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Study of the interaction of electron paramagnetic spins with nuclear spins*

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NMR measurements are reported here on a particular Ce^{3+}-doped CaF_2 crystal which, when analyzed in the light of existing relaxation theory, yield explicit expressions for the effective magnetic moment of the paramagnetic spin, its associated autocorrelation time, and the contribution of the surrounding shifted nuclei to the second moment of the nuclear-resonance line shape. Additional more direct measurements of this cross second moment using both Mansfield's coherent-double-pulse technique and a free-induction-decay decomposition agree with the moment predicted by the above analysis to within experimental error. Some common pitfalls in the interpretation and comparison with theory of such data are also pointed out. Finally, attention is called to serious inconsistencies between the autocorrelation times resulting from this analysis and impurity-spin–lattice relaxation times obtained from EPR measurements on similar systems.

I. INTRODUCTION

Many investigators have studied the interaction of electron paramagnetic spins with nuclear spins in nominally diamagnetic solids since the work of Rollin[1] and Bloembergen.[2] Studied in particular has been the Bloembergen model in which spin-lattice relaxation of nuclei occurs by diffusion of their Zeeman energy to the vicinity of an electron spin, where energy is then transferred from the nuclear spin system to the electron spin, which is assumed strongly coupled to the lattice. This latter feature of the model which attempts to describe the process at the site of the impurity has itself received considerable attention but still has not been resolved completely. Simply, the picture is as follows: The electron impurity magnetic moment fluctuates owing to the lattice interaction with an autocorrelation time τ_c, thus producing a fluctuating magnetic field at the nearby nuclear-spin sites which in turn produces transitions of the nuclear spins among their Zeeman levels. It is widely asserted that τ_c is identical with the spin-lattice relaxation time T_{1e} for the impurity spin. However, this latter assertion has never really been demonstrated experimentally. In fact, we present evidence that the assertion is, in general, not correct. An earlier paper[3] from this laboratory suggested that, by combining with existing theory both nuclear T_1 data and second-moment measurements taken as functions of temperature, one can determine the τ_c of the impurity as a function of temperature. Measurements and calculations performed in this manner are reported for Ce^{3+}-doped CaF_2 in the present paper.

II. THEORY

A. Linewidth

Theoretical calculations of the nuclear resonance linewidth of a system of nuclear spins in a solid with dipolar interactions are in excellent agreement with experiment. If electron paramagnetic impurities of sufficient concentration are present in the sample, they may further broaden the nuclear resonance line. Day, Grimes, and Weatherford[3] have used Rorschach's[4] theory for the magnetic moment of the impurity effective in interacting with the nuclear spins to obtain an expression for that part of the second moment of the nuclear resonance line due to the impurities. The impurity contribution to the second moment is given by

$$\langle \Delta\omega^2 \rangle_{IJ} = \gamma_I^2 (\mu_{\mathrm{eff}})^2 N_J N_I^{-1} \sum_i (1 - 3\cos^2\theta_{ij})^2 r_{ij}^{-6} , \tag{1}$$

where N_I is the density of resonant spins, γ_I is their magnetogyric ratio, N_J is the density of paramagnetic ions, and μ_{eff} is the z component of the magnetic moment of the paramagnetic ion effective in broadening the resonance of the nuclear spins. Rorschach assumes the autocorrelation function for the impurity magnetic moment is

$$K(\tau) = \langle \mu_z \rangle^2 + (\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2)\, e^{-\tau/\tau_c} ,$$

from which the spectral density of its fluctuating magnetic moment is calculated to be

$$\begin{aligned} J(\omega) &= \int_{-\infty}^{\infty} K(\tau) e^{i\omega\tau}\, d\tau \\ &= \langle \mu_z \rangle^2\, 2\pi\delta(\omega) + (\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2) \frac{2\tau_c}{1 + \omega^2\tau_c^2} . \end{aligned} \tag{2}$$

The square of the average z component of the moment effective in perturbing the nuclei is given by

$$\mu_{\mathrm{eff}}^2 = \frac{1}{2\pi} \int_{-\Delta\omega}^{+\Delta\omega} J(\omega)\, d\omega$$

$$= \langle \mu_z \rangle^2 + \frac{2}{\pi} (\langle \mu_z^2 \rangle - \langle \mu_z \rangle^2) \tan^{-1}(\Delta\omega)\tau_c \;, \tag{3}$$

where $\Delta\omega$ is the halfwidth at half-maximum of the nuclear resonance line. For the case of equally spaced Zeeman energy levels and values of the argument of the Brillouin function small compared to unity, a statistical mechanical analysis produces simplified expressions for $\langle \mu_z \rangle$ and $\langle \mu_z^2 \rangle$, which in turn simplify (3):

$$\mu_{\text{eff}}^2 = \left(\frac{J(J+1)\gamma_J^2 \hbar^2 B_0}{3kT} \right)^2 + \frac{2}{\pi} \left(\frac{J(J+1)\gamma_J^2 \hbar^2}{3} \right) \times \tan^{-1}(\Delta\omega)\tau_c . \tag{4}$$

J is the angular momentum quantum number of the paramagnetic ion, γ_J is its magnetogyric ratio, k is the Boltzmann constant, T is the temperature, and B_0 is the magnetic field intensity.

B. Spin-lattice relaxation

The relaxation of nuclear spins by paramagnetic impurities has been studied by numerous investigators. In this paper, we follow the notation and theoretical treatment given by Lowe and Tse.[5] Their general expression for T_1 for the single-paramagnetic-center model is

$$T_1^{-1} = \frac{4\pi\lambda N_J D \beta^2}{R} \times \frac{I_{-3/4}(\delta) K_{-3/4}(\Delta) - I_{-3/4}(\Delta) K_{-3/4}(\delta)}{I_{-3/4}(\delta) K_{1/4}(\Delta) + I_{1/4}(\Delta) K_{-3/4}(\delta)} \;, \tag{5}$$

where λ is a parameter which characterizes the average spatial distribution of the magnetization about an impurity, $I_{\pm\nu}(z)$ and $K_{\pm\nu}(z)$ are the modified Bessel functions,

$$\delta = \tfrac{1}{2}(\beta/b)^2 \;, \tag{6}$$

and

$$\Delta = \tfrac{1}{2}(\beta/R)^2 \;. \tag{7}$$

Furthermore, D is the spin-diffusion coefficient,

$$\beta = (\overline{C}/D)^{1/4} \;, \tag{8}$$

$$\overline{C} = \tfrac{2}{5} J(J+1)\gamma_J^2 \hbar^2 \gamma_I^2 \tau_c (1 + \omega_0^2 \tau_c^2)^{-1} \;, \tag{9}$$

$$R = [3/(4\pi N_J)]^{1/3} \;, \tag{10}$$

$$b = (\tfrac{3}{2} a \mu_{\text{eff}} / B_1)^{1/4} \;, \tag{11}$$

B_1 is the "local" magnetic field, a is the lattice constant ($a = 5.45 \times 10^{-8}$ cm), $\omega_0 = \gamma_I B_0$, and the other quantities have been given in Sec. II A.

In order for the single-paramagnetic-center model to apply, the condition $R > b$, or $\Delta \ll 1$, must be satisfied. The largest value of Δ encountered in this work is 0.03. In this case ($\Delta \ll 1$), Eq. (5) becomes

$$T_1^{-1} = 8\pi\lambda N_J D \beta \frac{\Gamma_{(3/4)}}{\Gamma_{(1/4)}} \frac{I_{3/4}(\delta)}{I_{-3/4}(\delta)} \;. \tag{12}$$

Consequently, there are only two limiting cases of interest: Case I: $R > b \gg \beta$ or $\delta \ll 1$ and $\Delta \ll 1$. This is called the rapid-diffusion case, where (12) is approximated by

$$T_1^{-1} \simeq \tfrac{4}{3} \pi N_J \overline{C} / b^3 \;. \tag{13}$$

Case II: $R \gg \beta \gg b$ or $\delta \gg 1$ and $1 \gg \Delta$. This is called the diffusion-limited case, where (12) becomes

$$T_1^{-1} \simeq \tfrac{8}{3} \pi N_J \overline{C}^{1/4} D^{3/4} \;. \tag{14}$$

Equations (13) and (14) can be used to determine the temperature dependence of τ_c provided D, and the concentration and type of impurity are known. The basic difficulty comes about when one tries to decide which case applies in a given temperature range. The method employed here is to assume that Eq. (13) applies in the liquid-helium temperature region. Then by equating (13) to the empirical temperature dependence of T_1, the temperature dependence of τ_c can be computed. Using this expression for τ_c, δ can be evaluated at liquid-helium temperatures, thereby checking the validity of the use of Eq. (13). An additional test can be made by using the computed temperature dependence of τ_c to calculate the contribution of the paramagnetic ions to the second moment of the nuclear resonance line and comparing it with the second moment determined from experiment.

III. EXPERIMENTAL APPARATUS

The 25-MHz phase-coherent pulse NMR spectrometer employed in the present experiments utilized a single coil probe and followed generally the conventional design practices described in recent literature. The probe tuned circuit, which had a higher Q (approximately 25) than any of the other band-pass elements in the spectrometer, determined its bandwidth of 1 MHz. The rotary B_1 of the sample coil was 17–20G. Inhomogeneity of the B_1 field over the sample volume was measured to be less than 1% by observing the maximum remanent transverse magnetization $M(\tau)$ in a doped water sample immediately after terminating an rf pulse of arbitrary length τ. The basic $\frac{1}{4}\lambda$ duplexing scheme described by Lowe and Tarr[6] was used. Recovery time of the spectrometer, with the above parameters realized, was 3–5 μsec. Phase-sensitive detection was employed, with the resulting detected free precession signals being read out directly on a storage oscilloscope.

The solid examined in these experiments was a CaF_2 single crystal containing, according to the

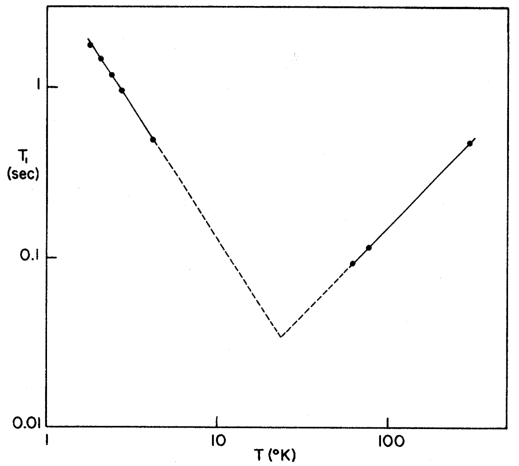

FIG. 1. Spin-lattice relaxation time of ^{19}F in CaF_2: Ce^{3+} vs temperature with [100] $\| \vec{B}_0$.

stoichiometric estimation of the manufacturer,[7] 7×10^{18} cm^{-3} Ce^{3+} impurity ions. However, using neutron-activation analysis,[8] a concentration of 1.02×10^{19} cm^{-3} of cerium ions was obtained. This latter number was used for N_J in all subsequent calculations. According to Optovac, the crystal studied was grown in conditions under which the Ce^{3+} ions in CaF_2 occupy almost exclusively substitutional sites of tetrogonal symmetry with charge compensation by an additional F^- ion in the nearest interstitial site. Temperature control was effected by controlling the vapor pressure over a liquid helium or nitrogen bath surrounding the sample. Thus, measurements were made over the temperature ranges 1.8–4.2 K, 62–77 K, and 297 K.

IV. EXPERIMENTS AND THEIR INTERPRETATION

Figure 1 shows a log-log plot of T_1 versus temperature for a B_0 field of 6.24 kG oriented parallel to the [100] crystalline axis. Data points on the graph were taken using both $\frac{1}{2}\pi - \tau - \frac{1}{2}\pi$ and $\pi - \tau - \frac{1}{2}\pi$ pulse methods with good agreement between the two. To determine the temperature dependence of τ_c, it is convenient to characterize the experimental values of T_1 by making a simple two-parameter fit to the data. Namely,

$$T_1 = 4.6 T^{-1.5} \text{ sec for } 1.8 \le T \le 4.2 \text{ K} \tag{15}$$

and

$$T_1 = 1.3\times 10^{-3}\, T \text{ sec for } 62 \text{ K} < T < 297 \text{ K}. \tag{16}$$

Clearly, T_1 had a minimum between 4.2 K and 62 K. If the temperature at which the minimum occurs can be ascertained and if the diffusion-limited case is known to apply, then τ_c can be determined unambiguously because $\tau_c = \omega_0^{-1}$ at this point. Frequently it is not known that these conditions prevail and some other approach must be followed such as the one used by Tse and Lowe.[9] In any case, by equating (15) to either (13) or (14), it is possible to obtain an equation for τ_c as a function of the temperature for $1.8 \text{ K} \le T \le 4.2$ K.

First we shall assume T_1 is diffusion limited ($\delta \gg 1$ and $\Delta \ll 1$) in the helium temperature range. Using (9) for $\bar{C}$ with $J(J+1)\gamma_J^2 \hbar^2 \gamma_I^2 = 3.135\times 10^{-31}$ cgs units, Kim's[10] value for the diffusion constant $D = 1.3\times 10^{-12}$ cm^2 sec^{-1}, and $N_J = 1.02\times 10^{19}$ ions cm^3, we get $\tau_c = 0.27\, T^{-6}$ or $\tau_c = 4.9\times 10^{-5}$ at $T = 4.2$ K. Now if this value of τ_c is used to calculate δ at 4.2 K, we get $\delta = 6.4\times 10^{-3}$ which is not consistent with the conditions set on the diffusion-limited case. Next we shall assume T_1 is given by the rapid-diffusion case ($\delta \ll 1$ and $\Delta \ll 1$). Equating (13) to (15) and eliminating b by using (11), we have

$$4.6\, T^{-1.5} = \frac{3}{4\pi N_J C}\left(\frac{3a\,\mu_{\text{eff}}}{2B_1}\right)^{3/4} \quad . \tag{17}$$

Here B_1 is the "local field" and is 2.08 G for CaF_2 when $\vec{B}_0 // [100]$; μ_{eff} is given by (4). When these quantities are substituted into (17), the temperature dependence of τ_c can be computed. This has been done by computer using the value of the constants above with the result shown in Fig. 2. The curve can be approximated by a two-parameter fit, giving

$$\tau_c = \frac{(4.4\pm 1.0)\times 10^{-7}}{T^{0.87\pm 0.10}} \quad , \tag{18}$$

with T in degrees Kelvin and τ_c in seconds. Using this result for τ_c we have $0.12 \le \delta \le 0.30$ and $0.02 \le \Delta \le 0.03$ for $1.8 \text{ K} \le T \le 4.2$ K from (6) and (7) respectively. The approximation that $\Delta \ll 1$ is justified. At 4.2 K, δ has its maximum value of 0.3 which is certainly not very small compared to 1. However, as shown in Fig. 1 of Rorschach's paper,[4] the ratio $I_{+3/4}(\delta)/I_{-3/4}(\delta)$ changes rapidly between $\delta = 3$ and $\delta = 0.5$.

$$\frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})}\,\frac{I_{+3/4}(\delta)}{I_{-3/4}(\delta)} \simeq \frac{4}{3}\left(\tfrac{1}{2}\delta\right)^{3/2}\left(1 - \tfrac{6}{7}\,\delta^2\right) \tag{19}$$

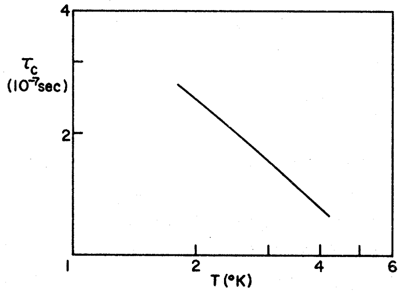

FIG. 2. Temperature dependence of the autocorrelation time τ_c of Ce^{3+} between 1.8 and 4.2 K.

for small δ, and less than an 8% difference exists between the assumed form of T_1 in Eq. (13) and the more exact expression of Eq. (12) at 4.2 K. Furthermore, λ has been taken as 1 which according to Eq. (33) of Lowe and Tse[5] is in error by less than 5%. Thus, the assumption that the rapid-diffusion case applies in the low-temperature region is borne out.

As a further test of the validity of the expression for τ_c, we can compare the calculated second moment to the experimental values. The substitution of (18) into (4) gives

$$\mu^2_{\text{eff}} \simeq \left(\frac{0.56}{T^2} + \frac{7.0\times 10^{-2}}{T^{0.87}}\right)\times 10^{-40} \text{ cgs units} \quad (20)$$

for $1.8\text{K} \leq T \leq 4.2$ K. The contribution of the paramagnetic ions to the second moment of the fluorine resonance linewidth can be calculated from Eq. (1). Assuming that each Ce^{3+} ion is located at a Ca substitutional site, we evaluated the lattice sum in (1) to three decimal places by a computer calculation. The total sum thus obtained is 3.84×10^{45} cm^{-6}, which when substituted into (1) along with (20) yields

$$\langle \Delta\omega^2 \rangle_{IJ} = 5.0\times 10^{10}\left(\frac{0.56}{T^2} + \frac{7.0\times 10^{-2}}{T^{0.87}}\right)\left(\frac{\text{rad}}{\text{sec}}\right)^2 . \quad (21)$$

There exist several methods for independently obtaining the above quantity experimentally. It is pertinent at this point to identify some rather subtle limitations which can plague all such measurements of NMR lineshape parameters. In computing the above-mentioned lattice sum in Eq. (1), we summed over all the nuclear spins surrounding an impurity. However, in direct measurements of $\langle \Delta\omega^2 \rangle_{IJ}$, the resonance frequency of spins close to the impurity may be shifted out of the range of observation of the spectrometer. If one is using a cw spectrometer, the signal component from the shifted nuclei appears in the wings of the resonance line and is usually lost in the noise. On the other hand, if one is using a pulse spectrometer, the nuclei near the impurity will contribute a frequency component to the free-induction decay (FID) which may lie outside the bandwidth of the receiver system. It is also possible to fail to observe the nearby nuclear spins if the spectral density of the $\frac{1}{2}\pi$ pulse at the resonance frequency of these spins is not sufficiently intense to rotate their magnetization into the transverse plane where they can contribute to the FID signal. In short, one must assume one of the following two courses of action in order to make a realistic comparison of theory with experiment: (a) make the effective spectrometer bandwidth large enough to "see" all the spins or (b) truncate the lattice sum in (1) such that nuclear spins not observed by the particular spectrometer in question are also not included in the sum.

A reasonable criterion for determining the situation that applies can be had by equating the effective half-bandwidth $\Delta\Omega$ of the spectrometer to the shift in the resonance frequency of a nuclear spin situated at a distance d from a paramagnetic impurity:

$$\Delta\Omega = \gamma_I\, \mu_{\text{eff}}/d^3 \ . \quad (22)$$

As quoted previously, the bandwidth of the receiving system in our spectrometer is approximately 1 MHz. Thus, the effective spectrometer bandwidth is determined by the more narrow spectral distribution of the transmitter pulse. The Fourier transform of a rectangularly modulated rf pulse of length τ is given by

$$B_1(\omega) = \alpha \sin\tfrac{1}{2}(\Delta\Omega)\tau/\tfrac{1}{2}(\Delta\Omega)\tau \ , \quad (23)$$

where α is a normalizing factor, $\Delta\Omega = \omega - \omega_0$, and ω_0 is the carrier frequency as well as the Larmor frequency of a free nuclear spin. If, immediately after a $\frac{1}{2}\pi$ pulse, only those nuclear spins in the ensemble which are rotated at least $\frac{1}{6}\pi$ away from B_0 contribute appreciably to the linewidth, then the condition set on the power spectrum of B_1 is that

$$\gamma_I B_1(\omega')\tau = \tfrac{1}{6}\pi \ . \quad (24)$$

Hence,

$$B_1(\omega') = \tfrac{1}{3}B_1(\omega_0) \ . \quad (25)$$

Substituting (25) into (23), we have

$$\sin\tfrac{1}{2}(\Delta\Omega')\tau/\tfrac{1}{2}(\Delta\Omega')\tau = \tfrac{1}{3} \ . \quad (26)$$

The solution of (26) is

$$\tfrac{1}{2}(\Delta\Omega')\tau \simeq \tfrac{3}{4}\pi \ , \quad (27)$$

which, for our $\frac{1}{2}\pi$ pulses of 3.5 μsec, yields $(2\pi)^{-1}$ $\Delta\Omega' = 0.2$ MHz. Using (27) to solve (22) for d, we find

$$d^3 = 1.8\times 10^{-2}\ \mu_{\text{eff}} \ . \quad (28)$$

Using Eq. (20) with $T = 4.2$ K, d becomes 3.5×10^{-8} cm. That is, nuclei within d of the Ce^{3+} ion do not contribute to the FID. This value for d at 4.2 K excludes only the nearest neighbors, which for $[100]//\vec{\text{B}}_0$ do not contribute to the lattice sum if there is no lattice distortion, because $(1 - 3\cos^2\theta) = 0$ for these spins. Consequently, Eq. (21) evaluated at $T = 4.2$ K gives

$$\langle \Delta\omega^2 \rangle_{IJ} = 2.59\times 10^9 \ (\text{rad/sec})^2 \ ,$$

which should compare favorably with the measured result if the theory is correct. However, at 1.8 K, d becomes 4.4×10^{-8} cm approaching closely the next-nearest-neighbor distance of 4.5×10^{-8} cm. This suggests that the next-nearest-neighbor fluorine nuclei may not participate in the FID and these spins should be eliminated from the lattice sum. In this case, Eq. (1) with $T=1.8$ K gives

$$\langle \Delta\omega^2\rangle_{IJ}=2.45\times10^9\,(\text{rad/sec})^2 \quad (T=1.8\text{ K}) .$$

Additional exclusion of the next-next-nearest-neighbors yields

$$\langle \Delta\omega^2\rangle_{IJ}=1.88\times10^9(\text{rad/sec})^2 \quad (T=1.8\text{ K}) .$$

Mansfield[11] has shown previously that if the phase-coherent pulse sequence $\frac{1}{2}\pi-\tau-\frac{1}{2}\pi$ (where $\tau<T_2$) is applied to a system composed of two spin species, the second magnetic species gives rise to a cross-coupling transient signal, the initial slope of which is proportional to the cross second moment. More specifically,

$$\langle \Delta\omega^2\rangle_{IJ}=\frac{1}{\tau S_0}\,\frac{dS}{dt}\bigg|_0 , \tag{29}$$

where τ is the spacing between pulses, S_0 is the initial signal height after the first pulse, and $dS/dt|_0$ is the slope of the signal evaluated immediately after the termination of the second $\frac{1}{2}\pi$ pulse. For all but the liquid-helium temperatures the transient was not observed in this sample, indicating that

$$\langle \Delta\omega^2\rangle_{IJ}<10^8(\text{rad/sec})^2$$

for $T\geq 62$ K. This is estimated from the minimum detectable signal using Eq. (29). This is in agreement with the prediction of Eq. (1) where μ_{eff} is expected to be very small because T is large and τ_c is small. At both 4.2 K and 1.8 K, the cross second-moment measurements using the Mansfield technique gave

$$\langle \Delta\omega^2\rangle_{IJ}=2.4\times10^9(\text{rad/sec})^2 ,$$

with no change observed outside the limits of experimental accuracy. This number is in good agreement with $\langle \Delta\omega^2\rangle_{IJ}$ calculated at 4.2 K using the entire lattice sum and the value calculated at 1.8 K excluding the next-nearest-neighbor spins.

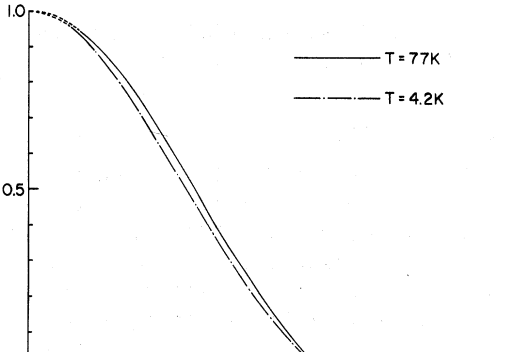

FIG. 3. Free-induction-decay curves of ^{19}F in CaF$_2$: Ce^{3+} with [100] $\parallel \vec{B}_0$ at $T=4.2$ and 77 K. The dashed portions of the curves represent extrapolation back to zero as described in the text.

As a further check on the theory, FID curves were taken at 4.2 K and 77 K. The curves were photographed from the oscilloscope, then projected onto graph paper for comparison at the two temperatures. The results are shown in Fig. 3. The FID curve obtained at 77 K was extrapolated from 3.5 μsec back to zero by fitting the function $G(t)=A\,e^{-1/2a^2t^2}(\sin bt)/bt$ of Abragam[12] where the first zero crossing of 21.3 μsec determined b and a was calculated by setting $a^2+\frac{1}{3}b^2$ equal to the theoretical value for the second moment. The agreement between the assumed functional form for $G(t)$ and the experimental curve was within 1% over the time interval between 3.5 and 21.3 μsec. Consequently, the second moment at 78 K is the same as given by Van Vleck.[13] At 4.2 K the first zero crossing for $G(t)$ was observed to be 21.3 μsec as at 78 K. An attempt was made to fit an Abragam function to the FID at 4.2 K but it was found that a fit could be made only over the region from 7 to 16 μsec while the experimental curve before 7 μsec deviated considerably from the Abragam function. However, it was found that a Gaussian curve for $G(t)$ fit extremely well between 3.5 and 13 μsec. This permitted a determination of the signal height at zero time and the total second moment which was 10.34×10^9 (rad/sec)^2. Consequently, the inpurity contribution to the second moment from the FID curve analysis is

$$\langle \Delta\omega^2\rangle_{IJ}=2.2\times10^9\,(\text{rad/sec})^2$$

at 4.2 K. This is again in fairly good agreement with the calculated value and the number determined by the Mansfield method. Table I summarizes the comparison of calculated and measured contributions to the second moment of the fluorine line by the cerium ions.

Bierig, Weber, and Warshaw[14] have used ESR techniques to measure the spin-lattice relaxation time of the Ce^{3+} ion with tetragonal site symmetry in CaF$_2$ as a function of temperature for several different Ce^{3+} concentrations.

Crozier,[15] using crystals supplied by Optovac, Inc. (as were ours), reported the site symmetry to be tetragonal with the Ce^{3+} ion having the same ground-state configuration as reported by Weber and Bierig[16] and Baker, Hayes, and Jones.[17] We can then safely assume that our sample was similar to that of Bierig *et al.*[14] For their sample having a concentration (1.1×10^{19} cm^{-3}) closest to that of the present sample, they found a dominant tempera-

TABLE I. Summary of results for $\langle \Delta\omega^2 \rangle_{IJ}$ of $CaF_2 : Ce^{3+}$ with [100] $\parallel \vec{B}_0$.

Temperature (K)	$\langle \Delta\omega^2 \rangle_{IJ}$ (measured) $(rad/sec)^2$	$\langle \Delta\omega^2 \rangle_{IJ}$ (calculated) $(rad/sec)^2$
78	$< 10^8$	$< 5\times 10^7$
4.2	2.4×10^9 (Mansfield method) 2.2×10^9 (FID's)	2.6×10^9 (all spins included)
1.8	2.4×10^9 (Mansfield method)	11.0×10^9 (all spins included) 2.5×10^9 (excluding next-nearest neighbors) 1.9×10^9 (excluding next-next-nearest neighbors)

ture dependence of

$$T_{1e} = 1.7\times 10^{-3} T^{-1} \quad (1.8\ \mathrm{K} \le T \le 6\ \mathrm{K}),$$

with the numerical coefficient decreasing slowly for larger concentrations. This value is to be compared, albeit quite unfavorably, with the autocorrelation time found in this work and given in Eq. (17) as

$$\tau_c = \frac{4.4 \pm 1.0}{T^{0.87\pm 0.10}} \times 10^{-7} \quad .$$

Although the temperature dependence for τ_c and T_{1e} compare well, it is not possible to reconcile the factor of 3×10^3 difference in the magnitude of the two numbers.

V. CONCLUSIONS

There is no detectable broadening of the fluorine nuclear resonance line due to doped Ce^{3+} magnetic moments in CaF_2 at temperatures of 62 K and above, while at helium temperatures there is considerable broadening. At 4.2 K, direct measurements of the cross second moment of the ^{19}F resonance due to the interaction with the Ce^{3+} spins using Mansfield's coherent double-pulse technique and a free induction decay decomposition agree within experimental error.

Measurements of T_1 and the cross second moment of the ^{19}F nuclear resonance have demonstrated that the autocorrelation time and the spin-lattice relaxation time of Ce^{3+} magnetic moment are inconsistent and differ by 10^3 at helium temperatures. It may be that although the Ce^{3+} magnetic moment is changing Zeeman states slowly, the component of the magnetic moment along the external magnetic field direction is fluctuating rapidly. It would be this rapid fluctuation which would be associated with the autocorrelation time.

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[1] B. V. Rollin, Nature (Lond.) 160, 436 (1947).

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

[3] S. M. Day, G. B. Grimes, Jr., and W. Weatherford, Phys. Rev. 139, 515 (1965).

[4] H. E. Rorschach, Jr., Physica (Utr.) 30, 38 (1964).

[5] I. J. Lowe and D. Tse, Phys. Rev. 166, 279 (1968).

[6] I. J. Lowe and C. E. Tarr, J. Phys. E 1, 320 (1968).

[7] Optovac, Inc., North Brookfield, Mass.

[8] The authors would like to thank Professor John L. Meason for his generous help in performing the neutron-activation analysis of this crystal.

[9] D. Tse and I. J. Lowe, Phys. Rev. 166, 292 (1968).

[10] K. H. Kim, Ph.D. thesis (University of Pittsburgh, 1969) (unpublished).

[11] P. Mansfield, Phys. Rev. 137, 961 (1965).

[12] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, 1961), p. 120.

[13] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

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

[15] M. H. Crozier, Phys. Rev. 137, A1781 (1965).

[16] M. J. Weber and R. W. Bierig, Phys. Rev. 134, A1492 (1964).

[17] J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. Lond. 73, 942 (1959).