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Effect of a Strong Radio-Frequency Field on the Transverse Relaxation Time in Paramagnetic Solids[*]

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We report the experimental measurement of the transverse relaxation time T_2 in saturated spin systems as a function of the applied rf magnetic field. These data are compared with the predictions of current theories and the value of the exchange frequency, or local field, is determined.

The spin decoupling in paramagnetic solids caused by the stirring effect of strong rf fields has been considered by many authors.[1-7] One conclusion which is drawn in all of these articles is that there should be an increase in the transverse relaxation time T_2 with increase in rf magnetic field. Such an increase has never been observed experimentally in electron-spin systems of solid materials. The relaxation time T_2 has generally been deduced from the linewidth $\Delta\omega$ of the electron-spin-resonance (ESR) absorption line by making use of the relation

$$\Delta\omega \sim \frac{1}{T_2} . \tag{1}$$

This expression is valid only for spin systems very far from saturation.

We have recently suggested that saturated spin systems can be studied conveniently by investigating the second-harmonic emission from them.[8] In particular, we have shown that transverse relaxation times for both saturated and unsaturated spin systems can be deduced from measurements of the phase of the harmonic signal. We present the first experimental measurements of T_2 as a function of the applied rf magnetic field in various samples of solid solutions of diphenylpicrylhydrazyl, (DDPH) in polystyrene. In our notation, T_{20} and T_{2e} represent the transverse relaxation times for unsaturated and saturated spin systems, respectively.

Let us consider a spin system containing paramagnetic impurities of spin $S=\frac{1}{2}$ in a static magnetic field $H_0=\omega_0/\gamma$ and an rf magnetic field H_{rf} of frequency ω polarized at an angle $\frac{1}{2}\pi-\theta$ with respect to the direction of the static field. We have shown[8] both experimentally and theoretically that such spin systems emit radiation at the second harmonic of the driving rf magnetic field. The harmonic spectrum has two lines resonating at $\omega=\omega_0$ and $\omega=\frac{1}{2}\omega_0$, respectively. The harmonic signal is phase coherent, the phase angle being a function of the external static magnetic field.

For the line resonating at $\omega=\omega_0$, the phase angle is given by

$$\tan\Phi_1=\frac{T_{2e}^{-1}}{\omega-\omega_0} . \tag{2}$$

Near the resonance $\omega\sim\omega_0$, the spin system is strongly perturbed by the rf field so that it is generally in a state of heavy saturation. The saturation factor $(T_2S)^2=\gamma^2H_{\mathrm{rf}}^2\,T_1\,T_2$ can be of the order of 10 or more; T_{2e} as given by Eq. (2) is therefore the effective transverse relaxation time, and is equal to T_{20} only at very low input-power levels.

For the line resonating at $\omega=\frac{1}{2}\omega_0$ the phase angle of the harmonic signal is given by

$$\tan\Phi_2=\frac{T_{20}^{-1}}{2\omega-\omega_0} . \tag{3}$$

T_{20} in Eq. (3) is essentially the same as the one obtained by using Eq. (1) because near $\omega=\frac{1}{2}\omega_0$ the spin system is very far from saturation.

In order to make clear some points that will be useful in later discussion, we wish to emphasize that Eqs. (2) and (3) have been inferred from an analysis of a two-level homogeneously broadened system and, strictly, are valid only for such a system. An inhomogeneously broadened line can be thought of as the envelope of many homogeneous lines, or spin packets, each with a width of T_2^{-1} and resonating at $\omega_0+\epsilon$, where ϵ has zero mean and a variance of ϵ_0^2. The harmonic signal in this case is the sum of many lines distributed symmetrically about the central one and with decreasing intensity. One can show that the value of T_{20}^{-1} deduced from Eq. (3) for this case is equal to the total width ϵ_0. On the other hand, the value of T_{2e}^{-1} deduced from Eq. (2) is equal to the width of the central spin packet resonating at $\omega=\omega_0$; this is true as long as the saturation factor S, satisfies the condition S

TABLE I. Summary of observed weak-field relaxation time T_{20} for samples of DPPH variously diluted in polystyrene. The parameter $\langle H_{\mathrm{eff}}^2\rangle^{1/2}$, determined by fitting the observed variation of T_{2e} with rf magnetic field strength, is listed in the last column.

DPPH sample No.	Nominal conc. spin/cm^3	$10^8 T_{20}$ (sec)	$\langle H_{\mathrm{eff}}^2\rangle^{1/2}$ (G)
1	6×10^{20}	4 ± 0.04	>100
2	5×10^{20}	2 ± 0.02	>100
3	3×10^{20}	0.8 ± 0.08	33 ± 3
4	2×10^{20}	0.6 ± 0.06	23 ± 2
5	6×10^{19}	0.47 ± 0.05	9 ± 0.9
6	2×10^{19}	0.4 ± 0.04	5 ± 0.5
7	$<10^{18}$	0.3 ± 0.03	...

$> T_{2e}^{-1}, \epsilon_0$.

The experimental apparatus used to produce the harmonic emission and to measure the phase of the harmonic radiation has been described previously.[8] All measurements were made using a fundamental frequency of 2.7 GHz at liquid-helium temperature.

Our choice of DPPH is based on the fact that its electron-paramagnetic-resonance (EPR) spectrum has inhomogeneously broadened lines which are exchange narrowed at high concentrations. DPPH has the unpaired electron near two almost equivalent nitrogen nuclei so that in very diluted samples the electron Zeeman levels have a hyperfine structure with $I=2$ which consists of five lines. In liquid solutions, that is, in low-viscosity solvents, the hyperfine lines are well resolved and have intensity ratios 1:2:3:2:1 with an individual full width of 5 G and a separation of 8 G.[9] In solid solutions, that is, in high-viscosity solvents, the spectrum is poorly resolved. It consists of a strong central line and two pairs of weak satellite lines with a relative separation of approximately 22 G.[10] One of our samples of very diluted DPPH in solid polystyrene, No. 7, with a concentration less than 10^{18} spins/cm^3, shows at 4.2 °K an EPR spectrum consisting of a single broad line with a half-width ϵ_0 of 18 G. The satellite lines are clearly distinguishable in the wings of the line at 22 and 44 G from line center, although they are not well resolved. At this concentration, both the homogeneous dipolar and the exchange interactions are probably negligible. DPPH molecules in solid polystyrene are frozen in an ensemble of random orientations. The residual linewidth ϵ_0 is believed[10] to arise from the $I_z=0$ hyperfine line, which has a half-width of 3.3 G, inhomogeneously broadened by g anisotropy, by orientation-dependent parameters of the $\vec{\mathrm{I}}\cdot\vec{\mathrm{S}}$ interaction, and by the overlap of the hyperfine lines. With increasing concentration dipolar and exchange interactions come into play with different roles. The former tends to broaden the spectrum, while the latter mixes the hyperfine components and, at the same time, it narrows the total linewidth. Pure DPPH shows a single line with full width 3 G, which is less than that of a single hyperfine component in the absence of exchange interaction.

We have investigated the harmonic spectra of samples of DPPH Nos. 1–6 diluted in solid polystyrene with the nominal concentrations listed in Table I. The sensitivity of our apparatus was not high enough to investigate samples with concentrations less than that of sample No. 6. For sample No. 7 only the phase of the $\omega=\frac{1}{2}\omega_0$ line could be studied. The value of T_{20} deduced from these measurements agrees with that deduced from the EPR linewidth.

Figure 1(a) shows the harmonic signal as a function of the external magnetic field for sample No. 5 of DPPH. The average input power is approximately 20 mW which, with the parameters of our cavity, corresponds to a peak rf field H_{rf} of approximately 35 G in the cavity. Figure 1(b) shows the phase angle of the harmonic signal as a function of the external magnetic field. Equation (2) shows that the value of T_{2e} can be deduced from the data at the left-hand side of Fig. 1(b) by making use of the relation

$$T_{2e}=\frac{1}{\gamma(H_{02}-H_{01})}\,. \tag{4}$$

H_{02} and H_{01} are the values of the static field for which the phase angle is 45° and 135°. Similarly, the value of T_{20} can be deduced from the data at the right-hand side of Fig. 1(b) by making use of Eq. (3).

Figure 2 shows the transverse relaxation time T_{2e} as a function of the input-power level (or rf magnetic field) for our six samples of DPPH. Several observations are in order. Very concentrated samples show T_{2e} to be independent of the input-power level. For less concentrated samples, T_{2e} increases roughly linearly with the power. For more diluted samples of DPPH, T_{2e} is again linearly dependent on the input power but with a greater slope, and it is obvious that T_{2e} tends to T_{20} at very low power levels. Our experimental data are fitted by the formula

$$T_{2e}=T_{20}\,(1+H_{\mathrm{rf}}^2/H_{\mathrm{eff}}^2), \tag{5}$$

where H_{eff}^2 is a constant determined in the fitting. Our results are in good quantitative agreement with the theory on the stirring effect of strong rf fields as developed by Tomita[4] and recently by Strandberg.[7]

In order to compare their results with our data on DPPH, we must distinguish between concentrated DPPH and diluted DPPH. Concentrated DPPH is characterized by strong exchange nar-

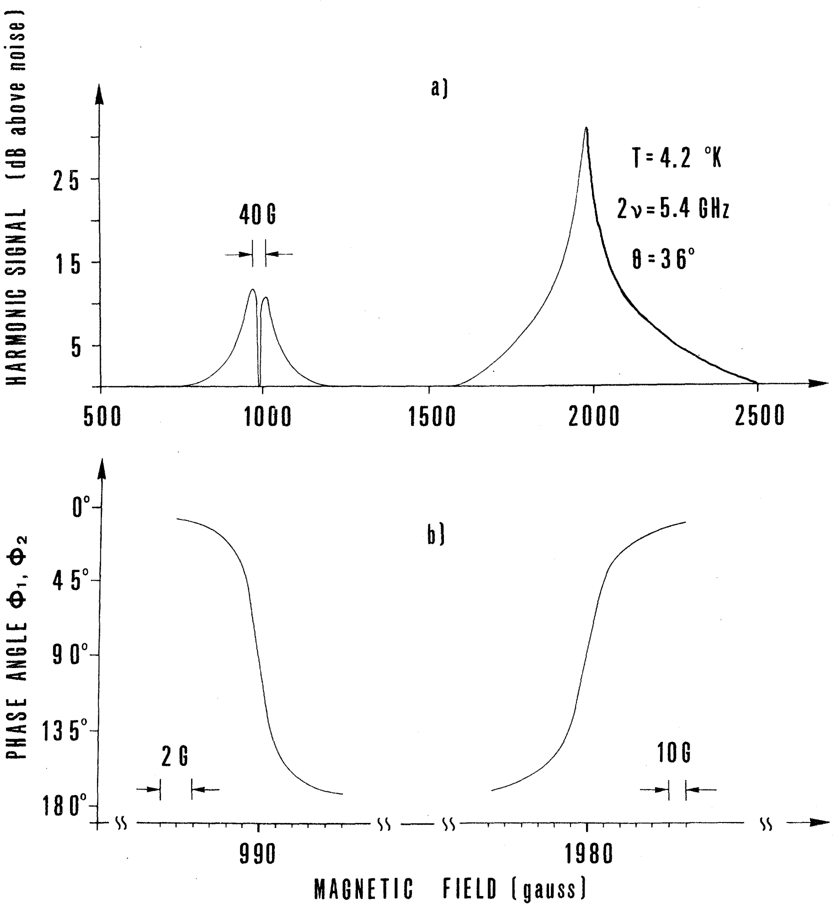

FIG. 1. (a) Harmonic signal as a function of the external magnetic field for sample No. 5 of diluted DPPH. (b) Phase variation of the harmonic signal as a function of the external field. Note the scale expansion. The average input power is 20 mW and corresponds to a peak rf field $H_{rf} \approx 35$ G in the cavity. Measurements are taken point by point.

rowing,[11] so that the five hyperfine components have lost all their individuality and are mixed in a single narrow line. The correlation time τ_c is defined as the reciprocal of the exchange frequency ω_E. In this case, τ_c fulfills condition A of Tomita,[4] $\tau_c \ll (\gamma^2 \langle \Delta H_D^2 \rangle)^{-1/2}$, where $\langle \Delta H_D^2 \rangle$ is the mean square dipolar width. The transverse relaxation time does not depend on the input-power level for $\gamma H_{rf} \ll 1/\tau_c$, while for $\gamma H_{rf} > 1/\tau_c$, Tomita[4] and Strandberg[7] predict the following rf dependence of T_{2e}:

$$T_{2e} = T_{20}\left(1 + \frac{\gamma^2 H_{rf}^2}{\omega_E^2}\right). \qquad (6)$$

For the samples with strong exchange narrowing, Nos. 1–4, H_{eff}^2 is thus a direct measure of ω_E^2/γ^2.

The exchange frequency could also be determined from the narrowing of the linewidth in these samples, if a satisfactory calculation of the dipolar width could be made. If one assumes a random orientation of the DPPH molecules and a uniform expansion of the DPPH lattice with dilution, the homogeneous dipolar spin-spin contribution to the mean square width is $\langle \Delta H_D^2 \rangle = (3.5 \times 10^{-20}\, C)^2$ G^2, where C is the concentration. This factor is $(0.7)^2$, $(2.1)^2$, $(7)^2$, $(11)^2$, $(18)^2$, and $(22)^2$ G^2 for sample Nos. 6–1, respectively. The inhomogeneous contribution to the mean square linewidth[10] comes from g-anisotropy and direction-dependent constants of the hy-

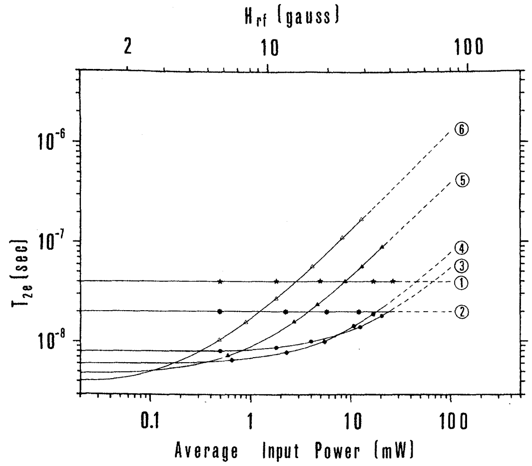

FIG. 2. T_{2e} as a function of the input rf power (or H_{rf}) for the samples of DPPH in solid solution of polystyrene listed in Table I. Sample numbers are indicated on the right-hand side.

perfine interaction and is probably independent of concentration. This contribution is very likely equal to the square of the half-width of the line observed in the very diluted solutions of DPPH in solid polystyrene, $\epsilon_0^2 = (18\ \mathrm{G})^2$.

Correlation-time-narrowing theory states that the exchange frequency is related to T_{20} and to the mean square linewidth as

$$\omega_E = \gamma^2 \langle \Delta H^2 \rangle T_{20} \quad \text{for} \quad \omega_E^2 \gg \gamma^2 \langle \Delta H^2 \rangle \tag{7}$$

and

$$\omega_E \approx \gamma \langle \Delta H^2 \rangle^{1/2} (\gamma \langle \Delta H^2 \rangle^{1/2} T_{20} - 1) \quad \text{for} \quad \omega_E^2 \approx \gamma^2 \langle \Delta H^2 \rangle . \tag{8}$$

Here

$$\langle \Delta H^2 \rangle = \langle \Delta H_D^2 \rangle + \epsilon_0^2 . \tag{9}$$

One can then estimate ω_E/γ to be 545, 205, 42, 20, 9.6, and 5.4 G for sample Nos. 1–6. These are in reasonable agreement with the values of H_{eff} determined from our experiments, which are reported in Table I.

The agreement must be fortuitous for sample Nos. 5 and 6. If these estimates are correct, the exchange field is the order of the dipolar and hyperfine fields. This situation is not covered by Eq. (6), which requires that the exchange field be large compared to the dipolar and hyperfine fields.

Tomita's prediction for case B is valid for systems with small exchange fields, $\omega_E^2 \ll \gamma^2 \langle \Delta H^2 \rangle$. For this situation, his prediction is that $H_{\mathrm{eff}}^2 = \langle \Delta H^2 \rangle^{1/2} \omega_E/\gamma$. If this expression is used to derive a value for ω_E from the measured H_{eff}^2, using for $\langle \Delta H^2 \rangle$ the total mean square homogeneous and inhomogeneous fields, the values deduced for ω_E/γ are 4.5 and 1.4 G. These exchange fields are too small to explain the linewidth at low power levels. If only the mean square field seen by the central line component is used to derive values for ω_E/γ, they are too large.

According to Strandberg[7] the mean square effective field, $\langle H_{\mathrm{eff}}^2 \rangle$ for a single spin packet, for any magnitude of exchange field is given by

$$\langle H_{\mathrm{eff}}^2 \rangle = \langle \Delta H_D^2 \rangle_I + \tfrac{1}{3} \langle \Delta H_D^2 \rangle_H + \frac{\omega_E^2}{\gamma^2} , \tag{10}$$

where $\langle \Delta H_D^2 \rangle_H$ is the homogeneous mean square dipolar field and $\langle \Delta H_D^2 \rangle_I$ is the inhomogeneous mean square dipolar field. If we equate this expression to the measured H_{eff}^2 for sample Nos. 5 and 6 of DPPH, we calculate ω_E/γ to be 8 and 3.8 G, respectively. These values are acceptable since they account for the linewidths of these diluted samples at low input-power levels. For sample No. 5, an inhomogeneous mean square width of $(18\ \mathrm{G})^2$, a dipolar mean square width of $(2.1\ \mathrm{G})^2$, and 8 G of exchange field predict a linewidth of 12 G for this sample at very low input-power level. This is in agreement with the value 12 G deduced from T_{20}. Sample No. 6, with an inhomogeneous mean square width of $(18\ \mathrm{G})^2$, a dipolar mean square width of $(0.7\ \mathrm{G})^2$, and 3.8 G of exchange field, is predicted to have a line 15 G wide. This also is in agreement with the value 14 G deduced from T_{20}.

In summary, it seems reasonable to say that we obtain quantitative understanding of the effect of strong rf fields on the transverse relaxation time of spin systems with inhomogeneous broadening over a wide variation of the effective exchange frequency.

Conversations with C. Cusumano are appreciated.

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