

SPIN DIFFUSION

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1. INTRODUCTION

IN this paper we consider magnetic relaxation and dynamic polarization of nuclei in a diamagnetic crystal with small concentration of paramagnetic atoms. The following are examples of such systems:

- 1) A dilute paramagnetic salt (for example, lanthanum-magnesium double nitrate, in which a small fraction of the lanthanum atoms is replaced by cerium or neodymium atoms).
- 2) An oxide or halide of a non-transition metal with a small concentration of a transition metal (for example, Al_2O_3 with a small amount of Cr_2O_3 added).
- 3) An alkali-halide crystal with F centers.
- 4) A crystal containing free radicals.

The concept of nuclear spin diffusion was first introduced by Bloembergen.^[1] He has shown that spin diffusion plays an important role for nuclear magnetic relaxation in a diamagnetic crystal with small paramagnetic-atom concentration. It was shown later that spin diffusion plays an important role also for the dynamic polarization of nuclei in such a crystal. The investigation of the diffusion of nuclear spin has become of great interest, because the method of dynamic polarization is at the present time the most powerful method of polarization of light nuclei.

We review first the theory of direct relaxation and dynamic polarization of nuclei, owing to their dipole-dipole interaction with the magnetic ions. We then describe the mechanism of nuclear-spin diffusion, after which we present the theory of magnetic relaxation and dynamic polarization of nuclei with account of spin diffusion. At the end of the paper we compare theory with experiment.

2. NUCLEAR MAGNETIC RELAXATION WITHOUT ACCOUNT OF SPIN DIFFUSION

Since the concentration of magnetic ions in a crystal is assumed to be sufficiently small, there is a large number of nuclei* (of the given type) for each magnetic ion. In this connection, the average distance between the magnetic ion and the nucleus is sufficiently large and their dipole-dipole interaction prevails over the contact interaction. In addition, the Zeeman energy of the nuclear spin will be much larger than the energy of the interaction between the spins of the nucleus and the magnetic ion.

We denote by N the concentration of the magnetic ions (their number per unit volume of the sample), and by n the concentration of the nuclei (of the given type); $n \gg N$. We denote further by R the radius of the sphere per magnetic ion. We obtain

$$\frac{4\pi}{3} R^3 N = 1. \quad (2.1)$$

\mathbf{S} and \mathbf{I} will denote the spin operators of the electron shell of the magnetic ion and of the nucleus. We confine ourselves to examination of the case $I = 1/2$, since almost all the experiments have been carried out on protons or F^{19} nuclei.

A strong, external, uniform and constant magnetic field H is applied to the crystal, and the z axis is chosen along its direction. The Zeeman (Larmor) frequencies of the spins of the magnetic ion and of the nucleus are given by the formulas

$$\omega_e = \gamma_e H, \quad \omega_n = \gamma_n H, \quad (2.2)$$

*We are referring throughout not to the nuclei of the magnetic ions, but to the nuclei of the host lattice.

where γ_e is the absolute magnitude of the gyromagnetic ratio of the magnetic-ion shell, and γ_n is the gyromagnetic ratio of the nucleus.

For reorientation of the nuclear spin it is necessary that the energy of interaction of this spin with the environment be a function of the time. In other words, it is necessary that the nucleus be acted upon by a time-varying local magnetic field. The Fourier component of this field with frequency equal to the Larmor frequency of the nucleus ω_n causes reorientation of its spin.

In the case when the nuclear relaxation is due to the interaction between the nuclei and the magnetic ions, a distinction is made between relaxations of types I and II.^[2,3] In the case of relaxation of type I, the change in the energy of interaction of the spins of the nucleus and of the magnetic ion in time is due to a change in the vector joining them (both in magnitude and in direction), that is, to the motion. In the case of relaxation of type II, we can neglect the motion of the nucleus and of the magnetic ion. The time dependence of the energy of interaction of their spins will in this case be governed by the relaxation of the magnetic-ion spin.

In this review we consider only the case of relaxation of type II, due to dipole-dipole interaction between the spins of the nucleus and the magnetic ion.

For simplicity we shall first investigate the case $S = 1/2$ (for brevity we shall sometimes refer to the electron instead of to the shell of the magnetic ion).

Let us calculate the time of nuclear-spin relaxation for the case when the condition $\omega_n \tau_e \gg 1$ is satisfied (we are following^[2], see also^[3-5]) where τ_e is the time of spin lattice relaxation of the magnetic ion.

We consider a system consisting of one electron and one nucleus. This system has four states (see Fig. 1, which shows the case $\gamma_n > 0$), whose energies are given by the formula

$$E(b') - E(b) = E(a') - E(a) = \hbar\omega_e,$$

$$E(b') - E(a') = E(b) - E(a) = \hbar\omega_n$$

(in the energy levels we take into account the Zeeman energies of the electron and of the nucleus, while the spin-spin interaction energy is neglected).

The introduction of such a system is to some degree arbitrary, since there are many nuclei per mag-

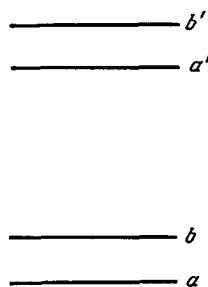


FIG. 1

netic ion. Further, the introduction of the energy levels a , a' , b , and b' is meaningful only when the Zeeman energy of the nucleus ($\hbar\omega_n$) is much larger than the width of the level (\hbar/τ_e), that is, if $\omega_n \tau_e \gg 1$.

Neglecting spin-spin interaction, we have (if $\gamma_n > 0$)

$$a = (-, +), b = (-, -), a' = (+, +), b' = (+, -),$$

where, for example, $(-, +)$ denotes the state with $S_z = -1/2$ and $I_z = +1/2$.

The dipole-dipole interaction of the spins \mathbf{S} and \mathbf{I} leads to a mixing of the wave functions. Since $\omega_n \ll \omega_e$, we can confine ourselves to a calculation of the mixing of the states with identical S_z and with values of I_z differing by unity. Application of perturbation theory yields

$$\begin{aligned} a &= (-, +) + \alpha(-, -), & a' &= (+, +) - \alpha(+, -), \\ b &= (-, -) - \alpha^*(-, +), & b' &= (+, -) + \alpha^*(+, +), \end{aligned} \quad (2.3)$$

where

$$\alpha = \frac{3}{4} \frac{g\beta \sin \vartheta \cos \vartheta e^{i\varphi}}{Hr^3}; \quad (2.4)$$

where r , ϑ , and φ are polar coordinates of the nucleus relative to the electron (the polar axis is directed along \mathbf{H}), g is the magnetic-ion g -factor, and β is the Bohr magneton ($g\beta = \hbar\gamma_e$). In order of magnitude we have

$$|\alpha| \sim \frac{H_{loc}}{H} \ll 1,$$

where $H_{loc} \approx g\beta/r^3$ is the local magnetic field produced by the electron at a distance r .

The interaction between the electron spin and the lattice causes spin reorientation. This interaction can be described by introducing a time-dependent relaxation Hamiltonian $\mathcal{H}_{rel}(t)$. The matrix elements of this operator differ from zero only when $\Delta S_z = \pm 1$ and $\Delta I_z = 0$. The probability (per unit time) of electron spin reorientation as a result of the perturbation $\mathcal{H}_{rel}(t)$ is, by definition $1/2\tau_e$ (without account of the Boltzmann factor). However, owing to the mixing of the states, we shall have not only transitions in which only S_z changes (the transitions $a \leftrightarrow a'$ and $b \leftrightarrow b'$), but also transitions in which I_z changes simultaneously with S_z (transitions $a \leftrightarrow b'$ and $a' \leftrightarrow b$).*

It is easy to see that the ratio of the matrix element of the transition $a' \leftrightarrow b$ (flip-flip transition, $S_z + I_z$ changes by ± 2) or $a \leftrightarrow b'$ (flip-flop transition, $S_z + I_z$ does not change) to the matrix element of the transition $a \leftrightarrow a'$ or $b \leftrightarrow b'$ has an absolute value $2|\alpha|$.

*The interaction between the electron spin and the lattice can be represented in the form $g\beta\mathbf{H}' \cdot \mathbf{S}$, where \mathbf{H}' is the effective fluctuating magnetic field due to the lattice vibrations. The component of \mathbf{H}' along the z axis does not produce any transitions in this case, and the magnitude of the component of \mathbf{H}' perpendicular to the z axis is defined by the requirement that the probability (per unit time) of the transition of the electron spin under the influence of the perturbation $g\beta\mathbf{H}' \cdot \mathbf{S}$ be equal to $1/2\tau_e$.

Taking into account the fact that the transitions $a \leftrightarrow a'$ and $b \leftrightarrow b'$ cause the spin-lattice relaxation of the electron spin with a relaxation time τ_e , we obtain

$$[T_n^{\text{dir}}(r)]^{-1} = \frac{4|a|^2}{\tau_e} = \frac{9}{4} \left(\frac{g\beta}{Hr^3} \right)^2 \frac{\sin^2 \vartheta \cos^2 \vartheta}{\tau_e}, \quad (2.5)$$

where $T_n^{\text{dir}}(r)$ is the nuclear relaxation time due to the interaction between the nuclear spin and the spin of an electron situated at a distance r from it. We note that $T_n^{\text{dir}}(r)$ is the longitudinal nuclear relaxation time, while the transverse nuclear relaxation time is not connected with the magnetic ions and is determined by the dipole-dipole interaction of the nuclei.

We take account further of the following fact. For reorientation of the nuclear spin it is immaterial what causes the reorientation of the spin of the magnetic ion. We denote by τ the correlation time of the quantity S_z . τ is determined approximately from the formula

$$\frac{1}{\tau} = \frac{1}{\tau_e} + \frac{1}{\tau_s}, \quad (2.6)$$

where τ_s is the spin-spin relaxation time of the magnetic ion.

In the case when the spin-spin relaxation of the magnetic ion is important, it is necessary to replace τ_e in (2.5) by τ . The result obtained in this case is valid if $\omega_n \tau \gg 1$. This condition means that the Zeeman energy of the nucleus greatly exceeds the width of the electronic levels* (which is of the order of \hbar/τ). In other words, this condition means that the probability of electron-spin reorientation during one Larmor period of the nuclear spin is small.

A more general calculation, for arbitrary $\omega_n \tau$ and arbitrary S , is given in^[1] (see also^[3]).

Calculation yields (see Appendix A)

$$[T_n^{\text{dir}}(r)]^{-1} = 3(\gamma_n g \beta)^2 S(S+1) r^{-6} \sin^2 \vartheta \cos^2 \vartheta \frac{\tau}{1 + (\omega_n \tau)^2}. \quad (2.7)$$

Let us assume that $\omega_n \tau = \tau \gamma_n H \gg 1$ (this has been the case in almost all the experiments performed to date). We also average over the angle ϑ (the average of $\sin^2 \vartheta \cos^2 \vartheta$ is equal to 2/15). We obtain

$$T_n^{\text{dir}}(r) = \frac{r^6}{C}, \quad (2.8)$$

where

$$C = \frac{2}{5} \frac{(g\beta)^2 S(S+1)}{\tau H^2}. \quad (2.9)$$

If, in particular, $S = 1/2$, then

$$C = \frac{3}{10} \frac{(g\beta)^2}{\tau H^2}. \quad (2.10)$$

We note that $C/2r^6$ gives a probability (per unit time) of relaxation reorientation of the spin of the nucleus located at a distance r from the magnetic ion,

due to the electron relaxation and the dipole-dipole interaction.

The value of τ_e depends on the temperature and on the external field, but does not depend on N . To the contrary, the value of τ_s does not depend on the temperature or on the field, but depends on N . The order of magnitude of τ_s can be estimated from the formula

$$\frac{\hbar}{\tau_s} \sim \frac{\beta^2}{(2R)^3} = \frac{\pi}{6} N \beta^2. \quad (2.11)$$

If the concentration of the magnetic ions is sufficiently small, and the temperature is not too low, we have $\tau_e \ll \tau_s$ and $\tau = \tau_e$. In the opposite limiting case of sufficiently high concentrations and sufficiently low temperatures we have $\tau_s \ll \tau_e$ and $\tau = \tau_s$.

According to the foregoing, in the case when $\tau_s < \tau_e$, the relaxation of the nuclei is caused by the time-varying local magnetic field, and the dependence of the local field on the time is brought about by the spin-spin relaxation of the magnetic ions. Therefore, the Zeeman energy of the relaxing nuclei will be transmitted to the system of electronic spins. Owing to the cross-relaxation process, this energy will be ultimately transmitted to the lattice.

An interesting situation should occur in the case when the concentration of the magnetic ions is such that $\tau_s < \tau_e$ but, on the other hand, the specific heat of the system of the magnetic ions is smaller than that of the system of nuclear spins*. In this case, the system of electronic spins will heat up during the course of the magnetic relaxation and magnetic resonance of the nuclei, provided only the cross-relaxation processes have no time to transfer the excess energy from the electron spins to the lattice.

We note further that formula (2.6) for τ is valid if $\hbar \gamma_e H / 2kT$ is smaller than or of the order of unity. In the opposite case it is necessary to take into account the fact that the transition “-” \rightarrow “+” of the magnetic-ion spin is hindered by a Boltzmann factor, so that the value of the first term in (2.6) is changed, and that the spin-spin relaxation of the magnetic ions is made difficult because the majority of the spins have the same direction. The latter circumstance changes the magnitude of the second term in (2.6).

The time of direct nuclear relaxation, given by (2.8), depends on r . Averaging $[T_n^{\text{dir}}(r)]^{-1}$ over r , we can obtain an expression for the average relaxation time, but the result obtained does not agree with experiment. This can be seen at least from the fact that according to experiment, the relaxation of the total nuclear magnetic moment of the sample is exponential, a fact which cannot be derived from the foregoing analysis.

*We are speaking here of that part of the electron-level width, which is due to the so called homogeneous broadening.

*Since the ratio of the magnetic moments of the magnetic ion and of the nucleus is of the order of 10^3 , satisfaction of the second condition requires that the relative concentration of the magnetic ions be, roughly speaking, less than 10^{-6} .

We shall see below that an account of spin diffusion changes completely the results concerning the nuclear magnetic relaxation.

3. INDUCED DYNAMIC NUCLEAR POLARIZATION WITHOUT ACCOUNT OF SPIN DIFFUSION

We return to Fig. 1 and formulas (2.3). An alternating field of frequency ω_e , applied perpendicular to the main field, gives rise to the transitions $a \leftrightarrow a'$ and $b \leftrightarrow b'$ (ordinary electron paramagnetic resonance). However, owing to the mixing of the wave functions, the alternating fields with frequencies $\omega_e + \omega_n$ and $\omega_e - \omega_n$ also give rise to transitions (forbidden transitions). The alternating field with frequency $\omega_e + \omega_n$ gives rise to the transitions $a \leftrightarrow b'$, while the alternating field with frequency $\omega_e - \omega_n$ causes the transitions $a' \leftrightarrow b$. However, as is well known, it is more convenient to determine in the experiment the frequency of the alternating field and to vary the magnitude of the main field. We then have

$$\left. \begin{aligned} &\text{for } H = H^* = \frac{\omega}{\gamma_e} \text{ transitions } a \leftrightarrow a', b \leftrightarrow b', \\ &\text{for } H = H_+ = H^* \left(1 + \frac{\gamma_n}{\gamma_e}\right) \\ &\quad \text{transitions } a' \leftrightarrow b \text{ (} H_+ \text{-transitions),} \\ &\text{for } H = H_- = H^* \left(1 - \frac{\gamma_n}{\gamma_e}\right) \\ &\quad \text{transitions } a \leftrightarrow b' \text{ (} H_- \text{-transitions).} \end{aligned} \right\} \quad (3.1)$$

By $G(H - H^*)$ we denote the function which gives the line shape of ordinary electron paramagnetic resonance, and whose integral is normalized to unity. The probability (per unit time) of an electron-spin transition due to an alternating field with amplitude $2H_1$ is (see, for example, [3,4])

$$w = \frac{\pi}{2} \gamma_e H_1^2 G(H - H^*). \quad (3.2)$$

Recalling that the ratio of the matrix element of the transition $a \leftrightarrow b'$ or $a' \leftrightarrow b$ to the matrix element of the transition $a \leftrightarrow a'$ or $b \leftrightarrow b'$ is equal to $2|\alpha|$, we obtain for the probability (per unit time) of the forbidden transitions under consideration

$$2|\alpha|^2 \pi \gamma_e H_1^2 G(H - H_{\pm}).$$

But according to (2.4) and (2.10) (we are averaging $|\alpha|^2$ over ϑ)

$$2|\alpha|^2 = \frac{C\tau}{2r^6}.$$

Thus, the probability (per unit time) of simultaneous reorientation of the spins of the electron and of the nucleus, separated by a distance r , due to the alternating field, is Γ_{\pm}/r^6 , where [4,6]

$$\Gamma_{\pm} = \frac{\pi}{2} \gamma_e H_1^2 G(H - H_{\pm}) \tau C. \quad (3.3)$$

Let $H \approx H^*$, and let the amplitude of the alternating

field H_1 satisfy the condition

$$2w\tau_e = \pi \gamma_e H_1^2 G(H - H^*) \tau_e > 1.$$

In such a case there will be noticeable saturation of the usual electron paramagnetic resonance (that is, of the transitions $a \leftrightarrow a'$ and $b \leftrightarrow b'$). It is easy to see, however, that the nuclei will not become polarized in this case, in view of the equality of the flip-flop ($a \leftrightarrow b'$) and flip-flip ($a' \leftrightarrow b$) relaxation-transition probabilities. [2,3,5] In other words, the Overhauser effect does not take place in the case of a diamagnetic crystal with a small concentration of paramagnetic atoms.

Assume now that $H \approx H_+$. The alternating field causes transitions $a' \leftrightarrow b$. Since the population of the state b is larger there will be more $b \rightarrow a'$ transitions than $a' \rightarrow b$ transitions. However, the transitions $b \rightarrow a'$ disturb the equilibrium between the electronic spins and the lattice. Owing to the spin-lattice relaxation, the electronic spin will flip from the state “+” to the state “-”, and the same electronic spin can further, under the influence of the alternating field, cause the flipping of another nuclear spin. Thus, if the relaxation time of the electronic spin is sufficiently small, and the relaxation time of the nuclear spin is sufficiently large, there can be unilateral transfer of the nuclear spins from the state “-” to the state “+”. It is easy to see that in the limiting case, if, first, we can neglect nuclear relaxation compared with electronic relaxation, and if the condition $\Gamma \gg C$ is satisfied* [or $\pi \gamma_e H_1^2 G(H - H_+) \tau \gg 1$], then the effective gyromagnetic ratio of the nucleus will be equal to γ_e . Similarly, in the case when $H \approx H_-$ it will be equal to $-\gamma_e$. If $\hbar \gamma_e H \ll kT$, we find that the polarization of the nuclei increases by a factor $\pm \gamma_e / \gamma_n$ †.

The phenomenon which we have considered, which consists in the polarization of the nuclei upon saturation of the forbidden transitions (resulting from the mixing of the wave functions by the dipole-dipole interaction of the spins of the magnetic-ion shell and of the nucleus) was discovered in France in 1958 [7,8] (see also the books and reviews [3,4,5,9]).

Various names were proposed for this phenomenon: effet solide, [3] double effet, [9] and dynamic polarization of nuclei [4] (we note, however, that the Overhauser effect is also one of the methods of dynamic polarization of nuclei).

We believe that this phenomenon is best called induced dynamic polarization of nuclei. Indeed, in the

*Since Γ/r^6 is the probability of simultaneous flipping of the spins of the nucleus and of the electron under the influence of an alternating field, and $C/2r^6$ is the probability of relaxation flipping of the nuclear spin, then the condition $\Gamma \gg C$ is the condition for saturation of the forbidden transition.

†If $\gamma_n < 0$, all the foregoing statements remain valid; it is merely necessary to take into account the fact that in this case $H_+ < H^*$ and $H_- > H^*$.

Overhauser effect the nuclear polarization is not brought about directly by the alternating field, but by relaxation; in the effect which we are considering however, the nuclear polarization is brought about directly by the alternating field.

The probability of simultaneous flipping of the spins of the electron and of the nucleus depends on the distance between them. In^[4,6,9] a simple model was investigated, in which this probability is averaged and a system consisting of N electronic and n nuclear spins is considered. For the intensification of the nuclear polarization one obtains, if the condition $\Gamma \gg C$ is satisfied, the expression

$$\rho = \pm \frac{\gamma_e}{\gamma_n} \left(1 + \frac{n\tau_e}{NT_n} \right)^{-1}. \quad (3.4)$$

The foregoing results, which pertain to induced dynamic polarization, are valid also when the width of the electron paramagnetic resonance is much smaller than the nuclear Larmor frequency. Indeed, in this case the usual electronic resonance (the transitions $a \leftrightarrow a'$ and $b \leftrightarrow b'$), the H_+ transition ($a' \leftrightarrow b$), and the H_- transition ($a \leftrightarrow b'$) are well resolved. In the opposite case, when the width of the electronic resonance is larger than or of the order of the nuclear Larmor frequency, an additional complication arises, connected with the fact that the alternating field causes simultaneously all three types of transitions. The expression obtained in this case for the intensification of the nuclear polarization depends on whether the broadening of the electronic resonance is homogeneous or inhomogeneous.

Let us analyze briefly the case of inhomogeneous broadening.^[3,4,6,9,19]

Let the frequency of the alternating field be fixed and equal to ω . The function $G(H - H^*)$ gives the shape of the EPR line (its integral is normalized to unity). $H^* = \omega/\gamma_e$ is the field corresponding to the center of the paramagnetic resonance (Fig. 2). By $H_{1/2}$ we denote the width of the electron paramagnetic resonance (the total width at half the height).

In the case of inhomogeneous broadening we can assume that the electronic line consists of narrow spin packets with width δ , and different spin packets relax and are saturated independently of one another. Assume that the following conditions are satisfied:

$$\delta \ll H_{1/2}, \quad \delta \ll \frac{\gamma_n}{\gamma_e} H^*.$$

The function $G(H - H^*)$ gives the distribution of the resonant fields over the sample* (for fixed constant frequency ω), brought about by the distribution of the local field.

Assume that we apply to the sample an external field H_0 . Figure 2 shows three packets, whose centers correspond to H_0 , H_+ , H_- , where (we are considering the case $\gamma_n > 0$)

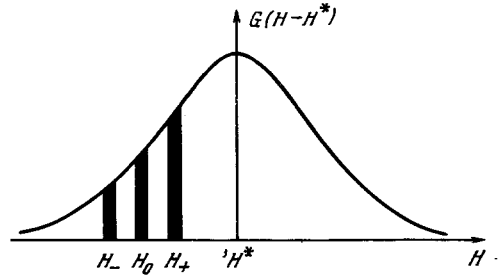


FIG. 2

$$H_{\pm} = H_0 \pm \frac{\gamma_n}{\gamma_e} H_0.$$

$G(H_0 - H^*)\delta$ gives the fraction of the spins which execute the transition corresponding to ordinary paramagnetic resonance. $G(H_- - H^*)\delta$ gives the fraction of the spins for which the resonant field is equal to $H_- = H_0 - \gamma_n H_0/\gamma_e$. Since the field applied to the sample is H_0 , these spins will experience a H_+ transition. Analogously, $G(H_+ - H^*)\delta$ gives the fraction of the spins which execute the H_- transition. Thus, if the conditions $\Gamma \gg C$ and $n\tau \ll NT_n$ are satisfied, we obtain for the amplification coefficient of the nuclear polarization

$$\rho(H_0) = \frac{\gamma_e}{\gamma_n} [G(H_- - H^*) - G(H_+ - H^*)] \delta. \quad (3.5)$$

Recognizing that the function $G(H - H^*)$ is symmetrical with respect to $H = H^*$, we find that ρ vanishes when $H_0 = H^*$. Further, $\rho < 0$ when $H_0 < H^*$ and $\rho > 0$ when $H_0 > H^*$.

If, in particular, the nuclear Larmor frequency is considerably smaller than the width of the electronic resonance (that is, $\gamma_n H^*/\gamma_e \ll H_{1/2}$), we can expand in (3.5) in powers of $H_+ - H_-$ and obtain

$$\rho(H_0) = -2\delta H_0 \left(\frac{dG}{dH} \right)_{H_0}. \quad (3.6)$$

Thus, in this limiting case ρ does not depend on γ_n . Further, ρ is proportional to dG/dH , and therefore ρ is maximal for those values of the external field, at which the slope of the electronic resonance curve is maximal. Finally, it is clear that the effect of the overlap of the transitions reduces the amplification coefficient ρ compared with its value in the absence of overlap.

In^[9] there is a detailed analysis of cases when the function G has Gaussian or Lorentzian shape. The same paper considers the case when the nuclear Larmor frequency is of the order of $H_{1/2}$ and also the case of a broad, homogeneously broadened electron-resonance line.

In^[11,12], account is taken of the cross-relaxation transitions between the different spin packets of the inhomogeneously broadened line. In^[13] these results are compared with the experimental data.

We note a recent paper,^[14] in which induced dynamic polarization was considered for the case of a broad, homogeneously broadened electronic-resonance

*That is, of the resonant values of the external field.

line, using the theory of saturation of the magnetic resonance developed in^[15].

The method of induced dynamic polarization has distinct advantages over the Overhauser method.^[3,4,9] The presence of mechanisms of relaxation of nuclear spin, for which the spin of the magnetic ion does not become reoriented, decreases the maximum dynamic polarization attainable when the Overhauser method is applied. On the other hand, when the method of induced dynamic polarization is used, these processes are insignificant (more accurately, their role can be suppressed by increasing the microwave power), provided their probabilities do not approach the probabilities of the purely electronic relaxation transitions. The method of induced polarization does not call for the application of large concentrations of magnetic centers; finally, this method is very effective for polarization of the lightest nuclei, which is very important from the point of view of the requirements of nuclear and elementary-particle physics.

Basing ourselves on the statements made in the beginning of this section, we can conclude that the effect of induced dynamic polarization takes place (and the Overhauser effect does not take place) if the relaxation of the nuclei is a dipole-dipole relaxation of type II, and the dipole-dipole interaction between the nucleus and the magnetic ion varies with time (owing to the spin flip of the magnetic ion) slowly compared with the Larmor precession of the nucleus, that is, if $\omega_n\tau$ is sufficiently large. In the opposite case, the induced dynamic polarization does not take place, but instead the Overhauser effect takes place.

Since ω_n is proportional to H , systems are possible which give the Overhauser effect for weak fields and the effect of induced dynamic polarization for strong fields.

The foregoing can be formulated differently.^[9] Assume that the relaxation of the nuclei is a dipole-dipole relaxation of type II. The operator of the energy of the interaction of the spins of the nucleus and of the magnetic ion can be represented in the form of a sum of static and fluctuating parts. If the static part predominates appreciably in this sum, then, according to the statements made in the beginning of this section, the Overhauser effect will not take place. On the other hand, the static part of the dipole-dipole interaction causes mixing of states with different I_z , and therefore an alternating field with frequency $\omega_e \pm \omega_n$ gives rise to induced dynamic polarization of the nuclei.

On the other hand, if the static part of the interaction is negligibly small compared with the fluctuating part, then we can also neglect the effect of mixing of the states, and therefore the effect of induced dynamic polarization will not take place (in other words, an alternating field with frequency $\omega_e \pm \omega_n$ produces no transitions). But an alternating field with frequency ω_e causes the electron spins to flip, and this in turn, owing to the fluctuating part of the dipole-dipole

interaction, leads to the polarization of the nuclei, that is, the Overhauser effect takes place.

We note in conclusion that all the results concerning induced dynamic polarization, presented in the present section, are valid only when the nuclear Zeeman frequency greatly exceeds the width of the electron paramagnetic resonance, due to the homogeneous broadening, that is, if $\omega_n\tau$ is sufficiently large, (it is actually only in this case meaningful to introduce the levels a , a' , b , and b').

4. NUCLEAR SPIN DIFFUSION

We have seen that the probabilities of nuclear spin flip, due to the relaxation ($C/2r^6$) or to the alternating field (Γ/r^6) depend on the distance from the nucleus to the magnetic ion r . Therefore, both in relaxation and in induced dynamic polarization, the component of the nuclear magnetization along the z axis (which we denote by M) will be a function of position. In the presence of a mechanism which makes it possible to transport nuclear magnetization (that is, excess spin), the quantity M will diffuse.

Such a mechanism is insured by flip-flop transitions of neighboring nuclei, due to their dipole-dipole interaction. An important fact is that in flip-flop transition of neighboring nuclei, the total Zeeman energy of their spins does not change, and therefore this process takes place without the lattice participating.

The question of the diffusion of the nuclear spin was considered in detail by Bloembergen.^[1] We note that the nuclei do not move during spin diffusion, only the excess of the nuclear spin projection diffuses. In the case of a nuclear spin equal to one half (in our review we consider only this case), it is always possible to introduce the concept of spin temperature T_S . In the problems considered by us T_S will be a function of position, and in place of the diffusion of nuclear magnetization we can speak of the diffusion of nuclear spin temperature.

Spin diffusion plays a very important role in the relaxation and induced dynamic polarization of nuclei in a diamagnetic crystal with a small concentration of paramagnetic ions.

Let us first consider the relaxation phenomenon. Assume that at the initial instant of time $t = 0$ an external constant field* H is superimposed on the sample. Then when $t = 0$ the spin temperature is infinite, that is, the sample contains an equal number of nuclear spins directed parallel and antiparallel to the external field. Since the time of direct relaxation of the nucleus (due to the magnetic ion) is proportional to the sixth power of the distance from the magnetic

*Or else when $t < 0$ a field H and an alternating field which completely saturated the nuclear resonance were applied to the sample. At the instant of time $t = 0$ the alternating field is turned off.

ion, the nuclei located near the paramagnetic ions will come rapidly into equilibrium with the lattice. This is the reason for the appearance of a gradient of spin temperature (near the paramagnetic ions T_S is equal to the lattice temperature, and far from the ions T_S is infinite). The presence of the gradient of T_S gives rise to the diffusion of the nuclear spins that are antiparallel to the external field toward the paramagnetic ions (in the case $\gamma_n > 0$). On approaching the magnetic ions, a fraction of the nuclear spins, directed antiparallel to the field, will reverse direction. Thus, the direct relaxation and diffusion will bring the system of nuclear spins into equilibrium with the lattice.

The situation is similar also in the case of induced dynamic polarization. The probability of spin flip due to the alternating field is inversely proportional to the sixth power of the distance from the magnetic ion. Therefore nuclei located near the magnetic ions are polarized very rapidly after application of the microwave field to the sample. Because of the resultant spin-temperature gradient, this polarization propagates also towards the far nuclei.

To construct a mathematical theory of spin diffusion, let us consider first a one-dimensional model. Assume that we have a linear chain of spins, with the distance between neighboring spins equal to a . We denote by W the probability (per unit time) of a flip-flop transition of a neighboring pair of oppositely directed nuclear spins.

We align the x axis with the chain and denote by $P_{\pm}(x)$ the probability that at the point x the spin is directed upward (downward). We introduce, further, the quantity

$$p(x) = P_+(x) - P_-(x). \quad (4.1)$$

The z -component of the magnetization M can be expressed in terms of p :

$$M = \frac{1}{2} n h \gamma_n p. \quad (4.2)$$

Introducing the spin temperature T_S , we have

$$\frac{P_+}{P_-} = \exp\left(\frac{\hbar \omega_n}{k T_S}\right), \quad p = \text{th} \frac{\hbar \omega_n}{2 k T_S}. \quad (4.3)^*$$

Let us consider three nuclear spins located at the points $x - a$, x , and $x + a$. For the process wherein nuclei located at the points x and $x + a$ go over from the state with spin projections $(-1/2, +1/2)$ into the state with projections $(+1/2, -1/2)$ we can readily obtain

$$\frac{\partial P_+(x)}{\partial t} = -\frac{\partial P_-(x)}{\partial t} = W P_+(x+a) P_-(x).$$

Considering further all the possible transitions with participation of the nuclear spin located at the point x , and confining ourselves here to interaction with the nearest neighbors, we obtain

$$\begin{aligned} \frac{\partial p(x)}{\partial t} = & 2W \{P_-(x)[P_+(x+a) + P_+(x-a)] \\ & - P_+(x)[P_-(x+a) + P_-(x-a)]\}. \end{aligned}$$

This equation can be readily transformed into

$$\frac{\partial p(x)}{\partial t} = W [p(x+a) + p(x-a) - 2p(x)]. \quad (4.4)$$

Assuming that $p(x)$ (and therefore also the spin temperature) varies little over a distance on the order of a , we can expand $p(x \pm a)$ in powers of a . Thus, we have, going over from p to M ,

$$\frac{\partial M}{\partial t} = W a^2 \frac{\partial^2 M}{\partial x^2}.$$

An account of the interaction of the spin with all the spins leads in the case of a linear chain to the equation

$$\frac{\partial M}{\partial t} = \frac{1}{2} \sum_n' W(na) (na)^2 \frac{\partial^2 M}{\partial x^2}, \quad (4.5)$$

where $W(na)$ is the probability of the flip-flop transition of a pair of identical nuclei, located at a distance na from each other; the summation is over all the integer (positive and negative) values of n ; the prime denotes that we have left out from the sum the term with $n = 0$.

In the three-dimensional case we find that the diffusion $M(r, t)$ is described by the equation

$$\frac{\partial M}{\partial t} = D \Delta M, \quad (4.6)$$

where D is the coefficient of diffusion of the nuclear spin.

In analogy with the case of the one-dimensional chain, it is necessary for (4.6) to be valid in the three-dimensional case that the relative change of M over a distance a be considerably smaller than unity. On the other hand, the applicability of (4.6) does not impose any limitations at all on the degree of polarization of the nuclei.

In fact, D is a symmetrical tensor of second rank, the components of which depend on the angles between the external field and the crystal axes. But in the case of a cubic single crystal, and also in the case of a polycrystalline sample or powder of any crystal system, D reduces to a scalar. We shall henceforth confine ourselves to a consideration of the case of a cubic crystal.

If we confine ourselves to an account of flip-flop transitions of nearest neighbors, we have

$$D \approx W a^2, \quad (4.7)$$

where W is the probability (per unit time) of a flip-flop transition of a pair of nearest identical nuclei, and a is the distance between them.

We shall henceforth use an estimate of W , obtained for a cubic crystal as a result of averaging over the directions (see Appendix C):

*th = tanh.

$$W \approx \frac{1}{30T_2}, \quad D \approx \frac{a^2}{30T_2}, \quad (4.8)$$

where T_2 is the transverse time of nuclear relaxation.*

Usually in a solid $T_2 \approx 10^{-5}$ sec and $a = (2-3) \times 10^{-8}$ cm. This yields $D \approx (1-3) \times 10^{-12}$ cm²/sec. Thus, the diffusion coefficient of the nuclear spin is exceedingly small.

The time required to transport the value M over a distance r is of the order r^2/D . For macroscopic values of r , the times are astronomical. For $r = 10^{-6}$ cm, however, this time is of the order of one second.

It is easy to calculate the coefficient of spin diffusion for a cubic single crystal with account of the anisotropy effects and of the fact that the flip-flop transitions take place not only for nearest identical neighbors. Assuming that the position of each nucleus is a symmetry center of the lattice, we can readily generalize (4.7) (see^[16,17]):

$$D = \frac{1}{6} \sum_j' W_{ij} r_{ij}^2, \quad (4.9)$$

where W_{ij} is the probability (per unit time) of the flip-flop transition of a pair of identical nuclei (i, j), and r_{ij} is the distance between them.† The summation is over all the nuclei j which are identical with the nucleus i (the prime indicates that the term $j = i$ is left out of the summation), and the sum does not depend on the position of the nucleus i . We note that (4.9) yields the diffusion coefficient of the nuclei of the type i .

Calculating W_{ij} (see Appendix C), we obtain

$$D = \frac{1}{48 \sqrt{2}} \hbar^2 \gamma_n^4 T_2 \sum_j' r_{ij}^4 (1 - 3 \cos^2 \vartheta_{ij})^2, \quad (4.10)$$

where ϑ_{ij} is the angle between the external field and the vector r_{ij} joining the nuclei i and j .

This expression can be transformed into (see Appendix B)

$$D = \lambda \frac{\sqrt{\pi}}{96} \hbar^2 \gamma_n^4 S^{-1/2} \sum_j' r_{ij}^4 (1 - 3 \cos^2 \vartheta_{ij})^2, \quad (4.11)$$

where S is the second moment of the nuclear resonance line of the nuclei of type i ‡ (that is, the mean square of the deviation of the nuclear-resonance frequency from the resonance frequency in the external field), due to the dipole-dipole interaction with the neighboring nuclei; λ —constant of the order of unity;*** in the case of a resonance line with Gaussian shape $\lambda = 1$.***

The value of S is given by a formula derived by

*The estimate $D \approx a^2/30T_2$ is used in the majority of papers on spin diffusion. However, in our opinion, this estimate yields a value of D too small by an approximate factor of 2 – 2.5 (see Appendix D).

†In^[16] formula (4.9) is given without the factor 1/6.

‡The nuclear-resonance width ΔH is of the order of $\gamma^{-1} S^{1/2}$.

***In the case of a resonance line with non-Gaussian shape, λ depends on the orientation of the crystal relative to the external field.

***It is stated in^[17] that in the case of a resonance line with Gaussian shape $\lambda = 3/\sqrt{2\pi}$.

Van Vleck^[18] [see Appendix B, formula (B.1)], which consists of two terms; the first is due to identical nuclei and the other to nonidentical nuclei (possessing spins).

In the case of a lattice in which all the nuclei possessing spins are identical (for example, in the case of CaF_2 , spin is possessed only by the F^{19} nuclei, which are located at the points of a primitive cubic lattice), there remains in S only the first term, and we obtain

$$D \propto \frac{\sum_j' r_{ij}^4 (1 - 3 \cos^2 \vartheta_{ij})^2}{\left[\sum_j' r_{ij}^6 (1 - 3 \cos^2 \vartheta_{ij})^2 \right]^{1/2}}. \quad (4.12)$$

A detailed analysis of this formula shows that the dependences of the numerator and the denominator on the orientation of the crystal relative to the direction of the external field do not differ greatly, and therefore the anisotropy of D will in this case be relatively small (see Appendix D for details). In the case of a lattice with nuclear spins of two sorts (for example, an alkali-halide crystal), the expression for S for nuclei of type i contains two terms, with the term due to the spins of the second sort predominating (since the spins of the second sort are the nearest neighbors). The dependences of the numerator and denominator of (4.11) on the crystal orientation will differ noticeably from each other, and therefore the anisotropy of the spin-diffusion coefficient will be considerably stronger than in the case of a lattice with identical spins.

We have assumed above that W , and therefore also D , is constant (that is, we have assumed that D does not depend on the position of the point in the crystal). In fact, however, D is a function of the distance r from the nearest magnetic ion, and when r is small $D(r)$ decreases with decreasing r .^[1,19] This is connected with the fact that the Zeeman frequencies of the nuclei located near the magnetic ions differ appreciably from one another (owing to the magnetic field produced by the ion). This hinders the flip-flop transitions of the neighboring nuclei, for in such a transition the total Zeeman energy of the spins is not conserved. It can be stated that near each magnetic ion there is a diffusion barrier, inside of which the diffusion of the nuclear spin is strongly hindered.

In the future we shall use for the function $D(r)$ the model of a rectangular well:

$$D(r) = \begin{cases} 0 & r < \delta, \\ \text{const} = D & r > \delta. \end{cases} \quad (4.13)$$

It remains to estimate the radius of the diffusion barrier δ .

The magnetic field due to the magnetic ion at a distance r is of the order of $\hbar \gamma_e / r^3$. The difference of these fields at points occupied by the neighboring nuclei (located along the radius) is of the order $\hbar \gamma_e a / r^4$.*

*In view of the crudeness of the estimates presented below, we neglect the factor 3 which results from the differentiation.

The width of the nuclear magnetic resonance is of the order of the magnetic field produced by the nucleus at the neighboring nucleus, that is, of the order of $\hbar\gamma_n/a^3$.

We can introduce the distance from the magnetic ion, at which the field produced by the magnetic ion is of the order of the width of the nuclear magnetic resonance. This distance is of the order of $(\gamma_e/\gamma_n)^{1/3}a$. The nuclei located in a sphere of such radius and centered about the magnetic ion have strongly shifted Zeeman frequencies (the shift of the Zeeman frequency exceeds the width of the nuclear magnetic resonance). These nuclei therefore do not participate in the nuclear magnetic resonance.

One can also introduce the distance from the magnetic ion, for which the difference of the Zeeman frequencies of the neighboring nuclei (located along the radius) is of the order of the width of the nuclear magnetic resonance. This distance is of the order of $(\gamma_e/\gamma_n)^{1/4}a$. For nuclei located in a sphere of such a radius and with its center on the magnetic ion, the flip-flop transitions, and consequently diffusion, are strongly hindered.

In view of the approximate nature of our analysis, we shall not distinguish between the two aforementioned lengths. Thus, we assume $\delta \sim (\gamma_e/\gamma_n)^\alpha a$, where $\alpha = 1/4 - 1/3$. In the future, in numerical estimates, we shall use the geometric mean of the two introduced lengths, that is, we shall assume that $\alpha = z/24$. We note that for an electron and a proton $\gamma_e/\gamma_n = 660$ and $\delta = 6.62 a$.*

Everything said concerning δ is valid if $\tau > T_2$. Indeed, in this case the nucleus is acted upon by the static magnetic field produced by the magnetic ion (since the direction of the nuclear spin does not change within a time of the order of T_2). If, however, $\tau < T_2$, this field averages out and it is necessary to replace in the foregoing expressions γ_e by $\gamma_e(\hbar\gamma_e H/2kT)$ (if $\hbar\gamma_e H < 2kT$). Thus,†

$$\delta \sim \left(\frac{\gamma_e}{\gamma_n}\right)^\alpha a \quad \text{when } \tau > T_2 \text{ or } \hbar\gamma_e H > 2kT, \quad (4.14a)$$

$$\delta \sim \left(\frac{\gamma_e}{\gamma_n} \frac{\hbar\gamma_e H}{2kT}\right)^\alpha a \quad \text{when } \tau < T_2 \text{ and } \hbar\gamma_e H < 2kT. \quad (4.14b)$$

*In fact, when we deal with the function $D(r)$, it is more correct to employ a value $\alpha = 1/4$. On the other hand, in the case of the function $A(r)$ (see Sec. 5, item 9), it is more accurate to use the value $\alpha = 1/3$.

†We note that almost everywhere when we say "larger than" or "smaller than" we imply in fact "considerably larger" and accordingly "considerably smaller."

‡The foregoing reasoning pertains to the case $S = 1/2$. In the general case we have

$$\delta \sim \left(2S \frac{\gamma_e}{\gamma_n}\right)^\alpha a \quad \text{for } \tau > T_2,$$

$$\delta \sim \left(2S \frac{\gamma_e}{\gamma_n} B_s \left(\frac{S\hbar\gamma_e H}{kT}\right)\right)^\alpha a \quad \text{for } \tau < T_2$$

(B_s is the Brillouin function). If $\tau < T_2$ and $S\hbar\gamma_e H < kT$, we obtain

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

If we take into account the fact that the width of the nuclear resonance is $\Delta H \sim \hbar\gamma_n/a^3$, we obtain for the dependence of δ on the width

$$\delta \propto (\Delta H)^{-\alpha}. \quad (4.15)$$

In fact $D(r)$ is a smooth function of r . The form of this dependence can be determined by using cross-relaxation theory. It is easy to see that it is necessary to substitute in formula (4.9) for the probability W_{ij} an expression that differs from formula (C.2) by an exponential factor that takes into account the difference between the Zeeman frequencies of the nuclei i and j . If on the other hand we confine ourselves to an account of flip-flop transitions of the nearest neighbors, the generalization of formula (4.7) gives for $D(r)$ an expression proportional to $\exp(-\text{const}/r^8)$. However, when $D(r)$ has such a form, the equation describing the diffusion of the nuclear spin can be solved only by numerical methods. We shall therefore use the square-well model for the function $D(r)$.

We neglect also the dependence of the radius of the diffusion barrier δ on the angle ϑ between the external electric fields and the vector joining the magnetic ion and the nucleus (see Sec. 5, item 8).

The concentration of the magnetic ions is assumed to be so small (a criterion will be given below) that the crystal can be regarded as consisting of individual systems, each of which is a magnetic ion surrounded by a large number of nuclear spins. Each such system can be regarded in this case as a sphere of radius R , given by formula (2.4).

We denote by \mathfrak{M} the summary z component of the nuclear magnetic moment of the sphere belonging to one magnetic ion

$$\mathfrak{M} = \int M dV, \quad (4.16)$$

where the integration is over the volume of a sphere of radius R with center at the magnetic ion (the summary z -component of the nuclear moment of the entire sample is equal to $NV\mathfrak{M}$, where V is the volume of the sample).

As was indicated above, nuclei located in a sphere of radius δ do not participate in the nuclear magnetic resonance. Therefore the experimentally measured quantity $\mathfrak{M}_{\text{exp}}$ differs from the expression (4.16) in the fact that a sphere of radius δ is excluded from the integration. However, the difference between \mathfrak{M} and $\mathfrak{M}_{\text{exp}}$ is negligible if $\delta \ll R$.* The latter condition is always satisfied if the concentration of the magnetic ions is not too large.

5. NUCLEAR MAGNETIC RELAXATION WITH ACCOUNT OF SPIN DIFFUSION

1. We now proceed to consider nuclear magnetic relaxation. We shall follow here our papers^[20-22].

*It is readily found that $\mathfrak{M}_{\text{exp}} = \mathfrak{M} - \mathfrak{M}_0 (\delta/R)^3$.

The z component of the nuclear magnetization $M(r, t)$ satisfies the equation^[1]

$$\frac{\partial M}{\partial t} = D \Delta M - 2AM - C \sum_m |\mathbf{r} - \mathbf{r}_m|^{-6} (M - M_0). \quad (5.1)$$

In this equation M_0 is the equilibrium value of M , A is the probability (per unit time) of nuclear spin flip under the action of the radio-frequency field saturating the nuclear resonance, and \mathbf{r}_m is the radius vector of the m -th paramagnetic ion. The first term in the right side of (5.1) describes the variation (in time) of M , due to the diffusion; the second and the third terms give the variation of M due to the saturating field and relaxation, respectively. Further, we have

$$M_0 = n \frac{(\hbar \gamma_n)^2 H}{4kT}, \quad (5.2)$$

$$A(H) = \frac{\pi}{2} \gamma_n h_1^2 g \left(H - \frac{\omega}{\gamma_n} \right), \quad (5.3)$$

where $2h_1$ is the amplitude, ω the frequency of the radio-frequency field saturating the nuclear resonance, and $g(H - \omega/\gamma_n)$ a function which gives the nuclear resonance line shape, and whose integral is normalized to unity. In particular, at exact resonance (we take into account the fact that $\pi g(0) = T_2 \gamma_n$)

$$A = \frac{1}{2} \gamma_n^2 h_1^2 T_2. \quad (5.3a)$$

In (5.1) it is assumed that nuclear relaxation is due exclusively to the magnetic ions under consideration. If in addition there is also a magnetic nuclear relaxation not connected with the magnetic ions (the so-called extraneous relaxation), with a partial relaxation time T_d , it is necessary to add to the right side of (5.1) the term $(M_0 - M)/T_d$.

We note that in the most general case, when we have a sample of noncubic symmetry and we take into account the spatial dependence of the diffusion coefficient due to the diffusion barrier, the first term of the right side of (5.1) is replaced by the expression

$$\sum_{\alpha, \beta=1}^3 \frac{\partial}{\partial x_\alpha} \left(D_{\alpha\beta} \frac{\partial M}{\partial x_\beta} \right).$$

Recently, Buishvili and Zubarev^[23] presented a quantum-statistical derivation of (5.1), using the method of the statistical operator for the nonequilibrium system, developed in^[24]. The results are given in Appendix E.

2. Our purpose is to determine the law governing the relaxation of the summary nuclear magnetic moment (more accurately, the summary z -component of the moment) of the sample.

Let us consider a stationary case in the absence of a saturating alternating field. We assume that the concentration of the magnetic ions is small, and also take account of the rapid decrease of the probability of relaxation of the nucleus with increasing distance from the magnetic ion; we can conclude that each nucleus experiences noticeable relaxation only from

the nearest magnetic ion, and therefore we confine ourselves in the sum over m to one term (the validity of this analysis is discussed in item 7 of the present section). In other words, we consider a system consisting of one magnetic ion, surrounded by a large number of nuclei. Choosing the origin at the center of the magnetic ion, we obtain

$$\Delta M - \beta r^{-6} (M - M_0) = 0, \quad (5.4)$$

where

$$\beta = \frac{C}{D}. \quad (5.5)$$

The general solution of Eq. (5.4), possessing central symmetry, is of the form

$$M(r) = M_0 - M_0 r^{-1/2} \left[AI_{-1/4} \left(\frac{\beta^{1/2}}{2r^2} \right) - BI_{1/4} \left(\frac{\beta^{1/2}}{2r^2} \right) \right]; \quad (5.6)$$

A and B are the integration constants, and $I_p(x)$ is given by the formula

$$I_p(x) = i^{-p} J_p(ix), \quad (5.7)$$

where $J_p(x)$ is the Bessel function.

Using the well-known expression for the function $I_p(x)$ for small values of the argument*, we can easily obtain the asymptotic form of (5.6) for $r \gg \beta^{1/4}$ (the expansion is in powers of the quantity β/r^4):

$$M(r) = M_0 - M_0 \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}} \left[\left(1 - \frac{B}{A} \frac{b}{r}\right) + \frac{\beta}{12r^4} \left(1 - \frac{3B}{5A} \frac{b}{r}\right) \right], \quad (5.8)$$

where b is a quantity with the dimension of length:

$$b = \frac{\pi\beta^{1/4}}{2^{5/2} \left[\Gamma\left(\frac{5}{4}\right) \right]^2} = 0.68 \left(\frac{C}{D} \right)^{1/4}. \quad (5.9)$$

We introduce the quantity F (with dimension of length) by means of the formula

$$\frac{F}{b} = \frac{B}{A}. \quad (5.10)$$

Neglecting in (5.8) the term proportional to $(b/r)^5$, we obtain

$$M(r) = M_0 \left\{ \left[1 - \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}} \right] + \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}} \left[\frac{F}{r} - \frac{\beta}{12r^4} \right] \right\}. \quad (5.11)$$

The solution $M(r)$ contains two constants: A and F . For the problem to be stationary it is necessary that for large r the quantity M be maintained artificially

*When $x \ll 1$ we have

$$I_p(x) = \frac{x^p}{2^p \Gamma(p+1)} \left[1 + \frac{x^2}{4(p+1)} \right],$$

and when $x \gg 1$

$$I_p(x) = \frac{e^x}{\sqrt{2\pi x}} \left[1 - \frac{4p^2 - 1}{8x} \right].$$

constant, and not equal to M_0 (if we stipulate in our stationary problem that M be equal to M_0 for large r , we obtain automatically that $M = M_0$ for all r). This boundary condition for large values of r makes it possible to determine the constant A . We shall see below that the constant A drops out of the expression for the relaxation time of the summary z -component of the nuclear magnetic moment of the sample (in other words, the relaxation time of the summary moment does not depend on the boundary condition when r is large).

To determine the constant F , on the other hand, it is necessary to impose on the exact solution, that is, on expression (5.6), a suitable boundary condition for small r (see below).

In particular, if $M(\infty) = 0$, then (5.11) yields $A = \pi\beta^{1/8}/4\Gamma(5/4)$ and we have, further

$$M(r) = M_0 \left(\frac{F}{r} - \frac{\beta}{12r^4} \right). \quad (5.12)$$

If in (5.11) we neglect the term proportional to $(b/r)^4$, we obtain

$$M(r) = M_0 \left[1 - \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}} \left(1 - \frac{F}{r} \right) \right]. \quad (5.13)$$

In particular, if $M(\infty) = 0$, then (5.13) yields*

$$M(r) = M_0 \frac{F}{r}. \quad (5.14)$$

In what follows, in calculating the flux of the nuclear moment and of the magnetic moment of the sphere per magnetic ion, we shall use formula (5.13). In order for our analysis to be correct, it is necessary to satisfy the conditions

$$b \sim \beta^{1/4} \ll R, \quad F \ll R. \quad (5.15)$$

The first of these conditions is required in order that formula (5.13) be applicable in the greater part of the volume of the sphere of radius R and with center at the magnetic ion. The second condition, on the other hand, is necessary to satisfy the inequality

$$|M(R) - M(\infty)| \ll M_0;$$

only in this case can we assume that each nucleus is acted upon only by the nearest magnetic ion.

3. According to (5.13), the flux of the nuclear magnetic moment† through a sphere of radius r is (for $r \gg \beta^{1/4}$) equal to

*It is physically more sensible to employ the boundary condition not at $r = \infty$, but at $r = R$, since there is a sphere with radius R for each magnetic ion. If we stipulate that $M(R) = M_1 \neq M_0$, then (5.13) yields

$$M(r) = \left(1 - \frac{F}{R} \right)^{-1} \left[\left(M_1 - M_0 \frac{F}{R} \right) + (M_0 - M_1) \frac{F}{r} \right].$$

†In all that follows we take nuclear magnetic moment (flux of nuclear magnetic moment, summary nuclear magnetic moment of a sphere with radius R or of a sample) to mean the z -component of the nuclear magnetic moment.

$$D \cdot 4\pi r^2 |\text{grad } M| = 4\pi DF M_0 \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}}.$$

For the summary nuclear moment of a sphere of radius R with center at the magnetic ion, Eq. (5.13) yields

$$\mathfrak{M} = \frac{4\pi}{3} R^3 M_0 \left[1 - \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}} \right] + 2\pi FR^2 M_0 \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}}.$$

Recognizing that the equilibrium value of \mathfrak{M} is

$$\mathfrak{M}_0 = \frac{4\pi}{3} R^3 M_0,$$

we obtain

$$\mathfrak{M}_0 - \mathfrak{M} = \frac{M_0}{N} \frac{4\Gamma\left(\frac{5}{4}\right)A}{\pi\beta^{1/8}} \left(1 - \frac{3F}{2R} \right).$$

Thus, the flux of nuclear moment through a sphere of radius R can be expressed in the following fashion:

$$\frac{4\pi NDF}{1 - \frac{3F}{2R}} (\mathfrak{M}_0 - \mathfrak{M}).$$

Neglecting the quantity $3F/2R$ compared with unity, we obtain finally for the flux the expression:

$$4\pi NDF (\mathfrak{M}_0 - \mathfrak{M}). \quad (5.16)$$

In the stationary case, the flux of nuclear moment through the sphere of radius R is equal to the summary nuclear moment "emitted" by the magnetic ion per second. The stationary behavior is ensured in this case by the conditions at large distances from the ion, where there is a sink of nuclear moment if $M(R) < M_0$. [If $M(R) > M_0$, the magnetic ion "absorbs" the nuclear moment and a source of moment exists at large distances.]

In the nonstationary problem of the relaxation (restoration) of the nuclear magnetic moment after turning off the saturating alternating field (or after turning on the constant field H in the absence of a saturating field), the situation is entirely different. There are no sinks or sources of nuclear moment at large distances from the ions at all. In the nonstationary problem (5.16) gives the summary magnetic moment "emitted" by the magnetic ion per second. But this very quantity will be equal to the change in the summary magnetic moment \mathfrak{M} of the sphere of radius R per second due to relaxation.

We see therefore that it follows from (5.1) that

$$\frac{\partial \mathfrak{M}}{\partial t} = \frac{1}{T_n} (\mathfrak{M}_0 - \mathfrak{M}) - 2A\mathfrak{M}, \quad (5.17)$$

where

$$T_n = \frac{1}{4\pi NDF} = \frac{R^3}{3DF}. \quad (5.18)$$

Since the nuclear magnetic moment of the sample differs from the nuclear magnetic moment of a sphere of radius R by a constant factor (equal to NV), we can

take \mathfrak{M} in (5.17) to mean the nuclear magnetic moment of the sample. In this case \mathfrak{M}_0 will be the equilibrium nuclear moment of the sample:

$$\mathfrak{M}_0 = VM_0.$$

Thus, we have proved that the summary nuclear magnetic moment of the sample \mathfrak{M} has a single relaxation time T_n . Thus the problem of determining the relaxation time T_n has been reduced to the problem of finding the value of F .

We see from the foregoing that the fact that the relaxation is exponential follows from the fact that in the stationary problem, without a saturating field, the flux of magnetic moment through a sphere of radius R and with center at the magnetic ion, is proportional to $\mathfrak{M}_0 - \mathfrak{M}$. The latter circumstance, on the other hand, follows from the fact that when $r \gg b$ we have

$$M(r) = M(\infty) + \frac{\text{const}}{r}.$$

In the absence of a saturated field we have

$$\mathfrak{M}(t) = \mathfrak{M}_0 + [\mathfrak{M}(0) - \mathfrak{M}_0] e^{-t/T_n}. \quad (5.19)$$

In the presence of a field that saturates the nuclear resonance we have

$$\mathfrak{M}(t) = \mathfrak{M}_s + [\mathfrak{M}(0) - \mathfrak{M}_s] \exp \left[- \left(\frac{1}{T_n} + 2A \right) t \right], \quad (5.20)$$

where \mathfrak{M}_s is the stationary value of \mathfrak{M} :

$$\mathfrak{M}_s = \frac{\mathfrak{M}_0}{1 + 2AT_n}. \quad (5.21)$$

Thus, the value we obtain for T_n satisfies also the other definition of the relaxation time

$$T_n = (2A_{1/2})^{-1}, \quad (5.22)$$

where $A_{1/2}$ is that value of A at which $\mathfrak{M}_s = \mathfrak{M}_0/2$.

4. At large values of r Eq. (5.4) yields $\Delta M = 0$. This equation is satisfied by expression (5.13), which is also the asymptotic form (when $r \gg b$) of the exact solution of Eq. (5.4). On the other hand, the second term of (5.4) prevails when r is small. Thus, if $b > \delta$, diffusion plays the principal role when $r > b$ and direct relaxation when $r < b$. In other words, roughly speaking, b is that distance from the magnetic ion, up to which the direct relaxation of the nuclei is effective.

It is clear from the foregoing that if $\delta \ll b$, the presence of a diffusion barrier plays no role whatever; on the other hand, if $b < \delta$, the diffusion barrier is very appreciable and must lead to a slowing down of the relaxation.

To take into account the diffusion barrier, we impose upon $M(r)$ the boundary condition

$$\frac{dM}{dr} = 0 \quad \text{for } r = \delta, \quad (5.23)$$

which expresses the vanishing of the diffusion nuclear-moment flux at $r = \delta$. Substitution of (5.6), with account of (5.10), yields

$$\frac{F}{b} = \frac{I_{-1/4}(x) + 4xI'_{-1/4}(x)}{I_{1/4}(x) + 4xI'_{1/4}(x)},$$

where

$$x = \frac{\beta^{1/2}}{2\delta^2} = 1.08 \left(\frac{b}{\delta} \right)^2. \quad (5.24)$$

Using the well-known formula which expresses the derivative of the Bessel function* we obtain

$$\frac{F}{b} = \frac{2xI_{3/4}(x)}{2xI_{5/4}(x) + I_{1/4}(x)}; \quad (5.25)$$

(5.24) and (5.25) express F as a function of b and δ . Substitution in (5.18) yields the relaxation time T_n .

Using the expression for the Bessel functions at large and small values of the argument, we obtain in the limiting cases

$$F = b, \quad T_n = \frac{1}{4\pi NDb} = 1.6 \frac{(bR)^3}{C} \quad \text{for } b > \delta, \quad (5.26a)$$

$$F = \frac{C}{3D\delta^3} = 1.6 \frac{b^4}{\delta^3},$$

$$T_n = \frac{0.05}{NDb} \left(\frac{\delta}{b} \right)^3 = \frac{(\delta R)^3}{C} \quad \text{for } b < \delta. \quad (5.26b)$$

The result (5.26a) was obtained in a different manner by deGennes^[25] (see Appendix F), while the result (5.26b) was obtained by Blumberg^[19] (see Appendix G).

If δ/b is small, the diffusion barrier is insignificant. We can assume D constant for all r and impose on (5.6) the requirement $M(0) = M_0$. Recognizing that $I_{1/4}(x)$ and $I_{-1/4}(x)$ become infinite when $x = \infty$ and that their difference vanishes, we reach the conclusion that the requirement $M(0) = M_0$ yields $A = B$. Using (5.10), we obtain $F = b$.

We note also that if $\delta \ll b$, the conditions $M(0) = M_0$, $M(\delta) = M_0$, $dM/dr|_0 = 0$, and $dM/dr|_\delta = 0$ lead to identical results.

In the case of large δ/b , the result (5.26b) can be obtained directly by imposing the condition (5.23) on the function (5.11).

Using (2.1), (2.9), (5.9), and (5.26), we obtain the dependence of T_n on the concentration of the magnetic atoms, the field intensity, and the temperature:

$$T_n \propto N^{-1} \tau^{1/2} H^{1/2} \quad \text{for } b > \delta, \quad (5.27a)$$

$$T_n \propto N^{-1} \tau H^2 \delta^3 \quad \text{for } b < \delta. \quad (5.27b)$$

According to (2.9), (4.14), and (5.9), the quantity b decreases with decreasing temperature, and δ increases. Therefore, at sufficiently high temperatures we have $b > \delta$, and at sufficiently low ones $b < \delta$.

If, in particular, $b < \delta$ and $\tau_S < \tau_e$ (that is, $\tau \approx \tau_S$), then (2.11), (4.14), and (5.27b) yield

$$T_n \propto N^{-2} H^2 \quad \text{when } \tau > T_2 \quad \text{or } \hbar \gamma_e H > 2kT, \quad (5.27c)$$

$$T_n \propto N^{-2} H^{2+3a} T^{-3a} \quad \text{when } \tau < T_2 \quad \text{and } \hbar \gamma_e H < 2kT. \quad (5.27d)$$

* $\frac{dI_p(x)}{dx} = \frac{p}{x} I_p(x) + I_{p+1}(x)$.

We use the following terminology.^[19] When $b > \delta$, we say that diffusion-limited relaxation takes place; if $b < \delta$, we say that rapid diffusion takes place. The latter designation is connected with the fact that if $b < \delta$, the diffusion in the region where it is possible ($r > \delta$) is rapid compared with the direct relaxation.*

Comparison of (5.26a) with (5.26b) shows that in the case when $\delta > b$ the relaxation time contains an additional factor $(\delta/b)^3$, which greatly retards the relaxation of the summary magnetic moment of the sample.

The physical cause of the slowing down of the relaxation in the case $\delta > b$ is obvious. In the region $b < r < \delta$ there is no diffusion (since $r < \delta$), and the direct relaxation is slow (since $r > b$).

In other words, the inequality $\delta > b$ denotes that the diffusion of the nuclear Zeeman energy to the magnetic ion (to a distance δ) is more rapid than the transfer of this energy to the magnetic ion. Therefore, if the ratio δ/b is sufficiently large, the system of nuclei located in the region $\delta < r < R$ soon reaches internal equilibrium, after which this system will gradually approach equilibrium with the lattice. Consequently, when $\delta < r < R$ the nuclear magnetization M will be a function of the time but not of the position^[19] (for more details see Appendix G).

In the stationary problem which we are considering, if δ/b is sufficiently large, we have [we choose a solution satisfying the condition $M(\infty) = 0$]

$$M(\delta) = M_0 \frac{3F}{4\delta} = M_0 \frac{\beta}{4\delta^4} = 1.17M_0 \left(\frac{b}{\delta}\right)^4 \ll M_0. \quad (5.28)$$

$M(\delta)$ decreases with increasing δ , owing to the decrease in the role of the direct relaxation at a distance δ .

Numerical calculations, based on formulas (5.18) and (5.25), are given in^[26]. The quantity T_n is represented in the form $T_n = \text{const} \cdot x^{-1}$ [x is given by (5.24)]. The plot of n against x shown in Fig. 3 is a result of these calculations.

In the limiting case of large x ($b \gg \delta$) we have $n = 0.5$; for small x ($b \ll \delta$) $n = 2$. We see from the curve that these limiting values are obtained (approximately) quite rapidly: when $b = 1.5\delta$ we have $n \approx 0.58$ and when $\delta = 2b$ we have $n \approx 1.9$.

We note finally, that if extraneous nuclear relaxation also takes place, with a partial relaxation time T_d , then the summary time of nuclear relaxation T_n is given by the formula

$$T_n^{-1} = T_d^{-1} + 4\pi NDF. \quad (5.29)$$

5. In calculating the relaxation time we have used the model of a square well for the function $D(r)$. More accurately, a calculation which takes into account the presence of the diffusion barrier should be carried out in the following fashion. It is first necessary to determine $D(r)$, using the cross-relaxation theory

*This is precisely why T_n does not depend on D when $b < \delta$.

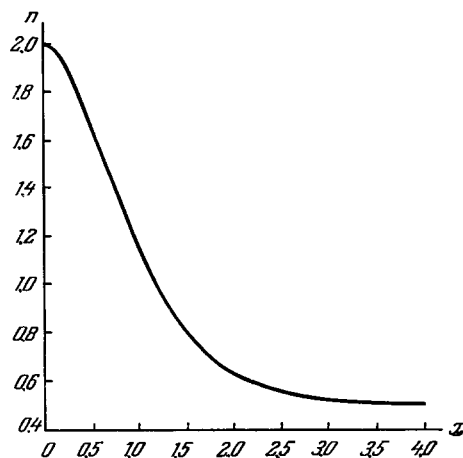


FIG. 3

(see Sec. 4). Then the diffusion term in the equation for $M(r, t)$ will be equal to

$$\text{div}(D(r) \text{grad } M) = D(r) \Delta M + (\text{grad } D, \text{grad } M).$$

Thus, we add to the right side of (5.1) the term $(\text{grad } D, \text{grad } M)$. In place of (5.4) we obtain

$$D(r) \Delta M + (\text{grad } D, \text{grad } M) - Cr^{-6}(M - M_0) = 0. \quad (5.30)$$

It is then necessary to find the centrally-symmetrical solution of (5.30), satisfying the conditions $M(0) = M_0$ (this condition expresses the fact that nuclei located near the magnetic ions are in equilibrium with the lattice) and $M(\infty) = 0$. It is necessary to find the asymptotic behavior of this solution, which will take the form (5.14), since for sufficiently large r we have $D(r) = \text{const}$. We thus obtain F and then, using (5.18), we obtain T_n . However, Eq. (5.30) with variable $D(r)$ can be solved only by numerical means.

We must note in this connection that such a calculation is meaningful only if we take into account, simultaneously with the dependence of the diffusion coefficient on r , also the barrier anisotropy effects (see below). Indeed, it can be assumed that effects produced by the barrier anisotropy will be of the same order of magnitude and possibly even stronger than the effects due to the smooth decrease of the diffusion coefficient on approaching the magnetic ion.

In view of the foregoing, it is desirable to replace this procedure by solving (5.4) with constant D when $r > \delta$ and with the corresponding boundary condition when $r = \delta$. The condition (5.23) which we have employed follows from the continuity of the nuclear-moment flux density [that is, from the expression $-D(r) \text{grad } M$], if we assume that $D(r) = 0$ when $r < \delta$.

It is clear in this case that the result (5.26a) is not connected with the use of the square-well approximation for the function $D(r)$ (since the diffusion barrier plays no role when b is considerably larger than δ). On the other hand, the result (5.26b) will be more accurate to a coefficient which, roughly speaking, is of the order of unity.

In Appendix H, the stationary problem is considered for the case when $D(r) = D_1$ for $r < \delta$ and when $D(r) = D$ for $r > \delta$.

6. Let us examine the conditions for the applicability of the analysis presented in this section.

The nuclear-spin diffusion plays an essential role when $r > \max(b, \delta)$. For the macroscopic description of the spin diffusion to be valid it is necessary that the latter quantity be appreciably larger than a . For our analysis to be correct it is also necessary that $\delta \ll R$;^{*} we take into account, further, Eq. (5.15) and the fact that $F \leq b$. We then obtain the following conditions for the validity of our analysis:

$$a \ll \max(b, \delta) \ll R. \quad (5.31)$$

It is also necessary to satisfy the condition

$$T_n = \frac{R^3}{3DF} \gg T_n^{\text{dir}} [\max(b, \delta)] = C^{-1} [\max(b, \delta)]^6,$$

or

$$[\max(b, \delta)]^6 \ll \frac{R^3 b^4}{F}.$$

This inequality, however, follows automatically from the inequality $(b, \delta) \ll R$.

7. According to (5.18), (5.26), and (5.31) we have

$$T_n = \frac{R^3}{3DF} \gg \frac{R^2}{D}; \quad (5.32)$$

where R^2/D is the time during which the nuclear spin diffuses over a distance of the order of R . We can alternately write (5.32) in the form

$$(DT_n)^{1/2} = R \left(\frac{R}{3F} \right)^{1/2} \gg R. \quad (5.32a)$$

$(DT_n)^{1/2}$ is the distance covered by the nuclear spin during the relaxation time T_n . We find therefore that prior to the relaxation the nuclear spin has time to stay near a large number of magnetic ions.

This raises the question of the validity of retaining only one term in the sum over the magnetic ions in (5.1) in the analysis of the stationary problem [see (5.4)].

Direct relaxation of the nuclei plays an important role only for those nuclei, the distance of which from the nearest magnetic ion is smaller than or of the order of $\max(b, \delta)$. On the other hand, we assume that the condition $(b, \delta) \ll R$ is satisfied. Therefore, inside a sphere centered about a certain magnetic ion and having a radius R we can neglect the relaxation due to the other ions.

The stationary problem which we have considered above has an auxiliary character. We have proved with its aid that the nuclear magnetic moment "emitted" per unit time by the magnetic ion is proportional to the deviation of the magnetic moment of a sphere of radius R from its equilibrium value.

When the nuclear spin goes over from the vicinity

of one magnetic ion into the vicinity of another (this takes place within a time of the order of R^2/D), the magnetic ion causing the spin relaxation changes. This circumstance, however, does not play any role in the stationary problem.

De Gennes, considering the case of absence of a diffusion barrier, takes into account the action on the nuclear spin of all the magnetic ions.^[25] The result obtained by him coincides in this case with (5.26a). However, de Gennes' calculation is difficult to generalize to the case when the diffusion barrier exists.

8. Let us discuss briefly the possibility of taking into account the effect of angular anisotropy in diffusion theory.

The quantity D (we are referring to the diffusion coefficient far from the magnetic ions) depends on the orientation of the crystal relative to the external field. The quantities C and δ also depend, generally speaking, on the orientation of the crystal (owing to the dependence of the correlation time τ and the width of the nuclear resonance ΔH on the orientation). But C and δ depend also on the angle ϑ between the vector \mathbf{r} , which joins the nucleus and the nearest magnetic ion, and the direction of the external magnetic field.* Since we introduce the quantity δ , it is clear here that we are again dealing with the square-well model for the function $D(r)$, but with an anisotropic radius of the diffusion barrier.

It is clear that the difficult problem is to take into account the dependence of C and δ on the angle ϑ . On the other hand, the fact that some quantities depend on the orientation of the crystal raises no difficulty, since these values are fixed for a given crystal orientation.

If we average all the quantities over the angle ϑ , then the results obtained in the present section will be valid[†], but in the final formulas it is necessary to take into account the dependence of D , C , and δ on the orientation of the crystal.

In the case when $b > \delta$, we obtain for the dependence of T_n on the orientation of the crystal, in accordance with (5.26a) and (4.11) (we neglect the dependence of τ on the orientation of the crystal),

$$T_n \propto D^{-3/4} \propto S^{3/8} \left[\sum_j r_{ij}^{-4} (1 - 3 \cos^2 \theta_{ij})^2 \right]^{-3/4}. \quad (5.33)$$

According to the statements made in Sec. 4, we expect the anisotropy of T_n to be stronger in the case of a lattice containing two or more species of nuclei with spins, than in the case of a lattice in which all the nuclei having spins are identical.

*More accurately speaking, we are referring not to the quantity C given by formula (2.9), but to the quantity obtained after averaging over the angle ϑ , that is, we are referring to the quantity $(15/2) C \sin^2 \vartheta \cos^2 \vartheta$.

[†]We are referring to a cubic single crystal. In the case of a single crystal of a different system, the quantity D , as noted above, will be a second-rank symmetrical tensor.

*Indeed, the solution (5.6) of (5.4) is valid only when $r > \delta$.

In the case $b < \delta$, according to (5.26) and (4.15), we obtain for the dependence of T_n on the crystal orientation

$$T_n \propto \delta^3 \propto (\Delta H)^{-3\alpha} \propto S^{-\frac{3}{2}\alpha}. \quad (5.34)$$

We now proceed to consider effects due to the dependence of C and δ on the angle ϑ . When averaging over the angle ϑ we obtain for $D(\mathbf{r})$ a spherical square well (4.13) and the barrier is represented by a spherical surface centered about the magnetic ion with radius δ . We now consider how to proceed if we do not carry out averaging over the angle; the z-component of the field acting on a nucleus is given by the formula

$$H \pm \frac{3}{4} \frac{\hbar \gamma e}{r^3} (1 - 3 \cos^2 \vartheta),$$

where the two signs preceding the second term correspond to the two possible spin directions of the magnetic ion*. Using for the determination of δ the procedure developed in Sec. 4, we get for the dependence of δ on ν :

$$\delta = \text{const} \cdot |1 - 3 \cos^2 \vartheta|^\alpha, \quad (5.35)$$

where the order of magnitude of the constant is given by (4.14); the dependence of the constant on the orientation of the crystal relative to the external field is given by the formula

$$\text{const} \propto (\Delta H)^{-\alpha}. \quad (5.35a)$$

(5.35) yields, in spherical coordinates, the equation of the surface that represents the diffusion barrier.

According to (5.35), δ vanishes at an angle $\vartheta_0 = \cos^{-1}(1/\sqrt{3}) = 54^\circ 44'$. 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 near the magnetic ion the spin diffusion will essentially occur in directions which make angles close to ϑ_0 to the direction of the external field.

When solving the stationary equation for M it is necessary to take into account the dependence of C on ϑ . Further, it is necessary to impose on the solution of the equation a boundary condition that calls for the vanishing, on the surface representing the diffusion barrier, of the derivative M with respect to the normal to this surface. From the asymptotic form of the obtained solution we can determine the total flux of nuclear moment through a sphere of radius R centered at the magnetic ion (when finding the summary flux we integrate over the angles, so that the angle ϑ drops out), making it possible to calculate the relaxation time T_n .

The foregoing pertains to an account of the effects due to the anisotropy of the barrier in the approxima-

tion in which we use for the diffusion barrier a square well. In the exact analysis of the problem it is necessary first, using the cross-relaxation theory, to determine the function $D(r, \vartheta)$. It is then necessary to solve the stationary equation for M with variable D , with account of the dependence of C on ϑ and with the boundary condition $M(0) = M_0$. Using, finally, the asymptotic form of the obtained solution, we can determine the summary nuclear-moment flux through a sphere of radius R , and the relaxation time T_n . The relaxation of the summary moment will be exponential (if the conditions for the applicability of the diffusion analysis are satisfied), since we have again for the dependence of M on r when r is large

$$M = M(\infty) + \frac{\text{const}}{r}.$$

9. We now consider the question of the values of the alternating-field amplitude (saturating the magnetic resonance) at which Eq. (5.17) is valid. The term $2A\mathfrak{M}$ of this equation is obtained by integrating the term $2AM$ of (5.1), if A is assumed to be constant. The quantity A is in fact not constant, for when $r < \delta$ the nuclei have strongly shifted Zeeman frequencies. In analogy with (4.13), we assume that

$$A(r) = \begin{cases} 0 & r < \delta, \\ \text{const} = A & r > \delta. \end{cases} \quad (5.36)$$

Taking (5.36) into account, we obtain in place of (5.17)

$$\frac{\partial \mathfrak{M}}{\partial t} = \frac{\mathfrak{M}_0 - \mathfrak{M}}{T_n} - 2A\mathfrak{M} + 2A\mathfrak{M}_0 \left(\frac{\delta}{R}\right)^3.$$

Thus, for the applicability of (5.17) we must satisfy the condition

$$2AT_n \left(\frac{\delta}{R}\right)^3 \ll 1 \quad \text{or} \quad A \ll A_{1/2} \left(\frac{R}{\delta}\right)^3. \quad (5.37)$$

If we neglect the extraneous relaxation, this condition takes the form

$$A \ll \frac{CF}{b^4 \delta^3}, \quad (5.38)$$

which gives in the two limiting cases

$$2A < [T_n^{\text{dir}} (\sqrt{b\delta})]^{-1} = \frac{C}{b^3 \delta^3} \quad \text{when } b > \delta, \quad (5.39a)$$

$$2A < [T_n^{\text{dir}} (\delta)]^{-1} = \frac{C}{\delta^6} \quad \text{when } b < \delta. \quad (5.39b)$$

The latter condition can be readily understood. To satisfy this condition, for small values of r the decrease of $A(r)$ does not play any role. Indeed, even if $A(r)$ were not to decrease, the alternating field still would not cause any noticeable saturation when $r \lesssim \delta$.

10. Assume that a saturating alternating field is applied to the sample at the instant $t = 0$. We are now interested in whether the equation $\partial \mathfrak{M} / \partial t = (\mathfrak{M}_0 - \mathfrak{M}) / T_n$ will describe the relaxation of $\mathfrak{M}(t)$ for all t (see^[19]).

If the relaxation of $\mathfrak{M}(t)$ is exponential in the non-

*We note, however, that the assumption that the spins of the magnetic ions are directed only parallel and antiparallel to the external field is inaccurate.

stationary case, then the corresponding relaxation time will coincide with the value of T_n calculated by us. To this end it is necessary that the diffusion play an essential role; this requires in turn that when $r > \max(b, \delta)$ the value of grad M be noticeably different from 0.* We conclude therefore that the exponential relaxation takes place for those values of t , for which the conditions differ greatly from the condition of total saturation when $r \approx \max(b, \delta)$.†

It is easy to see that $(Ct)^{1/6}$ is the distance from the magnetic ion reached by the direct relaxation within a time t , and $(C/2A)^{1/6}$ is the distance from the magnetic ion at which the probabilities of spin flip of the nucleus, due to the relaxation and to the alternating field, are equal to each other.

Recognizing that $M(r, t)$ is always equal to M_0 when $r < \delta$, we find that when $b < \delta$ then, no matter how large A , the relaxation of $\mathfrak{M}(t)$ will be exponential for all t . The same will take place if

$$\delta < b \text{ and } 2A < [T_n^{\text{dir}}(b)]^{-1} = \frac{C}{b^6} \left(\text{i.e.} \left(\frac{C}{2A} \right)^{1/6} > b \right).$$

Assume now that

$$\delta < b \text{ and } 2A > [T_n^{\text{dir}}(b)]^{-1} = \frac{C}{b^6} \left(\text{i.e.} \left(\frac{C}{2A} \right)^{1/6} < b \right).$$

At the instant when the saturating field is turned on saturation will take place of the resonance when $r > \max[\delta, (C/2A)^{1/6}]$. We can easily obtain the following approximate formulas:‡

$$\mathfrak{M}(t) = \frac{4\pi}{3} N \mathfrak{M}_0 \max \left[\delta^3, \left(\frac{C}{2A} \right)^{1/2} \right] \text{ for } 0 < t < \max \left(\frac{\delta^6}{C}, \frac{1}{2A} \right), \quad (5.40a)$$

$$\mathfrak{M}(t) = \frac{4\pi}{3} N \mathfrak{M}_0 (Ct)^{1/2} \text{ for } \max \left(\frac{\delta^6}{C}, \frac{1}{2A} \right) < t < \frac{b^6}{C}. \quad (5.40b)$$

When $t > b^6/C$, the relaxation of $\mathfrak{M}(t)$ will be exponential with a relaxation time T_n .

It is clear from the derivation of (5.40) that these formulas are approximate; they are accurate to within coefficients of the order of unity [we note in this connection that in^[19] formula (5.40b) contains an additional factor $\pi^{1/2}$].

11. We have assumed during the entire course of the analysis that the direct relaxation of the nuclei is due to dipole-dipole interaction of the spins of the nucleus and of the magnetic ion. In the case of a local

electron center (F center in an alkali-halide crystal, donor or acceptor center in a semiconductor), the wave function of the electron propagates over sufficiently large distances; it is therefore not excluded that if the external magnetic field is sufficiently small, the direct relaxation of the nucleus will in some cases be due to hyperfine interaction. The question was considered in^[27]. It is assumed that $T_n^{\text{dir}}(r)$ is proportional to $\exp(-\alpha r)$, where α is connected with the radius of the wave function of the local electronic center.

6. INDUCED DYNAMIC POLARIZATION OF NUCLEI WITH ACCOUNT OF SPIN DIFFUSION

Spin diffusion was first taken into account in induced dynamic polarization in^[28] (see also^[4,6]), but without account of the presence of the diffusion barrier. We have analyzed spin diffusion in induced dynamic polarization and took the diffusion barrier into account in^[22,29].

We confine ourselves to the case $S = I = 1/2$.

In the case of induced dynamic polarization, the z -component of the nuclear magnetization $M(r, t)$ satisfies the equation

$$\frac{\partial M}{\partial t} = \frac{M_0 - M}{T_d} + D \Delta M - C \sum_m |\mathbf{r} - \mathbf{r}_m|^{-6} (M - M_0) - 2AM - \Gamma_{\pm} \sum_m |\mathbf{r} - \mathbf{r}_m|^{-6} \left(M_{\mp} \frac{\gamma_e}{\gamma_n} M_0 \right). \quad (6.1)$$

Let us consider the case where the transitions corresponding to the fields H_+ , H^* , and H_- do not overlap and a field close to H_+ or H_- is applied to the sample. The upper and lower signs in (6.1) are taken for the case of the H_+ and H_- transitions. We shall henceforth leave out the plus and minus sign of Γ .

The physical meaning of the last term of (6.1) is obvious: it determines the change in the nuclear magnetization due to the H_{\pm} transitions. In the H_{\pm} transition, the microwave field "strives" to equate M with $\pm \gamma_n M_0 / \gamma_e$. The physical meaning of the remaining terms of (6.1) was analyzed above.

We rewrite (6.1) in the following fashion:

$$\frac{\partial M}{\partial t} = D \Delta M - (C + \Gamma) \times \sum_m |\mathbf{r} - \mathbf{r}_m|^{-6} \left[M - (C + \Gamma)^{-1} \left(C \pm \frac{\gamma_e}{\gamma_n} \Gamma \right) M_0 \right] + \frac{M_0 - M}{T_d} - 2AM.$$

We have seen above that (5.1) leads to (5.17). We obtain now analogously

$$\frac{\partial \mathfrak{M}}{\partial t} = 4\pi N D \bar{F} \left[\left(C \pm \frac{\gamma_e}{\gamma_n} \Gamma \right) (C + \Gamma)^{-1} \mathfrak{M}_0 - \mathfrak{M} \right] + \frac{\mathfrak{M}_0 - \mathfrak{M}}{T_d} - 2A\mathfrak{M}, \quad (6.2)$$

where

$$\bar{b} = 0.68 \left(\frac{C + \Gamma}{D} \right)^{1/4} = b \left(\frac{C + \Gamma}{C} \right)^{1/4}, \quad (6.3)$$

* r denotes the distance to the nearest magnetic ion.

† If for $r \approx \max(b, \delta)$ the saturation of the nuclear resonance is complete, then $M \approx 0$ and grad $M \approx 0$ when $r > \max(b, \delta)$, and no spin diffusion will take place.

‡ We can alternately write (5.40) in the form

$$\mathfrak{M}(t) = \frac{\mathfrak{M}_0}{R^3} \max \left[\delta^3, \left(\frac{C}{2A} \right)^{1/2}, (Ct)^{1/2} \right] \text{ for } 0 < t < \frac{b^6}{C}.$$

$$\bar{F} = F(\bar{b}, \delta). \quad (6.4)$$

We define here $F(\bar{b}, \delta)$ as in (5.25). More generally speaking, if we do not use the square-well model for the function $D(r)$, it is necessary to define \bar{F} as a result of the substitution $b \rightarrow \bar{b}$ in the dependence of F on b .

In order for (6.2) to be correct it is necessary to satisfy the condition [compare with (5.31)]

$$a \ll \max(\bar{b}, \delta) \ll R. \quad (6.5)$$

If $C > \Gamma$, then $\bar{b} \approx b$. On the other hand, $\bar{b} \approx 0.68(\Gamma/D)^{1/4}$ if $C < \Gamma$; \bar{b} is in this case the distance from the magnetic ion, up to which the direct induced dynamic polarization is effective.

Assume that $A = 0$ (that is, no radio frequency field capable of saturating nuclear resonance is applied to the sample*). Equation (6.2) can be rewritten

$$\frac{\partial \mathfrak{M}}{\partial t} = \frac{\mathfrak{M}_s - \mathfrak{M}}{T_s}, \quad (6.6)$$

where

$$\mathfrak{M}_s = \frac{T_d^{-1} + 4\pi N D \bar{F} (C + \Gamma)^{-1} \left(C \pm \frac{\gamma_e \Gamma}{\gamma_n} \right)}{T_d^{-1} + 4\pi N D \bar{F}} \mathfrak{M}_0, \quad (6.7)$$

$$T_s^{-1} = T_d^{-1} + 4\pi N D \bar{F}. \quad (6.8)$$

Solution of (6.6) yields

$$\mathfrak{M}(t) = \mathfrak{M}_s + [\mathfrak{M}(0) - \mathfrak{M}_s] e^{-t/T_s}. \quad (6.9)$$

It follows therefore that \mathfrak{M}_s is the stationary value of the moment of the sample, and T_s is the time necessary to establish stationary dynamic polarization.

Using (5.29) and (6.8), we have

$$\frac{T_n}{T_s} = \frac{T_d^{-1} + 4\pi N D \bar{F}}{T_d^{-1} + 4\pi N D F}. \quad (6.10)$$

We introduce further the nuclear-polarization amplification coefficient by means of the formula†

$$\eta = \frac{\mathfrak{M}_s}{\mathfrak{M}_0} - 1. \quad (6.11)$$

We then obtain

$$\eta = \eta_m \frac{\Gamma}{C + \Gamma} \frac{4\pi N D \bar{F}}{T_d^{-1} + 4\pi N D \bar{F}} = \eta_m \frac{\Gamma}{C + \Gamma} \left(1 - \frac{T_s}{T_d} \right), \quad (6.12)$$

where

$$\eta_m = \pm \frac{\gamma_e}{\gamma_n} - 1. \quad (6.13)$$

Formula (6.12) shows that η increases with decreasing C and with increasing T_d , which can be readily understood. A decrease in C means a decrease in the role of the nuclear relaxation brought about by the magnetic ions; an increase in T_d means

*In experiments, a radio frequency field with frequency equal to the frequency of the nuclear resonance is applied for the measurement of the degree of polarization of nuclei. We assume that the amplitude of this field is small enough so that $2AT_n \ll 1$. In this case we neglect the term $2A\mathfrak{M}$ in (6.2).

† $\eta = \rho - 1$, where ρ is the quantity introduced in Sec. 3.

a decrease in the role of the extraneous nuclear relaxation. On the other hand, a decrease in the role of nuclear relaxation should intensify the effect of the induced dynamic polarization.

If the extraneous relaxation can be neglected, then (6.12) simplifies to

$$\eta = \eta_m \frac{\Gamma}{C + \Gamma}. \quad (6.12a)$$

We note that the maximum polarization amplification coefficient η_m is found to be the same as in the simple model which takes no account of spin diffusion (see Sec. 3).

In limiting cases we obtain from (6.8) and (6.12) the following results; we make use of the expressions for the function $F(b, \delta)$ in the two limiting cases [see (5.26)], and also of formula (6.3).

When $\bar{b} > \delta$ we have

$$\eta = \eta_m \frac{\Gamma}{C + \Gamma} \frac{8.5N(C + \Gamma)^{1/4} D^{3/4}}{T_d^{-1} + 8.5N(C + \Gamma)^{1/4} D^{3/4}}, \quad (6.14a)$$

$$T_s^{-1} = T_d^{-1} + 8.5N(C + \Gamma)^{1/4} D^{3/4}, \quad (6.15a)$$

which coincides with the results of earlier work.^[4,28]

When $\bar{b} < \delta$ we have

$$\eta = \eta_m \frac{\Gamma}{C + \Gamma} \frac{4.2N(C + \Gamma)\delta^{-3}}{T_d^{-1} + 4.2N(C + \Gamma)\delta^{-3}}, \quad (6.14b)$$

$$T_s^{-1} = T_d^{-1} + 4.2N(C + \Gamma)\delta^{-3}. \quad (6.15b)$$

Since Γ increases with increasing microwave power, at sufficiently large power \bar{b} will greatly exceed δ and the diffusion barrier will be insignificant. The diffusion barrier is very important at not too high values of the microwave field power (if in addition $b < \delta$), and will lead to a decrease in the nuclear polarization.

We note that in the present section we have assumed that $\hbar\gamma_e H \ll 2kT$. If this condition is not satisfied, it is necessary to replace γ_e/γ_n in the last term of (6.1) by the expression $\tanh(\hbar\gamma_e H/2kT) \times [\tanh(\hbar\gamma_n H/2kT)]^{-1}$. It is easy to see that all the results obtained by us remain valid, except that formula (6.13) is replaced by

$$\eta_m = \pm \frac{\text{th} \frac{\hbar\gamma_e H}{2kT}}{\text{th} \frac{\hbar\gamma_n H}{2kT}} - 1. \quad (6.16)$$

If the H_{\pm} transitions overlap, we can generalize the analysis given in the present section, retaining in (6.1) both the term proportional to Γ_+ and the term proportional to Γ_- . It is easily seen that in this case the results of (6.4) and (6.8) remain in force, while (6.3) and (6.12) are replaced by (we are considering the case when $\hbar\gamma_e H \ll 2kT$):

$$\bar{b} = 0.68 \left(\frac{C + \Gamma_+ + \Gamma_-}{D} \right)^{1/4}, \quad (6.17)$$

$$\eta = \frac{\left(\frac{\gamma_e}{\gamma_n} - 1 \right) \Gamma_+ - \left(\frac{\gamma_e}{\gamma_n} + 1 \right) \Gamma_-}{C + \Gamma_+ + \Gamma_-} \frac{4\pi N D \bar{F}}{T_d^{-1} + 4\pi N D \bar{F}}. \quad (6.18)$$

If we neglect unity compared with γ_e/γ_n , formula (6.18) reduces to

$$\eta = \frac{\gamma_e}{\gamma_n} \frac{\Gamma_+ - \Gamma_-}{C + \Gamma_+ + \Gamma_-} \frac{4\pi N D \bar{F}}{T_d^{-1} + 4\pi N D \bar{F}}. \quad (6.19)$$

The latter results are in our opinion applicable in the case of a broad inhomogeneously broadened line of electron paramagnetic resonance.

We have indicated in Sec. 3 that the analysis presented there of the induced dynamic polarization is valid only if the condition $\omega_n \tau \gg 1$ is satisfied. Therefore our analysis is not valid for a broad, homogeneously broadened EPR line. This question was recently considered in^[14].

7. COMPARISON OF THEORY WITH EXPERIMENT

We proceed to a comparison of the experimental data on nuclear magnetic relaxation with theory.

The first experiments on spin diffusion were set up by Bloembergen.^[1] The experiments were made in the temperature interval 1–300°K at alternating-field frequencies 9.5 and 30.5 Mc. The relaxation time was determined from the time dependence of the nuclear resonance signal after turning off the alternating field that saturated the nuclear resonance. The experiments were carried out with potassium-aluminum and cesium-aluminum alums, with alkali-halide crystals, with CaF₂, etc. The most detailed measurements were made with potassium-aluminum alums, in which a small fraction of the aluminum atoms was replaced by chromium atoms. The dependence of the relaxation time of the protons on the temperature, on the external field, and on the concentration of the chromium atoms was measured. The dependence on N and on T was of the form $T_n \propto N^{-1} \tau_e^\beta$, where $\beta = 0.5-0.7$. Unfortunately, however, the values of τ_e were taken from data by others. In the experiments with CaF₂ (with iron added) the nuclear relaxation time turned out to be, within the limits of errors, independent of the orientation of the crystal relative to the external field, in agreement with the theory (see Sec. 5, item 8).

Experiments with single-crystal LiF^[30] have shown that irradiation of the crystal with x rays causes a reduction in the relaxation times of both the Li⁷ and the F¹⁹ nuclei, owing to the production of F centers. The same reference reports measurements of the dependence of T_n on the orientation of the crystal relative to the external field. These measurements were made at room temperature with the condition $b > \delta$ satisfied. In addition to the anisotropy of T_n , a measurement was made of the anisotropy of the nuclear-resonance width. It turned out that T_n increases with increasing nuclear resonance width, in agreement with (5.33).

Measurements of the field dependence of the relaxation time of the F¹⁹ nuclei in LiF are reported in^[31]. The measurements were made at 300 and 77°K with $\tau_e \ll \tau_s$ and $\delta \ll b$. It was found that $T_n \propto H^{1/2}$,

which agrees with the theoretical result (5.27a) (at the temperatures in question, the electronic relaxation is two-phonon and therefore τ_e does not depend on H). Experiments with NH₄HSO₄ with a small amount of (NH₄)₂CrO₄ added are reported in^[19]. Measurements were made of the time variation of the restoration of the proton signal after turning off the radio frequency field that saturated the proton resonance. The measurements were made at room temperature, with $\delta < b$. It was found that at small values of the time t the proton signal is proportional to $t^{1/2}$, which, in accord with (5.40b), follows from the theory if $\delta < b$. By using (5.40b), the value of C was determined and τ_e estimated. An experiment was also made with a sample in which no magnetic impurity was introduced. For this sample, the relaxation turned out to be exponential for all t; this fact can be explained by assuming that the proton relaxation in this sample is not due to the magnetic ions.

An investigation of the anisotropy of the nuclear relaxation times in several alkali-halide crystals with small amounts of iron added is the subject of^[16]. The measurements were made at room temperature, in a field of 4400 Oe. Under these conditions $\delta \ll b$. According to the theory, the dependence of T_n on the crystal orientation is given by (5.33). According to the statements made above (see Sec. 4 and Sec. 5, item 8), the anisotropy of T_n should be noticeable in the case of a lattice containing two types of nuclei with spins. For LiF crystals, the results of the experiments agree with the theory* (there is agreement both for the Li⁷ and for the F¹⁹ nuclei). In the case of NaCl and KBr, no anisotropy of the relaxation time was observed, a fact attributed by the author to the predominance of the quadrupole relaxation mechanism.

Borghini^[32] measured the relaxation times of the protons and cerium ions in lanthanum-magnesium double nitrate, in which 0.5 per cent of the lanthanum was replaced by cerium. The measurements were made in the temperature interval 1.5–2.1°K, in a 13.5 kOe field. It was found that $T_n \propto T^{-2}$ and $\tau_e \propto T^{-7}$. The result does not agree with theory (since under the experimental conditions $\delta > b$ and $\tau_s < \tau_e$); it must be noted, however, that the temperature interval was too small to draw any conclusions concerning the temperature dependence of the relaxation times.

The relaxation time of the protons in lanthanum-magnesium double nitrate, in which a small fraction of the lanthanum atoms was replaced by cerium atoms, was measured in^[6]. The cerium concentration was varied in the range of 0.05–10 per cent. The measurements were made in the temperature interval 1.6–4.2°K, and in a field of 3650 Oe. The dependence

*The authors failed to take into account, however, that the quantity b which enters in formula (5.26a) depends on D [see formula (5.9)]. They assume therefore that $T_n \propto D^{-1}$ whereas in fact $T_n \propto D^{-3/4}$.

of the relaxation time of the protons on the cerium concentration and on the temperature was measured. The value of τ_e was measured along with T_n . It was found that $T_n \propto N^{-2}\tau_e^{1/2}$ (with $\tau_e \propto T^{-14}$) which contradicts the theory.

Reference^[17] is devoted to the measurement of the relaxation time of F^{19} nuclei in LiF, irradiated by gamma rays from Co^{60} to produce F centers. The measurements were made at room temperature and at an alternating field frequency 6.4 Mc. The relaxation time of the F^{19} nuclei was measured as a function of the concentration of the F centers for two orientations of the external field, namely with H parallel to [100] and [110]. For the same crystal orientations, a measurement was made of the shape and width of the resonance line of F^{19} . The concentration of the F centers was determined by optical methods. It was found that when $N < 2 \times 10^{16} \text{ cm}^{-3}$, $T_n \propto N^{-1}$. Carrying out a numerical estimation of the sums in formula (5.33) the authors found that at these concentrations the ratio of the values of T_n for two crystal orientations is in good agreement with theory. It was further found that when $N > 2 \times 10^{16} \text{ cm}^{-3}$, T_n ceases to depend on N, a fact attributed by the authors to the formation of clusters of F centers near the dislocation lines.

In^[33] experiments are reported with an Al_2O_3 crystal with a Cr_2O_3 impurity; the relative concentration of Cr_2O_3 was 0.035 per cent. The spin of Al^{27} is 5/2. Owing to the quadrupole effects, the six Zeeman levels of the Al^{27} nucleus are not equidistant and five lines are obtained in the nuclear resonance spectrum. In the first approximation, the quadrupole splitting is proportional to $1-3\cos^2\vartheta$, where ϑ is the angle between the external field and the symmetry axis of the intracrystalline electric field. Therefore, when $\vartheta = \vartheta_0 = \cos^{-1}(1/\sqrt{3}) = 54^\circ 44'$, the Zeeman levels will be approximately equidistant. The authors have shown that in this case T_n should be determined, if $b > \delta$, by the same formula (5.26a) as in the case when the nuclear spin is 1/2. The measurement was made at $T = 80^\circ\text{K}$ and $H = 9 \text{ kOe}$. The obtained value $T_n = 0.8 \text{ sec}$ is in good agreement with (5.26a). However, the numerical estimates made by the authors show that for the values of the physical quantities chosen by the authors, b is in fact smaller than δ .

Paper^[26] is devoted to a measurement of the relaxation times of the protons and P^{31} nuclei in KH_2PO_4 as functions of the temperature (in the interval $4.2-375^\circ\text{K}$) and of the external field. Measurements were also made of the anisotropy of the relaxation time of the protons. The experimental data are in good agreement in the entire temperature interval with the diffusion theory that takes no account of the barrier (that is, with the case $\delta < b$). However, as pointed out by the author, when $T = 4.2^\circ\text{K}$ b is in fact smaller than δ .

Kessenikh et al.^[34,35] (see also^[12]) measured the

relaxation times of the protons in irradiated polyethylenes. Along with T_n , they measured also the spin-lattice relaxation time of the magnetic center. The measurements were made at 77, 4.2, and 1.6°K . The external magnetic field was 3450 Oe. The concentration of the paramagnetic centers was varied in the interval $(2.8-8.5) \times 10^{18} \text{ cm}^{-3}$. The value of T_n was determined from the time dependence of the proton sample after turning off the high frequency field producing the dynamic polarization. Measurements were also made of T_n by observing the restoration of the signal after turning off the radio frequency field that saturated the proton resonance.

For the dependence of T_n on the magnetic-center concentration, they found $T_n^{-1} \propto N^\beta$ where $\beta = 1-2$.

Formula (2.10) yields (we are substituting $g = 2$) $C = 0.87 \tau^{-1} \times 10^{-47} \text{ cm}^6/\text{sec}$. The estimate (4.14a) yields (we choose $a = 2.3 \text{ \AA}$) $\delta = 15 \text{ \AA}$.

Let us compare theory and experiment for samples with $N = (5.2-5.9) \times 10^{18} \text{ cm}^{-3}$ at $T = 4.2^\circ\text{K}$. Formula (2.1) yields $R \approx 35 \text{ \AA}$. According to (2.11) we obtain $\tau_s \approx 4 \times 10^{-6} \text{ sec}$ which is appreciably smaller than τ_e ($\tau_e \approx 0.4 \text{ sec}$ when $T = 4.2^\circ\text{K}$); therefore $\tau = \tau_s$. Then $C = 2 \times 10^{-42} \text{ cm}^6/\text{sec}$. Assuming that $D = 2.5 \times 10^{-12} \text{ cm}^2/\text{sec}$, we obtain according to (5.9) that $b \approx 2 \text{ \AA}$. Using, finally, formula (5.26b), we obtain $T_n \approx 70 \text{ sec}$, which is in good agreement with the experimental value (40-80 sec).

Further, in accordance with the same paper, at helium temperatures the relaxation time T_n is inversely proportional to the temperature. It is easily seen that such a dependence follows approximately from the theory if τ_s is considerably smaller than T_2 [see formula (5.27d)]. According to experiment, the proton resonance line has a Gaussian form and its width (between points corresponding to half the maximum) is 17.5 Oe, yielding $T_2 \approx 6 \times 10^{-6} \text{ sec}$. Recognizing that the foregoing estimate of τ_s is quite crude, and taking also into account the fact that we do not know the values of τ/T_2 at which the estimate (4.14b) becomes valid, we can conclude that with respect to the temperature dependence there is no contradiction between theory and experiment [we note, however, that if δ is estimated by means of (4.14b), we obtain for the foregoing sample at 4.2°K a value T_n 6 sec, which is much smaller than the experimental value]. In^[36] measurements are reported of the relaxation time of the protons in lanthanum-magnesium nitrate, in which 0.8 per cent of the atoms of lanthanum are replaced by cerium atoms. The measurements were made in the temperature interval $0.3-1.7^\circ\text{K}$, with an external field 3.5 kOe. The measurement yielded $T_n^{-1} \propto T^{1.45}$; in other words, T_n increases with decreasing temperature somewhat more rapidly than predicted by theory.

Jeffries and his co-workers measured the relaxation time of protons in lanthanum-magnesium double nitrate, in which one per cent of the lanthanum atoms

was replaced by neodymium atoms^[4] (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 the temperature interval 1.3–4.2°K and at fields ranging from 1 to 20 kOe. The external field made an angle 40° with the direction of the symmetry axis of the intracrystalline field. T_n was measured by determining the time dependence of the proton signal after turning off the high-frequency field producing the dynamic polarization. τ_e was also measured.

Under the conditions of these experiments $\delta \gg b$. Comparing the results of the experiments with theory, Jeffries concludes that the diffusion theory leads to values of T_n which are three orders of magnitude larger than the experimental data. However, if one recognizes that under the conditions of the experiments in question $\tau_s \ll \tau_e$, one finds that in fact the theoretical value of T_n is two orders of magnitude smaller than the experimental data.

The resonance of the F^{19} nuclei in single-crystal CaF_2 containing a manganese impurity is investigated in^[37]. The angular anisotropy of the nuclear-resonance line width was measured. This was followed by investigation of the time dependence of the restoration of the nuclear resonance signal after turning off the saturating field. At room temperature, a region of $t^{1/2}$ and a region of exponential signal growth were obtained in agreement with the theory (the condition $\delta < b$ was satisfied). The experimentally obtained value of T_n agrees approximately with formula (5.26a).

We see therefore that the diffusion theory is in accord with the experiments made at relatively high temperatures (when $b > \delta$), as regards experiments made at helium temperatures, (when $b < \delta$), the diffusion theory agrees qualitatively with some and contradicts others. This disparity is possibly connected with the fact that under the conditions of these experiments δ/R is insufficiently small and consequently the criterion for the applicability of our analysis breaks down. The disparity may possibly also be due to the approximations employed by us, particularly the crude estimates (4.14), and by failure to take into account the anisotropy of the diffusion barrier.

As regards induced dynamic polarization of the nuclei, we are unable at present to compare the results of the diffusion theory with experiment, since most experiments were made under conditions when the H_+ and H_- transitions overlap (with the broadening of the electron paramagnetic resonance not being purely homogeneous). In the latest papers by the Jeffries group^[4] microwave fields are used with a wavelength of approximately 4 mm, and there is thus no overlap. However, no data are given in the review^[4] on the dependence of the coefficient of intensification of the nuclear polarization and the growth time of the induced dynamic polarization [see formulas (6.8) and (6.12)] on the temperature, external field, concentra-

tion of the magnetic atoms, and microwave power. In a recent review, Abragam and Borghini^[14] likewise present no experimental data on the dynamic polarization in sufficient detail to be able to make a detailed comparison between theory and experiment.

We mention, finally, investigations of nuclear polarization in a liquid adsorbed on a solid containing magnetic centers, following application of an alternating field that gives rise to forbidden transitions.^[9,38,39] As a result of the forbidden transitions, direct polarization takes place of the nuclei of the liquid, located near the solid surface. This polarization is furthermore transported inside the liquid, but not by slow spin diffusion, but by the much more rapid molecular diffusion.

8. CONCLUSION

We have already noted in the introduction that interest in the investigation of spin diffusion has greatly increased because of the success of the method of induced dynamic polarization of nuclei. We note in this connection that the Jeffries group has attained a proton polarization of 70 per cent.^[4] The sample was lanthanum-magnesium double nitrate in which one per cent of the lanthanum ions were replaced by neodymium ions. The experimental conditions were as follows: $H = 20 \text{ kOe}$, $T = 1.5^\circ\text{K}$, external field perpendicular to the symmetry axis of the intracrystalline field, microwave-field frequency 74 Gc, microwave power approximately 100 MW.

Reports have already (more accurately, finally) been published concerning the first experiments with a target containing polarized protons. Abragam and his co-workers^[40] measured the spin correlation in the scattering of polarized incident protons (with energy 20 MeV) by protons of a polarized target (lanthanum-magnesium double nitrate, in which 0.3 per cent of the lanthanum is replaced by cerium), with a degree of proton polarization equal to 20 per cent.

The Berkeley group^[41] investigated scattering of 250-MeV pions by protons of a polarized target (lanthanum-magnesium double nitrate, in which 1 per cent of the lanthanum is replaced by neodymium) with a proton polarization of approximately 25 per cent*.

We must note, however, that lanthanum-magnesium double nitrate is by far not an ideal proton target. Although this target contains a sufficiently large number of hydrogen atoms ($3.7 \times 10^{22} \text{ cm}^{-3}$), the interpretation of the experiments is hindered by the fact that many more protons are contained in the other target nuclei.

From this point of view, more convenient targets are the various hydrocarbon compounds (polyethylene,

*A detailed description of the experiments made with polarized-target protons can be found in^[4,14].

polystyrene), containing as magnetic centers a free-radical impurity. However, so far no strong proton polarization could be obtained for such substances.

An ideal target for nuclear research is solid hydrogen. Experiments were set up in which solid H₂ was bombarded (with gamma quanta, x rays); this yields a H₂ lattice into which a small amount of atomic hydrogen has been introduced. However, further experiments have shown that the microwave field which should cause the forbidden transitions does not lead to the polarization of the protons (H₂ molecules*). The explanation of this fact follows (see, for example, [4]). The ground state of the H₂ molecule (state with zero rotational quantum number K) is the para state, in which the summary spin of the two protons is 0. It is clear that there can be no talk of a spin flip of one of the protons of the molecule by means of the microwave quantum; indeed, such a transition is a para-ortho transformation, and the energy required for it is larger by many orders of magnitude than the energy of the microwave-field quanta.

It is well known, however, that when hydrogen is cooled to helium temperatures, it is possible to store in it, for a sufficiently long period of time, an appreciable quantity of ortho hydrogen (we note that in our case this will be difficult, since the atomic hydrogen is a catalyst which accelerates the ortho-para conversion), and one can raise the question of the polarization of the spins of the protons which are contained in the ortho-hydrogen molecules. However, in the ortho state the rotational quantum number of the molecule is K = 1.

In view of the small mass of the protons, this rotation is rapid, and it causes a sufficiently fast relaxation of the proton spins. As we have already seen in Sec. 3, rapid relaxation of the nuclei (that is, small T₁), destroys the dynamic polarization.

The situation is entirely different in the case of solid D₂ or HD. The ground state of the D₂ molecule is the ortho state, and the summary spin of the two protons is equal to two with a probability of 5/6 and to zero with a probability of 1/6. On the other hand, in the case of the HD molecule there are no limitations whatever connected with the symmetry. The solid D₂ and solid HD are highly promising polarized targets provided no trouble is caused by the fact that the electron spin-lattice relaxation time is large because of the lack of spin-orbit interaction. For details and references concerning polarization of pure hydrogen targets we refer the reader to the reviews [4,14].

*We note that the resonant frequencies of the protons of atomic and molecular hydrogen differ greatly. Indeed, in the case of atomic hydrogen the energy of the hyperfine interaction of the spins of the electron and the proton is much larger than the Zeeman energy of the proton.

In the derivation of (2.7) we follow the book [3].

From the energy operator of the dipole-dipole interaction between the magnetic ion and the nucleus we separate the term V, which is proportional to S_ZI,

$$V = \hbar A S_Z I_+, \tag{A.1}$$

where

$$A = -\frac{3}{2} \frac{\hbar \gamma_e \gamma_n}{r^3} \sin \theta \cos \theta e^{-i\varphi}. \tag{A.2}$$

We introduce the correlation function of the operator AS_Z

$$G(t) = A^2 \langle S_Z(0) S_Z(t) \rangle \tag{A.3}$$

and its Fourier transform

$$J(\omega) = \int_{-\infty}^{+\infty} G(t) e^{-i\omega t} dt. \tag{A.4}$$

According to the general theory of magnetic relaxation, we have for the relaxation time of the nucleus

$$[T_n^{\text{dir}}(r, \theta)]^{-1} = 2J(\omega_n). \tag{A.5}$$

Thus

$$[T_n^{\text{dir}}(r, \theta)]^{-1} = \frac{9}{2} \frac{(\hbar \gamma_e \gamma_n)^2 \sin^2 \theta \cos^2 \theta}{r^6} \int_{-\infty}^{+\infty} \langle S_Z(0) S_Z(t) \rangle e^{-i\omega_n t} dt. \tag{A.6}$$

We assume that the correlation is exponential, with a correlation time τ . Then

$$\langle S_Z(0) S_Z(t) \rangle = \frac{1}{3} S(S+1) e^{-\frac{|t|}{\tau}} \tag{A.7}$$

and we obtain (2.7) of the main text.

However, if $\hbar \gamma_e H/kT$ is not small, then (A.7) is not correct. Indeed, in this case $\langle S_Z \rangle \neq 0$, $\langle S_Z^2 \rangle \neq (1/3)S(S+1)$.

This circumstance can be easily taken into account. [42] Indeed, when $t = 0$ the correlator $\langle S_Z(0) S_Z(t) \rangle$ is equal to $\langle S_Z^2 \rangle$, and when $t = \infty$ it becomes equal to $\langle S_Z \rangle^2$. Assuming that the correlator changes exponentially in time, we can write

$$\langle S_Z(0) S_Z(t) \rangle = \langle S_Z \rangle^2 + (\langle S_Z^2 \rangle - \langle S_Z \rangle^2) e^{-\frac{|t|}{\tau}}. \tag{A.8}$$

For J(ω) we obtain

$$J(\omega) = A^2 \left[2\pi \delta(\omega) \langle S_Z \rangle^2 + \frac{2\tau}{1+(\tau\omega)^2} (\langle S_Z^2 \rangle - \langle S_Z \rangle^2) \right]. \tag{A.9}$$

On the other hand,

$$\begin{aligned} \langle S_Z \rangle &= -S B_s \left(\frac{S \hbar \gamma_e H}{kT} \right), \\ \langle S_Z^2 \rangle - \langle S_Z \rangle^2 &= S^2 B_s' \left(\frac{S \hbar \gamma_e H}{kT} \right) \end{aligned} \tag{A.10}$$

(B_s is the Brillouin function, and the prime denotes differentiation with respect to the argument).

According to (A.5), (A.9), and (A.10) there appears in the right sides of (2.7) and (2.9) an additional factor

$$\frac{3S}{S+1} B_s' \left(\frac{S \hbar \gamma_e H}{kT} \right). \tag{A.11}$$

The replacement of the quantity C by the factor

(A.11) leads to a corresponding change in T_n [see formulas (5.26)]. Thus, when $\hbar\gamma_e H > 2kT$ we have an additional increase in T_n with increase of the ratio H/T .

Formulas (A.9) and (A.10) were used in^[42] to calculate the dependence of the diffusion-barrier radius δ on τ/T_2 and a more accurate formula than our formula (4.14) was obtained.

APPENDIX B

We present certain results of the well-known paper by Van Vleck, devoted to the theory of the line width of magnetic resonance in a rigid lattice.^[18] We shall consider the case of nuclear resonance (we confine ourselves here only to an account of the dipole-dipole interaction of the spins).

The mean-square width of the nuclear resonance line of nuclei of this type (with spin I and gyromagnetic ratio γ_n) is given by the formula

$$S = \langle (\Delta\omega)^2 \rangle = \frac{3}{4} I(I+1) \hbar^2 \gamma_n^4 \sum_j' r_{ij}^{-6} (1-3 \cos^2 \theta_{ij})^2 + \frac{1}{3} \hbar^2 \gamma_n^2 \sum_k I_k (I_k+1) \gamma_k^2 r_{ik}^{-6} (1-3 \cos^2 \theta_{ik})^2; \quad (B.1)$$

here the summation in the first term is over all the nuclei which are identical with the nucleus i (the prime denotes that the term with $j = i$ has been omitted from the sum); r_{ij} is the distance between the nuclei i and j ; θ_{ij} is the angle between the vector \mathbf{r}_{ij} and the external magnetic field. The summation in the second term is over nuclei which are not identical with the nucleus i ; I_k and γ_k are the corresponding spin and gyromagnetic ratio.

For a cubic crystal we can derive the following formula^[18,16]

$$\sum_j' r_{ij}^{-p} (1-3 \cos^2 \theta_{ij})^2 = \frac{1}{2} (a_p + b_p \Lambda), \quad (B.2)$$

where

$$\Lambda = \lambda_1^4 + \lambda_2^4 + \lambda_3^4; \quad (B.3)$$

λ_1 , λ_2 , and λ_3 are the direction cosines of the external magnetic field relative to the cubic axes of the crystal; the quantities a_p and b_p are given by the formulas

$$a_p = \sum_j' r_{ij}^{-p} [7-9(\mu_{1ij}^4 + \mu_{2ij}^4 + \mu_{3ij}^4)], \\ b_p = \sum_j' r_{ij}^{-p} [-9+15(\mu_{1ij}^4 + \mu_{2ij}^4 + \mu_{3ij}^4)] \quad (B.4)$$

(μ_{1ij} , μ_{2ij} , and μ_{3ij} are the direction cosines of the vector \mathbf{r}_{ij} relative to the cubic axes).

Let us consider the case of a cubic crystal in which all the nuclei that possess spins are identical. (B.1) and (B.2) yield

$$S = \frac{3}{8} I(I+1) \hbar^2 \gamma_n^4 (a_6 + b_6 \Lambda). \quad (B.5)$$

The quantities a_p and b_p depend on whether the

cubic lattice is primitive (Γ_C), body-centered (Γ_C^V), or face-centered (Γ_C^f). A numerical estimate yields for the Γ_C lattice

$$S = 12.4 \hbar^2 \gamma_n^4 a^{-6} I(I+1) (\Lambda - 0.19) \quad (B.6a)$$

for the Γ_C^f lattice

$$S = 5.7 \hbar^2 \gamma_n^4 a^{-6} I(I+1) (2.12 - \Lambda); \quad (B.6b)$$

where a is the distance between the nearest nuclei.

In the case of a powder or of a polycrystal of the cubic system, it is necessary to average the expression $(1-3 \cos^2 \theta_{ij})^2$ [or else it is necessary to replace in (B.5) Λ by $3/5$]. As a result we obtain

$$S = \frac{3}{5} I(I+1) \hbar^2 \gamma_n^4 \sum_j' r_{ij}^{-6} = \frac{3}{8} I(I+1) \hbar^2 \gamma_n^4 \left(a_6 + \frac{3}{5} b_6 \right). \quad (B.7)$$

Numerical estimates yield

$$\sum_j' r_{ij}^{-6} = g a^{-6}, \quad (B.8)$$

where $g = 8.4$ for the Γ_C lattice, 14.2 for the Γ_C^V lattice, and 14.4 for the Γ_C^f lattice. We thus obtain

$$S = \frac{3}{5} I(I+1) \hbar^2 \gamma_n^4 g a^{-6}. \quad (B.9)$$

For a Gaussian line, the distribution function relative to $\Delta\omega = \omega - \omega_n$ is of the form [we recognize that $\pi\varphi(0) = T_2$]

$$\varphi(\Delta\omega) = \frac{T_2}{\pi} \exp \left\{ -\frac{T_2^2 (\Delta\omega)^2}{\pi} \right\}. \quad (B.10)$$

We thus have for a Gaussian line

$$S = \langle (\Delta\omega)^2 \rangle = \frac{\pi}{2T_2^2}. \quad (B.11)$$

We note that for a non-Gaussian line the expression ST_2^2 depends on the orientation of the crystal relative to the external field.

(B.9) and (B.11) give in the case of a Gaussian line (for a powder)

$$T_2 = \left[\frac{5\pi}{6I(I+1)g} \right]^{1/2} \frac{a^3}{\hbar\gamma_n^2}. \quad (B.12)$$

In the case of a spin $I = 1/2$ we obtain for the Γ_C lattice

$$T_2 = 0.65 \frac{a^3}{\hbar\gamma_n^2}, \quad (B.13a)$$

and for the Γ_C^V and Γ_C^f lattices

$$T_2 = 0.49 \frac{a^3}{\hbar\gamma_n^2}. \quad (B.13b)$$

APPENDIX C

We separate from the energy operator of the dipole-dipole interaction of the nuclei i and j the term V_{ij} which causes the flip-flop transitions^[1,3]:

$$V_{ij} = -\frac{(\hbar\gamma_n)^2}{4r_{ij}^3} (I_i^+ I_j^- + I_i^- I_j^+) (1-3 \cos^2 \theta_{ij}). \quad (C.1)$$

In the case of a flip-flop transition of a pair of

identical nuclei, the number of final states per unit interval of frequency is $T_2/\sqrt{2\pi}$.^{*} For the probability (per unit time) of the flip-flop transition of the pair of nuclei (i, j) we obtain

$$W_{ij} = \frac{2\pi}{\hbar^2} \left| \left(\pm \frac{1}{2}, \pm \frac{1}{2} \left| V_{ij} \right| \mp \frac{1}{2}, \pm \frac{1}{2} \right) \right|^2 \frac{T_2}{\sqrt{2\pi}}$$

Since $I = 1/2$, this yields

$$W_{ij} = \frac{1}{8\sqrt{2}} \hbar^2 \gamma_n^4 r_{ij}^{-6} (1 - 3 \cos^2 \theta_{ij})^2 T_2 \quad (C.2)$$

We consider a crystal in which all nuclei with spins are identical. The formula (B.1) yields (we substitute $I = 1/2$)

$$S = \frac{9}{16} \hbar^2 \gamma_n^4 \sum_j' r_{ij}^{-6} (1 - 3 \cos^2 \theta_{ij})^2 \quad (C.3)$$

According to (C.2) and (C.3)

$$\sum_j' W_{ij} = \frac{\sqrt{2}}{9} S T_2 \quad (C.4)$$

Assuming that the nuclear-resonance line is Gaussian, we apply (B.11) and obtain

$$\sum_j' W_{ij} = \frac{\pi}{9\sqrt{2}T_2} \quad (C.5)$$

According to (4.7), it is necessary, in order to determine the coefficient of spin diffusion D, to calculate the probability W of the flip-flop transition of the pair of nearest identical nuclei. It is easy to see that W is equal to the ratio of the expression in (C.5) to the quantity g which enters in (B.7) (g plays the role of the effective number of nearest neighbors). This procedure however, is valid only if averaging is carried out over the directions (in particular, this procedure is exact for a powder or a polycrystal of the cubic system).

As a result we obtain for the Γ_C lattice

$$D = \frac{a^2}{34T_2},$$

and for the Γ_C^V and Γ_C^f lattices

$$D = \frac{a^2}{53T_2}.$$

In most papers on spin diffusion the estimate used is

$$D = \frac{a^2}{30T_2} \quad (C.6)$$

^{*}We take into account the fact that $\varphi(0) = T_2/\pi$ (see Appendix B). The factor $\sqrt{2}$ is the result of the fact that for a system of two identical nuclei the total width of the state is $\sqrt{2}$ times larger than for one nucleus (this statement, however, is accurate only for a Gaussian distribution). An alternate proof of this statement is as follows. The number of the final states per unit frequency interval is

$$\int \int \delta(\omega_i - \omega_j) \varphi(\omega_i - \omega_n) \varphi(\omega_j - \omega_n) d\omega_i d\omega_j = \int [\varphi(\Delta\omega)]^2 d\omega = \frac{T_2}{\sqrt{2\pi}},$$

where we use for $\varphi(\Delta\omega)$ formula (B.10).

For a cubic crystal we get from (4.11), (B.2), and (C.3) (we are considering a crystal in which all spin-possessing nuclei are identical)

$$D = \frac{\lambda \sqrt{\pi}}{72 \sqrt{2}} \hbar \gamma_n^2 \frac{a_4 + b_4 \Lambda}{\sqrt{a_6 + b_6 \Lambda}} \quad (D.1)$$

A numerical estimate of the quantities a_4 , b_4 , a_6 , and b_6 leads to the following results (we are considering a Gaussian line, $\lambda = 1$): for the Γ_C lattice

$$D = 9.3 \cdot 10^{-2} \frac{\hbar \gamma_n^2}{a} \frac{\Lambda + 0.27}{\sqrt{\Lambda - 0.19}}, \quad (D.2a)$$

and for Γ_C^f

$$D = 5.3 \cdot 10^{-2} \frac{\hbar \gamma_n^2}{a} \frac{4.04 - \Lambda}{\sqrt{2.13 - \Lambda}} \quad (D.2b)$$

For the lattice Γ_C (for example F^{13} in the CaF_2 lattice) it follows from (D.2a) that the ratio of the values of D when the external field is directed along [100], [110], and [111] respectively is 1:1:1.15, that is, the anisotropy of D is small.

On going over to a powder (or a polycrystal), it is necessary to replace Λ in (D.2) by $3/5$. Using, further, formulas (B.13), we obtain the values of D for powders or polycrystals of the cubic system. In particular, for the Γ_C lattice

$$D = \frac{a^2}{12T_2}, \quad (D.3a)$$

and for Γ_C^f

$$D = \frac{a^2}{13.5T_2} \quad (D.3b)$$

We assume that these estimates of the coefficient D are more accurate than the estimate (4.8). Indeed, the estimates (D.3) take account of the fact that flip-flop transitions take place not only for the nearest identical nuclei.

APPENDIX E

We present the main results obtained by Buishvili and Zubarev,^[23] in which a quantum statistical derivation of the Bloembergen equation (5.1) is given.

We consider a crystal in which the spin-possessing nuclei are identical. The Hamiltonian of the system is of the form (there is no alternating field)

$$\mathcal{H} = -\hbar \gamma_n H \sum_i I_i^z + \frac{1}{2} \sum_{ij}' U^{\alpha\beta}(i, j) I_i^\alpha I_j^\beta + \sum_{im} V^{\alpha\beta}(i, m) I_i^\alpha S_m^\beta + \mathcal{H}_e \quad (E.1)$$

The indices i and j number the nuclei while m numbers the magnetic ions; repeated Greek indices imply summation from unity to 3 (x, y, z); $U^{\alpha\beta}$ and $V^{\alpha\beta}$ are operators whose explicit form can be readily determined by using the formula for the dipole-dipole interaction energy (we note that the diagonal components of the tensors $U^{\alpha\beta}$ and $V^{\alpha\beta}$ are real, while the

off-diagonal components are pure imaginary); \mathcal{H}_e is the Hamiltonian of the lattice and of the magnetic ions (with the exception of the Hamiltonian of their dipole-dipole interaction with the nuclei).

Using the method of the statistical operator of the non-equilibrium system, developed in^[24], the authors obtain for the z-component of the nuclear magnetization the equation

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial x_\alpha} \left(D_{\alpha\beta} \frac{\partial M}{\partial x_\beta} \right) - L(\mathbf{r})(M - M_0), \quad (\text{E.2})$$

In the absence of a diffusion barrier, the tensor $D_{\alpha\beta}$ is given by the formula

$$D_{\alpha\beta} = \frac{1}{2} \sum_j' x_{ij}^\alpha x_{ij}^\beta W_{ij}, \quad (\text{E.3})$$

where

$$W_{ij} = \frac{V\pi}{16h^2\sqrt{S}} [U^{zz}(i, j)]^2. \quad (\text{E.4})$$

In the case of a Gaussian nuclear-resonance line, calculation of (E.4) leads to formula (C.2). Further, in the case of a cubic crystal, we can replace $x_{ij}^\alpha x_{ij}^\beta$ in (E.3) by $(1/3)r_{ij}^2 \delta_{\alpha\beta}$. Thus, (E.3) reduces to $D_{\alpha\beta} = D\delta_{\alpha\beta}$, where D is given by (4.9).

When account is taken of the diffusion barrier, each term of the sum (E.3) is multiplied by an appropriate exponential, the argument of which is proportional to the square of the difference of the resonance frequencies of the nuclei i and j.

The quantity L which enters in (E.2) is given by

$$L(\mathbf{r}) = -\frac{1}{2h^2} \sum_{mm'} V^{-z}(\mathbf{r}-\mathbf{r}_m) V^{+z}(\mathbf{r}-\mathbf{r}_{m'}) K_{mm'}(\omega_n). \quad (\text{E.5})$$

where

$$V^{\pm z} = V^{xz} \pm iV^{yz}, \quad K_{mm'}(\omega) = \int_{-\infty}^{+\infty} \langle S_m^z(0) S_{m'}^z(t) \rangle e^{-i\omega t} dt. \quad (\text{E.6})$$

It can be shown that

$$\begin{aligned} & -\frac{1}{2h^2} \sum_m V^{-z}(\mathbf{r}-\mathbf{r}_m) V^{+z}(\mathbf{r}-\mathbf{r}_m) K_{mm}(\omega_n) \\ &= \frac{15}{2} C \sum_m |\mathbf{r}-\mathbf{r}_m|^{-6} \sin^2 \vartheta_m \cos^2 \varphi_m \end{aligned}$$

(ϑ_m and φ_m are the polar angle and the azimuth of the vector $\mathbf{r}-\mathbf{r}_m$ relative to the external field \mathbf{H}). Thus, if we average over the angle ϑ_m , the diagonal part of $L(\mathbf{r})$ reduces to the term $C \sum_m |\mathbf{r}-\mathbf{r}_m|^{-6} (M - M_0)$ of Eq. (5.1).

Analogously, the off-diagonal part of $L(\mathbf{r})$ reduces to the expression

$$\frac{15}{2} C \sum_{mm'}' |\mathbf{r}-\mathbf{r}_m|^{-3} |\mathbf{r}-\mathbf{r}_{m'}|^{-3} \sin \vartheta_m \cos \vartheta_m \sin \vartheta_{m'} \cos \vartheta_{m'} e^{i(\varphi_m - \varphi_{m'})}.$$

This result can also be obtained by following the procedure of Appendix A, and taking in place of (A.1) an expression summed over the magnetic ions:

$$V = h \sum_m A_m S_m^z I^+,$$

where

$$A_m = -\frac{3}{2} \frac{\hbar \gamma_e \gamma_n}{|\mathbf{r}-\mathbf{r}_m|^3} \sin \vartheta_m \cos \vartheta_m e^{-i\varphi_m}.$$

However, the off-diagonal part of $L(\mathbf{r})$ can be neglected if the magnetic-ion concentration is not too large.

APPENDIX F

We present a derivation of formula (5.26a) as written by deGennes^[25] (see also^[3,26]).

1. We start with Eq. (5.1). Considering the stationary case in the presence of a saturating field and confining ourselves to one term in the sum over the magnetic ions, we obtain

$$D \Delta M - Cr^{-6} (M - M_0) - 2AM = 0,$$

or

$$\Delta M - \beta r^{-6} (M - M_0) - L^{-2}M = 0, \quad (\text{F.1})$$

where

$$L = \left(\frac{D}{2A} \right)^{1/2}. \quad (\text{F.2})$$

We solve (F.1) under the boundary conditions

$$M(0) = M_0, \quad M(\infty) = 0.$$

We shall show below that the condition $b \ll L$ is always satisfied. When $r \gg b$ we can neglect the relaxation term in (F.1), and the equation takes the form

$$\Delta M - L^{-2}M = 0, \quad (\text{F.3})$$

with a centrally-symmetrical solution satisfying the condition $M(\infty) = 0$ and proportional to $r^{-1} \exp(-r/L)$. To determine the proportionality coefficient it is necessary to make this equation continuous with the solution of (F.1) for small values of r . On the other hand, when $b \ll r \ll L$ the term $L^{-2}M$ in (F.1) plays no role and the solution is equal to $M_0 b/r$ [see (5.14); since we disregard the diffusion barrier, we have $F = b$]. Thus, when $r \gg b$

$$M(r) = M_0 \frac{b}{r} \exp\left(-\frac{r}{L}\right). \quad (\text{F.4})$$

The factor $\exp(-r/L)$ is brought about by the presence of the saturating field. This factor is important when r is of the order of or larger than L . It is essential that these distances greatly exceed b .

2. We circumscribe a sphere of radius b around each of the magnetic ions. We assume that the nuclear spins are continuously in equilibrium with the lattice inside these spheres, and that in the volume outside these spheres we can neglect direct relaxation. Thus, we obtain in place of (F.1)

$$\begin{aligned} \frac{\partial M}{\partial t} &= D \Delta M - 2AM & \text{when } |\mathbf{r}-\mathbf{r}_m| \gg b, \\ M &= M_0 & \text{when } |\mathbf{r}-\mathbf{r}_m| \leq b. \end{aligned} \quad (\text{F.5})$$

3. Let us consider the stationary case. We solve (F.3) for $r > b$ with the conditions

$$M(b) = M_0, \quad \left. \frac{dM}{dr} \right|_R = 0.$$

The centrally-symmetric solution can be written in the form

$$M(r) = \frac{1}{r} [c_1 \operatorname{sh} kr + c_2 \operatorname{ch} kr], \quad k = \frac{1}{L} = \left(\frac{2A}{D} \right)^{1/2}. \quad (\text{F.6})^*$$

The boundary conditions yield

$$c_1 = \frac{b}{kb + \Delta} M_0, \quad c_2 = \Delta = \frac{kR - \operatorname{th} kR}{1 - kR \operatorname{th} kR}. \quad (\text{F.7})$$

We define T_n by means of the formula [see (5.22)]

$$T_n = (2A_{1/2})^{-1}. \quad (\text{F.8})$$

According to the meaning of $A_{1/2}$, taking k in (F.6) to mean

$$k = \left(\frac{2A_{1/2}}{D} \right)^{1/2} = (DT_n)^{-1/2}, \quad (\text{F.9})$$

we should have

$$\int_b^R M(r) r^2 dr = \frac{1}{2} \int_b^R M_0 r^2 dr,$$

which yields

$$k^2 = \frac{6b\Delta}{(kb + \Delta) R^3}. \quad (\text{F.10})$$

Let us assume that $kR \ll 1$ (this assumption will be justified below); we then have $\delta = (kR)^3/3$ and simple transformations yield

$$k^2 = \frac{3b}{R^3}. \quad (\text{F.11})$$

Since $b \ll R$, we obtain $kR \ll 1$ (and all the more $kb \ll 1$). Then (F.9), (F.11), and (2.1) yield

$$T_n = \frac{R^3}{3Db} = \frac{1}{4\pi NDb}. \quad (\text{F.12})$$

We thus obtain (5.26a) of the main text.

4. Reference^[25] also considers the problem of pure relaxation, and solves (F.5) in the absence of the term $2AM$. The result of this analysis shows that the total nuclear magnetic moment of the sample relaxes exponentially, with the relaxation time given by (F.12).

APPENDIX G

We present a derivation of the expression for T_n for $b \ll \delta$, given in^[19].

If the ratio δ/b is sufficiently large, then the diffusion in the layer $\delta < r < R$ will be much faster than direct relaxation of the nuclei located at distances of the order of δ from the magnetic ion. In such a case an internal equilibrium will be established in the system of nuclei located in the spherical shell $\delta < r < R$ (we are referring to all spherical shells about each of the magnetic ions of the specimen), and subsequently this shell will gradually enter into equilibrium with the lattice. Because of this, the nuclear magne-

tization M in the layer $\delta < r < R$ will be a function of t only, and not of r . The relaxation time of the nuclear magnetic moment of the specimen can be obtained by averaging C/r^6 over all the ions located at a distance $r > \delta$ from the nucleus. Thus,

$$T_n^{-1} = \int_{\delta}^{\infty} \frac{C}{r^6} N dV = \frac{4\pi N}{3} C \delta^{-3}.$$

Using (2.1), we obtain formula (5.26b).

APPENDIX H

For a better explanation of the physical nature of the solution of the problem with the diffusion barrier, we present a solution of Eq. (5.4) for the following form of the function $D(r)$:

$$D(r) = \begin{cases} D_i & \text{when } r < \delta, \\ D & \text{when } r > \delta. \end{cases} \quad (\text{H.1})$$

We introduce the notation

$$\beta_i = \frac{C}{D_i}, \quad \beta = \frac{C}{D}. \quad (\text{H.2})$$

When $r > \delta$, the solution is given by (5.6); when $r < \delta$, the solution is given by a similar formula, but the argument of the functions $I_{\pm 1/4}$ will be $\beta_i^{1/2}/2r^2$, and the corresponding coefficients will be denoted by A_i and B_i .

The boundary conditions are of the form $M(0) = M_0$ and $M(\infty) = 0$. When $r = \delta$ it is necessary to join together the expression for $M(r)$ and $D(r)dM/dr$. The aggregate of these four conditions determines the coefficients A , B , A_i , and B_i .

The condition $M(0) = M_0$ yields $A_i = B_i$. From formula (5.8) we find again that the condition $M(\infty) = 0$ yields $A = \pi\beta^{1/8}/4\Gamma(5/4)$. Further, we replace B in (5.10) by F . After applying the conditions $M(0) = M_0$ and $M(\infty) = 0$, we are left with two undetermined constants A_i and F , which are determined from the conditions for continuity.

In the general case we obtain rather cumbersome formulas, so that we confine ourselves to the case $\delta \ll \beta_i^{1/4}$. Then, when $r < \delta$

$$M(r) = M_0 \left[1 - A_i \frac{2^{1/2} r^{1/2}}{\pi^{1/2} \beta_i^{1/4}} \exp \left(-\frac{\beta_i^{1/2}}{2r^2} \right) \right],$$

$$\frac{dM}{dr} = -M_0 A_i \frac{2^{1/2} \beta_i^{1/4}}{\pi^{1/2} r^{3/2}} \exp \left(-\frac{\beta_i^{1/2}}{2r^2} \right), \quad (\text{H.3})$$

(the differentiation gives rise to one more term, which, however, we can neglect).

Comparing the conditions for the continuity of M and $D(r)dM/dr$ at $r = \delta$, and eliminating A_i from these two relations, we obtain a connection between the external values of M and dM/dr at $r = \delta$

$$M'(\delta + 0) = -\frac{\beta}{\beta_i^{1/2} \delta^3} [M_0 - M(\delta)] \quad (\text{H.4})$$

[in place of $M(\delta + 0)$ we can write $M(\delta)$, since $M(r)$ is continuous at $r = \delta$].

*sh = sinh, ch = cosh.

If D_i tends to zero, that is, β_i tends to infinity, then (H.4) yields $M'(\delta + 0) = 0$. In other words, if $D(r) = 0$ when $r < \delta$, we obtain for the external solution the boundary condition (5.23) at $r = \delta$.

Assume now that the following conditions are satisfied

$$b = 0.68\beta^{1/4} \ll \delta \ll \beta_i^{1/4}.$$

Then we use for $r < \delta$ formula (H.3), and for $r > \delta$ formula (5.12):

$$M(r) = M_0 \left(\frac{F}{r} - \frac{\beta}{12r^4} \right). \quad (\text{H.5})$$

Comparing the continuity conditions and again eliminating the quantity A_i , we obtain

$$\frac{F - \frac{\beta}{3\delta^3}}{1 - \frac{F}{\delta} + \frac{\beta}{12\delta^4}} = \frac{\beta}{\beta_i^{1/2}\delta}, \quad (\text{H.6})$$

which expresses in implicit form F in terms of β , β_i , and δ .

In the limit as $D_i \rightarrow 0$ and $\beta_i \rightarrow \infty$ (H.6) yields

$$F = \frac{\beta}{3\delta^3}, \quad (\text{H.7})$$

that is, we obtain (5.26b).

Expressing A_i in terms F , we readily obtain a formula for $M(r)$ for r smaller than but close to δ :

$$M(r \lesssim \delta) = M_0 \left\{ 1 - \left(1 - \frac{3F}{4\delta} \right) \exp \left[- \frac{\beta_i^{1/2}(\delta - r)}{\delta^3} \right] \right\}. \quad (\text{H.8})$$

It follows from the last formula that the decrease of $M(r)$ from a value M_0 to a value $M(\delta) \ll M_0$, occurs essentially in a layer $(\delta - \delta^3 D_i^{1/2} / C^{1/2}, \delta)$. In the limit as $D_i \rightarrow 0$, the thickness of this layer tends to 0.

Notes added in proof. 1. The nuclear-relaxation diffusion theory development in Sec. 5 does not agree primarily with low-temperature measurements, when samples are used with magnetic-ion concentrations such that $\tau_s \ll \tau_l$ is satisfied (see Sec. 7). It is therefore possible that the theory disagrees with experiment because we have assumed (see Sec. 2) that $\tau = \tau_s$ when $\tau_s < \tau_l$. We must, however, take into account that a low magnetic-impurity concentration the energy of the electron spin-spin interactions will be smaller than the energy of the nuclear Zeeman interactions. Because of this, the "electronic spin-spin interactions-lattice" region may turn out to be narrow for the transfer of energy from the nuclear spins to the lattice. Then, when $\tau_s < \tau_l$ the effective τ will not be equal to τ_s , but will lie between τ_s and τ_l , which leads (see Sec. 7) to a better agreement between theory and the experimental data on the Jeffries group.

2. In a recent paper, M. Goldman [Phys. Rev. A138, 1675 (1965)] investigated the relaxation of protons in para-dibromobenzene. The nature and the concentration of the magnetic impurity were unknown (the impurity concentration, however, was so small that $\tau_l \ll \tau_s$ and $\tau = \tau_l$ for all T). The dependence of the relaxation time of the protons T_p on the field (in the interval from 0 to 140 Oe) was determined at $T = 4.2^\circ\text{K}$. It was found that with increasing field the relation $T_p \propto H^{1/2}$ gives way to a relation $T_p \propto H^2$. This result agrees with (5.27a), (5.27b), and (4.14a), if it is assumed that τ_l does not depend on H and that $\tau_l > T_2$. It is noted in the paper that the experimentally obtained relation $T_p(H)$ agrees well with the theoretical curve for the square-well model.

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