CONNECTION OF ELECTRON SPIN-SPIN INTERACTIONS WITH POLARIZATION AND NUCLEAR SPIN RELAXATION IN RUBY

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The relationship between electron cross relaxation (ECR) and the shape of the EPR line of the Cr^{3+} ion, on the one hand, and dynamic polarization (NDP) and spin-lattice relaxation of Al^{27} in ruby, on the other, is studied experimentally in ruby at helium temperatures. The appearance of NDP during saturation of the EPR line in the center (without detuning) is observed. Complete correlation between this effect and the ECR conditions in the Cr^{3+} spectrum is demonstrated. The degree of saturation transfer between transitions of the Cr^{3+} spectrum with close frequencies depends, under ECR conditions, on the nuclear polarization and can be artificially increased by saturating the Al^{27} NMR. The shape of the EPR line indicated by a weak signal directly after pulsed saturation is also uniquely related to the magnitude of the NDP under ECR conditions. Investigation of Al^{27} nuclear spin-lattice relaxation as a function of the orientation of the external field indicates the presence of shortened relaxation time regions arranged symmetrically with respect to the points of coincidence of various EPR spectral lines. The results obtained are discussed on the basis of the concept of an electron spin-spin temperature (T_{ss}). A consistent interpretation of the whole set of data is proposed under the assumption of the existence of direct thermal contact (independent of the microwave field) between the electron spin-spin interaction system and the Zeeman reservoir of the lattice nuclei. Estimates confirm the correctness of such an assumption for ruby.

INTRODUCTION

A new approach to magnetic resonance in solids, based on the concept of the temperature T_{ss} of the spin-spin interaction reservoir, has recently gained wide acceptance. It was preceded by the idea of Redfield[1] concerning a single spin temperature in a coordinate system rotating together with the strongly saturating high frequency field. In 1961–62, Provotorov developed a theory of magnetic resonance at any degree of saturation[2] (the only requirement was smallness of the high frequency field compared with the local field H_L in the substance) and a cross-relaxation theory[3]. In both these papers, account was taken of the existence of two, in general different temperatures, T_{ss} and T_Z, corresponding to different parts of the spin-system Hamiltonian: the secular parts of the energy of the spin-spin interactions (SS reservoir) and the Zeeman energy of the spins in an external magnetic field (Z reservoir).

Among the other investigations devoted to various aspects of this problem[4-7], we note the experiments[4,6] in the field of nuclear magnetic resonance (NMR), which confirm directly or indirectly the new theory. Subsequently, the T_{ss} concept, extended to include electron spins, has entered into the theory of nuclear dynamic polarization (NDP) in solids ("effet solide")[8-12] and has found some confirmation in experiments on NDP[13] and electron paramagnetic resonance (EPR)[14,15].

If it is assumed that the T_{ss} notion is applicable under real conditions for both nuclear and electron spins (for example, in crystals with sufficient concentration of paramagnetic impurities), then we should apparently expect manifestations of an interrelationship between the phenomena (which so far have been regarded as independent), whereby the behavior of T_{ss} plays a major role. The purpose of the present work was to investigate experimentally such an interrelation between the electron cross relaxation (ECR), the EPR line shape upon saturation, NDP and spin lattice relaxation of nuclei, and also to analyze theoretically these phenomena on the basis of the concept of the electronic T_{ss}.

Some preliminary results of this work are contained in[16,17].

I. NUCLEAR POLARIZATION UNDER ECR CONDITIONS

1. The purpose of this series of experiments was to obtain polarization of the nuclei of a crystal lattice in ECR in a system of impurity ferromagnetic ions. As is well known, in ECR between two transitions with frequencies ν_{e1} and ν_{e2} ($m\nu_{e1} \approx n\nu_{e2}$, where m and n are integers), the difference energy $h(m\nu_{e1} - n\nu_{e2}) \equiv h\Delta$ goes over to the electron SS reservoir. If $w_{cr} \gg \tau_{1e}^{-1}, (\tau_1')^{-1}$, where w_{cr} is the ECR probability, and τ_{1e} and τ_1' are the times of the spin-lattice relaxation of the electronic Zeeman (Z_e) and SS systems, the following relation should be satisfied (see[3,7])

$$m\nu_{e1}T_{e1}^{-1} - n\nu_{e2}T_{e2}^{-1} = \Delta T_{ss}^{-1}, \tag{1}$$

where T_{e1} and T_{e2} are the spin temperatures of the Zeeman systems Z_{e1} and Z_{e2}. For a non-equidistant multilevel system, the spin temperature T_{ij} for the transition ij is introduced in accordance with the linear-approximation formula ($h\nu_{ij} \ll kT$)

$$\frac{N}{R}\frac{h\nu_{ij}}{kT_{ij}} = N_i - N_j,$$

where N_{ij} are the populations of the levels i and j; $N = \sum_{i=1}^{R} N_i$, and R is the number of levels.

If the condition $T_{e1} \neq T_{e2}$ is maintained in some manner (for example, by applying a microwave field to one of the electronic transitions), then the temperature T_{SS} can change strongly[7]. In this case the task of obtaining NDP reduces merely to transferring this temperature to the Zeeman system Z_n of the crystal-lattice nuclei (we assume that Z_n forms a reservoir with a single spin temperature T_n). Such an equalization of T_n and T_{SS} is possible theoretically[10,11], when the NMR frequency ν_n is of the same order as γH_L (γ is the electron spin spectroscopic splitting factor).

2. The experiments were performed at temperatures T_0, equal to 1.9 and 4.2°K on ruby crystals (Al_2O_3: Cr^{3+}), some parameters of which are listed in the table, where $\delta\nu_{23}$ and $\delta\nu_0$ are the widths of the EPR lines in the transitions 2–3 at θ = 60° and (+ or − ½) at θ = 0 respectively (θ—angle between H_0 and the crystal axis; the spins are numbered upward). The relaxation times are given for 1.9°K.

Certain characteristics of investigated crystals

C, at. %	$\delta\nu_{23}$, MHz	$\delta\nu_0$ MHz	τ_{1e}, msec*	τ_{1n}, sec**
0.02	57.5	33.5	250	20.6
0.03	61.0	38.0	200	10.2
0.08	81.5	50.5	50	0.07

*For transition 2—3 at θ = 62°.
**At θ = 66°, H_0 = 3340 Oe (provided that $\nu_{23} = \nu_{12}$).

The experimental setup has made it possible to observe simultaneously the EPR of the Cr^{3+} ion in the 3 cm band and the NMR of Al^{27} (nuclear spin I = 5/2). For Al^{27} we have γ_n = 1110 Hz/Oe, so that in fields $H_0 \sim 10^3$–10^4 Oe, the frequency ν_n falls in the right band $\sim\gamma H_L$.

In order to separate the expected effect from the "ordinary" NDP, connected with the saturation of the "forbidden" electron-nuclear transitions at frequencies $\nu_e \pm \nu_n$[18,8], the EPR was saturated strictly at the center of the absorption line. At the magnetic-field modulation (50 Hz) necessary to indicate the EPR and NMR, such a saturation was ensured by short (0.1 msec) periodic microwave pulses. The intervals between pulses (20 msec) were as a rule much shorter than τ_{1e}, so that the saturation was in fact stationary.

3. The expected effect of intensification of the nuclear polarization was actually observed when the angle θ corresponded to the ECR conditions in the spectrum of Cr^{3+} ion (we shall henceforth call this effect, for brevity, "nuclear cross relaxation polarization" or NCRP). Figure 1 shows the intensification of the nuclear polarization $E \equiv T_0/T_n$ as a function of θ at T_0 = 1.9°K and C = 0.03 at.%. The 2–3 transition of the EPR spectrum was saturated; when θ was varied, the field H_0 was also adjusted so as to make ν_{23} = const.

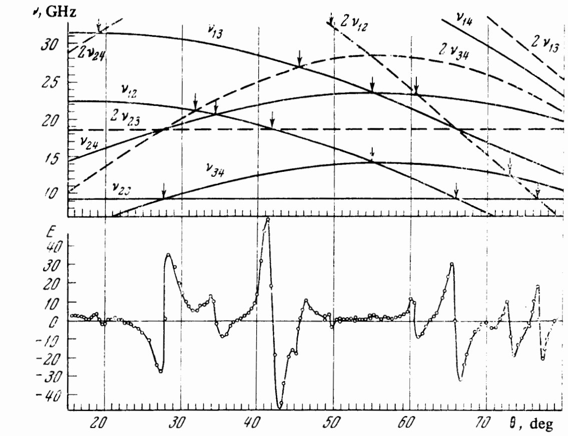

FIG. 1. Top—diagram of resonance frequencies of the EPR spectrum of ruby under the condition ν_{23} = const = 9.3 GHz (dashed-doubled frequencies). The arrows designate the ECR points. Bottom—dependence of NDP of Al^{27} on the orientation of $\mathbf{H_0}$ upon saturation of the center of the 2-3 line.

In the upper part of Fig. 1 is shown the dependence of the frequencies of the EPR spectrum in ruby, calculated from the known tables[19] for the case when ν_{23} = 9.3 GHz (the doubled frequencies are also shown). The points of intersection of the curves on this figure, designated by arrows, correspond to the ECR conditions.

Comparison of this diagram with the experimental E (θ) plot revealed a complete correlation between the ECR conditions and the occurrence of NDP. It is typical that the behavior of E agrees with the expected course of T_{SS}^{-1}. Thus, when ν_{23} exceeds somewhat the frequency of the second transition, which takes part in the ECR (i.e., $\Delta > 0$), $E < 0$ is observed, and vise-versa; when $\Delta = 0$ we have $E \approx 1$ (see, for example, the vicinity of the points θ equal to 28 and 66°). Similar regularities are characteristic of the harmonic and combination ECR: $\theta \approx 42°$, $2\nu_{23} \approx \nu_{12}$; $\theta \approx 76.5°$, $\nu_{23} = 2\nu_{12}$; $\theta \approx 49.5°$, $\nu_{24} + \nu_{23} \approx 2\nu_{12}$; $\theta \approx 71.5°$, $\nu_{13} + \nu_{23} \approx 2\nu_{34}$ (in the latter case $\nu_{24} + \nu_{23} > 2\nu_{34}$ all the time, and consequently $E < 0$).

NCRP is also observed when the 2–3 transition does not take direct part in the ECR, but saturation of this line leads to a change of the Zeeman spin temperatures of other transitions of the spectrum ($\theta \approx 19°$, 31.6°, etc.). In the "symmetrical" orientation $\theta \approx 54.5°$, no NCRP is observed; this, obviously, is connected with the fact that saturation of the transition 2–3 changes the temperatures of the interacting transitions T_{12} and T_{34} (and also T_{13} and T_{24}) to an equal degree.

4. Figure 2 shows a fragment of the overall picture of the NCRP in the vicinity of θ = 66° ($\nu_{23} \approx \nu_{12}$), for different chromium concentrations. We see that a decrease of C from 0.03 to 0.02% leads to an increase of $|E|_{max}$ from 30 to 45 with simultaneous reduction of the distance between the maxima of the polarization in approximately the same proportion. At C = 0.08%, the NCRP vanishes practically completely (in this case, however, no complete saturation of EPR is reached, since τ_{1e} is comparable with the intervals between the pulses, so that the values of E are somewhat lower).

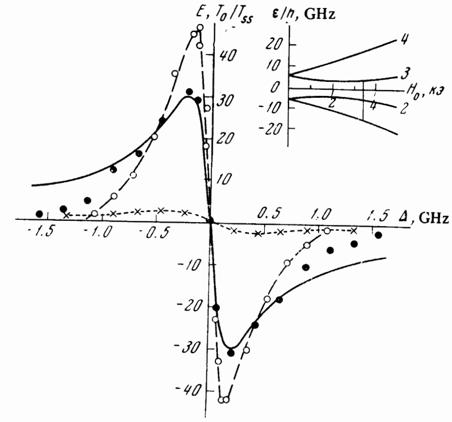

FIG. 2. Dependence of NDP of Al^{27} on the detuning Δ between the transitions 2-3 and 1-2 of the EPR spectrum of ruby near $\theta = 66°$ (upper right-energy level scheme of Cr^{3+}): ● – C = 0.03%, ○ – C = 0.02%, × – C = 0.08%. Solid line-result of calculation of T_0/T_{SS} by means of formulas (2) and (3) for C = 0.03%.

An increase of T_0 to 4.2°K had practically no influence on the NCRP picture.

5. As is well known[20], NDP in ruby can be attained also by the "usual" method, i.e., by saturating the EPR line on the wings. We note, however, that in this case, also, non-strictly-resonant saturation of the line should lead to a change of T_{SS}[2,7].

In our experiments, the dependence of E on the detuning Δ' of the saturating signal relative to the line center had, as a rule, an unusual form: owing to the NCRP effect, the function $E(\Delta')$ passed through unity at $\Delta' \neq 0$. The "usual" symmetrical $E(\Delta')$ picture was observed only for those values of θ, where there was no ECR. Thus, at $\theta = 52°$ and C = 0.03% we obtained $|E|_{max} = 15$ at $\Delta' = \pm 145$ MHz; however, at such large values of Δ', saturation of EPR was no longer reached, so that the presented values are undoubtedly underestimated.

II. CONNECTION OF NDP WITH SATURATION TRANSFER IN ECR

1. Unlike the earlier ECR theory[21], according to which cross relaxation leads to equalization of T_{1e}^{-1} and T_{2e}, it follows from (1) that the tendency of cross relaxation consists in the tendency of the expression $(m\nu_{e1}T_{e1}^{-1} - n\nu_{e2}T_{e2}^{-1} - \Delta T_{SS}^{-1})$ to vanish; if one of the transitions is saturated ($T_{e1}^{-1} \to 0$), we have

$$T_{ss}^{-1} = -n\frac{\nu_{e2}}{\Delta}T_{e2}^{-1}. \tag{2}$$

By measuring T_{e2}^{-1} under conditions of $T_{e1}^{-1} = 0$, we can, consequently calculate T_{SS}^{-1} by means of formula (2) and then compare it with the experimentally measured nuclear temperature T_n.

2. Such measurements were made in the vicinity of $\theta = 66°$ at C = 0.03%, $T_0 = 1.9°$K. Deep modulation of the magnetic field has made it possible to observe simultaneously both close EPR lines--the transitions 2--3 and 1--2, with the transition 2--3 saturated by the method described earlier (I, 2), and the temperature T_{12} of the transition 1--2 measured by determining the amplitude of the 1--2 line. The results of the measurements, as a function of $\Delta = \nu_{23} - \nu_{12}$, are shown in Fig.

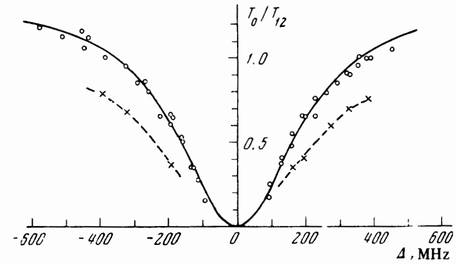

FIG. 3. Dependence of the temperature T_{12} of the 1-2 transition upon saturation of the 2-3 line on the detuning $\Delta = \nu_{23} - \nu_{12}$ near $\theta = 66°$ (C = 0.03%): ○ – without NMR saturation, × – with partial NMR saturation. The solid line corresponds to formula (3).

3. The experimental points are well described by the formula

$$T_0/T_{12} = A[1 + (\Delta_0/\Delta)^2]^{-1} \tag{3}$$

with $\Delta_0 = 210$ MHz, A = 1.35 (A > 1, since the transition 1--2 "cools off" when the transition 2--3 is saturated, owing to the presence of a common level for these transitions).

Formula (3) was then used to calculate T_{SS}^{-1} from (2). The solid line of Fig. 2 shows the result of the calculation. We see that when $|\Delta| \lesssim 700$ MHz, the experimental values of E fit very well the calculated T_0/T_{SS} curve.

3. Thus, serious arguments appear in favor of the proposed equalization of T_{SS} and T_n in NDP. The result is important also for the understanding of the gist of the ECR, since the theoretical conclusion that the weakening of the saturation transfer with increasing detuning may be unconnected with the decrease of w_{cr} is confirmed. In our case there is an appreciable region ($|\Delta| \lesssim 700$ MHz) where the ECR has a high probability, but its result is not so much the equalization of T_{12} and T_{23} (i.e., saturation transfer), as a growth of $|T_{SS}^{-1}|$. We note that in this case, in spite of the strong ECR, the amplitude of the first (faster) exponential in the usual experiments on measurements of relaxation time by the pulsed saturation method (see, for example,[22]), will be insignificant.

When $|\Delta| \gtrsim 700$ MHz, the condition $W_{cr} \gg \tau_{1e}^{-1}$ $(\tau_1')^{-1}$ is apparently violated, and E decreases in comparison with the calculated curve.

4. During the course of the described measurements it was noted that at the first instants after the saturating pulses are turned on, the 1--2 transition is saturated to a greater degree than after a certain time (~10 sec), when the stationary value of T_{12} has been established. The time variation of T_0/T_{12} is fully correlated with the establishment of the stationary value of E, thus confirming the uniqueness of the correspondence between T_n, T_{SS}, and T_{12}.

In this connection, the thought arose of the possibility of an external influence on the saturation transfer in ECR by "artificially" changing T_n. To this end, we have partly saturated the NMR signal by a strong high frequency field, i.e., we forced a decrease of $|T_n^{-1}|$, counting on decreasing also $|T_{SS}^{-1}|$. The values of T_0/T_{12} measured under these conditions ($T_{23}^{-1} = 0$) are also shown in Fig. 3. We see that NMR saturation has

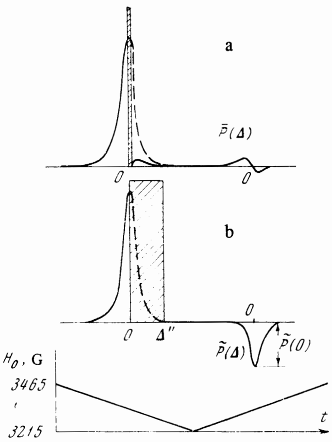

FIG. 4. Shape of EPR line indicated by a weak signal directly after pulsed saturation (C = 0.03%): a—short pulse at the center of the line, b—passage of line on saturation from the center to Δ''. Dashed—equilibrium line shape. Below—variation of external magnetic field during the observation process.

actually influenced the ECR result, increasing the degree of saturation transfer from 2—3 to 1—2.

III. DNP AND THE EPR LINE SHAPE IN SATURATION

1. The absorption (P) at the frequency $\nu_e + \Delta'$ ($|\Delta'| \ll \nu_e$) is given by (see[2])

$$P(\Delta') = W_0(\Delta')\left[\frac{\nu_e}{T_e} + \frac{\Delta'}{T_{ss}}\right], \tag{4}$$

where $W_0(\Delta')$ is the normalized absorption probability in the vicinity of ν_e, and T_e is the temperature of the system Z_e.

If $|T_{SS}^{-1}| \gg T_0^{-1}$, then the line shape will be significantly altered compared with the equilibrium shape (see[2,7]). In this connection, it is of interest to investigate $P(\Delta')$ for NDP, and thus approach the question of the connection between T_{SS} and T_n from still another point of view.

We note that (4) holds true only for a homogeneous EPR line. In ruby, on the other hand, at C = 0.03%, the major part of the line width is due to the influence of the nuclear spins from the nearest surroundings of the Cr^{3+} ion[22], so that the contribution of the inhomogeneous broadening is large. Nonetheless, we shall base ourselves for the time being on (4); a certain justification for this procedure is the strong cross relaxation inside the line contour. In Sec. V, article 8, we shall return to this question.

2. The observation of the EPR line shape was carried out under conditions when the Z_e system was saturated. In this case $T_e^{-1} = 0$, and the shape of the absorption line, indicated by the weak (unsaturated) signal, was determined only by the state of the SS system. The value of E was set by the prior NDP; then, at the instant of the passage of the magnetic field through the center of the 2--3 line, a short saturating pulse was turned on, and the indication of the line shape (which we denote in these experiments by $\overline{P}(\Delta')$), was carried out during the return passage of the modulation of the magnetic field.

It is seen from Fig. 4a that the line shape indicated in this manner includes absorption and stimulated emission sections. It has turned out that $\overline{P}(\Delta')$ is determined completely by the degree of polarization of the nuclei at the instant of indication, and is well described by the formula

$$\overline{P}(\Delta') = P_0(\Delta')E\Delta'/\nu_e, \tag{5}$$

where $P_0(\Delta')$ determines the equilibrium line shape. Obviously, when $T_e^{-1} = 0$ expressions (5) and (4) are compatible when $T_{SS} = T_n$. To obtain the form of $\overline{P}(\Delta')$ it was sufficient to apply a single pulse saturating the EPR by at least 80—90%.

We note that the occurrence of the signal of the type $\overline{P}(\Delta')$ following multiple repetition of the indicated procedure is possible also without preliminary NDP, if NCRP takes place. This provides a new method of observing ECR.

3. Pulsed saturation of EPR on the absorption line wing (with a detuning Δ'' relative to the center) also leads to effects connected with the degree of polarization of the nuclei. Observation of the $\tilde{P}(\Delta')$ line shape immediately after such a saturation has shown that an absorption or stimulated emission signal arises at the frequency ν_e, depending on the relative signs of Δ'' and E. The amplitude $\tilde{P}(\Delta')$ increased when a successive saturation of the line was employed, first at the center and then with a detuning Δ''.

This was attained in practice by lengthening the saturating pulse to 3--4 msec, so that its leading front corresponded to the center of the line and its trailing edge to the detuning Δ''(Fig. 4b). Just as in the preceding experiment, $\tilde{P}(\Delta')$ depended on the value of E at the instant of indication, and therefore correlated with the ECR conditions (a concrete example of such a correlation was demonstrated by us in[16]).

The dependence of $\tilde{P}(0)$ on the position of the trailing edge of the pulse, i.e., on Δ'' at a specified value of E, has turned out to be well described for the formula

$$\tilde{P}(0) = -P_0(0)E\Delta''/\nu_e. \tag{6}$$

To explain this result we recognize that saturation at the frequency $\nu_e + \Delta''$ denotes, in accordance with (4), that $\nu_e/T_e + \Delta''/T_{SS} \to 0$. It follows therefore that $\tilde{P}(0)/P_0(0) = P_0/T_e = -(\Delta''/\nu_e)(T_0/T_{SS})$, and (6) is obtained directly provided only $T_{SS} = T_n$. A more detailed discussion of these experiments will be presented in section V, articles 5—7. We note here only that, besides demonstrating the connection between T_{SS} and T_n, the described procedure makes it possible to determine E from (6) in general without observing an NMR signal.

IV. SPIN LATTICE RELAXATION OF NUCLEI

1. We proceed to the question of the connection between the temperatures T_{SS} and T_n in the absence of a saturating microwave field, i.e., under conditions of free relaxation of the spin system to the lattice.

Figure 5 shows the results of measurements of the time τ_{1n} in ruby samples with a chromium concentration 0.02 and 0.03 at.%, near the angle $\theta = 66°$ and at $H_0 \approx 3340$ Oe, i.e., under ECR conditions $\nu_{23} \approx \nu_{12}$. The time τ_{1n} was determined from the decrease of E after turning off the microwave power causing the NDP. Within the limits of measurement accuracy (± 10%), the relaxation process was described by a single exponential.

The most interesting feature of the results is the appreciable (up to 50%) decrease of τ_{1n} on both sides of the point $\theta = 66°$ ($\nu_{23} = \nu_{12}$). The region of the

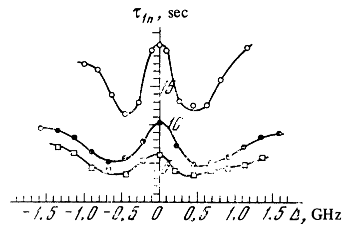

FIG. 5. Dependence of the time τ_{1n} of the spin-lattice relaxation of the nuclei on the detuning $\Delta = \nu_{23} - \nu_{12}$ near $\theta = 66°$: ●–C = 0.03%, T_0 = 1.9°K; □–C = 0.03%, T_0 = 4.2°; ○–C = 0.02%, T_0 = 1.9°K.

shortened values of τ_{1n} extends up to $|\Delta|$ = 1.2 GHz for C = 0.03% and 0.8 GHz for C = 0.02%.

The shortening of τ_{1n} in ECR was already observed earlier[23], but at that time the two regions of accelerated relaxation on both sides of $\Delta = 0$ were not noted, and this has left its imprint on the interpretation of this phenomenon.

In a sample with C = 0.08%, we obtained $\tau_{1n} \approx 70$ msec (at 1.9°K), i.e., $\tau_{1n} \sim \tau_{1e}$ (see the table). No clear cut dependence of τ_{1n} on the ECR conditions was noted in this case. Measurements of τ_{1n} at those angles θ at which the ECR had no effect have shown that the time $\tau_{1n} \sim H_0^2$ for C = 0.02 and 0.03%.

2. To interpret the foregoing results, we assume that effective coupling between the SS and Z_n reservoirs exists also in the absence of a microwave field and leads to equalization of the temperatures T_{ss} and T_n. In this case the spin-lattice relaxation of the nuclei can be visualized as a two-step process[11], consisting of the equalization of T_n and T_{ss} and joint relaxation of Z_n and SS to the lattice. If the second part of this process is due to the thin-lattice relaxation of the SS reservoir, then under ECR conditions with detuning $\Delta \neq 0$, when the SS system is coupled with the electronic Zeeman system, an additional outflow into the lattice is produced for the nuclei (via Ze), and this leads to a reduction of τ_{1n}[14]. A more detailed analysis of these experiments will be given in Section V, article 8.

The closeness of τ_{1n} to τ_{1e} at C = 0.08% is due apparently to the large probability of the ECR process, which practically couples all the transitions of the EPR spectrum with one another. In this case the SS and Z_e systems are apparently no longer isolated; the nuclei give up their energy to the joint electron system, the specific heat of which is large, and the joint relaxation of the electrons and the nuclei to the lattice proceeds with a common time $\sim\tau_{1e}$.

Obviously, under such conditions it is difficult to maintain a temperature difference between different parts of the common spin system, as is confirmed by the sharp weakening of the NCRP (Fig. 2), and can be compared with the "concentration quenching" of quantum paramagnetic amplifiers (see, for example,[22]).

V. DISCUSSION OF RESULTS AND CERTAIN THEORETICAL ESTIMATES

1. In the qualitative explanation of the experimental results we have assumed thermal equilibrium between the SS and Z_n reservoirs. Let us analyze the conditions under which this assumption is valid. Equations[11], which describe NDP in the presence of a microwave field at a frequency $\nu_e + \Delta'$ (let $\Delta' > 0$) and under the conditions $\gamma H_L \sim \nu_n$, can be written in the form

$$\frac{\partial}{\partial t}\frac{\nu_e}{T_e} = -W_0\left(\frac{\nu_e}{T_e}+\frac{\Delta'}{T_{ss}}\right) - W_+\left(\frac{\nu_e}{T_e}+\frac{\nu_n}{T_n}+\frac{\Delta'-\nu_n}{T_{ss}}\right) - \frac{1}{\tau_{1e}}\left(\frac{\nu_e}{T_e}-\frac{\nu_e}{T_0}\right),$$

$$\frac{\partial}{\partial t}\frac{1}{T_{ss}} = -\frac{\Delta'}{(\gamma H_L)^2}W_0\left(\frac{\nu_e}{T_e}+\frac{\Delta'}{T_{ss}}\right) - \frac{\Delta'-\nu_n}{(\gamma H_L)^2}W_+\left(\frac{\nu_e}{T_e}+\frac{\nu_n}{T_n}+\frac{\Delta'-\nu_n}{T_{ss}}\right) - \frac{1}{\tau_{sn}}\left(\frac{1}{T_{ss}}-\frac{1}{T_n}\right) - \frac{1}{\tau_1'}\left(\frac{1}{T_{ss}}-\frac{1}{T_0}\right),$$

$$\frac{\partial}{\partial t}\frac{\nu_n}{T_n} = -\frac{\tilde{N}_e}{\tilde{N}_n}W_+\left(\frac{\nu_e}{T_e}+\frac{\nu_n}{T_n}+\frac{\Delta'-\nu_n}{T_{ss}}\right) - \frac{c_{ss}}{c_{zn}}\frac{1}{\tau_{sn}}\left(\frac{\nu_n}{T_n}-\frac{\nu_n}{T_{ss}}\right) - \frac{1}{\tau_{nl}}\left(\frac{\nu_n}{T_n}-\frac{\nu_n}{T_0}\right) \quad (7)$$

(the diffusion terms of[11] have been omitted). Here c_{ss} and c_{zn} are the specific heats of the SS and Z_n systems,

$$c_{ss}/c_{zn} = \tilde{N}_e(\gamma H_L)^2/\tilde{N}_n\nu_n^2, \quad \tilde{N}_e/\tilde{N}_n = N_eS(S+1)/N_nI(I+1);$$

N_e, N_n and S, I are respectively the numbers and spins of the electrons and nuclei; τ_{nl} is the time of the "extraneous" spin lattice relaxation of the nuclei (besides the SS reservoir). Two terms in (7) lead to equalization of the temperatures T_n and T_{ss}. One of them, introduced in[8,9], is proportional to the probability $W_\pm$ of the "forbidden" electron-nuclear transitions (in our case we chose W_+ in the vicinity of the frequency $\nu_e + \nu_n$); only in the case when these transitions are saturated by the microwave field is nuclear polarization attained, i.e., T_n shifts to the value of T_{ss}. The second term, proportional to τ_{sn}^{-1}, has been introduced in[10,11] and ensures equalization of T_n and T_{ss} independently of the microwave field, owing to the direct coupling of the SS and Z_n reservoirs and their "relaxation" to each other. This term ($\sim\tau_{sn}^{-1}$) leads to the same results as the term with $W_\pm$, but now all that is required for the NDP is the shift of T_{ss}, which is already assured by the saturation of the allowed EPR transition. Indeed, a stationary solution of (7) under the condition that the allowed transition is saturated ($W_0\tau_{1e} \gg 1$) and with allowance for $W_+ \ll W_0$, is given by

$$\frac{1}{T_{ss}} \approx -\frac{1}{T_0}\left\{\left(\frac{\tilde{N}_e}{\tilde{N}_n}W_+\tau_{nl}+\frac{c_{ss}\tau_{nl}}{c_{zn}\tau_{sn}}\right)\left(\frac{\Delta'\nu_e\tau_1'}{(\gamma H_L)^2\tau_{1e}}-\frac{c_{zn}\tau_1'}{c_{ss}\tau_{nl}}\right)+\frac{\Delta'\nu_e\tau_1'}{(\gamma H_L)^2\tau_{1e}}\right\}\left\{\left(\frac{\tilde{N}_e}{\tilde{N}_n}W_+\tau_{nl}+\frac{c_{ss}\tau_{nl}}{c_{zn}\tau_{sn}}\right)\left(\frac{\Delta'^2\tau_1'}{(\gamma H_L)^2\tau_{1e}}+1+\frac{c_{zn}\tau_1'}{c_{ss}\tau_{nl}}\right)+\frac{\Delta'^2\tau_1'}{(\gamma H_L)^2\tau_{1e}}+1\right\}^{-1}, \quad (8)$$

and the expression for $1/T_n$ differs from (8) only in that the last term in the numerator is replaced by the sum $(-\Delta'^2\tau_1'/(\gamma H_L)^2\tau_{1e} + 1)$. We see that under the condition

$$\frac{\tilde{N}_e}{\tilde{N}_n}W_+\tau_{nl} \gg 1 \text{ and (or) } \frac{c_{ss}}{c_{zn}}\frac{\tau_{nl}}{\tau_{sn}} \gg 1 \quad (9)$$

the temperatures T_n and T_s become equalized:

$$\frac{T_0}{T_n} \approx \frac{T_0}{T_{ss}} \approx -\left[\frac{\Delta' \nu_e \tau_1'}{(\gamma H_L)^2 \tau_{1e}} - \frac{c_{zn}\tau_1'}{c_{ss}\tau_{nl}}\right]\left[\frac{\Delta'^2 \tau_1'}{(\gamma H_L)^2 \tau_{1e}} + 1 + \frac{c_{zn}\tau_1'}{c_{ss}\tau_{nl}}\right]^{-1}. \quad (10)$$

Naturally, $|1/T_{ss}|$ is now smaller than in the case when there are no nuclear spins and the microwave field saturates only the electronic system[7]. However, if the "extraneous" relaxation of the nuclei in the lattice can be neglected, i.e., if

$$c_{zn}\tau_1' / c_{ss}\tau_{nl} \ll 1, \quad (11)$$

we obtain from (10) the same strongly shifted value of T_{ss} as in the absence of coupling with the nuclei (when W_+, $\tau_{sn}^{-1} \to 0$): in the stationary regime, under condition (11), the nuclear system does not decrease $|T_{ss}^{-1}|$, in spite of its large specific heat.

2. So far, in the experimental investigations of NDP ([13] and others), the term with τ_{sn}^{-1} was not taken into account, and we shall therefore discuss its role in greater detail. The physical meaning of the direct coupling between the Z_n and SS reservoirs lies in their mutual exchange of energy as the result of modulation of the local magnetic fields at the locations of the nuclei, during spin-spin relaxation of the electrons. The probability of relaxation of the nuclei in the SS system, maintained by the microwave field at a constant temperature T_{ss}, is practically equal to $(c_{ss}/c_{zn})\tau_{sn}^{-1}$ and its order of magnitude is $\sigma\tau_{2e}^{-1}$, where σ is the "hindrance" factor for the electron-nuclear transition and τ_{2e} is the time of the electronic spin-spin relaxation. On the other hand, if the only possible mechanism of "extraneous" relaxation of the nuclei in the lattice are the electron-nuclear transitions connected with the spin-lattice relaxation of the electrons, then $\tau_{nl}^{-1} \sim \sigma\tau_{1e}^{-1}$.

Inasmuch as $\tau_{2e}^{-1} \gg \tau_{1e}^{-1}$, condition (9) is certainly satisfied (even without saturation of the forbidden transitions)[10], and in the stationary regime we have $T_n \approx T_{ss}$. Estimates indicate also that the condition (11) is satisfied, which reduces at $\tau_{1e} \approx 2\tau_1'$ to the requirement $2c_{ss}/c_{zn} \gg \sigma$. Indeed, $\sigma \sim (\delta H_n/H_0)^2$, where δH_n is the NMR line width due to the local fields of the electron spins; in our experiments $H_0 \sim 3 \times 10^3$ Oe and $\delta H_n \sim 10$ Oe, i.e., $\sigma \sim 10^{-5}$. On the other hand, $c_{ss}/c_{zn} \sim 10^{-2}$ (see article 8 of this section).

Thus, in the interpretation of the experiments we are justified in using the formulas for the stationary value of T_{ss}[7], derived without allowance for the nuclear spins.

We note that the elementary act of direct energy transfer from the nuclei to the SS reservoir can be represented in simplified form as a simultaneous flipping of two electron and one nuclear spins; the Zeeman energy of the latter goes over in this case to the SS system. This mechanism can also be regarded as a sui generis cross relaxation between the "forbidden" and allowed transitions. If we now transfer this model to the electron spins pertaining to different spin packets in the inhomogeneously broadened EPR line, we arrive at the process considered in[24]. The model of the authors of[24] leads, however, to a relatively low probability of the "electron-nuclear cross relaxation" $w_{en} \sim \sigma w_{cr}$. In those cases when $\nu_n \sim \gamma H_L$, the probability of this process can be apparently neglected in comparison with $\tau_{sn}^{-1} c_{ss}/c_{zn}$, inasmuch as $w_{cr} \ll \tau_{2c}^{-1}$.

3. In accordance with the conclusions of article 2, we shall interpret the experimental data on NCRP with the aid of expressions for T_{ss}, in which the influence of the nuclei is disregarded. These formulas, which are close to those obtained for two types of spins in[7], have been modified for spins of the same kind with a multilevel non-equidistant spectrum. We present the result of the calculations for the cross relaxation between the transitions ij and kl at $m\nu_{ij} - n\nu_{kl} = \Delta \ll \nu_e$, where ν_e is the frequency of any of the transitions. Assuming stationary microwave saturation of one of the transitions of the spectrum under the condition $w_{cr} \gg 1/\tau_{1e}, 1/\tau_1'$, we obtain the stationary value of T_{ss} in the form

$$\frac{\Delta}{T_{ss}} \approx \left[1 + \left(\frac{\Delta_0}{\Delta}\right)^2\right]^{-1}\left(\frac{m\nu_{ij}}{T_{ij}^*} - \frac{n\nu_{kl}}{T_{kl}^*}\right), \quad (12)$$

where T_{ij}^* and T_{kl}^* are the Zeeman temperatures at the transitions ij and kl, established under the influence of the microwave field without the cross-relaxation process. The parameter Δ_0, as can be readily seen from (12), is the value of the detuning Δ corresponding to the maximum of $|1/T_{ss}|$ as a function of $|\Delta|$; assuming an exponential spin-lattice relaxation for the transitions ij and kl with times τ_1^{ij} and τ_1^{kl}, it takes the form

$$\Delta_0 = \gamma H_L\left(\frac{\alpha\tau_1^{ij} + \beta\tau_1^{kl}}{\tau_1'}\right)^{1/2}, \quad (13)$$

where α and β are numbers that depend on the type of cross relaxation and on the location of the transition saturated by the microwave field. We indicate below the calculated values of Δ_0 for certain cases of cross relaxation in ruby ($S = 3/2$) in saturation of the 2–3 transition, which, as can be readily shown, leads to the following expressions for T^*:

$$\frac{\nu_{23}}{T_{23}^*} = 0, \quad \frac{\nu_{12}}{T_{12}^*} \approx \frac{\nu_{12}}{T_0} + \frac{\nu_{23}}{2T_0}\frac{\tau_1^{12}}{\tau_1^{23}}, \quad \frac{\nu_{34}}{T_{34}^*} \approx \frac{\nu_{34}}{T_0} + \frac{\nu_{23}}{2T_0}\frac{\tau_1^{34}}{\tau_1^{23}}. \quad (14)$$

Calculation yields in this case, for simple and harmonic cross relaxations, $\nu_{23} \approx \nu_{12}$ and $2\nu_{23} \approx \nu_{12}$

$$\Delta_0 = \frac{3\sqrt{2}}{2}\gamma H_L \sqrt{\frac{\tau_1^{12}}{\tau_1'}}. \quad (15')$$

For $\nu_{23} \approx 2\nu_{12}$ the value of Δ_0 turns out to be twice as large. When $m\nu_{12} \approx n\nu_{34}$ we have

$$\Delta_0 = \sqrt{\frac{3}{2}}\gamma H_L\left[\frac{m(3m+n)\tau_1^{12} + n(3n+m)\tau_1^{34}}{\tau_1'}\right]^{1/2}. \quad (15'')$$

4. Comparison of expressions (12)–(15) with the general NCRP picture shows that there is a good correspondence between the theoretical values of T_0/T_{ss} and the measured value of E. Not only the general course, but many details of the $E(\theta)$ dependence coincide with the predictions of the theory for the value of T_{ss}^{-1}. Thus, the relation between the values of $|E|_{max}$ near the points of the simple ($\theta \approx 28$ and 66°) and harmonic ECR (2 : 1 at $\theta \approx 77^\circ$ and 1 : 2 at $\theta \approx 42^\circ$)

in which the transition 2—3 takes part, is given by (see Fig. 1)

$$E^{1:1}_{max} : E^{2:1}_{max} : E^{1:2}_{max} \approx 3 : 2 : 5,$$

which corresponds to (12)—(15) under the condition that all the partial probabilities of the spin-lattice relaxation w_{ij} are equal (this ensures also equality of the times τ_1^{ij} and τ_1^{kl}). We note that this uncovers a possibility of estimating the ratios of the quantities w_{ij} from the NCRP results.

From the experimental values of Δ_0 we can, using expressions (13) and (15), determine the value of γH_L. It follows from Fig. 2 that Δ_0 is approximately equal to 210 and 150 MHz respectively for C equal to 0.03 and 0.02%. Assuming $\tau_1' \approx \tau_{1e}/2$, we obtain from (15′) for these concentrations $\gamma H_L \approx 70$ and 50 MHz. These values greatly exceed $\delta\nu_0$ (see the table); the possible causes of this discrepancy will be discussed below.

5. The conclusion that T_{ss} and T_n can become equalized independently of the saturation of the "forbidden" electron-nuclear transitions is reached also on the basis of experiments aimed at observing the EPR line shape (see section II, article 2). In fact, a single application of a microwave pulse of duration $\tau_p \ll \tau_{1e}$, preceding the observation of the form $\overline{P}(\Delta')$, can lead to saturation of the "forbidden" transition only in the case when $t_p W_\pm \gg 1$. In our experiments, however, the line shape shown in Fig. 4a was observed already at a relatively low power of the saturating pulse, at which only the condition $t_p W_0 \approx 5-10$ was satisfied. Inasmuch as $W_\pm/W_0 \ll \tau_{1e}/\tau_{1n}$ (the equal sign holds in the limiting case when τ_{1n} is determined entirely by the spin-lattice relaxation of the electronic Zeeman system), it follows that $t_p W_\pm \lesssim 10^{-1}$ for C = 0.03% and $T_0 = 1.9°$K, i.e., the microwave pulse does not have time to saturate the "forbidden" transition. Since actually the ratio $W_\pm/W_0 \sim \sigma$ is even smaller according to the estimate given above, $\sigma \sim 10^{-5}$), in can be stated that the shift of T_{ss}, up to values of T_n, does not arise in these experiments under the influence of the microwave pulse, but exists already before its turning on, being due to the direct coupling between the SS and Z_n reservoir.

6. This, in particular, constitutes the difference between our procedure and that of Lamb et al.[25], who observed the influence of polarization of nuclear spins on the EPR line shape during its continuous saturation. Under these conditions, the separation of the mechanisms corresponding to the terms $W_\pm$ and τ_{sn}^{-1} becomes impossible. We note that the interpretation of the "distant ENDOR" phenomenon, proposed in[25], is insufficient, since it does not take into account the role of the electron spin-spin interactions, and particularly the cross relaxation between the spin packets in the EPR line. Moreover, it remains unclear how the nuclear spin diffusion can proceed from the nearest neighbors of the paramagnetic ion to the distant nuclei, which have an entirely different resonance frequency. These contradictions can be easily eliminated by assuming that the SS reservoir is in thermal contact with both the close and distant nuclei, and that $T_n = T_{ss}$.

7. To explain the results of the experiments described in section III, article 3, it is also necessary to assume that T_{ss} is determined by the temperature of the Z_n system. Inasmuch as the specific heat c_{zn} is large, T_n cannot be altered in practice within the time of action of one saturating pulse; as to $|T_{ss}^{-1}|$, this quantity should first increase under the influence of the saturating field to a value (see[7]) $\Delta''\nu_e[(\Delta'')^2 + (\gamma H_L)^2]^{-1} T_0^{-1}$, and then tend, with a time constant $\sim \tau_{sn}$, to a stationary value $|T_n^{-1}|$ (this also follows from[7], if it is recognized that when $\tau_{sn} \ll \tau_{1e}, \tau_1'$ the nuclei assume the role of the lattice for the SS system)[1)]. Simultaneously, the stationary value of T_e^{-1} is also established with the same time constant, i.e., $\tilde{P}(0)$. It is clear that if $t_p \sim \tau_{sn}$ or shorter, then $\tilde{P}(0)$ will not have time to reach the stationary value (6). This apparently can explain the weakening of the effect in the case when the saturation with detuning Δ'' is effected with a short pulse, if it assumed that $\tau_{sn} \sim t_p = 0.1$ msec.

8. Let us now discuss the mechanism of the spin lattice relaxation of the nuclei. We estimate first the quantity

$$\tau_{sn} \sim \frac{c_{ss}}{c_{zn}} \sigma^{-1} \tau_{2e}, \tag{16}$$

which determines the time of relaxation of the SS system to the Z_n system. At C = 0.03%, the contribution of the homogeneous broadening of the EPR line is ~ 3 Oe[22], i.e., $\tau_{2e} \sim 3 \times 10^{-8}$ sec; assuming $\sigma \sim 10^{-5}$ and $c_{ss} \ll c_{zn}$, we obtain $\tau_{sn} \ll 3 \times 10^{-3}$ sec. Thus, the relation $\tau_{sn} \ll \tau_1'$, which is necessary to shift T_{ss} during the process of nuclear relaxation to the temperature T_n[11], is satisfied. Another condition formulated in[11], namely $(c_{zn}/c_{ss})\,\tau_{sn} \ll \tau_{nl}$ is also satisfied (see Sec. V, article 2), and it can be assumed that in our experiments the spin-lattice relaxation of the nuclei actually proceeds via the SS reservoir, the "bottle neck" of the relaxation process being the SS-lattice section (see Sec. IV, article 2). In this case, as shown in[11], the following relation holds true

$$\tau_{1n}^{-1} \approx \frac{c_{ss}}{c_{zn}} (\tau_1')^{-1} + \tau_{nl}^{-1}. \tag{17}$$

Assuming that (11) is satisfied, we neglect τ_{nl}^{-1} and obtain

$$\frac{c_{zn}}{c_{ss}} = \frac{\tilde{N}_n \nu_n^2}{\tilde{N}_e (\gamma H_L)^2} = \frac{2\tau_{1n}}{\tau_{1e}} \tag{18}$$

For C = 0.03%, $H_0 = 3340$ Oe, and $\nu_n = 3.7$ MHz we have $c_{zn}/c_{ss} \approx 10^2$ and $\gamma H_L \approx 32$ MHz. For C = 0.02% we obtain in exactly the same manner $\gamma H_L \approx 30$ MHz. The obtained values of γH_L are in good agreement with the width of the EPR line $\delta\nu_0$ (see the table), which undoubtedly argues in favor of the proposed interpretation. The fact that these values turn out to be much closer to the total line width than to the homogeneous width confirms the remark above (Sec. III, article 1) that the entire EPR line, in spite of the ap-

[1)]It must be emphasized that rapid passage through resonance (i.e., one overtaking the couplings between the electron spins and the lattice and its analogues, for example nuclei) under microwave saturation condition is at each instant an isentropic process, and not adiabatic in the quantum-mechanical sense (after Ehrenfest [26]). The well known fact that a negative Zeeman temperature can be obtained as the result of a complete isentropic passage through the EPR line is also evidence in favor of the existence of an electronic spin-spin temperature.

preciable fraction of inhomogeneous broadening, should behave as one entity. Apparently, this means that the energy of the hyperfine interaction of the chromium ion with the nearest nuclei, which is responsible for the inhomogeneous broadening of the line, must be included in the SS reservoir. The experimentally observed dependence $\tau_{1n} \backsim H_0^2$ also agrees with (17), inasmuch as $c_{zn} \backsim \nu_n^2 \backsim H_0^2$.

Using (16) and (18), we can now estimate τ_{sn} more accurately. For C = 0.03% we obtain $\tau_{sn} \sim 30$ μsec; this value agrees with the estimate made in Sec. V, article 7.

9. We now proceed to analyze the data on the spin-lattice relaxation of Al^{27} nuclei under ECR conditions in ruby. The equations of this process can be written by adding to the cross-relaxation equations[3,7] terms that take into account the direct coupling of the SS with the nuclei. Let us consider the cross relaxation between spins of two kinds k and 1, $\nu_k - \nu_l = \Delta$, and assume, to simplify the calculation, that $\tau_{1e}^k = \tau_{1e}^l = \tau_{1e}$. Then, denoting

$$x = \Delta/T_{ss}, \quad \xi = \frac{\nu_k}{T} - \frac{\nu_l}{T_l}, \quad \eta = \frac{\nu_n}{T},$$
$$\alpha = \frac{\tilde{N}_k \tilde{N}_l}{\tilde{N}^2} \frac{\Delta^2}{(\gamma H_L)^2},$$

where $\tilde{N} = \tilde{N}_k + \tilde{N}_l$, we obtain the system of equations

$$\dot{\xi} = -w_{cr}(\xi - x) - \frac{1}{\tau_{1e}}(\xi - \xi_0),$$
$$\dot{x} = \alpha w_{cr}(\xi - x) + \frac{1}{\tau_{sn}}\left(\frac{\Delta}{\nu_n}\eta - x\right) - \frac{1}{\tau_1'}(x - x_0),$$
$$\dot{\eta} = -\frac{c_{ss}}{c_{zn}}\frac{1}{\tau_{sn}}\left(\eta - \frac{\nu_n}{\Delta}x\right) - \frac{1}{\tau_{nl}}(\eta - \eta_0).$$

An approximate calculation with allowance for w_{cr}, $\tau_{sn}^{-1} \gg \tau_{1e}^{-1}, (\tau_1')^{-1}$, and $c_{ss} \ll c_{zn}$, yields

$$\tau_{1n}^{-1} = \frac{c_{ss}}{c_{zn}}\left(\frac{\alpha}{\tau_{1e}} + \frac{1}{\tau_1'}\right) + \tau_{nl}^{-1}. \quad (19)$$

Comparing τ_{1n} from (19) with the initial $(\tau_{1n})^0$ in the absence of ECR (for which it suffices to put $\alpha = 0$ in (19)), we note that τ_{1n} is appreciably shortened symmetrically on both sides of the point $\Delta = 0$; this was indeed observed in the experiment.

An analogous approximate calculation for ECR between transitions in a non-equidistant four-level spectrum (similar to the ruby spectrum) yields the same formula (19) with $\alpha = \Delta^2/18(\gamma H_L)^2$. From an analysis of (19) it may appear that τ_{1n} should decrease without limit with increasing $|\Delta|$. This, however, is only the consequence of the approximations made. It can be shown that at sufficiently large Δ, when w_{cr} decreases and the "bottle neck" of the relaxation process arises already in the section SS → ξ, it is necessary to replace α/τ_{1e} in (19) by αw_{cr}. On the other hand, if w_{cr} is very large even in the case of large $|\Delta|$, then $\tau_{1n} \to \tau_{1e}$, as is observed at C = 0.08%.

10. Remark concerning the value of γH_L. It was noted above that the value of γH_L determined from Δ_0 in NCRP experiments, greatly exceeds $\delta\nu_0$, and also γH_L determined from relaxation measurements. It seems to us that this discrepancy may be connected with the influence of the distant wings of the EPR line, due to the relatively strong spin-spin interactions of the closely-located pairs or groups of ions (of course, we are not referring here to the strongly coupled "exchange pairs," whose energy is comparable with or exceeds $h\nu_e$). Such interactions should apparently no longer be included in the SS reservoir, and the coupling with them can be effected only via cross relaxation. A rigorous allowance for the distant wings of the line calls for the construction of the corresponding theory, which so far is nonexistent.

Another possible cause of the increase of Δ_0 may be the "extraneous" relaxation (outside the SS reservoir), not accounted for in the calcuation, with a time τ_{nl}^l. It is also possible that introduction of single temperature T_n is too rough an approximation at the considered paramagnetic-impurity concentrations.

CONCLUSIONS

1. The aggregate of the obtained experimental data on NDP and spin-lattice relaxation of nuclei in ruby can be interpreted under the assumption that there exists an electronic spin-spin temperature T_{ss}, which becomes equalized with the Zeeman temperature of the nuclei T_n as the result of the SS-Z_n thermal contact. In EPR saturation, this connection between T_n and T_{ss} leads to nuclear polarization, and in the absence of microwave power it leads to spin-lattice relaxation of the nuclei.

The described model has enabled us not only to describe consistently many of the observed phenomena, but also to predict some new effects, including NDP during cross relaxation in the electronic system (NCRP) and the influence of power at the NMR frequency on the saturation transfer in electronic cross relaxation.

2. The main difficulty in our interpretation is the difference between the values of γH_L, obtained in the analysis of experiments in the presence and in the absence of saturating microwave power. This problem is connected, in our opinion, with the need for consistently taking into account the contribution of the inhomogeneous broadening of the EPR line in these two cases, i.e., with the development of a theory of NDP in magnetically-diluted crystals at $\gamma H_L \sim \nu_n$.

3. The connection observed by us between the electronic cross relaxation, NDP, and the EPR line shape under saturation conditions makes it possible to use new methods for the investigation of each of these phenomena. In particular, an exceedingly sensitive method is created for the study of electronic cross-relaxation processes by observing nuclear polarization, etc. It is possible that the control of the electronic cross-relaxation process by saturating the NMR signal will also find an application in research practice.

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186