will not describe properly the entire ground term. That is, cases 4 and 5 will not predict accurately the positions of the missing multiplets. For this reason the Hamiltonian of case 3 may be more useful in certain cases, but in any event the use of a Hamiltonian derived from fundamental considerations is generally (but not necessarily) to be preferred over phenomenological Hamiltonians. Hence, case 3 was chosen as the standard model to which the other models were compared.

It is useful to compare how well the spin-orbit and B_{lm} might describe other physical phenomena in addition to the energy levels. The parallel component of a g factor, $g_{||}$, for the ground Γ_2 state was calculated for each case. Table X shows that $g_{||}$ of case 3 is 17.915 and is in agreement to about 0.8% with the $g_{||}$ measured in a previous EPR study,[6] yielding $g_{||}=17.777\pm 0.005$. The $g_{||}$ factors, determined using the other Hamiltonians of cases 1, 2, 4, and 5 do not agree as well, but are still within about 1.2% of the measured value.

In summary, the parameters for case 3 as given in Table IX yield theoretical energy levels compatible with the experimental energy levels for the ground term of Tb^{3+} in $CaWO_4$. These parameters also yield results consistent with the $g_{||}$-factor measurement of the ground state. A comparison of the various theoretical models shows that the B_{lm} are affected considerably when J mixing and term mixing are neglected, as they are in cases 1 and 2. Such effects are considered by the effective Hamiltonian (case 3) and the range over which the B_{lm} may vary is indicated by the results obtained for cases 4 and 5.

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Measurement of the Nuclear Spin Diffusion Coefficient in CaF_2†

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Measurements are reported of the spin-lattice relaxation time T_1 at 80°K and at room temperature for F^{19} spins in CaF_2 doped with one U^{3+} ion per 9×10^3 fluorine atoms. T_1 was found to be strongly dependent on the orientation of magnetic field with respect to the crystalline axes. Observation at 80°K of the recovery of nuclear magnetization for very short times after saturation indicated a $t^{1/2}$ behavior, as predicted by Blumberg for the diffusion-limited regime of relaxation via paramagnetic impurities. The magnetization which starts out proportional to $t^{1/2}$ consists of spins near a paramagnetic impurity, i.e., those relaxed by direct contact with the paramagnetic ions rather than by diffusion of Zeeman energy via the nuclear dipole-dipole interaction. The latter measurements, coupled with the T_1 measurements, yield values for the effective spin-diffusion coefficient of 0.77×10^{-12} cm²/sec when the dc magnetic field is in the [111] direction, and 4.2×10^{-12} cm²/sec when it is in the [100] direction. These results are in disagreement with present theories, which predict little variation in the effective diffusion coefficient with orientation of the applied field.

INTRODUCTION

WORK in recent years has underlined the importance of transport of nuclear Zeeman energy in solids by the dipole-dipole interactions among nuclear spins, a process usually referred to as nuclear spin diffusion. We wish to report here some experimental results which, while confirming the approximate magnitude of theoretical predictions of the effective spin-diffusion coefficient, disagree strongly with the theoretical prediction of the effect of magnetic field orientation on the diffusion coefficient.

Nuclear spin diffusion is an important phenomenon in the domain of solid-state physics, as is illustrated by at least three examples: The first is as a mechanism enhancing spin-lattice relaxation by paramagnetic impurities. In many insulators the main coupling of the nuclear spins to the lattice is via the electron spins of the paramagnetic impurities. The rate for relaxation of a single nuclear spin by an electron spin is Cr^{-6}, where C is a function of the two magnetic moments, the angle between the applied magnetic field and the line joining the two spins, the correlation time of the electron spin states, and the Larmor frequency of the nuclear spins,[1] and r is the distance between the nuclear spin

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and the electron spin. However, most of the nuclear spins are much too far away from any impurity spin to explain the observed relaxation times by such an interaction. As shown by Bloembergen,[1] there is another interaction, viz., the dipole-dipole interaction among nuclear spins, which can rapidly transport Zeeman energy from the region around an impurity to regions far away from any impurity.

The other two obvious examples of nuclear spin diffusion are in the dynamic polarization of nuclear spins[2] and in nuclear double-resonance experiments.[3] In both of these one wishes to see an effect on a numerous set of nuclear spins due to rf radiation applied to a relatively rare set of spins: in the first case electron spins, in the second a set of rare nuclear spins. In both, as in the case of spin-lattice relaxation, the strong interspecies coupling occurs between near neighbors and the effect is then distributed among the numerous species by nuclear spin diffusion. In the case of dynamic polarization of nuclear spins, there is some reason to ask whether the process of distribution of polarization will be a diffusion process or not, although it certainly is a transport process. In several attempts to derive a diffusion equation from a microscopic equation of motion for the nuclear spin system, the assumptions of high spin temperature and small magnetization gradient have had to be made.[4,5]

OBSERVATION OF SPIN DIFFUSION

We chose to measure the effective spin diffusion coefficient D by measuring the spin-lattice relaxation time T_1 of F^{19} spins in CaF$_2$, in which the fluorine sites form a simple cubic lattice. The experimental procedure consisted of carefully measuring the fluorine magnetization in an applied magnetic field of 7.2 kOe after saturation and observing a departure from exponential recovery.

Various relationships between the spin-lattice relaxation time T_1, the electron spin-nuclear spin coupling constant C, and the effective diffusion coefficient D, have been derived by several authors. The common approach is to assume that the paramagnetic impurities are so far apart that one may solve the equation of motion for magnetization density for the case of one single paramagnetic impurity in a sea of nuclear spins. Including both direct and diffusion relaxation, the relevant macroscopic differential equation is

$$\partial\rho/\partial t = D\nabla^2\rho - Cr^{-6}\rho, \qquad (1)$$

where ρ is the difference between $m(\mathbf{r}, t)$, the magnetization density at the position $\mathbf{r}$ at time t, and m_0, the equilibrium magnetization density. The paramagnetic impurity is taken to be at the origin.

The simplest approach to solving Eq. (1) is to assume that there exists some radius a such that the direct interaction magnetizes the nuclear spins inside the radius a to the equilibrium value m_0, in a very short time, while the value of m for $r>0$ remains zero. Thus we arrive at an initial (i.e., $t=0$) condition $m=m_0$ for $r<a$, $m=0$ for $r>a$. One then assumes a boundary condition, namely, that the magnetization current, proportional to the gradient of $m(\mathbf{r}, t)$, be zero at $r=R\equiv(3/4\pi N)^{1/3}$, where N is the concentration of impurities per unit volume. Lastly, one assumes that for $r>a$, only the diffusion term of Eq. (1) is important. Thus one has an eigenvalue problem, given a differential equation plus an initial condition and a boundary condition. It is easy to show that the solution is of the form $m/m_0 = 1-\sum_n A_n\phi_n \exp(-k_n^2Dt)$, where t is now the time after saturation. The set of ϕ_n contain the spatial dependence and are normalized so that the integral of ϕ_n over the sphere of volume N^{-1} is unity. The A_n depend, of course, on the initial condition, i.e., exactly what the derivatives of m are at the beginning. The k_n depend only on the boundary conditions on m—in this case spherical symmetry and zero current at $r=R$—and are obtained from the transcendental equation

$$kR + \tan ka = (1 - kR \tan ka) \tan kR. \qquad (2)$$

Hence the solution for the total magnetization M, as a function of time, may be regarded as a sum of modes, each with a characteristic time constant equal to $(k_n^2D)^{-1}$. The higher n is, the shorter is the characteristic time and the smaller the amplitude of the mode. The amplitudes and characteristic times of the first five modes were found for a range of values of a/R by using a "search" process on an IBM 7040 digital computer. For values of $a\ll R$, the first mode, which dominates the usual observed relaxation, is characterized by $1/T_1 \approx 4\pi NaD/(1-3a/R)$. If higher modes are provoked by an initial magnetization density variation, then a careful measurement of the recovery of magnetization as a function of time after saturation should reveal them, thus providing a value of D.

A second, more sophisticated approach, proposed by de Gennes[6] and by Khutsishvili[7] and used in both the case of equilibrium magnetization in the presence of a small rf field on resonance and that of recovery of magnetization after saturation, essentially involves solving the differential equation for m in two regions: One is for small r and ignores the diffusion term and the other is for large r and ignores the direct interaction

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term. The two solutions are then matched to produce a solution for all $\boldsymbol{r}$. In this process a parameter

$$\beta=0.68(C/D)^{1/4} \tag{3}$$

must be introduced, and the resulting relaxation rate is given by the expression

$$1/T_1=4\pi N\beta D, \tag{4}$$

where β is the pseudopotential of de Gennes, and has the physical significance of being approximately the radius at which there is a shift from a predominance of direct interaction to one of relaxation by spin diffusion. This approach is valid where $\beta \gg b$, where b is the spin-diffusion barrier, representing the region within which spin diffusion does not occur because the local dc field due to the paramagnetic impurity has shifted the nuclear spins out of the resonance line.[8]

Blumberg[8] later showed that the assumption that $b \gg \beta$ led also to an exponential recovery of magnetization described by the rate $1/T_1=4\pi NC/3b^3$. This is the "rapid diffusion" case, where the relaxation is no longer limited by diffusion, but rather is limited by the rate at which the electron spin relaxes its nuclear spin neighbors. Blumberg[8] also showed that in the case of spin-diffusion limited relaxation, for very small values of time t, the observed total magnetization should be given by

$$M=M_0(\tfrac{4}{3}\pi^{3/2})NC^{1/2}t^{1/2}. \tag{5}$$

This expression gives the magnetization due to direct interaction relaxation, with the assumption that the impurities are far apart. Obviously for sufficiently small times this term will be comparable with, or even larger than, the magnetization due to diffusion, which will start out as M_0t/T_1.

As Bloembergen pointed out,[2] and later theories have agreed,[4,5,9] although spin diffusion itself is anisotropic (because of the anisotropy of the dipole-dipole interaction), the effective value of D (i.e., averaged over all directions), which is what one sees when measuring T_1, should depend very little on the orientation of the crystal with respect to the applied dc field. Hence one should be able to distinguish the regime $\beta \gg b$ from $\beta \ll b$ by looking at the orientation dependence of T_1,[10] or by looking for a $t^{1/2}$ behavior of the magnetization for short times after saturation. Previous attempts to measure D by observing a $t^{1/2}$ behavior[8] have been hampered by the necessity of high impurity concentration in order to elicit a visible $t^{1/2}$ behavior and the necessity of complicated compounds in order to get the high concentration of impurities.

EXPERIMENTAL RESULTS

The experimental results that we wish to present here are simply a very accurate measurement of the magnetization recovery of F^{19} spins in CaF_2 after saturation, at sufficiently short times that a $t^{1/2}$ behavior was distinguishable from a t behavior. The saturation of the fluorine magnetization was accomplished by applying seven intense, 90° rf pulses. The magnetization M at a time t was later measured by applying a single 90° rf pulse and then gating a boxcar integrator during the ensuing free precession signal. The F^{19} resonance frequency was 28.667 MHz. One plots the observed M versus t and hopes to see a deviation from $M_0[1-\exp(t/T_1)]$. Initial rough estimates indicated that it would be easier to see higher diffusion modes (i.e., starting out proportional to t, but with a characteristic time constant different from T_1, as measured for longer times) than it would be to observe a $t^{1/2}$ behavior. The problem with either is that the optimum range of t is from 10^{-4} to 10^{-2} times T_1, and the magnitude of either higher diffusion modes or $t^{1/2}$ would be of the order of 1–20% of the *observed* signal, which itself would be of the order of 0.1% of M_0. Obviously one must look at a lot of free-precession signals. Of course one may repeatedly integrate over many free-precession signals, but any drift (i.e., noise with a frequency less than the inverse of the gate time) will become a problem. Therefore, the capacitor of the boxcar integrator was made reversible by means of a Haller Rel 51 ceramic-mounted DPDT relay. When the capacitor is in one sense, a (variable) time t occurs between the last pulse of the saturation burst S, and the single 90° measuring pulse M. This is called the signal mode. When the capacitor is in the opposing sense, a time of about 350 μsec comes between S and M, a time long enough for spin-spin equilibrium to be established, but too short for any perceptible magnetization to have developed. This is called the test mode. The capacitor is reversed after each measuring pulse M. Thus low-frequency noise is subtracted out and high-frequency noise is integrated to zero.

It should also be pointed out that beginning the experiment cycle by saturating the nuclear magnetization avoids the necessity of waiting several T_1's between cycles. It was thus possible to observe in a reasonable amount of time the several hundred thousand free-induction signals needed to distinguish a departure from simple exponential recovery.

Systematic errors were checked for by reversing the phase between the pulse sequence and the direction of the reversible capacitor and by reversing the phase of the synchronous detector reference signal. A correction of 1% (for 200 reversals) to the gross observed magnetization compensated for the signal lost due to nonreversible stray capacitance in parallel with the reversible capacitor.

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The first results are shown as the points in Fig. 1 and were taken in CaF_2, doped with U^{3+} (one U^{3+} per 9×10^3 F^{19}) supplied by the Harshaw Chemical Co. The temperature was 80°K and the dc magnetic field was applied along the crystal's [111] direction. The results are not consistent with the "eigenvalue problem" model, mentioned above, for any reasonable value of the diffusion barrier b (which is assumed equal to the parameter a in the model). A least-squares fit of the expression $At^{1/2}+Bt$ was made, with the results as shown in Table I along with the values of T_1 measured for long times (i.e., 0.2 to 2.0 times T_1). In the figure t is actually the difference in time between S and M in the two modes. That is, if τ is the time between S and M, then t is the difference between τ for the signal mode and τ for the test mode. The "best values"—obtained by weighting each point by the inverse of the square of its uncertainty—are $A_{111}=(1.13\pm0.05)\times10^{-2}\ \mathrm{sec}^{-1/2}$ and $B_{111}=0.599\pm0.06\ \mathrm{sec}^{-1}$. The value of B should be $1/T_1$, which is 0.652. That B is actually less than $1/T_1$ is reasonable since $1/T_1$ is the appropriate value for relaxation when the direct process is negligible, i.e., after the magnetization in the neighborhood of the impurity has reached the equilibrium value. But A and B are measured before this situation obtains, and therefore the relaxation rate due to diffusion should be somewhat less.

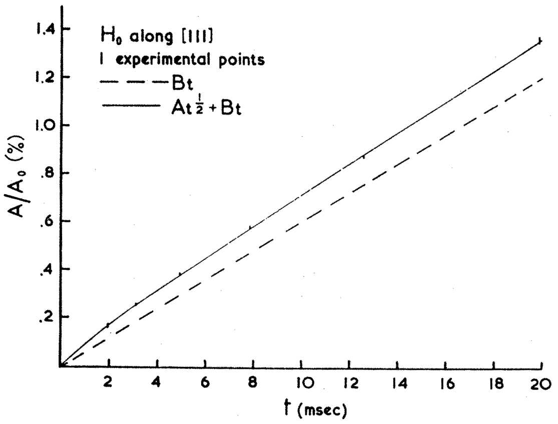

FIG. 1. F^{19} magnetization in CaF_2, relative to the equilibrium value, as a function of time after saturation, for $\mathbf{H}_0$ along the [111] direction. The size of the experimental points indicates the standard error.

Using Eqs. (3)–(5), and the measured values of $T_1(111)$ and $A(111)$ from Table I, one obtains $D(111)=0.77\times10^{-12}\ \mathrm{cm}^2/\mathrm{sec}$. In reality, it is difficult to ascribe a precision to this number. Formally, since D is proportional to $T_1^{-4/3}N^{-2/3}A^{-2/3}$, the numerical uncertainty of D is dominated by the uncertainty of N(~10%) and A(~5%). In reality, it is the formulas which are probably less precise, since D and C are really averages over discrete points of anisotropic quantities and, at least for short times, the pertinent distances are relatively small multiples of the interfluorine spacing. It therefore seems probable that the theoretical formulas contribute as much uncertainty as the experiment.

TABLE I. Results of best fit of $At^{1/2}+Bt$ to experimental data, corresponding relaxation times, and resulting diffusion coefficients.

	$\mathbf{H}_0$ along [111]	$\mathbf{H}_0$ along [100]
A:	$(1.13\pm0.05)\times10^{-2}\ \mathrm{sec}^{-1/2}$	$(0.49\pm0.18)\times10^{-2}\ \mathrm{sec}^{-1/2}$
B:	$0.599\pm0.058\ \mathrm{sec}^{-1}$	$1.53\pm0.25\ \mathrm{sec}^{-1}$
T_1:	1.533 ± 0.009 sec	0.645 ± 0.004 sec
D:	$0.77\times10^{-12}\ \mathrm{cm}^2/\mathrm{sec}$	$4.2\times10^{-12}\ \mathrm{cm}^2/\mathrm{sec}$

We next repeated the experiment with the dc field along a [100] direction of the crystal, with the results as shown in Fig. 2. The precision of the points is poorer than for Fig. 1 because of fewer experiments per point and also the shorter T_2 for $\mathbf{H}_0$ in the [100] direction reduces the integrating time and hence the intrinsic signal-to-noise ratio. The best values for a least-squares fit of $At^{1/2}+Bt$ are $A(100)=(0.49\pm0.18)\times10^{-2}\ \mathrm{sec}^{-1/2}$ and $B(100)=1.53\pm0.25\ \mathrm{sec}^{-1}$. $1/T_1$ is 1.550. The resulting value for $D(100)$ is $4.2\times10^{-12}\ \mathrm{cm}^2/\mathrm{sec}$.

The experimental uncertainty in $D(100)/D(111)$ is about 28%. With the assumption that the uncertainty introduced by treating C and D as averaged quantities is not significantly greater, our results lead to the conclusion that the effective diffusion coefficient is highly dependent on magnetic field orientation with respect to the crystal axes. As will be seen, the order-of-magnitude agreement with theory is good, but the orientation dependence disagrees strongly with theory.

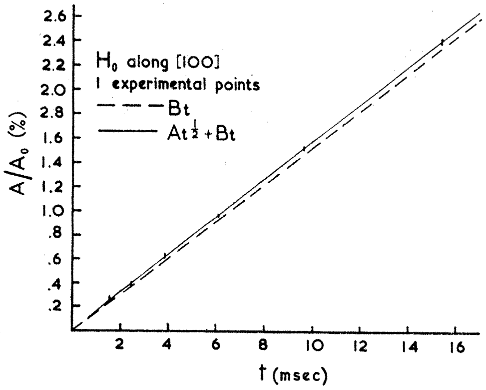

FIG. 2. F^{19} magnetization in CaF_2, relative to the equilibrium value, as a function of time after saturation, for $\mathbf{H}_0$ along the [100] direction. The size of the experimental points indicates the standard error.

DISCUSSION OF RESULTS

Recent efforts[4,5,9] to calculate an effective diffusion coefficient yield a result of the form

$$D = C\tau\gamma^4 I(I+1) \sum_j r_{ij}^{-4}(1-3\cos^2\theta_{ij})^2, \qquad (6)$$

where C is a numerical coefficient of the order of 0.05, τ is the coherence time of the interaction which is responsible for the diffusion of Zeeman energy (usually set equal to the spin-spin relaxation time T_2), γ is the gyromagnetic ratio of the nuclear spins, I is the spin of the nuclear spins, r_{ij} is the distance between the ith and jth nuclear spins, and θ_{ij} is the angle between the applied magnetic field and the vector joining the ith and jth spins.

The three references differ only in the numerical coefficient C. When this expression is evaluated for the F^{19} spins in CaF_2, the theoretical result is

$$D(111) = 1.5\times 10^{-12}\ \text{cm}^2/\text{sec},$$

$$D(100) = 1.3\times 10^{-12}\ \text{cm}^2/\text{sec}.$$

A more recent theoretical result[11] yields a value for $D(100)/D(111)$ of about 0.91 for a simple cubic lattice. Hence the magnitude of our experimental results is in good agreement with theory, but the orientation dependence is bad. References 4, 5, and 9 are all considerably different, only having in common the assumption that $\tau = T_2$. This assumption is patently incorrect, and several efforts are under way to improve on this assumption.

There are several factors involved which could cause our experimental results to be misleading. These include: the distance dependence and the anisotropy of the diffusion barrier, which in effect causes some regions close to the impurity spin to have a T_2 shorter than others, and also causes some observable nuclear spins to be in poor diffusion contact with their neighbors; the orientation dependence of the expectation value of the electron-spin magnetization, $\langle S_z\rangle_{\text{av}}$, which causes a change in the diffusion barrier; and the anisotropy of the electron spin-nuclear spin interaction. Our estimates of the effects caused by these factors indicate that they do not play a significant role in our results. Variations in the electron spin-lattice interaction are not of importance since the first part of our experiment consists of measuring the magnetization of the nuclear spins due to direct interaction with the electron spins. The second part is the measurement of T_1, which depends on both the direct interaction of electron spins with nuclear spins and the diffusion of the resulting nuclear magnetization from these spins to the less favorably located fluorine spins. In detail, our results say that while the magnetization due to direct interaction is somewhat larger when the dc field is along a $\langle 111\rangle$ axis, the diffusion of the magnetization is much more rapid when the dc field is along a $\langle 100\rangle$ axis; i.e., $1/T_1(100) > 1/T_1(111)$.

Therefore, we conclude that the magnetization in the vicinity of the electron spins for short times after saturation is about the same for the two orientations of $\mathbf{H}_0$, and that it is the difference in average diffusion coefficient which accounts for the difference in the T_1's.

As a partial check to ensure that we were in the diffusion-limited regime—although the presence of $t^{1/2}$ behavior in the magnetization is already evidence of this fact—we measured T_1 for the F^{19} spins at room temperature. Raising the temperature has the effect of reducing the diffusion barrier since thermal motion will reduce the value of $\langle S_z\rangle_{\text{av}}$ at the neighboring sites. T_1 for $\mathbf{H}_0$ along the [100] direction was 1.02±0.02 sec, T_1 for $\mathbf{H}_0$ along the [111] direction was 3.52±0.02 sec. Thus the anisotropy remains as the temperature is raised. Since the observed anisotropy of T_1 at high temperatures and the anisotropy of D are both in conflict with any of the theories we have seen to date, we hope that this work will encourage further efforts, both theoretical and experimental, to resolve this inconsistency.

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