Spin Relaxation of F-Center Electrons*

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Several possible mechanisms leading to spin transitions in the electron-nuclear spin system of an F-center electron and its neighboring nuclei have been examined. Calculations show that the most probable transition is one in which the electron spin changes, but the nuclear spin does not change, and which results from the second-order perturbation of the spin-orbit coupling of the electron due to lattice vibrations. The spin-lattice relaxation time of the F-center electrons in NaCl at 300°K has been measured at 70, 2950, and 8300 gauss. The relaxation time is 2×10^{-6} second, independent of the magnetic field, in approximate agreement with the theory.

I. INTRODUCTION

THE relaxation rate of the spin of an electron trapped in a negative ion vacancy (F center) has been measured[1,2] for a few of the crystals which exhibit F centers, but no theoretical treatment of this phenomenon has been made. It will be the purpose of this paper to examine the theory of the various electron spin-lattice and electron-nuclear transitions rates, and to present the results of some experiments on the spin-lattice relaxation time of the F-center electrons in NaCl. It will be shown that the theory and experiment are in approximate agreement.

Since an F-center electron has a relatively large hyperfine coupling[3] to the nuclei which surround the negative ion vacancy, the designation of the Zeeman states of the electron must include not only the m_S value of the electron spin but also the m_I values of the coupled nuclear spins. There will then be more than two levels in the Zeeman energy system, and the definition of "relaxation time" becomes ambiguous unless the transitions by which relaxation is taking place are specified. To simplify the problem of nomenclature, we will consider an electron spin which is coupled with only one neighboring nucleus, and we will take the nucleus to have spin one-half. This system will include all the essential features of an actual physical case of an electron coupled to six or eight neighboring nuclei of spin $\geq \frac{1}{2}$. The levels of the simplified system appear in Fig. 1. The separation of the $(\frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, -\frac{1}{2})$ levels is not the same as the separation of the $(-\frac{1}{2}, -\frac{1}{2})$ and $(-\frac{1}{2}, \frac{1}{2})$ levels and varies with the orientation of the magnetic field with respect to the line joining the center of the vacancy with the nucleus under consideration. We will define relaxation times for this system to characterize the six possible transition rates shown in Fig. 1. It will be assumed that the transition probability does not

depend upon the initial value of m_S and m_I except for the Boltzmann difference between upward and downward transitions. Thus there will be four characteristic rates for this system. The nomenclature we will use is given in Table I.

If the transition $(-\frac{1}{2}, -\frac{1}{2}) \rightarrow (\frac{1}{2}, \frac{1}{2})$, for example, is saturated with microwave power, there are three possible ways by which the Zeeman energy can be transmitted to the lattice. The electron can flip independently of the nucleus in a characteristic time T_S, or the electron can undergo an electron-nuclear $\Delta M = 0$ or $\Delta M = 2$ transition preceded or followed by a nuclear spin flip. If the latter processes are independent, they would lead to electron spin relaxation having characteristic times T_{X0} or T_N, whichever is larger, and the larger of T_{X2} and T_N, respectively. Thus to understand the spin-lattice relaxation process, we must obtain estimates of the magnitudes of all four of these characteristic times.
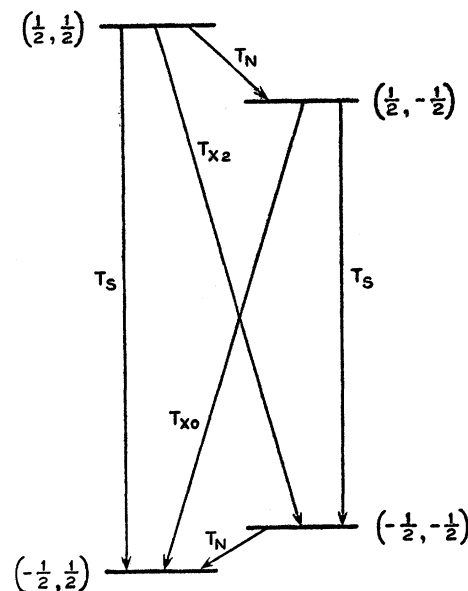

FIG. 1. Zeeman energy level diagram of one electron coupled by anisotropic hyperfine interaction to a nucleus of spin one-half for arbitrary orientation of the magnetic field. The levels are labeled (m_S, m_I).

[1] A. M. Portis, Phys. Rev. 91, 1071 (1953).
[2] A. M. Portis, Phys. Rev. 100, 1219 (1955).
[3] A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. 91, 1066 (1953); N. W. Lord, Phys. Rev. 105, 756 (1957); and Phys. Rev. Letters 1, 170 (1958); G. Feher, Phys. Rev. 105, 1122 (1957).

TABLE I. Nomenclature of transitions in the
electron-nuclear Zeeman system.

Transition		Characteristic
Δm_S	Δm_I	time
± 1	0	T_S
± 1	∓ 1	T_{X0}
± 1	∓ 1	T_{X2}
0	± 1	T_N

Van Vleck[4] has considered several ways in which spin relaxation can occur for paramagnetic ions in a crystal. This treatment cannot readily be adapted to the *F* center as the states split by an electric crystal field which are necessary for the operation of the Van Vleck mechanism are not well understood for the *F* center if indeed they exist at all. Pines, Bardeen, and Slichter and Abrahams[5] have considered several relaxation mechanisms in relation to donor states in silicon which might be applicable to the *F* center. They have computed values for relaxation rates based on the fluctuation of the hyperfine interaction and have found that these rates are much too slow. We shall show later that this is also the case for the *F*-center electron.

We will use the spin Hamiltonian[6]

$$\mathcal{H} = \mu_e \mathbf{H} \cdot \mathbf{S} + \mu_I \mathbf{H} \cdot \mathbf{I} + A \mathbf{I} \cdot \mathbf{S}$$
$$+ b[3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r}) - \mathbf{I} \cdot \mathbf{S}] + \lambda \mathbf{L} \cdot \mathbf{S}, \quad (1)$$

where $\mathbf{r}$ is the unit vector relating the nucleus to the center of the vacancy. This Hamiltonian, when combined with the Hamiltonian for the crystal energy, provides matrix elements for spin transitions of various types.

1. The value of A, as will be shown later, is a function of the relative positions of the vacancy and the neighboring nucleus, and thus the lattice vibrations make the hyperfine coupling time-dependent. The first-order perturbation of $A(t)\mathbf{I} \cdot \mathbf{S}$ on (1) has nonvanishing matrix elements $\langle I_{\pm} S_{\mp} \rangle$ and leads to transitions of the type $\Delta m_S = \pm 1$, $\Delta m_I = \mp 1$, in which the electron and nucleus flip in opposite directions.

2. The anisotropic hyperfine coupling can be made time-dependent in two ways. The coupling coefficient b is dependent upon the geometry in a manner similar to A, and thus $b(t)[3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r}) - \mathbf{I} \cdot \mathbf{S}]$ perturbs the remainder of (1) to give matrix elements $\langle I_z S_{\pm} \rangle$, $\langle S_z I_{\pm} \rangle$, $\langle S_{\pm} I_{\mp} \rangle$, and $\langle S_{\pm} I_{\mp} \rangle$, by a first-order perturbation. This perturbation can then cause transitions in which either the electron or the nucleus flips alone, or both flip simultaneously. Secondly, the value of S_z can be time-dependent if the electron spin is undergoing transitions caused by one of the other perturbations. In this case, we have $b\{3(\mathbf{I} \cdot \mathbf{R})[\mathbf{S}(t) \cdot \mathbf{r}] - \mathbf{S}(t) \cdot \mathbf{I}\}$ as the perturbing

[4] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).
[5] D. Pines, J. Bardeen, and C. P. Slichter, Phys. Rev. **106**, 489 (1957); E. Abrahams, Phys. Rev. **107**, 491 (1957).
[6] See for example, B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108. We have assumed that the effects of crystalline fields may be neglected.

Hamiltonian. By a first-order perturbation, this leads to matrix elements in which the nuclear spin flips in a manner not correlated with any electron spin flips.

3. Since λ is also a function of the geometrical dimensions of the system, lattice vibrations will cause λ to be time-dependent. The perturbation term $\lambda(t)\mathbf{L} \cdot \mathbf{S}$ in Eq. (1) has no nonvanishing matrix elements in first-order perturbation but has, in second order, the matrix elements $\langle S_{\pm} \rangle$. Thus this process leads to transitions of the type $\Delta m_S = \pm 1$, $\Delta m_I = 0$.

II. DEVELOPMENT OF THEORY

A. Perturbation of Isotropic Hyperfine Coupling

We shall now make an estimation of the transition rate caused by fluctuations in the isotropic hyperfine coupling. It will be assumed that the lattice temperature is high enough so that the Raman or two-phonon transition is more important than the direct or one-phonon transition.[7] Then the transition probability is given by

$$P = \frac{2\pi}{\hbar^2} \int_0^{\omega_m} \rho^2(\omega) \langle |\mathcal{H}'|^2 \rangle d\omega. \quad (2)$$

The matrix element of $\mathcal{H}'$, the fluctuating part of the Hamiltonian, is to be taken between states characterized by (m_S, m_I, n, m) and $(m_S \pm 1, m_I \mp 1, n \pm 1, m \mp 1)$, where the parameters represent the quantum numbers of the electron and nuclear spin and the quantum numbers of excitation of the two lattice oscillators involved. The brackets denote an average over all final lattice oscillator states. Since energy must be conserved in this process, the energy difference of the two phonons must equal the energy change of the Zeeman system. We will have assumed that, in that portion of the phonon spectrum where the density of oscillators is large, the Zeeman energy difference can be neglected with respect to the energy of either phonon. A Debye spectrum will be chosen for $\rho(\omega)$, and ω_m will be chosen to be $\kappa\theta/\hbar$, so that the total number of lattice oscillators has the correct value when θ is the Debye temperature. The Debye spectrum gives

$$\rho(\omega) = 9\omega^2 \hbar^3 V / \kappa^3 \theta^3 a^3, \quad (3)$$

where V is the volume of the crystal and a is the internuclear distance. We take the amplitude of a given vibration as

$$q^2 = \frac{2\hbar}{3\omega M[\exp(\hbar\omega/\kappa T) - 1]}. \quad (4)$$

The fraction of q appearing as a relative displacement between neighboring nuclei is $\omega a q/v$, where v is the velocity of sound. For an approximate value of P, the effects of the different modes and polarizations of the phonons may be disregarded, as well as the average over

[7] For a review of the details of deriving the transition probabilities of one-phonon and two-phonon processes, see A. K. Saha and T. P. Das, *Theory and Application of Nuclear Induction* (Saha Institute of Nuclear Physics, Calcutta, 1957), Chap. 4.

the angular distribution of phonon momenta which would be necessary for a precise determination of the transition probability. Then

$$\langle|\mathfrak{IC}'|^2\rangle\cong\left(m_Sm_I\frac{d^2A}{dr^2}\frac{2\hbar a^2\omega}{3v^2M[\exp(\hbar\omega/\kappa T)-1]}\right)^2. \quad (5)$$

To determine the radial derivatives of the hyperfine coupling coefficient, one must know the wave function of the F-center electron as a function of lattice spacing. Gourary and Adrian[8] have calculated wave functions for the F-center electron for values of the lattice spacing corresponding to all the alkali halides. Thus, by interpolations, it would be possible to obtain the wave function as a function of spacing and compute $A(r)$. This is an unnecessarily complicated procedure, however, in view of the approximations which were made concerning the phonon spectrum. It is assumed that the value of A is computed as given by the calculations of Blumberg and Das[9]. These calculations employ the relation

$$A_\alpha=\frac{16\pi\beta\mu_I}{31}\langle\psi_F-\sum_i\langle\alpha_i|F\rangle\psi_{\alpha i}|\delta(\mathbf{r}_\alpha)|\psi_F$$
$$-\sum_i\langle\alpha_i|F\rangle\psi_{\alpha i}\rangle, \quad (6)$$

where ψ_F is the F-center wave function computed from an electrostatic potential neglecting overlap effects,[8] and $\psi_{\alpha i}$ is the wave function of electron i on neighboring ion α. Blumberg and Das found that the greatest contribution to A was made from the terms

$$\langle\alpha_i|F\rangle^2\langle\psi_{\alpha i}|\delta(\mathbf{r}_\alpha)|\psi_{\alpha i}\rangle.$$

The latter bracket is an intrinsic property of the ion itself and does not depend upon vibrational coordinates. The term $\langle\alpha_i|F\rangle^2$ then represents the major factor in A which does depend upon geometrical coordinates. It is assumed that when that part of a crystal containing an F center undergoes a compression due to a lattice phonon, the shape and extent of ψ_F is not changed appreciably, since, with the neighboring ions vibrating in practically random phases, the volume of the vacancy remains roughly constant. What is changed, however, is the overlap of the wave function $\psi_{\alpha i}$ of the ion core electron i on ion α, with ψ_F due to the displacement of $\psi_{\alpha i}$ with respect to ψ_F. Thus,

$$\frac{d}{dr}\langle\alpha_i|F\rangle=\langle\alpha_i|F\rangle\frac{1}{\psi_F}\frac{d\psi_F}{dr}. \quad (7)$$

Using the Type III wave function of Gourary and Adrian[8] gives

$$\psi_F=\frac{Na\sin(\xi r/a)\exp(-\eta)}{\xi\eta r}, \quad r<a,$$
$$\psi_F=\frac{Na\sin(\xi)\exp(-\eta r/a)}{\xi\eta r}, \quad r>a,$$
$$\quad (8)$$

[8] B. S. Gourary and F. J. Adrian, Phys. Rev. 105, 1180 (1957).
[9] W. E. Blumberg and T. P. Das, Phys. Rev. 110, 647 (1958).

where ξ and η are variation parameters. For NaCl, the variation calculation gives $\xi=2.36$ and $\eta=2.38$. Using this wave function,

$$\frac{d^2A}{dr^2}=2[(\eta+1)^2+\xi^2+1]\frac{A}{a^2}=\frac{36A}{a^2} \quad (9)$$

is obtained.

The complete expression for the transition probability is now, combining (3), (5), and (9),

$$P\cong\frac{2\pi}{\hbar^2}\int_0^{\omega m}\left(\frac{9\omega^2\hbar^3v}{\kappa^3\theta^3a^3}\right)^2$$
$$\times\left(\frac{36Am_Sm_I}{a^2}\frac{2\hbar a^2\omega}{3v^2M[\exp(\hbar\omega/\kappa\tau)-1]}\right)^2d\omega. \quad (10)$$

Using the relation $\kappa\theta a=(6\pi^2)^{\frac{1}{3}}\hbar v$ for a cubic lattice, this expression may be simplified to

$$P\cong7\times10^4\frac{A^2T^{*7}}{\rho^2v^3a^7}\int_0^{1/T^*}\frac{x^6dx}{(e^x-1)^2}. \quad (11)$$

Here the density ρ has been written for M/V and T^* for T/θ. For $T=300°$K and $A/h=66$ Mc/sec, $P=4\times10^2$ sec^{-1}. This would give a value of $T_{X0}=1/2P\cong10^{-3}$ sec.

B. Perturbation of Anisotropic Hyperfine Coupling

An argument similar to the above can be carried out for the fluctuation of the anisotropic hyperfine coupling. This will not be repeated here, but the result is the same as (11) with A^2 replaced by b^2. For the same values of the experimental parameters and $b/h=2.5$ Mc/sec,[10] T_S, T_N, T_{X0}, $T_{X2}\cong1$ sec is obtained.

If, on the other hand, S_z is made to be time-dependent by another relaxation mechanism, there is another perturbation process leading to nuclear spin transitions, and we shall obtain an estimate of T_N due to it. This process is similar to the well-known dipole-dipole transition, discussed by Bloembergen,[11] for the relaxation of nuclei by paramagnetic impurities which has the form

$$P=\frac{3}{2\pi}(\gamma_N\gamma_e\hbar)^2S(S+1)r^{-6}\cos^2\theta\sin^2\theta\frac{\tau}{1+\omega^2\tau^2}. \quad (12)$$

Here θ is the angle between the magnetic field and the line joining the two dipoles, and τ is the correlation time of the component of the electron or paramagnetic ion spin parallel to the magnetic field. In the case considered here, this interaction is enhanced, since the anisotropic hyperfine interaction is larger than the classical dipole-dipole interaction between two dipoles separated by a distance a, i.e., $b>\mu_e\mu_Na^{-3}$. Disregarding the angular

[10] Calculated from the F-center wave function. F. J. Adrian, W. E. Blumberg, and T. P. Das, Bull. Am. Phys. Soc. 2, 317 (1957).
[11] N. Bloembergen, Physica 25, 386 (1949).

factor, the enhanced probability may be written as

$$P \cong \frac{b^2}{\hbar^2} \frac{T_S}{1+\omega^2 T_S^2}. \tag{13}$$

For $b/h = 2.5$ Mc/sec, $\omega = 2\pi \times 10^7$ sec^{-1}, and $T_S = 2 \times 10^{-6}$ sec, this gives $P = 3 \times 10^4$ or $T_N = 1.6 \times 10^{-5}$ sec.

C. Perturbation of the Spin-Orbit Coupling

The ground-state wave function of the F-center electron is primarily of s character. The existence of a g shift[12] for the electron spin resonance shows, however, that there is an admixture of states of higher angular momentum. The calculations of Blumberg and Das[9] show that the admixture of $l>0$ states into the s state ψ_F is adequately taken into account by the Löwdin[13] orthogonalization process by which the function ψ_F is made orthogonal to wave functions of all the ion core electrons on neighboring ions.

Blumberg and Das made the approximation that

$$\Delta g = (2/E_F) \sum_{\alpha i} \langle F | \alpha_i \rangle^2 \lambda_{\alpha i} \langle \alpha_i | L_z^2 | \alpha_i \rangle, \tag{14}$$

which says in effect that the F-center electron appears to have the spin-orbit coupling of the ion core electrons reduced by $\langle \alpha_i | F \rangle^2$, the square of the overlap of the computed F-center wave function with the wave function of the ion core electron. Here E_F is the F-band energy.

The summation in (14) represents the average spin-orbit coupling of the F-center electron and it may be taken equal to the λ of the spin Hamiltonian (1). For NaCl, λ has the value 13 cm^{-1}. Since the angular momentum is quenched in the ground state, the effect of the term $\lambda \mathbf{L} \cdot \mathbf{S}$ vanishes in first order, and a second-order perturbation must be used to compute the relaxation transitions.

In (14) it will be noted that $\lambda_{\alpha i}$ and $\langle L_z^2 \rangle$ are intrinsic properties of the ion itself, and only the part $\langle F | \alpha_i \rangle^2$ is dependent upon the geometry of the lattice vacancy and the F-center wave function. The time-dependence of λ arising from changes in $\langle F | \alpha_i \rangle$ due to lattice vibrations leads to the relaxation transitions.

We now need the second-order matrix elements of $\mathcal{K} = \lambda \mathbf{L} \cdot \mathbf{S}$ connecting the different Zeeman and vibrations states of the spin system and lattice oscillator system. These will be given by

$$\langle \mathcal{K} \rangle = \sum_j \frac{\langle \mathcal{K}_{ij} \rangle \langle \mathcal{K}_{jf} \rangle}{E_j - E_f}, \tag{15}$$

where we have lumped all the quantum numbers designating a state of the complete system into a single index: initial state i, intermediate state j, and final state f.

There are only a finite number of bound states j in the sum, and these states have an energy greater than the F-band energy E_F but less than the binding energy of the F-center electron, which is only slightly larger than E_F. The free states will make no contribution to the sum in (15) as the angular momentum of these states is zero. Thus $E_j - E_f$ may be replaced by E_F in (15) and the matrix sum carried out to obtain

$$|\mathcal{K}| \cong |\mathcal{K}_{if}^2| / E_F. \tag{16}$$

Proceeding exactly as in Sec. IIA, that part of the perturbing Hamiltonian interacting with two phonons is obtained:

$$|\mathcal{K}'| \cong \frac{m_s^2}{E_F} \frac{d^2\lambda^2}{dr^2} \frac{2\hbar a^2 \omega}{3v^2 M [\exp(\hbar\omega/\kappa T) - 1]}. \tag{17}$$

The derivatives of the spin-orbit coupling coefficient λ are obtained in an analogous manner to the derivatives of A previously evaluated. This gives

$$d^2\lambda^2/dr^2 = [12(\eta+1)^2 + 4(\xi^2+1)]\lambda^2/a^2 = 162\lambda^2/a^2. \tag{18}$$

Now, combining (3), (17), and (18) into (2), we obtain

$$P \cong \frac{2\pi}{\hbar^2} \int_0^{\omega_m} \left(\frac{9\omega^2\hbar^3 V}{\kappa^3\theta^3 a^3} \right)^2$$
$$\times \left(\frac{162\lambda^2 m_s^2}{a^2} \frac{2\hbar a^2 \omega}{3v^2 M[\exp(\hbar\omega/\kappa T) - 1]} \right)^2 d\omega. \tag{19}$$

As before, introducing $\rho = M/V$, $T^* = T/\theta$ and $\kappa\theta a = (6\pi^2)^{\frac{1}{3}}\hbar v$ gives the final expression for the transition probability,

$$P \cong 1.4 \times 10^6 \frac{\lambda^4 T^{*7}}{\rho^2 v^3 a^7 E_F^2} \int_0^{1/T^*} \frac{x^6 dx}{(e^x - 1)^2}. \tag{20}$$

For F centers in NaCl at $T = 300°$K, this gives $P = 4 \times 10^4$ sec^{-1} or $T_S \cong 10^{-5}$ sec.

It must be emphasized here that there are two distinct sources of approximation involved in the preceding treatment. First there is the question of the detailed nature of vibrational amplitudes and phases near a lattice imperfection. First, one might say that, since the ions neighboring the vacancy are not subject to as strong restoring forces as the ions in the bulk medium, the vibrational amplitudes of these ions would be larger and thus tend to decrease the value of T_S. Moreover, in this treatment, the phase difference between the vibration of different ions has been neglected. Above the Debye temperature, one can assume that even neighboring ions vibrate with random phases for the purpose of computing an order-of-magnitude estimate of the transition probability.

Second, there is the question of the detailed nature of the spin-orbit interaction itself. We have proceeded as if the entire interaction were due to the overlap of ψ_F with the $l>0$ electrons of the nearest neighboring ions only.

[12] C. A. Hutchison, Jr., and G. A. Noble, Phys. Rev. **87**, 1125 (1952).
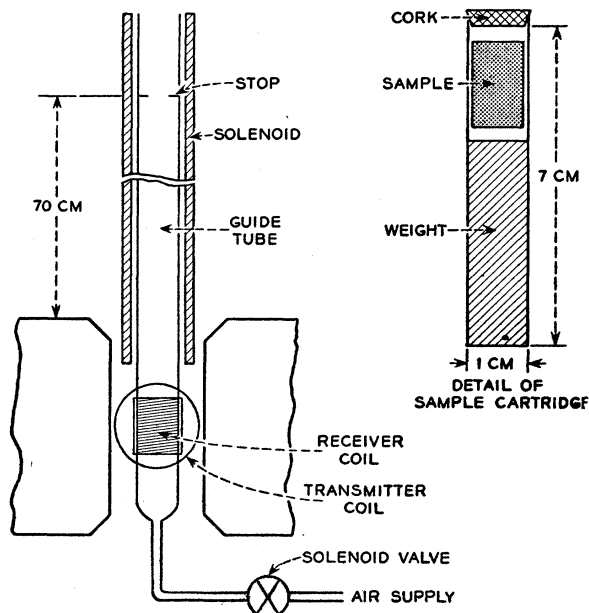[13] Per-Olov Löwdin, J. Chem. Phys. **18**, 365 (1950).

FIG. 2. Schematic diagram of sample transport system. The cartridge containing the sample fits inside the glass guide tube and can be made to travel between the receiver coil and upper stop by means of compressed air.

For the case of KCl, calculations[14,15] show that the six nearest K^+ ions contribute more than twice as much to the spin-orbit interaction as the eight nearest Cl^- ions. For heavier potassium halides, however, the contribution from the halide ions increases to a much greater proportion relative to that of the K^+ ions, which remains roughly the same for all the K halides. For F centers in LiF, on the other hand, there is no contribution at all to the spin-orbit interaction from the Li^+ ions in this model, as these contain no $l > 0$ electrons, and the principal contribution is made from the eight nearest F^- ions. Adrian's more exact model of the spin-orbit coupling shows that there is indeed a small contribution to λ from the Li^+ ions. The effects on the relaxation due to the next-nearest and more remote neighbors have been neglected since, at greater distance, ψ_F becomes less curved, and the value of $d^2\lambda/dr^2$ decreases.

It is seen from the several preceding rough calculations that the value of T_S (1.2×10^{-5} sec) due to the spin-orbit-phonon process is much smaller than the T_S (1 sec) arising from the hyperfine-phonon process. Also, the value of T_S is much smaller than the smallest calculated value of either the larger of T_{X0} and T_N (10^{-3} sec) or the larger of T_{X2} and T_N (1 sec), so that excess Zeeman energy in the electron spin system is transmitted to the lattice predominantly by means of an electron spin flip in which the nuclear spin quantum numbers are not changed.

14 F. J. Adrian, Phys. Rev. 107, 488 (1957).
15 A discussion of the various contributions to the g shift will be found in B. S. Gourary and F. J. Adrian, Solid-State Physics, edited by F. Seitz and D. Turnbull [Academic Press, New York (to be published)].

III. EXPERIMENT

The spin-lattice relaxation time T_S of F-center electrons in NaCl has been measured at 300°K at three values of the magnetic field by three entirely different methods. At very low fields an experimental determination of T_S was made by observing the relaxation of the Na^{23} nuclei in the bulk of the crystal. At 2950 gauss, an X-band microwave electron resonance experiment using slow passage techniques yielded T_S by the observation of the relative values of the absorption and dispersion mode signals. At 8300 gauss, a K-band microwave electron resonance experiment, using fast passage techniques, was used to calculate T_S by obtaining the dispersion mode signal as a function of modulation field amplitude. Each of these methods will be discussed separately.

A. Low Field Measurement

As has been discussed by Bloembergen,[11] the presence of unpaired electron spins in a crystal may have a large effect upon the relaxation rate of the nuclei in the crystal. A pulsed nuclear resonance experiment[16] was performed at 9100 gauss (10.6 Mc/sec for the Na^{23} nuclei) on a pure Harshaw quality NaCl single crystal and on a similar crystal[17] which contained approximately 10^{18} F-center electrons per cm^3 to determine the nuclear spin-lattice relaxation time of each. These two crystals exhibited the same relaxation time, 12 sec, indicating that the F-center electrons were not effective in relaxing the nuclei at this magnetic field. The reason for this is that the factor $T_S/(1+\omega^2 T_S^2)$ in the expression for the electron-induced transition probability is too small. At lower values of the field, where ω becomes of the order of $1/T_S$, the relaxation effects of the electrons should be increased.

It would thus appear desirable to measure the nuclear relaxation as a function of the magnetic field by changing the frequency of the nuclear spectrometer. This, however, presents some severe experimental difficulties, since the sensitivity of nuclear resonance apparatus is proportional to H^2, and lowering the field would reduce the signal-to-noise ratio of the experiment. Therefore, a procedure[18] was adopted which would allow the field at which the nuclear spin population was measured to remain at 9100 gauss but allowing the field at which relaxation took place to vary. The sample was placed in a small cylindrical cartridge which fitted inside a long glass tube. The tube passed through the receiver coil of the nuclear resonance apparatus in the center of the magnet gap and extended vertically well into the fringe

16 The equipment used for this experiment has been described in detail by E. G. Wikner, thesis, University of California, 1959 (unpublished).
17 The author is grateful to A. M. Portis for furnishing the NaCl crystals containing the F centers.
18 This procedure, which is a refinement of one first used by R. V. Pound and N. F. Ramsey [Phys. Rev. 81, 278 (1959)], has been previously described by the author [W. E. Blumberg and E. L. Hahn, Bull. Am. Phys. Soc. 3, 318 (1958)].

FIG. 3. Block diagram of sequence generator. To the right is shown the sequence of events during one cycle of the apparatus. The height of the free induction tail H is a measure of the nuclear magnetization remaining after relaxation for a time T_R.
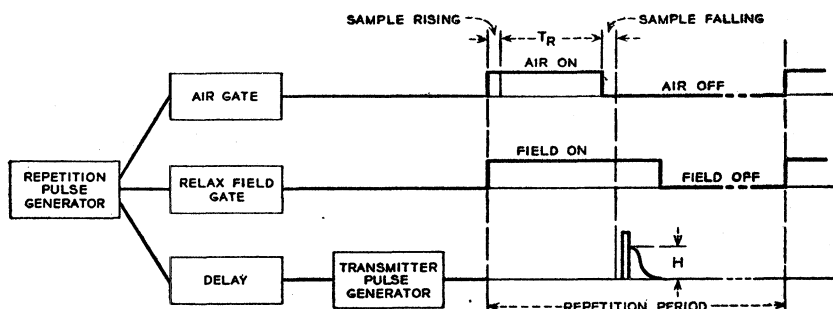
field of the magnet. The tube was fitted with appropriate stops at each end such that the two limits of travel of the cartridge in the tube were the exact center of the receiving coil and a point 70 cm from the gap of the magnet, where the fringe field was approximately two gauss. The cartridge could be made to travel from the receiver coil to the upper stop outside the magnet by means of compressed air. When the air pressure was removed, the cartridge would fall back into the magnet gap. A solenoid was wound on a long cylindrical form which would cover the glass tube from the receiving coil to a point 25 cm beyond the upper stop. A schematic diagram of the apparatus is shown in Fig. 2. The sample could be transported from the nuclear resonance apparatus to the field of the solenoid, where it could relax for any desired time interval and then be returned to the magnet for a measurement of the nuclear spin population. The trip up and down required about 0.4 second each way. This rate was slow enough so that the transiton from the high horizontal field to the lower vertical field was adiabatic at all times.

To eliminate the human reaction time from the experiment, the entire apparatus was programmed to run automatically. The block diagram of the sequence generator and the program of the air pressure, solenoid field, and nuclear resonance apparatus are shown in Fig. 3. At the start of a cycle, the air and the solenoid current were turned on simultaneously. The sample rose and relaxed in the field of the solenoid for a predetermined time, after which the air was turned off, allowing the sample to fall. After the sample had returned to the receiver coil, a delayed pulse triggered the radiofrequency transmitter to measure the nuclear spin population. An additional delay of 0.1 sec was made to allow for variations in falling time. The sweep of the oscilloscope was triggered by the transmitter, and the nuclear free induction signal was presented on the cathode-ray tube where it could be photographed. When the oscilloscope had completed its trace, the solenoid current was turned off. After the completion of one cycle, a sufficient time elapsed to insure that the nuclear spin system returned to thermal equilibrium before another cycle was begun.

While the preliminary data from the experiment was taken photographically, it was found that a more precise measurement could be made by using an electronic data

sampler[19] which measured the height of the free-induction signal and fed this information to a Brown recording potentiometer. The apparatus was gated so that the recorder held the value of the signal from one cycle until the next cycle was completed. In practice, the sequence generator was allowed to complete about 10 cycles at a given value of the solenoid field before changing to a new value, and an average of the signals was taken from the recorder.

Results for one set of measurements are shown in Fig. 4. Here the ordinate is the fraction of the nuclear magnetization remaining after a time T_R (2.5 seconds in this case) multiplied by $\exp(+T_R/T_1)$, and the abscissa is the Larmor frequency of the Na^{23} nuclei. For the values of the solenoid field H_R used, we have neglected $\mu H_R/\kappa T$ with respect to $\mu H_0/\kappa T$. Thus, if the only relaxation processes present are those taken into account by the measurement of $T_1 = 12$ sec at high fields, the ordinate of each experimental point should be unity. It will be seen that this is true for the NaCl sample without F centers, but an additional relaxation process appears at low fields for the sample containing the F centers. Seven such runs were made for different values of T_R on samples of two different concentrations[20] of F centers. The additional relaxation rates occurring
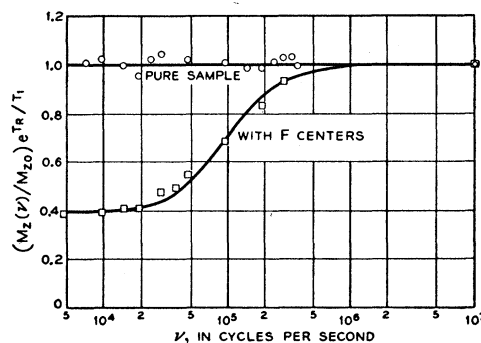

FIG. 4. Results of a run in which the time T_R spent in the low field was 2.5 sec. The ordinate is proportional to the nuclear magnetization remaining after return to the large magnetic field. The effects of relaxation due to the F centers become important for $\nu \lesssim 10^5$ cps ($H_R \cong 100$ gauss).

[19] E. G. Wikner, reference 16.

[20] The concentrations of the two samples were measured by microwave Faraday rotation and are 4.4×10^{17} and 2.3×10^{18} F centers per cm^3, as reported in D. Teaney, W. E. Blumberg, and A. M. Portis, following paper [Phys. Rev. 119, 1851 (1960)].

at low fields were in the ratio of $6.7:1\pm20\%$, while the ratio of the F-center concentration calculated from measurements of microwave Faraday rotation is 5.2, with an error of approximately 20%. If the nuclear relaxation is occurring by a process in which the diffusion of nuclear spin energy to the F center plays a large role, the relaxation rate should be proportional to the concentration of unpaired electrons.[21] The data from the various runs were combined and are shown in Fig. 5. The ordinate y of each plot similar to Fig. 4 was observed to have a low field plateau y_0 for each run. The ordinate of Fig. 5 is taken as $\ln(1-y)/\ln(1-y_0)$. Thus, the vertical scale of Fig. 5 is the power spectrum of S_z, $J(\omega)=(1+\omega^2 T_S^2)^{-1}$ normalized to $J(0)=1$. Since the power spectra of S_x and S_y are spread over a frequency range of the line width of the F-center resonance, ~500 Mc/sec, they are assumed to have negligible effect. It will be noted that, within the experimental scatter of the points, all the data lead to the same $J(\omega)$ independent of the time the sample was allowed to relax and the concentration of F centers. The solid curve is drawn to have the Lorentz form $J(\nu)=(1+4\pi^2\nu^2 T_S^2)^{-1}$, with T_S chosen to be 2×10^{-6} sec for the best fit. The scatter of the points allows the determination of T_S to be made within $\pm20\%$. This measurement of T_S is taken to be appropriate to 70 gauss, where $J(\omega)=\frac{1}{2}$. However, the good fit to the Lorentizan curve indicates that T_S is a constant in the range 10 to 400 gauss.

The value of T_S obtained above is the true spin-lattice relaxation time and contains no contribution from the spin-spin relaxation time T_{SS} due to interaction between F centers. Since T_{SS} depends[22] upon the sixth power of the average distance between F centers, it should vary inversely as the concentration squared, but no concentration dependence was observed in this experiment. An
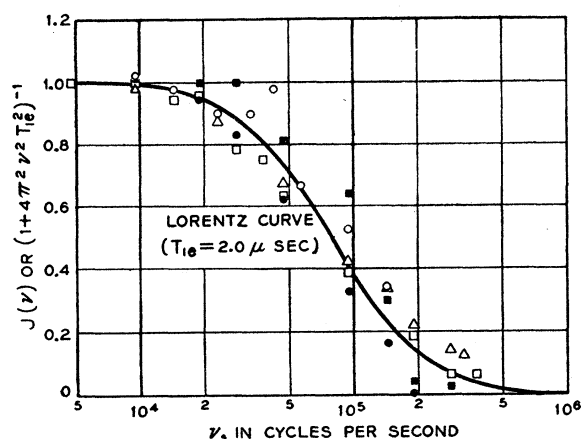

FIG. 5. The combined results of relaxation measurements for different time intervals and different sample concentrations. The open points represent data from the sample of higher concentration, and the solid points are from the more dilute sample. The Lorentz curve crosses $J(\nu)=\frac{1}{2}$ at $\nu=8.0\times10^4$ cps or 70 gauss.

[21] W. E. Blumberg, Phys. Rev. 119, 79 (1960).
[22] P. W. Anderson, Phys. Rev. 109, 1492 (1958).

estimate of T_{SS} is $\Delta\omega(\hbar/N\mu_2^2)^2\cong1$ sec, where $\Delta\psi$ is the total line width of the F-center resonance and $N\mu_e^2/\hbar$ is the mean dipolar line width of N electrons per cm³.

If the value of T_S were a strong function of the magnetic field, the data in Fig. 5 would be skewed with respect to the Lorentz curve, and the value of T_S obtained by setting $J(\omega)=\frac{1}{2}$ would be in error. As we shall see by measurements at higher fields, T_S is not a strong function of the magnetic field.

B. X-Band Measurement

Using X-band microwaves, a slow passage saturation experiment was performed which was exactly analogous to that reported by Portis[1] for F centers in KCl. The microwave apparatus used has been discussed by Portis and Teaney.[23] The measurement of the microwave parameters and their use in computing the microwave magnetic field H_1 is discussed in the following article.[20] Under the experimental conditions of this measurement, the value of the average microwave field in the sample was 0.53 gauss at maximum power. As Portis[1] has shown, the ratio of dispersion signal to absorption signal for an inhomogeneously broadened Gaussian line is

$$\chi'/\chi''=1.65/(1+\gamma_e^2 H_1^2 T_S^2)^{\frac{1}{2}}. \tag{21}$$

Here we have assumed $T_{SS}\gg T_S$ and that for the electron $T_1=T_2=T_S$. There is no apparent reason why, in the absence of a spin-spin interaction, there should be any difference between the longitudinal and transverse relaxation times of the F-center electron.

The absorption and dispersion signal amplitudes are shown in Fig. 6. At maximum microwave power, the ratio of dispersion to absorption signals is 16. This gives, from (21), $T_S=1.7\times10^{-6}$ sec. Uncertainties in the measurement of the microwave power and cavity Q are estimated to place limits of error on T_S of $\pm50\%$.

C. K-Band Measurement

A measurement of the electron spin-lattice relaxation time at a magnetic field of 8300 gauss (23.5 kMc/sec) was carried out using a technique proposed by Portis[24] and used to measure T_S of F centers in LiF.[2] The technique consists of observing the behavior of the dispersion mode electron resonance signal as a function of magnetic field modulation amplitude, followed by fitting this function with a theoretical expression containing T_S as a parameter.

In several different regions, defined by the relative magnitudes of the experimental variables, the dispersion mode signal has different forms. If the magnetic field is being modulated by the addition of a field of amplitude $H_m\cos\omega_m t$, the dispersion mode signal will have a com-

[23] A. M. Portis and D. Teaney, J. Appl. Phys. 29, 1692 (1958).
[24] A. M. Portis, Technical Note No. 1, Sarah Scaife Radiation Laboratory, University of Pittsburgh, November 15, 1955 (unpublished).

Fɪɢ. 6. Peak absorption and peak-to-peak dispersion signals for F-center electron resonance in NaCl at 8300 Mc/sec. The value of the microwave field H_1 at 0 db is 0.53 gauss in the rotating frame of the electrons.
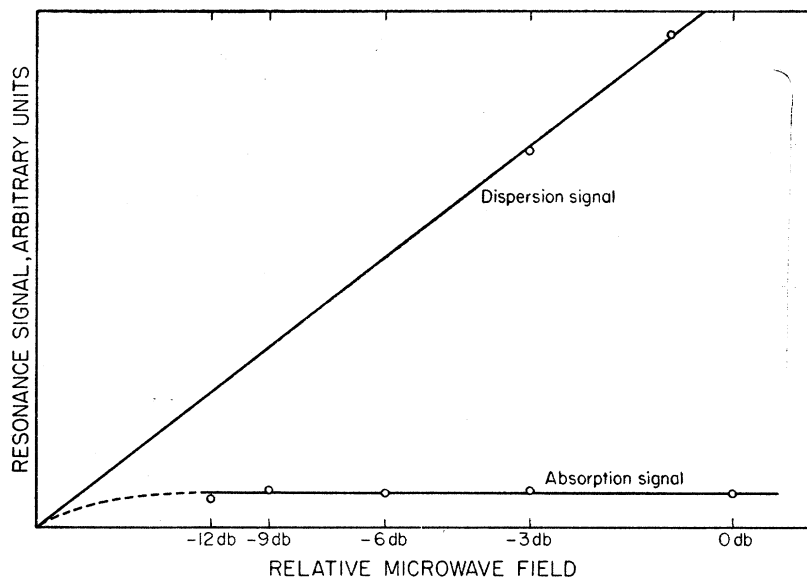
ponent at frequency ω_m and at a phase difference ψ with respect to the modulation field. Assume that H_1 is large enough to ensure saturation of individual spin packets in the resonance line, i.e., $\gamma H_1 T_S > 1$, and that the passage through a given spin packet is adiabatic, i.e., $\omega_m H_m < \gamma H_1^2$. Under these conditions, Portis[24] has shown that the strength of the dispersion signal is given by

$$S_d = \frac{\pi \chi_0}{4(2\pi)^{\frac{1}{2}}} \frac{\omega}{\Delta\omega} \zeta \sin\omega_m t, \qquad (\zeta < 1), \quad (22)$$

$$S_d = \frac{\chi_0}{(2\pi)^{\frac{1}{2}}} \frac{\omega}{\Delta\omega} \ln[\zeta + (1+\zeta^2)^{\frac{1}{2}}] \sin\omega_m t, \quad (\zeta > 1). \quad (23)$$

Here χ_0 is the static spin susceptibility and ζ has been written for $H_m \omega_m T_S / H_1$. There is a small transition region near $\zeta = 1$ where both expressions become approximate. Note that both expressions have time-dependence $\sin\omega_m t$ and thus are $\pi/2$ out of phase with the modulation field.

One could place the sample in a position of uniform H_1 and increase the value of H_m until the signal changed from a linear dependence upon H_m to a logarithmic dependence. The position H_m' of this break would give $T_S = H_1 / \omega_m H_m'$. However, because of the dilute nature of F-center samples, a rather large sample must be used, and the achievement of a uniform microwave field is difficult, especially at the higher frequencies.

In this experiment, no attempt was made to create a uniform microwave field. The sample was cut to exactly fill a resonant rectangular cavity. The coupling of the cavity to the waveguide was varied until the cavity was matched ($\beta > 0.99$) in order to obtain the maximum H_1. The value of H_1, calculated as indicated in the following article,[20] was 9.4×10^{-2} gauss at the position of maximum intensity in the cavity. According to the position in the crystal, the microwave field varied from zero to H_1. The value of the microwave field as a function of position will be denoted by $h(r)$. In some parts of the crystal where h was very small, the adiabatic passage condition was violated. This case gives a complicated dispersion signal which decreases with increasing H_m.[25] It is assumed that for $\omega_m H_m > \gamma h^2$ there is a negligible dispersion signal component $\pi/2$ out of phase with the modulation field. A phase-sensitive detector[26] was used to detect the resonance signal. The phase of the detector was adjusted to accept signals differing in phase by $\pi/2$ from the modulation field, which varied sinusoidally at a frequency of 1050 cps.

To obtain the theoretical dependence of the signal on modulation amplitude, Eqs. (22) and (23) must be averaged over the volume V of the entire cavity. This was accomplished by numerical evaluation of the following integrals.

$$S_d = \frac{\chi_0}{(2\pi)^{\frac{1}{2}} V} \frac{\omega}{\Delta\omega} \sin\omega_m t \left\{ \frac{\pi}{4} \int_{h = H_m \omega_m T_S}^{h = H_1} \zeta d^3 r \right.$$

$$\left. + \int_{h = (H_m \omega_m/\gamma)^{\frac{1}{2}}}^{h = H_m \omega_m T_S} \ln[\zeta + (1+\zeta^2)^{\frac{1}{2}} d^3 r] \right\}. \quad (24)$$

The parameter ζ now has the meaning $H_m \omega_m T_S / h(r)$. The integrals are to be carried out over the entire volume of the cavity. The limits of the integrals are given in terms of the microwave field at the boundary between the three regions: (1) that contributing a linear signal; (2) that contributing a logarithmic signal; and (3) that contributing no signal.

[25] M. Weger, Phys. Rev. (to be published).

[26] The author is indebted to D. N. Langenberg and T. W. Moore for permitting the use of their equipment for this experiment. The entire K-band spectrometer has been described in detail by X. Langenberg, thesis, University of California, 1959 (unpublished).
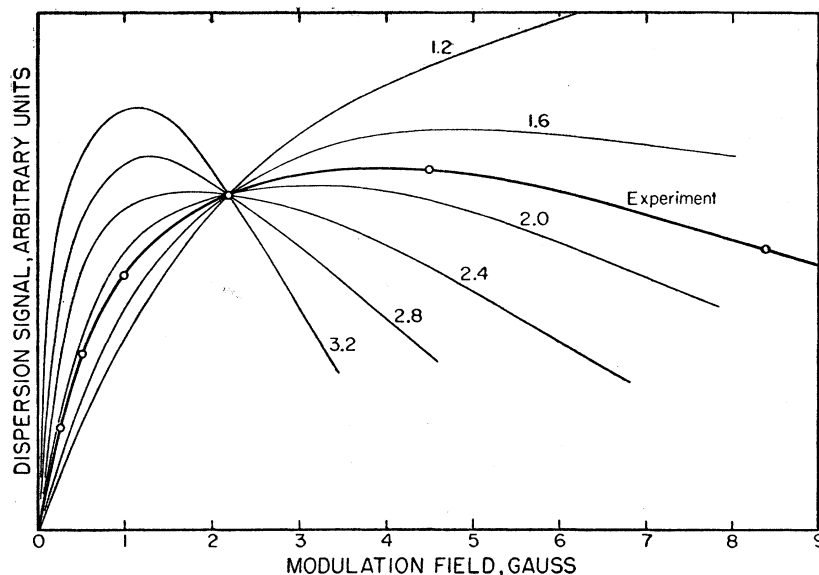
The experimental curve is plotted in Fig. 7, along with several theoretical curves calculated from (24) with T_S, in microseconds, as a parameter. Since no measurement was made of the absolute signal intensity, the theoretical curves have been normalized to one of the experimental points. It can be seen that the experimental data fits with a value of T_S of approximately 1.8×10^{-6} sec. The uncertainty in determining the microwave parameters places estimated limits of accuracy of $\pm 50\%$ on this value.

TABLE II. Summary of measured T_S for NaCl.

Magnetic field (gauss)	70	2950	8300
T_S, microseconds	2.0±0.4	1.7±0.9	1.8±0.9

By way of summary, the three measured values of T_S are listed in Table II. It is noted that the value of T_S is practically independent of the magnetic field, as would be predicted from (20). The agreement between the theory and experiment is considered within the range of the approximations made in treating the lattice vibrations and the nature of the spin-orbit interaction. It would be interesting to measure the values of T_{X0}, T_{X2}, and T_N by cross-saturation experiments to see whether the orders of magnitude estimated in Sec. II for these times are correct.

ACKNOWLEDGMENTS