

Nuclear Magnetic Relaxation in LiF at High Temperatures

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(Received 11 June 1963)

Measurements of T_1 and T_2 , the spin-lattice and spin-spin relaxation times, are reported for Li^7 and F^{19} nuclei in a single crystal of LiF. $T_1(\text{Li})$ has been measured from room temperature to the melting point (1120°K) and the other quantities from 830°K to the melting point. Above 620°K, relaxation is caused exclusively by the diffusion of Li and F ions. $T_1(\text{Li})$, $T_2(\text{Li})$, and $T_1(\text{F})$ are mainly determined by ν_{Li} , the jump frequency of Li ions, and $T_2(\text{F})$ mainly by ν_{F} . Using a theory of relaxation developed elsewhere, ν_{Li} and ν_{F} are obtained for the region of intrinsic diffusion as $\nu_{\text{Li}} = 1.7 \times 10^{16} \exp(-1.81 \text{ eV}/kT)$ and $\nu_{\text{F}} = 4.5 \times 10^{17} \exp(-2.2 \text{ eV}/kT)$. For the extrinsic region, the motional activation energy of Li ions is obtained as 0.71 eV. The values of ν_{Li} are in good agreement with those obtained from conductivity measurements; to our knowledge, ν_{F} has never been measured by other methods. Below 620°K quadrupolar relaxation due to lattice vibrations and relaxation by paramagnetic impurities become important, and rough values are obtained for these contributions to $T_1(\text{Li})$. Large angular variations of T_1 and T_2 are observed in the region of relaxation due to atomic diffusion. $T_2(\text{Li})$ and $T_1(\text{Li})$ vary by a factor of 2 and 1.5, respectively, as a function of crystal orientation, in good agreement with theoretical prediction. A crude measurement of $T_1(\text{Li})$ in molten LiF is discussed.

I. INTRODUCTION

THE profound effect of diffusion on nuclear magnetic relaxation has been recognized since the earliest days of nuclear resonance. Frequently, in solids, the relaxation of a nucleus is affected only by the relative motions of nearby nuclei, hence, in principle, one could get a better microscopic picture of the diffusion process than is possible with ionic conductivity or radioactive tracer diffusion measurements. In practice, however, few nuclear-relaxation experiments have yielded diffusion parameters of comparable precision to those obtained by these other methods. Because of the indirect nature of the measurement, it cannot be on an equal footing with other methods until the theory of nuclear relaxation via diffusion is quantitatively understood. Many different relaxation mechanisms may be operative over the same temperature range, and it is not always obvious how to separate their effects. If a mechanism which is independent of diffusion predominates over a large temperature range, the amount of diffusion information obtainable may be greatly restricted. The latter situation prevails in many solids consisting of nuclei with large quadrupole moments. The most quantitative work to date seems to have been the relaxation measurements on metals by Holcomb and Norberg,¹ and Spokas and Slichter,² and the theoretical work of Torrey.³ Their success stems from the fact that magnetic dipolar relaxation due to translational diffusion is the dominant relaxation mechanism over a sizeable temperature range. The dipolar interaction strength is well known, and a theory of relaxation could be developed based on a simple microscopic model for diffusion. By contrast, the quadrupolar interaction

strength is not well known, it can arise from a variety of sources, such as minute traces of impurities or lattice imperfections, and the mechanisms through which it operates are varied, and in many cases uncertain.

LiF is an ideal solid for studying the effects of diffusion on nuclear relaxation. The Li^7 nucleus has a very small quadrupolar interaction, F^{19} has none, and both nuclei have large magnetic dipole moments. Both T_1 and T_2 , the spin-lattice and spin-spin relaxation times, can be measured for both nuclei, thus there are four quantities available to determine the diffusion of the two chemical species. This redundancy provides a good check on the internal consistency of the relaxation theory used, or alternatively, it might reveal a significant diffusion parameter other than ν_{Li} and ν_{F} , the jump probabilities per second, or jump frequencies of lithium and fluorine ions. A theoretical calculation somewhat different from Torrey's is described in another paper,⁴ and did, in fact, give good internal agreement.

At temperatures below 600°K, quadrupolar relaxation of lithium becomes significant, but we will not consider this in any detail. In a future publication we shall discuss extensive relaxation measurements in NaCl, where relaxation is largely quadrupolar, and all of the above mentioned difficulties appear. Measurements by others of relaxation in ionic crystals will be cited in the NaCl paper, since they were principally concerned with quadrupolar relaxation.

II. APPARATUS AND PROCEDURE

T_1 and T_2 were measured by conventional coherent rf pulse techniques similar to those described elsewhere.² The nonstandard units are a crystal oscillator and rf gate,⁵ a nonblocking receiver and phase detector,⁶ and a

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¹ D. F. Holcomb and R. E. Norberg, *Phys. Rev.* **98**, 1074 (1955).

² J. J. Spokas and C. P. Slichter, *Phys. Rev.* **113**, 1462 (1959).

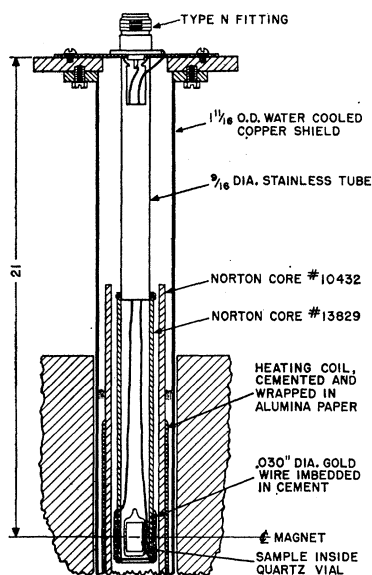
³ H. C. Torrey, *Phys. Rev.* **92**, 962 (1953); **96**, 690 (1954).

⁴ M. Eisenstadt and A. G. Redfield, following paper, *Phys. Rev.* **132**, 635 (1963).

⁵ R. J. Blume, *Rev. Sci. Instr.* **32**, 554 (1961).

⁶ R. J. Blume (to be published).

FIG. 1. The rf head and furnace.



boxcar integrator.⁷ The pulsed rf magnetic field H_1 was typically 20 G. It was found most convenient to use a single coil to provide H_1 and pick up the nuclear induction signal, hence, a bridge circuit was used to cancel the rf pulse at the receiver. All data were taken at 10.75 or 4.17 Mc/sec.

T_1 was usually measured by applying a 180° pulse followed by a 90° pulse a known time later. The size of the free induction tail following the 90° pulse is a measure of the recovery of the spin system towards thermal equilibrium. Occasionally a 90° - 90° or a 180° - 90° - 180° sequence was used. For the longest values of $T_1(\text{Li}^7)$ it was more expedient to demagnetize the nuclei with a succession of 90° pulses, and then measure their recovery with a 90° pulse. No dependence of the measured T_1 on the particular pulse sequences was observed. T_2 was measured by the spin-echo method whenever feasible. The shorter values were obtained by a direct measurement of the shape of the free induction tail. Each value of T_1 or T_2 was obtained from at least six points on a semilogarithmic plot of induction amplitude versus delay time. A good fit of these points to a straight line always obtained; the slope of the line is the relaxation time. Except for the shortest T_2 and longest T_1 values, the accuracy was always 10% or better.

The rf head and furnace are shown in Fig. 1. The furnace consists of 0.020-in.-diam platinum-rhodium wire noninductively wound on a threaded Alundum⁸ core and cemented in place. The wire was wound over an 8-in. length, which was adequate to keep the temperature gradient small. At 800°C the temperature was 5° less than its maximum value when the rf head was displaced 1 in. from the center of the furnace. The

core was wrapped in ceramic paper⁹ until it fit snugly inside a water cooled copper jacket. The whole assembly fit inside the $1\frac{3}{4}$ -in. gap of a magnet. Power for the heater was rectified and filtered to about 5% ac. To reach 800°C , 5.5 A at 85 V were required; the furnace was operated as high as 900°C on occasion. Magnetic fields due to the heater current caused no difficulty.

The rf head for operation at 10.75 Mc/sec consisted of 10 turns of 0.030-in.-diam gold wire wound on a threaded Alundum core. It was necessary to cement the coil in place to eliminate a spurious coherent signal generated by an acoustical vibration due to applying a large rf current in a magnetic field. The core was attached to a stainless steel tube and a suitable mount. For 4.17 Mc/sec operation, 24 turns of wire were used on a core with a more closely spaced thread. The Q of the coil was high to at least 900°C .

The LiF sample was a single crystal made by the Harshaw Company. It was turned on a lathe to a cylindrical shape, $\frac{3}{8}$ -in. diam and $\frac{3}{4}$ in. long. The cylinder axis was a cube axis of the crystal. The sample was sealed off in a quartz vial under about one-half atmosphere of spectroscopically pure argon, and placed coaxially inside the rf coil. At temperatures close to the melting point LiF vapors attacked the quartz to some extent, but this had no effect on the data, which was reproducible after 100 h of running time. The only impurities known to affect the data were divalent metal ions and paramagnetic ions. From the high-temperature data, one can determine that the molar concentration of divalent metal ions was about 3×10^{-6} , and from the large value of $T_1(\text{Li})$ obtained at 300°K , the concentration of paramagnetic ions must be much less than 10^{-6} . Such long relaxation times in Harshaw LiF crystals have also been observed by Low,¹⁰ Mahendroo,¹¹ and Andrew.¹²

Temperatures were measured with a Pt, Pt-Rh thermocouple in contact with the sample vial, and were held constant to 1°C during the course of a run. The rf head and furnace were operated in air. The sample was not annealed, and no special efforts were made to heat or cool the crystal slowly.

The crystal was oriented with one cube axis perpendicular to the magnetic field H_0 . The orientation of the other axes was not measured directly, but could be deduced by measuring the angular variation of T_1 and T_2 at one temperature. Because of crystalline symmetry, T_1 and T_2 must have maximum or minimum values when H_0 is parallel to a $[100]$ axis, and the reverse for a $[110]$ direction. The relative angles of rotation were accurate to $\pm 5^\circ$. The remainder of the data was taken

⁹ Fiberfrax Ceramic Fiber, Carborundum Company, Niagara Falls, New York.

¹⁰ F. J. Low and C. F. Squire, *J. Phys. Chem. Solids* **5**, 85 (1958).

¹¹ P. P. Mahendroo and A. W. Nolle, *Phys. Rev.* **126**, 125 (1962).

¹² E. R. Andrew, K. M. Swanson, and B. R. Williams, *Proc. Phys. Soc. (London)* **77**, 36 (1961).

⁷ R. J. Blume, *Rev. Sci. Instr.* **32**, 1016 (1961).

⁸ Norton Company, Refractories Division, Worcester 6, Mass.

at a single angle, which was determined from the data as $22^\circ \pm 5^\circ$.

III. DATA AND RESULTS

From 620 to 1120°K, relaxation is caused exclusively by the magnetic dipolar interaction between spins. The time variation of the interaction arises from the diffusion of lithium and fluorine ions, whose jump frequencies per second we denote by ν_{Li} and ν_F . In another paper⁴ we have derived expressions for T_1 and T_2 based on a random walk model, and will only give the final results here. These numerical results apply to LiF in the low-temperature region, i.e., where ν_{Li} , $\nu_F \ll \omega_0$, the Larmor frequency of the measured nuclei. Most of the data falls in this region. The values are for $\Theta = 0^\circ$ and 45° , where Θ is the angle between \mathbf{H}_0 and the [100] axis, for rotations in the (001) plane. For $\Theta = 0^\circ$,

$$\begin{aligned} T_1^{-1}(\text{Li}^7) &= 3.53 \times 10^{-7} \nu_{Li} + 2.90 \times 10^{-7} (\nu_{Li} + \nu_F), \\ T_1^{-1}(\text{F}^{19}) &= 26.0 \times 10^{-7} \nu_F + 77.0 \times 10^{-7} (\nu_{Li} + \nu_F), \\ T_2^{-1}(\text{Li}^7) &= 59.7 \times 10^7 \nu_{Li}^{-1} + 309 \times 10^7 (\nu_{Li} + \nu_F)^{-1}, \\ T_2^{-1}(\text{F}^{19}) &= 44.0 \times 10^8 \nu_F^{-1} + 145 \times 10^8 (\nu_{Li} + \nu_F)^{-1}; \end{aligned} \quad (1)$$

and for $\Theta = 45^\circ$,

$$\begin{aligned} T_1^{-1}(\text{Li}^7) &= 3.22 \times 10^{-7} \nu_{Li} + 6.83 \times 10^{-7} (\nu_{Li} + \nu_F), \\ T_1^{-1}(\text{F}^{19}) &= 23.7 \times 10^{-7} \nu_F + 60.8 \times 10^{-7} (\nu_{Li} + \nu_F), \\ T_2^{-1}(\text{Li}^7) &= 71.4 \times 10^7 \nu_{Li}^{-1} + 107.5 \times 10^7 (\nu_{Li} + \nu_F)^{-1}, \\ T_2^{-1}(\text{F}^{19}) &= 52.5 \times 10^8 \nu_F^{-1} + 50.6 \times 10^8 (\nu_{Li} + \nu_F)^{-1}. \end{aligned} \quad (2)$$

In the above evaluations, the Larmor frequency of the measured nuclei was 10.75 Mc/sec, and the lithium-fluorine interatomic spacing was taken as 2.07 Å, its value at 1000°K. Since this distance appears as r^{-6} , lattice expansion is of some importance, and values obtained from the literature¹³ were used in computing the temperature dependence of ν_{Li} and ν_F . The first terms in the above equations refer to the interaction between like nuclei, and the second terms, unlike. The contribution of like interactions has a small angular dependence, presumably because of the high coordination number of nearest neighbor nuclei, but the angular variation for unlike neighbors is considerable. As discussed in the theoretical paper, the angular dependence of T_1^{-1} and T_2^{-1} must be of the form $A + B \sin^4 \Theta$, so from the above equations, the relaxation times can be determined for any angle.

Equations (1) and (2) are accurate results for a random walk model, however, the motion of the nuclei are subject to spatial and temporal correlations. Estimates of corrections for correlation effects are given in the theoretical paper,⁴ and these corrected values should be good to within 10%, hence, they were used to reduce

¹³ A. Gott, Ann. Phys. (N. Y.) 41, 520 (1942).

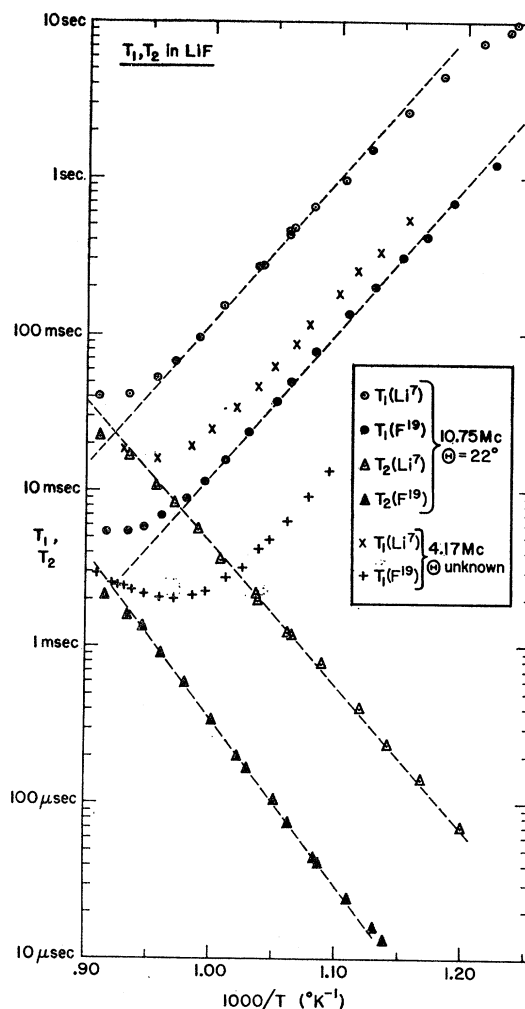


FIG. 2. The measured values of T_1 and T_2 versus $1000/T$ for the temperature region of relaxation via ionic diffusion.

the data. The equations, for $\Theta = 22^\circ$, become

$$\begin{aligned} T_1^{-1}(\text{Li}^7) &= 1.85 \times 10^{-7} \nu_{Li} + 3.68 \times 10^{-7} (\nu_{Li} + \nu_F), \\ T_1^{-1}(\text{F}^{19}) &= 13.6 \times 10^{-7} \nu_F + 51.6 \times 10^{-7} (\nu_{Li} + \nu_F), \\ T_2^{-1}(\text{Li}^7) &= 100 \times 10^7 \nu_{Li}^{-1} + 278 \times 10^7 (\nu_{Li} + \nu_F)^{-1}, \\ T_2^{-1}(\text{F}^{19}) &= 74.4 \times 10^8 \nu_F^{-1} + 131 \times 10^8 (\nu_{Li} + \nu_F)^{-1}. \end{aligned} \quad (3)$$

The high-temperature data are shown in Fig. 2. Only the data taken at 10.75 Mc/sec were analyzed. The general behavior is as expected for relaxation via a thermally activated jumping process. At low temperatures, $T_1 \sim \omega_0^2 \tau_c$ and $T_2 \sim \tau_c^{-1}$, where the correlation time τ_c can be roughly defined as the time for the interaction between two spins to change appreciably. Here τ_c will be the inverse of $2\nu_{Li}$ or $2\nu_F$ for interactions between like nuclei, and $\nu_{Li} + \nu_F$ for unlike nuclei. The jump frequencies will be of the form $\nu = \nu_0 \exp(-\Delta E/kT)$, where ΔE is an activation energy for diffusion. If $\nu_F \ll \nu_{Li}$, a logarithmic plot of $T_1(\text{Li})$,

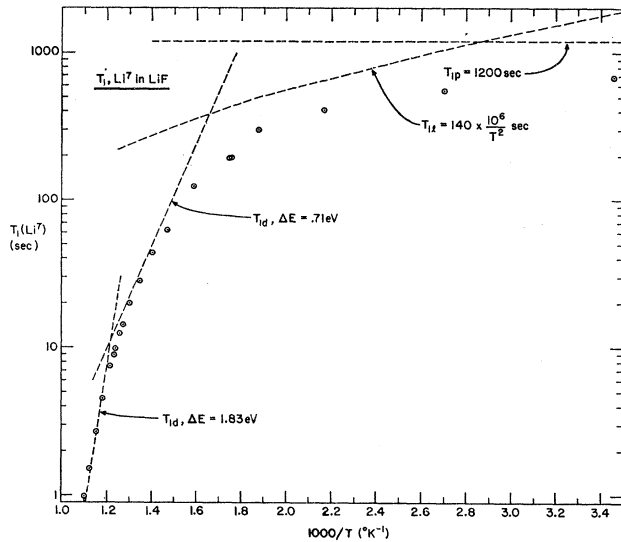


FIG. 3. The measured values of $T_1(\text{Li}^7)$ from 910°K to room temperature. The dashed lines are the best fit to the data of T_{1p} , relaxation by paramagnetic impurities; T_{1l} , quadrupolar relaxation via lattice vibrations; and T_{1d} , dipolar relaxation via ionic diffusion.

$T_1(\text{F})$, and $T_2(\text{Li})$ versus T^{-1} would have a low-temperature asymptote whose slope is $(\Delta E)_{\text{Li}}$, and a plot of $T_2(\text{F})$ would have a slope $(\Delta E)_{\text{F}}$. This can be seen from the forms of Eqs. (3). From the measurements, we obtain $\nu_{\text{F}} \approx 0.2\nu_{\text{Li}}$, hence, both terms must be included in Eqs. (3) to determine accurate jump frequencies, but $T_1(\text{Li})$, $T_1(\text{F})$, and $T_2(\text{Li})$ will be determined mainly by ν_{Li} and $T_2(\text{F})$ by ν_{F} .

When $\tau_c \approx \omega_0^{-1}$, T_1 will have a minimum, and at higher temperatures, T_1 should increase with a slope $\sim \Delta E_{\text{Li}}$. T_2 should show a small kink at the T_1 minimum, and then become equal to T_1 at higher temperatures. LiF melts before the high-temperature asymptote is reached, but the T_1 minimum and T_2 kink can be observed. Some T_1 data taken at 4.17 Mc/sec are also shown in Fig. 2; T_1 is shorter, and the minimum occurs at a lower temperature, as expected. These data were not analyzed since Θ was not determined.

Figure 3 shows $T_1(\text{Li})$ from 910°K to room temperature. The slope of the high-temperature data begins to decrease at $T \approx 800^\circ\text{K}$. This change in slope corresponds to the characteristic "knee" found in conductivity and diffusion plots, the region where the number of vacancies in the crystal becomes constant, and equal to the number of divalent metal impurities present. The activation energy here is the energy of motion of an ion, whereas the higher temperature activation energy is the energy of motion plus the energy of formation of a vacancy. At 700°K the slope begins to decrease markedly with decreasing temperature, and $T_1(\text{Li})$ approaches a constant value near room temperature. The low-temperature data can be fit with a combination of two relaxation mechanisms, $T_1^{-1} = T_{1p}^{-1} + T_{1l}^{-1}$,

where T_{1p} is a constant contribution of 1200 sec due to paramagnetic impurities, and $T_{1l} = 140 \times 10^6 T^{-2}$ sec, quadrupolar relaxation due to lattice vibrations. The existence of these mechanisms in alkali-halide crystals has been well established. The low-temperature values of T_1 are not very accurate, and the values given above for T_{1p} and T_{1l} are probably only good to about 40%, but they are important as a correction factor to obtain the jump frequencies in the region of impurity-controlled diffusion.

Using Eqs. (3) we solve for ν_{Li} and ν_{F} by a simple iteration. The final value of ν_{F} is determined from the $T_2(\text{F})$ equation, using a mean value of ν_{Li} determined from the other three equations. Similarly, the first three equations are used to obtain ν_{Li} , using values of ν_{F} for the relevant temperatures. The final values are shown in Fig. 4. The internal agreement of the three determinations of ν_{Li} is excellent. The best fit of the low-temperature asymptotes for the region of intrinsic diffusion yield $\nu_{\text{Li}} = 1.7 \times 10^{16} \exp(-1.81 \text{ eV}/kT)$ and $\nu_{\text{F}} = 4.5 \times 10^{17} \exp(-2.2 \text{ eV}/kT)$. The long dashed line is ν_{Li} as determined from Haven's conductivity data,¹⁴ and the agreement is quite good. His values have been corrected for the contribution of ν_{F} , since he assumed it was negligible. The short dashed lines are values obtained from the data without applying correlation corrections. The jump frequencies are about 30% lower than values obtained from a conductivity measurement.

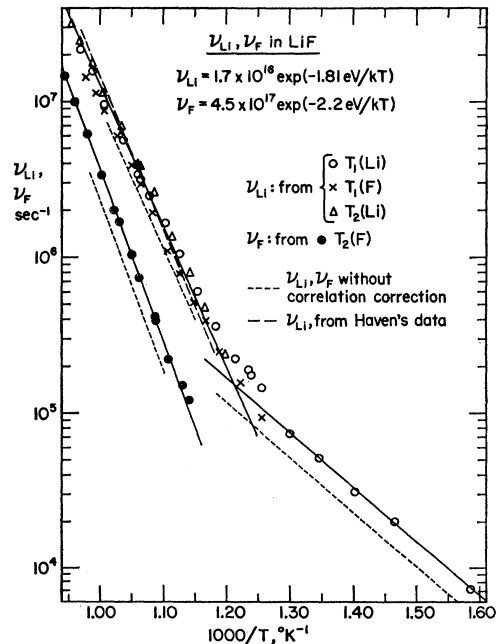


FIG. 4. Values of ν_{Li} and ν_{F} derived from the data using Eqs. (3). The values of ν_{Li} obtained from Haven's conductivity data are shown as a long dashed line. The short dashed lines are obtained from the data without applying a correlation correction.

¹⁴ Y. Haven, Rec. Trav. Chim. 69, 1471 (1950).

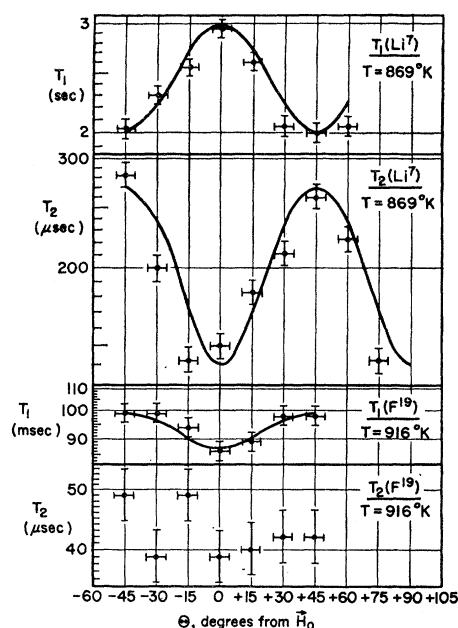


FIG. 5. The variation of relaxation times with orientation of the magnetic field. The solid curves are the best fit to the data of curves of the form $A + B \sin^4 \Theta$.

This disparity is about the same as is found between tracer diffusion and conductivity measurements. To our knowledge, there has been no previous measurement of fluorine diffusion in LiF.

The region below the "knee" is of limited accuracy, since much of it depends on knowing the quadrupolar contribution to relaxation. The turning point depends on the divalent metal impurity content of the crystal, which was not known, but the slope is independent of impurity content until impurity-vacancy association occurs. The data yield a motional activation energy of 0.71 eV, in good agreement with Haven's value of 0.65 eV. Haven gets the concentration of thermal vacancies as $c_v = 5.0 \times 10^2 \exp(-1.34/kT)$. Since the "knee" occurs roughly at a temperature where the concentration of thermal vacancies is equal to the concentration of divalent metal impurities, we obtain an impurity concentration for our sample as 3×10^{-6} , a typical amount for Harshaw crystals.¹⁵ In calculating ν_{Li} in this region, we have assumed $\nu_F = 0$. At the very worst, this would introduce a 10% error, but there is reason to expect ν_F to approach zero, due to the "salting-out" effect.¹⁶ However, if there were an appreciable concentration of positive-negative vacancy pairs, ν_F would show a "knee" similar to ν_{Li} . Unfortunately, there are no $T_2(F)$ data with which to determine this. Relaxation-time measurements on doped LiF crystals, which would have

¹⁵ As discussed by R. W. Dreyfus, in *The Art and Science of Growing Crystals*, edited by J. J. Gilman (John Wiley & Sons, Inc., New York 1963), Chap. 21.

¹⁶ A. B. Lidiard, *J. Phys. Chem. Solids* **6**, 402 (1958).

turning points at much higher temperatures, might shed light on the question of pairs.¹⁷

The derived values of ν_{Li} begin to deviate from a straight line at the highest temperatures, since the condition $\nu_{Li}, \nu_F \ll \omega_0$ on which Eqs. (3) are based is no longer fulfilled. The region where $\nu_{Li}, \nu_F \approx \omega_0$ could be treated by the theory, but it would be laborious, and there is not enough data to warrant it.

Figure 5 shows the angular variation of T_1 and T_2 at fixed temperatures well below the T_1 minimum. The solid curves are of the form $A + B \sin^4 \Theta$, and are normalized to fit the data. Since absolute values of Θ were not directly measured, the combined T_1 and T_2 data were shifted along the Θ axis until the best fit to the above curves was obtained. The $T_2(F)$ data were rather poor, due to their small values. The other quantities have maxima or minima at the same angle, and have the correct periodicity required by symmetry. The most significant quantity for comparison with theory is the ratio of relaxation times at $\Theta = 0^\circ$ and $\Theta = 45^\circ$, since for a fixed temperature this ratio will be independent of jump frequencies. The comparison is shown in Table I, and the agreement is good.

TABLE I. Comparison of theoretical and experimental ratios of relaxation times for [100] and [110] orientations.

		Theory	Experiment
Li ⁷ , T = 869°K	$T_1^{-1}[100]/T_1^{-1}[110]$	0.62	0.67
	$T_2^{-1}[100]/T_2^{-1}[110]$	1.93	2.0
F ¹⁹ , T = 916°K	$T_1^{-1}[100]/T_1^{-1}[110]$	1.25	1.1
	$T_2^{-1}[100]/T_2^{-1}[110]$	1.08	≈ 1

IV. MOLTEN LiF

A brief attempt to measure T_1 in the molten salt was made, and a crude value of $T_1(Li)$ was obtained. Two serious difficulties prevented an accurate determination of T_1 . The conductance¹⁸ of molten LiF is about $8 \Omega^{-1} \text{cm}^{-1}$, hence it is necessary to subdivide the sample in order to maintain a high enough Q and allow the rf field to penetrate the entire sample. Furthermore, molten LiF is highly reactive, and a quartz container is decomposed in a very short time. Following Yim and Feinleib, we used boron nitride as a container material. A BN cylinder consisting of twenty 0.042-in.-diam holes and a tight-fitting BN cap was constructed, and LiF powder was pressed into the holes. The nuclear-resonance signal from the melt was adequate, however, the molten salt was extremely fluid, creeping up through the threaded cap, and also through the walls themselves. The sample remained in the container long enough to make only one measurement. At $T = 1132^\circ\text{K}$, $T_1(Li) = 7 \pm 2$ sec. This corresponds to an increase in ν_{Li} of

¹⁷ N. Laurance, *Phys. Rev.* **120**, 57 (1960).

¹⁸ E. W. Yim and M. Feinleib, *J. Electrochem. Soc.* **104**, 626 (1957).

about 400 in the melt. The electrical conductivity of the solid¹⁴ at the melting point is $3 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ and the liquid¹⁸ is $8.4 \Omega^{-1} \text{ cm}^{-1}$, an increase of about 3000. Our observed increase in $T_1(\text{Li})$ is also large, but not as large as might be expected. We cannot say much else about molten LiF.

V. CONCLUSIONS

We have obtained jump frequencies of lithium and fluorine ions in a LiF single crystal over a wide temperature range with an accuracy comparable to conductivity and diffusion methods. As an added advantage, both quantities could be obtained for the same crystal by the

same set of measurements. It should be possible to extend this work to doped LiF crystals, or to other crystals containing nuclei with small quadrupolar interactions and reasonable magnetic moments.

ACKNOWLEDGMENTS

Several illuminating discussions were held with R. L. Garwin and C. P. Slichter. R. J. Blume and W. V. Kiselewsky developed most of the electronics for the experiment. Finally, we wish to thank A. G. Redfield for numerous suggestions on both the theoretical and experimental aspects of this work, and for his hospitality during the author's stay in his laboratory.

Nuclear Spin Relaxation by Translational Diffusion in Solids

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(Received 11 June 1963)

Expressions for T_1 and T_2 have been derived for dipolar relaxation via atomic diffusion using the general theory of nuclear spin relaxation. General methods of evaluating the autocorrelation functions of various terms in the dipole-dipole Hamiltonian are discussed, and cubic symmetry requirements are given. A random walk model is used for the calculation, but rough estimates are made of the effects of correlation in direction and time of successive jumps of atoms for the vacancy mechanism of diffusion; if account were taken of these correlations, the derived relaxation times might change by a factor of nearly 2. Detailed computations are made only in the limits of high and low field. The random walk model yields an expression for T_1 in the high-field limit identical to that given by Torrey. Zero-frequency spectral densities needed for computation of T_2 , and also T_1 at low field, are expressed as lattice sums involving only the dipolar interaction and the sum of the probabilities of n -step random walks between lattice points (an extension of the Polya problem). Detailed computations of T_1 and T_2 have been made for two or more species of spins diffusing on an NaCl or fcc lattice. The angular dependence of T_1 and T_2 may be large for the NaCl lattice in the high-field limit. The agreement with Torrey's theory for T_1 in the fcc lattice is good.

I. INTRODUCTION

THE possibility that nuclear magnetic resonance would be a useful technique for the study of atomic diffusion was suggested in the early paper of Bloembergen, Purcell, and Pound¹ and such studies have been made on a number of solids. The simplest theory of relaxation due to diffusion can be expressed by the formulas²

$$T_1^{-1} \approx \langle \omega_i^2 \rangle \tau_c (1 + \omega_0^2 \tau_c^2)^{-1}, \quad (1)$$

$$T_2^{-1} \approx \langle \omega_i^2 \rangle \tau_c \times \frac{1}{2} [1 + (1 + \omega_0^2 \tau_c^2)^{-1}]. \quad (2)$$

Here ω_0 is the resonance angular frequency, τ_c is of the order of the jump time for diffusion, and ω_i is the strength of the interaction of the nucleus with the per-

turbation responsible for relaxation, in frequency units. These expressions are based on the assumption of an autocorrelation function for the interaction of the simple form $\langle \omega_i^2 \rangle \exp(-t/\tau_c)$, as discussed in Sec. 5.7 of Ref. 2. They are applicable only to the "motionally narrowed" region of temperature; that is, where $\tau_c \ll \omega_i^{-1}$. This is the only region we will consider in this paper. For nuclei having spin $\frac{1}{2}$ or a small electric quadrupole moment, relaxation occurs via the magnetic dipolar interaction between spins, and ω_i is of the order of the rigid lattice linewidth, typically a few kc/sec. If relaxation occurs because of electric quadrupolar interactions, ω_i may be many Mc/sec. For systems in which ω_i is reasonably well known, Eqs. (1) and (2) can predict τ_c from T_1 and T_2 measurements to within an order of magnitude. For more precise results, it is necessary to use a more complicated correlation function based on a detailed model of the microscopic diffusion process. We will develop such a formulation in this paper. We restrict ourselves to the case of relaxation via magnetic dipolar interactions, because the form and

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¹ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

² C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, Inc., New York, 1963).