connected by energy transfer leads to a qualitative interpretation of the experimental results. The correct temperature dependences of the intensity and lifetime measurements are predicted and the initial rise and double-exponential decay patterns of the R_1 line at low temperatures are explained. When the two systems are strongly coupled, the ratio of the energy transfer probabilities in the two directions is proportional to an exponential factor.

An examination of the mechanism for the energy transfer through the overlap of the transitions indicates from very rough calculations that quadrupole-quadrupole interactions can be responsible for the energy transfer over ionic separations of 10 Å. This theory must be modified to obtain the correct temperature dependence for the ratio of the transition probabilities in the two directions. Phonon-assisted energy transfer leads to the experimentally observed temperature dependence and is efficient enough for quadrupole-quadrupole interaction to account for the efficiency of the observed energy transfer over the estimated chromium ion separations for these samples.

ACKNOWLEDGMENTS

The author would like to thank C. O. Dugger for the crystals used in this investigation and J. R. Weiner for determining their impurity content by neutron-activation analysis. He also would like to acknowledge O. M. Clark and T. J. Reichenbach for their assistance with the experiments.

PHYSICAL REVIEW VOLUME 173, NUMBER 2 10 SEPTEMBER 1968

Nuclear-Spin-Diffusion Relaxation to a Finite Density of Paramagnetic Impurity Ions*†

EIICHI FUKUSHIMA‡ AND EDWIN A. UEHLING
University of Washington, Seattle, Washington 98105

(Received 1 April 1968)

The effect of a finite concentration of paramagnetic impurity ions on nuclear-spin-diffusion relaxation is studied theoretically and experimentally. It is found that in the spin-diffusion limited case, which is the one of greatest interest here, the equation for the relaxation rate can be modified in such a way as to permit a moderately simple description of the relaxation for all normal ion densities. The modification consists in the replacement of certain exponents in the usual relaxation-rate expression for small ion densities by other exponents which are determined numerically when a single parameter has been specified. This parameter is $x=N^{1/3}(C/D)^{1/4}$, where N is the concentration of the ions, C/r^6 is the transition probability of the nuclei due to the dipole-dipole interaction between an ion and a nucleus, and D is the spin-diffusion coefficient. It is shown also that the amount of nonexponential behavior in the relaxation recovery depends on this same parameter, and that the effects of finite ion density on the way in which T_1 depends on ion concentration, frequency, and temperature can be studied at the same time as the nonexponential behavior. Applications are made both to results of pulse NMR experiments which are reported here for the first time and to the results of experiments that have been reported by other workers.

I. INTRODUCTION

IN spite of extensive studies of spin-diffusion relaxation by nuclear-magnetic-resonance (NMR) methods which have been in progress for a period of nearly 20 years since the concept was first introduced by Bloembergen[1] in 1949, it has not yet been possible experimentally clearly to distinguish the various limiting cases predicted by the theory nor to make wholly satisfactory determinations of various parameters on which the magnitude of the relaxation depends. Reasons for this are to be found partly in the difficulty of making independent determinations of such quantities as the paramagnetic ion density and the electron relaxation time, and partly in the inadequacy of the theory with respect to such considerations as the dependence of relaxation on ion density, on the magnitude of the diffusion-barrier radius, and on other factors.

Thus it is not surprising that much of the experimental work has been devoted to the study of the one case which appears most often, namely, the so-called diffusion-limited case, and to have been restricted, even within the range of validity of this case, to the mere determination of sets of numerical values for the parameters which are mutually consistent and are physically reasonable. In most cases even the electron relaxation time τ was permitted to be determined, along with all other quantities, from the measurements of nuclear spin-lattice relaxation

* This research was supported by the National Science Foundation.

† This work was based on a part of a thesis submitted by Eiichi Fukushima in partial fulfillment of the requirements for a Ph.D degree at the University of Washington.

‡ Present address: University of California, Los Alamos Scientific Laboratory, Los Alamos, N.M. 87544.

[1] N. Bloembergen, Physica 15, 386 (1949).

time T_1 alone. In a few cases, as, for example, in the measurements of Guzzle and Mahendroo,[2] this determination of τ was based on the prediction that T_1 must pass through a minimum as a function of temperature when $\omega\tau=1$, where ω is the Larmor frequency of the nuclear magnetic moment. In a few other cases, as, for example, in the measurements of Leifson and Jeffries,[3] the electron relaxation time was measured independently, and in one case, the measurements of Day, Grimes, and Weatherford,[4] the combination of T_1 and second-moment measurements was used to determine τ.

But in most of the studies τ was unknown and its value was simply inferred from the data on nuclear relaxation. Nevertheless, significant checks of the proposed theories were possible and much has been learned about the range of validity of the two important limiting cases predicted by the theory, about the nature of the departure of the relaxation from strict exponential behavior, and about the dependence of relaxation on the concentration of the paramagnetic impurity ions. As a background for the considerations to be described in this paper, we will mention the major steps in the development of the theory and then review briefly the experimental situation insofar as it deals with the three dependences which have just been mentioned.

Following the original paper of Bloembergen[1] in which he wrote down the diffusion equation, solved it numerically, and also introduced the concept of the diffusion-barrier radius, the further development of the theory took place in five major steps. They were (a) an analytic solution of the stationary-state spin-diffusion equation found by Khutsishvili[5]; (b) the analysis of de Gennes[6] which led to a solution of the time-dependent equation and the demonstration of approximate equivalence of the two solutions; (c) the recognition by Blumberg[7] of the importance of the diffusion-barrier radius under some conditions and his derivation of the expression for the relaxation rate, which he called the rapid-diffusion case under these conditions; (d) the analysis of the inherently nonexponential character of the relaxation by Blumberg[7]; and (e) the generalization of the relaxation problem by Khutsishvili,[8] Silsbee,[9] and Rorschach[10] which led to the concept of two limiting cases, i.e., diffusion-limited and rapid-diffusion.

Studies of spin-diffusion relaxation show that the case most generally realized is that of diffusion-limited relaxation. A few examples are (a) the measurements of Winter[11] on fluorine in LiF at 77 and 300°K; (b) the observations of Jones[12] on the protons in KH_2PO_4 at 4.2, 77, and 300°K; and (c) that part of the data above the diffusion-limited–rapid-diffusion transition temperature in the experiment of Goldman[13] on protons in p-$C_6H_4Br_2$. But, only in a few situations has the opposite extreme of rapid diffusion been observed. Examples are to be found in the studies of Beal and Hatton[14] on fluorine in natural CaF_2 at temperatures below 1°K, and in those of Day, Otsuka, and Josephson[15] on fluorine in CaF_2 and of Goldman,[13] mentioned above, in both of which a transition from diffusion-limited to rapid-diffusion with decrease of temperature seems to be indicated. In addition to these experiments there are some which yield results which are intermediate between the two extreme cases. These include the experiments of Leifson and Jeffries[3] and of Guzzle and Mahendroo.[2] These experiments will be discussed, briefly, in Sec. VI. The experiment of Jones,[12] mentioned above, on protons in KH_2PO_4 is notable because there is no indication of a transition from the diffusion-limited to the rapid-diffusion case even at 4.2°K, where the parameters are expected to be such that the transition should have been completed at a much higher temperature.

Some of these results may be suggestive only of the difficulties of a complete interpretation of the data in the absence of independent determinations of the values of various parameters. But as we will show they may be consequences also of application of the theory to situations in which the concentration of ions is sufficiently high that the results of theoretical analyses based on small concentrations is no longer valid. In addition, there may be difficulties at very low temperatures because of the way in which the diffusion-barrier radius is used in the usual calculations.[16]

Turning now to the possibility of nonexponential behavior of the relaxation, we find the situation rather confused. Such a nonexponential behavior was first predicted by Blumberg[7] and shown to be a consequence of the finite concentration of paramagnetic ions. Blumberg expressed the nonexponential character of the relaxation as a $\sqrt{t}$ dependence in the magnetization recovery at small t, and he demonstrated the existence of a $\sqrt{t}$ dependence with a further dependence on concentration by making observations on the proton relaxation in polycrystalline NH_4HSO_4

[2] T. L. Guzzle and P. P. Mahendroo, Phys. Rev. **150,** 361 (1966).
[3] O. S. Leifson and C. D. Jeffries, Phys. Rev. **122,** 1781 (1961).
[4] S. M. Day, G. B. Grimes, Jr., and W. Weatherford, Phys. Rev. **139,** A515 (1965).
[5] G. R. Khutsishvili, Tr. Inst. Fiz. Akad. Nauk Gruy. SSR **4,** 3 (1956).
[6] P. G. de Gennes, J. Phys. Chem. Solids **7,** 345 (1958).
[7] W. E. Blumberg, Phys. Rev. **119,** 79 (1960).
[8] G. R. Khutsishvili, Zh. Eksperim. i Teor. Fiz. **42,** 1311 (1962) [English transl.: Soviet Phys.—JETP **15,** 909 (1962)].
[9] H. B. Silsbee, quoted in Ref. 16, pp. 7–8.
[10] H. E. Rorschach, Jr., Physica **30,** 38 (1964).
[11] J. Winter, Compt. Rend. **249,** 2192 (1959).
[12] E. D. Jones, Ph.D. thesis, University of Washington, 1962 (unpublished).
[13] M. Goldman, Phys. Rev. **138,** A1675 (1965).
[14] B. T. Beal and J. Hatton, Phys. Letters **15,** 210 (1965).
[15] S. M. Day, E. Otsuka, and B. Josephson, Jr., Phys. Rev. **137,** A108 (1965).
[16] E. Fukushima, Ph.D. thesis, University of Washington, 1967, pp. 8–9 (unpublished).

doped with Cr ions. Similar results have been obtained by Akhmedov and Dautov[17] in a natural single crystal of CaF_2. But a nonexponential recovery can arise from other causes, as, for example, from an inhomogeneous distribution of paramagnetic ions in the sample, and the existence of such nonexponential recoveries are easily demonstrated. Furthermore, any reasonable form of the magnetization recovery with time may be made to look like a $\sqrt{t}$ dependence over a limited range. Clearly, one needs a better criterion for use in isolating the intrinsic nonexponential recovery of spin-diffusion relaxation and one would like to relate the departure from exponential behavior to the magnitude of the spin-diffusion parameters on which it depends. One of the objectives of this paper is to define a parameter which measures the amount of nonexponential behavior and to define a technique for measuring it which excludes other contributory causes of nonexponential behavior.

Finally, we consider the dependence of the nuclear relaxation time on the concentration of the paramagnetic impurity ions. It has sometimes been regarded as a triumph that the relaxation rate is observed to vary linearly with the paramagnetic ion concentration N, as predicated by the approximate solutions of existing theories. An example is the measurement of T_1 for F^{19} in LiF containing F centers, by Josephson and Strandberg.[18] They find $1/T_1 \propto N$. But in some other cases the departure from linearity has been striking. Thus, in the low-temperature measurements of Leifson and Jeffries[3] on the proton relaxation rate in the hydrated rare-earth magnesium nitrates, the relaxation rate has been found to vary approximately as N^2 for concentration of Ce ions in excess of 1%. Also, the measurements of Swanenberg, van den Heuvel, and Poulis[19] yield a relaxation rate $1/T_1 \propto N^q$, where q is at least 1.4 and the concentration of Ce ions is between 0.1 and 5%. It should be mentioned that other mechanisms have been suggested which give rise to a relaxation behavior such that the relaxation rate is not proportional to the ion concentration N. In particular, Khutsishvili[20] has pointed out that it is possible to have $1/T_1 \propto N^2$ for N sufficiently large at low enough T. This, in principle, is true under the conditions of rapid diffusion and τ long compared with the electron spin-spin relaxation time, the latter being a function of N.

In this paper we wish to investigate the consequences of having non-negligible concentration of impurities insofar as nonexponential behavior and T_1 are concerned.[21] In doing this we will, for simplicity, restrict ourselves to the most frequently realized case of diffusion-limited relaxation. We will first show that the existing theories of spin-diffusion relaxation already contain the solution for finite values of the ion concentration, provided only that a parameter $\rho = 0.68(C/D)^{1/4}$, where C is a measure of the direct interaction of the nuclei with paramagnetic ions and D is the nuclear-spin-diffusion coefficient, is smaller than the radius of the average-size sphere controlled by each of the paramagnetic ions. We will then define a parameter Δ which measures the over-all departure from nonexponential behavior. This parameter has the advantage of being unambiguously determined from the data and of being correlated with the dependence of relaxation rate on temperature and magnetic field in a way which easily permits the recognition of an intrinsic contribution, in distinction to nonexponential behavior due to all other causes. Finally, in the experiments we use rare-earth S-state ions as impurity centers in order to put the temperature region of large ρ, at which the nonexponential behavior is maximized, sufficiently high so that even in the adjacent temperature ranges of smaller ρ the relaxation will be diffusion-limited. The reason that S-state ions accomplish this objective is that their relaxation times are much longer and the dependences of the relaxation times on temperature much slower than for non-S-state ions.[22–24]

The various topics to be considered are presented in the following order: Sec. II, a resume of the theoretical background; Sec. III, the theory for the case of finite ion densities; Sec. IV, description of the experiment; Sec. V, results and discussion; Sec. VI,

[17] A. G Akhmedov and R. A. Dautov, Fiz. Tverd. Tela **6**, 529 (1964) [English transl.: Soviet Phys.—Solid State **6**, 415 (1964)].

[18] B. Josephson and M. W. P. Strandberg, J. Phys. Chem. Solids **23**, 67 (1962).

[19] T. J. B. Swanenberg, G. M. van den Heuvel, and N. J. Poulis, Physica **33**, 707 (1967).

[20] G. R. Khutsishvili, Fiz. Tverd. Tela **5**, 2713 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1983 (1964)].

[21] As this paper was being prepared, we learned of the work of I. J. Lowe and D. Tse, who have treated the problem of relaxation due to finite concentration of ions in a wider scope than it is treated here [Phys. Rev. **166**, 279 (1968); **166**, 292 (1968)]. They start by obtaining solutions to the spin-diffusion equation subject to boundary conditions that are less restrictive than those which have been used previously, as a consequence of which the concentration of ions may be made indefinitely large and the parameter ρ can take any value in relation to other lengths which enter into the problem. This brings in additional cases beyond those considered previously. Solutions for the different cases are then developed in a power series yielding correction terms for several cases of interest which provide for different dependences of relaxation rate on parameters than have been known previously. Our procedure is different. Instead of a power-series development, we express the relaxation in terms of the usual relation but with exponents whose values depend on the concentration. Insofar as the diffusion-limited case is concerned, the two procedures give results which do not appear to differ greatly. Both predict dependences of the relaxation rate on N and C which vary more rapidly and on D which vary less rapidly than in the standard diffusion-limited expression for small N. In addition, these authors obtained nonexponential recovery of magnetization in the rotating frame which are analogous to our observations in the laboratory frame. We wish to thank the authors for the privilege of seeing their manuscript in advance of publication.

[22] R. W. Bierig, M. J. Weber, and S. I. Warshaw, Phys. Rev. **134**, A1504 (1964).

[23] K. Horai, J. Phys. Soc. Japan **19**, 2241 (1964).

[24] C. Huang, Phys. Rev. **139**, A241 (1965).

examination of results of other experiments; and Sec. VII, summary.

II. REVIEW OF EXISTING THEORY

In a pioneering article[1] Bloembergen wrote down a diffusion equation for the magnetization which has become the starting point for all subsequent theoretical treatments of the problem. In the absence of an external field, the equation is

$$\dot{M}(r,t)=D\nabla^2M(r,t)-(C/r^6)M(r,t), \qquad (1)$$

where M is the fractional magnetization difference from the thermal equilibrium magnetization, D is the spin-diffusion coefficient, and C/r^6 is the dipole-dipole transition probability of a nucleus due to a paramagnetic ion at a distance r. The diffusion mechanism is that of energy-conserving mutual spin flips of pairs of nuclei so that D is proportional to a transition probability for such an $I_{i+}I_{j-}$ process. The direct transition probability C/r^6 is a consequence of random-field variations at the nucleus due to spin flips of the ion. A straightforward calculation with the assumption of random correlation, and consequently a correlation function exponentially dependent on the time with a single correlation time τ_c yields[25]

$$C=\tfrac{2}{5}(\gamma_S\gamma_I\hbar)^2f(\theta)\tfrac{1}{4}g^2J(J+1)\tau_c/(1+\omega^2\tau_c^2), \qquad (2)$$

where ω is the angular Larmor frequency of the nucleus, θ is the angle between the external static field H_0 and the line joining the ion with the nucleus, and J is written instead of the usual S because the orbital angular momentum is not quenched for the rare-earth ions.

In this work, τ_c is taken to be the spin-lattice relaxation time τ of the paramagnetic ion, which varies rapidly with changes in temperature T. Under many conditions, C can be averaged over θ, in which case $f(\theta)$ can be set equal to unity. C is the source of most of the dependences of the various parameters associated with the spin-diffusion process on resonance frequency and temperature. As a function of τ, it goes through a maximum when $\omega\tau=1$.

It should be remarked that several assumptions have already gone into Eq. (1). One is that the system can be considered to be a continuum. Another is that any given nucleus is primarily influenced by one paramagnetic ion. A third assumption is that D is independent of r. This is a good assumption at most temperatures where τ is less than the nuclear transverse relaxation time T_2, and, as will be seen later, the condition is fulfilled easily for the present experiment. Physically, this assumption has to do with the fact that D involves mutual transitions which conserve energy, and the transition probability for this process is independent of the location of the pairs of nuclei except when they are near an ion where the Zeeman energy levels of two neighboring nuclei may be affected differently by the magnetic field of the ion. However, at moderately high temperatures, for which $\tau\ll T_2$, the effective local static field at the nuclei due to the ions is an average over electron-spin orientations, so that the region of diminishing D is very small. One can then neglect this region of small D if the effects of the direct interaction in relaxing the nuclei are of greater extent, and this is almost always the case in experiments performed at moderate temperatures.

Equation (1) can be solved in the limits of small and large r. The two solutions are then joined and appropriate boundary conditions are used to get the usual form of the relaxation rate,[5,6] for constant D,

$$1/T_1=8.5NC^{1/4}D^{3/4}, \qquad (3)$$

where N is the concentration of paramagnetic ions. Situations in which this relation is presumed to be valid are classified as belonging to the diffusion-limited case. One expects it to be the most common case at moderate temperatures in dilute samples.

Another aspect of the spin-diffusion-relaxation problem which has been treated previously is the $\sqrt{t}$ dependence of the magnetization in the early stages of recovery from complete saturation. This effect was first predicted by Blumberg.[3] Neglecting the diffusion term in Eq. (1), he obtained a solution for the average magnetization as a function of time which is of the form

$$M(t)=1-7.4NC^{1/2}t^{1/2} \qquad (4)$$

for small t.

III. THEORY FOR THE CASE OF FINITE ION DENSITY

In this section, a general solution of the diffusion equation will be obtained in the diffusion-limited case and expressions derived for the experimentally verifiable quantities. It will be assumed that the conventional method[6] of solving Eq. (1) for small r and then joining the solution to the asymptotic solution $1-\rho/r$, with the result

$$\rho=0.68(C/D)^{1/4}, \qquad (5)$$

is a valid procedure. Therefore, the third term in Eq. (1) will be replaced by an equivalent boundary condition, and the problem of concern reduces to that of solving the equation

$$\dot{M}(r,t)=D\nabla^2M(r,t), \qquad (6)$$

[25] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, England, 1961), p. 380.

with the boundary conditions

$$M(\rho, t)=0, \tag{7}$$

$$M'(R, t)=0, \text{ where } \tfrac{4}{3}\pi R^3 N=1 \text{ and } M'=dM/dr, \tag{8}$$

and

$$M(r, 0)=1, \quad r>\rho. \tag{9}$$

The solution which consists of normal modes is

$$M(r, t)=\sum_{n=0}^{\infty} A_n f_n(r)\exp(-\alpha_n t). \tag{10}$$

The space-dependent part of the solution is

$$f_n(r)=[\sin k_n(r-\rho)]/r, \quad \text{where} \quad k_n^2=\alpha_n^2/D. \tag{11}$$

It is orthogonal to the other f's and satisfies the boundary condition at ρ. Application of Eq. (8) in order to make the solution satisfy the boundary condition at $r=R$ yields

$$\tan k_n(R-\rho)=k_n R \tag{12}$$

to be satisfied by the k_n's. Because $M(r, t)$ is not the quantity measured in experiments, we define

$$M(t)=\int_\rho^R M(r, t)r^2dr \Big/ \int_\rho^R r^2dr$$

$$=\sum_{n=0}^{\infty} B_n \exp(-\alpha_n t) \tag{13}$$

as the fractional deviation of the average magnetization from unity, which is its value at $t=0$. Equations (9), (10), and (13) yield the following relations:

$$B_n=\left(\int_\rho^R f_n(r)r^2dr\right)^2 \Big/ \int_\rho^R r^2dr \int_\rho^R [f_n(r)]^2r^2dr$$

$$=J_n^2/VK_n \tag{14}$$

and

$$\sum_{n=0}^{\infty} B_n=1. \tag{15}$$

One obtains, upon performing the integration and with the aid of Eq. (12),

$$J_n=\rho/k_n,$$

$$K_n=\tfrac{1}{2}[R\sin^2 k_n(R-\rho)-\rho], \tag{16}$$

and

$$V=\tfrac{1}{3}(R^3-\rho^3).$$

The k_n's as given by Eq. (12) are to be found graphically. If we define $y_n=k_nR$ and $x=\rho/R$, then it is evident that the larger y_n's behave alike and are given by

$$y_n\approx\tfrac{1}{2}\pi(2n+1)/(1-x), \quad n>0 \tag{17}$$

while the smallest y_n behaves differently from the others. In the simplest case of very small argument, the left side of Eq. (12) can be expanded to give

$$y_0^2\approx 3x. \tag{18}$$

If Eq. (17) is substituted into Eqs. (14) and (16), the approximate result for large n is

$$B_{n\neq 0}\approx[6x^2/(1+x+x^2)][(2n+1)(\pi/2)^2]^{-1}. \tag{19}$$

Although this is a general expression, there is an upper limit imposed on x by the first two assumptions after Eq. (2). One can make $B_{n\neq 0}$ as small as one wishes by making x small so that, in that limit of $x\to 0$, the magnetization given in Eq. (13) recovers exponentially with a rate given by α_0. This recovery rate, evaluated with the use of k_0 obtained from Eq. (18), is the diffusion-limited expression previously given as Eq. (3).

If the condition of very small x is violated, Eq. (18) ceases to be valid, thus invalidating Eq. (3) for the relaxation rate, and $B_{n\neq 0}$ as given by Eq. (19) no longer can be neglected.

If Eq. (18) is invalid, no exact analytic form of y_0 is possible and y_0 versus x must be solved numerically from Eq. (12). This results in an approximate expression $y_0\approx Gx^{(1.35+0.50)}$, where G is a slowly varying function of x. Therefore, one can write an analytic expression for the relaxation rate as a function of x which is valid in a limited range of x within which G does not change very much. Such an expression has the form

$$1/T_1=\text{const}\times N^{(2+4p)/3}C^pD^{(1-p)}, \tag{20}$$

where $p=0.68x+0.25$. In general, the relaxation rate for the case in which x is not negligible varies more rapidly with N and C and less rapidly with D than in the standard diffusion-limited expression for vanishing x.

The criterion which may be used to decide whether or not x is negligible depends on the relative sizes of the two terms in the expression for p. Thus, one might expect that the usual diffusion-limited expression would be valid for $x\ll 0.37$. This is essentially equivalent to the criterion which was recognized when the usual expression was originally derived, namely, $x\ll 1$. However, neither the consequences of not adhering strictly to the restriction nor the ease with which this restriction can be violated has been investigated before, to our knowledge.

This result, that the relaxation rate at moderate temperatures can vary as N^q with q larger than unity for the diffusion-limited case, is somewhat surprising and is a new theoretical result. (See also Ref. 21, however.)

If $B_{n\neq 0}$ no longer can be neglected, the time behavior of magnetization is given by the nontrivial form of Eq. (13). $M(t)$ can be calculated for short times if, initially, the zeroth normal mode is neglected and the sum of Eq. (13) carried out with

$B_{n\neq 0}$ of Eq. (19). When the contribution from B_0 is put back into the sum, the result for short times is identical to the expression of Eq. (4) derived by Blumberg.

Traditionally, Eq. (4) has been used to check the nonexponential effect, namely, magnetization is monitored as a function of time and then is plotted against $\sqrt{t}$ to verify the equation. The weakness of using this procedure lies in the fact that, even for an exponential recovery, a plot of magnetization as a function of $\sqrt{t}$ yields a curve which looks like a straight line over a range of values of t which is not very different from that for which Eq. (4) is supposed to hold. Therefore, it is an ambiguous test of the theory.

Another difficulty associated with the interpretation of past experiments was caused by the ever-present possibility of nonexponential recovery due to some other mechanism besides that of the direct relaxation to the paramagnetic ion. A very common cause of this sort of recovery is due to a nonuniform distribution of the ions in the crystal.

These difficulties can be bypassed by studying the fractional magnitude of the nonexponential recovery Δ as a function of the temperature or applied magnetic field. This quantity should be an unambiguous index of the magnitude of nonexponential recovery which is intrinsic to the recovery mechanism. Furthermore, nonexponential recoveries due to other causes are not expected to depend on temperature and field and, consequently, they may be separated from the effect which we desire to study.

If Δ is taken to be the contribution to the magnetization due to all but the lowest normal mode at $t=0$, then we can write

$$\Delta=\sum_{n=1}^{\infty} B_n \approx 0.56x^2(1+x+x^2)^{-1} \qquad (21)$$

from Eq. (19). Thus, Δ varies as x^2 for small x and has a value of about 0.2 when x has a value near unity. Nonexponential behavior is unambiguously present if Δ is as large as 5%. This requires a value of x of the order of $\frac{1}{3}$.

The general form of Δ should be obtainable also from Eq. (4) by an alternative definition

$$1-\Delta=M(t_0), \qquad (22)$$

where t_0 is some time after which the recovery is exponential. If this time is taken to be the time constant of the next-to-longest mode, i.e., α_1^{-1}, then it follows that

$$\Delta\approx 0.8x^2(1-x). \qquad (23)$$

This is in sufficiently good agreement with the result of Eq. (21) if x is not too large.

From these considerations, one finds that the effects of nonexponential recovery are maximized by maximizing x. Since $x=\rho/R$, a peak in Δ may be found for a given ion concentration (fixed R) by varying T at constant ω, thus varying ρ. From Eqs. (2) and (5) a maximum will occur when $\omega\tau=1$. From Eqs. (2) and (3) this maximum in Δ will coincide with a minimum in T_1.

IV. EXPERIMENTAL PROCEDURE

Pulse NMR experiments were performed on rare-earth-doped CaF_2 crystals. The electronic instrumentation used was similar to that described by Clark.[26] Initially, the total fluorine magnetization is made zero in an external magnetic field of magnitude H_0 by a cluster of four rf magnetic field pulses at the Larmour frequency. Each pulse has magnitude H_1 and duration $t_x<T_2$ such that $\gamma_I H_1 t_x\approx\frac{1}{2}\pi$. The recovery of the magnetization is measured at any time thereafter by the use of a sampling pulse which displays a free-induction decay on an oscilloscope. The range of Larmor frequencies used was 5.5 to 20.0 Mc/sec.

The approximate temperature range used was 150 to 500°K. We used a glass double-wall sample Dewar which was similar to that described by Schreiber.[27] Nitrogen gas heated to the appropriate temperature from a liquid-nitrogen supply was passed around the sample to maintain its temperature.

Samples of CaF_2 single crystals doped with rare-earth ions were obtained from Optovac, Inc. of North Brookfield, Mass. All of them were oriented cylinders with approximate dimensions of 10 mm diam and 15 mm length.

The concentration of the impurities assigned to each crystal is that used in the preparation of the melt and no attempt was made to check these figures independently. Aside from the possible difficulties in trying to dope a crystal heavily, there exist thermodynamical reasons for an increasing probability of creating aggregates of ions with increasing nominal concentrations.[28] This effectively reduces the concentration of the ions as far as the relaxation process is concerned. Therefore, one expects the possibility of the divergence between the effective concentration of the ions and the nominal concentration to increase with an increase in the nominal concentration. This divergence should be in such a way that the effective concentration is less than the nominal concentration.

Two kinds of relaxation measurements were made. On the one hand, the recovery of magnetization was measured and 1 minus the fractional magnetization was plotted against elapsed time on semilog paper. From each such graph, T_1 and Δ were obtained for one temperature, frequency, and orientation. Because this is a time-consuming process, another method was used to provide data on the relative relaxation rates as a function of temperature. While the temperature

[26] W. G. Clark, Rev. Sci. Instr. **35**, 316 (1964).
[27] D. S. Schreiber, Rev. Sci. Instr. **35**, 1582 (1964).
[28] V. V. Osiko, Fiz. Tverd. Tela **7**, 1294 (1965) [English transl.: Soviet Phys.—Solid State **7**, 1047 (1965)].

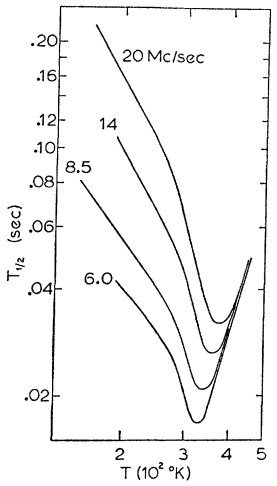

FIG. 1. Temperature dependences of $T_{1/2}$ at four frequencies for CaF_2:Gd^{3+} (0.01%) with $H_0 \parallel [111]$. The curves are the best fits through the experimental points. See Fig. 2 for the actual points taken at 6 Mc/sec.

of the sample was allowed to drift 1° per min, the time $T_{1/2}$ required for the magnetization to recover from zero to one-half of the maximum value was recorded, together with instantaneous value of the temperature. In this way, it was possible to plot out detailed curves of $T_{1/2}$ versus T. From the definitions, $T_{1/2}$, T_1, and Δ are related to each other by the equation

$$T_{1/2}=T_1 \ln[2(1-\Delta)], \quad t_0<T_{1/2} \qquad (24)$$

where t_0 was defined in connection with Eq. (22).

A more detailed description of the experimental procedure is given elsewhere.[29]

V. RESULTS AND DISCUSSION

In this section we will examine the results mainly for a Gd^{3+}-doped CaF_2 sample with a nominal Gd to Ca ratio of 0.01%.

Figure 1 is a plot of the temperature dependence of $T_{1/2}$ at four different frequencies for this sample with $H_0 \parallel [111]$. A similar plot with $H_0 \parallel [100]$ shows that at 6 Mc/sec the temperature dependence of $T_{1/2}$ is identical to the case with $H_0 \parallel [111]$, except that the values for $T_{1/2}$ are about 10% larger, with $H_0 \parallel [100]$. The $T_{1/2}$ minima of Fig. 1 are assumed to occur at points corresponding to $\omega\tau=1$, where τ is the spin-lattice relaxation time of the Gd^{3+} ions. If this is indeed the case, then the values of τ at the temperatures corresponding to the $T_{1/2}$ minima can be obtained from Fig. 1, and this is useful information for comparing the results with the theory. There are changes in the slopes of Fig. 1 at about 280°K for all four frequencies. Above these breaks, the $T_{1/2}$ minima are quite symmetric with magnitudes of the slopes on both sides equal to about ± 3. The data taken at the lower frequencies exhibit steeper and deeper minima because of the prominence of the nonexponential component of recovery near the $T_{1/2}$ minima at the lower frequencies.

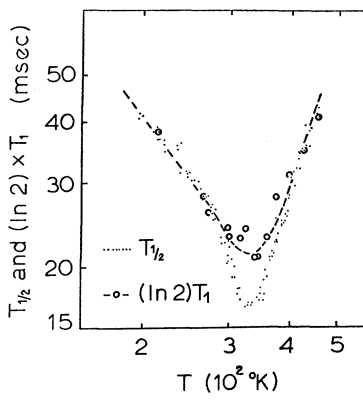

FIG. 2. Temperature dependence of measured $T_{1/2}$ and T_1 ln2 for CaF_2:Gd^{3+} (0.01%), $H_0 \parallel [111]$, at 6 Mc/sec. The dashed line is a fit to the T_1 ln2 points.

[29] Reference 16, Chap. VII.

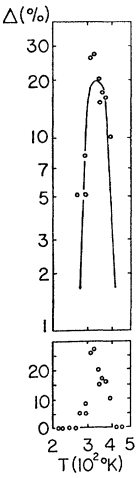

FIG. 3. Temperature dependence of Δ for CaF_2:Gd^{3+} (0.01%), $H_0 \parallel [111]$, and 6 Mc/sec. The semilog plot is included to show the $\Delta=0$ points.

The temperature dependence of $T_{1/2}$ at 6 Mc/sec is shown in Fig. 2 together with the measured T_1's reduced to the equivalent $T_{1/2}$ scale. The effect of the nonexponential recovery is very evident as the difference between the two sets of points. It is also evident that the maximum in Δ does correspond to the minimum in T_1.

The measured values of Δ at 6 Mc/sec are plotted against temperature in Fig. 3. The dependence is very rapid. The maximum slopes have magnitudes of about 19. It should be pointed out that Eq. (24) does not apply here because the condition $t_0<T_{1/2}$ is violated near the Δ maximum for 6 Mc/sec.

Further data on the dependence of T_1, $T_{1/2}$, and Δ on ω and T for CaF_2:Gd^{3+} (0.01%) and graphical representations of various relations which can be extracted from the data are given in Figs. 4–9.

Nonexponential recovery was found also in two samples of Eu^{2+}-doped CaF_2 (0.01 and 1.0%) at room temperature and above. This is to be expected since Eu^{2+}, like Gd^{3+}, is an S-state ion. However, the range

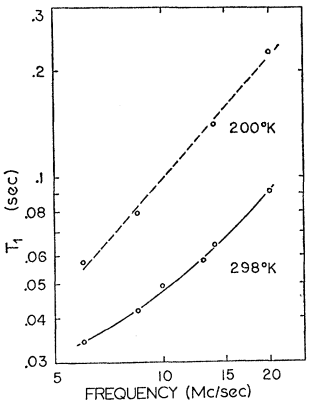

FIG. 4. Frequency dependences of T_1 at 200 and 298°K for CaF_2:Gd^{3+} (0.01%), H_0 || [111]. The points at 200°K are calculated from the $T_{1/2}$ data.

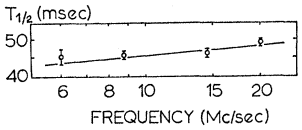

FIG. 5. Frequency dependence of $T_{1/2}$ at 450°K for CaF_2:Gd^{3+} (0.01%), with H_0 || [111].

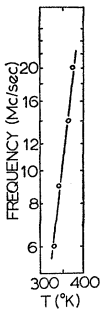

FIG. 6. The NMR frequency versus temperature at which the $T_{1/2}$ minima occur for CaF_2:Gd^{3+} (0.01%) sample with H_0 || [111].

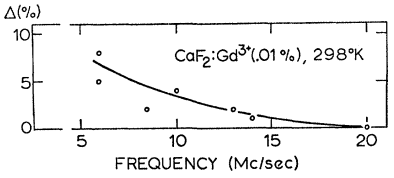

FIG. 7. Frequency dependence of Δ at 298°K for CaF_2:Gd^{3+} (0.01%) with H_0 || [111].

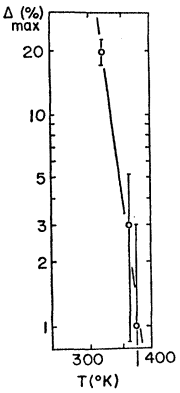

FIG. 8. The values of maximum Δ plotted against the temperature at which the maximum occurs for CaF_2:Gd^{3+} (0.01%) with H_0 || [111].

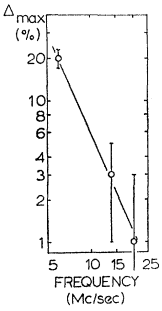

FIG. 9. Maximum value of Δ at a given NMR frequency plotted against that frequency for CaF_2:Gd^{3+} (0.01%) with H_0 || [111].

of temperatures over which the condition $\omega\tau\approx 1$ can be fulfilled at values of ω used in this experiment was too high to permit the same kind of investigation as was performed on the Gd^{3+}-doped samples. Conversely, experiments performed in the room-temperature range on a non-S-state Nd^{3+}-doped crystal of CaF_2 (1.0%) always showed strictly exponential recovery. This also was to be expected because such ions have much smaller values of τ in the room-temperature range than the S-state ions. The net result is that we are left with the data on the Gd^{3+}-doped sample as given in Figs. 1–9 as a basis for further study. An analysis of these data is given in the next few paragraphs.

We start by assuming that, on the basis of Eqs. (2) and (20), the dependence of $1/T_1$ on ω and τ is most likely to be of the form

$$1/T_1 = \text{const}\times[\tau/(1+\omega^2\tau^2)]^p, \tag{25}$$

where

$$\tau = \text{const}\times\omega^n T^{-m}. \tag{26}$$

Using Figs. 2 and 4–6 and Eqs. (25) and (26), we can obtain several relations involving products of the exponents m, n, and p. They are

$$mp=3, \quad p(n+2)=1,$$
$$pn=-\tfrac{1}{10}, \quad m/(n+1)=8.6.$$

One obtains values of the exponents m, n, and p in Eqs. (25) and (26) from these relations, which are uncertain by something of the order of ±20%. Using the average values, one finds, for the CaF_2: Gd^{3+} sample used in this experiment,

$$1/T_1 = \text{const}\times[\tau(1+\omega^2\tau^2)]^{0.55}, \tag{27}$$

$$\tau = \text{const}\times\omega^{-0.25}T^{-6}. \tag{28}$$

Equation (27) is an approximate relation which applies only in a limited range of ω and τ such that $\omega\tau\approx 1$. Outside of this range, p will have smaller values. Equation (28) applies in the temperature range 280 to 450°K.

The empirical value for p equal to 0.55 obtained in the experiment with CaF_2: Gd^{3+} (0.01%) corresponds to a value for x of about 0.44. If, for this crystal, $N\approx 2.5\times 10^{18}$ cm^{-3}, then this, in turn, corre-

sponds to a ρ of about 33 Å. On the other hand, the maximum value of ρ, computed from Eqs. (2) and (5) at a frequency of 6Mc/sec, turns out to be 25 Å if D is taken to be 5×10^{-12} cm^2 sec^{-1}. The agreement is satisfactory.

Going back to Eq. (20) and calculating the predicted magnitude of T_1 by using p equal to 0.55 and the values of parameters given above, one obtains a value which agrees with the experimental value to within a factor of 2. This result, however, would appear to have somewhat less significance than the qualitatively correct interpretation of frequency and temperature dependence as described above.

The value of D used above is based on a frequently used expression given, for example, by Khutsishvili.[30] It is in close agreement with a more recent calculation of Lowe and Gade.[31]

According to Eq. (28) the relaxation time of the Gd^{3+} ion at room temperature varies as $\omega^{-0.25}$ and T^{-6}. No results of measurements of τ in this range near the Debye temperature have been reported previously. The temperature dependence is close to the T^{-5} dependence reported by Bierig *et al.*[22] and Huang[24] at much lower temperatures for S-state rare-earth ions in CaF_2. No frequency dependence has been predicted or observed before. The actual values of τ obtained ir this work for Gd^{3+} seem to fall between the extrapolations of the data of Bierig *et al.*[22] and Horai.[23]

We now turn to the results for Δ. The qualitative results which were described at the beginning of this section behave in the manner expected from the discussion of Sec. III. Quantitatively, the picture is not wholly clear, as the following discussion will show.

Suppose it is assumed that

$$\Delta = \text{const}\times[\tau/(1+\omega^2\tau^2)]^q. \tag{29}$$

Then, with the additional assumption that Eq. (28) for the Gd spin-lattice relaxation time is correct, it is possible to get estimates for q from the various dependences of Δ. The predicted relations are

$$\Delta = \text{const}\times\omega^{-(7/4)q}T^{6q}, \quad \omega\tau>1$$

$$\Delta_{\max} = \text{const}\times T_0^{-6q}, \quad \omega\tau=1$$

and

$$\Delta_{\max} = \text{const}\times\omega_0^{-q}, \quad \omega\tau=1$$

where ω_0 and T_0 denote the values of ω and T when $\omega\tau=1$.

The values of q obtained by a comparison of these relations with the experimentally determined $\Delta(T)$, $\Delta(\omega)$, $\Delta_{\max}(T_0)$, and $\Delta_{\max}(\omega_0)$, as found in Figs. 3 and 7–9, are 3, 1, 3, and 2, respectively. The uncertainties are of the order of 40% because of difficulties in the measurement of Δ. But even allowing for a wide range of error in this determination, there is still a considerable discrepancy between a value of q determined in this way and the value $q=\frac{1}{2}$ predicted by Eq. (21), according to which $\Delta\propto x^2\propto\rho^2\propto C^{1/2}$. The source of this disagreement is not understood.

VI. DISCUSSION OF OTHER DATA

We consider briefly the published data of Guzzle and Mahendroo,[2] Bierig, Weber, and Warshaw,[22] and Leifson and Jeffries.[3]

Guzzle and Mahendroo measured the fluorine T_1 in several rare-earth-doped CaF_2 samples as a function of temperature in the range of 25–300°K. They found, for example, that the minimum in T_1 at 29.5 Mc/sec for CaF_2:Tb^{3+} occurs at 41°K. Typical data for a crystal containing Tb^{3+} ions in a large concentration of about 2×10^{19} cm^{-3} are replotted in Fig. 10. We extract from this curve two kinds of information: (a) the slope of the curve on either side of the minimum is approximately equal to ±3; and, (b) if $\omega\tau=1$ at the T_1 minimum, τ is equal to 5.4×10^{-9} sec at $T=41$°K.

In order to provide an interpretation of these data along the lines which have been described above, it would be helpful to have information of the variation of τ for Tb^{3+} with temperatures around 41°K. Some information on the temperature dependence can be obtained considering the data of Guzzle and Mahendroo together with the paramagnetic resonance data of Bierig *et al.*[22] The latter measured the ion spin-lattice relaxation time of Tb^{3+} in CaF_2 over a range of temperatures below 10°K. A replot of their data points and published smooth curve is shown in Fig. 11 as the set of small circles and solid smooth curve extending downward to $T\sim10$°K. The other datum point shown is the previously mentioned point of Guzzle and Mahendroo at 41°K.

The next step is to interpolate between the two sets of data points. The heavy dashed curve was obtained by Guzzle and Mahendroo, using the stand-

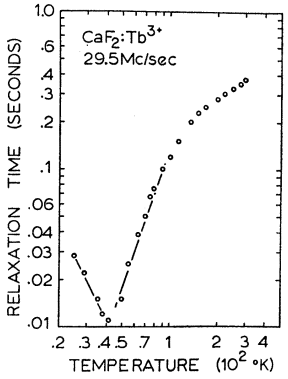

FIG. 10. Temperature dependence of T_1 in CaF_2:Tb^{3+} at 29.5 Mc/sec from data of Guzzle and Mahendroo (Ref. 2).

[30] G. R. Khutsishvili, Usp. Fiz. Nauk **87**, 211 (1965) [English transl.: Soviet Phys.—Usp. **8**, 743 (1966)].
[31] I. J. Lowe and S. Gade, Phys. Rev. **156**, 817 (1967).

ard spin-diffusion equation, Eq. (3), and their T_1 data on the F^{19} relaxation. The slope of this curve is about -10. The dotted curve is merely an extrapolation of the low-temperature curve of Bierig *et al.* to the one point at 41°K. It has a slope -5.

We now give reasons for choosing the curve of slope -5 in preference to the one of slope -10, and then draw a further conclusion. We first note that the non-Kramers Tb^{3+} ion is expected to relax by a Raman process with $T_1 \propto T^{-7}$.[22] Thus, the predicted slope on this basis is between the two curves appearing on Fig. 11. Then we use the data of Guzzle and Mahendroo on T_1 below 41°K and interpret it in terms of Eq. (20). This is the same procedure as used above to interpret the T_1 data on CaF_2: Gd^{3+}. In this case we find $p \approx 0.6$. Since $\omega\tau > 1$ in this range, $1/T_1 \propto \tau^{-p} \propto T^{-np}$. But we have previously observed that in this case $1/T_1 \propto T^{-3}$. This leads to $n \approx 5$, the slope of the dotted curve in Fig. 11. Thus, we again find that an interpretation of spin-diffusion relaxation using Eq. (20) gives better results than would have been obtained using Eq. (3). That the values of p are about the same in the two cases which have been analyzed here is not unexpected in view of the relative ion concentrations and the fact that p is not very sensitive to changes in C.

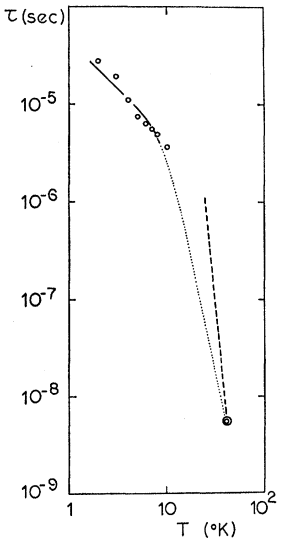

FIG. 11. Temperature dependence of Tb^{3+} electron spin-lattice relaxation time in CaF_2. The small circles are the points from the EPR measurements of Bierig *et al.* (Ref. 22) and the solid line is their fit to these points. The isolated point at 41°K is from the NMR data of Guzzle and Mahendroo (Ref. 2). The steep dashed line is a rough sketch of the temperature dependence of τ calculated in Ref. 2 with the use of the usual diffusion-limited expression for T_1 together with the NMR data. The dotted line is drawn to join the 41°K point to the best fit curve of Bierig *et al.*

Leifson and Jeffries[3] measured the paramagnetic spin-lattice relaxation time τ of Ce in

$$(La, Ce)_2Mg_3(NO_3)_{12} \cdot 24H_2O$$

and found that $\tau = \text{const} T^{-14}$ for T between 1.9 and 2.3°K. They also measured the proton spin-lattice relaxation time and found that $T_1 = \text{const} \times T^{-7}$ for T between 1.9 and 4.2°K. The four relative concentrations used ranged from 5×10^{-4} to 5×10^{-2}. $\omega\tau$ was greater than 1 at 4.2°K. If it is again assumed that $1/T \propto [\tau/(1+\omega^2\tau^2)]^p$, then their data yield $p = \frac{1}{2}$, a result which is similar to others discussed in this and the previous section.

VII. SUMMARY

The criterion for the validity of the spin-diffusion-limited relaxation and the consequences of violating this criterion have been reexamined. We found the general expression for the spin-lattice relaxation rate to be given by Eq. (20). This reduces to the usual diffusion-limited expression in the limit of small N.

We have also derived an expression for a newly defined quantity Δ which is a measure of the nonexponential component of recovery. We found that Δ should be a maximum where x is a maximum, and thus it is convenient to look for a nonzero Δ at the same time that the departure from the usual diffusion-limited case is being studied.

An experiment yielded results generally consistent with the above except in the exact dependences of Δ on T and on ω. These dependences were too rapid to be consistent with the predictions of our theory, but at least the qualitative picture seems to be correct. Our observation of Δ as a function of T and of ω is the first study of its kind. It unambiguously establishes the existence of the phenomenon of nonexponential recovery which was first predicted by Blumberg.[7]

ACKNOWLEDGMENT

Henry B. Silsbee made valuable contributions to this work in its early stages.