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THE EFFECT OF COLOR CENTERS ON THE NUCLEAR SPIN-LATTICE RELAXATION TIME IN LITHIUM FLUORIDE*

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Abstract.—The dependence of the spin-lattice relaxation time of fluorine nuclei in lithium fluoride on the concentration of radiation-induced color centers has been investigated under rigidly controlled conditions. *F*-center concentrations have been determined from ultraviolet absorption spectra. The data agree with the theoretical predictions for diffusion-limited relaxation, with respect to the dependence on both the concentration of color centers and the diffusion constant for nuclear-spin diffusion. Some linewidth measurements were made for the fluorine resonance; data were obtained with the [110] crystalline axis parallel to the d.c. magnetic field.

I. INTRODUCTION

THE EFFECTS of paramagnetic impurities on the spin-lattice relaxation time of the nuclear spins in crystalline solids were first investigated systematically by BLOEMBERGEN⁽¹⁾. His experiments, which were carried out on a variety of complex salts, including calcium fluoride and some alkali halides containing paramagnetic impurities such as chromium and iron, clearly established the fact that minute quantities of paramagnetic impurities are responsible for the relatively short relaxation times observed in many crystalline solids.

One of the objectives of his investigation was to determine the dependence of the nuclear spin-lattice relaxation time, T_1 , on the concentration of paramagnetic ions present in the crystals that he used. For chemical impurities present in small concentrations, such an investigation presents several difficulties. First, a different crystal must be used to obtain each datum (at a given tempera-

ture), and the measurement is destructive because the crystal must be chemically analyzed after the relaxation measurements have been made. Second, it becomes increasingly difficult to obtain accurate measurements of the impurity concentration at low concentrations for which the theoretical predictions would have their greatest significance. There is also the question of the degree of uniformity of the mean density of the impurities. Moreover, it would be desirable to work with substances that are relatively easy to treat theoretically, such as the alkali halides; substances that contain accurately known amounts of uniformly distributed chemical impurities are difficult to obtain.

These difficulties can be circumvented by beginning with alkali halide crystals of high purity and then coloring them with high-energy radiation. It is well established that the *F*-centers produced in this way consist of an electron trapped in a halogen ion vacancy in the lattice.^(2,3) Such a configuration is paramagnetic and its properties have been investigated by using paramagnetic-resonance techniques.^(4,5,6) *F*-center concentrations can be obtained from ultraviolet absorption data.⁽⁷⁾

In the experiment that is described here, the

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relaxation time for fluorine nuclei in a large single crystal of lithium fluoride was measured as a function of F -center concentration. Experimental evidence⁽⁶⁾ indicates that paramagnetic centers other than F -centers are not produced in any appreciable concentrations under the conditions of temperature and irradiation employed. Lithium fluoride was chosen because of the permanency of the radiation-induced coloring and because there can be no possible complication from quadrupole effects if the nuclear spin is $1/2$, as is the case with fluorine. The theoretically predicted dependence of T_1 on the nuclear spin diffusion constant is verified.

The theory of the relaxation process of a system of nuclear spins in a crystalline lattice containing magnetic impurities in high dilution has been considered by several authors.^(1,8-10) We take as a model a single impurity spin surrounded by a lattice of nuclei. The interactions that make important contributions to the process by which such a system approaches equilibrium are the magnetic dipole interactions among the nuclei themselves and the dipole interaction between the electronic magnetic moment of the impurity, and the nuclear magnetic moments of the surrounding nuclei.

Spin-spin interaction between nuclei of the same species permits them to exchange Zeeman energy by mutually flipping each other and gives rise to the phenomenon of spatial spin diffusion.⁽¹⁾ In the absence of impurities, the z -component (parallel to the applied d.c. magnetic field) of the nuclear magnetic moment per unit volume, considered as a function of time and position, satisfies a diffusion equation in which the diffusion constant is given by

$$D = \frac{1}{16} \gamma_n^3 \hbar^2 \lambda (\overline{\Delta H^2})^{-1/2} \sum_{j \neq i} r_{ij}^{-4} (1 - 3 \cos^2 \theta_{ij})^2. \quad (1)$$

In this expression, a nucleus is arbitrarily labeled i , and the sum is extended over all other like nuclei in the lattice; r_{ij} is a vector drawn from the i^{th} to the j^{th} nucleus, making an angle θ_{ij} with the applied d.c. magnetic field H_0 ; γ_n is the nuclear magnetogyric ratio; λ depends on the shape function of the particular resonance that is being considered and for a Gaussian line shape it will be independent of the direction of H_0 ; $(\overline{\Delta H^2})$ is

second moment of the resonance line, which can be calculated from an expression developed by VAN VLECK⁽¹¹⁾,

$$\begin{aligned} \overline{\Delta H^2} &= \left(\frac{2\pi}{\gamma} \right)^2 \overline{\Delta \nu^2} \\ &= \frac{3}{4} I(I+1) \gamma^2 \hbar^2 \sum_{i \neq j} r_{ij}^{-6} (1 - 3 \cos^2 \theta_{ij})^2 \\ &\quad + \frac{1}{3} \sum_k \hbar^2 \gamma_k^2 I_k(I_k+1) r_{ik}^{-6} (1 - 3 \cos^2 \theta_{ik})^2. \end{aligned} \quad (2)$$

In equation (2), the index j is summed over all nuclei undergoing resonance, k is summed over all other nuclei present, and I is the corresponding nuclear spin in units of \hbar .

In the presence of a paramagnetic ion, an additional term appears in the diffusion equation as a result of the dipole interaction between the impurity spin and the surrounding nuclear moments. For the diffusion-limited case, the transfer of spin energy from the system of nuclear spins to the lattice is limited by the rate of diffusion of nuclear spin energy and, except for a short initial period, the z -component of nuclear magnetization will exponentially approach equilibrium with the lattice,⁽¹¹⁾ with a time constant given by

$$T_1 = 0.12 N_p^{-1} C^{-1/4} D^{-3/4}. \quad (3)$$

Here, N_p is the concentration of paramagnetic impurities, and C is given by

$$C = \left(\frac{1}{5\pi} \right) (\gamma_p \gamma_n \hbar)^2 S(S+1) \tau (1 + \tau^2 \nu^2)^{-1},$$

where γ_p and S are the magnetogyric ratio and the spin of the impurity, respectively, and τ is the correlation time of the z component of its spin.

II. EXPERIMENTAL PROCEDURE AND APPARATUS

Lithium fluoride (LiF) crystals of high purity were obtained from the Harshaw Chemical Company in the shape of right circular cylinders with the [001] crystalline axis lying along the axis of the cylinder.

F -centers were introduced into one of these crystals by exposing it to the radiation emitted

by Co^{60} . A Co^{60} source emits almost monochromatic gamma radiation at an energy of approximately 1.2 MeV. The absorption coefficient for gamma radiation of this energy in LiF is small and a uniform coloration was obtained throughout the crystal. Twenty-five seconds of irradiation produced a change of approximately 0.18 cm^{-1} in the maximum F -band absorption coefficient.

0.0001 in. Even so, the unirradiated crystals were observed to have different absorption coefficients in the region between $205 \text{ m}\mu$ and $240 \text{ m}\mu$, and small corrections were made on the F -band absorption curves in this range. The product of the F -center concentration and the oscillator strength can be obtained from the maximum absorption coefficient and the width of the absorption curve at

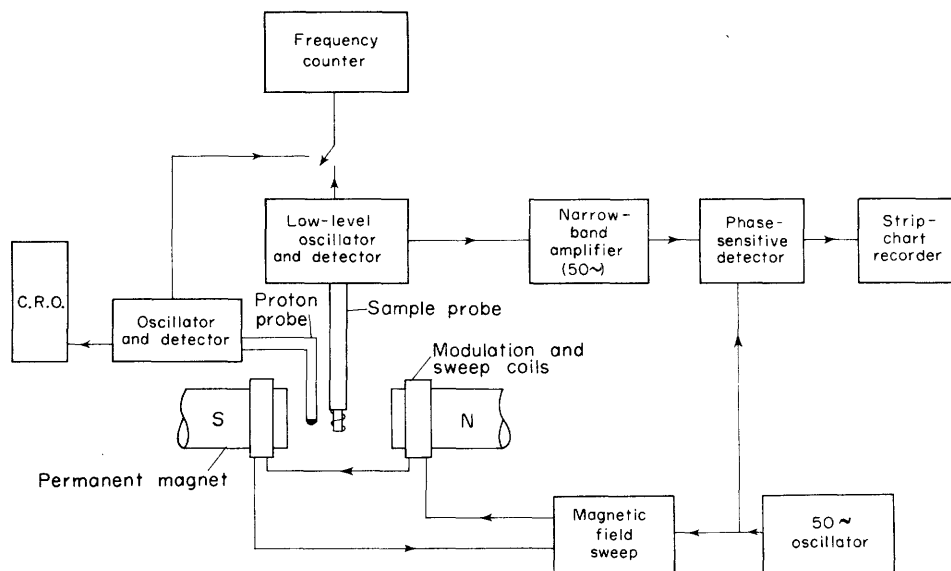


FIG. 1. Block diagram of nuclear magnetic resonance spectrometer.

All ultraviolet absorption measurements were made with a Cary spectrophotometer. This is a double-beam instrument from which a continuous plot of the absorption coefficient against wavelength can be obtained. It is desirable to obtain only that part of the absorption coefficient arising from the presence of color centers in the crystal. Therefore the instrument was adjusted to read zero over the whole range of wavelengths to be investigated when two identical unirradiated LiF crystals were placed in the beams. One of these calibration crystals was then replaced by the irradiated crystal, and the range of wavelengths was again traversed.

To implement these measurements, three crystals were ground to the same length and the ends were polished. The finished length was 1.004 in. and the end faces were parallel within

half-maximum by using Smakula's equation.⁽⁷⁾ Accurate relative concentrations can be obtained in this way.

The line shapes and spin-lattice relaxation times of all of the crystals were examined before irradiation was begun. The crystal with the longest "intrinsic" T_1 was selected to undergo irradiation, and it was irradiated for 25 sec in a Co^{60} source. Next, its ultraviolet spectrum was recorded. Finally, the spin-lattice relaxation time was measured with a radiofrequency spectrometer for two different orientations of the crystal in the magnetic field H_0 . The process was repeated until the maximum F -band absorption coefficient had risen to approximately 2.0 cm^{-1} , which is close to the maximum value that could be measured accurately with the spectrophotometer. This occurred after 325 sec of irradiation. Also, the whole

resonance line was traversed periodically so that any change in the line shape would be detected.

To obtain data at higher F -center concentrations, another set of three crystals, ground to a length of approximately 0.2 in. and polished, was prepared from one of the unused crystals in the original shipment. Two of these were used to calibrate the spectrophotometer (as described above), and the third was irradiated for 325 sec. Measurement confirmed that the third crystal had the same F -center concentration as the original test crystal. Irradiation of both the original test crystal and the new specimen was continued. Higher F -center concentrations were determined from the F -band absorption spectrum of the new crystal and corresponding measurements of T_1 were made on the original crystal.

As a precautionary measure to avoid bleaching, test crystals were stored in darkness and handled in subdued light. However, an extra crystal, which had been given a single 300 sec irradiation, showed no change in the F -band absorption spectrum over a period of months. It was also standard procedure to obtain the ultraviolet spectra and measure T_1 within 12 hr of irradiation.

A block diagram of the spectrometer used for all radiofrequency measurements is shown in Fig. 1. The low-level oscillator to which the sample probe is attached is of the type developed by POUND and WATKINS⁽¹²⁾. Their circuit was modified slightly to obtain stable oscillation at sufficiently low levels that the saturation factor⁽¹³⁾ did not influence any of the measured relaxation times. With the sample coil used, the saturation factor was estimated to be greater than 0.99 for all measurements.

T_1 was measured from direct observations of the recovery of the nuclear spin system from saturation. At a field of $H_0 = 4012$ G, the operating frequency was adjusted to give a maximum output signal with a modulation field of 7 G peak-to-peak applied. After several minutes, the output of a laboratory signal generator operating at the same frequency was connected directly across the sample coil for approximately 30 sec. The fluorine resonance is homogeneously broadened and the transverse relaxation time is of the order of 10^{-5} sec, so that the entire resonance was saturated. The signal generator was then disconnected, and the growth of the output signal was

observed for a time interval of $10T_1$ duration. This procedure was repeated four to seven times for each orientation of the crystal, and the results were averaged to obtain T_1 .

The sample coil used in these experiments consisted of 12 uniformly spaced turns of 16-gauge copper wire wound on a thin-walled glass form that was approximately 1 in. long. The measured Q was 240. When in use the coil was mounted so that the axis of the cylindrical LiF crystal inside it was perpendicular to the magnetic field H_0 . Before irradiation, the test crystal was rotated in the coil until the observed linewidth of the resonance was minimized. In this orientation the $[110]$ axis is parallel to H_0 . A rotation of 45° then brings the $[100]$ axis parallel to H_0 . The crystal was marked to identify these orientations for later experiments. All measurements were made at room temperature.

III. RESULTS AND CONCLUSIONS

The experimental results are summarized in Fig. 2. The product of F -center concentration and f , the oscillator strength for F -band transitions in LiF, is plotted against the inverse of the spin-lattice relaxation time of the fluorine nuclei, T_1 , for two orientations of the crystal in the magnetic field H_0 . The oscillator strength is between 0.7 and 1.0, but has not yet been accurately determined.

The curves are linear for $(N_p f)$ less than $2 \times 10^{16} \text{ cm}^{-3}$. The experimental points in this region represent a series of 13 irradiations of 25 sec duration each. The fit to a straight line is very good in this region, and thus the dependence of T_1 on N_p predicted by equation (3) is confirmed. The curves satisfy the equation

$$(N_p + N_0)f = \frac{K}{T_1}, \quad (N_p f) \leq 2 \times 10^{16} \text{ cm}^{-3}. \quad (4)$$

Both curves are extrapolated to obtain the intercept with the $(N_p f)$ axis, which is nearly the same for both curves. The intercepts yield a value of N_0 , an effective F -center concentration that would produce the observed relaxation times in the unirradiated crystal. The slope K varies with crystal orientation. The values measured from the curves are $K_{110} = 1.11 \times 10^{18} \text{ sec cm}^{-3}$ and $K_{100} = 1.38 \times 10^{18} \text{ sec cm}^{-3}$, ± 3 per cent.

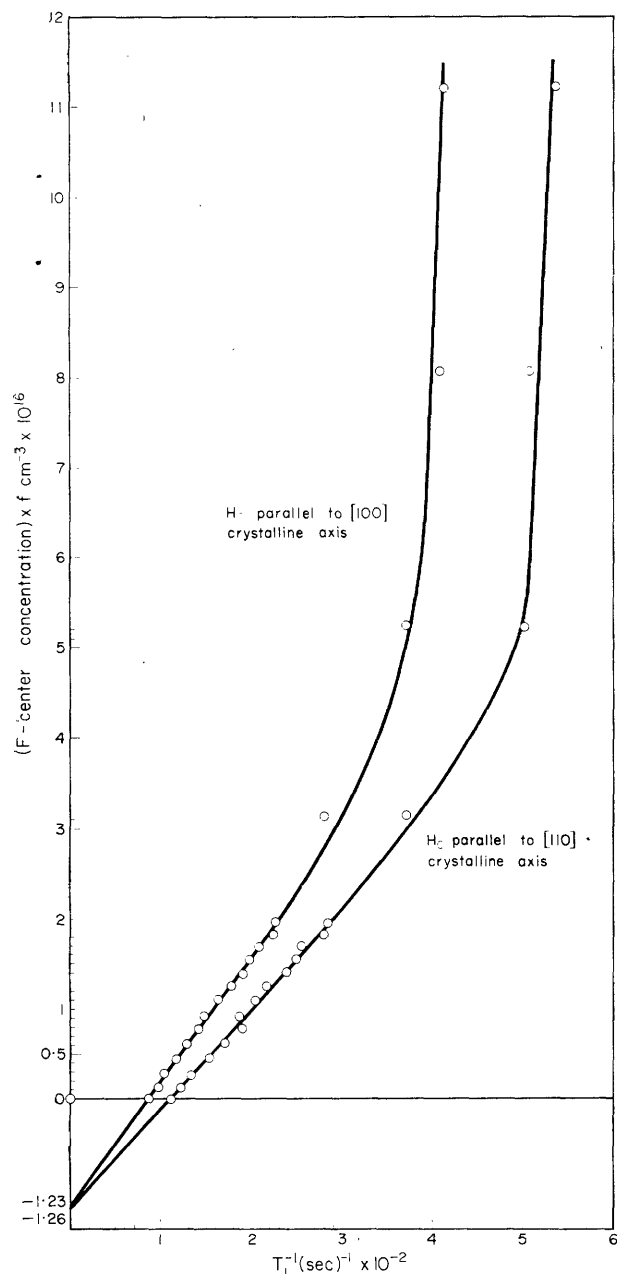


FIG. 2. Product of F -center concentration and oscillator strength plotted against the inverse of the spin-lattice relaxation time, T_1 , for fluorine nuclei in lithium fluoride for two orientations of the crystal in the magnetic field H_0 .

According to equation (3), K should be inversely proportional to $D^{3/4}$. The quantity λ in equation (1) has not been determined, so that D has not been calculated. However, it is of interest to calculate the ratio $(D_{100}/D_{110})^{3/4}$ under the assumption that λ is not a function of the crystal orientation in the magnetic field H_0 (as would be the case if the line shape were Gaussian for both orientations). Using equation (2), we obtain

$$(\overline{\Delta H^2})_{[100]}^{1/2} = 5.20 \text{ G}, \quad (\overline{\Delta H^2})_{[110]}^{1/2} = 3.70 \text{ G}.$$

The sums in equation (1) converge rather slowly. Term-by-term summation is carried out for $r_{ij} \leq \sqrt{50}b$, where b is the interionic spacing; the rest of the contribution is estimated by an integral under the assumption of a uniform density of fluorine nuclei of $1/4b^3 \text{ cm}^{-3}$. We obtain

$$\left[\sum_j r_{ij}^{-4} (1 - 3 \cos^2 \theta_{ij})^2 \right]_{100} = 4.11b^{-4},$$

$$\left[\sum_j r_{ij}^{-4} (1 - 3 \cos^2 \theta_{ij})^2 \right]_{110} = 4.85b^{-4},$$

so that $(D_{100}/D_{110})^{3/4} = 0.69$, and $(K_{110}/K_{100}) = 0.80$. Thus it appears that λ changes only slightly for the two orientation considered.

If the line shape were Gaussian, then we would have $\lambda = 1/\sqrt{8}$. An order-of-magnitude calculation of K can be carried out by using this value of λ and assuming that $\tau = 10^{-6} \text{ sec}$. For a resonance frequency of about 6.4 mc/s , $b = 10^{-8} \text{ cm}$, $\gamma_p = 1.8 \times 10^7 \text{ sec}^{-1} \text{ G}^{-1}$, $\gamma_n = 10^4 \times \text{sec}^{-1} \text{ G}^{-1}$ and $S = 1/2$, equation (3) gives $K \approx 2 \times 10^{18}$, which is in accord with the observed values.

We may ask whether the relaxation is truly diffusion-limited in this case, since BLUMBERG has shown that T_1 is also inversely proportional to N_p in the case of rapid diffusion in which the transfer of magnetic energy from the nuclear spin system to the lattice is limited by the paramagnetic impurity.⁽¹⁰⁾ However, $T_1 \propto (\overline{\Delta H^2})^{-1/2}$ for the rapid-diffusion case; this proportionality indicates that T_1 should decrease as the crystal is reoriented in the magnetic field, H_0 , so as to increase the linewidth. In the present experiment, T_1 was found to increase with such a reorientation. This variation is consistent with equation (3), and we conclude that this is a diffusion-limited case.

Referring again to Fig. 2, we see that for $(N_p f)$ greater than $5 \times 10^{16} \text{ cm}^{-3}$ the relaxation time becomes virtually independent of F -center concentration. Theoretically, such behavior is not to be expected until the impurity concentration rises to 0.1 per cent, or approximately 10^{19} impurities per cm^3 .

A possible source of this discrepancy might come from assuming that the paramagnetic centers are uniformly distributed throughout the lattice. The actual distribution is random, and this will give rise to some clustering which might reduce the mean effectiveness of paramagnetic centers in promoting relaxation. However, this is not the case. The relaxation time for a random distribution of paramagnetic centers is the same, within a negligible factor, as that for a uniform distribution. This equality arises from the fact that the Poisson distribution for finding one paramagnetic ion within a radius r is sharply peaked near $R_0 = (4\pi/3N_p)^{-1/3}$:

$$P(1|r) = \frac{4}{3}\pi r^3 N_p \exp[-(4/3)\pi r^3 N_p].$$

Furthermore, the relaxation time for a random distribution with r the variable of spacing, written in terms of the relaxation time, T_0 , for uniform distribution of paramagnetic ions, with $N_p^{-1} = 4/3\pi R_0^3$, is given by

$$T(r) = T_0 R_0^3 / r^3.$$

If we weight this relaxation time by the number of nuclei (or volume of the crystal) relaxed by a paramagnetic ion having a radius of influence r , and average, we have

$$\begin{aligned} \langle T_{\text{random}} \rangle &= \frac{\int_0^\infty T(r) P(1|r) r^2 dr}{\int_0^\infty P(1|r) r^2 dr} \\ &= \frac{T_0}{1 + \frac{4}{3}\pi b^3 N_p} \approx T_0. \end{aligned}$$

Thus, in order to explain the saturation of the relaxation time with N_p at the density that we observe, a clustering *greater* than that produced by a *random* distribution must be evoked.

From this point of view, there is good reason

to suppose that the distribution of vacancies in the crystal is not random. Vacancies tend to cluster around dislocation lines in a crystal, provided that they are sufficiently mobile to migrate. For a light alkali halide such as LiF, one would expect the vacancies to have negligible mobility at room temperature (that is, the activation energy necessary for ion-vacancy movement is very much greater than kT). However, clustering probably occurs during annealing after the crystal is grown from the melt, and it is reasonable to suppose that the crystal received from Harshaw Chemical Company has a distribution of halogen ion vacancies which is not random. Certainly, if a clustering argument is invoked to explain the data, the degree of clustering must be greater than that produced by a random distribution.

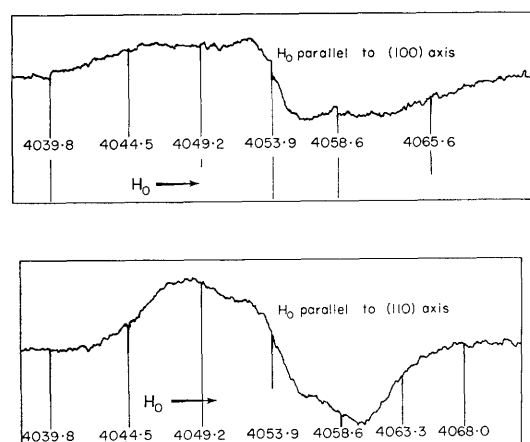


FIG. 3. Traces of the derivative of the fluorine absorption line in lithium fluoride for two orientations of the crystal in the magnetic field H_0 .

Figure 3 shows typical traces of the derivative of the fluorine absorption for two orientations of the crystal in the magnetic field, H_0 . These traces were made under unsaturated conditions with a modulation field of 2 G peak-to-peak. The slight asymmetry is spurious, resulting from non-linearity in the field sweep. There was no apparent change in the line shape as a result of irradiation.

For the field H_0 parallel to the $[110]$ crystalline axis, the second moment of the resonance line was measured with the use of the method of PAKE

and PURCELL⁽¹⁴⁾. We obtained $(\overline{\Delta H^2})^{1/2} = 3.9 \pm 0.3$ G. The width of the trace between points of maximum and minimum slope is 12.6 G. The ratio of these two values is 3.2; this is considerably different from the value of 2, which would be obtained if the line shape were Gaussian.

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