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Nuclear relaxation and nuclear-nuclear double resonance in systems with inhomogeneous EPR broadening

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Nuclear relaxation and nuclear-nuclear double resonance are considered in an electron-nuclear spin system in which the degree of inhomogeneity of the EPR broadening can be varied. The case closest to the qualitative experimental results [J.van Houten, W. Th. Wenckebach, and J. J. Poulis, Physica **92B**, 201, 210 (1977) and **100B**, 35 (1980); J. van Houten, Dissertation, Leiden (1979)] is singled out from among several limiting cases. Good quantitative agreement between theory and experiment is found.

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1. INTRODUCTION

A number of investigations have been made[1-3] of the relaxation of the protons of the water of hydration in copper-Tutton's salt containing a certain amount of D_{2O}:

$$(Cu_f, Zn_{1-f})Cs_2(SO_4)_2 \cdot 6(H_y, D_{1-y})_2O,$$

where $f \approx 0.5\%$, and y ranges from 6 to 100%, as well as nuclear-nuclear double resonance with participation of protons, deuterons, and cesium nuclei.

The copper Tutton's salt crystal contain Cu^{2+} ions with electron ($S = \frac{1}{2}$) and nuclear ($I^{Cu} = 3/2$) spins. In addition, there are the spins of the protons ($I_p = \frac{1}{2}$), of the deuterons ($I_d = 3/2$), and of the cesium nuclei $I_{Cs} = 7/2$). Since the Cu^{2+} ions occupy two magnetically nonequivalent positions in the lattice, the EPR spectrum of Cu^{2+} consists of two sets of lines that coincide if the constant magnetic field is directed along the crystal axis K_1 or K_3. Each of the two sets consists of four lines due to the hyperfine interaction of the electron and nuclear spins of the Cu^{2+} ions. The EPR lines are inhomogeneously broadened by the hyperfine interaction of Cu^{2+} with ligand protons and deuterons.

The most essential feature of the experimental results is the dependence of the proton-relaxation time T_{1p} and of the nuclear-nuclear double resonance coefficient Q on the orientation of the constant magnetic field relative to the crystal axes K_1 and K_3. This phenomenon was explained[1-3] on the basis of the assumption that in the bottleneck in the proton relaxation to the lattice are two thermal contacts: 1) the contact of the proton Zeeman subsystem with the electron dipole-dipole pool (EDDP); 2) the contact of the proton Zeeman subsystem with the "difference" Zeeman energies of the electron spins, which is effected with the aid of a three-spin process with participation of two electron spins and one nuclear spin [first described by Kessenikh and Manenkov[4] and usually called electron-nuclear cross relaxation (CR)]. It was assumed that as a result of the effective electron cross relaxation, the EDDP and the difference Zeeman electron energies combine into a single "non-Zeeman" pool [usually called the local-field pool (LFP)[5]].

This model, however, did not describe the experimentally observed[1-3] overall decrease of T_{1p} in the angle region near the axes K_1 and K_3, and did not explain the presence of a maximum in the angular dependence of the nuclear-nuclear double resonance coefficient Q. To resolve the latter contradiction it was proposed[3] that the EDDP and the difference Zeeman energies are not in equilibrium with each other in the nuclear-nuclear double resonance process.

The purpose of the present paper is a study of the nuclear relaxation of nuclear-nuclear double resonance in spin systems in which it is possible to vary the de-

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gree of inhomogeneity of the broadening, and to explain the experimental results[1-3] on the basis of a unified approach developed for the description of electron-nuclear spin systems of solids under conditions of inhomogeneous EPR broadening.[6]

We note beforehand that the equations of the preceding paper[6] do not include a term corresponding to direct relaxation of the nuclei to the EDDP.[7] The direct relaxation of nuclear spins to the EDDP in the case of inhomogeneous EPR, under conditions of rapid spectral diffusion, has already been considered in a number of studies,[8,9] but since it is possible for spectral diffusion to be ineffective in experiment, it makes sense to consider this question in greater detail.

2. DIRECT RELAXATION OF NUCLEI TO THE EDDP

The rate of direct relaxation of nuclei to an EDDP is given by

$$T_{1D}^{-1}=\frac{\pi}{4N_I}\sum_{inm}|V^{+z}(im)|^2 f_z(\omega_I), \tag{1}$$

where $f_z(\omega)$ is the Fourier transform of the correlation function $\langle S_{ni}^z S_{mi}^z(t)\rangle/\langle(S_{ni}^z)^2\rangle$, where $\langle A\rangle=\mathrm{Sp}A/\mathrm{Sp}1$, and $V^{+z}(im)$ is the electron-nuclear interaction constant.

In the model of independent spin packets

$$\langle S_{ni}^z S_{ni}^z(t)\rangle=\langle S_{ni}^z\exp(iH_d't)S_{ni}^z\exp(-iH_d't)\rangle;$$
$$H_d'=\sum_{nn'ij}A_{ij}S_{ni}^z S_{n'j}^z+\sum_{nij}B_{ij}S_{ni}^+S_{nj}^-, \tag{2}$$

where H_d' is the secular part, relative to the Zeeman energy of an individual packet, of the *dd* interaction of the nuclear spins.

In the case of rapid spectral diffusion

$$\langle S_{ni}^z S_{ni}^z(t)\rangle=\langle S_{ni}^z\exp[i(H_{dd}+H_\Delta)t]S_{ni}^z\exp[-i(H_{dd}+H_\Delta)t]\rangle;$$
$$H_{dd}=H_d'+\sum_{n\neq n'ij}B_{ij}S_{ni}^+S_{n'j}^-, \tag{3}$$

where H_{dd} is the secular part, relative to $\sum_n\sum_{i=1}^{N_n}S_{ni}^z$, of the dipole (*dd*) interaction, and

$$H_\Delta=\sum_i\Delta_i S_i^z,\quad \Delta_i=\omega_i-\omega_0$$

(ω_0 is the center of gravity of the EPR spectrum).

We consider first the correlation function (3) and show that if the inhomogeneous broadening prevails over the homogeneous, then this function reduces to (2). In fact, we represent $S_{ni}^z(t)$ in the form

$$S_{ni}^z(t)=\exp(iH_\Delta t)\tilde{S}_{ni}^z(t)\exp(-iH_\Delta t),$$

where $\tilde{S}_{ni}^z(t)$ satisfies the equation

$$\frac{d\tilde{S}_{ni}^z(t)}{dt}=\frac{1}{i}[\tilde{S}_{ni}^z(t),H_{dd}(t)],$$
$$H_{dd}(t)=\exp(-iH_\Delta t)H_{dd}\exp(iH_\Delta t). \tag{4}$$

It is obvious that

$$\langle S_{ni}^z\exp[i(H_{dd}+H_\Delta)t]S_{ni}^z\exp[-i(H_{dd}+H_\Delta)t]\rangle=\langle S_{ni}^z\tilde{S}_{ni}^z(t)\rangle.$$

We substitute $H_{dd}(t)$ in (4) in explicit form

$$H_{dd}(t)=H_d'+\sum_{ijn\neq n'}B_{ij}\exp[i(\Delta_i-\Delta_j)t]S_{ni}^+S_{n'j}^-$$

and, recognizing that the inhomogeneous broadening exceeds the homogeneous (i.e., $|B_{ij}/(\Delta_i-\Delta_j)|$ can be regarded as a small parameter), we apply to (4) the Bogolyubov-Krylov averaging method.[10] The averaged equation takes the form

$$\frac{d\tilde{S}_{ni}^z(t)}{dt}=\frac{1}{i}[\tilde{S}_{ni}^z(t),\bar{H}],$$

where the average Hamiltonian is given in first approximation[11] by $\bar{H}=H_d'$ (the time-dependent term is made to vanish by the averaging).

The sought correlator (3) thus reduces to (2), and both in the case of fast spectral diffusion and in the model of independent spin packets, to calculate T_{1D} it is necessary to calculate the correlation function (2). We use for this purpose the method of moments. For the ratio $M_4/3M_2^2$ we obtain

$$\frac{M_4}{3M_2^2}=(g_nf)^{-1}\{0.8-0.1(S^2+S)^{-1}\}\sum_{i'}{}'B_{ii'}^4\Big/\Big\{\sum_{i'}{}'B_{ii'}^2\Big\}^2$$
$$+\frac{1}{3}[2.5+4g_n^{-1}]\Big[1-\sum_{i'}{}'B_{ii'}^4\Big/\Big\{\sum_{i'}{}'B_{ii'}^2\Big\}^2\Big]$$
$$-\frac{2}{3}[1+2g_n^{-1}]\sum_{i'j'}{}'B_{ii'}^2B_{i'j'}B_{ij'}\Big/\Big\{\sum_{i'}{}'B_{ii'}^2\Big\}^3$$
$$+2\sum_{i'ij'}{}'B_{ii'}B_{ij}B_{i'j'}^2\Big/\Big\{\sum_{i'}{}'B_{ii'}^2\Big\}^3,$$

where f is the dilution. Under the conditions of the experiments of Refs. 1–3, the fraction of the Zn sites occupied by Cu is $f\approx 0.5\%$. The summation is over all the zinc sites, and the prime on the summation sign means that quantities B with equal indices are excluded from the summation; g_n is the fraction of the spins of the n-th packet.

Just as in the case of homogeneous broadening, at sufficiently low concentrations of the electron spins ($f<1\%$) the first term predominates and $M_4/3M_2^2\gg 1$, so that $f_z(\omega)$ is Lorentzian, and the corresponding correlation time τ_{sn} is given by

$$(\tau_{sn})^{-1}=\frac{\pi}{6}M_2^{1/2}\left(\frac{3M_2^2}{M_4}\right)^{1/2}\approx\pi\left\{\frac{2S(S+1)}{3[0.8-0.1(S^2+S)^{-1}]}\right\}^{1/2}$$
$$\times\Big\{\sum_{i'}{}'B_{ii'}^2\Big\}^{1/2}\Big\{\sum_{i'}{}'B_{ii'}^4\Big\}^{-1/2}g_nJ\propto\frac{\Delta}{\Delta^*}J, \tag{5}$$

where Δ is the width of the spin packet, and Δ^* is the inhomogeneous EPR width, i.e., the correlation time is proportional to the degree of inhomogeneity of the EPR broadening. Such a dependence of the correlation time on the inhomogeneous width follows from the results of the earlier studies[8,9] for the particular case of an anamalously large inhomogeneous width. Under real experimental conditions no such case takes place, from which it follows that the τ_{sn} obtained from Refs. 8 does not depend[1)] on Δ^*. The generally incorrect result of Refs. 8 and 9 follows from the fact that in the calculation of the second moment account was taken also of nonsecular terms of the type

$$\sum_{nn'ij}B_{ij}S_{ni}^+S_{n'j}^-,$$

which increased the second moment substantially. This is the cause of the previously obtained[8,9] incorrect requirements that account must be taken of the inhomogeneous broadening, even though the final result, as noted above, remains qualitatively the same for anomalously large Δ^*.

When account is taken of (5), the rate of indirect relaxation (1) depends on the electron density and on the degree of inhomogeneity of the EPR broadening in the following manner:

$$T_{1D}^{-1} \propto \begin{cases} f^2 \sum_n g_n^2 \sim \dfrac{\Delta}{\Delta^*} f^2, & \text{if} \quad \omega_I^2 \tau_{sn}^2 \gg 1 \\ \sum_n 1 \sim \dfrac{\Delta^*}{\Delta}, & \text{if} \quad \omega_I^2 \tau_{sn}^2 \ll 1 \end{cases} \tag{6}$$

Under the experimental conditions,[1-3] $\omega_I^2 \tau_{sn}^2 \gg 1$ so that, as seen from (6), in contrast to the suggestions of the authors of Refs. 1 to 3, the direct relaxation depends significantly on the degree of inhomogeneity, i.e., on the angle Φ between the constant magnetic field and the axis K_1 or K_3.

3. THE EQUATIONS

We introduce the notation

$$\xi_{nn'} = \frac{\omega_n \beta_n - \omega_{n'} \beta_{n'}}{\Delta_{nn'}}, \quad C_{nn'} = \tilde{N} g_n g_{n'} \Delta_{nn'}^2,$$

where $\Delta_{nn'} = \omega_n - \omega_{n'}$; β_n is the reciprocal temperature of the electron spin packet of frequency[2)] ω_n, $\tilde{N} = NS(S+1)/3$, and N is the number of the paramagnetic centers. The $\xi_{nn'}$ are linear transforms of the thermodynamic parameters, and can therefore also be regarded as thermodynamic parameters (these parameters were introduced in Atsarkin's book[12]).

Taking the remarks made above into account, we rewrite the equations of the preceding paper[6] in the form

$$\begin{aligned} \frac{d}{dt}\left(\sum_{n'<n} C_{nn'}\xi_{nn'}\right) &= -\frac{1}{T_{SL}}\left(\sum_{n'<n} C_{nn'}\xi_{nn'} - C_\Delta \beta_L\right) \\ &\quad - \sum_{n'<n} \tilde{N} g_n g_{n'} \Delta_{nn'}^2 W_{nn'}^{CR} (\xi_{nn'} - \beta_D) \\ &\quad + \sum_{k;n'<n} g_n g_{n'} \tilde{N}_k \omega_k \Delta_{nn'} W_{nn'k}^{CR} X; \\ C_D \frac{d\beta_D}{dt} &= -\sum_k C_D \frac{\beta_D - \beta_k}{T_{Dk}} - C_D \frac{\beta_D - \beta_L}{T_{DL}} \\ &\quad + \sum_{n'<n} \tilde{N} g_n g_{n'} \Delta_{nn'}^2 W_{nn'}^{CR} (\xi_{nn'} - \beta_D) \\ &\quad - \sum_{k;n'<n} g_n g_{n'} \tilde{N}_k \omega_k (\Delta_{nn'} - \omega_k) W_{nn'k}^{CR} X; \\ \frac{d\beta_k}{dt} &= -\frac{\beta_k - \beta_D}{T_{kD}} - 2W_k \beta_k - \sum_{n'<n} g_n g_{n'} W_{nn'k}^{CR} X; \\ X &= \beta_k - \beta_D - \frac{\Delta_{nn'}}{\omega_k}(\xi_{nn'} - \beta_D), \end{aligned} \tag{7}$$

where β_k ($k = p, d, \mathrm{Cs}$) are the reciprocal temperatures of the Zeeman subsystems of the protons, deuterons, and of the cesium nuclei; $\tilde{N}_k = N_k I_k (I_k + 1)/3$; $C_D = \tilde{N}\omega_D^2$ is the heat capacity of a unified EDDP having a reciprocal temperature β_D; T_{kD}^{-1} is the rate of direct relaxation of the k-th nuclei to the EDDP; $T_{Dk}^{-1} = C_k T_{kD}^{-1}/C_D$; $C_k = \tilde{N}_k \omega_k^2$ is the heat capacity of the k-th nuclei,

$$C_\Delta = \sum_{n'<n} C_{nn'} = \tilde{N}(5A^2 + x^2)/4$$

is the total heat capacity corresponding to the difference Zeeman electron energies, A is the hyperfine interaction constant, and x is the distance between the centers of the different sets,

$$W_{nn'k}^{CR} \equiv W_{nn'k}^{CR}(\Delta_{nn'} - \omega_k)$$

is the probability of the electron-hole CR,

$$W_{nn'}^{CR} \equiv W_{nn'}^{CR}(\Delta_{nn'})$$

is the probability of the electron CR, W_k is the probability of a transition under the influence of the RF field, T_{SL}^{-1} and T_{DL}^{-1} are the rates of the spin-lattice relaxation of the electrons of the Zeeman and dipole subsystems, and β_L is the reciprocal temperature of the lattice.

4. PROTON RELAXATION

We shall discuss the question of proton relaxation by starting from Eqs. (7) and assuming that $T_{1\rho}$ is determined by measuring the restoration of the proton-resonance signal after saturation by a short strong RF field, as was the case in the experiments of Refs. 1-3. In view of the complexity of Eqs. (7), we consider $T_{1\rho}$ for several limiting cases.

1. *Strong I–D coupling.* Assume that in the course of the proton relaxation the strong direct relaxation of the nuclei from the EDDP establishes rapidly a single temperature $\beta_k^{-1} = \beta_D^{-1} = \beta^{-1}$. Then the experimentally measured time $T_{1\rho}$ is determined by the time dependences of β and $\xi_{nn'}$, described by the equations

$$\begin{aligned} \frac{d}{dt}\left(\sum_k C_k + C_D\right)\beta &= -\sum_{n'<n} (\beta - \xi_{nn'}) L_{\xi_{nn'}}^{\beta} - \frac{C_D}{T_{DL}}(\beta - \beta_L), \\ \frac{d}{dt}\left(\sum_{n'<n} C_{nn'}\xi_{nn'}\right) &= -\sum_{n'<n} (\xi_{nn'} - \beta) L_{\xi_{nn'}}^{\beta} - \frac{1}{T_{SL}}\left(\sum_{n'<n} C_{nn'}\xi_{nn'} - C_\Delta \beta_L\right), \end{aligned} \tag{8}$$

$$L_{\xi_{nn'}}^{\beta} = g_n g_{n'}\left\{\tilde{N}\Delta_{nn'}^2 W_{nn'}^{CR} + \sum_k \tilde{N}_k \Delta_{nn'}^2 W_{nn'k}^{CR}\right\}. \tag{9}$$

a) If the two- and three-spin CR is neglected, the proton relaxation becomes similar to the case of homogeneous broadening of an EPR line. Once equilibrium is established between I and D, relaxation to the lattice takes place at a rate

$$C_D \Big/ \left(C_D + \sum_k C_k\right) T_{DL}. \tag{10}$$

Since C_D is practically independent of the degree of inhomogeneity of the broadening, the final relaxation of the protons is independent of the angle Φ under the experimental conditions of Refs. 1 to 3.

This results in an interesting situation. The point is that, as shown in Sec. 2, direct relaxation of the nuclei to the EDDP depends strongly on the degree of inhomogeneity of the EPR spectrum. Therefore at certain angles the bottleneck can be the contact of the lattice with the (nuclei + EDDP) system, while for other angles, corresponding to a larger inhomogeneity of the EPR

spectrum, the bottleneck may turn out to be the direct I–D relaxation. Inasmuch as in experiment[1-3] the proton relaxation depends on the angle [a condition not satisfied by Eq. (10)], the EDDP is more strongly connected with the difference energies than with the lattice:

$$\sum_{n'<n} g_n g_{n'} W_{nn'}^{CR} \Delta_{nn'}^2 / \omega_D^2 \gg T_{DL}^{-1}.$$

We must therefore take into account the electronic CR.

b) Assume now that the first to be established is the equilibrium within the entire spin system, followed by relaxation to the lattice, so that in the course of relaxation β and $\xi_{nn'}$ first relax to a common value

$$C_\Delta \beta_L \Big/ \Big(\sum_k C_k + C_\Delta + C_D\Big),$$

which differs greatly from β_L if $\sum_k C_k \gg C_\Delta$, and finally the system goes into equilibrium with the lattice during a second relaxation stage, at a rate

$$C_\Delta \Big/ \Big(\sum_k C_k + C_\Delta + C_D\Big) T_{SL}. \tag{11}$$

The quantity C_Δ decreases smoothly with decreasing angle $|\Phi|$ and reaches a minimum at $\Phi = 0$; the relaxation (11) behaves similarly. This is precisely the explanation offered by Atsarkin, Mefed, and Rodak[13] for the experimentally observed decrease of the rate of nuclear relaxation with decreasing $|\Phi|$, inasmuch as under the conditions of their experiment the nuclear subsystem had a large heat capacity.

c) Assume now that the $\xi_{nn'}$ do not break away from the lattice. This is the situation at $\sum_k C_k \lesssim C_\Delta$ and at not too low temperatures, when the rate of the electronic spin-lattice relaxation is high enough. Equations (8) then describe the relaxation of the combined (nuclei + EDDP) system to the lattice, and the measured relaxation rate $T_{1\rho}^{-1}$ is determined by the two- and three-spin CR:

$$T_{1\rho}^{-1} = \Big\{\sum_k C_k\Big\}^{-1} \sum_{n'<n} g_n g_{n'} \Delta_{nn'}^2 \Big(N W_{nn'}^{CR} + \sum_k N_k W_{nn'k}^{CR}\Big). \tag{12}$$

At $W_{nn'k}^{CR} = 0$ expression (12) goes over into the corresponding expression of Atsarkin, Mefed, and Rodak,[13] in which the electron-nuclear CR was neglected, since it was not at resonance under their experimental conditions.

It is necessary to take into account in (12) the fact that owing to the relation $\omega_k \ll A$ the electron-nuclear CR can take place only between nearest EPR lines from various sets; we designate these distances by Δ_m. Then (12) describes the minima in the angular dependence of $T_{1\rho}(\Phi)$ at $\Delta_m = \omega_p$, where $W_{nn'p}^{CR}$ is maximal. The minima in the angular dependence of $T_{1\rho}(\Phi)$ at $\Delta_m = \omega_d$ and $\Delta_m = \omega_{Cs}$, which were predicted by (12), should not be observed, since the corresponding angles Φ agree, within the limits of experimental error, with the angles Φ_r, where $\Delta_m = 0$, and the number of crossings of the EPR lines is equal to r. The angle structure of $T_{1\rho}(\Phi)$ with minima at $\Delta_m = \omega_p$ should appear against the background of a smooth decrease of $T_{1\rho}$ with decreasing $|\Phi|$ [this total decrease of $T_{1\rho}(\Phi)$ has a minimum at $\Phi = 0$], due to the enhancement of the cross relaxation when the degree of homogeneity of the EPR broadening is decreased [the term

$$\sum_{n'<n} g_n g_{n'} \Delta_{nn'}^2 W_{nn'}^{CR}$$

in (12) increases with increasing r].

2. *Effective electronic CR.* Assume that the electronic CR is effected so rapidly that we can always assume $\beta_D = \xi_{nn'} = \beta$ in the proton relaxation process. Then the measured time $T_{1\rho}$ is determined by two thermal contacts: between the protons and the LFP and between the LFP and the lattice:

$$\frac{d}{dt}(C_\Delta + C_D)\beta = -\sum_k (\beta - \beta_k) L_{\beta_k}^{\beta} - (\beta - \beta_L)\left(\frac{C_\Delta}{T_{SL}} + \frac{C_D}{T_{DL}}\right),$$

$$\frac{d}{dt} C_k \beta_k = -(\beta_k - \beta) L_{\beta_k}^{\beta}; \tag{13}$$

$$L_{\beta_k}^{\beta} = C_k\Big(T_{kD}^{-1} + \sum_{n'<n} g_n g_{n'} W_{nn'k}^{CR}\Big).$$

a) If the LFP relaxation to the lattice is much faster than the establishment of equilibrium of the nuclei in the LFP, then

$$T_{1\rho}^{-1} = T_{pD}^{-1} + \sum_{n'<n} g_n g_{n'} W_{nn'p}^{CR}. \tag{14}$$

At $T_{pD}^{-1} \propto \sum_n g_n^2$ (see Sec. 2) and at an angular dependence $T_{1\rho}(\Phi)$ [see (14)], dips similar to those observed at the angles Φ_{mp} should appear at the angles Φ_r, and their depths should increase with increasing r. On the other hand, the values of $T_{1\rho}$ at the angles Φ_{flat} should not depend on r [Φ_{flat} are the angles corresponding to the flat parts of the $T_{1\rho}(\Phi)$ plot].

b) If the coupling of the nuclei with LFP is more effective that the LFP relaxation to the lattice, and the duration of the RF pulse is shorter than the time of contact of the nuclei with the LFP, then the initial conditions for the proton relaxation take the form

$$\beta_p(0) = 0, \quad \beta(0) = \beta_d(0) = \beta_{Cs}(0) = \beta_L,$$

and β and β_p relax first to a common value

$$\gamma = \frac{C_\Delta + C_D + C_{Cs} + C_d}{C_\Delta + C_D + C_{Cs} + C_d + C_p}\,\beta_L. \tag{15}$$

For sample with high proton density we have $\gamma \ll \beta_L$, so that the final proton relaxation rate will be the rate of the relaxation to the lattice

$$C_\Delta \Big/ \Big(\sum_k C_k + C_\Delta\Big) T_{SL}. \tag{16}$$

For low proton densities the relaxation practically terminates at the first stage and the relaxation rate is determined by the rate of the thermal contact of the nuclei from the FLP [expression (14)].

3. We propose finally that in the CR process, notwithstanding the temperature difference between the EDDP and the lattice, the difference subsystems are not detached from the lattice in the course of the proton relaxation.

a) We consider the limiting case when

$$\sum_{n'<n} g_n g_{n'} W^{CR}_{nn'} \Delta^2_{nn'}/\omega_D^2 \gg T_{Dk}^{-1}. \quad (17)$$

In this case the EDDP is rapidly unified with the difference Zeeman energies that have the lattice temperature, and the rate of the proton relaxation is determined by the thermal contacts of the protons with the LFP and coincides with (14). The angular dependence of (14) has been discussed in subsection 2a of this section.

b) In the opposite case, the nuclei are rapidly joined to the EDDP, and $T_{1\rho}^{-1}$ characterizes the relaxation of the unified (nuclei + EDDP) system to the lattice, and coincides with (12). The corresponding angular dependence is discussed in subsection 1c of the present section.

5. NUCLEAR-NUCLEAR DOUBLE RESONANCE

We proceed to a discussion of nuclear-nuclear double resonance in an electron-nuclear spin system of the same type as in copper-Tutton's salt. The experiments on stationary nuclear-nuclear double resonance are usually performed in the following manner: a strong RF field is used to saturate the NMR of one species of nuclei (deuteron or cesium resonance in the experimental case of Refs. 1–3), and after the stationary state is reached the relative change of the NMR signal of the second species of nuclei (protons in Refs. 1–3) is measured in comparison with the resonant value

$$Q = 1 - (\beta_p)_{st}/\beta_L, \quad (18)$$

where $(\beta_p)_{st}$ is the stationary value of β_p as $W_k \to \infty$ (k stands for d or Cs).

We consider now nuclear-nuclear double resonance, using Eqs. (7) for the same limiting cases that were used in the analysis of proton relaxation.

1. *Strong I–D coupling.* Calculating the nuclear-nuclear double resonance signal we find that $Q \sim 1$ and does not depend on the angle Φ, as expected.

2. *Effective electronic* CR. In this case Q takes the form

$$Q_{k\to p} = \left(T_{1k}^{-1} + \sum_{n'<n} g_n g_{n'} W^{CR}_{nn'k}\right) \Big/ \left(T_{kD}^{-1} + \sum_{n'<n} g_n g_{n'} W^{CR}_{nn'k} + C_\Delta C_k^{-1} T_{SL}^{-1}\right). \quad (19)$$

Of greatest interest in the study of the angular dependence of A is the case when

$$C_\Delta C_k^{-1} T_{SL}^{-1} \gg T_{kD}^{-1}.$$

We assume also that $\omega_k^2 \tau_{sn}^2 \gg 1$ (this condition is satisfied in Refs. 1–3). Then the angular dependence of $Q(\Phi)$ should have maxima at the angles Φ_r and Φ_{mk} (under the experimental conditions in Refs. 1–3 Φ_{mk} practically coincides with Φ_r); these maxima are due respectively to the terms T_{kD}^{-1} and $W^{CR}_{nn'k}$. This angle structure should be observed against the background of a smooth decrease of $Q(\Phi)$ with decreasing $|\Phi|$ (owing to the decrease of C_Δ).

3. Under conditions when the difference subsystems remain at equilibrium with the lattice, the expression for Q is very unwieldy in the case of an arbitrary angle Φ. We therefore write down and expression for Q at the angle $\Phi = 0$ and the angles Φ_{mp} and Φ_{flat} closest to it:

$$(Q_{k\to p})_0 = \left[(T_{Dk}^{-1})_0 + \sum_{n'<n} g_n g_{n'} W^{CR}_{nn'k}(\omega_k) C_k C_D^{-1}\right] \Big/ \left[(T_{Dk}^{-1})_0 + \sum_{n'<n} g_n g_{n'} W^{CR}_{nn'k}(\omega_k) C_k C_D^{-1} + (T_D^{-1})_0\right];$$

$$(Q_{k\to p})_{flat} = (T_{Dk}^{-1})_{flat}/[(T_{Dk}^{-1})_{flat} + (T_D^{-1})_{flat}]; \quad (20)$$

$$(Q_{k\to p})_{mp} = (T_{Dk}^{-1})_{mp} \Big/ \left\{[(T_{Dk}^{-1})_{mp} + (T_D^{-1})_{mp}] \times \left(1 + T_{pD} \sum_{n'<n} g_n g_{n'} W^{CR}_{nn'p}(0)\right) + \frac{C_p}{C_D} \sum_{n'<n} g_n g_{n'} W^{CR}_{nn'p}(0)\right\};$$

$$C_D T_D^{-1} = \sum_{n'<n} g_n g_{n'} \{\tilde{N} \Delta^2_{nn'} W^{CR}_{nn'} + \tilde{N}_k \Delta_{nn'} (\Delta_{nn'} - \omega_k) W^{CR}_{nn'k}\}, \quad (21)$$

where $(T_D^{-1})_{0,flat,mp}$ are obtained from (21) by the respective substitutions $\Delta_m = 0$, $W^{CR}_{nn'k} = 0$, and $\Delta_m = \omega_p$.

From the expression for A at an arbitrary angle Φ and from (20) it follows that the angular dependence should have maxima at the angles Φ_r and minima at the angles Φ_{mp}, against the background of a smooth decrease of $Q(\Phi)$ with decreasing $|\Phi|$, due to the increase of T_D^{-1} with decreasing $|\Phi|$.

6. CONCLUSION

The picture of the minima of $T_{1\rho}$ at angles Φ_{mp} against a background of a general decrease of $T_{1\rho}$ with decreasing $|\Phi|$, observed[1-3] in all deuterated samples in a wide range of fields and temperatures, and in a non-deuterated sample in strong fields and high temperatures, can be explained by assuming that in the course of the proton relaxation the difference subsystems do not become detached from the lattice, and the bottleneck is the contact between the (nuclei + EDDP) subsystem and the lattice. The angular dependence of $T_{1\rho}$ for this case, investigated with the aid of (12), agrees well with the experimental data. The relaxation behavior in Refs. 1–3 must be rejected, for according to it the angular dependence of $T_{1\rho}$ should have at the angles Φ_r additional minima due to the direct relaxation of the nuclei to the EDDP, but no such minima were observed in experiment.

No angle structure was observed in a nondeuterated sample in a weak field and at low temperature. In this case, just as in the experiments of Ref. 13, even the difference subsystems cannot be assumed to be at equilibrium in proton relaxation, owing to the large heat capacity of the proton subsystem and the slow electronic spin-lattice relaxation. The final time of the proton relaxation must therefore be determined by Eq. (10) or (11), the first of which does not depend on Φ, and the second decreases smoothly with decreasing $|\Phi|$, having a minimum at $\Phi = 0$. The cited experimental values do not depend on Φ, but the angle interval is too small for the relation given by (11) to become noticeable. To determine which of these situation is realized we must therefore study $T_{1\rho}$ in a larger angle interval.

We proceed now to consider the nuclear-nuclear double resonance experiments described by van Hou-

ten,[3] who stipulated an angular dependence $Q(\Phi)$ for deuteron-proton and cesium-proton resonances. A characteristic feature of this angular dependence is the presence of a maximum at $\Phi=0$ and of a minimum at $\Phi=\Phi_{mp}$, with

$$(Q_{h\to p})_0\approx 2(Q_{h\to p})_{flat};\quad (Q_{h\to p})_{mp}<(Q_{h\to p})_{flat}.$$

This angular dependence follows from (20), which was derived under the assumption that in the standard nuclear-nuclear double resonance process the difference subsystems remain at equilibrium with the lattice (this assumption, as noted above, leads to agreement between the theory and the experiments on proton relaxation).

The angular behavior of the nuclear-nuclear double resonance in this model is physically quite clear. At $\Phi=0$ the proton subsystem is heated by the deuteron (or cesium) subsystem via the EDDP because of the direct I–D coupling and of the electron-nuclear CR (the latter is possible, since $\Phi_{md}\sim\Phi_{mCs}\approx 0$). At Φ_{flat} there is no electron-nuclear CR, and the I–D coupling becomes weaker, so that Q decreases. At Φ_{mp} the proton subsystem is resonantly drained into the difference subsystems whose temperature is equal to that of the lattice, via the three-spin system, as a result of which a sharp minimum appears in the $Q(\Phi)$ angular dependence.

We now carry out a numerical comparison with the experimental results[3] on nuclear-nuclear double resonance. Substituting in (20) van-Houten's numerical data:

$$f=0.69\%,\ y=12\%,\ \nu_p=30\ \text{MHz},\ \nu_d=3.75\ \text{MHz},\ A=270\ \text{MHz},$$
$$(T_{1p})_{flat}=70\ \text{sec},\ (T_{1p})_0=55.5\ \text{sec},\ (T_{1p})_{mp}=40\ \text{sec},\ (Q_{d\to p})_{flat}=0.3$$

and assuming that the electronic CR is effective over a distance $\lesssim A$, we obtain

$$(Q_{d\to p})_0\approx 0.53;\quad (Q_{d\to p})_{mp}\approx 0.11$$

as against the respective experimental values 0.55 and 0.09.

Using the experimental data for cesium-proton resonance:

$$f=0.52\%,\ y=50\%,\ \nu_{Cs}=3.75\ \text{MHz},\ (Q_{Cs\to p})_{flat}=0.125,$$

we obtain

$$(Q_{Cs\to p})_0\approx 0.26.\quad (Q_{Cs\to p})_{mp}\approx 0.017$$

as against the experimental 0.2 and 0.075, respectively.

Thus, on the basis of previously derived equations,[6] assuming that an important role in nuclear relaxation is played by electronic CR, we have succeeded in describing in a unified manner the experimental results of Refs. 1–3.

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[1)] That the need for taking the inhomogeneous broadening in Ref. 8 is a stringent condition was called to our attention by V. A. Atsarkin.

[2)] We shall assume that in each of the eight inhomongeneously broadened EPR lines in copper-Tutton's salt there takes place a rapid spectral diffusion, so that each of these lines can be assigned a single temperature β_n^{-1} in the course of the proton relaxation and the nuclear-nuclear double resonance.

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