

SPIN DIFFUSION AND NUCLEAR MAGNETIC RELAXATION IN A CRYSTAL CONTAINING A MAGNETIC IMPURITY

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NUCLEAR spin diffusion plays an important role in the relaxation and the dynamic polarization of nuclei in a nonmetallic diamagnetic crystal with small concentration of magnetic impurity (see [1-3]). Investigations of nuclear spin diffusion have gained greatly in interest in connection with the fact that the method of dynamic polarization (the so-called solid effect) turns out to be a most powerful method of obtaining a polarized proton target.

The concept of nuclear spin diffusion was introduced in [4,5]. The nuclear spin diffusion was further developed in [6-10].

In this review we summarize the results of the theory of relaxation of nuclei in nonmetallic diamagnetic crystals containing a relatively small amount of paramagnetic atoms, and compare the results of this theory with the experimental data published since 1964 (earlier experiments were considered in our review [3]). At the end of the review we consider the role of the dipole-dipole reservoir of magnetic ions in the process of relaxation of nuclear spins.

I

We present the main results of the diffusion theory of nuclear magnetic relaxation in the case of a nuclear spin equal to 1/2 [9,3]. The nuclear relaxation time T_n (the relaxation time of the total nuclear magnetic moment of the sample) is given by the formulas*

$$T_n = \frac{1}{4\pi NDb} = 1,6 \frac{(bR)^3}{C} \text{ for } b > \delta, \tag{1a}$$

$$T_n = \frac{0,05}{NDb} \left(\frac{\delta}{b}\right)^3 = \frac{(\delta R)^3}{C} \text{ for } b < \delta. \tag{1b}$$

In these formulas N is the concentration of the magnetic ions and R is the radius of the sphere occupied by one magnetic ion, with

$$\frac{4\pi}{3} R^3 N = 1. \tag{2}$$

C is given by the formula

$$C = \frac{2}{5} (\gamma_n g \beta)^2 S(S+1) \frac{\tau}{1 + (\tau \gamma_n H)^2}. \tag{3}$$

Further, S , g , and γ_e represent respectively the effective spin, the g -factor, and the gyromagnetic ratio of the magnetic ion, β is the Bohr magneton, γ_n is the gyromagnetic ratio of the nucleus, τ is the correlation time of the quantity S_z (the z axis is chosen along the direction of the external magnetic field H), and $\omega_n = \gamma_n H$ is the frequency of the nuclear resonance.

We note that the time of direct relaxation of the nucleus, due to the magnetic ion located at a distance r away from it, is given by the expression $T_{dir}(r) = r^6/C$. We note also that in the derivation of formula (3) it was assumed that the correlation function of S_z is exponential with a correlation time τ .

In most of the experiments performed to date, the condition $\tau \gamma_n H \gg 1$ is satisfied. In this case we can use in lieu of (3) the simpler formula

$$C = \frac{2}{5} \frac{(g\beta)^2 S(S+1)}{\tau H^2}. \tag{4}$$

The quantity b in (1) is given by

$$b = 0,68 \left(\frac{C}{D}\right)^{1/4}. \tag{5}$$

D is the coefficient of diffusion of the nuclear spin, at a distance from the magnetic ion such that the shift of the nuclear Zeeman frequency, due to the local field of the magnetic ion, is negligibly small. If we neglect the effects of angular anisotropy, then D is given by the formula

$$D = l \frac{a^2}{T_2}, \tag{6}$$

where a is the distance between the neighboring nuclear spins and T_2 is the time of the transverse nuclear relaxation. The values given for the numerical coefficient l in most papers are 1/30 and 1/50. Our estimates show (see [3]), however, that this value is underestimated. In particular, for a simple cubic lattice we obtain $l \approx 1/12$. We note that a detailed calculation of D was performed in [11]. The numerical estimates were made for a simple cubic lattice. If we neglect the weak anisotropy, then we obtain $D = 0.15 \hbar \gamma_n^2 / a$. But for a primitive cubic lattice, neglecting anisotropy, we have [3] $T_2 = 0.65 a^2 / \hbar \gamma_n^2$. We thus arrive at formula (6) with $l \approx 1/10$.

Formula (1b) was obtained within the framework of the square-well model for a diffusion barrier. δ is the radius of the diffusion barrier and is given by the formulas

$$\delta \sim \left(2S \frac{\gamma_e}{\gamma_n}\right)^\alpha a \text{ for } \tau > T_2 \text{ or } S \hbar \gamma_e H > kT, \tag{7a}$$

$$\delta \sim \left[2S \frac{\gamma_e}{\gamma_n} B_s \left(\frac{S \hbar \gamma_e H}{kT}\right)\right]^\alpha a \text{ for } \tau < T_2; \tag{7b}$$

B_s is the Brillouin function, and $\alpha = 1/4 - 1/3$.*

If, in particular, $\tau < T_2$ and $S \hbar \gamma_e H < kT$, then

*More accurately, $\alpha = 1/4$ if we consider the barrier for spin diffusion, and $\alpha = 1/3$ if we consider barrier for spin transitions caused by a resonant radio-frequency field [3]. These two quantities will be denoted by δ (1/4) and δ (1/3), respectively.

*)Almost everywhere in the article, the symbols " $>$ " or " $<$ " mean "appreciably larger than" and "appreciably smaller than" respectively.

$$\delta \sim \left[\frac{2}{3} S(S+1) \frac{\gamma_e}{\gamma_n} \frac{\hbar \gamma_e H}{kT} \right]^\alpha a. \quad (7c)$$

We denote by τ_l and τ_s the spin-lattice and spin-spin relaxation times of the magnetic ion. The value of τ_l depends on T and H, and also on N.* τ_s is practically independent of T and H, but depends on N.

The assumption that the correlator S_z depends exponentially on the time is well confirmed by experiment in the case when the reorientation of the magnetic-ion spin is due to interaction between the ion and the lattice. However, it is not clear beforehand whether the assumed exponential dependence is valid in the case when the spin reorientation is due mainly to spin-spin interaction.

Melikin^[13] calculated the second and fourth moments of the Fourier component of the correlator S_z for the case when the reorientation of the spin of the magnetic ion is due to spin-spin interaction. The formula obtained for the ratio M_4/M_2^2 shows that at a relative magnetic-impurity concentration smaller than 1–2%, the dependence of the Fourier component of the correlator on the frequency is Lorentzian (more accurately, it can be said that this dependence is given by a cut-off Lorentzian curve with a cutoff frequency much higher than ω_n), which leads to an exponential dependence of the correlator on the time. For a cubic crystal and $S = 1/2$ we obtain for τ_s the expression†

$$\frac{1}{\tau_s} = \kappa \frac{\hbar \gamma_e^2}{a^3} f, \quad (8)$$

where f is the relative concentration of the magnetic impurity, κ is a coefficient of the order of unity, which depends on the time of the lattice and on the orientation of the external field relative to the crystal axis. For a primitive cubic lattice in the case of an external field directed along [100] we have $\kappa = 1.8$.

Let us assume that^[8,11]:

$$\frac{1}{\tau} = \frac{1}{\tau_l} + \frac{1}{\tau_s}. \quad (9)$$

If $\tau_l < \tau_s$, we have $\tau \cong \tau_l$, but if $\tau_s < \tau_l$, then we have $\tau \cong \tau_s$. It must be recognized, however, that in the case $\tau_s < \tau_l$, the dipole-dipole reservoir of the magnetic ions may become heated upon relaxation of the nuclei. This possibility will be disregarded for the time being (see Ch. VIII).

The criterion for the validity of the aforementioned result is given by

$$a < \max(b, \delta) < R. \quad (10)$$

For the dependence of T_n on N, H, and T we obtain (in the case when $\tau \gamma_n H \gg 1$)

* According to the Kronig–Van Vleck theory of spin-lattice relaxation, τ_l should not depend on N. According to experiment, on the other hand, τ_l at first remains constant with increasing N, and then decreases (for example, in the case of ruby, τ_l begins to decrease at a chromium concentration of approximately 0.03 at.%). Details on spin-lattice relaxation and on the dependence of τ_l on N can be found in the monograph^[12].

† In the review^[3] we used, for a rough determination of the order of magnitude of τ_s , the formula

$$\hbar/\tau_s = \beta^2/8R^3 = \pi N \beta^2/6.$$

For a primitive cubic lattice $R^3 = 3a^3/4\pi f$; thus, (8) leads to a value of τ_s which is smaller by one order of magnitude than given by formula (8a).

$$T_n \propto N^{-1} \tau^{1/4} H^{1/2} \quad \text{for } b > \delta, \quad (11a)$$

$$T_n \propto N^{-1} \tau H^2 \delta^3 \quad \text{for } b < \delta. \quad (11b)$$

For an arbitrary value of $\tau \gamma_n H$, we obtain

$$T_n \propto N^{-1} \left[\frac{1 + (\tau \gamma_n H)^2}{\tau} \right]^{1/4} \quad \text{for } b > \delta, \quad (12a)$$

$$T_n \propto N^{-1} \frac{1 + (\tau \gamma_n H)^2}{\tau} \delta^3 \quad \text{for } b < \delta. \quad (12b)$$

Recognizing that τ decreases with increasing temperature (if $\tau_l < \tau_s$) or remains constant (if $\tau_s < \tau_l$), we find that the dependence of T_n on H at a certain temperature (when the condition $\tau \gamma_n H \cong 1$ is satisfied) can have a minimum.

If $b > \delta$, then we can say that we are dealing with the case of relaxation by limited diffusion; on the other hand if $b < \delta$, then we say that fast diffusion takes place. The transition from the first region to the second occurs when the field is increased if the temperature is constant, and when the temperature is decreased if the field is constant.

For arbitrary values of b/δ we have for T_n the formula

$$T_n^{-1} = 4\pi N D F = \frac{3DF}{R^3}, \quad (13)$$

where*

$$\frac{F}{b} = \frac{2x I_{3/4}(x)}{2x I_{3/4}(x) + I_{1/4}(x)}, \quad x = 1.08 \left(\frac{b}{\delta} \right)^2. \quad (14)$$

We note that the formula for T_n can be reduced to the form^[15]

$$T_n^{-1} = 4\pi N D b \frac{I_{3/4}(x)}{I_{-3/4}(x)}. \quad (15)$$

Finally, if we have also extraneous relaxation of the nuclei (i.e., relaxation due not to the magnetic ions under consideration but to other causes) with a partial relaxation time T_d , then T_n is given by

$$T_n^{-1} = T_d^{-1} + 4\pi N D F. \quad (16)$$

In the derivation of (3) we did not take into account the fact that when the magnetic-ion spins are strongly polarized the probability of relaxation of the nuclear spins should decrease. Therefore formula (3) is valid only if $S\hbar \gamma_e H < kT$.

An analysis presented in^[15] shows that if $S\hbar \gamma_e H > kT$, then an additional factor $[3S/(S+1)]B'_S(S\hbar \gamma_e H/kT)$ appears in the right side of formula (3), leading to an additional growth of T_n with increasing H/T. In the case when $S = 1/2$, this factor coincides with the factor $1 - P_0^2$ introduced in^[16,17] (P_0 —degree of spin polarization of the magnetic ion). In^[15] there was also obtained an approximate formula for the dependence of the radius of the diffusion barrier δ on H/T and τ/T_2 :

$$\delta = \left\{ 2S \frac{\gamma_e}{\gamma_n} \left[B_S^2(y) + B'_S(y) \frac{2}{\pi} \arctg \frac{2\pi\tau}{\beta T_2} \right]^{1/2} \right\}^\alpha a, \quad y = \frac{S\hbar \gamma_e H}{kT}, \quad (17)$$

where $\beta = 30-50$ (see^[18]).

* $I_p(x) = i^p J_p(ix)$, where J_p is the Bessel function.

At sufficiently large H/T , formula (17) goes over into (7a). At sufficiently small τ/T_2 , formula (17) goes over into (7b). On the other hand, at sufficiently large τ/T_2 formula (17) coincides with (7a) only in the case $S = 1/2$. On the other hand, if $S > 1/2$, then the limiting value of δ at large τ/T_2 depends, in accordance with (17), on H/T .

In^[17], the relation between T_n and τ_l was considered for the case when an appreciable role is played in the spin-lattice relaxation of the magnetic ions by the phonon bottleneck effect. The concept of the diffusion-barrier radius δ is meaningful only as an order of magnitude estimate. This is connected, first, with the fact that the diffusion barrier is not rectangular; second, when introducing δ we have neglected the anisotropy effect (see below). Further, in obtaining the value of the radius of the diffusion barrier we have equated the value of the local field, produced at a distance δ by the magnetic ion (or the difference of the local field at distances δ and $\delta + a$) to the local field produced by the neighboring nucleus. Finally, the value of the local field itself was assumed equal to the ratio of the magnetic moment to the cube of the distance. Further, in formula (8) for τ_s , the numerical coefficient κ is known only for one particular case. It follows therefore that if either the condition $\delta > b$ or the condition $\tau_s < \tau_l$ is satisfied (or both together), our results cannot claim to yield the absolute values of T_n with great accuracy. They should give the correct dependence of T_n on the magnetic-ion concentration, on the temperature, on the external field, and the correct order of magnitude.

II

In the general case D is a symmetrical tensor of second rank, and its components depend on the orientation of the crystal relative to the external field. However, in the case of a cubic single crystal, and also of a polycrystalline sample or powder, D reduces to a scalar quantity.

In the review article^[3] we presented a formula (4.11) based on perturbation theory, giving the dependence of D for a cubic crystal on its orientation (see also^[19]). We note that two papers^[10,11] are devoted to a quantum-statistical derivation of the Bloembergen spin-diffusion equation. In these papers, expressions were obtained for the tensor of the spin diffusion coefficient. The expression obtained in^[10] for D takes into account the effects due to the diffusion barrier. In the absence of the barrier and in the case of a cubic crystal, this expression for D reduces to formula (4.11) of^[3]. On the other hand, the result obtained in^[11] does not reduce in the case of a cubic crystal to this formula. However, as indicated above (see Ch. I), the results almost coincide after averaging over the angles (at least for a primitive cubic lattice).

The diffusion barrier is in fact anisotropic. For the dependence of δ on ϑ (the angle between the vector joining the magnetic ion with the nucleus and the direction of the ion spin) we have^[3]

$$\delta(\vartheta) = \text{const} \cdot |1 - 3 \cos^2 \vartheta|^\alpha, \quad (18)$$

where the constant depends on the angle between the ion spin and the external field.

According to (18), δ vanishes at the so-called magic

value $\vartheta_0 = \cos^{-1}(3^{-1/2}) = 54.7^\circ$. It is clear that at low temperatures, for angles ϑ close to ϑ_0 , we have $\delta < b$, and for other directions $\delta > b$. Therefore the spin diffusion near the magnetic ion will occur mainly in directions lying inside a narrow cone.

III

Blumberg^[8] has shown that after strong saturation the relaxation of the total magnetic moment of a sample may not be exponential for small values of the time t . Let us analyze this question in greater detail.

Assume that a radio-frequency field saturating the NMR is applied to the sample. We denote by $2A$ the probability, per unit time, of the reorientation of the spin of the nucleus under the influence of this alternating field. We have (see, for example,^[3])

$$A = \frac{\pi}{2} \gamma_n h_1^2 g \left(H - \frac{\omega}{\gamma_n} \right), \quad (19)$$

where ω is the frequency, $2h_1$ the amplitude of the radio-frequency field (applied perpendicular to the main field), and $g(H - \omega/\gamma_n)$ a function giving the NMR line shape, the integral of which is normalized to unity.*

Assume that at the instant of time $t = 0$ the saturating field is turned off; in order for the relaxation of the total nuclear magnetic moment $\mathfrak{M}(t)$ of the sample be exponential with a relaxation time T_n given by formulas (1), it is necessary that the spin diffusion play an important role. This in turn requires that $\text{grad } M$ not be too small when $r \gtrsim \max(b, \delta)^\dagger$ (r —distance to the nearest magnetic ion). It follows therefore that the relaxation of $\mathfrak{M}(t)$ will be exponential in the case when no complete saturation of the resonance takes place at $r \cong \max(b, \delta)$. Since the quantity r^6/C gives the time of direct relaxation over a distance r , we find that $(Ct)^{1/6}$ is the distance from the magnetic ion, which the direct relaxation reaches within a time t .

When $r < \delta$ we have $M(r, t) = M_0$ for all t . Therefore, if $b < \delta$, no matter how large A , the relaxation of $\mathfrak{M}(t)$ will be exponential for all t . Indeed, M changes from a value equal to M_0 to a small value when $r \approx \delta$, and therefore the spin diffusion is turned on immediately after the saturating field is removed.

The relaxation of $\mathfrak{M}(t)$ is exponential for all t also when $\delta < b$, but $2A < C/b^6$; indeed, in this case there is no complete saturation of the resonance when $r = b$.

On the other hand, if $\delta < b$ and $2A > C/b^2$, then the relaxation of $\mathfrak{M}(t)$ at small t will not be exponential. Indeed, at the initial instant of time after the saturating field is turned off, at $r = b$, there is almost complete saturation, and therefore there is practically no spin diffusion. The relaxation becomes exponential only when $t > b^6/C$, i.e., after the process of direct relaxation reaches a distance b from the magnetic ion. This case was considered by us in^[3], but the qualitative considerations used there lead to an inexact result when $t < \delta^6/C$.

*An important role is played in the NMR saturation by the presence of the nuclear dipole-dipole reservoir^[20]. We can disregard this circumstance, however, since we are interested below in the relaxation of the nuclei after the saturating field is turned off.

[†] $M(r, t)$ is the component of the nuclear magnetization along the z axis.

We therefore present a more rigorous analysis.

Assume that the conditions $\delta < b$ and $2A > c/\delta^6$ are satisfied. At the instant $t = 0$, in the entire sample, with the exception of spheres with radii δ around all the magnetic ions, complete saturation of the nuclear resonance takes place. When $t < b^6/C$, we can neglect the diffusion term in Eq. (5.1) of^[3], and we obtain

$$\frac{\partial M}{\partial t} = -Cr^{-6}(M - M_0).$$

Recognizing that $M(r > \delta, t = 0) = 0$, we have for $r > \delta$

$$M(r, t) = M_0 [1 - \exp(-Ctr^{-6})]. \quad (20)$$

The integral $\int_0^R M(r, t) dV$ gives the nuclear magnetic moment of a sphere with center in the magnetic ion and with radius R , after subtracting the sphere with radius δ . Taking into account the fact that the magnetic moment of the spheres with radii δ around the magnetic ions are not revealed in NMR experiments (in view of the strong shift of the Larmor frequency), we obtain for the experimentally measured value of \mathfrak{M} (the upper limit in the integral can be replaced by infinity)

$$\mathfrak{M}(t) = 4\pi N \mathfrak{M}_0 \int_0^\infty [1 - \exp(-Ctr^{-6})] r^2 dr$$

($\mathfrak{M}_0 = VM_0$ is the equilibrium nuclear magnetic moment of the sample, V is the volume). The integration yields

$$\mathfrak{M}_s(t) = \frac{4\pi}{3} N \mathfrak{M}_0 (Ct)^{1/2} [\pi^{1/2} \Phi(\mu^{1/2}) - \mu^{-1/2} (1 - e^{-\mu})], \quad (21)$$

where $\Phi(x)$ is the probability integral, and

$$\mu = Ct\delta^{-6}. \quad (22)$$

In the limiting cases we obtain^{[2], [8]}

$$\mathfrak{M}(t) = \frac{4\pi}{3} N \mathfrak{M}_0 Ct/\delta^3 \quad \text{for } t < \delta^6/C, \quad (23a)$$

$$\mathfrak{M}(t) = \frac{4\pi}{3} N \mathfrak{M}_0 [(\pi Ct)^{1/2} - \delta^3] \quad \text{for } \delta^6/C < t < b^6/C. \quad (23b)$$

In order to observe experimentally the non-exponential relaxation it is necessary, besides satisfaction of the condition $\delta < b$, also that the ratio b/R not be too small (otherwise the value of $\mathfrak{M}(t)$ remains practically unchanged within a time b^6/C), i.e., the concentration N should not be too small. On the other hand, however, b/R should nevertheless be smaller than unity, for otherwise the aforementioned analysis will not be correct.

IV

Let us consider briefly the so-called homogeneous model of relaxation^[8, 22].

The reciprocal time of direct relaxation of the i -th nucleus is given by the expression $C \sum_k r_{ik}^{-6}$, where r_{ik} is the distance from the i -th nucleus to the k -th magnetic ion; the summation is over all the magnetic ions of the sample. In the case when the nuclear magnetization of the sample does not depend on the position, the spin diffusion is immaterial and we can average the latter expression over all nuclei (of a given type) of the sample. This averaging leads to the expression

$$\frac{C}{nV} \sum_{ik} r_{ik}^{-6},$$

where n is the concentration of the nuclei. But

$$\sum_{ik} r_{ik}^{-6} = NV \sum_i r_{ih}^{-6} = nV \sum_h r_{ih}^{-6}.$$

We thus obtain

$$T_n^{-1} = C \sum_h r_{ih}^{-6} = C \frac{N}{n} \sum_i r_{ih}^{-6}. \quad (24)$$

It is physically clear that if the time diffusion of the nuclear spin over a distance R , i.e., the quantity R^2/D , is sufficiently small, then an internal equilibrium in the nuclear-spin system is rapidly established (within a time of the order of R^2/D) in the greater part of the sample, and the nuclear magnetization will not depend on the position. In such a case, the relaxation time of the nuclear moment of the sample, T_n , will not depend on the spin-diffusion coefficient.

We denote by r_m the distance from the magnetic ion to the nearest nucleus (it is clear that $r_m \sim a$). Assume that the conditions $\delta > r_m$ and $R^2/D < T_{\text{dir}}(\delta) = \delta^6/C$ are satisfied. We can use for T_n formula (24), summing with respect to i the nuclei located at a distance $\geq \delta$ from the magnetic ion. We change over to integration, making the substitution $\sum_i (...) \rightarrow \int (...) n dV$ (this substitution is, in general, permissible if δ/r_m is sufficiently large). We obtain

$$T_n^{-1} = 4\pi n C \int_\delta^\infty \frac{dr}{r^4}, \quad (25)$$

or

$$T_n^{-1} = \frac{C}{(\delta R)^3}.$$

We thus arrive at the result (1b).*

We must, however, note the following. When (5) is taken into account, the condition $R^2/D < \delta^6/C$ yields $b^2 R < \delta^3$, i.e., $b < \delta(\delta/R)^{1/2}$. On the other hand, the result (1b) is valid when the less stringent condition $b < \delta$ is satisfied. Thus, the homogeneous model, although it does yield the correct result for T_n in the considered limiting case, it results in a more stringent criterion than the true criterion.

Formula (1b) can be rewritten in the form

$$T_n^{-1} = [T_{\text{dir}}(\delta)]^{-1} \left(\frac{\delta}{R}\right)^3. \quad (26)$$

In this formula $(\delta/R)^3$ gives the ratio of the number of nuclei located in the layers $0 < r < \delta$ and $\delta < r < R$.

Assume now that the following conditions are satisfied:

$$\delta < r_m, \quad \frac{R^2}{D} < T_{\text{dir}}(r_m) = \frac{r_m^6}{C}.$$

To find T_n , we can again use formula (24), but in the sum over i , the minimum distance will already be r_m , so that it is not permissible to change over from summation to integration.

Let us consider a case in which the magnetic ion replaces in the lattice one of those nuclei, whose relaxation is investigated. Then the sum over i in (24) can be expressed in terms of the second moment P of the nuclear resonance line of the polycrystalline sample or powder. We have (see, for example, Appendix B of^[3])

*We note that by taking b as the lower limit of the integral in (25), we arrive at the result (1a) without the numerical factor 1.6.

$$P = \frac{9}{20} h^2 \gamma_n^4 \sum_i r_{in}^{-6}$$

Using also formula (4) for C, we readily obtain (we consider the case $S = 1/2$)

$$T_n^{-1} = \frac{2N}{3\pi} \left(\frac{\gamma_n}{\gamma_n} \right)^2 \frac{P}{\tau \omega_n^2} \quad (27)$$

The criterion $R^2/D < r_m^6/C$ yields $b^2 R < r_m^2$, i.e., $b < r_m (r_m/R)^{1/2}$. Apparently, however, in order for the result (27) to be valid it is sufficient to satisfy (in addition to the condition ($\delta < r_m$)) the less stringent condition $b < r_m$.

The result (27) cannot be obtained by solving the spin-diffusion equation, for when $b, \delta < r_m$ the macroscopic description of the diffusion is not valid. To avoid misunderstandings, we note that the relative concentration of the magnetic impurity is connected with the quantity N/n by the relation

$$f = \nu \frac{N}{n}, \quad (28)$$

where ν is the number of nuclei (the relaxation of which we are dealing with) per atom replaced by an impurity. For example, $\nu = 1$ for ruby (Al_2O_3 with chromium impurity) and $\nu = 24$ for lanthanum-magnesium double nitrate ($\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$) with cerium or neodymium impurity (since we are dealing with proton relaxation).

V

Jeffries^[23,24] proposed the so-called influence-sphere model to explain the experimental data on proton relaxation in dilute paramagnetic salts.

We consider a sphere centered about a magnetic ion with radius R . We denote by r the distance from the point to the magnetic ion, and break up the sphere into three regions: $0 < r < r_m$, $r_m < r < \delta$, and $\delta < r < R$. We assume that $r_m < \delta < R$, and in addition that $\delta > b$. The overwhelming majority of the nuclei are in region III, and region I does not contain any nuclei at all. In region III, owing to the spin diffusion, internal equilibrium is rapidly established in the system of nuclear spins. It is assumed in^[23,24] that in region II it is possible to introduce a nuclear relaxation probability averaged over r ; it is assumed further that the nuclei of region III are in thermal contact with the magnetic ion only via the nuclei of region II, and a corresponding cross-relaxation time is introduced. Comparing the equations for the time variation of the polarizations of the nuclei of regions II and III, and solving these equations approximately, we find that the relaxation time of the summary nuclear moment (which can be assumed to coincide with the relaxation time of the nuclei of region III) is given by the formula

$$T_n^{-1} = \langle T_{\text{dir}}^{-1}(r) \rangle_{r_m, \delta} \left(\frac{\delta}{R} \right)^3 \quad (29)$$

In this formula $\langle T_{\text{dir}}^{-1}(r) \rangle_{r_m, \delta}$ is the average value of the probability of direct relaxation for the interval (r_m, δ) . Calculation of this mean value yields

$$T_n^{-1} = \frac{C}{(r_m \delta)^3} \quad (29a)$$

It seems to us that introduction of a time of cross relaxation between the nuclei of regions II and III is doubtful. However, inasmuch as the cross relaxation time

drops out of the final result, this assumption does not play an essential role.

The weak point of the influence-sphere model, in our opinion^[25], is the introduction of the averaged relaxation probability for the nuclei of region II. Indeed, in typical cases $\delta/r_m = 2-4$, and the times of direct relaxation at distances r_m and δ differ very strongly. In region III, the spin diffusion is very appreciable, and in region II the diffusion is suppressed. Therefore the decisive role in the relaxation of the nuclei of region III is played by the probability of direct relaxation at the boundary of the regions II and III, i.e., $T_{\text{dir}}^{-1}(\delta)$. The direct formula is therefore not (29) but (26), leading to the result (1b) (see^[25]).

As indicated above (see Ch. IV), in the case when $b, \delta < r_m$, the value of T_n is given by formula (24), in which the minimum distance for summation over i is r_m . Replacement of summation by integration leads to the result (29a). In this case, however, first, the replacement of summation by integration is incorrect, and second, under the experimental conditions^[23] we have $\delta > r_m$.

We note, finally, that two spherical surfaces of radius $\delta(1/3)$ and $\delta(1/4)$ are introduced in^[23], in order to refine the influence-sphere model (see Ch. I). It is assumed in that paper, however, that $\delta(1/3) < \delta(1/4)$, whereas actually the opposite inequality holds.

VI

We proceed to consider the experimental results on nuclear relaxation in a crystal containing a magnetic impurity. We confine ourselves to the result published since 1965.

In^[26] is reported an investigation of the relaxation of F^{19} nuclei in CaF_2 . The measurements were made in the temperature interval $2-20^\circ\text{K}$, and also at temperatures 63 and 78°K . Fields from 300 to 5500 Oe were used. The experiments were made both with single-crystal samples and with powders. The nature and the concentration of the magnetic impurity were unknown (the concentration, however, is so small that even at 2°K the condition $\tau_l \ll \tau_s$ is certainly satisfied, and therefore also $\tau = \tau_l$).

The authors measured the dependence of T_n on the temperature, field, crystal orientation, and simple dimensions. According to the experiment, $T_n \propto HT^{-7/4}$ at $2 < T < 14^\circ\text{K}$ and $H < 2$ kOe. This result can be explained approximately by assuming that $\tau \gamma_n H > 1$, $\delta > b$, and $\tau < T_2$, and assuming that the magnetic ion is not of the Kramers type and its relaxation is of the single-phonon type (this yields $\tau \propto H^{-2} T^{-1}$). Indeed, using (7c) and (11b), we obtain $T_n \propto H^{3/4} T^{-7/4}$ (if we assume that $\alpha = 1/4$). At $14 < T < 20^\circ\text{K}$, and also when $H > 3$ kOe, the dependence of T_n on H turns out to be stronger, a fact which the authors attribute to the effect of the phonon bottleneck and to relaxation of the magnetic ion.

The relaxation of protons in para-dibromobenzene was investigated in^[27]. The experiments were performed at helium temperatures (in the interval $2.7-4.2^\circ\text{K}$). The nature and concentration of the impurity, unfortunately, were unknown (the concentration, however, was so low that at all temperatures $\tau_l \ll \tau_s$ and $\tau = \tau_l$). Fields from 0 to 140 Oe were used. In such a weak field, the equilibrium proton signal is small,

and therefore it is difficult to determine T_n from the growth of the signal after the saturating field is turned off. The protons were polarized by thermal mixing with the bromine nuclei in a weak field H , after which the proton signal was measured under conditions of rapid passage (the author measured in this case the dependence of the signal on the time of stay in the field H).

The dependence of the relaxation time on the field was measured at $T = 4.2^\circ \text{K}$. In a weak field, however, the employed procedure determines the spin-temperature relaxation time (in a weak field, the system is characterized by a single spin temperature). This time is a combination of the relaxation times of the Zeeman and dipole-dipole interaction. Knowing the local field, it is possible, by using the measured values of the relaxation time of the Zeeman interaction, as was indeed done. It turns out that this correction must be used in a field smaller than 20 Oe.

Figure 1 shows, in a log-log scale, the obtained dependence of T_n on H . The figure also shows two lines with slopes $1/2$ and 2 . It is seen from the figure that when the field increases a change takes place from a dependence $T_n \propto H^{1/2}$ to a dependence $T_n \propto H^2$ (the deviation of the experimental points from the $T_n \propto H^{1/2}$ dependence in a field weaker than 2 Oe can be disregarded, for in such a weak field the aforementioned recalculation is too rough). This result can be readily understood by assuming that $\tau\gamma_n H > 1$, that τ_1 is independent of H , and that $\tau_1 > T_2$ (see formulas (7a) and (11)). The central point of this transition (the point of intersection of the two straight lines) corresponds to a field of 35 Oe. This field corresponds to $\delta^3 = 1.6b^3$ (see formulas (1a) and (1b)). Using this fact, the author estimates from experiment the value of $\delta^3 D$ and obtains a reasonable value for it. Further, using the known value of the ratio δ/b in a field of 35 Oe, he plots the dependence of T_n on H in accordance with formulas (13) and (14). It is shown in Fig. 1. We see that the agreement between theory and experiment is good, on the basis of which it is concluded in^[27] that the rectangular barrier model is a good approximation.

In the same investigation, the temperature dependence of T_n in the temperature interval $2.7-4.2^\circ \text{K}$ in a 50 Oe field. We note that according to the theory, when $\tau\gamma_n H > 1$, $\delta > b$, and $\tau > T_2$, we have $T_n \propto \tau$ (see formulas (7a) and (11b)). The experimental data fits well the curve $T_n \propto T^{-9}$. It follows therefore that the magnetic ion is a Kramers ion, and its relaxation is of the Raman two-phonon type.*

The influence of light radiation on the relaxation of cadmium nuclei in CdS, which is a photoconducting compound, is investigated in^[28]. The light causes photoelectrons to appear in the conduction band, some of which are captured by the lattice defects or by the impurities. The centers capturing the photoelectrons, in the case when the latter are paramagnetic, cause the relaxation of the nuclei of the main lattice. The relaxation can be produced also by the band photoelectrons, if their concentration is sufficiently large. Thus, illumination of a photoconductor should lead to a decrease of the

*In view of the low value of the external field, the single-phonon relaxation is negligibly small compared with the two-phonon relaxation.

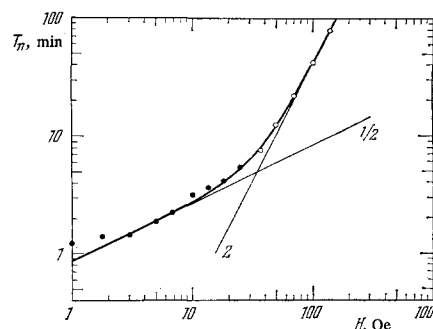


FIG. 1. Dependence of the proton relaxation time on the magnetic field in paradibromobenzene at $T = 4.2^\circ \text{K}$ [27].

relaxation time of the nuclei of the main lattice.

The experiment was performed at a temperature 4.2°K and at the external-field values 4, 7.4, and 9.7 kOe. The relaxation times of the nuclei Cd^{111} and Cd^{113} were determined from the rate of recovery of the nuclear signal after the saturating field was turned off. According to the measurements, for the sample employed by the authors, $T_n(\text{Cd}^{113}) \cong 3000$ min in darkness. As a result of illumination, T_n decreases to 30 minutes. After the illumination is turned off, T_n increases to 400 minutes. Further illumination of the crystal with red light restores the initial value of T_n .

The analysis performed by the authors shows that the decrease of T_n following illumination with white light is due to the paramagnetic centers produced as a result of capture of photoelectrons by lattice defects or impurities. The decrease of T_n due to the bandphotoelectrons is negligible, in view of the smallness of their conservation. The fact that the initial value of T_n is not restored after the white light is turned off is attributed by the authors to the fact that at low temperature a fraction of the electrons remains captured by the defects. Illumination of the crystal with red light causes a release of these electrons (the energy of the red-light quantum is insufficient for the formation of new photoelectrons). According to the experiment, T_n increases slowly with increasing external fields, in qualitative agreement with the diffusion theory (in the case when $b > \delta$).

A detailed investigation of the relaxation of protons in dilute paramagnetic salts was made by Jeffries and co-workers. In one of the investigations of this group^[16], they measured the relaxation time of the photons in lanthanum-magnesium double nitrate, in which 1% of the lanthanum atoms was replaced by neodymium atoms (in order to get rid of the hyperfine structure, the isotope Nd^{142} was introduced). This concentration corresponds to $N = 1.6 \times 10^{19} \text{cm}^{-3}$. The measurements were made in a temperature interval $1.3-4.3^\circ \text{K}$ and at an external-field intensity 1–20 kOe. The external field was inclined 40° to the symmetry axis of the intracrystalline field. By way of an example we point out that at a temperature 2°K and in a field of 5 kOe we have $T_n \cong 10^3$ sec. Simultaneously with T_n they measured also τ_1 .

Under the conditions of these experiments, $\delta \gg b$, so that it is necessary to use formula (1b) for T_n . Substituting τ_1 for τ in (4), the authors arrive at values of T_n that exceed the experimental data by three orders of

magnitude. However, $\tau_S \ll \tau_I$ under the conditions of these experiments. However, substituting τ_S for τ in (4), we arrive at values of T_n smaller by three orders of magnitude than the experimental data.

In another investigation^[29], the Jeffries group measured the relaxation time of the protons in the same salt in the temperature interval 0.5–3°K and in an external-field interval 10–50 kOe. The external field was applied perpendicular to the symmetry axis of the intercrystal-line field. In this investigation, τ_I was not measured. By way of an example we indicate that at 1.5°K and in a field of 19.5 kOe, the obtained value was $T_n \cong 40$ hours. As noted by the authors, such large values of T_n are very convenient from the point of view of conservation of the proton spin direction following dynamic polarization by a high-frequency field.

We note a very interesting investigation^[23] of proton polarization occurring following rotation of an yttrium ethyl sulfate crystal, in which 2% of the yttrium atoms are replaced by ytterbium atoms (even isotope Yb^{172}). Besides investigating the polarization occurring upon rotation, the authors also measured the proton relaxation time in the temperature interval 1.4–4.3°K for an external field 0.05–20 kOe and for different crystal orientations.

To explain the results obtained in^[16,23,29], they introduced the influence-sphere model, which we have discussed in sufficient detail above (see Ch. V).

In^[30], the relaxation time of F^{19} was measured in an NaF crystal containing Mn^{2+} as an impurity. The impurity concentration ranged from 10^{18} to 10^{19} cm⁻³. The measurements were made in the temperature interval 2–1380°K and at external-field values 3.2, 5.7, and 9.7 kOe. We confine ourselves to results obtained at room temperature and below.

The authors observed magnetic resonance due to the manganese impurity. A line having a hyperfine structure was observed, and also a broad structureless line. It was possible to saturate only the line having the hyperfine structure, and consequently the dependence of τ_I on the temperature and on the field could be measured only for the centers producing this line. The authors have shown further that at temperatures above 170°K the measured plots of T_n and τ_I against the temperature satisfy the relation that follows from the diffusion theory of nuclear relaxation. Below 170°K, the theoretical values of T_n obtained by using the measured values of τ_I exceed the measured values of T_n . The authors conclude that at a temperature below 170°K the paramagnetic relaxation causing the relaxation of the F^{19} nuclei is connected with centers that produce a broad structureless EPR line. The authors assume that these centers are pairs or larger aggregates of manganese ions.

Reference 31 is devoted to an investigation of the relaxation of In^{115} nuclei in p-InSb. The measurements were made in the temperature interval 1–4.2°K for an external field 0.3–10 kOe, and in the acceptor-concentration interval 10^{14} – 10^{17} cm⁻³. It is important that the samples contained also a compensating donor impurity. The most interesting results were obtained for medium concentrations of the acceptor impurity (2×10^{15} – 2×10^{16} cm⁻³). The authors show that the experimental data can be explained by assuming that the relaxation of

the nuclei is caused by the time variation of the local field on the nuclei, due to hopping of the hole from one acceptor impurity atom to another. We note that such hopping is possible because the sample contains compensating donor impurities, which causes a certain fraction of the acceptor atoms to be in the ionized state.

This effect was investigated in greater detail in^[32], where a study was made of the relaxation of the Si^{29} nuclei (spin 1/2, abundance 4.7%) in n-Si. The measurements were made at temperatures 1.3 and 4.2°K and in the field interval from 50 to 3300 Oe. In all the samples, the concentration of the donor impurity (phosphorus) was the same, $N_d = 6 \times 10^{16}$ cm⁻³. The concentration N_a of the acceptor impurity (boron) varied in such a way that the compensation coefficient $K = N_a/N_d$ assumed values 0.13, 0.33, and 0.67 for different samples. Measurements were made of the dependence of T_n on the temperature, external field, and K . For the dependence of T_n on H at $T = 4.2^\circ K$, they obtained $T_n \propto H^{1/2}$, which agrees with formula (11a) if it is assumed that τ is independent of H . At helium temperatures and at a donor impurity concentration 6×10^{16} cm⁻³, almost all the "extra fifth" electrons of the donor atoms will be localized. In compensated n-Si, however, some of the electrons will be captured by the acceptor atoms and therefore several of the donor atoms will be ionized.

The authors introduced the following model to explain the experimental data on the dependence of T_n on the temperature and on K . Let us consider a pair made up of a neutral and ionized donor atoms, located near an ionized (electron-capturing) acceptor atom. In^[33], the probability of the transition of the electron from one donor atom to the other was calculated. In such a transition, the local field acting on the nearby Si^{29} nucleus changes. The authors of^[32] calculated the time of direct relaxation of the Si^{29} nucleus, due to the hopping of the electron; using then the results of the spin-diffusion theory, they obtained finally an expression for T_n .

Calculation shows that $T_n \propto K$ at small values of K (when $K \ll 1$), $T_n^{-1} \propto 1 - K$ at large K (i.e., when $1 - K \ll 1$), and T_n^{-1} goes through a maximum when $K = 0.5$. These results can be readily understood. If $N_a \ll N_d$, then the number of centers causing the relaxation of the nuclei is proportional to the acceptor concentration N_a ; on the other hand, if $N_a \cong N_d$, then the number of centers causing a relaxation is proportional to the concentration of the neutral donors, i.e., to $N_d - N_a$.* The results of the experiment fit approximately the theoretical curve (but it is difficult to speak of good agreement, since K assumes only three values in the experiment). The authors also calculated the ratio of the values of T_n for two temperatures and obtained a value close to the measured one.

In^[18] they measured the temperature dependence of the relaxation time of F^{19} nuclei in CaF_2 doped with neodymium. The neodymium concentration was 5×10^{-3} wt.%. The measurements were made in an external field of 1.5 kOe and in the temperature interval 2–300°K. Two orientations of the external field along

*The number of centers causing the nuclear relaxation is proportional to $N_d(N_d - N_a) N_a$. Recognizing that N_d is fixed, we arrive at the indicated results.

the [100] and [110] directions were used. At $T = 16^\circ\text{K}$, T_n goes through a minimum. The spin-lattice relaxation time of the neodymium ions was not measured.

To analyze the results of his measurement, the author uses formula (15). Thus, the author determines the dependence of τ on T . At temperatures below 50°K , this dependence is described by formula (9), in which τ_l corresponds to the resonant relaxation process via an intermediate level located 65 cm^{-1} above the ground level.

An interesting transition effect was observed in^[34]. The experiment was performed with lanthanum-magnesium double nitrate, in which 1% of the lanthanum atoms were replaced by neodymium atoms (Nd^{142} isotope). The measurements were made in the temperature interval $1.5\text{--}2.5^\circ\text{K}$. The forbidden transition of the " Nd^{3+} ion plus proton system" was saturated, the transition energy (divided by Planck's constant) being equal to the sum of the Larmor frequencies of the neodymium ion and the proton. In other words, a saturating microwave field was applied (frequency 8.8 MHz), and the external field was set equal to H_- (see the review^[3]). It is known that in an H_- transition the protons are negatively polarized, and accordingly an emission signal in the proton resonance measurement setup. When the microwave field was turned off, the emission signal decreased, and then the signal became positive and the polarization of the protons tended to its equilibrium value. The time variation of the signal was simply exponential. For the proton relaxation time T_n , a value on the order of several hundred seconds was obtained (450 sec at $T = 2.02^\circ\text{K}$ and 220 sec at $T = 2.42^\circ\text{K}$).

In the second experiment, after reaching the stationary negative polarization of the protons (which exceeded in absolute magnitude the equilibrium thermal polarization by about 300 times), the external magnetic field was rapidly changed as a result of the H_- transitions, and made equal to H_+ . As a result, the emission signal decreased. At the instants when the proton signal became equal to zero, the microwave field was turned off. The measurements have shown that initially the emission signal is partially restored. The maximum signal exceeds the equilibrium signal in absolute magnitude by 3–4 times, and this maximum is reached approximately 100 sec after turning off the microwave field. The authors note that the signal growth in time cannot be described by a single exponential, or even by a sum of several exponentials. The emission signal decreases after the maximum is reached, vanishes at a certain instant of time, after which an absorption signal appears, which in the limit tends to the equilibrium signal. During this second stage, the change of the signal with time is simply exponential, and the time constant coincides with the previously measured value of T_n . This effect is observed only below 2.5°K .

The authors present the following interpretation of the observed effect. At first, all the protons are negatively polarized as a result of the H_- transitions. Switching the external field from the value H_- to the value H_+ produces H_+ transitions. Since the probability of direct reorientation of the proton spin decreases rapidly with increasing distance from the neodymium ion, the change of the polarization direction begins for the protons located near the magnetic ions. At the instant when the

microwave field is turned off, the protons located near the neodymium ions have positive polarization exceeding the thermal polarization; on the other hand, most protons have a negative polarization, and the total nuclear magnetic moment of the sample is equal to zero. The nuclear relaxation starts at that instant. The protons close to the ions have positive polarization exceeding the thermal polarization and relax rapidly. On the other hand, the relaxation of most protons is connected with the spin diffusion and is slower. It is clear therefore that the average sample polarization is at first negative, and that this process is not exponential in time. Then, owing to the spin diffusion, the contribution of the relaxation of most protons becomes noticeable. The total nuclear magnetic moment of the sample begins to decrease (in absolute magnitude), passes through zero, and then tends to an equilibrium value. It is clear that this process will be exponential with a relaxation time T_n .

The relaxation time of F^{19} in samples of CaF_2 doped with Tb^{3+} , Tm^{3+} , and Sm^{3+} was measured in^[35]. The measurements were made in the temperature interval $28\text{--}300^\circ\text{K}$, the frequency of the alternating field was 29.5 MHz (the corresponding value of the external field was 7.3 kOe), and the external field was directed along the [111] axis. Preliminary measurements have shown that at room temperature the relaxation times in all the samples were much lower than in a sufficiently pure CaF_2 sample. This indicates that in all these samples the relaxation of the F^{19} nuclei is due mainly to the introduced magnetic impurity.

Let us describe the results obtained for a sample with a Tb^{3+} concentration $1.9 \times 10^{19}\text{ cm}^{-3}$. At such a concentration and at $T > 28^\circ\text{K}$ we have $\tau_l \ll \tau_s$ and $\tau = \tau_l$. According to the experiment, the relaxation time, T_n has a minimum at a temperature of 41°K . Assuming that the minimum corresponds to a value of $\omega_n\tau$ equal to unity, the authors determine the value of τ at 41°K . Using the obtained value of τ and the corresponding value of T_n , the authors, using formula (1a) ($\delta < b$ at 41°K), determined the diffusion coefficient D . Using, further, the obtained value of D and the measured values of T_n , the authors determined the dependence of τ_l on T for the temperature interval $28\text{--}300^\circ\text{K}$. The authors note that their $\tau_l(T)$ curve and the $\tau_l(T)$ curve obtained in^[36] in the temperature interval $2\text{--}10^\circ\text{K}$, by the pulsed EPR saturation method, are "joined together" satisfactorily.

Similar results were obtained for a sample of CaF_2 doped with Tm^{3+} . In the case of a sample doped with samarium, the curve obtained for the temperature dependence of T_n had a single maximum and a single minimum. The reason for such a behavior of the $T_n(T)$ curve is unclear.

Reference 37 is devoted to the measurement of the dependence of T_n on the temperature, the external field, and the orientation of the crystal under conditions when the spin polarization of the magnetic ion is large and it is necessary to take into account in T_{dir} the factor $1 - P_0^2$ (see Ch. I). The measurements were made with lanthanum-magnesium double nitrate, in which 0.01% of the lanthanum atoms was replaced by dysprosium atoms ($S = 1/2$, Dy^{162} isotope). External fields in the interval $5.7\text{--}20\text{ kOe}$ were used, the temperature varied

in the interval 1.1–1.9°K, and the external field was applied parallel and perpendicular to the symmetry axis of the intracrystalline field.

According to the theory we have (when $\omega_n \tau \gg 1$)

$$C \propto \frac{1-P_3}{\tau H^2}.$$

This yields

$$T_n^{-1} \propto \left[\frac{1-P_3}{\tau H^2} \right]^\mu, \quad (30)$$

where $\mu = 1/4$ when $b > \delta$ and $\mu = 1$ when $b < \delta$. The concentration of the dysprosium is so small that it can be assumed that $\tau = \tau_I$.

The experimentally obtained values of the ratios $T_n(20 \text{ kOe})/T_n(12 \text{ kOe})$ (at $T = 1.1^\circ \text{K}$) and $T_n(1.1^\circ \text{K})/T_n(1.9^\circ \text{K})$ (at $H = 20 \text{ kOe}$) in parallel and perpendicular orientations were compared with the values of these ratios that follow from formula (30). The author, however, did not measure τ_I , which he obtained by extrapolating the data of [38]. A comparison shows that the measured values of these ratios lie in all cases between the theoretical values corresponding to $\mu = 1/4$ and $\mu = 1$.

In [39] they measured the temperature dependence of the relaxation time of the F^{19} nuclei in BaF_2 and SrF_2 crystals containing Mn^{2+} as an impurity. The temperature dependence of the spin-lattice relaxation time of the Mn^{2+} ions was also measured. The measurements were made in a field of 3.3 kOe and in the temperature range from that of helium to 79°K. The Mn^{2+} concentration measured by determining the EPR intensity varied for different samples in the interval $(2-8) \times 10^{17} \text{ cm}^{-3}$. However, the measurement of the concentration by an optical method has led to much larger values. This indicates that an appreciable fraction of the manganese ions is combined into pairs or even larger "clusters."

The measurement results show that the $T_n(T)$ curve has a minimum. The minima take place at temperatures close to 30° and 50°K for BaF_2 and SrF_2 respectively. These temperatures satisfy approximately the condition $\omega_n \tau = 1$ if the measured values are used for τ_I . At temperatures above 25°, the experimental data agree qualitatively with the theoretical results. At lower temperatures there is no agreement, and this is attributed by the authors to the presence of "clusters" of manganese ions, or to the presence of another impurity.

Reference 21 is devoted to an investigation of the relaxation of protons in solid organic substances containing free radicals as an impurity. The matrices employed were tetrahydrofuran (C_4H_8O), toluene ($C_6H_5-TH_3$), diphenyl ($C_6H_5-C_6H_5$) and o-terphenyl ($C_6H_4(C_6H_5)_2$), and the free radicals were DPPH (diphenyl picryl hydrazyl) and BPA (bis-diphenyl p-chlor-phenylalyl). The radicals were dissolved in the matrix above its melting temperature. Good homogeneity in the radical distribution was obtained by rapid cooling to 77°K. Special investigations have shown that toluene and o-terphenyl are obtained in the vitreous state, while tetrahydrofuran and diphenyl are obtained in the polycrystalline state.

The measurements were made at 14.5 MHz, the temperature varied in the interval 4.2–77°K (most measurements were made at 77°K), and the radical concentration N was varied in the interval 10^{18} – 10^{19} cm^{-3} . The authors measured the recovery of $\mathfrak{M}(t)$ in time after

pulsed saturation of the proton resonance. In all cases, regions of $\mathfrak{M}(t) \propto t$, $\mathfrak{M}(t) \propto t^{1/2} - \text{const}$, and an exponential region were observed. Further, according to the measurements, the coefficient of t and of $t^{1/2}$ respectively, and also the relaxation probability T_n^{-1} in the exponential region, are proportional to the radical concentration N . Thus, by using formulas (23a), (23b), and (1a) it is possible to determine from the experimental data the values of C , D , and δ , for which reasonable values are obtained. Values in the interval 10^{-14} – $10^{-16} \text{ cm}^2 \text{ sec}^{-1}$ are obtained for the spin-diffusion coefficient. The small values of D are due to the fact that for solid organic substances the distance between the protons of the neighboring molecules is relatively large. In this connection, the authors note that formula (6) does not hold for solid organic substances, for the quantity T_2 , unlike D , is determined mainly by the intramolecular interactions.

The obtained values of b and δ are rather large. For example, for diphenyl (with BPA impurity) the authors obtain $b = 34 \text{ \AA}$ and $\delta = 17 \text{ \AA}$ at 77°K. In this connection, the validity of the theory at the employed concentrations is somewhat doubtful. Indeed, for example at $N = 10^{18} \text{ cm}^{-3}$, it is found that $R = 62 \text{ \AA}$, and thus, b/R exceeds one-half.

Reference 40 is devoted to an investigation of the relaxation and dynamic polarization of protons in lanthanum magnesium double nitrate, in which 0.1% of the lanthanum atoms are replaced by neodymium atoms (Nd^{142} isotope). The samples were bombarded with 146-MeV protons. The measurements were made at temperatures 4.2 and 1.3°K in fields 2.5 and 9.2 kOe. The integral irradiation dose was varied up to 3×10^{12} protons/cm².

The EPR line resulting from the irradiation was investigated. The value obtained for the g-factor was 2.002 (the g-factor of the line due to the neodymium ion is 2.7, so that these two lines do not overlap). The line width does not depend on the temperature and on the irradiation dose, but increases rapidly with increasing field. It turned out further that the integral intensity of the EPR signal, meaning also the concentration of the centers resulting from the irradiation (and responsible for the EPR) are proportional to the irradiation dose. An estimate shows that the maximum dose corresponds to an center concentration on the order of $3 \times 10^{19} \text{ cm}^{-3}$.

The measurements have shown that the dynamic polarization of the proton decreases with increasing irradiation dose. This fact is connected by the authors with the occurrence of an additional channel for the relaxation of the protons by the defect centers and, in addition, to the shift of the Zeeman frequencies of the protons located near these centers.

The dependence of the relaxation time of the protons on the irradiation dose was measured in a field of 9.2 kOe and at a temperature 1.3°K. At all doses, the proton relaxation turned out to be exponential within the limits of errors. The measurements have shown that the proton relaxation rate T_n^{-1} is a linear function of the dose; in other words, the additional proton relaxation rate (compared with the relaxation rate in the non-irradiated sample) is proportional to the concentration of the defect centers produced by the radiation. This fact indicates that the additional relaxation of the pro-

tons is connected with the reorientation of the spins of the defect centers, due to their spin-lattice (and not spin-spin) relaxation.

An estimate yields* $b \cong 2 \text{ \AA}$ and $\delta \cong 16 \text{ \AA}$ (the estimate of δ was obtained from the observed decrease of the dynamic polarization of the proton as a result of the irradiation), so that formula (1b) should be used for the additional relaxation rate. The authors state that their data are in good agreement with this formula.

Concluding the review the experimental studies, we note that for many of them we were forced to confine ourselves to a qualitative comparison with the theory. This is due to the fact that only the values of T_n were measured in many experiments, and not the values of τ_j . In many experiments the dependence of T_n on the field was not measured. Finally, in some experiments the concentration or even the type of the magnetic impurity was unknown.

VII

In a class by itself are the brilliant experiments of Kessemeier and Norberg^[41] on nuclear relaxation due to a magnetic impurity in a rotating crystal.

We shall discuss first the question of the line width of NMR in a rotating crystal (see, for example,^[42,43], and also^[41]).

The external field, as throughout this review, is assumed to be much stronger than the local field, so that the condition $\omega_n \gg \sigma$ is satisfied ($\sigma = P^{1/2}$ is the statistical mean-square NMR line width). It is well known that in a strong field the shape and the width of the NMR line are determined by the secular part of the energy of the nuclear dipole-dipole interaction, i.e., by the part that commutes with the Zeeman energy operator. This secular part consists of two sums over pairs of nuclei†. The first sum contains terms proportional to $I_{1i}^z I_{1j}^z$, and the second sum (the so-called flip-flop part) contains terms proportional to $I_{1i}^+ I_{1j}^- + I_{1i}^- I_{1j}^+$.

We denote the angular velocity of the rotating crystal by Ω , and the angle between the directions of the external field and the rotation axis by θ . We introduce, further, the quantity

$$\Lambda(\theta) = \frac{1}{2}(3 \cos^2 \theta - 1).$$

When the crystal rotates, the secular part of the dipole-dipole interaction is a function of the time. A simple calculation shows that it can be represented in the form of a sum of three terms, one of which is independent of the time and is proportional to $\Lambda(\theta)$, and the other two depend on the time. Further, it turns out that the terms that depend on the time decrease with increasing Ω and become negligibly small when the condition $\Omega \gg \sigma/2\pi$ is satisfied. Thus, if the angle θ is chosen equal to the magic angle $\cos^{-1}(3^{-1/2}) = 54.7^\circ$, then the

*To calculate b it is necessary to know the spin-lattice relaxation time of the defect center τ_j . Measurements have shown that at a temperature 1.3° K in a field of 2.5 kOe, we have $\tau_j \cong 2 \times 10^{-3}$ sec. Assuming that the defect is of the Kramers type and its spin-lattice relaxation is due to a single-phonon process (this yields $\tau_j \propto H^{-4}$), the authors found that $\tau_j \cong 10^{-5}$ sec in a field of 9.2 kOe.

†A pair of non-identical nuclei produces only terms of the first kind.

secular part of the dipole-dipole interaction becomes very small at large values of Ω . Accordingly, the NMR line width should decrease with increasing Ω and tend to zero when $\Omega \gg \sigma/2\pi$. The latter conclusion, however, is valid only if the NMR line width is due only to the dipole-dipole interaction. On the other hand, if a certain contribution is made to the NMR width by some spin-spin interaction, which is invariant against rotation, then the width will tend not to zero but to a finite limit at large values of Ω .

We shall not discuss the results of experiments on the shape and width of the NMR line in a rotating crystal. We note only that such experiments make it possible to obtain information on rotation-invariant chemical shifts.

We proceed to the question of the relaxation of nuclei in a rotating crystal^[41]. According to formula (1) and (5), the relaxation time T_n depends on the three quantities δ , C , and D . The radius δ of the diffusion barrier does not change when the crystal rotates. It is easy to see, furthermore, that the relative change of C when the crystal rotates is of the order of Ω/ω_n , and therefore it can be assumed that C likewise remains unchanged. From the physical point of view, this is connected with the following circumstance: The quantity C describes the direct relaxation of the nucleus by the magnetic ion; in this process, the nucleus and the magnetic ion exchange an energy equal to $\hbar\omega_n$, which greatly exceeds the quantum $\hbar\Omega$ connected with the rotation. On the other hand, the spin-diffusion coefficient D is connected with the flip-flop transitions of pairs of neighboring nuclei. In the flip-flop transition of a pair of nuclei, the energy of this pair changes by an amount of the order of σ . If $\Omega > \sigma/2\pi$, the probability of the flip-flop transition, and with it the spin-diffusion coefficient D , should be smaller than in the static case.

The calculation of the value of D for a rotating crystal is similar to the calculation of the NMR line width. The interaction energy causing the flip-flop transitions represents that part of the secular dipole-dipole interaction which is the sum over the pairs of nuclei from the expression proportional to $I_{1i}^+ I_{1j}^- + I_{1i}^- I_{1j}^+$. For a rotating crystal, this interaction of energy again reduces to a term that does not depend on the time and is proportional to $\Lambda(\theta)$, and to two terms that depend on the time and decrease with increasing Ω . Thus, we find that at an angle θ equal to the magic angle the diffusion coefficient D will decrease with increasing Ω and tend to zero at large Ω . More accurately, if a certain contribution is made to the flip-flop transition probability by the spin-spin interaction, which is invariant against rotation, then $D(\Omega)$ will tend at large values of Ω not to zero but to a finite limit.

The value of $D(\Omega)/D(0)$ as a function of Ω was calculated in^[41] for a pure dipole-dipole interaction between the nuclei. Introducing further, in accordance with (4), the quantity $b(\Omega) = 0.68 C [D(\Omega)]^{-1/4}$, we can, using formulas (13) and (14), obtain an expression for $T_n(\Omega)$.

According to (1a) in the limit of diffusion-limited relaxation,

$$\frac{T_n(\Omega)}{T_n(0)} = \left[\frac{D(0)}{D(\Omega)} \right]^{3/4}.$$

In the fast-diffusion limit, the relaxation time T_n is

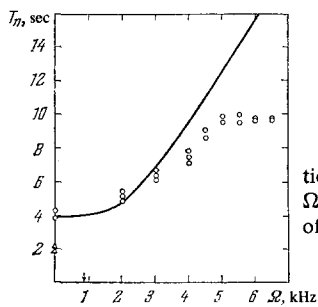


FIG. 2. Dependence of the relaxation time T_n on the angular velocity Ω for P^{31} nuclei in Mg_3P_2 in a field of 16,825 Oe [⁴¹].

independent of the diffusion coefficient, and therefore also of Ω . However, since $D(\Omega)$ decreases with increasing Ω , diffusion-limited relaxation will always take place when Ω is sufficiently large.

In setting up the experiments, a difficulty arises with the satisfaction of the condition $\Omega > \sigma/2\pi$. For example, for the NMR of F^{19} in CaF_2 we have $\sigma/2\pi \approx 10$ kHz. But when Ω is larger than 10 kHz, there is the danger of rupturing the crystal. It is therefore desirable to experiment with a material for which σ is relatively small. To this end it is necessary that the resonating nuclei have a small gyromagnetic ratio, that the average distance between them be relatively large, and that most other nuclei have zero spin. It is desirable furthermore to deal with nuclei having a spin equal to 1/2, so as to get rid of quadrupole effects.

The experiments were performed on P^{31} nuclei in Mg_3P_2 , Zn_3P_2 and AlP , and on Al^{27} in AlP . The value of $\sigma/2\pi$ for the P^{31} nuclei in Mg_3P_2 and Zn_3P_2 is 0.88 and 1.02 kHz, respectively. The samples used were in powdered form. The accuracy with which the angle θ was set equal to the magic angle was $\pm 0.5^\circ$. The angular velocity Ω was varied in an interval from 2 to 8 kHz. The measurements were performed at room temperature and at frequencies 15.9 and 25.0 MHz. The corresponding values of the resonant field of the P^{31} nucleus were 9225 and 16,825 Oe.

Pulsed saturation of the NMR was produced in the experiments, and a 90° pulse was applied at a time τ after the saturation. The magnitude of the signal was proportional to z-component of the magnetization at a time τ after the removal of the saturation. The dependence of the signal on τ turned out to be exponential, making it possible to determine $T_n(\Omega)$. The nature and the concentration of the magnetic impurity were unknown. However, diffusion-limited relaxation certainly takes place at room temperature.

Figure 2 shows the dependence of $T_n(\Omega)$ on Ω for P^{31} nuclei in Mg_3P_2 in a field of 16,825 Oe. The solid line shows the theoretical curve calculated for the dipole-dipole interaction.

We see thus that according to experiment, $T_n(\Omega)$ first increases with increasing Ω , after which the growth slows down and $T_n(\Omega)$ tends to a finite limit. According to the foregoing, this means that a certain contribution to the flip-flop transition probability is made by some spin-spin interaction that is invariant with respect to rotation. According to Fig. 2, $T_n(\infty)/T_n(0) \approx 2.5$. This yields $D(\infty)/D(0) \approx 0.3$.

The authors propose that the additional interaction is an exchange interaction between nuclei, due to the elec-

trons, and it is of the form

$$\hbar \sum_{\langle ij \rangle} J_{ij} I_i I_j.$$

The value of J for nearest nuclei can be estimated by using the asymptotic value of $D(\infty)/D(0)$. This yields $J \approx 0.33$ kHz for the P^{31} nuclei in Mg_3P_2 .

VIII

In Ch. II we have assumed that in the case $\tau_S < \tau_I$, when the spin orientation takes place, its Zeeman energy goes over into the energy of the dipole-dipole reservoir (DDR) of the system of magnetic ions. It must be recognized, however, that at low magnetic impurity concentrations, the heat capacity of the DDR will be smaller than the heat capacity of the nuclear Zeeman interactions. Because of this, the "DDR of the magnetic-ion system—lattice" section may turn out to be the "bottle-neck" in the transfer of the energy from the nuclear spins to the lattice.

Buishvili^[44] analyzed the relaxation of nuclei in a crystalline with magnetic impurities, with allowance for the possibility of changing the temperature of the DDR of the magnetic ions. He confined himself to the homogeneous problem (the nuclear magnetization was assumed to be independent of the position). We present the general line of reasoning in his paper, and analyze its results. We note that this reasoning is valid for arbitrary values of S and I .

The Hamiltonian of the system is written in the form

$$\mathcal{H} = \mathcal{H}_I + \mathcal{H}_d + \mathcal{H}_l + \mathcal{H}_{Id} + \mathcal{H}_{dl}, \quad (31)$$

where \mathcal{H}_I , \mathcal{H}_d , and \mathcal{H}_l are respectively the Hamiltonians of the Zeeman system of the nuclei, of the DDR of the magnetic ions (secular part), and of the lattice (it is assumed that the Zeeman degrees of freedom of the magnetic ions are in equilibrium with the lattice); \mathcal{H}_{Id} is the energy operator of the interaction between the spins of the nuclei and of the magnetic ions, and \mathcal{H}_{dl} is the energy operator of the interaction between the spins of the magnetic ions and the lattice.

The quantum equations of motion are (the square brackets denote a commutator)

$$\begin{aligned} \frac{d\mathcal{H}_I}{dt} &= -\frac{i}{\hbar} [\mathcal{H}_I, \mathcal{H}_{Id}] = K_I, & \frac{d\mathcal{H}_d}{dt} &= -\frac{i}{\hbar} [\mathcal{H}_d, \mathcal{H}_{dl}] = K_d, \\ \frac{d\mathcal{H}_d}{dt} &= -\frac{i}{\hbar} [\mathcal{H}_d, \mathcal{H}_{Id} + \mathcal{H}_{dl}] = K_d. \end{aligned} \quad (32)$$

Following Zubarev^[45], the statistical matrix of the system in the stationary nonequilibrium state can be written in the form

$$\rho = Q^{-1} \exp \left(- \left[\beta_I \mathcal{H}_I + \beta_d \mathcal{H}_d + \beta_l \mathcal{H}_l - \int_{-\infty}^0 e^{\epsilon t} dt \langle (\beta_I - \beta_l) K_I(t) + (\beta_d - \beta_l) K_d(t) \rangle \right] \right), \quad (33)$$

where Q is equal to the "trace" of the exponential, β_I , β_d , and β_l are the reciprocal temperatures of the nuclear Zeeman system, the DDR, and the lattice, respectively; $K(t)$ denotes the operator K in the Heisenberg representation; the transition to the limit $\epsilon \rightarrow +0$ should be made after the evaluation of the integral.

The mean value of K can be expressed by the formula

$$\bar{K} = \text{Sp}(\rho K). \quad (34)$$

Confining ourselves to the case of high temperatures,

we can expand the exponential in (33) in a series* and retain terms of first order of smallness. After calculating $\overline{K_I}$ and $\overline{K_d}$ and expressing further $\overline{\mathcal{E}_I}$ and $\overline{\mathcal{E}_d}$ in terms of β_I and β_d , we obtain the following system of equations (the dot denotes differentiation with respect to time)

$$\dot{\beta}_I = -\frac{\beta_I - \beta_d}{T_I} + \frac{\beta_d - \beta_I}{T_{Id}}, \quad \dot{\beta}_d = \frac{\beta_I - \beta_d}{T_{dI}} - \frac{\beta_d - \beta_I}{T_d}, \quad (35)$$

where

$$T_I^{-1} = \langle \overline{\mathcal{E}_I^2} \rangle^{-1} \int_0^1 d\lambda \int_{-\infty}^0 e^{e\lambda} \frac{\langle e^{-\beta_I \overline{\mathcal{E}_I} K_I K_I(t, \lambda \beta_I)} \rangle}{\langle e^{-\beta_I \overline{\mathcal{E}_I} K_I} \rangle} dt, \quad (36a)$$

$$T_d^{-1} = \langle \overline{\mathcal{E}_d^2} \rangle^{-1} \int_0^1 d\lambda \int_{-\infty}^0 e^{e\lambda} \frac{\langle e^{-\beta_d \overline{\mathcal{E}_d} K_d K_d(t, \lambda \beta_d)} \rangle}{\langle e^{-\beta_d \overline{\mathcal{E}_d} K_d} \rangle} dt, \quad (36b)$$

$$T_{Id}^{-1} = -\langle \overline{\mathcal{E}_I \mathcal{E}_d} \rangle^{-1} \int_0^1 d\lambda \int_{-\infty}^0 e^{e\lambda} \frac{\langle e^{-\beta_I \overline{\mathcal{E}_I} K_I K_d(t, \lambda \beta_I)} \rangle}{\langle e^{-\beta_I \overline{\mathcal{E}_I} K_I} \rangle} dt, \quad (37a)$$

$$T_{dI}^{-1} = -\langle \overline{\mathcal{E}_d \mathcal{E}_I} \rangle^{-1} \int_0^1 d\lambda \int_{-\infty}^0 e^{e\lambda} \frac{\langle e^{-\beta_d \overline{\mathcal{E}_d} K_d K_I(t, \lambda \beta_d)} \rangle}{\langle e^{-\beta_d \overline{\mathcal{E}_d} K_d} \rangle} dt, \quad (37b)$$

$$K(t, \gamma) = e^{-\gamma \overline{\mathcal{E}_I} K_I(t)} e^{\gamma \overline{\mathcal{E}_d} K_d}; \quad (38)$$

the symbol $\langle \rangle$ denotes

$$\langle A \rangle = \frac{\text{Sp } A}{\text{Sp } 1}. \quad (39)$$

T_I and T_d can be represented in the form

$$T_I^{-1} = T_{I\bar{I}}^{-1} + T_{I\bar{d}}^{-1}, \quad T_d^{-1} = T_{d\bar{I}}^{-1} + T_{d\bar{d}}^{-1}, \quad (40)$$

where

$$T_{I\bar{I}}^{-1} = -\langle \overline{\mathcal{E}_I^2} \rangle^{-1} \int_0^1 d\lambda \int_{-\infty}^0 e^{e\lambda} \frac{\langle e^{-\beta_I \overline{\mathcal{E}_I} K_I K_I(t, \lambda \beta_I)} \rangle}{\langle e^{-\beta_I \overline{\mathcal{E}_I} K_I} \rangle} dt, \quad (41a)$$

$$T_{d\bar{d}}^{-1} = -\langle \overline{\mathcal{E}_d^2} \rangle^{-1} \int_0^1 d\lambda \int_{-\infty}^0 e^{e\lambda} \frac{\langle e^{-\beta_d \overline{\mathcal{E}_d} K_d K_d(t, \lambda \beta_d)} \rangle}{\langle e^{-\beta_d \overline{\mathcal{E}_d} K_d} \rangle} dt. \quad (41b)$$

We note that

$$\frac{T_{dI}}{T_{Id}} = \frac{\langle \overline{\mathcal{E}_d \mathcal{E}_I} \rangle}{\langle \overline{\mathcal{E}_I^2} \rangle} = \frac{(2I+1)^N \text{Sp } \overline{\mathcal{E}_d^2}}{(2S+1)^N \text{Sp } \overline{\mathcal{E}_I^2}} = \frac{c_d}{c_I}, \quad (42)$$

where c_I and c_d are the heat capacities of the nuclear Zeeman system and of the DDR of the magnetic ions, respectively.

Calculation yields

$$T_I^{-1} = \frac{2\pi}{5} (\gamma_n g \beta)^2 S(S+1) \frac{N}{n} f(\omega_n) \sum_i r_{ik}^{-6}. \quad (43)$$

The summation takes place over the nuclei, and r_{ik} is the distance from the i -th nucleus to the k -th magnetic ion. $f(\omega)$ is given by the formula

$$f(\omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} \frac{\langle S_n^z S_n^z(t) \rangle}{\langle (S_n^z)^2 \rangle} e^{i\omega t} dt. \quad (44)$$

We assume that

$$\frac{\langle S_n^z S_n^z(t) \rangle}{\langle (S_n^z)^2 \rangle} = e^{-\frac{|t|}{\tau}}, \quad (45)$$

where τ is given by formula (9), and then

$$T_I^{-1} = \frac{2}{5} (\gamma_n g \beta)^2 S(S+1) \frac{\tau}{1 + (\omega_n \tau)^2} \sum_i r_{ik}^{-6} \frac{N}{n},$$

or (comparing with formula (24))

$$T_I^{-1} = C \frac{N}{n} \sum_i r_{ik}^{-6} = C \sum_k r_{ik}^{-6}. \quad (46)$$

*We expand the exponential (33) in terms of all the variables with the exception of $\beta_I H_I$.

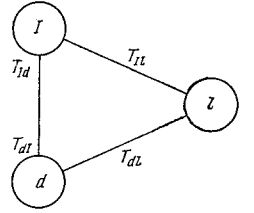


FIG. 3. Schematic picture of the relaxation with allowance for the dipole-dipole reservoir of the magnetic ion.

It is further easy to obtain the relation

$$\frac{c_d}{c_I} = \frac{NS(S+1)}{nI(I+1)} \left(\frac{\omega_d}{\omega_n} \right)^2, \quad (47)$$

where the quantity ω_d , which plays the role of the average DDR quantum, is given by the formula

$$\omega_d^2 = \frac{\langle \overline{\mathcal{E}_d^2} \rangle}{\hbar^2 \langle \sum_n S_n^z S_n^z \rangle}. \quad (48)$$

The relaxation picture is shown schematically in Fig. 3. I , d , and l denote respectively the nuclear Zeeman system, the DDR of the magnetic ions, and the lattice (the Zeeman degrees of freedom of the magnetic ions are combined with the lattice). $T_{I\bar{I}}$ and $T_{d\bar{d}}$ play the role of the partial relaxation times of the I and d systems with the lattice, respectively.

Equations of the type (35) are encountered in^[46,47], where their solutions are analyzed.* It follows from (35) that the relaxations of β_I and β_d are described by sums of two exponentials, $\exp(-\lambda_+ t)$ and $\exp(-\lambda_- t)$, where ($\lambda_+ > \lambda_-$)

$$\lambda_{\pm} = \frac{1}{2} \left(\frac{1}{T_d} + \frac{1}{T_I} \right) \pm \frac{1}{2} \left[\left(\frac{1}{T_d} - \frac{1}{T_I} \right)^2 + \frac{4}{T_{Id} T_{dI}} \right]^{1/2}. \quad (49)$$

It will become clear from what follows that for all the performed experiments it can be assumed that the condition $T_{d\bar{d}} \ll T_I$ is satisfied.

We confine ourselves to a consideration of particular cases^[44,25]. We are interested here in relaxation of β_I only.

Case I: $T_{Id} \gg T_{I\bar{I}}$. β_I relaxes with a relaxation time λ_-^{-1} , where

$$\lambda_- = T_I^{-1} = T_{I\bar{I}}^{-1}. \quad (50)$$

The nuclear spins relax directly with the lattice (more accurately, via the Zeeman degrees of freedom of the magnetic ions). The DDR of the magnetic ions does not take part in the relaxation of the nuclei.

Case II: $T_{dI} \gg T_{d\bar{d}}$. Assuming, in addition, that $T_{d\bar{d}} \ll T_I$, we find that β_I relaxes with a single relaxation time λ_-^{-1} , where

$$\lambda_- = T_I^{-1} = T_{I\bar{I}}^{-1} + T_{d\bar{d}}^{-1}. \quad (51)$$

The heat capacity of the DDR is in this case sufficiently large, and the reservoir is not heated by the relaxation of the nuclei.

Case III: $T_{Id} \ll T_{I\bar{I}}$, $T_{dI} \ll T_{d\bar{d}}$, $T_{dI} \ll T_{Id}$. β_I and

*It should be noted, however, that Eqs. (35) (but not (40)) differ from the corresponding equations of [46,47] in the permutation of T_{Id} and T_{dI} .

β_d first relax rapidly to a common value $(c_I + c_d)^{-1} [c_I \beta_I(0) + c_d \beta_d(0)]$, with a relaxation time λ_+^{-1} , where

$$\lambda_+ = T_{dI}^{-1} + T_{Id}^{-1} \cong T_{dI}^{-1}. \quad (52)$$

Further, β_I and β_d , remaining equal to each other, relax to β_I with a relaxation time λ_-^{-1} , where*

$$\lambda_- = \frac{c_d}{c_I} T_{dI}^{-1} + T_{Id}^{-1}. \quad (53)$$

Usually λ_-^{-1} is very small, so that only one relaxation time λ_-^{-1} is observed in the experiment.

In case III, the systems I and d are much more strongly coupled with each other than with the lattice. Then the heating of the DDR upon relaxation of the nuclei will be appreciable, thus slowing down the relaxation.

Two subcases are possible:

Subcase IIIa: $c_d/c_I \gg T_{dI}/T_{Id}$. The relaxation probability is

$$\lambda_- = \frac{c_d}{c_I} T_{dI}^{-1}. \quad (53a)$$

Subcase IIIb: $c_d/c_I \ll T_{dI}/T_{Id}$:

$$\lambda_- = T_{Id}^{-1}. \quad (53b)$$

In the latter case, the heating of the DDR is so strong that the nuclei relax directly with the lattice.

The relaxation process is described by four quantities with the dimension of time: T_{dI} , T_{Id} , T_{dI} , and T_{Id} . We have calculated above only the quantity T_I (formula (46)). For a complete solution of the problem it is necessary to find the quantities described by formulas (37) and (41). Let us see, however, what general conclusions can be drawn^[25]. It is known that $T_{dI} \cong \tau_I/2$ ^[20]. Therefore T_{dI} either remains unchanged, or decreases with increasing N (see Ch. I). Taking (40) into account, as well as the fact that $\dagger c_d \propto N^2$, we obtain $T_{dI}/T_{Id} \propto N^2$. From this we can apparently conclude that T_{dI} increases with increasing N .[‡] It can be assumed that when N increases T_{Id}/T_{dI} also increases. Indeed, at sufficiently small N the nuclear relaxation process does not affect the DDR, and therefore $T_{Id} < T_{dI}$; at sufficiently large N , the situation is reversed.

Further, τ_I is always so small that the satisfaction of the conditions $T_{dI} \ll T_{Id}$, T_{Id} should be expected in all cases. In all the performed experiments, the magnetic-ion concentration is so small that the condition $c_d \ll c_I$ is satisfied. According to (42) we obtain $T_{dI} \ll T_{Id}$. An important role for the sequel is played by the values of (T_{Id}/T_{dI}) and (T_{dI}/T_{Id}) . Let N_1 and N_2 be the solutions of the equations $T_{Id} = T_{dI}$ and $T_{dI} = T_{Id}$, respectively. N_1 and N_2 are functions of the tempera-

ture and of the external field. In addition, they depend strongly on the type of magnetic impurity and on the host substance. Taking the foregoing into account, we have:

$$\begin{aligned} T_{Id} < T_{dI} & \text{ when } N < N_1, \quad T_{Id} > T_{dI} & \text{ when } N > N_1, \\ T_{dI} > T_{Id} & \text{ when } N < N_2, \quad T_{dI} < T_{Id} & \text{ when } N > N_2. \end{aligned}$$

Let $N_2 < N_1$; then we get case I when $N < N_2$ and case II when $N > N_1$.^{*} Thus, if $N_2 < N_1$, then there is no region of N in which the heating of the DDR plays an important role in the relaxation of the nuclei. Let now $N_1 < N_2$. Then case I takes place when $N < N_1$, case III when $N_1 < N < N_2$, and case II when $N > N_2$. Thus, if $N_1 < N_2$, the heating of the DDR will play an important role in the relaxation of the nuclei for the intermediate values of N .

We note, however, that all these arguments are meaningful only if N_1 and N_2 are sufficiently small, since the entire theory is valid only at sufficiently low concentration of the magnetic impurity.

IX

In Ch. VI we compared the diffusion theory of nuclear relaxation with the experimental data published in 1965 and later. In the review^[3] we compared the theory with earlier experiments. With some of them, the theoretical results agree well. With others, there is only qualitative agreement. There are also experiments that deviate strongly from the theory as developed in Chapter I. It should be noted that the theory deviates principally from those low-temperature measurements in which rather large magnetic-ion concentrations are used ($N/n > 10^{-4}$). The discrepancy between theory and experiment is apparently due to the fact that in the theory it is necessary to take into account the possibility of heating of the DDR of the magnetic ions. To this end it is necessary to calculate the values of T_{Id} , T_{dI} , T_{Id} , and T_{dI} , and then carry out a quantitative analysis based on the results of Ch. VIII. However, generally speaking, the calculation should be carried out with allowance for spin diffusion. The disparity between theory and experiment in the case of helium temperatures and large N is possibly also due to another cause, namely to the fact that δ/R is not small enough under these conditions, and one of the criteria for the applicability of our theoretical analysis is violated. It is also possible that the discrepancy between theory and experiment is due in part to failure to take into account the anisotropy of the diffusion barrier.

In conclusion, we note once more that the theory (in the form expounded in Ch. I) is in fair agreement with many experiments performed at sufficiently low magnetic-impurity concentrations.

Recent interesting experimental papers^[49,50] indicate that in ruby, with a chromium concentration 0.05 at. % ($N/n = 5 \times 10^{-4}$) the coupling between the Zeeman system of the Al^{27} nuclei and the DDR of the chromium ions is much stronger than their coupling with the lattice. Ac-

*In the more general case, for an arbitrary value of the ratio c_d/c_I , we have

$$\lambda_- = \frac{c_d}{c_I + c_d} T_{dI}^{-1} + \frac{c_I}{c_I + c_d} T_{Id}^{-1}.$$

†For a regular distribution of the magnetic ions, $c_d \propto N^3$ (see [48]). However, if they have a random distribution, calculation leads to $c_d \propto N^2$ (this circumstance was pointed out to us by L.L. Buishvili).

‡The quantity T_{Id} , of course, decreases with increasing N , but there is every reason for assuming that this decrease is not faster than N^{-2} .

*More accurately, when $N < N_2$ we have the case I-II (II denotes the case opposite to the case I, i.e., satisfaction of the condition $T_{dI} > T_{Id}$), when $N_2 < N < N_1$ we have the case I-II, and when $N > N_2$ we have the case I-II.

cording to the statements made above (see Ch. VIII), the nuclear Zeeman system and the DDR are in equilibrium with each other, and relax together to equilibrium with the lattice. Indeed, it was shown in^[49] that the nuclear relaxation rate is described well by formula (53a). The experiment was performed at 4.2°K and 9 MHz.

In^[50] the EPR line in ruby was saturated under conditions of cross relaxation. It is known that cross relaxation leads to a change of the temperature of the magnetic-ion DDR, which in turn, in view of the strong coupling, should change the temperature of the Zeeman system of the Al²⁷ nuclei. The experiment was performed at 1.8°K and at 3.2 cm wavelength. The NMR signal of the Al²⁷ was measured in parallel. It was shown that the NMR signal is intensified, and that the maximum gain reaches 20–25.

It is of considerable interest to perform additional experiments on the relaxation of nuclei under conditions of strong coupling between the nuclear Zeeman system and the DDR of the magnetic ions.

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