at certain orientations of the magnetic field are caused either when the ground state crosses two consecutive excited states or when the ground state crosses one excited state for different crystallographically nonequivalent positions of RE ions with different splitting of terms due to different orientation of the oxygen dodecahedron relative to crystallographic axes.[2,8]

It is necessary to take it into account that the character of the magnetization anomalies associated with the crossing of levels in ferrimagnets is affected by the "magnetic Jahn–Teller effect,"[17,18] which causes deviation of the magnetization of the iron sublattice from the direction of the field. Therefore, it is apparently possible to consider from a single point of view both effects that account for the anomalies of magnetization in yttrium-holmium iron garnets in strong fields, i.e., crossing of the levels of the Ho^{3+} ion and formation of a noncollinear magnetic sublattice structure, (for details see[17]).

We thank K. P. Belov for his interest to this study, A. K. Zvezdin and A. I. Popov for valuable discussions, and A. S. Markosyan for growing the single-crystal iron garnets.

[1)]The plot of the magnetization along the [111] axis shows a jump in weak fields. Calculations suggest that it is associated with the first-order phase transition of the saturation along the hard axis in cubic ferromagnets with a positive magnetic anistropy constant.

[2)]Our measurements have shown that the width of hysteresis depends somehow, possibly because of relaxation phenomena, on the rate of field variation.

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Establishment of equilibrium between the electron dipole pool, the nuclear spins, and the lattice of a paramagnet

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The processes that take place when equilibrium is established in the electron-nuclear spin system of ruby crystals are investigated at helium temperatures. The existence of a strong coupling between the dipole-dipole pool (DDP) of the Cr^{3+} ions and the Zeeman subsystems of the ^{27}Al ions is confirmed. The parameters of this coupling are determined, as well as the rate of spin-lattice relaxation of the DDP, whose temperature was directly determined in the course of these processes by measuring the longitudinal magnetic susceptibility due to the cross relaxation of the Cr^{3+} ions. It is shown that the coupling between the DDP and the nuclei can be broken by modulation saturation of the DDP with an alternating longitudinal field. The results indicate that an appreciable fraction (up to 30%) of the ^{27}Al nuclei is coupled to the DDP more strongly than with the remaining nuclei, and for some reason makes no contribution to the observed NMR signal. A final interpretation of the results calls for a further development of the theory of nuclear relaxation, with allowance for spin diffusion.

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1. INTRODUCTION AND FORMULATION OF THE PROBLEM

It is known that in solids there can exist a strong coupling between the electron dipole–dipole pool (DDP) of a paramagnetic impurity and the Zeeman subsystem of the nuclear spins of the lattice (Z_n), and this coupling leads to equalization of the temperatures T_d and T_{Zn} of these subsystems. This phenomenon (the so-called "direct thermal contact" between the DDP and Z_n) was theo-

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retically predicted in 1964–65[1,2] and was soon observed experimentally in ruby crystals,[3] and later in other objects (see, e.g., the reviews[4–6]). It has turned out that at low temperatures the direct thermal contact with the DDP frequently ensures the most effective coupling channel between Z_n and the lattice, and can therefore play a decisive role in such important phenomena as the dynamic polarization and the spin-lattice relaxation of nuclei, ENDOR, etc.

To date, however, only the very existence of the thermal contact between the DDP and Z_n could essentially be established, while practically nothing is known at present concerning the kinetics of the establishment of equilibrium between these subsystems (and, incidentally, concerning the spin-lattice relaxation of the DDP).[1)] The point is that the only method of measuring T_d has so far been by observing the antisymmetrical component in the ESR absorption line (or in a group of lines connected with the effective cross relaxation).[4,5] This component, which is itself quite weak, is furthermore observed against the background of a strong symmetrical signal due to the Zeeman subsystem of the electron spins. This circumstance has not made it possible to trace reliably and with sufficient accuracy the variation of T_d during the transient processes, and consequently made it impossible to obtain information on the coupling between the DDP, Z_n, and the lattice.

Another method of determining T_d was recently proposed, based on a measurement of the longitudinal susceptibility of the paramagnet, and in particular the cross-relaxation susceptibility χ_{CR}, under conditions when the DDP is cooled.[8] We shall show that the use of this method can yield a detailed picture of the relaxation processes in the Z_n+DDP+lattice system. In view of the importance of this method in what follows, we shall dwell on the physical meaning of the quantity χ_{CR}.

It is known that an effective (i.e., rapid in comparison with the spin-lattice relaxation) cross relaxation (CR) between two spin subsystems α and β, having close resonance frequencies $\omega_\alpha \approx \omega_\beta$, causes a dynamic equilibrium to be established, characterized by the relation

$$\omega_\alpha/T_\alpha - \omega_\beta/T_\beta = \gamma_d \Delta_{\alpha\beta}, \tag{1}$$

where $\Delta_{\alpha\beta} = \omega_\alpha - \omega_\beta$; $\gamma_d \equiv 1/T_d$; T_α and T_β are the Zeeman temperatures of the subsystems α and β.[9,4]

In crystals containing paramagnetic ions with spin $S > 1/2$ and characterized by multilevel nonequidistant energy spectra, the subsystems α and β are usually various pairs of energy levels, and the detuning $\Delta_{\alpha\beta}$ depends strongly as a rule on the external magnetic field H_0. This means that any small increment δH of the field H_0 produces in such systems a change of $\Delta_{\alpha\beta}$, and this in turns upsets the equilibrium (1) and stimulates CR processes that lead ultimately to changes of the temperatures T_α and T_β, i.e., to a redistribution of the electron spins among the energy levels. Since, however, each level ε_i has its own corresponding value of the effective magnetic moment $\mu_i = -d\varepsilon_i/dH_0$ (we recall that in this case the dependence of ε_i on H_0 is in general nonlinear), it follows that this redistribution produces an increment δM_z to the total longitudinal magnetization of the sample, i.e., it leads to the appearance of a nonzero CR susceptibility $\chi_{CR} = \delta M_z/\delta H_0$.

It is clear even from (1) that χ_{CR} depends directly on γ_d; this is confirmed by exact calculations.[8] Without citing here the complete formulas, we confine ourselves to the expression for the imaginary part of the CR susceptibility χ''_{CR} when measured at a frequency $\Omega \gg \tau_{CR}^{-1}$, where τ_{CR} is the CR time:

$$\chi_{CR}''(\Omega) = B\gamma_d w_{CR}(\Delta_{\alpha\beta})/\Omega, \tag{2}$$

where B is a constant that depends on the values of μ_i in the CR region, and $w_{CR}(\Delta_{\alpha\beta})$ is the CR probability as a function of the detuning.

Thus, at fixed values of $\Delta_{\alpha\beta}$ and Ω, the quantity χ''_{CR} is directly proportional to γ_d and can serve as a direct "thermometer" for the DDP. This, incidentally, is the basis of the effect of "enhanced longitudinal susceptibility," in which the cooling of the DDP with the aid of microwave pumping leads to a sharp increase of χ_{CR}.[8] We note that "enhanced susceptibility" signals of another kind, connected with spin-lattice or spin–spin relaxation in a rotating coordinate frame (χ_1 and χ_s in[8]), are not suitable for the study of DDP relaxation since, in contrast to χ_{CR}, they vanish simultaneously when the microwave pump is turned off.

Taking into account the foregoing possibility of directly measuring T_d with the aid of χ''_{CR}, we shall discuss the experimental setup.

2. EXPERIMENTAL SETUP AND EXPECTED RESULTS

Figure 1 shows schematically the relations between the subsystems Z_n, DDP, and the lattice (the direct Z_n–lattice relaxation can usually be neglected[4]). This scheme ascribes to each subsystem, at any instant of time, a definite temperature; with respect to Z_n this assumption is quite stringent, since it confines the analysis to the case of rapid spatial diffusion of the nuclear spin.

Assume that the DDP and Z_n are initially in disequilibrium with the lattice, say "cooled" by the action of a microwave, and assume that at the instant $t = 0$ this field is turned off, and free relaxation to the lattice temperature $T_0 \equiv \gamma_0^{-1}$ takes place. The corresponding equations for the reciprocal temperatures γ_d and $\gamma_{Zn} \equiv T_{Zn}^{-1}$ are[2]

$$\dot\gamma_d = -\tau_{dn}^{-1}(\gamma_d - \gamma_{Zn}) - \tau_{dl}^{-1}(\gamma_d - \gamma_0), \tag{3a}$$

$$\dot\gamma_{Zn} = -\tau_{nd}^{-1}(\gamma_{Zn} - \gamma_d). \tag{3b}$$

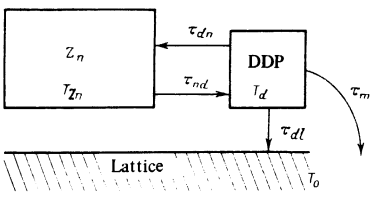

FIG. 1. Connections between the nuclear Zeeman subsystem (Z_n), the DDP, and the lattice.

Here τ_{dn}, τ_{nd}, and τ_{dl} are the characteristic relaxation times, the meaning of which is clear from Fig. 1, with $\tau_{nd}/\tau_{dn} = c_{Zn}/c_d \equiv k$, where c_{Zn} and c_d are the specific heats of Z_n and the DDP.

Under initial conditions $\gamma_d(0) = \gamma_{Zn}(0)$ the relaxation $\gamma_d(t)$ consists of two exponentials, "fast" and "slow," with amplitudes A_f, A_{sl}, and with respective times τ_f and τ_{sl}. Under the usually realized condition $k \gg 1$ we have

$$\tau_f^{-1} = \tau_{dn}^{-1} + \tau_{dl}^{-1}, \quad \tau_{sl} = \tau_{nd} + k\tau_{dl}, \quad A_{sl}/A_f = \tau_{dl}/\tau_{dn}. \tag{4}$$

Under the same conditions, the nuclear relaxation $\gamma_{Zn}(t)$ will be practically singly-exponential, with a time $\tau_{1n} = \tau_{sl}$.

Thus, by observing simultaneously the relaxation curves $\gamma_d(t)$ and $\gamma_{Zn}(t)$ we can verify the model of Fig. 1 and determine the material parameters τ_{dn}, τ_{dl}, and k of interest to us. It is clear from (4), however, that under the conditions of relaxation "bottleneck" on the DDP–lattice section (when the "bottleneck factor" is $\sigma \equiv \tau_{dl}/\tau_{dn} \gg 1$), the rapid exponential becomes unobservable and it is impossible to determine the time of coupling between Z_n and the DDP.

To get around this difficulty, we have employed a special procedure that allows the experimenter to regulate at will the rate of the DDP relaxation, and by the same token obtain the required relation between A_{sl} and A_f. We took into account the circumstance that a fraction of the energy of the alternating longitudinal field $h\cos\Omega t$ used to measure the susceptibility $\chi''_{CR}(\Omega)$ is absorbed by the electron spin system, causing additional heating of the DDP (we recall that χ''_{CR} is precisely the coefficient of this absorption). So long as the heating rate τ_m^{-1}, which is proportional to h^2, is small in comparison with τ_{dl}^{-1}, this effect can be neglected, but with increasing amplitude h the heating becomes substantial and must be taken into account by adding to the right hand side of (3a) the term $-\tau_m^{-1}\gamma_d$.

We note that this effect is identical to the "modulation saturation" of the DDP, which is described in[10], and is physically due to the nonadiabaticity of the change of $\Delta_{\alpha\beta}$ under the influence of a longitudinal field of frequency $\Omega \gtrsim \tau_{CR}^{-1}$.

Neglecting at $\gamma_d(0) \gg \gamma_0$ the difference between γ_0 and zero, we can assume that modulation saturation produces an additional coupling channel between the DDP and the lattice (Fig. 1), with τ_{dl}^{-1} replaced by the effective rate $(\tau_{dl}^e)^{-1} = \tau_{dl}^{-1} + \tau_m^{-1}$. It is clear that if h is increased sufficiently it is always possible to ensure satisfaction of the condition $\tau_{dl}^e \ll \tau_{dn}$, i.e. "lock" the DDP to the lattice and shift the relaxation bottleneck to the Z_n–DDP section. In this case, as is clear from (3) and (4), it becomes possible to measure directly the time τ_{nd}, which in this case becomes simply equal to τ_{sl} and τ_{1n}.

3. EXPERIMENT

The experiments were performed on ruby ($Al_2O_3 : Cr^{3+}$) crystals with chromium concentration 0.035 at.%, i.e., 1.75×10^{19} cm^{-3}, at temperatures 4.2 and 2.0 K. The choice of the substance was dictated by the presence of convenient variants of CR in the four-level system of the Cr^{3+} ion, and also by the fact that direct thermal contact between the DDP of the Cr^{3+} ions and Z_n of the ^{27}Al nuclei has already been observed in ruby earlier.[3]

We chose for the measurements three variants of CR in the ruby spectrum; information on these variants are given in Table I (θ is the angle between H_0 and the crystallographic axis; the subscripts of ω_{ij} label the energy levels of chromium in ascending order). The enhancement of χ''_{CR} in these variants was described by us earlier[11–13]; these references give also the dependences of ω_{ij} on H_0 in the CR region. We note that in case C ($H_0 = 0$) we have twofold degeneracy of the levels $\pm 1/2$ and $\pm 3/2$, so that we are dealing, strictly speaking not with CR in the usual sense, but with spin–spin relaxation in a zero field; this, however, does not affect the proportionality of χ''_{CR} and γ_d.

We determined χ''_{CR} by recording the absorption of the alternating longitudinal field $h\cos\Omega t$, measured at a frequency $\Omega \approx 2\pi \cdot 1$ MHz with the aid of a longitudinal coil wound around the sample and connected to a standard autodyne receiver. A second coil, crossed with the first, was used for simultaneous registration of the NMR from the ^{27}Al nuclei.

In all cases, the experiments were performed at $\Delta_{\alpha\beta} = 0$. This ensured satisfaction of the conditions of effective CR ($\tau_{CR} \ll \tau_{1e}$, τ_{dl}, where τ_{1e} is the time of the electron-Zeeman spin-lattice relaxation), and also yielded the maximum value of χ''_{CR} in accordance with (2). To observe the χ''_{CR} signal we used shallow modulation of the detuning $\Delta_{\alpha\beta}$ at a frequency 50 Hz, by suitably modulating the field H_0. As seen from (2), the function $\chi''_{CR}(\Delta_{\alpha\beta})$ has a maximum at $\Delta_{\alpha\beta} = 0$, so that a signal at double the modulation frequency was separated in the receiver. The amplitude of this low-frequency modulation (several oersteds) was low enough to avoid modulation saturation of the DDP.

The preliminary polarization of the ^{27}Al nuclei and the cooling of the DDP were effected by saturating the wing of one of the ESR lines at 9.3 GHz (in cases A and B) or 11.4 GHz (in case C). As already reported,[11,13] in all three cases this led to equalization of the temperatures T_d and T_{Zn}, and the amplication of the nuclear polarization reached 20. After turning off the microwave field, the χ''_{CR} and NMR signals, which were proportional to γ_d and γ_{Zn}, respectively, returned to the equilibrium values. These curves were recorded with an oscilloscope.

We begin the description of the results with variant A ($H_0 = 4500$ Oe). Figure 2 shows several $\chi''_{CR}(t)$ relaxation curves obtained at $T_0 = 4.2$ K with different amplitudes of the alternating longitudinal field h. It is seen that the relaxation process is doubly exponential, and with increasing h the characteristic times of both exponentials (τ_f and τ_{sl}) become shorter and the relative amplitude of the faster of the two increases. Simultaneous measurements of the NMR signals has shown that at all values of h the relaxation of the nuclei remains

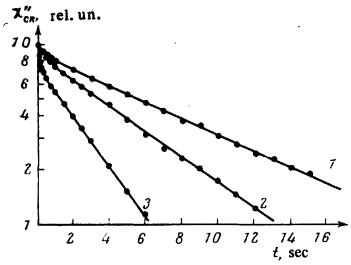

FIG. 2. Relaxation of longitudinal-susceptibility signal $\chi'_{CR}(\Omega)$ in variant A at $T_0 = 4.2$ K, $\Omega = 2\pi \cdot 1$ MHz, and longitudinal alternating field amplitudes h (in relative units): 1–1.0, 2–6.0, and 3–12.0. Points–experiment, curves–sums of two exponentials.

singly exponential, the time τ_{1n} decreasing with increasing h and always equal to τ_{s1} (this result was confirmed for each of the five NMR lines of ^{27}Al separated by the quadrupole splitting).

Plots of τ_{s1}, τ_f, and A_{s1}/A_f against h are shown in Figs. 3–5; it is seen from Fig. 3, in particular, that as h increases τ_{s1} tends to a constant value that should be identified, in correspondence with (3) and (4), with the time τ_{nd}.

A qualitative agreement is thus observed between the relaxation picture and the model of Fig. 1. The experimental values of τ_{s1}^{∞}, τ_{s1}^{0}, τ_f^0, and $(A_{s1}/A_f)^0$ are listed in Table I (the superscripts 0 and ∞ denote here and throughout the asymptotic values of the corresponding quantities as $h \to 0$ and $h \to \infty$).

Preliminary estimates made in a comparison of these data with (4) have shown that, despite the expectations, the condition $k \gg 1$ is not satisfied. A detailed reduction of the results was therefore carried out with the aid of an exact solution of the system (3), which leads to the following relations between the measured quantities and the material parameters of interest to us:

$$\tau_{dl} = \tau_{s1}^{0}\tau_f^{0}/\tau_{s1}^{\infty}, \tag{5}$$

$$k = (\tau_{s1}^{0} - \tau_{s1}^{\infty})(\tau_{s1}^{\infty} - \tau_f^{0})/\tau_{s1}^{0}\tau_f^{0}, \tag{6}$$

$$(A_{s1}/A_f)^0 = (\tau_{s1}^{0} - \tau_{s1}^{\infty})/(\tau_{s1}^{\infty} - \tau_f^{0}). \tag{7}$$

To find the unknowns τ_{dl} and k we used formulas (5) and (6) and the equality $\tau_{s1} = \tau_{nd}$, which remains in force for all k. The results obtained in this manner are given in Table I, where the values of the bottleneck factor σ are also indicated. We note immediately that the obtained value $k = 3.6$ turned out to be much less than the expected $k \sim 10^3$, while the time $\tau_{dl} = 2.0$ sec greatly exceeded $\tau_{1e} \approx 0.2$ sec, [14] results that are utterly unrealistic. We defer the discussion of these circumstances to Sec. 4.

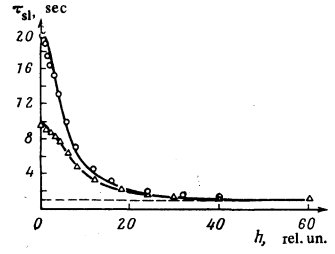

FIG. 3. Time constant τ_{s1} of the "slow" exponential vs the amplitude of the alternating field h in variant A: △–at 4.2 K, ○–2.0 K; curves–theory, dashed line–asymptotic value $\tau_{s1}^{\infty} = \tau_{nd}$.

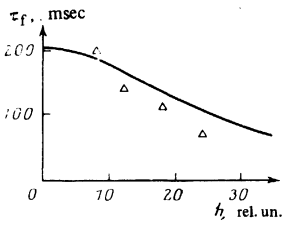

FIG. 4. Time constant τ_f of the "fast" exponential vs the amplitude of the longitudinal alternating field h in variant A at 4.2 K. Curve–theory.

Relation (7) is redundant and was used only as a control. Comparison of the "theoretical" value $(A_{s1}/A_f)^0_{theor}$ obtained from (7) with the experimental value, as seen from Table I, leads to good agreement, which undoubtedly argues in favor of the employed model.

Figures 3–5 show also the "saturation curves," i.e., the calculated dependences of all the measured quantities on the amplitude h. These curves were obtained with the aid of Eqs. (3) supplemented by the term $-\tau_m^{-1}\gamma_d$, using the previously obtained values of τ_{nd}, τ_{dl}, and k. The required coefficient of proportionality of τ_m^{-1} to h^2 was obtained from one of the points on the experimental plot of $\tau_{s1}(h)$ in Fig. 3. It is seen that the saturation curves also agree well with the experimental data.

Similar measurements were made at $T_0 = 2.0$ K. As seen from Fig. 3 and Table I, the lowering of the temperature has led to an increase of τ_{s1}^0 and σ, whereas the time $\tau_{s1}^{\infty} = \tau_{nd}$ remained unchanged. The same figure shows the calculated $\tau_{s1}(h)$ curve for 2.0 K, obtained under the assumption that k is independent of T_0 and that $\tau_{dl} \propto T_0^{-1}$. It is seen that the agreement between this curve and the experimental data is beyond any doubt.

We proceed to variant B ($H_0 = 1250$ Oe). Several relaxation curves for this case are shown in Fig. 6, and the results of the reduction of the data by the procedure described above are given in Table I. Figure 7 shows plots of $\tau_{s1}(h)$ for 4.2 and 2.0 K; just as before, the nuclear relaxation time τ_{1n} was always equal to τ_{s1}.

It is seen that this variant does not differ in principle from case A, but notice must be taken, besides the shortening of all the characteristic times, of an appreciable increase of the specific weight of the rapid expo-

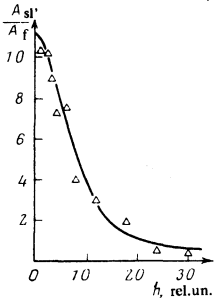

FIG. 5. Dependence of the ratio A_{s1}/A_f of the amplitudes of the "slow" and "fast" components on the amplitude of the longitudinal alternating field h in variant A at 4.2 K. Curve–theory.

TABLE I.

Variant	H_0, Oe	θ	CR conditions	T_0, K	$\tau_{s1}^{\infty}=\tau_{nd}$, sec	τ_{s1}^{0}, sec	τ_f^0, msec	$\left(\frac{A_{s1}}{A_f}\right)^0_{exp}$	$\left(\frac{A_{s1}}{A_f}\right)^0_{theor}$	τ_{dl}, sec	k	σ
A	4500	34°	$\omega_{12}=\omega_{24}$	4.2	1.0±0.05	10.0±0.1	200±20	10.5±1	11.2±1	2.0±0.2	3.6±0.3	7.1±1
				2.0	1.0±0.05	20.0±0.2	–	≫1	25±3	4.2±0.3	3.6±0.3	15.0±2
B	1250	26°	$\omega_{23}=\omega_{34}$, $\omega_{12}=\omega_{24}$	4.2	0.45±0.03	1.45±0.05	130±15	3.2±0.8	3.1±0.5	0.42±0.04	1.7±0.2	1.6±0.2
				2.0	0.45±0.03	2.45±0.05	160±20	4.8±1.5	6.9±1.5	0.87±0.08	1.5±0.2	2.9±0.3
C	0	–	$\pm 1/2$; $\pm 3/2$	4.2	–	0.060±0.005	–	≫1	–	0.060±0.005	≫1	≫1
				2.0	–	0.13±0.02	–	≫1	–	0.13±0.02	≫1	≫1

nential, thus indicating a decrease of the bottleneck factor σ.

The results for 2.0 K were reduced here independently of the data obtained at 4.2 K. As seen from Table I, the parameters τ_{nd} and k are again practically independent of temperature, whereas the time τ_{dl} has increased approximately in proportion to T_0^{-1}. We note that in this variant the CR conditions are more sensitive to exact settings of H_0 and θ, and the measurement error is therefore somewhat larger here.

Finally, in a zero magnetic field (case C) we have always observed a strictly singly-exponential $\chi''_{CR}(t)$ curve with a characteristic time τ_{s1} that decreased with increasing h. Simple estimates show that in this case $c_{Zn} \ll c_d$ (Z_n is in this case the quadrupole subsystem of the ^{27}Al nuclei), so that the nuclear spins cannot influence the DDP relaxation, and therefore the time τ_{s1}^0 is simply equal here to τ_{dl}. Numerical values of τ_{dl} are given in Table I and again attest to the relation $\tau_{dl} \propto T_0^{-1}$. We note that this experiment has made it possible in practice, for the first time, to measure directly the time τ_{dl} for an electron spin system.

Simultaneous observation of nuclear relaxation at $H_0 = 0$ at the frequency of the quadrupole splitting of ^{27}Al (715 kHz) has shown that this process follows at all values of h the same law as the relaxation of $\chi''_{CR}(t)$, i.e., a single exponential with a time $\tau_{1n} = \tau_{s1}$ is observed at all times. This indicates that the coupling between Z_n and the DDP is in this case so strong that it cannot be "broken" by modulation saturation.

4. DISCUSSION OF RESULTS

4.1. Specific heat and spin-lattice relaxation of DDP

As seen from the preceding section, the model of direct thermal contact, based on the simplest scheme of Fig. 1 and on Eqs. (3), is formally well confirmed in each of the investigated cases. However, as already remarked, the values of τ_{dl}^{A} and τ_{dl}^{B} obtained on the basis of this model greatly exceed τ_{1e}, a result that is utterly unlikely (the superscripts A, B, and C indicate from now on the variant to which the given quantity pertains). The values of k^A and k^B also contradict the reasonable estimates; furthermore, the dependence of k on H_0 turns out to be much weaker than the quadratic dependence that follows from the relation

$$k = N_n I(I+1)\omega_n^2 / N_e S(S+1)\omega_d^2, \qquad (8)$$

where the spin of the nucleus is $I = 5/2$, the electron spin is $S = 3/2$, ω_n and ω_d are the NMR frequency and the average ("local") DDP frequency, and N_n and N_e are the numbers of nuclei and electrons per unit volume.

All these patent contradictions can, however, be eliminated by a slight elaboration of the employed model. We assume for this purpose that the nuclear spins that land in the interior of some sphere centered about the Cr^{3+} ion and having a radius ρ ("close" nuclei) are so strongly coupled to the DDP that in the course of the relaxation they constantly have the temperature T_d, while the remaining ("remote") nuclei are much more strongly coupled to one another than to the DDP and the close nuclei, and are characterized by a single temperature T_{Zn}. Under these conditions the specific heat c_ρ of the close nuclei is actually added to the true specific heat c_d^* of the DDP to form the observed quantity c_d. On the other hand, the quantity c_{Zn} in Eq. (3) pertains now only to the remote nuclei, so that $c_{Zn} = c_{Zn}^* - c_\rho$, where c_{Zn}^* is the true specific heat of the entire nuclear subsystem. It is obvious that $c_\rho / c_{Zn}^* = (\rho/R_0)^3$, where $R_0 = (4\pi/3N_e)^{1/3} \approx 25$ Å is the radius of the "sphere of influence" of the paramagnetic ion.

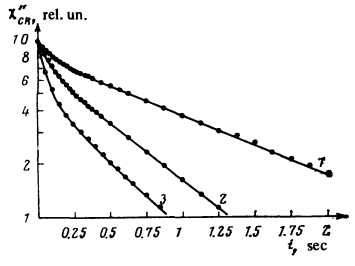

FIG. 6. Relaxation of the signal of the longitudinal susceptibility $\chi''_{CR}(\Omega)$ in variant B at $T_0 = 4.2$ K, $\Omega = 2\pi \cdot 1$ MHz, and longitudinal alternating-field amplitudes h (in relative units) 1.0 (1), 8.0 (2), and 12.0 (3).

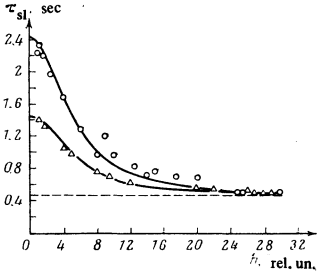

FIG. 7. Dependence of the time constant τ_{s1} on the amplitude of the longitudinal alternating field h in variant B. The notation is the same as in Fig. 3.

TABLE II.

Variant	τ_{dl}^*, sec	k^*	τ_{dn}^*, sec	$\frac{c_\rho}{c_{Zn}^*}$	ρ, Å	C, cm^6/sec	b, Å	D, cm^2/sec
A	$4\cdot10^{-2}$	230	$5.6\cdot10^{-3}$	0.24	15.0	$8.5\cdot10^{-41}$	15.5	$4\cdot10^{-14}$
B	$6\cdot10^{-2}$	18	$3.7\cdot10^{-2}$	0.33	17.5	$9\cdot10^{-40}$	25	—

Taking the foregoing into account, we easily obtain the relations

$$\tau_{dl}/\tau_{dl}^* = (c_d^* + c_\rho)/c_d^*,$$
$$k = \frac{c_{zn}^* - c_\rho}{c_d^* + c_\rho} = k^* \left(\frac{c_{zn}^*}{c_\rho} - 1 \right) \Big/ \left(\frac{c_{zn}^*}{c_\rho} + k^* \right), \quad (9)$$

where τ_{dl}^* is the true spin-lattice relaxation time of the DDP, and $k^* = c_{Zn}^*/c_d^*$ is the true ratio of the specific heats of Z_n and the DDP. Thus, the seeming slowing down of the DDP relaxation is now explained by the fact that the close nuclei, which have no drain of their own to the lattice, play the role of a ballast that makes the dipole subsystem heavier.

If we neglect next the direct contact between the close and remote nuclei via spin diffusion, and assume that the coupling between them is only via the DDP, then we obtain in addition

$$\tau_{dn}/\tau_{dn}^* = (c_d^* + c_\rho)/c_d^*,$$

where τ_{dn}^* is the true time of the DDP relaxation to the remote nuclei, while the previously obtained values of τ_{dn} and σ require no correction.[2)]

Substituting the values of τ_{dl} and k indicated in Table I for the variants A and B in Eqs. (9), recognizing that $c_{Zn}^* \propto H_0^2$, and assuming that $(\tau_{dl}^*)^B = \tau_{dl}^B = 60$ msec, we obtain the corrected values of the parameters of interest to us, which are listed in Table II (for 4.2 K).

The obtained values seem quite reasonable: some shortening of τ_{dl}^* in variant A corresponds fully to the expected dependence of the spin-lattice relaxation time on H_0 in ruby,[14] and from the value of k^* we find with the aid of (8) that $\omega_d \approx 2\pi \cdot 30$ MHz, in splendid agreement with the observed half-width of the ESR lines. It might seem that all the contradictions have been resolved, but unfortunately new complications arise now.

In fact, it follows from the values of c_ρ/c_{Zn}^* and ρ listed in Table II that from 20 to 30% of all the nuclei of the sample turn out to be of the close type, and this should lead to the appearance of a noticeable fast section in the nuclear relaxation, at least at large amplitudes h. This patently contradicts the experimental fact that the relaxation of the nuclei has always obeyed the simple $\exp(-t/\tau_{s1})$ law. We note that this difficulty cannot be attributed to an insufficiently well founded choice of the quantity $(\tau_{dl}^*)^B$ in the calculation, inasmuch as the obtained values of $c\rho/c_{Zn}^*$ are not very sensitive to variations of τ_{dl}^* within reasonable limits. It remains to assume that the close nuclei, for some reason, make no contribution at all to the observed NMR signal, but we are not yet in a position to explain this fact.

Leaving this question open, we note that in the investigated range of T_0 the radius ρ does not depend on the temperature.

From the obtained values of τ_{dl}^* we can obtain the important ratio $a \equiv \tau_{1e}/\tau_{dl}^*$, which plays an important role in the theory of spin temperature. A comparison of our data with τ_{1e}[14] yields $a \approx 4-5$, which differs substantially from the universally accepted value $a = 2-3$. We note that the use of the obtained value of a in the analysis of the old data on dynamic polarization of nuclei in ruby[3] yields, when the corresponding coefficients are taken into account,[16] a value $\omega_d \approx 2\pi \cdot 35$ MHz, which is in fair agreement with the estimate given above.

4.2. Rate of the direct Z_n–DDP thermal contact

Perhaps the most interesting result of the present study can be taken to be the direct measurement of the time τ_{nd}. As seen from Table I, in the investigated range this time is independent of T_0, and its dependence on H_0 is of the form $\tau_{nd} \propto H_0^{0.6}$. Let us compare these data with the theory.

It is known that when account is taken of spin diffusion, the time of relaxation of the nuclear magnetization to the DDP is described by the formulas[17]

$$\tau_{nd} = \delta^3 R_0^3/C \quad \text{at} \quad \delta > b, \quad (10a)$$
$$\tau_{nd} = 1.6\, b^3 R_0^2/C \quad \text{at} \quad b > \delta, \quad (10b)$$

where δ is the radius of the diffusion barrier, b is the potential radius of the paramagnetic ion, and C is the rate of direct relaxation of a nucleus located at unity distance from the ion.

Inasmuch as in our case the correlation time τ_c of the z component of the electron spin, is determined by the spin-spin interaction, it does not depend on T_0; furthermore, τ_c is much shorter than the time τ_{2n} of the nuclear transverse relaxation. It follows hence[17] that in the case (10a) we should observe a relation $\tau_{nd} \propto T_0^{-3/4}$, which does not agree with experiment. We therefore reject this case and proceed to the variant (10b).

Recalling that

$$b = 0.7\,(C/D)^{1/4}, \quad (11)$$

where D is the coefficient of nuclear spin diffusion, we see that formula (10b) actually ensures the observed independence of τ_{nd} of T_0. Taking furthermore into account the explicit expression for C,[17] we conclude that at $(\tau_c \omega_n)^2 \gg 1$ it follows from (10b) that $\tau_{nd} \propto H_0^{1/2}$, which is also in satisfactory agreement with experiment. Thus, it seems that in our case the inequality $b > \delta$ is realized ("diffusion-limited relaxation") and this, unfortunately, is in poor agreement with the employed model, in which the presence of fast diffusion outside a sphere of radius ρ is assumed.

To estimate the time τ_c we shall invoke data on the time of the resonant CR in ruby,[12] namely, $\tau_{CR} \approx 8 \times 10^{-7}$ sec. Since, obviously, $\tau_c < \tau_{CR}$ and, on the other hand $\tau_c > \omega_n^{-1}$, we have

$$10^{-7}\ \text{sec} < \tau_c < 8\cdot10^{-7}\ \text{sec},$$

i.e., $\tau_c \sim 3\times10^{-7}$ sec. Taking this value of τ_c, we obtain the values of C, b, and D listed in Table II.[3)] It is seen that the value $b^A = 15.5$ Å obtained in this manner is strikingly close to the previously obtained value $\rho^A = 15.0$ Å. This of course, favors our model, but the fact that $b^A = 0.6\ R_0$ does not allow us to regard this estimate as accurate enough (we recall that in the derivation of (10b) it was assumed that $(b/R_0)^4 \ll 1$).[17] In addition, at such large values of b/R_0 the nuclear relaxation should exhibit a noticeable non-exponential segment,[17] and this, as already noted, contradicts the experimental data.

In the case of variant B, a formal application of (10b) yields $b^B \approx R_0$. It is clear that formulas (10b) and (11) are not valid in this case; none the less, notice should be taken of the correlation between the behavior of the quantities ρ and b, which increase simultaneously with decreasing H_0 (Table II).

A special situation arises at $H_0 = 0$ (case C). Here owing to the degeneracy of the electronic levels $\pm 1/2$ and $\pm 3/2$, the contact between Z_n and the DDP is ensured not only by the "forbidden" electron-nuclear transitions due to the action of the operators $\hat{S}^z\hat{I}^{\pm}$, but also by the "allowed" electron-nuclear cross relaxation (operators of the type $\hat{S}^{\pm}\hat{I}^{\mp}$), which is much more effective, since it conserves the total mechanical momentum of the system. This argument agrees with the experimentally observed very strong coupling between Z_n and the DDP in this case.

Thus, by using a new method of measuring T_d, we have succeeded in obtaining much valuable information on the relaxation processes in the Z_n + DDP + lattice system. An appreciable part of the experimental facts fits well the framework of the direct thermal contact scheme modified in accordance with Sec. 4.1, but this model can nevertheless not be regarded as fully satisfactory. Its main weakness is that the real continuous spatial distribution of the nuclear polarization has been replaced by a steplike distribution, with a discontinuity at a sphere of radius ρ. It is obvious that such an idealization is justified only under the condition that the time of spin diffusion over a length on the order $R_0 - \rho$, namely $t_D \sim (R_0 - \rho)^2/D$, is small in comparison with all other relaxation times. Estimates show, however, that $t_D \sim \tau_t$, and one cannot exclude the possibility that the rate of relaxation on the initial sections of the $\chi''_{CR}(t)$ curves (Figs. 2 and 6) is in fact limited by the time t_D.

Unfortunately, the existing spin-diffusion theory,[17] when adapted to the presently available experimental methods, concerns itself only with the calculation of the integral behavior of the nuclear magnetization of the sample, and is therefore incapable of answering the questions that arise. One can hope that the procedure developed in this paper, which makes it possible to follow the behavior of the nuclear system so to speak "from the inside," i.e., from the side of the DDP and of the close nuclei, will stimulate further development of the theory.

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[1)] An exception is a paper by Goldman *et al.*,[7] where the time of the Z_n–DDP coupling is estimated on the basis of data on the thermal mixing of various nuclear spins.

[2)] The time of coupling between the DDP and the close nuclei is not determined in this model, and therefore τ^*_{dn} cannot be compared directly with the estimates of τ_{dn} based on the results of pulse experiments.[3,15]

[3)] In the calculation of C it is necessary to take into account the entire multilevel non-equidistant spectrum of the ^{27}Al nuclei, which leads in general to a complicated relaxation law for each of the transitions of the spectrum. It can be shown, however, that if the rate of the direct relaxation is determined by the matrix elements of the operator $\hat{S}^z\hat{I}^{\pm}$, and the temperatures of all transitions are the same at $t = 0$ (as is the situation in our case), then the relaxation for all levels follows the same exponential law, and to calculate C we can use the usual formula[17] derived for $I = 1/2$.

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