TABLE I. Numerical values of the integrals in Eqs. (7) and (8).

	Γ	α	$\frac{2\Gamma+\alpha}{3}$	Δ
Dyson[a]	$\frac{1}{5}$	0.516386[b]	0.31	...
Oguchi[c]	...	...	...	0.2
Wolfram and Callaway[d] and Table III of Slater and Koster[e]	0.2598[f]	0.4778[f]	0.332[f]	0.295[f,g]
Table I of Slater and Koster[e]	...	...	...	0.288[f]
Maradudin *et al.*[h]	0.185238[f]	0.516386[f,i]	0.29562[f]	0.29562[f]

[a] Reference 2.
[b] Watson's value.
[c] Reference 3.
[d] Reference 13.
[e] Reference 12.
[f] Compounded from related integrals.
[g] This is near the correct value because of cancellation of errors between the integrals from which it is compounded.
[h] Reference 14.
[i] Equal to Watson's value.

We thus conclude that for temperatures below those for which kinematic corrections are important (Wortis[5] gives a rough estimate that they will only be so in the $T^{(3/2)(2S+1)^4}$ term for a 3-dimensional ferromagnet, i.e., the T^{24} term for $S=\frac{1}{2}$, and even higher for larger spins) there is no evidence of any inconsistency between the boson models used by Dyson and by Oguchi. In practice Dyson's Hamiltonian is much the simpler to use as it involves only spin-wave pair interactions. Thus it enabled Dyson to sum the infinite series of ladder diagrams contributing to the T^4 term to give its exact dependence on S, whereas this would be exceedingly difficult using the Holstein-Primakoff method because of the need to cancel contributions between various orders of perturbation theory. This cancellation was shown to occur between contributions from the two graphs of Fig. 1 to order $1/S$ by Oguchi, but has not been demonstrated generally.

ACKNOWLEDGMENTS

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Spin-Spin Relaxation in LaF_3†

M. GOLDMAN* AND L. SHEN
Department of Physics, Washington University, St. Louis, Missouri

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The present work is a study by nmr pulse techniques of the motion of fluorine atoms in lanthanum trifluoride as a function of temperature, between 100 and 560°C. The experiments have been conducted with a single crystal of LaF_3. The model for the motions derived from this study is the following: There are two types of fluorine nuclei, the spins I and the spins S, located on different sublattices. Between 100 and 300°C, the motion of the spins I is fast (i.e., such as to be appreciable in times shorter than the reciprocal of the rigid-lattice line width), and the motion of the spins S is slow. There is an exchange of atoms between the two sublattices, the rate of which is slow up to about 300°C and fast at higher temperature. The ratio of populations of the spins I and S is $N_I/N_S=2$. Approximate values are derived for the activiation energies associated with these two types of motion.

I. INTRODUCTION

NUCLEAR magnetic resonance is a well-established tool for the study of motions in solids; detailed descriptions of its use in this respect, together with references to early works, can be found in general textbooks.[1-4] Its use is based on the fact that the averaging of spin-spin interactions between nuclei by atomic motions profoundly affects the line width and the spin-lattice relaxation of nuclear spin systems, as soon as the rate of change of the spin-spin interactions is faster than the static linewidth, typically a few kcps, although the method has been recently extended[5,6] to far lower rate values by the measurement of the spin-lattice relaxation time of the spin-spin interactions.

The present work consists of a study of the fluorine spin-spin relaxation in lanthanum trifluoride between 100 and 560°C, in a temperature range where atomic motions have a dominant influence on this relaxation. In a recent study[7] of the fluorine line shape in this com-

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* Present address: Centre d'Etudes Nucleaires de Saclay, France.

[1] E. R. Andrew, *Nuclear Magnetic Resonance* (University Press, Cambridge, England, 1955).

[2] A. K. Saha and T. P. Das, *Theory and Applications of Nuclear Induction* (Saha Institute of Nuclear Physics, Calcutta, India, 1957).

[3] A. Abragam, *The Principles of Nuclear Magnetism* (The Clarendon Press, Oxford, England, 1961).

[4] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row Publishers, New York, 1963).

[5] D. Ailion and C. P. Slichter, Phys. Rev. Letters **12**, 168 (1964).

[6] C. P. Slichter and D. Ailion, Phys. Rev. **135**, A1099 (1964).

[7] K. Lee and A. Sher, Phys. Rev. Letters **14**, 1027 (1965).

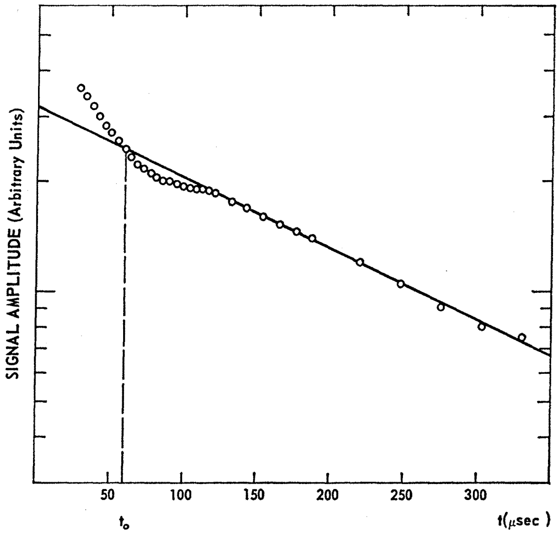

FIG. 1. Fluorine free decay signal in LaF$_3$. Temperature $t=182$°C. Orientation $H_0 \| c$ axis.

pound as a function of temperature, it was found that motional narrowing of the resonance line began at room temperature. Above this and in a substantial temperature range, the absorption signal was a superposition of a broad line and a narrow line, which seems to indicate the existence of two different kinds of fluorine nuclei. By using the pulse technique the present investigation verifies the existence of two types of nuclei, between which it is possible to observe cross relaxation. On the basis of the experimental results, the following model is proposed for the motions occurring in LaF$_3$.

There are two types of fluorine nuclei, I and S, on two different sublattices. Between 100 and 300°C, the motion of the spins I is fast and the motion of the spins S is slow. There is an exchange of atoms from one sublattice to the other which, below 300°C, is slow enough not to destroy the distinction between the spins I and the spins S and the difference in their relaxation behavior. Above 350°C this exchange becomes fast. The ratio of populations of the spins I and S is

$$N_I/N_S=2.$$

We shall first describe the experimental facts which suggest this model. Then we shall analyze its theoretical consequences before coming back to the experimental results for an overall check of consistency with theory.

II. EXPERIMENTAL METHODS

The experiments make use of the pulse technique. A strong pulse of rf field at the Larmor frequency of the fluorine nuclei rotates their magnetization and brings it perpendicular to the direction of the steady magnetic field. The free precession signal of the nuclei is then amplified, detected, displayed on an oscilloscope, and photographed.

Most measurements were performed at the frequency of 30 Mc/sec, and some were at 16 Mc/sec.

The pulse generator was of noncoherent type. The minimizing of rf pickup from the transmitter pulse to the receiver amplifier was achieved by the use of crossed coils.

The duration of a $\pi/2$ pulse could be made equal to 5 μsec, which corresponded to a rotating field H_1 of 12.5 G. The recovery time of the receiver after the pulse was of the order of 20 μsec.

The sample was heated by a flow of hot nitrogen gas. The heating system was similar to that described by Schreiber.[8] It consisted of a L-shaped Dewar made of quartz, which was fitted inside the receiver coil. The Dewar was coated with Hanovia No. 05 Platinum paint; the paint was scribed at the site of the sample and coils. The gas was heated by passing over a nichrome wire heater. The temperature was measured with a chromel-alumel thermocouple. It was continually adjusted and kept constant to within $\frac{1}{2}$°C during each run by changing the heater voltage or the gas flow.

III. SALIENT FEATURES OF THE EXPERIMENTAL RESULTS

The measurements have been performed on a single crystal of LaF$_3$ doped with 1% of Pr^{3+} and oriented, as a rule, with the applied field parallel either to the c axis or to the a axis of this hexagonal crystal. The fluorine spin-lattice relaxation time in this crystal ranges from about 100 msec at room temperature to about 15 msec at 560°C. With such short relaxation times it is possible

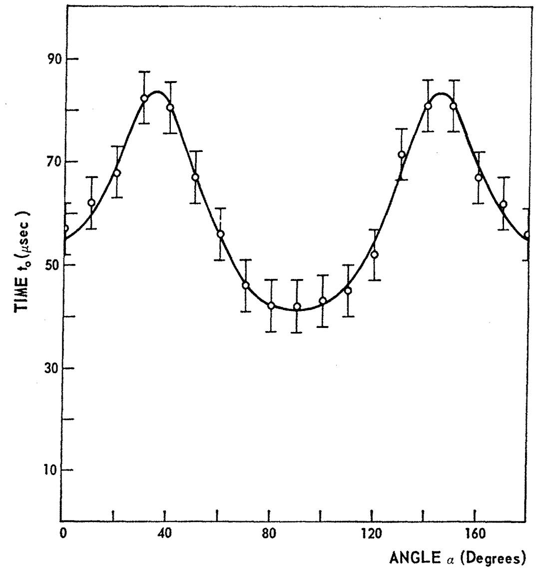

FIG. 2. Variation of the time t_0 at which the oscillatory part of the fluorine free decay is zero as a function of the angle α between the c axis and the magnetic field, in the a-c plane. Temperature $t=182$°C.

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[8] D. S. Schreiber, Rev. Sci. Instr. **35**, 1582 (1964).

to repeat the pulses several times per second, which facilitates the observation of the free decay. By comparison, the spin-lattice relaxation time T_1 in a powder sample of "pure" LaF_3 was found equal to 10 sec at room temperature.

The crystal structure of LaF_3 is not definitely known. X-ray measurements[9] have suggested a structure with two different fluorine sites, of relative populations 2:1. More recently, Anderson and Proctor[10] have shown, by a magnetic resonance study, that the symmetry of the electric field gradients at the sites of the lanthanum nuclei is not consistent with such a simple structure. They propose a model with four nonequivalent fluorine sites, with populations 3:3:2:1.

A. Free Precession Signal

The free precession signal is composite in the approximate temperature range between 90 and 300°C, and can be represented as the sum of an exponential decay and an oscillatory decay. As an example, Fig. 1 shows the shape of the free decay at $t = 182°C$, with $\mathbf{H}_0 \| c$ axis.

The time t_0 at which the oscillatory part of the decay is zero varies from 42 to 80 μsec when the magnetic field is rotated in the a-c plane, as shown on Fig. 2. This time t_0 is found to be independent of temperature. For a given orientation, the shape of the free decay is identical at 30 Mc/sec and at 16 Mc/sec. The oscillatory part of the decay thus does not arise from a beat between the signals of two types of nuclei with different chemical shifts. It is due to fluorine nuclei experiencing static dipole-dipole interactions.[11] The exponential part of the decay must arise from another type of nuclei, the dipole-dipole interactions of which are averaged by motion.

No evidence is found of a difference in Larmor frequencies between these two types of nuclei. The minimum time at which the first beat due to a difference in chemical shift could possibly occur is about 100 μsec, which would correspond to a maximum frequency shift of 2.5 kc/s. This is to be contrasted with the value of 3 kc/s found by Lee and Sher[7] at 16 Mc/sec using the cw technique. This discrepancy may arise from the difficulty of resolving an absorption signal into two lines when their widths are not very different.

The relative amplitude of the oscillatory part of the decay decreases with increasing temperature and becomes unobservable at about 350°C, above which the free decay signal is a single exponential.

B. Variation of T_2

When the temperature is increased, the time constant T_2 of the exponential part of the decay first increases, then decreases, then increases again, as shown on Fig. 3 for the orientation $\mathbf{H}_0 \| c$ axis. The same type of behavior has been found in a number of powder samples including pure LaF_3 and LaF_3 doped with 0.1% Pr^{3+}, 0.1% Nd^{3+}, and 0.1% Er^{3+}, in which the three domains of variation of T_2 occurred in about the same temperature ranges as in LaF_3 doped with 1% Pr^{3+}.

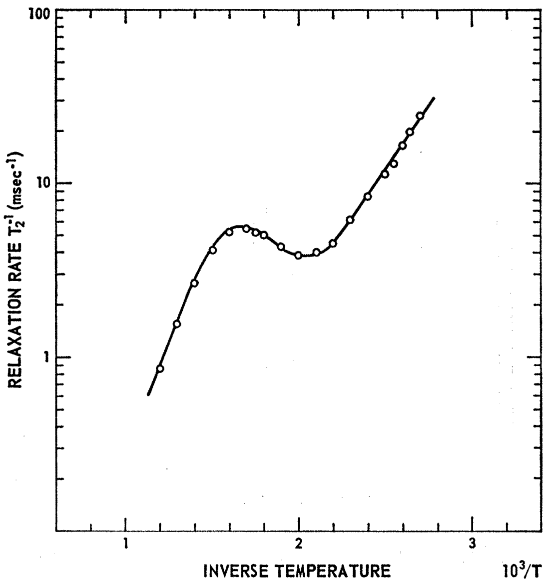

FIG. 3. Temperature dependence of the spin-spin relaxation time T_2 of the spins I, for the orientation $\mathbf{H}_0 \| c$ axis.

C. Cross Relaxation Between the Two Spin Species

The existence of composite absorption lines has already been observed, in previous magnetic resonance studies of motions in solids,[12,13] where the narrow component was found to increase at the expense of the broad one as the temperature was increased. This was attributed[12] to the existence of domains in the crystal where the motions were frozen, possibly by dislocations, imbedded in a sea of moving atoms; these domains were supposed to "melt" progressively as the temperature was increased, which explained the slow disappearance of the broad component.

In the present case, the composite decay arises from two types of fluorine nuclei which are intermingled at short distances from each other, that is, they are located on different sublattices. Indeed, if this is the case, there must be a cross relaxation between them, due to the operators $(I_+S_- + I_-S_+)$ of their dipole-dipole interactions. Such a cross relaxation is observed in experiments consisting of sequences of three $\pi/2$ pulses, as summarized on Fig. 4. We give here a simplified account of these experiments.

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[9] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1964), Vol. 2.

[10] L. O. Anderson and W. G. Proctor, Z. Krystall. (to be published).

[11] I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

[12] G. R. Miller and H. S. Gutowsky, J. Chem. Phys. **39**, 1983 (1963).

[13] J. G. Aston, Q. R. Stottemeyer, and G. R. Murray, J. Am. Chem. Soc. **82**, 1281 (1960).

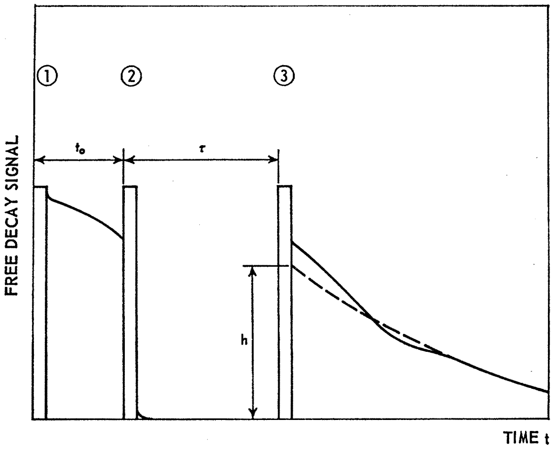

FIG. 4. Sequence of three $\pi/2$ pulses used for the observation of cross-relaxation. Pulses ① and ② are of opposite phases.

The first two pulses are used to create a situation with different longitudinal magnetizations I_z and S_z. We use a frame rotating around Oz, the direction of the steady field, with the fluorine Larmor frequency. Starting from thermal equilibrium, the first pulse rotates the magnetizations from the direction Oz to the direction Ox, along which they undergo free decay. At the time t_0 after this pulse, the magnetization S_x goes through zero, whereas the magnetization I_x has only partially decayed. The second $\pi/2$ pulse, in opposite phase with the first, is applied at this time t_0. It rotates the magnetization of the spins I back from the direction Ox to the direction Oz. The initial conditions thus prepared correspond to

$$S_z=0,$$
$$I_z\neq 0.$$

With the pulse generator used in these experiments, which was of noncoherent type, the coherence between the pulses was achieved by a fine tuning of the time interval between them.

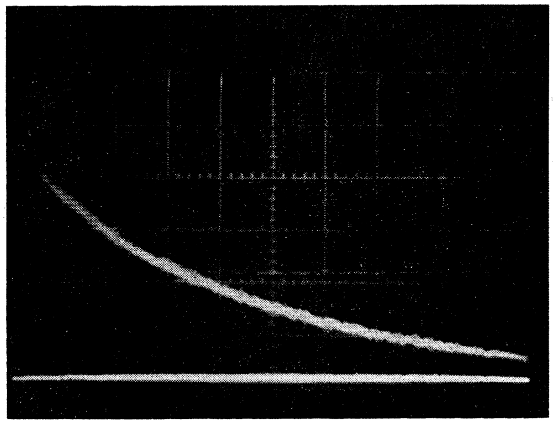

FIG. 5. Cross-relaxation experiment. Free decay signal observed after the third pulse. Temperature $t=182$°C. Orientation $\mathbf{H}_0\|c$ axis. Time interval between pulses ② and ③: $\tau=85$ μsec. Sweep rate: 50 μsec/cm.

A third $\pi/2$ pulses, applied a time τ after the second one, is used to measure I_z and S_z, from the shape and amplitude of the free decay signal.

It is observed that, when τ is short, the decay following this third pulse is exponential. As the time τ is increased, an oscillatory signal appears superimposed on the exponential part; this oscillatory signal increases with τ until the shape of the decay is the same as that after a single $\pi/2$ pulse. As an example, Figs. 5 and 6 show the free decay signals following the third pulse, for time intervals τ between the second and the third pulse equal to 85 μsec and 1.65 msec, respectively. These pictures were taken at a temperature $t=182$°C, with $H_0\|c$ axis.

The amplitude h of the exponential part of the decay varies, as a function of τ, as the difference of two exponentials. Such a variation is displayed on Fig. 7, corresponding to $t=162$°C and $H_0\|a$ axis. Figure 8 shows in more detail the region of decrease of the signal.

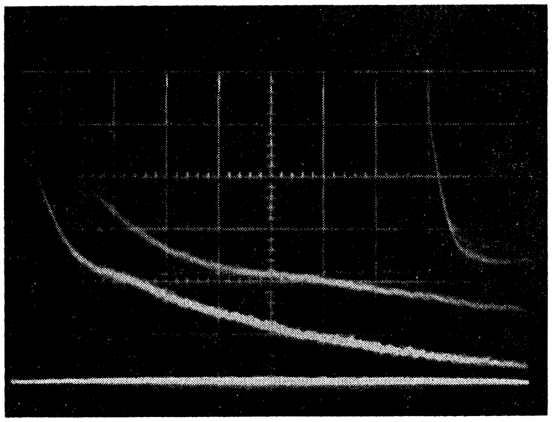

FIG. 6. Cross-relaxation experiment. Free decay signal observed after the third pulse. Temperature $t=182$°C. Orientation $\mathbf{H}_0\|c$ axis. Time interval between pulses ② and ③: $\tau=1.65$ msec. Sweep rates: 20 and 50 μsec/cm.

The nonhorizontal base line is extrapolated from the slow exponential increase displayed on Fig. 7.

The decrease, with a time constant T_m of a few hundred μsec, is due to cross relaxation between I_z and S_z. At the position of the minimum, the shape of the decay is the same as that after a single pulse. It does not change during the subsequent increase of the signal, which arises from spin-lattice relaxation. The spin-lattice relaxation time T_1 is always at least a hundred times longer than the cross-relaxation time T_m.

We call $h(0)$ the initial amplitude of the exponential signal, and $h(\infty)$ the equilibrium value it would reach in the absence of spin-lattice relaxation. In Fig. 9 are reported, as a function of $1/T$, the experimental values of $1/T_m$ and $h(\infty)/[h(0)-h(\infty)]$, for the orientation $\mathbf{H}_0\|c$ axis.

The measurements extend from 97°C ($10^3/T=2.7$) to 283°C ($10^3/T=1.8$). Below 97°C, the relaxation time T_2 is very short; the magnetization I_z following the second pulse is then very small and the signal-to-noise ratio is not good enough to allow any measurement. Above 283°C, the decrease of the exponential part from $h(0)$ to $h(\infty)$ is too small to allow any precise measurement.

The variation of T_m with temperature: an increase followed by a decrease closely parallels the observed variation of T_2. The cross relaxation is known to originate from the interaction between fluorine nuclei. The decrease of T_2 with increasing temperature, as well as that of T_m, must then be accounted for by a mechanism involving only fluorine nuclei.

Remark: The measurements of the spin-spin relaxation time T_2 are performed at low temperatures—from 97 to 283°C—using the three-pulse sequence, by observing the exponential free decay following the third pulse when it is applied shortly after the second pulse.

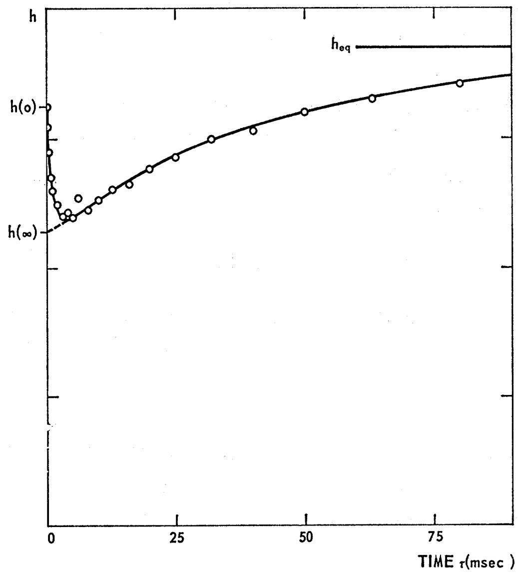

FIG. 7. Cross-relaxation experiment. Variation of the amplitude of the exponential part of the free decay following the third pulse as a function of the time interval τ between pulses ② and ③. The decrease is due to cross relaxation. The increase is due to spin-lattice relaxation. Temperature $t=162$°C. Orientation $H_0 \| a$ axis.

Indeed, especially at the lowest temperatures where T_2 is short, the presence of the oscillatory decay superimposed on the exponential decay makes it very difficult to measure with any precision the time constant of the latter.

IV. THEORETICAL INTERPRETATION

The cross-relaxation experimental results imply that there are two types of fluorine nuclei strongly interacting, which must then be located on different sublattices. The angular dependence and field independence of the oscillatory part of the decay indicate that it is due to nuclei experiencing static spin-spin interactions. The slow exponential part of the decay is due to nuclei, the spin-spin interactions of which are averaged by motion. Thermal expansion measurements[7,14] show that LaF_3 contains Shottky defects, and this motion is probably atomic diffusion. The difference in Larmor frequency between the two spin species is in any case far smaller than their linewidths, and is neglected. For fluorine nuclei, the indirect scalar interactions must be negligible and they are ignored.

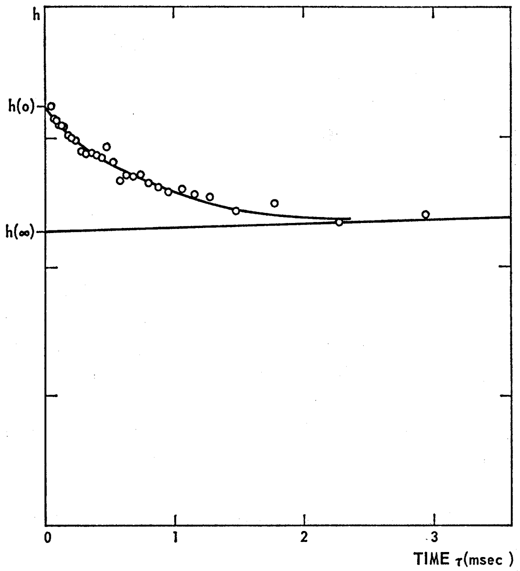

FIG. 8. Cross-relaxation experiment. Variation of the amplitude of the exponential part of the free decay following the third pulse as a function of the time interval τ between pulses ② and ③, in the domain where the amplitude decreases. The base line is extrapolated from Fig. 7. Temperature $t=162$°C. Orientation $H_0 \| a$ axis.

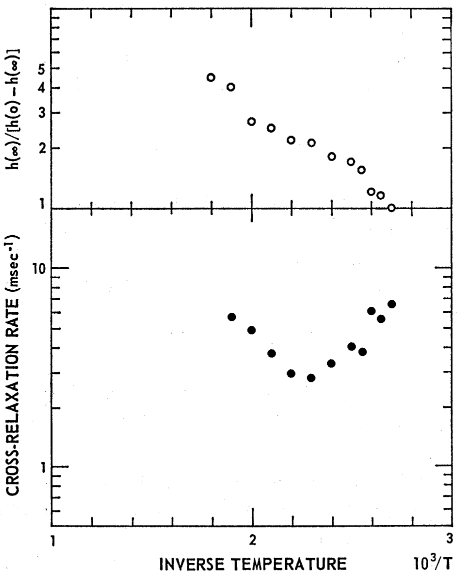

FIG. 9. Cross-relaxation experiment. Temperature variation of the cross-relaxation time T_m and of the ratio $h(\infty)/[h(0)-h(\infty)]$. Orientation $H_0 \| c$ axis.

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[14] A. Sher (private communication).

We call I the moving spins, N_I their number, and $\mathcal{A}$ their sublattice. Their motion essentially consists of jumps from one site in sublattice $\mathcal{A}$ to another site in sublattice $\mathcal{A}$. The corresponding mean jump time τ_1 is submitted, in the temperature range under study, to the conditions:

$$\Delta\omega\tau_1 \ll 1\,,$$

$$\omega_0\tau_1 \gg 1\,,$$

where $\Delta\omega$ is the resonance linewidth in the rigid lattice and ω_0 the fluorine Larmor frequency. The last condition implies that only the secular part of the dipole-dipole interactions is effective for the spin-spin relaxation of the fluorine nuclei.

We call S the "fixed" spins, N_S their number and $\mathcal{B}$ their sublattice. These spins actually need not be fixed, but, in the temperature range where an oscillatory decay is observed, their jump rate is smaller than the rigid lattice line width $\Delta\omega$.

The existence, for both T_2 and T_m, of a temperature range where they decrease with increasing temperature is interpreted in terms of a slow exchange of fluorine atoms between the sublattices $\mathcal{A}$ and $\mathcal{B}$: each fluorine atom in sublattice $\mathcal{A}$ jumps to a site in sublattice $\mathcal{B}$ with mean jump time τ_2 and, because in each sublattice the number of atoms is conserved, each atom in sublattice $\mathcal{B}$ jumps to a site in sublattice $\mathcal{A}$ with mean jump time $(N_S/N_I)\tau_2$.

At the temperatures where an oscillatory decay is observed, we have the condition:

$$\Delta\omega\tau_2 \gg 1\,.$$

Let us consider, for instance, the effect of these motions on the cross relaxation between I_z and S_z. This cross relaxation occurs both through the random modulation of their dipole-dipole interaction

$$(I_+S_- + I_-S_+)\,,$$

with correlation time of the order of τ_1, and by direct exchange of nuclei between the sublattices, with jump times τ_2 and $(N_S/N_I)\tau_2$.

The cross-relaxation rate T_m^{-1} is then of the form:

$$T_m^{-1} = \alpha\tau_1 + \beta/\tau_2\,.$$

Since τ_1 and τ_2 decrease with increasing temperature, T_m^{-1} must first increase and then decrease, as observed.

The effect of these motions is qualitatively the same on the spin-spin relaxation time T_2. When the temperature is further increased to values where $\Delta\omega\tau_2 < 1$, the structure of the decay is smeared out, the decay is a simple exponential for all nuclei, and T_2 increases again.

This problem is very similar to the problem of chemical exchange between sites experiencing different chemical shifts commonly met in high-resolution nmr.[15] However, in the present case, one of the spin species, the spins S in sublattice $\mathcal{B}$, experiences only show motions and its free decay is that of a solid. The second difference is that both spin species have the same Larmor frequency; incidentally, this situation makes it easier to observe phenomena by looking at the free decay signal instead of looking at the cw absorption line.

We now analyze in more detail the relaxation behavior expected from these types of motion. The succeeding steps of the analysis are:

(a) Influence of the dipole-dipole interactions on the spin-spin relaxation time and cross-relaxation time.

(b) Influence of atomic exchange between both sublattices on the same relaxation times.

(c) Analysis of the cross-relaxation experiment. This analysis, which can only be qualitative, gives an explanation for the variation of the ratio $h(\infty)/[h(0)-h(\infty)]$ as a function of temperature.

A. Influence of the Dipole-Dipole Interactions on the Relaxation Times

We restrict the analysis for the moment to the temperature range where we have

$$\Delta\omega\tau_2 > 1\,,$$

that is, where the spins I and S are experimentally distinguishable. We then also have, in this range:

$$\tau_2 \gg \tau_1\,.$$

We consider the relaxation of the spins I, for which all dipole-dipole interactions are averaged by motion. We use the methods and results of Abragam.[16]

1. Dipolar Coupling Between Pairs of Spins I

Their contribution to the spin-spin relaxation rate of the spins I is

$$(T_2^{-1})_{II} = \gamma^4\hbar^2 I(I+1)\times\tfrac{3}{8}J_{II}{}^0(0)\,, \tag{1}$$

where

$$J_{II}{}^0(\omega) = \textstyle\sum_{i,j} J_{I_iI_j}{}^0(\omega)/N_I \tag{2}$$

and $J_{I_iI_j}{}^0(\omega)$ is the Fourier transform of the correlation function of the factor $(1-3\cos^2\theta_{ij})r_{ij}^{-3}$ arising in the secular dipole-dipole interaction between the spins I_i and I_j.

The correlation time is of the order of the relative jump time between two spins I, which is $\frac{1}{2}\tau_1$. We then have:

$$(T_2^{-1})_{II} \propto J_{II}{}^0(0) \propto \tau_1\,.$$

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[15] See, for instance, J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959), Chap. 10.

[16] A. Abragam, Ref. 3, Chap. VIII.

2. *Dipolar Coupling Between the Spins I and S*

The correlation time of this coupling is of the order of the relative jump time between a spin I and a spin S which, since the spins S are practically not moving, is equal to τ_1.

An unusual phenomenon arises from the fact that both spins I and S have the same Larmor frequency, namely there is a cross relaxation between I_x and S_x in the rotating frame. Indeed, one usually considers unlike spins whose difference in resonance frequency is far larger than their linewidths. In that case, their transverse magnetizations do not change appreciably during a period of their differential precession, and cross relaxation between them averages to zero.

In the present case, the secular part of the dipole-dipole interaction between a spin I and a spin S is proportional to:

$$2I_zS_z-\tfrac{1}{2}(I_+S_-+I_-S_+).$$

Using Abragam's notations,[17] we get

$$A^{(0)}=\tfrac{1}{2}\gamma^2\hbar[2I_zS_z-\tfrac{1}{2}(I_+S_-+I_-S_+)].$$

If we consider the dipole-dipole interaction between a spin I^i and a spin S^μ, the standard calculation using this value of $A^{(0)}$ yields:

$$\begin{aligned}\frac{d}{dt}\langle I_x{}^i\rangle&=-\frac{5}{24}\gamma^4\hbar^2I(I+1)J_{I^iS^\mu}{}^0(0)[\langle I_x{}^i\rangle+\tfrac{4}{5}\langle S_x{}^\mu\rangle],\\ \frac{d}{dt}\langle S_x{}^\mu\rangle&=-\frac{5}{24}\gamma^4\hbar^2I(I+1)J_{I^iS^\mu}{}^0(0)[\langle S_x{}^\mu\rangle+\tfrac{4}{5}\langle I_x{}^i\rangle].\end{aligned}\tag{3}$$

We sum over all spins I and all spins S and we get finally:

$$\begin{aligned}\frac{d}{dt}\langle I_x\rangle&=-\frac{5}{24}\gamma^4\hbar^2I(I+1)J_{IS}{}^0(0)\left[\langle I_x\rangle+\frac{4}{5}\frac{N_I}{N_S}\langle S_x\rangle\right],\\ \frac{d}{dt}\langle S_x\rangle&=-\frac{5}{24}\gamma^4\hbar^2I(I+1)J_{IS}{}^0(0)\left[\frac{N_I}{N_S}\langle S_x\rangle+\frac{4}{5}\langle I_x\rangle\right].\end{aligned}\tag{4}$$

Since the decay of the spins S is faster than that of the spins I, we can consider, to first order, that this cross relaxation has only negligible effect on the decay of the spins I, and we have approximately, for the dipole-dipole contribution to the spin-spin relaxation rate:

$$(T_2{}^{-1})_{\rm DD}=\gamma^4\hbar^2I(I+1)[\tfrac{3}{8}J_{II}{}^0(0)+(5/24)J_{IS}{}^0(0)]\tag{5}$$

The consideration of this cross relaxation in the rotating frame proves however to be important for the interpretation of the cross relaxation along the applied field.

3. *Cross Relaxation Between I_z and S_z*

When the magnetizations I_z and S_z along the magnetic field are not equal, there is a cross relaxation between them, due to the operators $(I_+S_-+I_-S_+)$ of their dipole-dipole interactions.

Considering first the interaction between a spin I^i and a spin S^μ, and then summing over all spins I and all spins S, we find, for this contribution:

$$\begin{aligned}\frac{d}{dt}\langle I_z\rangle&=-\frac{1}{12}\gamma^4\hbar^2I(I+1)J_{IS}{}^0(0)\left[\langle I_z\rangle-\frac{N_I}{N_S}\langle S_z\rangle\right]\\ &=-W_{\rm DD}\left[\langle I_z\rangle-\frac{N_I}{N_S}\langle S_z\rangle\right].\end{aligned}\tag{6}$$

B. Influence of Atomic Exchange on the Relaxation Time

In the domain where the jump times between sublattices are long, i.e., when $\Delta\omega\tau_2\gg1$, it is a good approximation to consider that the only effect of the jumps is an exchange of magnetizations between the two spin species, at a rate which is the same along the magnetic field or in the rotating frame. This contribution to cross relaxation is simply added to the contribution from dipole-dipole interactions. This approach is the same as that used by Gutowsky, McCall and Slichter[18] in the study of chemical exchange by high-resolution magnetic resonance. However, in the present case, this procedure has a more restricted validity and can safely be used only at very low exchange rates since the dipole-dipole interactions between spins S can no longer be considered as static when $\Delta\omega\tau_2$ approaches unity and no proper treatment is available for the study of intermediate rate motions.

Summing all contributions, the evolution of the magnetizations in the rotating frame is governed by the equations:

$$\begin{aligned}(d/dt)\langle I_x\rangle&=-\delta_I\langle I_x\rangle+\epsilon_S\langle S_x\rangle,\\ (d/dt)\langle S_x\rangle&=\mathfrak{F}(t)+\epsilon_I\langle I_x\rangle,\end{aligned}\tag{7}$$

where

$$\begin{aligned}\delta_I&=(T_2{}^{-1})_{\rm DD}+\tau_2{}^{-1},\\ \epsilon_I&=\tau_2{}^{-1}-\tfrac{1}{6}\gamma^4\hbar^2I(I+1)J_{IS}{}^0(0),\\ \epsilon_S&=(N_I/N_S)\epsilon_I.\end{aligned}$$

$\mathfrak{F}(t)$ is the decay of the spins S due to the static interactions between pairs of spins S and to the fluctuating interactions between the spins S and the spins I.

As a first approximation, we neglect the effect of cross relaxation on the decay of the spins I, and their spin-spin relaxation time is equal to $\delta_I{}^{-1}$. Since we know that $J_{II}{}^0(0)$, $J_{IS}{}^0(0)\propto\tau_1$, we have:

$$T_2{}^{-1}\simeq\delta_I=\alpha\tau_1+\tau_2{}^{-1}.$$

Since both jump times decrease with increasing temperature, δ_I decreases first and then increases.

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[17] A. Abragam, Ref. 3, p. 289.

[18] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys. **21**, 279 (1953).

The evolution of the magnetizations along the magnetic field is governed by the equations:

$$(d/dt)\langle I_z\rangle = -W[\langle I_z\rangle - (N_I/N_S)\langle S_z\rangle],\qquad (d/dt)\langle I_z+S_z\rangle = 0, \tag{8}$$

where

$$W = \tau_2^{-1} + W_{\mathrm{DD}}. \tag{9}$$

Let I_0 and S_0 be the initial values of $\langle I_z\rangle$ and $\langle S_z\rangle$. We have at any time: $\langle I_z\rangle + \langle S_z\rangle = I_0 + S_0$, and we get:

$$(d/dt)\langle I_z\rangle = -W(1+N_I/N_S)\langle I_z\rangle + W(N_I/N_S)(I_0+S_0). \tag{10}$$

The decay time T_m which is measured in the cross-relaxation experiment is then given by

$$T_m^{-1} = W(1+N_I/N_S). \tag{11}$$

At low temperatures, when the contribution from dipole-dipole interactions is dominant, we have:

$$\delta_I/W \simeq (WT_2)^{-1} = \tfrac{5}{2} + \tfrac{9}{2}(J_{II}{}^0(0)/J_{IS}{}^0(0)). \tag{12}$$

At high temperatures, when the contribution from atomic exchange is dominant, we have

$$\delta_I/W \simeq (WT_2)^{-1} = 1. \tag{13}$$

At low temperatures, we also have

$$\epsilon_I = -2W. \tag{14}$$

C. Analysis of the Cross-Relaxation Experiment

This analysis is directed at explaining the variation of the factor $h(\infty)/[h(0)-h(\infty)]$ as a function of temperature observed in the cross-relaxation experiments. This effect arises from the cross relaxation between $\langle I_x\rangle$ and $\langle S_x\rangle$ in the rotating frame.

Since the decay of the spins S is not exponential and is due mainly to almost static dipole-dipole interactions, it is not possible to perform any rigorous calculation. Limited to an approximate, and thus only qualitative, treatment, we choose to simplify it as much as possible, and we very roughly approximate the decay signal due to the spins S by an exponential. We just add, as before, the contribution of atomic jumps to cross relaxation to the contribution of the dipole-dipole interactions. However crude such a procedure may be, it is hoped to give qualitatively the correct trend of the phenomena.

The evolution of the transverse magnetizations following a $\pi/2$ pulse is then assumed to be given by the following equations (from here on we drop the brackets in indicating expectation values):

$$(d/dt)I_x = -\delta_I I_x + \epsilon_S S_x,$$

$$(d/dt)S_x = -\delta_S S_x + \epsilon_I I_x.$$

δ_S approximates the decay of the spins S, and we have

$$\delta_S \gg \delta_I, \epsilon_I, \epsilon_S.$$

The signals I_x and S_x are sums of two decreasing exponentials, with rate constants which are, to first order, equal to

$$\lambda_1 = \delta_I - \epsilon_S\epsilon_I/(\delta_S-\delta_I), \tag{15}$$

$$\lambda_2 = \delta_S + \epsilon_S\epsilon_I/(\delta_S-\delta_I). \tag{16}$$

We call I_0 and S_0 the initial values of I_x and of S_x and we write:

$$I_x = A_1\exp(-\lambda_1 t) + A_2\exp(-\lambda_2 t) \tag{17}$$

$$S_x = B_1\exp(-\lambda_1 t) + B_2\exp(-\lambda_2 t). \tag{18}$$

Using the notation $\delta = \delta_S - \delta_I$, the slow components of I_x and S_x are given, to first order with respect to ϵ_I/δ and ϵ_S/δ, by

$$A_1 = I_0 + (\epsilon_S/\delta)S_0, \tag{19}$$

$$B_1 = (\epsilon_I/\delta)I_0. \tag{20}$$

The ratio of the amplitudes of the slow and fast components is equal to

$$\frac{A_1+B_1}{A_2+B_2} = \frac{I_0}{S_0} \times \frac{1+(\epsilon_I/\delta)+(\epsilon_S/\delta)(S_0/I_0)}{1-(\epsilon_S/\delta)-(\epsilon_I/\delta)(I_0/S_0)}. \tag{21}$$

It is equal to (I_0/S_0) only when there is no cross relaxation, i.e., when we have

$$\epsilon_I = \epsilon_S = 0.$$

The qualitative features of this simplified model, which should be true for the actual problem, are the following: Both the spins I and the spins S contribute to the slow part and also to the fast part of the decay. The ratio of the amplitudes of the slow and fast decays, which in the simplified model is the ratio $(A_1+B_1)/(A_2+B_2)$, increases as the cross relaxation becomes more important, that is, as we shall see, when the temperature is increased. This explains that the narrow line increases at the expense of the broad line when the temperature is increased, without necessitating any change in the ratio N_I/N_S of moving spins to fixed spins as a function of temperature.

In the cross-relaxation experiment, the second pulse is applied when the fast part of the decay goes through zero, that is it brings parallel to the steady magnetic field only that part of the magnetizations which contribute to the slow exponential decay. Then, just after this second pulse, the magnetization S_z is not zero, but instead I_z and S_z are proportional to the coefficients A_1 and B_1. These magnetizations vary with time under the effect of cross relaxation. We follow them by applying a third $\pi/2$ pulse at various times τ after the second one and by measuring the amplitude of the exponential part of the decay following this third pulse. By so doing, we do not measure I_z, but instead (A_1+B_1), that is a combination of I_z and S_z. These two effects: initial condition with $S_z \neq 0$, and measurement of a combination of I_z and S_z, are responsible for the observed variation of the ratio $h(\infty)/[h(0)-h(\infty)]$ with temperature.

The calculation of this ratio is performed in the appendix, within our simplified model and to first order in (ϵ_I/δ) and (ϵ_S/δ). The result is

$$h(\infty)/[h(0)-h(\infty)]=N_I/N_S[1+2(\epsilon_I+\epsilon_S)/(\delta_S-\delta_I)]. \tag{22}$$

This ratio varies with the relative rate of cross relaxation $(\epsilon_I+\epsilon_S)/(\delta_S-\delta_I)$. It is rigorously equal to N_I/N_S when there is no cross relaxation, that is, when

$$\epsilon_I=\epsilon_S=0.$$

This is apparent in Eq. (22), but also from the more correct Eq. (7), and is physically evident.

V. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY

Experiments have been performed at two orientations of the magnetic field with respect to the crystalline axis: parallel to the c axis and parallel to the a axis.

The cross-relaxation rate W between I_z and S_z is equal to

$$W=\tau_2^{-1}+W_{\mathrm{DD}}.$$

Let E_1 and E_2 be the activation energies associated with the two types of jumps, of jump times τ_1 and τ_2, respectively. We have

$$\tau_2^{-1}\propto\exp(-E_2/kT),$$
$$W_{\mathrm{DD}}\propto\tau_1\propto\exp(+E_1/kT).$$

The separation between these two contributions is possible on a logarithmic plot of W as a function of $1/T$.

In fact, what is measured is a mixing time T_m given by

$$T_m^{-1}=W(1+N_I/N_S),$$

which allows a determination of $W_{\mathrm{DD}}(1+N_I/N_S)$ and $\tau_2^{-1}(1+N_I/N_S)$.

On the other hand, the cross-relaxation rate ϵ_I in the rotating frame is equal to

$$\epsilon_I=\tau_2^{-1}-2W_{\mathrm{DD}}.$$

Then, ϵ_I and ϵ_S are zero when

$$\tau_2^{-1}=2W_{\mathrm{DD}},$$

that is, at a temperature T_0 which can be determined from the temperature variation of T_m. At this temperature, there is no cross relaxation in the rotating frame, and we must have:

$$h(\infty)/[h(0)-h(\infty)]=N_I/N_S.$$

Experimentally, we find the reciprocal temperatures:

$$10^3/T_0\simeq2.15 \quad \text{for} \quad \mathbf{H}_0\|c \text{ axis}$$
$$10^3/T_0\simeq2.25 \quad \text{for} \quad \mathbf{H}_0\|a \text{ axis},$$

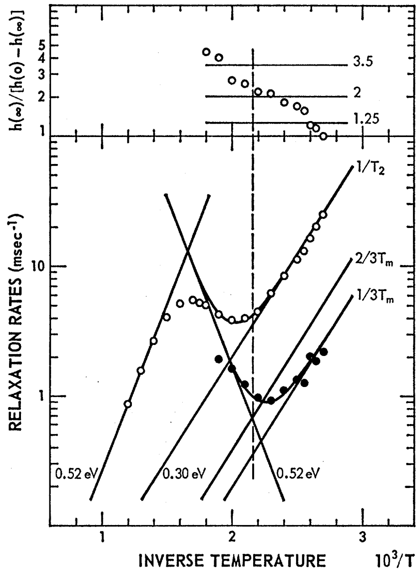

FIG. 10. Temperature variation of the quantities T_2^{-1}, $(3T_m)^{-1}$, and $h(\infty)/[h(0)-h(\infty)]$ for the orientation $H_0\|c$ axis. The solid curves correspond to a "best fit" of the experimental results to theory. The straight line $\frac{2}{3}T_m$, corresponding to the dipole-dipole contribution to the cross-relaxation in the rotating frame, is derived from this best fit and used to find the population ratio N_I/N_S, as explained in text.

with the corresponding mean value of the signal amplitude ratio:

$$h(\infty)/[h(0)-h(\infty)]\simeq2.3.$$

We believe that the actual ratio N_I/N_S is exactly equal to 2 since this would be the only possible value if the structure of LaF$_3$ was that proposed from x-ray studies, with two fluorine sites of relative populations 2:1. If we adopt the more complicated structure proposed by Anderson and Proctor,[10] with four fluorine sites of relative populations 3:3:2:1, the separation into two types I and S can yield the following ratios of populations:

$$N_I/N_S=5/4=1.25$$
$$=6/3=2$$
$$=7/2=3.5.$$

Again, from the cross-relaxation results, the only value we can select is:

$$N_I/N_S=2.$$

A value significantly different from 2 would imply that the unit cell is far larger than that proposed by Anderson and Proctor, which already contains 48 atoms. These considerations in addition to the imprecision of the measurements, lead us to conclude that N_I/N_S is indeed 2.

We then know that $W=(3T_m)^{-1}$. On Figs. 10 and 11 are reported for the orientations $\mathbf{H}_0\|c$ axis and $\mathbf{H}_0\|a$ axis, respectively, on a logarithmic scale and as a function of $1/T$, the experimental values of

$$T_2^{-1},\ (3T_m)^{-1} \ \text{and} \ h(\infty)/[h(0)-h(\infty)].$$

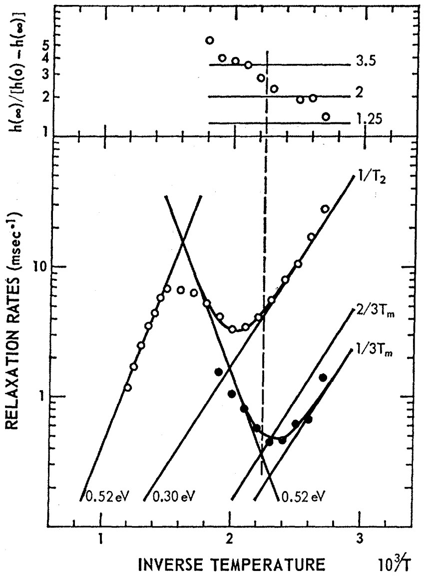

FIG. 11. Temperature variation of the quantities T_2^{-1}, $(3T_m)^{-1}$ and $h(\infty)/[h(0)-h(\infty)]$ for the orientation $H_0\|a$ axis. The solid curves correspond to a "best fit" of the experimental results to theory.

We can, with no inconsistency, fit the portions of $Ln(T_2^{-1})$ and $Ln(3T_m)^{-1}$ which increase with temperature to a common straight line, corresponding to τ_2^{-1}, which is the same for both orientations. Their decreasing portions, in the low-temperature region, can be fitted to parallel straight lines with the same slope for both orientations, corresponding to the dipole-dipole contributions to T_2^{-1} and W. The solid lines, on both figures, are the sums of the two exponentials.

In the low-temperature region we have:

$$(WT_2)^{-1} \simeq 10 \quad \text{for} \quad \mathbf{H}_0\|c \text{ axis},$$
$$\simeq 22 \quad \text{for} \quad \mathbf{H}_0\|a \text{ axis},$$

which corresponds to

$$J_{II}^0(0)/J_{IS}^0(0) \simeq 5/3 \quad \text{for} \quad \mathbf{H}_0\|c \text{ axis}$$
$$\simeq 13/3 \quad \text{for} \quad \mathbf{H}_0\|a \text{ axis}.$$

This ratio reflects the relative importance of the secular dipole-dipole interactions, $\mathcal{H}_{II}'$ and $\mathcal{H}_{IS}'$ within the system of spins I and between the spins I and the spins S, respectively. Its low value is a further indication that the distance between a spin I and a spin S nearest neighbor is comparable to the distance between two spins I nearest neighbors.

We get the following very approximate values for the activation energies associated with both types of motion:

$$E_1/k \simeq 3500°\text{K, i.e., } E_1 \simeq 0.30 \text{ eV},$$
$$E_2/k \simeq 6000°\text{K, i.e., } E_2 \simeq 0.52 \text{ eV}.$$

The value of T_2^{-1} goes through a maximum at $10^3/T \simeq 1.6$ to 1.7, depending on the orientation (that is approximately at the temperature where the structure of the free decay disappears), and then decreases with a slope corresponding to an activation energy of about 0.52 eV.

In this temperature range, we have

$$\Delta\omega\tau_2 \lesssim 1.$$

The experimental values of T_2^{-1} are far larger than the values extrapolated from the low-temperature region of decrease of T_2^{-1}, which means that in this high-temperature region the dominant contribution to T_2^{-1} comes from the modulation of the interactions between pairs of spins S. This is understandable since the rate of modulation of these interactions is the slowest.

Provided that the jump time of an atom from a site in sublattice $\mathcal{B}$ to another site in sublattice $\mathcal{B}$ is not shorter than its jump time $\tau_2/2$ to a site in sublattice $\mathcal{A}$, the relative jump time between two atoms in sublattice $\mathcal{B}$ is equal to $\tau_2/4$.

In this case, we must have

$$T_2^{-1} \propto \tau_2 \propto \exp(+E_2/kT).$$

In Figs. 10 and 11, we have taken as an explicit condition the fitting of the increasing portion of T_2^{-1} and its high-temperature decreasing portion to straight lines with slopes of equal absolute values. The fact that this is possible shows that we have no experimental way of detecting a third type of motion, the jump from one site in sublattice $\mathcal{B}$ to another site in sublattice $\mathcal{B}$, the mean jump time of which is the probably longer than τ_2.

The variation of the factor

$$h(\infty)/[h(0)-h(\infty)]$$

with temperature qualitatively follows the theoretical prediction: Below the temperature T_0, the cross-relaxation rates ϵ_I and ϵ_S are negative, and this factor is smaller than 2. Above this temperature, ϵ_I and ϵ_S are positive and the factor is larger than 2.

For the orientation $H_0\|c$ axis, for instance, the extreme measured values of this ratio: 4.5 for $10^3/T=1.8$ and 1 for $10^3/T=2.7$, correspond, respectively, after Eq. (22), to:

$$\epsilon_I/(\delta_S-\delta_I) = +0.21 \quad \text{and} \quad -0.08.$$

These values qualitatively show that a limited degree of cross relaxation is sufficient to account for the large variation of the factor $h(\infty)/[h(0)-h(\infty)]$ observed experimentally.

VI. CONCLUSION

A number of experimental results—the shape of the fluorine free decay, the temperature variation of T_2, the existence of a cross relaxation and the temperature variation of the cross-relaxation time T_m—shows that, in LaF_3, there are two types of fluorine nuclei located on different sublattices, one type moving fast, the other type moving slowly. A phenomenon suggested by the existence of temperature regions where T_2 and T_m increase with temperature is that there is a slow exchange of fluorine atoms between the two sublattices. From the theory of magnetic relaxation this model of atomic motions implies given relationships between the variations with temperature of T_2, T_m and $h(\infty)/[h(0)-h(\infty)]$. Both the theory and the experimental results are not accurate enough to provide a precise and detailed verification of these relationships, but they can be used to check qualitatively the over-all consistency of the proposed model. Such a consistency does exist, which helps to establish on a stronger basis this model for the motions. The existence of two types of motions for the fluorine atoms is not surprising, since it is natural that atoms located on different crystalline sites should experience different barriers to motion, but evidence for such composite motions is hardly attainable by other physical methods.

We have not performed any systematic study of the angular dependence of the measurable quantities: the relaxation times T_2 and T_m, the width and shape of the free decay of the spins S, and the width and shape of the free decay at low temperature, when all motions are frozen. The information yielded by such studies should help check the model of crystalline structure of $\mathrm{LaF_3}$ proposed by Anderson and Proctor,[10] and find which fluorine atoms are moving fast and which are moving slowly.

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APPENDIX

We calculate the ratio $h(\infty)/[h(0)-h(\infty)]$ using the simplified model, that is starting with Eqs. (19) and (20).

The transverse magnetizations just after the first pulse are equal to the equilibrium magnetizations:

$$I_z=I_{\mathrm{eq}};\ S_z=S_{\mathrm{eq}}=(N_S/N_I)I_{\mathrm{eq}}=(\epsilon_I/\epsilon_S)I_{\mathrm{eq}}.$$

At the time t_0 when the second pulse is applied, the magnetizations contributing to the slow part of the decay are

$$I_x=A_1\exp(-\lambda_1 t_0)=\alpha A_1.$$
$$S_x=\alpha B_1.$$

As a result of the second pulse, these become longitudinal magnetizations equal to

$$\begin{aligned} I_z(0)&=\alpha I_{\mathrm{eq}}(1+\epsilon_I/\delta),\\ S_z(0)&=\alpha I_{\mathrm{eq}}(\epsilon_I/\delta). \end{aligned}\tag{A1}$$

Due to cross relaxation these magnetizations tend toward the values:

$$\begin{aligned} I_z(\infty)&=N_I/(N_I+N_S)[I_z(0)+S_z(0)]\\ &=\epsilon_S/(\epsilon_I+\epsilon_S)[I_z(0)+S_z(0)],\\ S_z(\infty)&=\epsilon_I/(\epsilon_I+\epsilon_S)[I_z(0)+S_z(0)]. \end{aligned}$$

This yields, from Eq. (A1):

$$\begin{aligned} I_z(\infty)&=\alpha I_{\mathrm{eq}}(1+2\epsilon_I/\delta)\epsilon_S/(\epsilon_I+\epsilon_S),\\ S_z(\infty)&=\alpha I_{\mathrm{eq}}(1+2\epsilon_I/\delta)\epsilon_I/(\epsilon_I+\epsilon_S). \end{aligned}\tag{A2}$$

After the third pulse, we measure the exponential part of the decay, that is,

$$\begin{aligned} h&=A_1+B_1\\ &=(1+\epsilon_I/\delta)I_0+(\epsilon_S/\delta)S_0. \end{aligned}\tag{A3}$$

Initial Signal

When the time τ between the second and the third pulse is short, we have

$$\begin{aligned} I_0&=I_z(0)=\alpha I_{\mathrm{eq}}(1+\epsilon_I/\delta),\\ S_0&=S_z(0)=\alpha I_{\mathrm{eq}}(\epsilon_I/\delta). \end{aligned}$$

The initial signal is then

$$\begin{aligned} h(0)&=\alpha I_{\mathrm{eq}}[(1+\epsilon_I/\delta)^2+(\epsilon_I\epsilon_\delta/\delta^2)],\\ h(0)&\simeq\alpha I_{\mathrm{eq}}(1+2\epsilon_I/\delta). \end{aligned}\tag{A4}$$

Final Signal

At equilibrium, we have

$$I_0=I_z(\infty)\quad\text{and}\quad S_0=S_z(\infty).$$

This yields, for the final signals,

$$\begin{aligned} h(\infty)&=\alpha I_{\mathrm{eq}}(1+2\epsilon_I/\delta)\\ &\quad\times[\epsilon_S(1+\epsilon_I/\delta)+(\epsilon_I\epsilon_S/\delta)]/(\epsilon_I+\epsilon_S), \end{aligned}\tag{A5}$$

$$h(\infty)\simeq\alpha I_{\mathrm{eq}}(1+4\epsilon_I/\delta)\epsilon_S/(\epsilon_I+\epsilon_S).$$

We then have

$$h(0)-h(\infty)=\alpha I_{\mathrm{eq}}(1+2\epsilon_I/\delta-2\epsilon_S/\delta)\epsilon_I/(\epsilon_I+\epsilon_S)$$

and

$$\begin{aligned} h(\infty)/[h(0)-h(\infty)]&\\ &\simeq(\epsilon_S/\epsilon_I)[1+2(\epsilon_I+\epsilon_S)/\delta]\\ &=(N_I/N_S)[1+2(\epsilon_I+\epsilon_S)/(\delta_S-\delta_I)]. \end{aligned}\tag{A6}$$

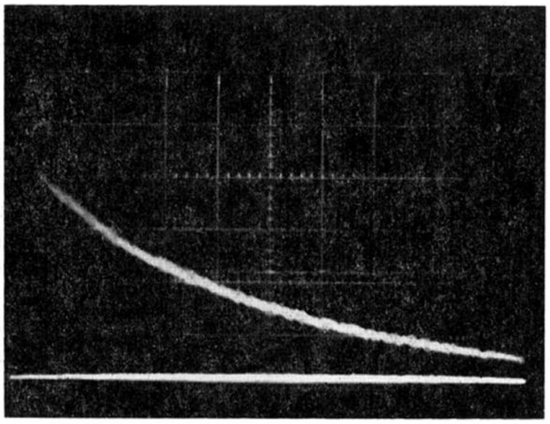

FIG. 5. Cross-relaxation experiment. Free decay signal observed after the third pulse. Temperature $t=182$°C. Orientation $\mathbf{H}_0 \| c$ axis. Time interval between pulses ② and ③: $\tau=85$ μsec. Sweep rate: 50 μsec/cm.

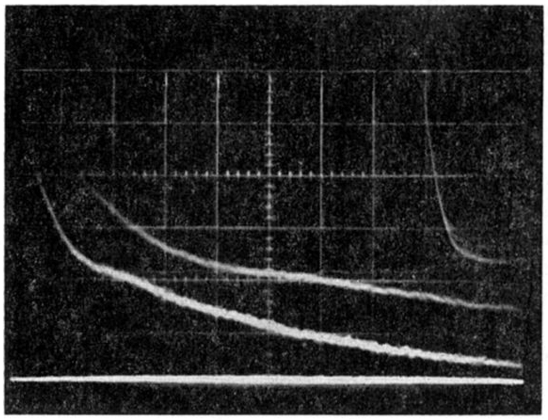

FIG. 6. Cross-relaxation experiment. Free decay signal observed after the third pulse. Temperature $t=182$°C. Orientation $\mathbf{H}_0 \| c$ axis. Time interval between pulses ② and ③: $\tau=1.65$ msec. Sweep rates: 20 and 50 μsec/cm.