The role of the dipole-dipole reservoir in electron-nuclear double resonance at distant nuclei

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The mechanism of "long-range" electron-nuclear double resonance involving the dipole-dipole reservoir of the electron spins is investigated in the case of homogeneous and inhomogeneous broadening of the EPR. Spectral diffusion is taken into account qualitatively. The theoretical estimates are found to be in satisfactory agreement with experiment.

1. The "long-range" electron-nuclear double resonance (LRENDOR) effect consists in the change of the pattern of saturation of the EPR under the action of a radio-frequency field saturating the NMR of "distant" nuclei. By "distant" nuclei, we mean those whose hyperfine interaction with the paramagnetic centers is negligibly small[1,2]. LRENDOR was first observed in ruby with inhomogeneous broadening of the EPR of the Cr^{3+} ions[1,2]. On application of a radio-frequency field saturating the resonance of the Al^{27} nuclei, a small increase of the imaginary part χ'' and a sharper decrease of the real part χ' of the complex susceptibility of the Cr^{3+} ions occurred. This behavior of the electronic susceptibility was regarded as the result of the effect of depolarization of distant nuclei on the intensity of forbidden transitions; this makes an observable, though small, contribution to the electronic absorption. The theoretical estimates made on the basis of these ideas in the framework of a model of independent spin packets were found to be too low compared with the experimental data.

On the other hand, as has been remarked by many authors[3,4], the pattern of the magnetic-resonance saturation in solids, generally speaking, depends substantially on the presence of the dipole-dipole reservoir (DDR) in the spin system. In particular, in the saturation of a homogeneously broadened magnetic resonance with detuning, the absolute value of the DDR temperature falls sharply, and this leads to different behavior of χ' and χ'' from that in the traditional theory. In addition, theory and experiment point to the presence of strong relaxational coupling between the nuclear Zeeman subsystem (NZS) and the DDR of the impurity ions in nonmetallic diamagnetic crystals with a paramagnetic impurity[4]. It is natural to expect, therefore, that the presence of this coupling can give a new, and in a number of cases more effective, mechanism of the LRENDOR.

The purpose of the present article is to give a consistent theoretical treatment of LRENDOR in the case of homogeneous and inhomogeneous broadening of the EPR and under conditions of strong relaxational coupling between the NZS and the DDR.

2. For clarity, first we shall consider LRENDOR in the case of homogeneous broadening of the EPR[5]. In[5] it was noted that, in the presence of strong relaxational NZS-DDR coupling, saturation of the NMR increases the width of the saturated EPR line. We shall make use of the results of this paper and shall discuss the question of the influence of saturation of the NMR on χ'' and χ'.

The stationary equations for the inverse temperatures of the subsystems have the form[5]

$$\frac{\beta_z-\beta_L}{T_{sL}}+2W_s\left[\beta_z+\frac{\Omega-\omega_0}{\omega_0}\beta_d\right]=0, \tag{1}$$

$$\frac{\beta_d-\beta_L}{T_{dL}}+\frac{\beta_d-\beta_I}{T_{dI}}+2W_s\frac{\omega_0(\Omega-\omega_0)}{\omega_d^2}\left[\beta_z+\frac{\Omega-\omega_0}{\omega_0}\beta_d\right]=0, \tag{2}$$

$$\frac{\beta_I-\beta_d}{T_{Id}}+\frac{\beta_I-\beta_L}{T_{IL}}+2W_I\beta_I=0. \tag{3}$$

Here β_Z, β_d, β_I and β_L are the inverse temperatures of the electron Zeeman subsystem, the DDR, the NZS and the lattice; $W_S \equiv W_S(\Omega_I - \omega_0)$ and $W_I \equiv W_I(\Omega_I - \omega_I)$ are the usual probabilities of EPR and NMR due to transverse magnetic fields with frequencies Ω and Ω_I; T_{sL}, T_{dL}, T_{Id}, T_{dI} and T_{IL} are the relaxation times.

To calculate the susceptibility, we make use of the formulas[3]

$$\chi''=\frac{\pi}{2}\chi_0\omega_0\varphi(\Omega-\omega_0)\frac{1}{\beta_L}\left[\beta_z+\frac{\Omega-\omega_0}{\omega_0}\beta_d\right], \tag{4}$$

$$\chi'=\frac{1}{2}\chi_0\left\{\frac{\beta_d}{\beta_L}+\omega_0 J_1(\Omega-\omega_0)\frac{1}{\beta_L}\left[\beta_z+\frac{\Omega-\omega_0}{\omega_0}\beta_d\right]\right., \tag{5}$$

where $\chi_0 = \beta_L\gamma^2NS(S+1)/3$ is the static susceptibility, S is the value of the electron spin, N is the number of electron spins, $\gamma > 0$ is the absolute value of the electron gyromagnetic ratio, $\varphi(\Omega - \omega_0)$ is the shape of the unsaturated EPR line and

$$J_1(x)=\int_{-\infty}^{\infty}\frac{\varphi(y)}{y-x}dy.$$

Neglecting the direct nuclear relaxation (we put $1/T_{IL} = 0$) and assuming that the DDR is more strongly coupled with the NZS than with the lattice ($T_{dL}/T_{dI} \gg 1$), we obtain the following expressions for χ'' and χ':

$$\chi''=\frac{\pi}{2}\chi_0\omega_0\varphi(\Omega-\omega_0)\left\{\frac{1}{T_{Id}}+2W_I\frac{T_{dL}}{T_{dI}}+\frac{\Omega-\omega_0}{\omega_0}\left(\frac{1}{T_{Id}}+2W_I\right)\right\}\frac{1}{Z}, \tag{6}$$

$$\chi'=\frac{1}{2}\chi_0\left\{\left(\frac{1}{T_{Id}}+2W_I\right)\left[1+2W_sT_{sL}\left(1-\frac{\omega_0(\Omega-\omega_0)}{\alpha\omega_d^2}\right)\right]+\omega_0J_1(\Omega-\omega_0)\left[\frac{1}{T_{Id}}+2W_I\frac{T_{dL}}{T_{dI}}+\frac{\Omega-\omega_0}{\omega_0}\left(\frac{1}{T_{Id}}+2W_I\right)\right]\right\}\frac{1}{Z}, \tag{7}$$

where

$$Z=\frac{1}{T_{Id}}+2W_I\frac{T_{dL}}{T_{dI}}+2W_sT_{sL}\left\{\frac{1}{T_{Id}}+2W_I\frac{T_{dL}}{T_{dI}}+\left(\frac{1}{T_{Id}}+2W_I\right)\frac{(\Omega-\omega_0)^2}{\alpha\omega_d^2}\right\},$$

and $\alpha = T_{sL}/T_{dL}$. By saturating the EPR ($2W_sT_{sL} \gg 1$) and denoting the values of χ'' and χ' in the absence of the radio-frequency field ($\beta_I = \beta_d$) by χ''_{0s} and χ'_{0s}, and the values of χ'' and χ' in the presence of a radio-frequency field saturating the NMR ($\beta_I = \beta_d = 0$) by χ''_s and χ'_s, we obtain the following expressions for χ''_s and χ'_s and for the absolute changes $\Delta\chi'' = \chi''_s - \chi''_{0s}$ and $\Delta\chi' = \chi'_s - \chi'_{0s}$:

$$\Delta\chi''=\chi_s''\frac{(\Omega-\omega_0)^2}{\alpha\omega_d^2+(\Omega-\omega_0)^2},\quad \Delta\chi'=\chi_s''\frac{(\Omega-\omega_0)s\Delta}{\alpha\omega_d^2+(\Omega-\omega_0)^2};$$
$$\chi_s''=\frac{1}{2}\chi_0\frac{\omega_0}{s\Delta}\frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2}{T_{dL}T_{dI}^{-1}\alpha\omega_d^2+(\Omega-\omega_0)^2}, \tag{8}$$

$$\chi_s'=\chi_s''\frac{\omega_0-\Omega}{\Delta}\left(1+\frac{s\Delta^2}{T_{dL}T_{dI}^{-1}\alpha\omega_d^2}\right). \tag{9}$$

Here $s=\omega_1^2T_{sL}/\Delta$ is the usual saturation parameter, Δ is the homogeneous width, $\omega_1=\gamma H_1$, H_1 is the half-amplitude of the linearly polarized transverse magnetic field, and it is assumed that[1)]

$$\omega_0|\omega_0-\Omega|/\alpha\omega_d^2\gg 1.$$

It follows from (8) that $\Delta\chi''$ is an intrinsically positive quantity, i.e., on saturation of the NMR an increase of the EPR absorption occurs. As regards $\Delta\chi'$, $\Delta\chi'>0$ for $\Omega>\omega_0$ and $\Delta\chi'<0$ for $\Omega<\omega_0$, and the absolute value of the dispersion signal decreases.

The relative changes of the susceptibilities are found to be equal to

$$\frac{\Delta\chi''}{\chi_s''}=\frac{(\Omega-\omega_0)^2}{\alpha\omega_d^2+(\Omega-\omega_0)^2}, \tag{10}$$

$$\frac{\Delta\chi'}{\chi_s'}=-\frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2s\Delta^2}{[\alpha\omega_d^2+(\Omega-\omega_0)^2](T_{dL}T_{dI}^{-1}\alpha\omega_d^2+s\Delta^2)}. \tag{11}$$

In obtaining these results, we have used the relation

$$J_1(x)=-\pi\Delta^{-1}x\varphi(x),$$

which is valid in the case when the shape of the unsaturated EPR line is Lorentzian with width Δ, i.e.,

$$\varphi(x)=\frac{\Delta}{\pi}\frac{1}{x^2+\Delta^2}.$$

If the unsaturated absorption line is Gaussian:

$$\varphi(x)=\frac{1}{\sqrt{2\pi}\Delta}\exp\left(-\frac{x^2}{2\Delta^2}\right),$$

then

$$\frac{\Delta\chi'}{\chi_s'}=-\frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2s\Delta}{\alpha\omega_d^2+(\Omega-\omega_0)^2}\times\left[T_{dL}T_{dI}^{-1}\alpha\omega_d^2\frac{\sqrt{2}}{\Omega-\omega_0}\Psi\left(\frac{\Omega-\omega_0}{\sqrt{2}\Delta}\right)+s\Delta\right]^{-1}, \tag{12}$$

where

$$\Psi(y)=\int_0^y e^{x^2}dx,$$

whereas $\Delta\chi''/\chi_s''$ keeps its previous form. For small detunings, when $\Psi(y)\approx y$, (12) coincides with (11). Under conditions of not very great dilution, when homogeneous broadening is realized, $\Delta^2\sim\alpha\omega_d^2$, and the estimates

$$\Delta\chi''/\chi_s''\sim 1,\quad |\Delta\chi'/\chi_s'|\gg 1.$$

are valid.

Thus, the presence of strong relaxational coupling between the NZS and the DDR in the case of a homogeneously broadened EPR ensures a significant relative change in the electronic susceptibility on saturation of the NMR. As the estimates show, saturation of the NMR has a stronger effect on χ' than on χ'', and so the experimental study of the behavior of the dispersion signal is of interest.

3. We now consider LRENDOR under conditions of inhomogeneously broadened EPR. Two cases are possible, corresponding to rapid and limited spectral diffusion. If the diffusion time T_d over the whole inhomogeneous line is much longer than the spin-lattice relaxation time T_{sL}, the spectral diffusion is said to be limited, but if $T_d\lesssim T_{sL}$, the spectral diffusion is said to be rapid[6].

A. Limited spectral diffusion

As follows from[7], under these conditions the contribution of the DDR to the absorption is small; for the LRENDOR effect, however, this can be the determining contribution, as is shown below. In the given case, the inhomogeneous line can be represented as an aggregate of spin packets. In the limit of a continuous distribution of Zeeman frequencies ω' of the packets, the stationary equations for the inverse temperatures $\beta(\omega')$ of the packets and of the single DDR, with the term coupling the DDR with the NZS taken into account, are of the form[7]

$$\frac{\beta(\omega')-\beta_L}{T_{sL}}+2W_s(\Omega-\omega')\left[\beta(\omega')+\frac{\Omega-\omega'}{\omega'}\beta_d\right]=0, \tag{13}$$

$$\frac{\beta_d-\beta_L}{T_{dL}}+\frac{\beta_d-\beta_I}{T_{dI}}+\frac{2}{\omega_d^2}\int(\Omega-\omega')g(\omega'-\omega_0)\times W_s(\Omega-\omega')[\omega'\beta(\omega')+(\Omega-\omega')\beta_d]d\omega'=0. \tag{14}$$

Replacing ω_0 by ω in (4) and (5) and multiplying both parts by $g(\omega'-\omega_0)$, after integration over ω' we obtain the following expressions for the susceptibilities χ_{in}' and χ_{in}'' in the case of inhomogeneous broadening of the EPR:

$$\chi_{in}''=\frac{\pi}{2}\chi_0\frac{1}{\beta_L}\int\omega'g(\omega'-\omega_0)\varphi(\Omega-\omega')\left[\beta(\omega')+\frac{\Omega-\omega'}{\omega'}\beta_d\right]d\omega', \tag{15}$$

$$\chi_{in}'=\frac{\chi_0}{2}\left\{\frac{\beta_d}{\beta_L}+\frac{1}{\beta_L}\int\omega'g(\omega'-\omega_0)J_1(\Omega-\omega')\left[\beta(\omega')+\frac{\Omega-\omega'}{\omega'}\beta_d\right]d\omega'\right\}. \tag{16}$$

Calculating the absolute changes $\Delta\chi_{in}''$ and $\Delta\chi_{in}'$ in the first approximation in the small parameter $\tilde{\Delta}/\Delta^*$, where $\tilde{\Delta}=\Delta\sqrt{s+1}$ is the saturated width of the packet and Δ^* is the inhomogeneous width of the EPR, we obtain

$$\Delta\chi_{in}''=\frac{\pi}{2}\chi_0\frac{\tilde{\Delta}}{\sqrt{s+1}}\Omega g^2(\Omega-\omega_0)\Psi^2\left(\frac{\Omega-\omega_0}{\sqrt{2}\Delta^*}\right)\frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2}{T_{dL}T_{dI}^{-1}\alpha\omega_d^2+\tilde{\Delta}^2}, \tag{17}$$

$$\Delta\chi_{in}'=\frac{\pi^{3/2}}{2}\chi_0\tilde{\Delta}\Omega g^2(\Omega-\omega_0)\Psi\left(\frac{\Omega-\omega_0}{\sqrt{2}\Delta^*}\right)\frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2}{T_{dL}T_{dI}^{-1}\alpha\omega_d^2+\tilde{\Delta}^2}. \tag{18}$$

In this case, in the calculation of the integrals appearing in the expressions for $\chi_{in,s}''$ and $\chi_{in,s}'$ (the electronic susceptibilities under conditions of saturated NMR) we can confine ourselves to the zeroth approximation in this parameter, which gives

$$\chi_{in,s}''=\frac{\pi}{2}\chi_0\frac{\Omega g(\Omega-\omega_0)}{\sqrt{s+1}},\quad \chi_{in,s}'=-\frac{\sqrt{\pi}}{2}\chi_0\Omega g(\Omega-\omega_0)\Psi\left(\frac{\Omega-\omega_0}{\sqrt{2}\Delta^*}\right). \tag{19}$$

As a result, the relative changes of the susceptibilities are found to be equal to

$$\frac{\Delta\chi_{in}''}{\chi_{in,s}''}=\tilde{\Delta}g(\Omega-\omega_0)\Psi^2\left(\frac{\Omega-\omega_0}{\sqrt{2}\Delta^*}\right)\frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2}{T_{dL}T_{dI}^{-1}\alpha\omega_d^2+\tilde{\Delta}^2}, \tag{20}$$

$$\frac{\Delta\chi_{in}'}{\chi_{in,s}'}=-\pi\tilde{\Delta}g(\Omega-\omega_0)\frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2}{T_{dL}T_{dI}^{-1}\alpha\omega_d^2+\tilde{\Delta}^2}. \tag{21}$$

As we should expect, the quantities $\Delta\chi_{in}''/\chi_{in,s}''$ and $\Delta\chi_{in}'/\chi_{in,s}'$ are proportional to the small parameter $\tilde{\Delta}/\Delta^*$, which, according to the results of the paper[7], characterizes the contribution of the single DDR to the stationary saturation of the inhomogeneous line under conditions of limited spectral diffusion. We note that, in the given case, unlike the homogeneous situation, $\Delta\chi_{in}'/\Delta\chi_{in,s}'$ and $\Delta\chi_{in}''/\chi_{in,s}''$ can turn out to be of the same order at sufficiently large detunings[2)].

B. Rapid spectral diffusion

In this case, the electron spin system can be represented[8,9,4] as a combination of two subsystems: the Zeeman subsystem

$$\mathcal{H}_z=\omega_0\sum_i S_i^z$$

and the reservoir of the local fields (LFR)

$$\mathcal{H}_D=\mathcal{H}_d+\sum_i \omega_i S_i^z,$$

where $\mathcal{H}_d$ is the secular part of the dipole-dipole interaction of the electron spins. Setting up the equations for the inverse temperatures of these subsystems in a manner analogous to that for the case of homogeneous broadening[5], we can convince ourselves that Eqs. (1)–(3) remain valid with the following replacements:

$$\omega_d^2\to\omega_D^2,\quad \varphi(\Omega-\omega_0)\to\tilde{\varphi}(\Omega-\omega_0),\quad T_{dL}\to T_{DL},\quad T_{dI}\to T_{DI}.$$

Here $\omega_D^2=\omega_d^2+\Delta^{*2}$, and $\tilde{\varphi}(\Omega+\omega_0)$ is the Fourier transform of the correlator

$$\tilde{\varphi}(t)=\frac{\langle S^+\exp(i\mathcal{H}_D t)S^-\exp(-i\mathcal{H}_D t)\rangle}{\langle S^+S^-\rangle}$$

(in the case $M_2\gg\Delta^{*2}$, where M_2 is the second moment due to the interaction $\mathcal{H}_d$, $\tilde{\varphi}(\omega)$ coincides with $\varphi(\omega)$; in the opposite case, $\tilde{\varphi}(\omega)$ coincides with the inhomogeneous lineshape $g(\omega)$); $1/T_{DL}$ and $1/T_{DI}$ are the rates of relaxation of the LFR to the lattice and to the NZS, and are given by the following expressions

$$\frac{1}{T_{DL}}=\frac{1}{\omega_d^2+\Delta^{*2}}\left(\frac{\Delta^{*2}}{T_{sL}}+\frac{\omega_d^2}{T_{dL}}\right),$$

$$\frac{1}{T_{DI}}=\frac{\mathrm{Sp}\,\mathcal{H}_I^2}{\mathrm{Sp}\,\mathcal{H}_D^2}\frac{\pi S(S+1)V^2}{3}\tilde{f}_z(\omega_I),$$

$$V^2\equiv\frac{1}{N_I}\sum_{in}|\mathcal{V}^{+z}(in)|^2;$$

$\mathcal{V}^{+z}(\mathrm{in})$ is the dipole-dipole interaction constant of the nuclei and electrons, secular with respect to the electron spins, and $\tilde{f}_z(\omega_I)$ is the Fourier transform of the correlator[9]

$$f_z(t)=\frac{\langle S_i^z\exp(i\mathcal{H}_D t)S_i^z\exp(-i\mathcal{H}_D t)\rangle}{\langle(S_i^z)^2\rangle}.$$

Calculations analogous to those given in Sec. 2 show that, for $T_{DL}/T_{DI}\gg 1$ (when the LRENDOR mechanism considered is valid), the quantities corresponding to (8) and (9) have the form

$$\begin{aligned}\Delta\chi''&=\chi_s''\frac{(\Omega-\omega_0)^2}{\alpha\omega_d^2+\Delta^{*2}+(\Omega-\omega_0)^2},\\ \Delta\chi'&=\chi_s''\omega_1^2T_{sL}\frac{\Omega-\omega_0}{\alpha\omega_d^2+\Delta^{*2}+(\Omega-\omega_0)^2};\end{aligned}\qquad(22)$$

$$\begin{aligned}\chi_s''&=\frac{1}{2}\chi_0\frac{\omega_0}{\omega_1^2T_{sL}}\frac{\Delta_s^2}{\Delta_s^2+(\Omega-\omega_0)^2},\\ \chi_s'&=\chi_s''\left\{\frac{\mathcal{J}_1(\Omega-\omega_0)}{\pi\tilde{\varphi}(\Omega-\omega_0)}-\frac{\omega_1^2T_{sL}(\Omega-\omega_0)}{\Delta_s^2}\right\},\end{aligned}\qquad(23)$$

where

$$\Delta_s=[T_{DL}(\alpha\omega_d^2+\Delta^{*2})/T_{DI}]^{1/2}.$$

As we should expect, saturation of the NMR under conditions of rapid spectral diffusion (RSD) and strong relaxational NZS-LFR coupling increases the width of the saturated EPR absorption line by a factor of $(T_{DL}/T_{DI})^{1/2}$ and makes it equal to Δ_S.

For the relative changes of the susceptibilities, we obtain

$$\begin{aligned}\left(\frac{\Delta\chi''}{\chi_s''}\right)^{\mathrm{RSD}}&=\frac{(\Omega-\omega_0)^2}{\alpha\omega_d^2+\Delta^{*2}+(\Omega-\omega_0)^2},\\ \left(\frac{\Delta\chi'}{\chi_s'}\right)^{\mathrm{RSD}}&=-\frac{\Delta_s^2\Delta_1^2}{(\Delta_1^2+\Delta_s^2)[\alpha\omega_d^2+\Delta^{*2}+(\Omega-\omega_0)^2]},\end{aligned}\qquad(24)$$

where we have introduced the notation

$$\Delta_1^2=\frac{\pi\omega_1^2T_{sL}(\omega_0-\Omega)\tilde{\varphi}(\Omega-\omega_0)}{\mathcal{J}_1(\Omega-\omega_0)}.$$

As for homogeneous broadening of the EPR also, $(\Delta\chi''/\chi_S'')^{\mathrm{RSD}}\sim 1$ (for $(\Omega-\omega_0)^2\sim\Delta^{*2}\gg\alpha\omega_d^2$) and, in contrast to the case of limited spectral diffusion, on saturation of the EPR does not depend on the amplitude of the oscillating field. In the limiting case $\Delta^{*2}\gg M_2$, we have

$$\tilde{\varphi}(x)\approx g(x),\quad \mathcal{J}_1(x)=-2\sqrt{\pi}\,g(x)\Psi(x/\sqrt{2}\,\Delta^*)$$

and

$$\begin{aligned}\left(\frac{\Delta\chi'}{\chi_s'}\right)^{\mathrm{RSD}}&=-\frac{\Delta_s^2\sqrt{\pi}\,\omega_1T_{sL}(\Omega-\omega_0)}{\alpha\omega_d^2+\Delta^{*2}+(\Omega-\omega_0)^2}\\ &\times\left[2\Delta_s^2\Psi\left(\frac{\Omega-\omega_0}{\sqrt{2}\,\Delta^*}\right)+\sqrt{\pi}\,\omega_1^2T_{sL}(\Omega-\omega_0)\right]^{-1}.\end{aligned}\qquad(25)$$

It is easy to see that $|\Delta\chi'/\chi_S'|^{\mathrm{RSD}}\gg 1$ for any relation between Δ_S and Δ_1. If we take $\alpha=2$ and $\Delta^{*2}=5A_Z^2/4$ (A_Z is the hyperfine interaction constant), then the expression for $(\Delta\chi''/\chi_S'')^{\mathrm{RSD}}$ coincides with the result of Wencebah[10], who studied LRENDOR in copper Tutton salts with the assumption that the reason for the inhomogeneous broadening is the hyperfine interaction of the electrons with the nearest nuclei.

4. It is of interest to estimate, at least roughly, the order of magnitude of the LRENDOR effect and to compare it with the results of the work of Lambe et al.[2], in which the experimental data obtained were interpreted on the basis of a model of independent spin packets. On the other hand, a number of experiments[4] show that, at such substantial concentrations of chromium (0.1%) in ruby, rapid spectral diffusion is realized. However, since the quantity $\Delta\chi''/\chi_S''$ should not depend in this case on the amplitude of the oscillating field, and the measurements performed in[2] display a dependence on the saturation parameter s, we may concur with the authors of[2] that, for some reason, limited spectral diffusion is occurring in the sample under consideration, and use the formulas (20) and (21) for the estimates.

It makes sense to consider two possibilities: weak ($T_{dL}T_{dI}^{-1}\times\alpha\omega_d^2\gg\tilde{\Delta}^2$) and strong ($T_{dL}T_{dI}^{-1}\alpha\omega_d^2\ll\tilde{\Delta}^2$) saturation. In the first case, according to (20) and (21), the LRENDOR effect increases like $\sqrt{s}$ with increasing s. Using the numerical data of[2]: s = 20, Δ = 0.2 MHz, Δ^* = 20 MHz, and assuming the detuning to be sufficiently large so that $\Psi\sim 1$, we obtain

$$\Delta\chi_{in}''/\chi_{in,s}''\approx 0.01,\quad \Delta\chi_{in}'/\chi_{in,s}'\approx -0.03,$$

which agrees, in order of magnitude, with the experimental results of[2]. In the case of strong saturation, the relative changes (20) and (21) of the susceptibilities decrease like $1/\sqrt{s}$ with increasing s. On the other hand, as s increases the effect of the LRENDOR proceeding via forbidden transitions increases, inasmuch as the forbidden transitions usually remain unsaturated on saturation of an allowed resonance. Thus, for strong saturation, forbidden transitions should turn out to be responsible for the LRENDOR. This circumstance explains the better agreement of the theoretical estimates of[2] with experiment in the case s = 200. It should be noted

that our estimates, like the estimates of[2], are highly approximate, since spectral diffusion is not taken into account.

5. We now consider the influence of spectral diffusion on LRENDOR involving the DDR. We shall make use of the results of[7], in which it was shown that, for $\tilde{\Delta} \ll 1/k$, where $1/k$ is the "spectral diffusion length," the width $\tilde{\Delta}$ of the "burnt-out" hole is replaced by $1/k$, and for the quantity β_d/β_L the estimate

$$\frac{\beta_d}{\beta_L} \sim \frac{k\omega_0}{(k\Delta)^2 k\Delta^* + 1}. \tag{26}$$

is valid. Comparing the relative changes of the susceptibilities with and without allowance for spectral diffusion, we obtain

$$\left(\frac{\Delta\chi_{in}''}{\chi_{in,s}''}\right)^{SD} \Big/ \frac{\Delta\chi''}{\chi_{in,s}''} = \left(\frac{\Delta\chi_{in}'}{\chi_{in,s}'}\right)^{SD} \Big/ \frac{\Delta\chi_{in}'}{\chi_{in,s}'} = \frac{1}{k\tilde{\Delta}} \frac{T_{dL}T_{dI}^{-1}\alpha\omega_d^2 + (1/k)^2}{T_{dL}T_{dI}^{-1}\alpha\omega_d^2 + \tilde{\Delta}^2} \left[(k\Delta)^2 + \frac{1}{k\Delta^*}\right]^{-1}, \tag{27}$$

which is greater than unity when the conditions $\tilde{\Delta} \ll 1/k \ll \Delta^*$ are fulfilled.

Thus, allowance for the spectral diffusion leads to amplification of the LRENDOR effect. This occurs principally because of the increase of the relative contribution of the DDR to the stationary absorption; in the case considered, this relative contribution is proportional to the parameter $1/k\Delta^* \gg \tilde{\Delta}/\Delta^*$.

[1)]It can be seen from (9) that saturation of the NMR in the presence of strong relaxational NZS-DDR coupling increases the width of the saturated EPR line by a factor of $\sqrt{T_{DL}/T_{dI}}$ and makes it equal to $\sqrt{T_{DL}/T_{dI}}\sqrt{\alpha}\omega_d$ [5].

[2)]Of course, these detunings should not be so large that the condition for saturation of the EPR is violated.

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