 \cdot 10^{-4}$
		77	$1.2 \cdot 10^{-4}$	180	86	$1.6 \cdot 10^{-3}$
$KCr(SO_4)_2 \cdot 12H_2O$						
$1.2 \cdot 10^{21}$	3/2	300	$3.0 \cdot 10^{-4}$	75	260	$2.7 \cdot 10^{-4}$
		77	$1.2 \cdot 10^{-3}$	230	240	$2.1 \cdot 10^{-4}$
0.03% Cr^{+3} Al_2O_3 *						
$1.4 \cdot 10^{19}$	3/2	300	$3.6 \cdot 10^{-6}$	11	38	$7.2 \cdot 10^{-4}$
$MnSO_4 \cdot 5H_2O$						
$3.3 \cdot 10^{21}$	5/2	300	$2.0 \cdot 10^{-3}$	12	345	$6.3 \cdot 10^{-6}$
		77	$7.8 \cdot 10^{-3}$	26	88	$3.7 \cdot 10^{-6}$
$FeCl_3$ in alcohol						
$9.0 \cdot 10^{20}$	5/2	77	$2.1 \cdot 10^{-3}$	130	135	$6.7 \cdot 10^{-5}$
$2.4 \cdot 10^{20}$		77	$5.7 \cdot 10^{-4}$	170	42	$3.3 \cdot 10^{-4}$
$3.0 \cdot 10^{19}$		77	$7.1 \cdot 10^{-5}$	85	28	$1.3 \cdot 10^{-3}$
DPPH, crystal						
$7.3 \cdot 10^{20}$	1/2	300	$3.8 \cdot 10^{-5}$	15	36	$4.3 \cdot 10^{-4}$
		77	$1.5 \cdot 10^{-4}$	32	36	$2.4 \cdot 10^{-4}$
DPPH in benzene						
$1.2 \cdot 10^{20}$	1/2	300	$6.2 \cdot 10^{-6}$	11	23	$1.2 \cdot 10^{-3}$
$1.5 \cdot 10^{19}$		300	$7.8 \cdot 10^{-7}$	7	40	$6.3 \cdot 10^{-3}$

*For ruby and for solution of DPPH in benzene, $\eta = 0.7$.

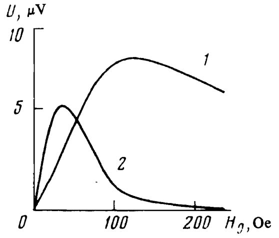

FIG. 6. Dependences of the signal on H_0 when $H_0 \parallel H_1$ for solutions: 1) $CuSO_4$ in glycerine, $c = 1$ mole/litter; 2) DPPH in benzene, $c = 0.05$ mole/liter; $T = 300$ °K.

tional to $\chi_0 - \chi_{ad}$, so that dilution of paramagnets and the associated reduction in χ_{ad} should increase, as found experimentally. Direct measurements of the time τ_c by altering the viscosity of Cu^{2+} solutions in glycerine through heating demonstrate a strong dependence of this effect on τ_c, which is in agreement with the theory of nonlinear relaxation effects in liquids.[3] Annealing of crystalline hydrates until they lose water of crystallization, which modifies the crystal lattice, and the associated changes in the relaxation times and mechanisms alter considerably the magnitude of the effects. This is in agreement with the relaxation nature of the effects.

According to[2,10,11], the relaxation times of the paramagnetic salts $KCr(SO_4)_2 \cdot 12H_2O$, $MnSO_4 \cdot 5H_2O$, and $FeNH_4(SO_4)_2 \cdot 12H_2O$ rises by a factor of several tens when the temperature is lowered from 300 to 77 °K and the value of ωT_1 changes in the same range from 1 to 40. This should reduce considerably the relaxation effects. However, such a reduction is either not observed experimentally or it is much less than that expected theoretically. This can be explained by assuming a change in the nature of the field dependence of the relaxation time or by postulating an increase in the contribution of nonlinear effects of other origin, since cooling to 77 °K satisfied better the adiabaticity conditions and also increases the saturation factor.

Thus, it is clear from our discussion that at high temperatures (~ 300 °K) and also for liquid solutions and dilute paramagnets the effects observed are indeed of relaxation origin. More precise conclusions on the nature of the observed effects in each specific case would require a detailed theoretical analysis allowing for the specific properties of each investigated substance. Moreover, it would be necessary to carry out further experimental studies of the nonlinear effects at difference frequencies of the exciting magnetic fields.

CONCLUSIONS

When the exciting power is 5 W, the magnitude of the effects under consideration $k = M_{2\max}/\chi_0 H_1$ reached 10^{-4}–10^{-2} for some of the investigated samples. The concentration sensitivity of the apparatus, determined for a solution of DPPH in benzene, was limited by the receiver noise (pass band 100 kHz, $U_n = 1.5$ μV) and was 5×10^{-3} mole/liter. Improvement of the apparatus by the use of lock-in detection and narrowing of the pass band of the receiver to 0.1 Hz should increase the sensitivity by a factor of 1000; an increase of the exciting power to 100 W should enhance the sensitivity further by a factor of 20 (on the assumption that $U_c \propto H_1^2$). Then, the sensitivity for a solution of DPPH in benzene should be 2.5×10^{-7} mole/liter, which would be comparable with the sensitivity of a high-grade ESR spectrometer. This example demonstrates the correctness of our earlier conclusions that the sensitivity of the method of recording higher harmonics could be made comparable with the sensitivity of the ESR method even for an ESR line width of ~ 10 Oe.

Thus, nonlinear effects in paramagnetic substances can be used to study these substances subject to further theoretical studies of the effects and improvement in the experimental methods for their detection. In particular, the nonlinear relaxation effects can give direct information on relaxation mechanisms.

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