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CONTRACT NO. AT(11-1)-1105
REPORT NO. CGO-1105-147

SPIN-LATTICE RELAXATION AND
ATOMIC MOTIONS IN LiF

BY
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A thesis submitted in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY
(Physics)

at the

UNIVERSITY OF WISCONSIN

1970

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SPIN-LATTICE RELAXATION AND ATOMIC MOTIONS IN LiF

JEROME WAGNER

Under the Supervision of Associate Professor P. R. Moran

Spin-lattice relaxation times of the ^7Li spins in LiF have been investigated using pulsed NMR techniques to determine the dominant mechanisms contributing to the normal high field relaxation, $1/T_1$, at laboratory fields of several kilogauss and also those contributing to the rotating frame relaxation, $1/T_{1\rho}$, corresponding to effectively low fields obtained by keeping the spins saturated. The experiments exhibit the very long intrinsic T_1 of LiF enabling one to achieve exceptional sensitivity to very dilute and very long correlation time interactions with defects and impurities and to study these interactions in the relatively low temperature region, $T < 400^\circ\text{K}$.

The most outstanding relaxation phenomena, and the one of principal interest in this work, is due to the motion of vacancies bound to divalent impurities; these effects are observed in $T_{1\rho}$ for temperatures greater than about 280°K and completely dominate $1/T_{1\rho}$ at temperatures greater than room temperature. The bound vacancy activation energy measured from the experiments is 0.43 eV, which is about 0.2 eV less than the activation energy of free vacancies. The mechanism dominating the relaxation at these temperatures is the fluctuating quadrupolar interaction between the vacancy and nearby spins.

A strong collision theory is developed to explain rotating frame quadrupolar relaxation in several different regimes of vacancy jump times, τ_v . The rf field dependence of $T_{1\rho}$ indicates that the τ_v 's that we observe are long enough that the quadrupolar interactions suffer no motional narrowing effects but remain sufficiently short that nuclei experiencing a large quadrupole interaction are effectively thermally isolated from other nearby nuclei for a time long compared with τ_v .

The dominant relaxation mechanism from nitrogen temperature to room temperature in both the laboratory frame and rotating frame measurements appears to be the interactions of both the Li and F spins with fast relaxing paramagnetic centers whose concentrations are only a few ppm. The relaxation behavior due to this process is in agreement with the theory of Lowe and Tse when one properly includes both nuclear spin species.

Above room temperature, the T_1 's in high field remain insensitive to the vacancy motion dominating $1/T_{1\rho}$, but they show some structure which is strongly temperature dependent though relatively small in magnitude. That this structure is sample dependent identifies its source as trace impurities, but the experimentally observed complexity precludes any easy identification or detailed interpretation.

Acknowledgements

It is my pleasure to thank Professor P. R. Moran for suggesting and directing the research discussed in this paper. His interest and encouragement were appreciated. Special thanks are due him for his work on the theoretical considerations to be discussed.

I would like to thank Sitapati Row Kasturi for his assistance in all phases of the experiment. I would also like to thank Bob Leach, Clarence Docken, Cliff Voight, Darrell Loper, Ervin Podgorsak, and Matt Weber for their help in the design, construction, performance and analysis of the experiment. Valuable discussions were held with Dr. Dave Lang. Dave Fields and Luis Barroilhet also provided assistance.

Special acknowledgements are made to Professor John Cameron, who was my major Professor during my first years of graduate school and who continued to support my work till the present. His advice and confidence in me were most valuable during my entire stay in graduate school.

Finally, I would like to thank my wife and family for their patience during the preparation of this paper.

This work was supported under grant AFOSR-69-1749 of the U. S. Air Force Office of Scientific Research and grant AT-(11-1)-1105 from the U. S. Atomic Energy Commission.

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GENERAL BACKGROUND

Research has been conducted to study diffusion and ultraslow atomic-like motions in crystals of lithium fluoride using nuclear magnetic resonance techniques. NMR techniques have been used for many years in studying internal motions in liquids and crystals. The important classic paper in this area is that of Bloembergen, Purcell, and Pound (BPP) in 1948.¹ Their experiments were based upon the idea that motions within a liquid will tend to disturb the "effective dipolar energy," that is, the energy due to the dipole-dipole interactions between spins of the system. These fluctuations in the dipolar field contribute to the spin-lattice relaxation rate, $1/T_1$, of the nuclear spins. The relaxation rate is proportional to the amplitude of the power spectrum of the fluctuations at the nuclear Larmor frequency ω ; this amplitude is largest when the correlation time, τ , of the fluctuations is approximately the inverse of the Larmor frequency. Therefore, looking at $1/T_1$ as a function of correlation time (or temperature), one will observe a peak at that point where $\omega\tau \approx 1$. The peak is easily observed only if T_1 from other processes is greater than the T_1 due to motion; i.e., $1/T_1)_{\text{diff}} > 1/T_1)_{\text{other}}$. Measurements of T_1 behavior on either side of this $1/T_1$ peak can be analyzed to give information about the characteristics of the internal motions. Torrey² carried out a more elegant calculation for the case of solids, but approached the problem in essentially the same manner by treating the fluctuations as a small perturbation with respect to the rest of the Hamiltonian

of the system.

Interpretation of experimental results based upon these theoretical treatments suffer from the difficulty that a perturbation approach is valid only if each jump contributes a small amount to the relaxation of the system. If each jumping atom were to act significantly to relax the crystal, the change in the energy would be large with each jump, and a perturbation calculation would be incorrect. Moreover, there is an experimental problem with BPP in solids at large static applied fields H_0 of several kilogauss; the relaxation rate in solids typically is increased significantly only in a relatively small region around $\omega\tau \approx 1$. Thus, since $\omega = \gamma H_0$ (where γ is the gyromagnetic ratio) is a high field Larmor frequency, to study internal motions of the solid by investigating the behavior of τ through its influence on T_1 , measurements must be done at very high temperatures, normally near the melting point. At lower temperatures other processes will dominate the relaxation. If the relaxation occurs at low applied fields, the spins are sensitive to slower atomic motions as the $\omega\tau \approx 1$ region is transformed to lower temperatures, but to obtain a magnetic resonance signal with a reasonable signal to noise ratio one must work at high fields.

In the experiments to be described here we use an approach developed by Slichter and Ailion^{4,5} (SA) which substantially helps to avoid both the theoretical and the experimental difficulties. In the long correlation time limit ($\omega\tau \gg 1$) where perturbation theory fails, SA showed that one can use a strong collision theory based upon a

spin temperature description. In this thesis a similar theory is developed to extend interpretation to the processes present in LiF. The conflict between high fields for detectability and low fields for sensitivity to slow motions is overcome by working with the spin system in high fields but simultaneously saturated by a resonant rf field. Under these conditions, the spins sense a small effective field equal to the resultant of the applied rf field H_1 and the dipolar local fields H_2 of the spins. Typically this effective field is 1/1000 of the static applied field H_0 . This general approach was justified initially by Redfield²² and is most easily treated theoretically by transforming the system into a reference frame rotating at the Larmor frequency. The formal details of this transformation and its use in interpreting measurements in terms of effectively low fields has been discussed amply in the literature.^{17,33,34} The relaxation phenomena observed in this manner have been called rotating frame relaxation and they allow one to investigate atomic motions in solids which are orders of magnitude too slow to be detected by using the BPP procedure.

The theoretical treatment of BPP may also be extended to quadrupolar relaxation by diffusing charges.^{3,21} In addition to changing the dipolar magnetic fields, the motion of atomic charges causes a variation in electric field gradients produced by those charges at the sites of nearby nuclei; the resulting fluctuations in the quadrupolar energy then act to relax the system. The mathematical approach to the problem is similar to the one used by BPP: one

calculates the effect of random statistical fluctuations in the Hamiltonian due to atomic motions. As the form of the quadrupolar Hamiltonian is similar to that of the dipolar Hamiltonian, the relaxation rate expressions calculated for the two interactions will be similar in form.

A great deal of work has been done on alkali halides in general and LiF in particular looking at relaxation times as a function of temperature,^{7,35} irradiation,³⁶ orientation,³⁷ and other parameters. Eisenstadt, for instance, has studied LiF at high temperatures⁷ and NaCl around the quadrupolar free vacancy peak.⁸ However, there has not been a careful study made of lithium fluoride in the temperature region near room temperature, nor have any rotating frame measurements been made. The relaxation in this region should be dominated by the lattice vibration-induced quadrupolar interactions in very pure samples¹⁹ or by paramagnetic impurities in the less pure crystal.¹⁸ Preliminary experiments showed that these background relaxation rates were exceptionally small in LiF so that we should expect correspondingly high sensitivity in effects due to slow atomic motions.

We also felt it worthwhile to look in this region for diffusion for possible correlation with thermoluminescent processes in lithium fluoride.³⁸ The use of thermoluminescence (TL) in radiation dosimetry has become very widespread in the last five years. Though its use has increased greatly, the basic microscopic TL mechanism in LiF is still not well understood. We hoped that an NMR investigation of the diffusional properties of LiF in a region near the useful TL region

might help resolve some questions concerning TL. As most good thermoluminescent LiF has a low temperature TL glow peak near 80°C ,³⁸ it was decided to investigate the relaxation times by looking for diffusional processes from near room temperature upto about 80°C in the high field experiments and from nitrogen temperature to about 80°C in the rotating frame work. The relevance of these results to thermoluminescence will be discussed in Appendix (3).

I. INTRODUCTION

In the experiments described here, NMR techniques were used to study spin-lattice relaxation rates for the ^7Li spins in LiF as a means of investigating slow atomic motions in the crystal in a temperature range from liquid nitrogen temperature up to about 80°C . Relaxation measurements were made of both the ordinary high field, or lab frame, and the effectively low field, or rotating frame, relaxation. This work is done on the lithium resonance as it is sensitive to both dipolar and quadrupolar interactions and since the fluorines in LiF have such a short T_2 so as to severely limit the experimental conditions under which they can be reliably observed.

The first approach for treating relaxation due to atomic motion was developed by Bloembergen, Purcell, and Pound¹ (BPP) and later refined by Torrey.² Reif³ extended the application to cases where quadrupolar interactions are present. Slichter and Ailion^{4,5} extended the region of usefulness in studying slow atomic motions to effectively low fields by making use of the rotating frame transformation to interpret relaxation occurring in the presence of saturating resonant rf fields.

In the Slichter and Ailion experiments, the rotating frame spin-lattice relaxation time, $T_{1\rho}$, is the quantity determined. Using the experimental techniques developed by Slichter-Ailion⁵ or Look and Lowe,⁶ the spin system may be tipped from being along the applied static field, H_0 , to being locked along the resultant of the rf field, H_1 , and the local field, H_ℓ . The rate of loss of the magnetization

that is spin locked along this effectively low field is denoted by $1/T_{1\rho}$ and differs, in general, from $(1/T_1)$, the relaxation rate along H_0 in the absence of applied rf fields.

Investigating T_1 at high temperatures has yielded much useful information concerning internal motions in the alkali halides.⁷⁻¹¹ Although $T_{1\rho}$ measurements have been recently employed with success on other substances,^{5,12,14} the only other rotating frame alkali halide work was done on NaCl by Kumano and Hanabusa¹⁵ in 1968. Both T_1 and $T_{1\rho}$ measurements should be useful in determining many properties of motion within alkali halide crystals and also in obtaining information about nuclear spin equilibration and relaxation. Activation energies, jump times, concentrations of moving entities can all be determined through the T_1 and $T_{1\rho}$ measurements. In systems having both dipolar and quadrupolar interactions, one might expect to learn about the relative strengths of the interactions.

In the present experiments, we are principally interested in the movement of extrinsic vacancies and vacancy related complexes in LiF. These studies are carried out to understand the basic considerations necessary in interpreting rotating frame relaxation in the alkali halides. Although these experiments do yield activation energies and jump time, we do not pursue a detailed investigation to determine their systematic variations.

The extraordinary sensitivity of rotating frame relaxation to internal motions is clearly revealed in this work. Even in our samples where paramagnetic impurities give background relaxation at least an order of magnitude greater than intrinsic lattice

vibration processes, we can observe vacancy motions at concentrations less than 10 ppm where the average vacancy jump time is about 10 ms. We wish to emphasize, however, that detection of such rare events must, as usual, be paid for in long data accumulation times. For a T_1 on the order of one half hour and several relaxation curve points necessary to specify $T_1\rho$ reliably, a single $T_1\rho$ versus T datum requires about 4 hours of experimental time. The time necessary to determine $(T_1)_{\text{Lab}}$ is even longer. The acquisition time alone represented by the graphs presented later is about 400 hours.

The theoretical treatment of SA is not directly applicable to the LiF system, and it is necessary to develop and extend the theory considerably. We must account for such considerations as large quadrupolar interactions in addition to the dipolar interaction, the effect of binding the moving vacancy to a divalent impurity, the possibility of non-equilibration among all the spins, and that LiF is a two spin species material. Kumano and Hanabusa have also treated the case of quadrupolar relaxation in the rotating reference frame, but their interpretation differs considerably from that derived in the theory section of this paper.

The remainder of the paper is organized into the following sections. In section II, we will give the experimental procedures used and the details of the experiment. In section III, we will develop the theoretical considerations necessary for an understanding of the experimental results. In section IV, we will present our results and their interpretation according to the theoretical

development. In the final section, we summarize our results and conclusions.

II. EXPERIMENTAL PROCEDURES

The experiments were performed on an 8 MHz pulsed NMR spectrometer which was constructed to employ a gated rf transmitter and phase coherent detection. A block diagram of the apparatus is shown in Fig.1. A field regulated 9" Magnion magnet was set at 4825 gauss for the ^7Li resonance.

The cross coil probe used is similar in design to that of Clark¹¹ and Ailion.¹⁶ The sample holder was machined from nylon which softens at about 100°C, placing an upper temperature limit on the present set of experiments. The transmitter coils were wrapped on a brass Faraday shield. A brass can, with a brass rod extending below it, fit over the sample holder and shield; the entire system was suspended in a dewar. A nichrome wire heater was wound on the extending brass rod. This rod, then, connected the rest of the probe to both the heat source (nichrome heater) and the cold liquid nitrogen reservoir in the dewar. A stable sample temperature was obtained by allowing the system to reach a steady state thermal equilibrium. The temperature was measured and monitored with a chromel-alumel thermocouple positioned on the top surface of the crystal. Once equilibrium was established, a stable temperature could be maintained both above and below room temperature for several hours with a stability better than $\pm 2^\circ\text{C}$. As the sample itself was not in direct contact with the thermal source, temperature gradients across the sample should be negligible.

The $T_{1\rho}$'s were measured using the pulse sequence described by

Ailion and Slichter.⁵ The spins are allowed to equilibrate for a time about equal to $(T_1)_{\text{Lab}}$. The static field, which specifies the z-direction, is pulsed about 25 gauss off resonance, and the rf is then turned on sharply. The field pulser adiabatically returns H_0 to the resonance value while the rf is on. As the spins are in the x-y plane, the free induction decay (FID) can be observed when the rf is sharply turned off after a waiting interval τ .

During this interval, which may be minutes, the spin system may be further adiabatically demagnetized in the rotating frame to approximately zero H_1 field. The H_1 field is varied adiabatically by modulating the voltage on the screen of the driver tube in the transmitter. For long $T_{1\rho}$'s this can be done manually, but for short $T_{1\rho}$'s the demagnetization to small H_1 was performed by an electronic modulator. For a given set of experimental conditions, the spin-locking process is repeated for several different time intervals τ and $T_{1\rho}$ is found from the equation

$M_x = (M_x)_{\text{initial}} \exp(-\tau/T_{1\rho})$; no observable deviation from this exponential dependence was detected.

The lab frame T_1 's are determined by measuring the FID signal after a very short spin-locking sequence as a function of time between these short spin-locking pulses. In this case, one observes an exponential growth to equilibrium with a time constant equal to T_1 .

The samples used were 0.5cm^3 ($0.7 \times 0.7 \times 1 \text{ cm}$) single crystals of LiF with normal ^6Li abundance (7.43%).* One crystal,

*The crystals were obtained from the Harshaw Chemical Co., Cleveland, Ohio.

denoted by LiF:Mg, was analyzed spectroscopically** to have about 100 ppm Mg^{++} doped into it plus trace impurities in the range of 1-10 ppm of the following: Al, Ca, Fe, Si, Ag. The other, denoted LiF-pure was of optical grade. However, due to the NMR measurements, thermoluminescent measurements, and the fact that other LiF has been obtained with a much longer T_1 , it is expected that similar amounts of trace impurities are present in the LiF:Mg and LiF-pure. The times necessary to do the measurements on purer crystals are prohibitively long, at least as viewed in relation to the primary motivations for undertaking the studies described here.

All experiments were performed with H_0 along the [110] crystalline axis. In this alignment, $H_\ell^2 = 15.4g^2$, obtained from a second moment calculation. This is about the same as the powder average H_ℓ^2 .

**The analyses were done by Harshaw and the Lawrence Radiation Laboratories, Livermore, California.

III. THEORY

A. Basic Interactions

We now attempt to describe the behavior of spin-lattice relaxation due to atomic motions for nuclei in an insulating solid. The approach is basically an extension of the treatment of Slichter and Ailion,¹ but we wish to include the following considerations. Because the electrostatic fields of defects in an insulator are not shielded to the extent they are in a metal and because quadrupolar interactions will be sensitive at lower temperatures to phenomena with much longer jump times than dipolar interactions, quadrupolar interactions may provide a dominant relaxation mechanism. Also, in a material with more than one type spin, the dipolar field and resulting rotating frame heat capacities of one specie, e.g., ^7Li in LiF , may be dominated by the interaction associated with another nuclear specie, e.g., ^{19}F in LiF .

For the purpose of clarity, we treat LiF explicitly and restrict our discussion to vacancy motion. However, generalization to other systems should be straightforward. The rotating frame Hamiltonian for the ^7Li system, under the application of a large static external field $H_0 \hat{z}$ and an rf field whose frequency ω is close to the Larmor frequency and whose amplitude has a component H_1 rotating in the Larmor sense, may be written¹⁷

$$H_r = H_r^0 + H' = -(\gamma_{\text{Li}} H_0 - \omega) I_z - \gamma_{\text{Li}} H_1 I_x + H_d^0 + H_Q^0 + H'. \quad (1)$$

In Eq. 1, the spin operators appearing in the Zeeman interaction are

the total ${}^7\text{Li}$ spin components, e.g., using h_0 to denote the effective z-component of magnetic field, $h_0 = (H_0 - \omega/\gamma_{\text{Li}})$,

$$-\gamma h_0 I_z = -\gamma h_0 \sum_j I_{zj}, \quad (2)$$

where the sum extends over all lithium spins.

H_d^0 is the secular part of the total dipole-dipole interactions:

$$H_d^0 = H_d^0(\text{Li-Li}) + H_d^0(\text{Li-F}) + H_d^0(\text{F-F}). \quad (3)$$

The total system interactions must be included in the effective dipolar Hamiltonian of the ${}^7\text{Li}$ because all such terms are intercoupled. Explicit expressions for the interaction terms in Eq. 3 may be found in many other papers and reference texts.¹⁷

H_Q^0 in Eq. 1 is the secular part of the ${}^7\text{Li}$ quadrupolar Hamiltonian:

$$H_Q^0 = \frac{eQ}{4I(2I-1)} \sum_{v,j} V_0(v,j)(3I_{zj}^2 - I_j^2). \quad (4)$$

The notation in Eq. 4 follows that adopted by Slichter;¹⁷ $V_0(v,j)$ represents the second derivative with respect to the z-coordinate of the electrostatic potential at nucleus "j" as produced by an impurity or defect at lattice position "v," and eQ denotes the quadrupole moment of the nucleus.

The final term in Eq. 1, H' , includes not only the nonsecular parts of the quasi-static dipolar and quadrupolar interactions but also such effects as lattice-vibration-induced dipolar and quadrupolar interactions and hyperfine interactions with small concentrations of paramagnetic defects. The fluctuations in these produce the normal "laboratory-frame" spin-lattice relaxation, T_1 . The

resulting relaxation rate $(1/T_1)$ and its dependence on the physical processes included in H' has been thoroughly analyzed elsewhere¹⁸⁻²¹ and these results will be referred to as needed.

One can, however, perform relaxation experiments with H_1 sufficiently large that the spin dynamics are dominated by the $(-\gamma H_1 I_x)$ term in Eq. 1 rather than by the relaxation effects arising from H' . In this case,²² the system is said to be "spin-locked" in the rotating frame; application of statistical or thermodynamic methods are valid only in the rotating frame representation defined by Eq. 1. The density matrix, ρ , of the system is then defined in terms of the rotating frame representation and in terms of a rotating frame spin temperature $(kT_s)^{-1} = \beta$.

$$\rho = \exp [-H_r^0 \beta] [\text{Tr}(\exp(-H_r^0 \beta))]^{-1} \quad (5)$$

It is important to realize that when we speak of the relaxation of the spin system we mean primarily the relaxation of β :

$$\partial_t \beta = -(1/T_{1\rho})_{\text{obs}} (\beta - \beta_{\text{eq}}) \quad (6)$$

We seek to describe the behavior of the total observed rotating frame relaxation rate $(1/T_{1\rho})_{\text{obs}}$ under conditions of resonant rf fields ($h_0 \approx 0$, $\beta_{\text{eq}} \approx 0$); in particular, we will look at how long correlation time fluctuations in H_d^0 and H_Q^0 contribute to $(1/T_{1\rho})_{\text{obs}}$.

First, let us note that

$$(1/T_{1\rho})_{\text{obs}} = (1/T_{1\rho}) + (1/T_1)' \quad (7)$$

where $(1/T_1)'$ is the contribution due to laboratory frame effects, H' . The relaxation rate $(1/T_{1\rho})$ is produced by changes in H_d^0 and H_Q^0 .

and it is this contribution we examine in the remainder of this section.

In our samples, vacancy motion would appear to be the predominant defect state contribution to $(1/T_{1\rho})$. Therefore, we will want to relate the average vacancy jump time, τ_v , to the interaction correlation times, τ_{cQ} and τ_{cd} . First, since the interaction H_Q^0 in Eq. 4 depends upon the spatial position of the vacancy, the quadrupolar interaction felt by a particular nucleus changes in a time τ_v ; thus $\tau_{cQ} \approx \tau_v$. In contrast, the interactions in H_d^0 are internuclear. In this case, the relevant time interval is the time during which the interaction between any pair of nuclei remains unchanged; $\tau_{cd} \approx \tau_v(N/N_v)$, where N is the total number of nuclei in the sample which can possibly change positions due to a vacancy jump and N_v is the number of vacancies. The consequences of $\tau_{cQ} \neq \tau_{cd}$ will be discussed later in this section.

B. Relaxation via Free Vacancy Motion

Case 1. Very large τ_v

The behavior of $(1/T_{1\rho})$ depends upon how interaction correlation times compare with other characteristic times of the system. We discuss first the case in which τ_v is large compared with both typical inverse frequency splittings generated by H_Q^0 and the characteristic time required for these quadrupolar split levels to approach thermal equilibrium with the bulk nuclei. The former condition insures that the nuclear spin alignment at a particular time can be described on the average in terms of their local interactions at that time; the

latter insures that the temperature describing this local alignment is the common rotating frame temperature of the entire spin system. This is the situation treated by SA for dipolar interactions only.

Following SA, we calculate the change in energy of the spin system induced by a single vacancy jump. We denote the energy change by $\langle \Delta E \rangle$, the quadrupole and dipole interactions before and after the jump as $H_d^0 + H_Q^0$ and $H_d^{0'} + H_Q^{0'}$, respectively, and we write the density matrix for $h_0=0$ in the high temperature limit from Eq. 5 and 1 as

$$\rho \approx [1 - (-\gamma H_1 I_x + H_d^0 + H_Q^0)\beta] / [\text{Tr}(1)] . \quad (8)$$

Then $\langle \Delta E \rangle$ is

$$\langle \Delta E \rangle = \text{Tr}[\rho(H_d^{0'} + H_Q^{0'})] - \text{Tr}[\rho(H_d^0 + H_Q^0)] , \quad (9)$$

which can be evaluated using Eq. 8, and we then obtain

$$\frac{\langle \Delta E \rangle}{\Delta t} = -\frac{N_v}{\tau_v} \frac{[\text{Tr}(H_d^0 H_d^{0'} + H_Q^0 H_Q^{0'}) - \text{Tr}(H_d^{02} + H_Q^{02})]\beta}{[\text{Tr}(1)]} , \quad (10)$$

where there are N_v vacancies jumping at an average rate $1/\tau_v$. Using the expression for the total spin energy, $\langle E \rangle$,

$$\langle E \rangle = -\text{Tr}[(\gamma H_1 I_x)^2 + H_d^{02} + H_Q^{02}]\beta / \text{Tr}(1) , \quad (11)$$

we can then identify

$$\langle \Delta E \rangle / \Delta t \langle E \rangle^{-1} = (\partial_t \beta) \beta^{-1} = -1/T_{1\rho}, \quad (12)$$

and thus obtain from Eqs. 10 and 11,

$$\frac{1}{T_{1\rho}} = \frac{N_V}{\tau_V} \frac{[\text{Tr}(H_d^{02} - H_d^0 H_d^{01}) + \text{Tr}(H_Q^{02} + H_Q^0 H_Q^{01})]}{\text{Tr}[(\gamma H_I I_X)^2 + H_d^{02} + H_Q^{02}]} \quad (13)$$

We first evaluate the denominator:

$$\text{Tr}[(\gamma H_I I_X)^2] = \text{Tr}[\gamma^2 H_I^2 (\sum_j I_{Xj})^2] = (\gamma H_I)^2 (2I+1) N \frac{1}{3} I(I+1); \quad (14)$$

$$\text{Tr}[H_d^{02}] = \text{Tr}[\frac{1}{2} \sum_{i,k} (H_{dik}^0)^2] = N \text{Tr}[\frac{1}{2} (\sum_k H_{dik}^0)^2]; \quad (15)$$

and

$$\text{Tr}[H_Q^{02}] = \text{Tr}[\sum_{v,\ell} (H_{Qv\ell}^0)^2] = N_V \text{Tr}[\sum_{\ell} H_{Qv\ell}^{02}]. \quad (16)$$

The trace of the cross terms in Eq. 15 vanish. The cross terms do not vanish in Eq. 16 but may be neglected for dilute concentrations of randomly dispersed vacancies. The trace on the right-hand side of Eq. 15 is that appearing in the VanVleck second moment¹⁷ and is defined by SA as the dipolar local field contribution,

$$\text{Tr}[\frac{1}{2} \sum_k (H_{dik}^0)^2] = (2I+1) N \frac{1}{3} I(I+1) \gamma^2 H_{\ell}^2. \quad (17)$$

By analogy, we can define an effective quadrupolar field contribu-

tion related to the trace in Eq. 17,

$$\text{Tr} \left[\sum_{\ell} (H_{Qv\ell}^0)^2 \right] \equiv (2I+1)^N \frac{1}{3} I(I+1) \gamma^2 H_Q^2 \quad (18)$$

The dipolar energy change term in the numerator of Eq. 13 can be evaluated as detailed by SA, who obtain the expression

$$\begin{aligned} \text{Tr}[H_d^{02} - H_d^0 H_d^{0'}] &= 2\text{Tr} \left[\frac{1}{2} \sum_j H_{dv'j}^0 (H_{dv'j}^0 - H_{dvj}^0) \right] \\ &= 2(1-p_d)(2I+1)^N \frac{1}{3} I(I+1) \gamma^2 H_d^2, \end{aligned} \quad (19)$$

where formal evaluation yields the dipolar order parameter, p_d , which takes into account both that the local fields are somewhat correlated as the nucleus moves from v' to v and that the jumping nucleus has a vacancy as a near neighbor. The quadrupolar energy change term in the numerator of Eq. 13 can be similarly treated:

$$\begin{aligned} \text{Tr}[H_Q^{02} - H_Q^0 H_Q^{0'}] &= \text{Tr} \left[\sum_j (H_Q^{02}(v,j) - H_Q^0(v,j) H_Q^0(v',j)) \right] \\ &= (1-p_Q) \text{Tr} \left[\sum_j (H_Q^0(v,j))^2 \right], \end{aligned} \quad (20)$$

which from Eq. 19 gives

$$\text{Tr}[H_Q^{02} - H_Q^0 H_Q^{0'}] = (1-p_Q)(2I+1)^N \frac{1}{3} I(I+1) \gamma^2 H_Q^2 \quad (21)$$

Finally, the expression for $(1/T_{1\rho})$ in Eq. 13 can now be written

$$\frac{1}{T_{1\rho}} = \frac{N_V}{N\tau_V} \frac{2(1-p_d)H_\ell^2 + (1-p_Q)H_Q^2}{(H_1^2 + H_\ell^2 + (N_V/N)H_Q^2)} \quad (22)$$

The form of the denominator reflects the fact that every nucleus in the sample sees roughly the same dipolar local fields, whereas only a small fraction of the nuclei suffer quadrupole interactions. From a perturbation theory approach in the limit of correlation times long compared with the typical inverse splitting frequencies, one can derive a local $(1/T_1)$ whose denominator is $(H_1^2 + H_\ell^2 + H_Q^2)$. However, when this local relaxation is distributed over the total spin system by a mechanism sufficiently rapid to maintain long range thermal equilibrium, the average $(1/T_{1\rho})$ is related to the local $(1/T_1)$ by the ratio of the local heat capacity to the bulk heat capacity. This then yields Eq. 22.

Case 2. Intermediate τ_V

We now consider the situation for which τ_V is still sufficiently large that $\gamma(H_1^2 + H_\ell^2 + H_Q^2)^{1/2}\tau_V \gg 1$ but for which the local field splittings are so large that τ_V is small compared with the time to achieve equilibration with the bulk. Thus, we imagine only local equilibrium in which the high temperature approximation for the density matrix is

$$\rho \approx \frac{[1 - \sum_j (-H_1 I_{xj} + \frac{1}{2} \sum_k H_{dj k}^0 + \sum_v H_Q^0(v,j)) \beta_j]}{\text{Tr}[1]} \quad (23)$$

This expression is similar to that in Eq. 8, except for the factor β_j , which indicates a local inverse temperature different from the bulk average β to the extent that $H_Q^0(v,j)$ provides a splitting large enough to give thermal isolation.

We assume a complete isolation model (very dilute vacancy concentration) in order to relate β_j to β : Prior to the appearance of the vacancy at position v , the density matrix for nuclei in the locality of v was

$$\rho = [1 - \sum_j (-\gamma H_1 I_{xj} + \frac{1}{2} \sum_k H_{djk}^0) \beta] / \text{Tr}(1) \quad (24)$$

At a certain time the vacancy arrives at position v , and at that instant the energy is

$$\begin{aligned} \langle E \rangle = & \text{Tr}[(1 - \sum_j (-\gamma H_1 I_{xj} + \frac{1}{2} \sum_k H_{djk}^0) \beta) (\sum_\ell (-\gamma H_1 I_{x\ell} \\ & + \frac{1}{2} \sum_m H_{d\ell m}^0 + \sum_v H_Q^0(v,\ell))] / \text{Tr}(1) \quad (25) \end{aligned}$$

In the time interval τ_v before the vacancy jumps away, the spins locally come into alignment along the new interactions so that the density matrix evolves to that given by the expression in Eq. 23. However, since the spins now seeing the interaction are isolated from the bulk, there is no energy change during the interval τ_v and the energy may be written

$$\begin{aligned}
\langle E \rangle = & \text{Tr} \left\{ \left[1 - \sum_j (-\gamma H_1 I_{xj} + \frac{1}{2} \sum_k H_{djk}^0 + \sum_v H_Q^0(v, j)) \right] \beta_j \right\} \\
& \times \left[\sum_\ell (-\gamma H_1 I_{x\ell} + \frac{1}{2} \sum_m H_{d\ell m}^0 + \sum_v H_Q^0(v, \ell)) \right] / \text{Tr}(1) .
\end{aligned} \tag{26}$$

By equating the expressions in Eqs. 25 and 26, one obtains

$$\begin{aligned}
& \sum_j \text{Tr} [\gamma^2 H_1^2 I_{xj}^2 + \frac{1}{2} \sum_k H_{djk}^0 + \sum_v H_Q^{02}(v, j)] \beta_j \\
& = \sum_j \text{Tr} [\gamma^2 H_1^2 I_{xj}^2 + \frac{1}{2} \sum_k H_{djk}^{02}] \beta .
\end{aligned} \tag{27}$$

To relate β_j and β , we will assume that the quadrupolar energy changes are of such short **range** that the dominant relaxation effects are confined to nuclei which are nearest neighbors of the moving vacancy. Then using the definition of H_Q^2 in Eq. 18, one can approximate from Eq. 27

$$\beta_j = \beta (H_1^2 + H_\ell^2) / (H_1^2 + H_\ell^2 + \alpha H_Q^2) , \tag{28}$$

where α is given in terms of the average nearest neighbor interactions by

$$\alpha \approx \langle \text{Tr} [H_Q^{02}(v, j)] \rangle_{nn} / \sum_j \text{Tr} [H_Q^{02}(v, j)] . \tag{29}$$

The condition that these local spins are isolated from the bulk necessarily implies that the local quadrupole interactions are very

much larger than dipolar interactions. We consequently neglect dipolar contributions to $\langle \Delta E \rangle$ and write

$$\frac{\langle \Delta E \rangle}{\Delta t} = -\frac{N_V}{\tau_V} \text{Tr} \left[\sum_j (H_{Qj}^{\circ 2} - H_{Qj}^{\circ} H_{Qj}^{\circ'}) \beta_j \right] / \text{Tr}[1] . \quad (30)$$

Identifying $(1/T_{1\rho})$ and using Eq. 29, we find

$$(1/T_{1\rho}) = \frac{N_V}{N\tau_V} \sum_j \frac{[\text{Tr}\{H_{Qj}^{\circ 2} - H_{Qj}^{\circ} H_{Qj}^{\circ'}\}]}{(H_1^2 + H_\ell^2 + \alpha H_Q^2)} \frac{(H_1^2 + H_\ell^2)}{(2I+1) \frac{N}{3} I(I+1) \gamma^2 (H_1^2 + H_\ell^2 + \frac{N_V}{N} H_Q^2)} \quad (31)$$

which in the limit of dilute vacancy concentrations, gives according to the definition in Eq. 21

$$(1/T_{1\rho}) = \frac{N_V}{N\tau_V} \frac{(1-p_Q) H_Q^2}{H_1^2 + H_\ell^2 + \alpha H_Q^2} . \quad (32)$$

It is useful to recall that αH_Q^2 in the denominator of Eq. 32 is approximately given by the average squared quadrupole splitting of the levels of a nucleus neighboring the defect,

$$\alpha H_Q^2 \approx (\gamma^2 h^2)^{-1} \langle H_Q^{\circ 2} \rangle_{\text{nearest neighbor levels}} . \quad (33)$$

Eq. 32 is essentially the same expression as that obtained by Kumano and Hanabusa; our derivations differ considerably, and these differences will be discussed further in Appendix 4.

Case 3. Large H_1 limit. In the limit that $H_1^2 \gg (H_\ell^2 + H_Q^2)$, the $(1/T_{1\rho})$ of Eq. 22 and 32 reduce to the same expression. However, only the parts of H_d° and H_Q° which do not commute with the dominant $(-\gamma H_1 I_x)$ term of the Hamiltonian are capable of rapidly transferring their energy fluctuations into spin realignment along H_1 ; just as with the lab frame relaxation, the parts of H_Q° and H_d° which are secular with respect to $-\gamma H_1 I_x$ remain effectively decoupled.

In this case, one must express the interactions as the sum

$$H_Q^\circ + H_d^\circ = (H_{Qn}^\circ + H_{dn}^\circ) + (H_{Qs}^\circ + H_{ds}^\circ), \quad (34)$$

where H_{Qs}° and H_{ds}° are the parts of their respective interactions which commute with I_x and which are also adjusted to have zero trace. For example, from Eq. 4 we can obtain

$$H_{Qn}^\circ = \frac{eQ}{4I(2I-1)} \sum_{v,j} V_0(v,j) (2I_z^2 - I_y^2 - \frac{1}{3}I^2), \quad (35)$$

and

$$H_{Qs}^\circ = \frac{eQ}{4I(2I-1)} \sum_{jv} V_0(v,j) (I_x^2 - \frac{1}{3}I^2). \quad (36)$$

Once again, one calculates the energy change occurring during a vacancy jump but uses H_{Qn}° and H_{dn}° terms in Eq. 34. The procedure leading to Eq. 22 now yields

$$(1/T_{1\rho}) = \frac{N_v}{N\tau_v} \frac{2(1-p_d)H_{\ell n}^2 + (1-p_Q)H_{Qn}^2}{H_1^2}, \quad (37)$$

where $H_{\ell n}^2$ and H_{Qn}^2 are calculated from Eqs. 17 and 18, respectively, except that only the H_{Qn}^o and H_{dn}^o parts are employed.

Case 4. Short τ_v . We now consider the limit in which $(\gamma H_Q)\tau_v \ll 1$, but $\gamma(H_{\ell}^2 + H_1^2)^{1/2} \frac{N\tau_v}{N_v} \gg 1$, and H_1 is of comparable magnitude to the local fields. In this situation, the quadrupole fluctuations are motionally narrowed, and a perturbation theory approach can be validly applied to show that the spins achieve in a time τ_v only a small partial alignment along the effective quadrupole interaction fields. This fractional alignment can be shown to be approximately

$\gamma^2(H_Q^2 + H_1^2 + H_{\ell}^2) \left(\frac{\tau_v}{T - p_Q}\right)^2$; because of the strong motional narrowing effect, the system is also effectively in the large H_1 limit with respect to the quadrupole interactions so that only the non-secular parts of H_Q^o contribute to the relaxation process. The quadrupolar contribution to $(1/T_{1\rho})$ can then be expressed as

$$(1/T_{1\rho})_Q = \left(\frac{N_v}{N}\right) \gamma^2 H_{Qn}^2 \frac{\tau_v}{T - p_Q} \quad (38)$$

On the other hand, for free vacancy diffusion inter-nuclear terms in H_d^o have a characteristic fluctuation time $\left(\frac{N\tau_v}{N_v}\right)$ which is assumed to be very long, and their contribution to $(1/T_{1\rho})$ will be that associated with Case 1. The total relaxation rate is thus given by

$$(1/T_{1\rho}) = \left(\frac{N_v}{N\tau_v}\right) \frac{2(1-p_d)\gamma^2 H_{\ell}^2}{H_1^2 + H_{\ell}^2} + \frac{N_v}{N} \frac{\gamma^2 H_{Qn}^2 \tau_v}{(1-p_Q)} \quad (39)$$

and when $(\gamma H_{Qn})^2 \tau_v^2 \ll 1$, the second term in Eq. 39 becomes negligible. In this case, the $(1/T_{1\rho})$ given by Eq. 39 is identical to that derived by SA.

C. Relaxation via Bound Vacancy Motion.

We shall now discuss what special considerations are necessary if the vacancies are bound to divalent impurities. This is very likely in the temperature range of the experiments, for example, with a nearest neighbor (nn) binding energy of 0.4eV, a divalent ion concentration of 100 ppm, and a temperature of 400°K, the probability of finding an unbound vacancy is less than 10^{-2} . Since the probability of thermally forming vacancies near room temperature is negligible, almost all vacancies present will be the result of charge compensation for divalent impurities.²³ Due to electrostatic attraction, the divalent charge and vacancy can form a bound complex. As indicated by other work,²⁴⁻²⁶ the vacancy binding energy is about equal for nearest neighbors or next nearest neighbors (nnn) of the impurity. Fig. 2 shows the type of complexes we are considering and the possible type of vacancy jumps. We shall neglect the type jump when the vacancy and divalent impurity exchange places.²⁵

The quadrupolar interaction will now be the result of an electric dipole (impurity-vacancy). The motion is then the re-orientation of this dipole. However, the previous sections equations relating to this, Eqs. 18 and 20, will still be correct provided the effects of both the vacancy and divalent impurity are included

in the evaluation of $(1-p_Q)$, i.e., $(1-p_Q)_{\text{complex}} \neq (1-p_Q)_{\text{free}}$.

If the divalent impurity has no magnetic moment (as is the case with Mg^{++}) then the correction again is in the evaluation of $(1-p_d)$ and is very straight forward. As in the quadrupolar case, $(1-p_d)_{\text{complex}} \neq (1-p_d)_{\text{free}}$. All of these order parameters will be evaluated in Appendix 1 for the specific case of this experiment.

For bound vacancies, we would also expect a shortening of the dipolar correlation time, τ_{cd} . Now, the number of nuclei that can possibly jump due to vacancy motion in the bound complex is "17", the number of spin positions where a vacancy is bound to the complex. Thus, $\tau_{cd} \approx 17\tau_v$ rather than $\tau_{cd} \approx \frac{N}{N_v} \tau_v$ for free vacancy diffusion. For our previous Case 4, the difference in the motional narrowing limits for quadrupole and dipole interactions will not be nearly as great for bound complexes as for free vacancy diffusion. This, however, does not change qualitatively the possibility of seeing a transition from quadrupolar dominated to dipolar dominated relaxation as τ_v decreases. Hence, the form of the approximate result given in Eq. 39 remains applicable to the case of bound vacancies.

Our previous calculations will seriously run into problems only if the vacancy motion is rapid enough to develop a spin diffusion bottleneck and thereby create very hot spots in the crystal. No such problems are expected in the current experiment. They would become apparent as a non-exponential decay of the magnetization.

IV. DISCUSSION

The data for $(1/T_1)_{\text{Lab}}$ and $(1/T_{1\rho})$ vs. temperature for both the nominally pure LiF and the 100 ppm Mg^{++} doped LiF are shown in Figs. 3 and 4. We shall discuss the low temperature (77°K to 200°K) regions of both graphs first. Another more pure crystal obtained from Harshaw was measured in this laboratory to have a T_1 of ≈ 2 hours, a value 4 to 5 times longer than the T_1 's presented in Fig. 3. A rough calculation of relaxation times via quadrupolar and dipolar interactions as a result of lattice vibrations yields times of approximately 10^4 - 10^6 sec. This is at least an order of magnitude larger than the times we measure. Therefore, all effects we see are extrinsic and due to defects present even in our nominally pure crystal.

The LiF-pure low temperature $(1/T_1)$ curve exhibits a small positive slope with T_1 running from about 2000 to 1000 seconds between room temperature and liquid nitrogen temperature. The LiF:Mg sample exhibits what appears to be qualitatively similar behavior except for the increased higher temperature structure and T_1 's of about a factor of 3 shorter than in the LiF-pure case. The magnitude of this low temperature relaxation rate and its relatively weak temperature dependence suggests that it arises from a type of paramagnetic impurity whose concentration is in the range of a few parts per million and whose electron spin relaxation rate is large compared with the nuclear Larmor frequency, i.e., $\omega_{\text{Li}} \tau_c \ll 1$. For example, Tse and Lowe¹² observe a low temperature lab frame

peak in Cerium doped CaF_2 due to the paramagnetic Ce^{3+} impurity. The slope of their graph in the $\omega\tau_c \ll 1$ region is very similar to ours.

In addition, Lowe and Tse^{18,12} show that, for relaxation due to paramagnetic centers in the short correlation time region, the ratio $(T_{1\rho}/T_1)$ should be ≈ 1 , going from 0.86 in the rapid diffusion-high temperature region to 1.62 in the diffusion limited-low temperature case. This was shown for fluorine in CaF_2 . In our case, however, we have a two spin species system. In laboratory frame relaxation experiments, the Li and F spin systems are decoupled, whereas in rotating frame relaxation, the F-F dipolar reservoir is well coupled to the Li spins²⁷ (see Eq. 3). Consequently paramagnetic impurity induced relaxation of the fluorine spins contributes to the observed $(1/T_{1\rho})$ of the Li system. The expected relaxation rate would be enhanced by the ratio of $\gamma_F^2/\gamma_{\text{Li}}^2$ times the relative heat capacities of the fluorine terms to the entire system. For our case, this yields a corrected ratio $(T_{1\rho}/T_1) \approx 0.2$ from the Lowe and Tse predictions; this value is in good agreement with the experimental results presented in Figs. 3 and 4.

Furthermore, both of our samples have traces (1-10 ppm) of various impurities, several of which are paramagnetic; the divalent diamagnetic impurity concentrations differ, on the other hand, by at least an order of magnitude. Thus we are confident in assuming that this low temperature background relaxation rate is not associated with the divalent impurity doping but can be attributed to fast relaxing paramagnetic interactions.

We also note that there appears to be more structure in the 200-250°K region for the LiF:Mg ($1/T_1$) vs T curves than for the LiF-pure sample. In the absence of further systematic experiments with larger and well-controlled paramagnetic impurity doping, little more can be said concerning the low temperature ($1/T_1$) behavior.

Let us now turn to the higher temperature regions of Figs. 3 and 4. Expanded temperature scale drawings of each are given in Figs. 5 and 6. The rotating frame graphs of both LiF-pure and LiF:Mg show a steep linear slope becoming visible at about 250°K. This would imply an $\omega\tau_c \gg 1$ region of an activated process. The ratio of the relaxation rates of the LiF:Mg to the LiF-pure is greater than an order of magnitude. We associate this process with the motion of vacancies introduced by the divalent impurities in the two samples. This relaxation mechanism is the principal motivation behind the experiments reported here. We will return shortly to a complete discussion of these results.

The high temperature lab frame curves (Fig. 5) show a great deal of structure. The clearest part is the apparent peak in the nominally pure LiF; we find this feature to be especially puzzling and interesting because of the considerations we discuss below. It is tempting to try and identify this with an activated process occurring within the crystal. If the base line is subtracted from this data, the peak becomes clearer as shown in Fig. 7. However, due to the relatively large base line relaxation rate and the errors

associated with it and the data, the uncertainties for this curve are very large. We have also plotted on this same figure, as an example, theoretical curves following the form of Cohen and Reif²¹ for quadrupolar relaxation via motion of external charges normalized to have the same peak value and temperature as our data. The theoretical shape for dipolar relaxation is very similar. Free vacancy activation energies for LiF are 0.65 eV.²⁸ However, if this motional peak were related to vacancies or divalent diamagnetic impurities, one would expect the LiF:Mg curve to show a significant enhancement in peak size. This is not seen. There does appear to be structure in this region in the LiF:Mg but none is easily identified with the LiF-pure peak. At best, any corresponding peak would be only a factor of 3 larger, far less than the factor of 13 seen in the rotating frame high temperature slopes.

Even though such structure, therefore, appears to be associated with some other trace impurity interactions and consequently not related to our principal interests, we find it puzzling that this peak does not appear in the rotating frame curves. One might expect it to occur at $\approx 225^\circ\text{K}$ with a magnitude of tens of seconds in the $T_{1\rho}$ data if it were the result of atomic motion effects. Even if it is assumed to be due to paramagnetic centers, Tse and Lowe¹² observe, in the $\omega\tau_c \gg 1$ region, $T_{1\rho}$ minima that are at least two orders of magnitude shorter and shifted to lower temperatures than the corresponding lab frame T_1 's. These would also be apparent and, yet, are not observed.

Sato⁹ has observed what we believe to be similar peaks in NaCl:Mn. He associates it with the decomposition of higher complexes into single complexes. It still would not be clear why the process would not transform into the rotating frame, unless there is some thermal quenching effect that is occurring.

Now let us return to the dominant feature of the rotating frame relaxation, the high temperature activated ($1/T_{1\rho}$) process seen in Fig. 6. These measurements were done with the system demagnetized; that is the relaxation occurs after the system is adiabatically demagnetized in the rotating frame to almost zero H_1 so that the heat capacity associated with H_1 is negligible with respect to H_z . H_1 is left on to keep the average magnetization "in the rotating frame." By subtracting the extrapolated low temperature base ($1/T_{1\rho}$) (shown as dotted lines in Fig. 6) in both the nominally pure and Mg^{++} -doped LiF, one obtains the results seen in Fig. 8. The apparent shoulder at the low temperature side in Fig. 6 is chosen as the base line because this gives the best fit of the lower temperature data to the straight line through the higher temperature data where logarithmic uncertainties due to the base line subtraction are negligible.

The activation energies obtained from the slopes of the LiF-pure and LiF:Mg lines in Fig. 8 are 0.41 ± 0.03 eV and 0.45 ± 0.03 eV, respectively. The error estimates are the standard deviations from a least squares fit of the data. These activation energies are of the same order as values for vacancy diffusion in LiF. The ratio

the $(1/T_{1\rho})$ in the two samples, as mentioned previously, is 13. We know from spectroscopic analysis that there are 100 ppm Mg^{++} doped into our LiF:Mg crystal and, therefore, the same number of charge compensating cation vacancies. In the nominally pure sample, we have trace impurities from 1 to 10 ppm of several impurities such as Mg^{++} , Ca^{++} , and so forth. The associated cation vacancies in the LiF would make a total vacancy concentration of about 10 ppm likely even in the pure sample. That the $(1/T_{1\rho})$ is a factor of 13 smaller in the LiF-pure crystal, thus supports our identification of this process as related to vacancy motion.

In addition, as a crude order of magnitude estimate for vacancy motion-induced relaxation we approximate Eq. 32 by $(1/T_{1\rho}) \approx \frac{N_V}{N_T} \tau_V^{-1}$ and assume that the jump times should be of the form $\tau_V = \frac{1}{\omega} \exp(E/kT)$. Using a typical vibrational frequency $\omega \approx 10^{12} \text{ sec.}^{-1}$, and employing the measured $E = 0.45 \text{ eV}$, we obtain $(1/T_{1\rho}) \approx 10$ for the LiF:Mg sample at 300°K . This value is in order of magnitude agreement with the experimental result.

We should also note that only this high temperature activated process differs drastically between crystals with an order of magnitude or more difference in divalent impurity concentrations. All other observable processes appear to change by at most a factor of three between the two crystals.

Essentially all the vacancies present in both crystals should be bound to impurities. Bassani and Fumi²⁹ have theoretically calculated the association energy of vacancies to divalent impurities

to be 0.35-0.40eV. R. Grant³⁰ has estimated from dielectric loss measurements on the LiF:Mg used in this experiment that the association energy is 0.37eV. Using these numbers, it is easily shown that almost all vacancies will bind themselves to divalent impurities at temperatures near room temperature. Work in NaCl^{15,24,25} has shown that bound vacancies moving so as to stay bound are activated with less energy than free vacancy motion. This is reasonable as the presence of the (++) impurity will distort the lattice near it, electrostatically pulling the anions toward it. This would also make the motion of a nn vacancy to a nnn or a nnn to a nn preferred. Therefore, we will identify the observed activated process with motion of bound vacancies around a divalent impurity. We will also identify 0.43eV as the activation energy for this process. The free vacancy activation energy for diffusion is 0.65eV as determined from ionic conductivity experiments.²⁸

Let us now inquire how this process can be interpreted in terms of theory previously discussed. First we wish to determine the correlation time regime in which our measurements are done. From Eqs. 22 and 32, we see that a plot of $T_{1\rho}$ vs. H_1^2 should help us in this identification. The results are shown in Fig. 9 for the LiF:Mg crystal at 46°C. As can be seen from this plot, it would be desirable to employ H_1 's near 20 gauss in order to obtain a more accurate value for the slope of $T_{1\rho}$ vs H_1^2 . However, this is very difficult because of the following experimental considerations. For this kind of measurement, we want to be in a region where the

$(1/T_{1\rho})$ is dominated by this activation process to avoid base $(1/T_{1\rho})$ errors. However, in this region, a 3% change in temperature would result in a factor of 2 change in the relaxation rate observed. Since the $T_{1\rho}$'s here are on the order of several seconds, the necessary temperature stability limits the amount of power that can be dissipated in the transmitter coils. These factors limit our maximum usable H_1 to ≈ 7 gauss, which is almost twice the dipolar local field.

The line drawn in Fig. 9 intersects the H_1^2 axis at $H_1^2 = -(19\text{gauss})^2$. The uncertainty is probably a few gauss. The dipolar local fields in the 110 -direction of LiF are about 4 gauss. From our theory, this would imply that we are in the intermediate τ_V region (case 2) where there is thermal isolation between the spins that see a large quadrupolar interaction and the bulk Li spins. We also expect that the relaxation is almost entirely quadrupolar in nature.

For a rough comparison with the value of 19 gauss obtained in the experiment we can estimate αH_Q^2 from Eq. 33 as follows: We use a point ion approximation to represent the vacancy, and assume an undistorted lattice. Using a Sternheimer shielding factor of 1 to represent the small polarizability of the Li ion and a quadrupole moment $Q = .04 \times 10^{-24} \text{eSU-cm}^2$ we obtain $\alpha H_Q^2 \approx (30)^2 \text{ gauss}^2$. That this crude estimation is quite near the experimental value of 19 gauss indicates that the semiquantitative model and approximations used for Case 2 are not inconsistent with the experimental observations.

As another check on the theory, one can estimate the vacancy jump times and compare them with both the local spin-spin relaxation time and the cross relaxation time, τ_{cr} , expected for equilibrations of the local and bulk spin systems. Assuming again for the LiF:Mg that $(1/T_{1\rho}) \approx N_V/N\tau_V$, we would expect jump times in the range from 10^{-4} sec. to 10^{-2} sec. corresponding to the data presented in Fig. 8. This verifies that $(\gamma H_Q)^2 \tau_V^2$ and even $(\gamma H_L)^2 \tau_V^2$ are much larger than one for all τ_V we measure. An estimate of τ_{cr} may be obtained by extrapolating the experimental results of Lang and Moran²⁷ for τ_{cr} between ^6Li and ^7Li in the adiabatically demagnetized state. For an order of magnitude estimate, one would expect, then, to have a τ_{cr} for our case of no shorter than about 10^{-2} sec. We do get to τ_V 's of 10^{-2} sec. It is interesting to speculate whether the shoulder on the $(1/T_{1\rho})$ which begins to emerge at about $(T_{1\rho}) \approx 100$ seconds can be attributed to the change over from Case 2 to Case 1. Once one gets well into the temperature region associated with Case 1, one would expect to see $(1/T_{1\rho})$ again be exponential with respect to inverse temperature and with the same activation. We cannot verify this satisfactorily because of the magnitude of the wide low temperature background (see Fig. 4). However, if one defines β_j in terms of an expansion in τ_V/τ_{cr} around β , one would predict that in the transition region from Case 1 to Case 2, $(1/T_{1\rho})$ should be independent of temperature. This produces a shoulder extending to higher temperatures similar to that observed in the experiments.

Explicit calculations for $2(1-p_d)$, $2(1-p_d)_{\text{complex}}$, $(1-p_Q)$, and $(1-p_Q)_{\text{complex}}$, are carried out in Appendix 1, and the values are 0.90, 0.88, 0.7^{-7} , and 0.3^7 , respectively. Therefore, our estimates of $(1-p)$ being ≈ 1 were quite reasonable. It is interesting that all the values are close to one except for $(1-p_Q)_{\text{complex}}$, which is significantly lower. This reflects that H_Q^0 for the bound vacancy case is composed of a term for the divalent impurity in addition to the vacancy term and that this divalent impurity term does not fluctuate.

Finally, let us comment on how the experiment done by Ailion and Slichter on Li metal fits into our theory. The motional peak that they see is strictly dipolar as it occurs at the temperature where T_2 in Li metal begins to show narrowing effects. Therefore, their data is taken in a system with very small N_v/N , but very short τ_v ; this corresponds to our case 4 where quadrupolar interactions may be neglected because their effects are largely suppressed by motional narrowing. In this region, our theory reduces to being the same as the one they develop.

V. SUMMARY AND CONCLUSIONS

The ^7Li NMR studies described above of the lab frame and rotating frame spin-lattice relaxation processes in LiF at temperatures below 400°K reveal an extraordinary sensitivity to very slow and very dilute dynamic interactions of the nuclear spins. This good sensitivity is due to the very small intrinsic ($1/T_1$) background in the rather pure LiF crystals, and one can easily observe processes caused by trace amounts (1-10 ppm) of both paramagnetic impurities and diamagnetic defects.

Below 280°K we observe in the experiments a generally featureless and weak temperature dependence of both ($1/T_1$) and ($1/T_{1\rho}$) and identify this behavior with spin diffusion to fast relaxing paramagnetic centers. The relation between T_1 and $T_{1\rho}$ in this temperature region agrees with the predictions of Lowe and Tse for paramagnetic centers in the $\omega T_C \ll 1$ region providing one accounts for the second specie, fluorine, in our experiment.

Above 280°K, the lab frame relaxation ($1/T_1$) shows observable structure which is small in magnitude, but strongly temperature dependent. In the LiF-pure sample, this structure appears to be a single activated peak; whereas in the 100 ppm doped LiF:Mg sample the structure, although of only somewhat larger magnitude, is considerably more complicated. Although we associate the source of these nuclear relaxation peaks with other trace concentration impurities, no more specific identification can be made. Because no associated relaxation processes can be observed

in the ($T_{1\rho}$) measurements, one must presume that the T_1 minima observed in this higher temperature range are not produced by a simple direct interaction with the Li nuclear spins.

Finally, as was the principal motivation for these experiments, in a temperature range from 280°K to 380°K we have observed motion of bound vacancies as reflected in their pronounced effect on the rotating frame relaxation. The measured activation energy is 0.43eV, about 0.2eV less than free vacancy activation energies determined from ionic conductivity experiments. This is consistent with the fact that, for relatively low temperatures and for the divalent ion concentrations in the samples, essentially all the vacancies should be bound to form a vacancy-ion complex. The relaxation can be attributed primarily to fluctuations in the quadrupolar interaction caused by the motion of the vacancy in the impurity-vacancy complex. A theory, which is an extension of Slichter-Ailion theory, was developed to meet this situation. From the H_1 dependence of $T_{1\rho}$, we conclude from our theoretical treatment that the quadruple splittings are large enough to produce almost complete isolation during a vacancy jump time of nuclei neighboring a vacancy from the more distant bulk nuclei. Although the experimental results are similar, this interpretation is considerably different than that used by Kumano and Hanabusa in their treatment of rotating frame bound-vacancy motion in NaCl.

Our theoretical analysis also predicts that the quadrupolar interactions will begin to become motionally narrowed and the

rotating frame relaxation dominated by dipolar interactions for vacancy jump times of about a factor of 10 shorter than those we obtain at the upper temperature limits of the present experiments.

APPENDIX 1

Calculation of Order Parameters

We will, in this Appendix, explicitly calculate the $(1-p_d)$ and $(1-p_Q)$ referred to in the paper for the cases of free and bound vacancy motion in the long correlation time, long τ_v , limit. We will do the $(1-p_d)$ calculation first to make use of analogy with Ailion's work; $(1-p_Q)$ should follow easily from this.

The methods we will use will be similar to SA except that we will be interested in a two spin species material and in a single crystal with the static field in the 110-direction. We will calculate the loss in dipolar energy, ΔE_d° , due to a free vacancy jump; v will refer to the initial position of the vacancy and v' , the final position. Then from Eqs. 8 and 9

$$\Delta E_d^\circ = -[\text{Tr} H_d^\circ (H_d^\circ - H_{dv}^\circ)] \beta / \text{Tr}\{1\} \quad (A1)$$

now

$$\text{Tr}\{H_d^{\circ 2}\} = \text{Tr}\{H_{d, \text{Li-Li}}^{\circ 2} + H_{d, \text{Li-F}}^{\circ 2} + H_{d, \text{F-F}}^{\circ 2}\}, \quad (A2)$$

as the cross terms vanish; also in general for a two spin specie

$$H_{dII}^\circ = \gamma_I^2 \hbar^2 \sum_{ij} \frac{(1-3\cos^2\theta_{ij})}{r_{ij}^3} (3I_{zi}I_{zj} - I_i I_j) \quad (A3)$$

$$H_{dIS}^\circ = \gamma_I \gamma_S \hbar^2 \sum_{ij} \frac{(1-3\cos^2\theta_{ij})}{r_{ij}^3} (I_{zi} S_{zj}),$$

where θ_{ij} is the angle between the internuclear vector $\vec{r}_{ij}$ and the applied magnetic field

We wish to identify this energy change ΔE_d^0 as $-\frac{2}{N}(1-p_d)\langle H_d^0 \rangle$ and therefore may write

$$\frac{2(1-p_d)}{N} = \frac{\text{Tr}\{H_d^{02} - H_d^0 H_{dv}^0\}}{\text{Tr}\{H_d^{02}\}} \quad (\text{A4})$$

The 2 is artificial in our case as will be seen; however for consistency with SA we will include it. Unlike SA, Eq. A4 does not reduce to strictly a geometrical problem because in a two species system the spin functions do not cancel. However, only the geometrical parts of Eq. A3 change. Therefore, we will write the dipolar terms as a strictly geometrical part, denoted by capital letters, times the product of the coefficients and the traces of the spin functions, denoted by script letters.

$$\begin{aligned} \frac{2(1-p_d)}{N} = & \left[\sum_{ij} (A_{ij}^2 - A_{ijv} A_{ij}) S_{ij}^2 + \sum_{jk} (B_{jk}^2 - B_{jk} B_{jkv}) T_{jk}^2 + \right. \\ & \left. \sum_{kl} (C_{kl}^2 - C_{klv} C_{kl}) U_{kl}^2 \right] / \left[\sum_{ij} A_{ij}^2 S_{ij}^2 + \sum_{jk} B_{jk}^2 T_{jk}^2 + \right. \\ & \left. \sum_{kl} C_{kl}^2 U_{kl}^2 \right] \quad (\text{A5}) \end{aligned}$$

where the first, second, and third terms refer to the Li-Li, Li-F, and F-F interactions, respectively.

Now, let us evaluate this expression. The F-F term in the

numerator will vanish. The Li-F term will reduce to a single sum over fluorines and involve only the moving lithium ion. The Li-Li double sum will reduce to twice the single sum as only the terms involving the moving Li ion will not cancel. Note that the 2 then arises from the fact that these are unrestricted sums in the definition of the H_d^0 's. Similar to SA, we may change from a sum over Li spins to a sum over lattice sites by subtracting off the vacancy position. Also, we must average over the possible directions of the jump. If there are G nearest neighbors, the numerator now looks like

$$\frac{2}{G} \sum_v \left[\sum_i (A_{iv}^2 - A_{iv} A_{iv}) - A_{vv}^2 \right] S_{iv}^2 + \frac{1}{G} \sum_v \left[\sum_k (B_{vk}^2 - B_{vk} B_{vk}) \right. \\ \left. \times T_{kv}^2 \right] \quad (A6)$$

where the sum i is over all Li lattice sites and the sum k is over all F sites.

The denominator is easily evaluated using Van Vleck second moments and relating these to the dipolar energy.³² The geometrical factors were evaluated for 500 spins using a GE Mark II computer with the following results:

$$\begin{aligned} \sum_{ij} A_{ij}^2 &= 98.4 \, N/a^6 \\ \sum_{ik} B_{ik}^2 &= 225.6 \, N/a^6 \\ \sum_{kl} C_{kl}^2 &= 98.4 \, N/a^6 \end{aligned} \quad (A7)$$

where N is the number of spins and a is the lattice constant.

$$\langle H_d^0 \rangle_{VV} = -N\hbar^2\beta[21.1 \times 10^8]. \quad (A8)$$

the sums in the numerator were also evaluated using the computer:

$$\begin{aligned} \frac{1}{G} \sum_V \sum_i A_{iV} A_{iV} &= 15.3/a^6 \\ \frac{1}{G} \sum_V A_V A_V &= 7.0/a^6 \\ \frac{1}{G} \sum_V \sum_k B_{V'k} B_{Vk} &= -12.0/a^6 \end{aligned} \quad (A9)$$

the numerator, using Van Vleck second moments, is

$$N\hbar^2\beta[19.0 \times 10^8] \quad (A10)$$

and finally $2(1-p_d) = 0.90$.

We may compare our value for the Li-Li interaction with that obtained by Ailion and Ho for nn jumps in an FCC lattice. Our value for $(1-p_d)$ would be 0.77. They get, depending on angle, 0.77-0.80. Therefore, our comparable results agree.

Let us now evaluate $(1-p_Q)$ for free vacancy motion defined in Eq. 20. The form of H_Q^0 ; from a point charge at r for a nuclei j at the origin in spherical coordinates is given by Slichter as

$$H_{Qj}^0 = \frac{eQ}{4I(2I-1)} e \frac{(3\cos^2\theta_{vj}-1)}{r_{vj}^3} [3I_{zj}^2 - I_j^2] \quad (A11)$$

where θ_{vj} is the angle between the z -axis (the static magnetic field direction) and the vector $\vec{r}_{vj}$. Thus, the total quadrupolar

interaction from a vacancy v is

$$H_Q^o(v) = \sum_j H_{Qj}^o = \frac{e^2 Q}{4I(2I-1)} \sum_j \frac{(3\cos^2\theta_{vj}-1)}{r_{vj}^3} [3I_{zj}^2 - I_j^2] \quad (A12)$$

We will assume a very dilute concentration of vacancies so there will be no cross terms. The geometrical factor is exactly the same form as in the dipolar case, but, as far as the quadrupolar interaction is concerned, this is a one spin specie and all spin factors will cancel. Denoting

$$D_{vj} = \frac{(1-3\cos^2\theta_{vj})}{r_{vj}^3}, \quad (A13)$$

We may write

$$(1-p_Q) = \frac{\frac{1}{\bar{G}} \sum_{v'} \sum_j (D_{vj}^2 - D_{vj} D_{v'j})}{\sum_j D_{vj}^2} \quad (A14)$$

The sum j is over Li spins. We have evaluated a mathematically equivalent expression in the dipolar case: there the expression involved the moving Li spin and the other spins; here the expression involves the moving vacancy and the other spins. Therefore we write $(1-p_Q) = 0.77$.

The extension of the previous calculations to the case of vacancies bound to a diamagnetic divalent impurity is straightforward. In the dipolar case, we must subtract the position of the

impurity from the Li-Li lattice sums and do a proper averaging. Only the Li-Li sums are involved. From Fig. 2, we can see the possible bound vacancy complexes considered and the possible types of jumps. From work on NaCl,²⁵ we would expect the interchange of the vacancy with the divalent ion to occur much less frequently than the other jumps and will be neglected. All other possible jumps will be assumed of equal probability for simplicity. A nn vacancy can jump to any one of six positions. A nnn can jump to any of four. The corrected first term in Eq. A6 is

$$\frac{1}{H} \frac{2}{G} \sum_{V, V'} \left[\sum_i (A_{iV}^2 - A_{iV} A_{iV'}) - A_{VV'}^2 \right] \quad (A15)$$

where H is the number of possible initial positions of the vacancy, G is the number of possible final positions of the vacancy, and the sum i is over Li lattice sites with the position of the divalent ion excluded. Due to the symmetry, this reduces to

$$\frac{2}{G} \sum_V \left[\sum_i (A_{iV}^2 - A_{iV} A_{iV'}) - A_{VV'}^2 \right] - \frac{2}{GH} \sum_{V, V'} (A_{DV}^2 - A_{DV} A_{DV'}) \quad (A16)$$

the first term in A16, as before, is $2(76.1)/a^6$. The second may be evaluated to give $2 \times 5.4/a^6$. Finally $2(1-p_d)_{\text{complex}} = 0.88$. As might be expected, the diamagnetic divalent impurity has little effect.

For the quadrupolar bound vacancy case, the impurity will also have a quadrupolar interaction with the spins. Therefore, the total quadrupolar interaction felt by a nucleus j near an

impurity vacancy complex is

$$H_{Qj}^{\circ} = H_{Qv}^{\circ} + H_{QD}^{\circ}, \quad (A17)$$

where D refers to the divalent ion. Again, we assume that any spin sees at most one complex. Then the change in quadrupolar energy due to a vacancy jump, ΔE_Q° , may be written

$$\Delta E_Q^{\circ} = -\text{Tr}\{[H_{Qv}^{\circ} + H_{QD}^{\circ}][H_{Qv}^{\circ} + H_{QD}^{\circ}] - (H_{Qv}^{\circ} H_{QD}^{\circ} + H_{QD}^{\circ} H_{Qv}^{\circ})\} \beta / \text{Tr}\{1\} \quad (A18)$$

$$= \text{Tr}\{(H_{Qv}^{\circ})^2 - H_{Qv}^{\circ} H_{Qv}^{\circ} + (H_{QD}^{\circ} H_{Qv}^{\circ} - H_{QD}^{\circ} H_{Qv}^{\circ})\} \beta / \text{Tr}\{1\} \quad (A19)$$

therefore,

$$(1-p_Q)_{\text{complex}} = \frac{\text{Tr}\{(H_{Qv}^{\circ})^2 - H_{Qv}^{\circ} H_{Qv}^{\circ} + (H_{QD}^{\circ} H_{Qv}^{\circ} - H_{QD}^{\circ} H_{Qv}^{\circ})\}}{\text{Tr}\{(H_{Qv}^{\circ})^2 + H_{QD}^{\circ} H_{QD}^{\circ} + 2H_{Qv}^{\circ} H_{QD}^{\circ}\}} \quad (A20)$$

As before, all but the geometrical factors cancel, and we must average over all possible initial and final positions of the vacancy. Doing this, we see that the second part of the numerator becomes identically zero as the averages over v and v' are over the same sites. The first part of the numerator is as in the bound dipolar case (Eq. A16) and is $70.7/a^6$.

The denominator is also easily evaluated. The form of the first two terms are the same as in the free case but we should

subtract the position of the impurity or vacancy from the sums, respectively. Both these terms are then $(98.4-5.3)/a^6=93.1/a^6$.

The last term may be done in two parts for when the vacancy is a nn and for the case when it is a nnn. We have already evaluated a similar expression in the former case (first equation in A9.)

The latter case is again evaluated using the computer and is $2 \times (-25.5)/a^6$; their average is $3.4/a^6$. Finally, $(1-p_Q)_{\text{complex}} = 0.37$. This is quite different than $(1-p_Q)_{\text{free}}$ because the part of the quadrupolar Hamiltonian associated with the divalent impurity is not fluctuating.

APPENDIX 2

Experimental Details

In this section we will expand on our experimental detail. A timing sequence diagram for the lab frame T_1 measurements is given in Fig. 10 and, for the rotating frame work, in Fig. 11. Textronix 160 series pulsters were used in the initial experiments for controlling all pulse lengths and time intervals, but most of these were finally replaced with a logic scheme pulse sequence using univibrators, J-K flip flops, counters, nandgates, and a timing module. This was accomplished by patchwiring a Heath Analog Digital Designer. A gated integrator with a digital output was used to obtain a digital value proportional to M_x from the free induction decay signal. The system was not used in the normal boxcar integrator mode due to the length of the T_1 's.

A pair of Helmholtz coils wrapped on the outside of the dewar were used for the field pulser coils. The design was similar to that of Lurie.³² The maximum field attainable was about 25 gauss. This was determined by observing the field of the proton resonance in water with the field pulse on. The h_0 field pulse was on for about 10 ms in the experiments. This produced no noticeable effects on the stability of the magnet. However, pulses of around 100 ms or so would tend to disturb the magnet's regulation as it would try to compensate for the h_0 .

The rf pulse for lab frame experiments was normally about 25 ms. This had no noticeable effect on the temperature. The magnitude of the rf was determined by observing the proton resonance for

successive 180° pulses in water. For rotating frame experiments on some of the longer $T_{1\rho}$'s, the rf was on for several (≈ 5) seconds. This did effect the thermocouple readings; however, this probably reflects little actual sample temperature effect on the bulk of the crystal as can be inferred from the fact that the thermocouple would come back shortly to a reading very near to the reading before the H_1 pulse. With H_1 demagnetized to almost zero field, the pulse length τ could be several minutes with no apparent change in the transmitter characteristics. With H_1 of large amplitude, as in the H_1^2 dependence experiment, the transmitter was not left on for more than 10 seconds because of the heating effect.

A picture of the probe and heater are shown in Fig. 12. The nichrome wire heater resistance was 5 ohms. Therefore, only a few volts were necessary to produce a couple of watts. It was never necessary to keep more than 5 watts going into the system to maintain temperatures up to 85°C . A temperature stability of $\pm 2^\circ\text{K}$ was deemed adequate as the T_1 's and $T_{1\rho}$'s did not change very rapidly with temperature except at temperatures above room temperature in the rotating frame case. In this region, two degrees is better than 1%, and the stability was better here. The thermocouple potential was recorded on a chart recorder with the scale at 10mV full scale and the speed about 4 minutes/cm. For Cr-Al, this would mean 2.5 degrees between small divisions near room temperature. This was the stability sought. The thermocouple becomes rather insensitive near liquid nitrogen temperatures. Therefore, the

observation of temperature stability is more difficult. There appeared to be very little D.C. drift in the recorder although this was corrected for every few hours.

APPENDIX 3

TL and Atomic Motions

One of the motivations to do this experiment was to see if information obtained about internal motions of the crystal might be related to the thermoluminescent process (TL) in LiF. Activation energies and frequency factors as well as thermal properties of TL peaks in LiF-TLD-100 (a commercial TL phosphor) as well as some other LiF phosphors have been measured.³⁸ It was hoped that with this information available, a study of diffusion in LiF using NMR techniques might show correlations with TL. Attempts to correlate TL with electron/hole activation using optical absorption data has not been very successful until recently.^{39,40}

In our model for TL, it was hypothesized that TL resulted from activation of a filled trap by some defect moving into the region about it. If this sensitive volume is ℓ^3 , the jumping rate of the defect is τ_d , and their number N_d , then the rate, r , at which the defect jumps into the volume ℓ^3 is just the probability that the defect is on an outside surface and jumps in times the jump rate.

$$r = [(6\ell^2 x_a) \times N_d] \times \frac{1}{6} \times \frac{1}{\tau_d} \quad (A21)$$

where a is the nearest neighbor distance. $\ell^2 = (fa)^2$ where f is a small number. Thus

$$r = f^2 a \frac{3N_d}{\tau_d}$$

$$= f \frac{2N_d}{N\tau_d} \quad (\text{A22})$$

Eq. A22 is of the same form as our expressions for $(1/T_{lp})$.

Therefore, if such processes are occurring, NMR would appear to be a good method to use in their investigation.

Our experimental results do not show an activated process relatable to TL. This is probably due to the fact that TL in LiF is not caused by the mechanism suggested or that we are not looking for the activation in the proper temperature region. Regardless, the use of NMR in investigation of luminescence processes might still prove useful if the above mentioned mechanism is the source of the luminescence.

APPENDIX 4

Discussion of Kumano and Hanabusa Theory

Let us now discuss how our approach differs from that of Kumano and Hanabusa¹⁵ in their paper on NaCl. First, we will note, that their equation for $T_{1\rho}$ due to quadrupolar interactions is stated with very little proof. That this equation (Eq. 1 in their paper) is the same form as the SA expression with H_ℓ^2 replaced by H_Q^2 (in our notation) leads one to the conclusion that the Japanese group did just this with no justification. We believe this to be conceptually wrong. As mentioned previously, although quadrupolar and dipolar relaxation are the results of the same physical process (motion of a vacancy) the dipolar is an internuclear interaction and all spins feel a dipolar interaction while the quadrupolar is an interaction between the vacancy and nearby spins and only nearby spins will sense it. Therefore, as shown in our approach, the form for $T_{1\rho}$ will not always follow the form given by SA theory.

From their paper, it is not clear in which region of τ_v their theory will apply. They state that the jumps are occurring slowly enough so that the spin system has time to come to thermal equilibrium between jumps. However, they then exclude from consideration the spins that are located in the neighborhood of the complexes as these cannot obtain the common spin temperature. From our approach it is clear that these quadrupolar broadened spins are the ones responsible for the form of the $T_{1\rho}$ and certainly

2

may not be ignored. For sufficiently slow jump rates, these spins should equilibrate with the rest of the spins. For faster jump rates, the near spins do not equilibrate between jumps with the bulk, but the near spins still control the relaxation rate. The far spins from the complex are essentially always at β and see effectively no quadrupolar field.

Kumano and Hanabusa also do not adequately define the H_Q^2 that they use. They say H_Q^2 is the local field for $\langle H_Q \rangle$. Does this include the near spins? From their statement about excluding those spins from considerations, one would expect that it does not. However, H_Q^2 should then be no larger in magnitude than H_L^2 . This is not what they observe or what we observe.

Finally, it would be interesting to compare their constant (β_k) with our expression $(1-p_Q)$. β_k is N/N_V times our $(1-p_Q)$ except that they are again eliminating the spins near the complex. They do not attempt explicitly to evaluate β_k but obtain a value from their data of $\beta_k \approx 1$ for all samples, independent of concentration. Our $(1-p_Q)$ including all spins is of order unity. Eliminating the spins near the vacancy would tend to make $(1-p_Q) \approx 0$. Therefore, a value of $\beta \approx 1$ or $(1-p_Q) \approx N_V/N$ is possible in this definition. However, this would imply that there should be no concentration dependence in $1/T_{1\rho}$. We observe one and so do they.

It seems clear that quadrupolar relaxation in the rotating frame is not a clear cut theoretical problem and has subtleties not found in the dipolar case.

Fig. 1. Block diagram of 8MHz pulsed NMR spectrometer.

Fig. 2. Types of vacancy-impurity complexes considered

- a) Vacancy a nn to impurity
- b) Vacancy a nnn to impurity

Arrows indicate possible types of vacancy jumps.

- + - Li ions in paper plane
- 0 - Li ions in plane above or below paper plane
- ++ - divalent impurity ion
- + - Li ion vacancy

(9)

(8)

Fig. 3. $(1/T_1)_{\text{Lab}}$ vs $(1000/T)$ for the ^7Li spins in LiF-pure
and LiF:Mg.
(Typical error bars are shown for a few points on all
data graphs.)

Fig. 4. $(1/T_{1\rho})$ vs $(1000/T)$ for the ^7Li spins in LiF-pure and LiF:Mg.

Fig. 5. $(1/T_1)_{\text{Lab}}$ vs $(1000/T)$, expanded temperature scale.

Fig. 6. $(1/T_{1\rho})$ vs $(1000/T)$, expanded temperature scale.

Fig. 7. $(1/T_1)_{\text{Lab}}$ vs $(1000/T)$ in region of peak in LiF-pure with the base line subtracted. Theoretical curves for quadrupolar relaxation following the form of Cohen and Reif (see text) are also shown.

Fig. 8. $(1/T_{1\rho})$ diff vs $(1000/T)$; the base relaxation rate has been subtracted. The activation energies obtained from the slopes are $0.45 \pm .03\text{eV}$ for the LiF:Mg and $0.41 \pm .03\text{eV}$ for the LiF-pure.

Fig. 9. T_1 vs H_1^2 at 46° for the LiF:Mg sample. The line drawn through the data intersects the x-axis at $H_1^2 = -350 \text{ (gauss)}^2$.

Fig. 10. Typical timing sequence for the $(T_1)_{\text{Lab}}$ experiments.

Fig. 11 Typical timing sequence for the $(T_{1\rho})$ experiments.

Fig. 12. A picture of the probe with brass can off (A) and the brass can with heater (B). Receiver coils are wrapped and cemented on nylon probe. Transmitter coils are wrapped using black tape on brass Faraday shield which fits over probe. Sample is shown schematically.

Nichrome wire is wound on mylar around brass rod in Piece B. Asbestos is wrapped around outside of nichrome.

Piece B screws onto Piece A.

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