[*] Research supported in part by the National Science Foundation.

[1] Several papers have been published on the observation of the oscillating dependence of $\epsilon_{1\alpha}$ on the atomic number. Descriptions and references are given in an earlier paper (see Ref. 2).

[2] W. K. Chu and D. Powers, Phys. Rev. 187, 478 (1969).

[3] P. D. Bourland, W. K. Chu, and D. Powers, Phys. Rev. B 3, 3625 (1971).

[4] The use of a polynomial curve fit was kindly suggested by L. Wine (private communication), Hollins College, Hollins College, Va., and author of the text *Statistics for Scientists and Engineers* (Prentice-Hall, Englewood Cliffs, N. J., 1964). It is, of course, desirable to use a curve based on some physical theory, but there exists no simple analytic function which represents ϵ over the entire energy interval 300 keV to 2 MeV. The polynomial curve fit at least allows a statistical analysis of the experimental data to be made; the curve-fit parameters should not be used outside the experimental energy region.

[5] P. K. Weyl, Phys. Rev. 91, 289 (1953).

[6] H. Bichsel, C. C. Hanke, and J. Buechner, Report No. USC-136-148, 1969 (unpublished).

[7] D. I. Porat and K. Ramavataram, Proc. Phys. Soc. (London) A252, 394 (1960).

[8] W. Whaling, in *Handbüch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 34, p. 193.

[9] P. D. Bourland and D. Powers, Phys. Rev. B 3, 3635 (1971).

[10] C. A. Sautter and E. J. Zimmerman, Phys. Rev. 140, A490 (1965).

[11] John T. Park and E. J. Zimmerman, Phys. Rev. 131, 1611 (1963).

[12] R. L. Wolke, W. N. Bishop, E. Eichler, N. R. Johnson, and G. D. O'Kelley, Phys. Rev. 129, 2591 (1963).

[13] H. K. Reynolds, D. N. F. Dunbar, W. A. Wenzel, and W. Whaling, Phys. Rev. 92, 742 (1953).

[14] J. B. Swint, R. M. Prior, and J. J. Ramirez, Nucl. Instr. Meth. 80, 134 (1970).

[15] C. C. Rousseau, W. K. Chu, and D. Powers, Phys. Rev. A (to be published).

[16] E. Bonderup, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 35, No. 17 (1967).

[17] J. Lindhard and A. Winther, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 34, No. 4 (1964).

[18] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

PHYSICAL REVIEW B VOLUME 4, NUMBER 1 1 JULY 1971

Nuclear Spin-Lattice Relaxation and Dynamic Polarization in γ-Irradiated LiF[†]

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(Received 12 February 1971)

The spin-lattice relaxation at 13.6 MHz of F^{19} nuclei in γ-irradiated LiF is investigated at 300, 77, and 4.2–1.7 °K. The crystals used have optically determined *F*-center concentrations of 7.0×10^{17}, 2.0×10^{18}, and 3.5×10^{18} cm^{-3}. The relaxation in the temperature range 4.2–1.7 °K is found to be characterized by a spin-diffusion regime intermediate to the slow- and rapid-diffusion cases. At 300 °K, the nuclear spin-lattice relaxation is found to be predominantly controlled by *F*-center spin-lattice relaxation. However, for the *F*-center concentrations used here, temperature-independent *F*-center spin-spin relaxation is found to control the nuclear spin-lattice relaxation below 10 °K. The variation of the F^{19} dynamic polarization as a function of microwave power at 1.7 °K is investigated for microwave magnetic field amplitudes up to 2.6 G. For this range of fields, the dynamic polarization process also is characterized by an intermediate spin-diffusion regime. Existing theory yields an expression giving the variation of the dynamic polarization time with microwave power, which is used to estimate the correlation time of the *F*-center-nucleus dipole-dipole interaction at 1.7 °K. Estimates are also obtained for the *F*-center spin-lattice relaxation time at 300 °K.

INTRODUCTION

Bloembergen[1] has shown that nuclear magnetic spin-lattice relaxation in insulating crystalline solids at low temperatures can be caused by short-range direct magnetic dipolar interactions between the nuclei and paramagnetic impurity ions in low concentrations augmented by a nuclear spin-diffusion process. Nuclear spin diffusion has been exhaustively investigated[2–5] and the current state of the theory is such that it gives acceptable agreement with experiment. In addition to producing nuclear spin-lattice relaxation, the paramagnetic ion-nuclear dipolar interactions cause a mixing of the zero-order magnetic energy states which allows simultaneous nucleus-ion spin transitions, forbidden in zero order, to be induced by application of microwave radiation. Stimulation of the forbidden transitions results in a change in the nuclear magnetic polarization, which may be maintained at a steady-state value significantly different from the thermal equilibrium value. The process of producing nuclear polarizations different from the thermal equilibrium polarization by microwave stimulation of the forbidden transitions is referred to as dynamic polarization.[6] The particular type of dynamic polarization to be dealt with in this paper is sometimes called the solid-state effect.[6]

The direct ion-nuclear dipolar interactions that produce dynamic polarization through the solid-state effect are of very short range and spin diffusion provides the mechanism whereby their effects are propagated throughout the bulk of the crystal. Jeffries[7] and Khutsishvili[8] have solved the spin-diffusion equation for the solid-state effect and have obtained an expression for a polarization time T_p, which characterizes the growth of the dynamic polarization as a function of paramagnetic ion concentration, nuclear spin-diffusion coefficient, the interaction correlation time, and the applied microwave power.

Since both nuclear spin-lattice relaxation and nuclear dynamic polarization caused by the solid-state effect arise from dipolar interactions between nuclei and the paramagnetic ions, nuclear spin-lattice relaxation time T_1, and T_p measurements, coupled with theoretical expressions for T_1 and T_p provide an indirect method of observing the magnetic behavior of the paramagnetic ion system. In particular, T_1 measurements can be used to determine the temperature dependence of the ion-nuclear interaction correlation time and if the ion concentration is accurately known, the value of the correlation time may be deduced. The theoretical expression for the variation of T_p with microwave power gives a result from which the value of the correlation time may be obtained without knowing the exact ion concentration or how the ions are distributed in the crystal, if T_1 is known.

For several reasons, LiF containing F centers is an excellent system for an investigation of nuclear spin-lattice relaxation in solids caused by paramagnetic impurities in low concentrations. First, high-purity single crystals with low background relaxation rates are available and F centers may be easily produced in them by γ irradiation at room temperature. Color centers in LiF are stable under the conditions of ordinary room lighting and temperature and no special handling or storage procedure is necessary. Further, relative F-center concentrations can be determined easily and accurately by optical absorption measurements.

Josephson and Strandberg[9] showed that F centers in LiF are effective in controlling nuclear spin-lattice relaxation at 300 °K. One purpose of the present work is to extend the study of nuclear spin-lattice relaxation for F^{19} in the LiF F-center system to liquid-helium temperatures. This indicates the character of the nuclear spin-diffusion process (i.e., slow or rapid diffusion). From this the temperature dependence of the F-center correlation time may be estimated. Early steady-state dynamic polarization experiments on the LiF F-center system[10] suggested that the system would be a good one to use for dynamic polarization rate studies. F-center clustering, the details of which are unknown, renders a large portion of the F centers ineffective in controlling nuclear spin-lattice relaxation, but this difficulty may be surmounted by T_p versus microwave power measurements. The second purpose of the work to be reported here is to study the dynamics of the F^{19} dynamic polarization at 1.7 °K by a series of T_p versus microwave power measurements and to relate the results to available theories. From these measurements, a value for the F-center correlation time is deduced. It will be shown that at low temperatures this correlation time is largely controlled by the spin-spin interactions of the F centers for concentrations giving a nuclear T_1 of the order of minutes or less.

Of other reports on dynamic polarization rates in solids,[11–13] only one by Karra, Clarkson, and Sato[12] studied the variation of the dynamic polarization rate with microwave power. The system they studied was the protons in $CuK_2SO_4 \cdot 6H_2O$ diluted with $ZnK_2SO_4 \cdot 6H_2O$. Even though their paramagnetic ion concentrations were at least two orders of magnitude larger than any value of N_0 in the present experiment, they found that temperature-dependent paramagnetic spin-lattice relaxation controlled the nuclear spin-lattice relaxation. Further, τ was on the order of microseconds. Since the copper ion is much more complex than an F center and since the water molecules are not distributed on a simple lattice, the rather different behavior of the $CuK_2SO_4 \cdot 6H_2O$ system as compared to the LiF F-center system should not seem unreasonable.

THEORETICAL BACKGROUND

In the absence of diffusion, nuclei at a distance r from a paramagnetic impurity have a relaxation time given (after an angular averaging) by Cr^{-6}, where the function C is proportional to the intensity at the nuclear Larmor angular frequency ω_n of the spectrum of the field-direction component of the impurity magnetization. If this spectrum has a correlation time τ, C contains the factor $\tau/(1+\omega_n^2\tau^2)$, which reduces to $(\omega_n^2\tau)^{-1}$ for $\omega_n\tau \gg 1$ as is the case here.

Approximate treatments of spin diffusion have been worked out by using a spin-diffusion coefficient D independent of r (and in most discussions, independent of direction) outside a sphere of radius $r = b$, but zero inside that sphere because of the detuning of the nuclei from each other by the strong field gradient near the impurity. In this case, a quasi-steady-state solution of the spin-diffusion problem can be obtained[2,4,5] for the neighboring nuclei around an isolated impurity and interpreted in terms of the relaxation of the observed bulk magnetization of a sample with N paramagnetic centers per unit volume. The nuclear spin-lattice relaxation time T_1 is given by[4,5]

$$T_1 = (8\pi N D \beta)^{-1}\left[\frac{\Gamma(\frac{1}{4})}{\Gamma(\frac{3}{4})}\,\frac{I_{-3/4}(\delta)}{I_{3/4}(\delta)}\right] , \qquad (1)$$

where $\delta \equiv \beta^2/2b^2$ and $\beta = (C/D)^{1/4}$ is the characteristic diffusion radius outside of which spin diffusion is the major relaxation mechanism. For the case $\omega_n \tau \gg 1$, T_1 increases monotonically with τ. The limiting case of rapid diffusion[2-5] (D so large with respect to C that the value of D is unimportant) corresponds to $\delta \ll 1$, while the case of slow diffusion[2,5] (relaxation limited primarily by the value of D) corresponds to $\delta \gg 1$. The quantity in square brackets in Eq. (1) approaches $6(b/\beta)^3$ for $\delta \ll 1$ and approaches $\Gamma(\frac{1}{4})/\Gamma(\frac{3}{4})$ for $\delta \gg 1$.

The dependence of D, b, and β on the nuclear linewidth ΔH results in a variation of T_1 with crystal orientation.[4,5] We find from Eq. (1) that for the case of slow diffusion the value of T_1 increases with a crystal reorientation that increases ΔH, and that the reverse occurs in the case of rapid diffusion. For $\delta \approx 0.6$, T_1 is insensitive to crystal reorientation.

In the present experiments, microwave power can be applied to the sample with magnetic field amplitude H_1, of the proper orientation and frequency to produce electron spin resonance (ESR) somewhere in the broad, inhomogeneously broadened F-center ESR line. For the electron spin subpopulations (packets[8]) at resonance, sufficiently large H_1 results in saturation, characterized by reduced electron polarization (increased electron spin temperature), by a transition rate much greater than the thermal value for transitions having $\Delta M_S = \pm 1$, $\Delta M_I = 0$, and by increased rate of packet shifting, representing the flips of nuclei adjacent to the F center in response to the reduced correlation time of the z component of electron magnetization. For certain spin packets not at resonance, the microwave signal results in forbidden transitions having $\Delta M_S = \pm 1$, $\Delta M_I = \mp 1$. These also contribute to packet shifting. The mixing of states required to make these transitions occur is produced by operators of the form $S_z(I_x \pm i I_y)$ which occur in the dipole-dipole interaction between the electron and a nucleus, but do not occur in interactions of the form $\vec{I}\cdot\vec{S}$. The forbidden transitions produce nuclear polarization,[7,8] but in opposite senses, so that a net change in nuclear polarization is obtained only when the microwave signal is applied away from the center of an inhomogeneously broadened electron resonance.[6-8,10] The theory of nuclear relaxation by spin diffusion, leading to Eq. (1), is easily modified[7,8] to include the effects of the forbidden transitions since these involve r^{-6} just as does thermally induced relaxation. In order to combine both causes of relaxation in a single relaxation rate T_p^{-1}, where T_p will be called the polarization time, it is necessary to replace C by $C + 2\Gamma_m$, where Γ_m is the average induced transition probability for the two forbidden transitions, proportional to microwave power. We find it convenient to express the polarization time as

$$T_p = (8\pi N D \bar{\beta})^{-1}\frac{\Gamma(\frac{1}{4})}{\Gamma(\frac{3}{4})}\,\frac{I_{-3/4}(\bar{\delta})}{I_{3/4}(\bar{\delta})} , \qquad (2)$$

where $\bar{\delta} \equiv \bar{\beta}^2/2b^2$ and $\bar{\beta}^4 = (C/D)[1 + 2(\Gamma_m/C)]$. In the limit of zero microwave power, $\bar{\delta} \to \delta$ and $\bar{\beta} \to \beta$.

From (1) and (2) we have

$$\frac{T_p}{T_1} = \left(1 + \frac{2\Gamma_m}{C}\right)^{-1/4} \frac{I_{-3/4}(\bar{\delta})\, I_{3/4}(\delta)}{I_{-3/4}(\delta)\, I_{3/4}(\bar{\delta})} . \qquad (3)$$

As shown in the Appendix, the ratio $2\Gamma_m/C$ is proportional to $f\tau$ times the microwave power, where f is the fraction of the paramagnetic centers affected by microwave pumping. Therefore, in principle Eq. (3) allows $f\tau$ to be evaluated from the experimental dependence of T_p/T_1 on microwave power, even when the concentration of paramagnetic centers is not known.

EXPERIMENTAL

All T_1 measurements were made by a direct-recovery method similar to that used by Josephson and Strandberg.[9] Dynamic polarization growth curves were made with a double-resonance cavity similar to one described by Doyle.[14] The cavity was in direct contact with a pumped liquid-helium bath at 1.7 °K. Microwave power (9.28 GHz) was supplied to the cavity through a "Strandlabs"[15] spectrometer which used the sample cavity as the automatic frequency control circuits (AFC) reference cavity.

A Robinson[16] oscillator was used to monitor the growth of the nuclear polarization. The external magnetic field H_0 was 3400 G (F^{19} resonant frequency ≈ 13.6 MHz). For this value of H_0 and a microwave frequency of 9.28 GHz, the steady-state value of induced enhancement was 3.

Microwave power was applied to the sample continuously during the course of the dynamic polarization time measurement operations. By means of an auxiliary set of coils, H_0 could be shifted between 3400 and 3500 G. At $H_0 = 3500$ G, the center of the F-center resonance was so disposed to the microwave frequency (9.28 GHz) that very little induced enhancement of nuclear polarization resulted. After a suitable length of time, during which the nuclear polarization had decayed to a value very nearly equal to the thermal equilibrium value, H_0 was

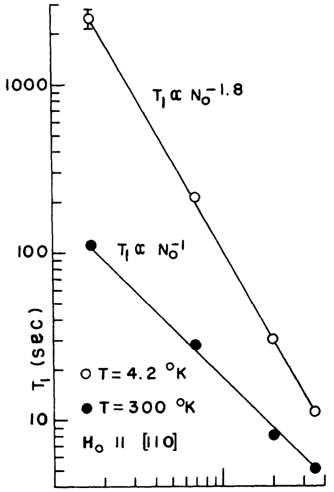

FIG. 1. Variation of the F^{19} spin-lattice relaxation time T_1 with the optically determined relative F-center concentration N_0.

shifted back to 3400 G and the growth of the nuclear polarization recorded.

The samples were made from Harshaw[17] vacuum ultraviolet grade LiF crystals and were irradiated by the Physics Department of the M. D. Anderson Hospital.[18] Initially, three crystals were irradiated with Co^{60} γ rays with an average intensity of 73 000 rad/min over the volumes of the crystals. The irradiation times were 80, 800, and 8000 sec. The F-center densities were such that plots of the F-center optical absorption could be used to determine the F-center densities using Smakula's formula.[19] Two other crystals were irradiated using an annular Cs^{137} source with an intensity of 7300 rad/min. The irradiation times of these crystals were 7000 and 17 000 min and the F-center concentrations were so large that optical absorption plots could not be used to calculate them. Co^{60} and Cs^{137} γ rays have been found[20] to impart equal amounts of energy for equal doses to LiF and it was assumed that they are equivalent F-center producers. From this we were able to estimate the F-center concentration in the last two samples by extrapolating the calculated F-center concentration versus dose curve to include the doses that they received. The two most heavily irradiated crystals were reddish brown in color while the other crystals were light green in color immediately after irradiation. Within a day, this green color disappeared, leaving the crystal yellow in color. LiF color centers have been found to be stable at room temperature and ordinary lighting,[9] so no special handling or storage was used.

RESULTS

Nuclear Spin-Lattice Relaxation

The unirradiated crystals had $T_1 > 3000$ sec at 300 °K. A series of T_1 measurements at various temperatures for different values of the optically determined F-center concentration N_0 was made to determine the nature of the spin-diffusion process in the crystals. As shown in Fig. 1, at 300 °K, T_1 is proportional to N_0^{-1} over the range 1.7×10^{17} to 3.5×10^{18} cm^{-3}, as predicted by Eq. (1) for the case where the correlation time to the electron-nuclear interaction is concentration independent.

Since F centers are known to aggregate in loose clusters[21] where they are not magnetically isolated from each other, the relationship $T_1 \propto N_0^{-1}$ appears fortuitous. ESR measurements on the crystals at 300 °K show that the relative F-center concentrations are consistent with the various values of N_0 but that the effective F-center concentration is one order of magnitude smaller than N_0. This suggests that as the radiation dose received by the crystals increases the number of F-center clusters per unit volume increases. This sort of behavior has been observed[22] for neutron-irradiated LiF.

Josephson and Strandberg[9] found that T_1 was independent of N_0 for $N_0 > 5 \times 10^{16}$ cm^{-3} and attributed this to F-center clustering. Their unirradiated crystals had a $T_1 \sim 100$ sec, which indicated a relatively high paramagnetic impurity background concentration. It is possible that in their crystals the F centers tended to cluster in the vicinity of the impurities in such a way that number of clusters per unit volume reached a saturation value and further irradiation simply caused the local density of the cluster to increase.

Figure 2 shows T_1 vs T for samples of three different F-center concentrations in the range 1.7–4.2 °K, together with values at 77 and 300 °K for these and a more dilute sample. To interpret these results, we consider that the correlation time τ for the interaction between the F center and a nucleus may be affected by both the spin-lattice relaxation time τ_{Sl} of the F centers and their spin-spin correlation time τ_{SS}, giving

$$\tau^{-1} = \tau_{SS}^{-1} + \tau_{Sl}^{-1} , \tag{4}$$

where τ_{SS} is temperature independent and τ_{Sl} ordinarily decreases with increasing temperature. At sufficiently high temperature, for a given F-center concentration, we expect the effect of τ_{Sl} to be dominant. Then, if there are no paramagnetic cross-relaxation processes making τ_{Sl} concentration dependent, we expect T_1 to vary as the reciprocal of F-center concentration. The 300 °K result in Fig. 1 shows this behavior, where the optically

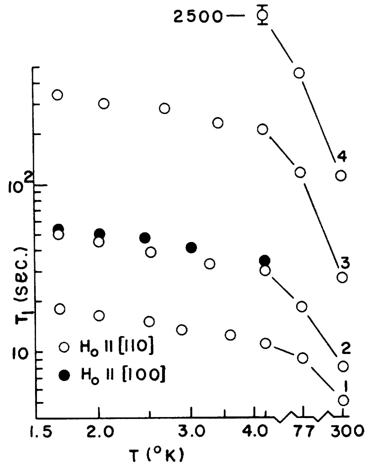

FIG. 2. Variation of the F^{19} spin-lattice relaxation time T_1 with the temperature T. $N_0 =$ (1) 3.5×10^{18} cm^{-3}, (2) 2.0×10^{18} cm^{-3}, (3) 7.0×10^{17} cm^{-3}, (4) 1.7×10^{17} cm^{-3}.

measured concentration is used. Moreover, the ratio $T_1(300\,°\mathrm{K})/T_1(77\,°\mathrm{K})$ is practically the same for the two lowest concentrations in Fig. 2, samples 3 and 4, as would be the case if T_1 is responding to the temperature dependence of a concentration independent τ_{sl}. For the most concentrated sample, however (sample 1), T_1 changes relatively little between 300 and 4.2 °K, suggesting that except near 300 °K the effect of τ_{sl} is not dominant for this sample. Therefore, at much lower temperatures the variation of T_1 occurs under conditions of nearly constant τ; that is, $\tau\approx\tau_{ss}$, and the residual variation of T_1 with temperature occurs through changes in the barrier radius.[5] This conclusion must apply to all samples studied below 4.2 °K, since they show closely similar behavior (approximately $T_1\propto T^{-0.5}$). That we have $\tau\approx\tau_{ss}$ at low temperature is further confirmed in Fig. 1 by the change in concentration dependence from $T_1\propto N_0^{-1}$ at 300 °K to $T_1\propto N_0^{-1.8}$ at 4.2 °K, for τ_{ss} is concentration dependent, whereas ideally τ_{sl} is not.

The results do not correspond to either of the limiting cases, $\delta\gg1$ or $\delta\ll1$. In Fig. 2, sample 2, T_1 is practically the same within experimental error for the [100] and [110] orientations at 1.7 °K, but at higher temperatures the [110] result is significantly smaller. Taking into account the discussion in the previous section, we then estimate $\delta = 0.6$ at 1.7 °K for the sample having $N_0 = 2.0\times10^{18}$ cm^{-3}. This value proves satisfactory for explaining the dynamic polarization results.

Dynamic Polarization

The dynamic polarization time T_p, as measured at 1.7 °K, is shown by the points in Fig. 3 for microwave power values in the range 10–200 mW. The curves are obtained by multiplying T_1 at 1.7 °K (Fig. 2) by T_p/T_1 calculated from Eq. (3). In the preceding section, δ at 1.7 °K for sample 2 was found to be 0.6. In evaluating $2\Gamma m/C$ (Appendix), the value of $f\tau = 0.9$ μsec was found to give the best fit to the data for sample 2 in Fig. 3. Values of δ for samples 1 and 3 were obtained by assuming that $\tau\propto N_0^{-1}$, which is ideally true for the spin-spin interaction of the electrons, and is approximately true in the present case as is shown in the discussion of Fig. 1. On this assumption, neglecting the variation[5] of b with τ, δ varies as $N_0^{1/2}$. The values of δ at 1.7 °K for samples 1 and 3 are 0.79 and 0.36, respectively. The values of $f\tau$ which then give the best fits to the data and are used in calculating the remaining curves of Fig. 3 are 0.6 μsec for sample 1 and 2.14 μsec for sample 3. Alternately, assuming that $f\tau$ varies as N_0^{-1} and then computing values of δ using $\delta\propto\tau^{-1/2}$ in conjunction with values of $f\tau$ and δ obtained for sample 2 gave somewhat poorer fits to the data than did the preceding process of analysis. The two slightly different approaches to analyzing the data are the only alternatives available in the absence of precise information on F-center concentration and distribution and accurate values of τ.

The minimum value of $f(=0.023)$ found in the Appendix can now be used to give an estimate of τ at 1.7 °K. For example, sample 1 has $f\tau = 0.6$ μsec, which gives $\tau\approx26$ μsec. τ for each sample has a constant value below 4.2 °K determined by the electron spin-spin interaction. For sample 1, T_1 is practically constant from 4.2 to 77 °K, indicating that τ also is nearly constant in this temperature range, as is $\delta(\approx1)$. On this basis, τ at 300 °K can be estimated. For sample 1, the ratio

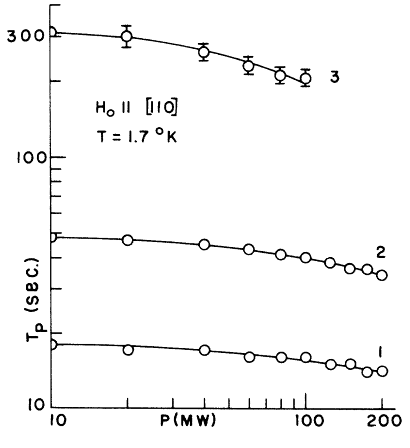

FIG. 3. Variation of the F^{19} dynamic polarization time T_p with microwave power P. $N_0 =$ (1) 3.5×10^{18} cm^{-3}, (2) 2.0×10^{18} cm^{-3}, (3) 7.0×10^{17} cm^{-3}. The curves were obtained from Eq. (3).

$T_1(77\,^\circ\mathrm{K})/T_1(300\,^\circ\mathrm{K})$ is 1.8. From Eq. (1), the ratio $\tau(77\,^\circ\mathrm{K})/\tau(300\,^\circ\mathrm{K})$ lies between 1.8 ($\delta \gg 1$) and $(1.8)^4$ ($\delta \ll 1$). According to this estimate, $\tau_{Sl} \approx 10^{-5}$ sec at 300 °K for all the samples.

This result differs appreciably from $\tau_{Sl} = 7 \times 10^{-7}$ sec which is deduced from room-temperature F^{19} relaxation measurements on irradiated LiF crystals by Josephson and Strandberg.[9] We suggest that this smaller value of τ is related to cross relaxation between F centers and the impurities responsible for the appreciable nuclear relaxation rate in their unirradiated crystals.

Other evidence suggests that one should obtain rather more than 10^{-5} sec for τ_{Sl} at 300 °K. Microwave measurements of F-center relaxation in[23] KCl extrapolate to $\tau_{Sl} = 3 \times 10^{-5}$ sec at 300 °K. A rapid passage experiment[24] with LiF F centers gave $\tau = 10^{-4}$ sec, although this result is not reducible in a simple way to τ_{Sl}. Saturation effects observed in the ESR measurements made to check F-center concentrations of the present samples indicate that $\tau_{Sl} \sim 10^{-4}$ sec if one were to assume a packet width of 1 G.

CONCLUSIONS

The spin-lattice relaxation of the F^{19} nuclei in irradiated LiF in the temperature range below 10 °K falls in the spin-diffusion regime intermediate to the slow- and rapid-spin-diffusion cases. This is also true for the dynamic polarization process for the range of microwave power explored. With increasing temperature, the slow-diffusion regime is approached and is substantially reached at 300 °K.

To obtain nuclear spin-lattice relaxation times on the order of 10 min or less at 4.2 °K, optically determined F-center concentrations greater than $N_0 = 4 \times 10^{17}$ cm^{-3} are required. For such concentrations, the correlation time of dipolar interactions between F centers and the F^{19} nuclei is equal to the temperature-independent spin-spin correlation time of the F centers and is given approximately by

$$\tau_{SS} = \mathrm{const} \times N_0^{-1} \ . \qquad (5)$$

The variation of the dynamic polarization time with microwave power has been explored at 1.7 °K and is adequately described by a suitable adaptation of the theory developed by Jeffries[7] and Khutsishvili.[8] Comparison of this theory with experiment yields a value of τ, the correlation time of the dipolar interactions between the F centers and the F^{19} nuclei from which the constant of proportionality in Eq. (5) was found to be $\sim 8 \times 10^{13}$ sec cm^{-3}. This evaluation is significant only within a factor of perhaps 2, because the theoretical functions in the expression for the polarization time as a function of microwave power [Eq. (3)] are not highly sensitive to τ. Also, the value given for τ is obtained on the assumption that the fraction of electron spins affected by the microwaves is determined by the area under the inhomogeneously broadened ESR curve of the F centers actually swept by the modulation field of the experiment. The value obtained for τ varies inversely with the value of this fraction.

At 300 °K, the spin-lattice relaxation of the F^{19} nuclei is controlled by the spin-lattice relaxation time of the F centers, which is found to be on the order of 10^{-5} sec from the nuclear relaxation data. Further, at 300 °K, $T_1 \propto N_0^{-1}$, but the values of N_0 are one order of magnitude too large to be compatible with the corresponding measured values of T_1 if $\tau \sim 10^{-5}$ sec. This is a result of F-center clustering. ESR measurements at 300 °K indicate that the relative effective F-center concentrations are consistent with the optically determined values of N_0, but that the effective F-center concentrations are at least one order of magnitude smaller than the corresponding values of N_0.

ACKNOWLEDGMENT

The authors wish to thank Dr. Peter R. Almond of the Physics Department of the M. D. Anderson Hospital and Tumor Institute, Houston, Texas, who supervised the irradiation of the crystals.

APPENDIX: EVALUATION OF $2\Gamma m/C$

In Eq. (3), $2\Gamma m/C$ is used for the more exact expression

$$(f_+\Gamma_+ + f_-\Gamma_-)/C \ , \qquad \text{(A1)}$$

where the f's are the fractions of the electrons affected by the microwave radiation as will be explained later. The microwave induced direct transition rates for the forbidden simultaneous nucleus-electron spin flips are given by $\Gamma_\pm r^{-6}$.[7,8] The $\Gamma_\pm$ used here are slightly different from those in Ref. 8 and are given by

$$\Gamma_\pm = \tfrac{1}{2}\pi\gamma_e H_1^2 G(H_\pm - H_0) C\tau \ . \qquad \text{(A2)}$$

In Eq. (A2), γ_e is the absolute value of the F-center electron gyromagnetic ratio, H_1 is the amplitude of the microwave field, and $G(H - H_0)$ is the envelope of the F-center resonance and is taken to be a Gaussian line[10,25] with a second moment of $(80)^2$ G^2. $H_\pm$ are given by

$$H_\pm = (\omega_e \pm \omega_n)/\gamma_e = H_e \pm \gamma_n H_0/\gamma_e \ , \qquad \text{(A3)}$$

where ω_e is the resonant angular frequency of the microwave cavity and the applied magnetic field H_0 is chosen to produce the desired enhancement condition.

Since H_1 is not constant over the volume of the sample, H_1^2 is replaced by $\langle H_1^2 \rangle$, the average of H_1^2 over the sample volume. The presence of the rf coil in the cavity used for the dynamic polarization experiments made exact calculation of $\langle H_1^2 \rangle$ as a function of microwave power P difficult, so an estimate was made by comparing ESR signal amplitudes made with a cavity of simple internal geometry with those made with the cavity containing the rf coil. In the absence of saturation, the ESR signal amplitude is proportional to $\langle H_1^2\rangle$ which can be calculated as a function of P in the simple cavity. For the cavity and rf coil arrangement used in the experiments, $\langle H_1^2\rangle = 32P$, with $\langle H_1^2\rangle$ in G^2 and P in W.

From Eq. (A3), since $\gamma_e \gg \gamma_n$, $H_+ = H_- = H_e = \omega_e/\gamma_e$, and $G(H_\pm - H_0)$ are replaced by $G(H_e - H_0)$. H_0 was chosen to be $H_e + 100 = 3400$ G. It is assumed that the fraction of the electron spins affected by the microwaves is given by (neglecting any contribution[7] from the microwave H_1)

$$f_+ \approx f_- \approx f = \int_{H_e - H_m}^{H_e + H_m} G(H - H_0)\, dH \ ,$$

where H_m is the amplitude of the sinusoidal modulation sweep field. Thus Eq. (A1) is replaced by

$$2\Gamma_m/C = \pi \gamma_e \langle H_1^2\rangle G(H_e - H_0) f \tau \ . \qquad \text{(A4)}$$

In the experiments, $H_e - H_0 = 100$ G, $H_m = 5$ G, and $\gamma_e = 1.76 \times 10^7\ \mathrm{G}^{-1}\ \mathrm{sec}^{-1}$. For $H_0 = 3400$ G, these values give $G(H_e - H_0) = 0.23\ \mathrm{G}^{-1}$ and $f = 0.023$. With these Eq. (A4) gives

$$2\Gamma_m/C = 4.1 \times 10^7 f P \tau \ . \qquad \text{(A5)}$$

Considering the uncertainties in the effective F-center concentration and the possibility of spin diffusion in the F-center electron system, the value of f given by Eq. (A4) must be regarded as a minimum estimate of the electrons affected by the microwaves.

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†Work supported in part by the National Science Foundation.

[1] N. Bloembergen, Physica 15, 449 (1949).

[2] P. G. de Gennes, J. Phys. Chem. Solids 3, 345 (1958).

[3] W. E. Blumberg, Phys. Rev. 119, 79 (1960).

[4] G. R. Khutsishvili, Zh. Eksperim. i Teor. Fiz. 42, 1311 (1962) [Sov. Phys. JETP 15, 909 (1962)].

[5] H. E. Rorschach, Physica 30, 38 (1964).

[6] A. Abragam, *Principles of Nuclear Magnetism* (Oxford U. P., London, 1961).

[7] C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience, New York, 1963).

[8] G. R. Khutsishvili, Usp. Fiz. Nauk 87, 211 (1965) [Sov. Phys. Usp. 8, 743 (1966)].

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

[10] M. Abraham, M. A. H. McCausland, and F. N. H. Robinson, Phys. Rev. Letters 2, 449 (1959).

[11] G. E. Schacher, Phys. Rev. 135, A185 (1964).

[12] J. S. Karra, R. Clarkson, and T. Sato, Phys. Rev. 175, 479 (1968).

[13] P. J. Bendt, Phys. Rev. B 2, 4375 (1970).

[14] W. T. Doyle, Rev. Sci. Instr. 33, 118 (1962).

[15] Manufactured by Strandlabs, Cambridge, Mass.

[16] F. N. H. Robinson, J. Sci. Instr. 36, 481 (1959).

[17] Harshaw Chemical Co., Cleveland, Ohio.

[18] The M. D. Anderson Hospital and Tumor Institute at Houston, Houston, Tex.

[19] J. J. Markham, in *Solid State Physics, Supplement* 8, edited by F. Seitz and D. Turnbull (Academic, New York, 1966).

[20] P. R. Almond, Physics Department, the M. D. Anderson Hospital, Houston, Tex. (private communication).

[21] H. Seidel and H. C. Wolf, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).

[22] R. E. Smallman and B. T. M. Willis, Phil. Mag. 2, 1018 (1957).

[23] D. W. Feldman, R. W. Warren, and J. G. Castle, Phys. Rev. 135, 470 (1964).

[24] J. S. Hyde, Phys. Rev. 119, 1483 (1960).

[25] W. C. Holton and H. Blum, Phys. Rev. 125, 89 (1962).