Similarly, Eq. (5) then becomes

$$\langle \mathbf{v}' \mid \exp(\pm i\mathbf{k}\cdot\mathbf{r}) \mid \mathbf{v}\rangle = \delta_{v_z',\,v_z\pm\hbar k_z/\mu}[\langle n' \mid \exp(\pm i\mathbf{k}\cdot\mathbf{r}_\perp) \mid n\rangle]$$
$$= \delta_{v_z',\,v_z\pm\hbar k_z/\mu}[\delta_{n',n} \pm i\langle n' \mid \mathbf{k}\cdot\mathbf{r}_\perp \mid n\rangle + \cdots], \tag{80}$$

where $\mathbf{r}_\perp$ is the position vector of the particle in a plane perpendicular to the uniform magnetic field $\mathbf{H}_0 = H_0\hat{\imath}_z$. Since the leading term in [ ] of Eq. (80) is $\delta_{n',n}$, to a first approximation we can use the above theory for a gas of charged-spin-$\frac{1}{2}$ particles (such as the electrons, the positrons, the protons, etc.) in a uniform magnetic field $\mathbf{H}_0 = H_0\hat{\imath}_z$, provided we make the following modifications:

$$\mathbf{v}\to v_z; \quad \mathbf{v}'\to v_z'; \quad \mathbf{v}_d\to\hat{\imath}_z\cdot\mathbf{v}_d; \quad \pm\hbar\mathbf{k}/\mu\to\pm\hbar k_z/\mu; \quad \mathbf{k}\cdot\nabla_v\to k_z(\partial/\partial v_z); \quad \mathbf{k}/\omega\to k_z/\omega;$$
$$\left(\frac{\omega - m\omega_s - \mathbf{k}\cdot(\mathbf{v}_d \pm \hbar\mathbf{k}/2\mu)}{k}\right) \to \left(\frac{\omega - m\omega_s - k_z(\hat{\imath}_z\cdot\mathbf{v}_d \pm \hbar k_z/2\mu)}{k_z}\right)$$

and consequently the right-hand side of Eqs. (26), (39), (41), (43), (45), (56b), (62), and (73) has to be multiplied by the factor (k/k_z). This factor arises from the modifications of the arguments of the Dirac δ functions over which an integration has already been performed. The g values (neglecting the radiative corrections[18,19]) for the electron, the positron, and the proton[15] are $+2$, -2, and 5.59, respectively.

In the above simple theory we found that when the induced emission exceeds the absorption, the system of spin-$\frac{1}{2}$ particles in a uniform magnetic field is unstable for radiations of frequencies $\omega \approx m\omega_s$, where m may take any one of the values 0, +1, or −1. It is, of course, interesting and physically instructive to seek an answer to the following question: What is the ultimate fate of the system once such an instability sets in? If one wishes to seek the answer to this question, then one must use the improved form of Eq. (9) due to Heitler and Ma.[3]

ACKNOWLEDGMENTS

It is a pleasure to thank Professor T. H. Stix for valuable suggestions, discussions, and encouragement. I also wish to thank Professor E. A. Frieman for discussions and encouragement.

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Nuclear-Magnetic-Resonance Free Induction Decay in a Two-Spin System*

Moses Lee,† D. Tse, W. I. Goldburg, and I. J. Lowe
Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania

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Measurements and calculations of the nuclear-magnetic-resonance free induction decay (FID) in sodium chloride are presented. The experiments consisted of the observation, by standard pulse techniques, of the FID in the sodium spin system at several crystal orientations. The calculation represents an extension of the method of Lowe and Norberg to the case where both nuclear species have arbitrary spin. Theory and experiment are in very good agreement. Quadrupolar effects due to intentional straining of the crystal could only be produced by rapid quenching from just below the melting point to room temperature. It thus appears that only in such severely strained crystals is quadrupolar broadening appreciable.

I. INTRODUCTION

We present here a calculation and measurement of the nuclear-magnetic-resonance (NMR) free-induction-decay function in a spin system containing two magnetic ingredients of arbitrary spin. The theory is an extension of the work of Lowe and Norberg,[1] who first calculated the free-induction-decay (FID) function for a one-ingredient, spin-$\frac{1}{2}$ system. Though the Lowe–Norberg (LN) calculation has been experimentally confirmed in the case of CaF_2,[1–3] their work has been subject to criticism[4] because it utilizes a perturbation expansion which lacks a clear-cut convergence criterion. It therefore seemed desirable to subject their method to additional experimental test in a spin system differing appreciably from calcium

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† Now at Davis and Elkins College, Elkins, West Virginia.

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

[2] D. E. Barnaal and I. J. Lowe, Phys. Rev. **148**, 328 (1966).

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fluoride. Sodium chloride was chosen for this study because of its structural simplicity, its ready availability in the form of single crystals of great purity, and, most importantly, because the spin-spin interaction parameters which enter the FID calculation are known. There exists only one experimental uncertainty in this work. The sodium nuclei, whose resonance was observed in these experiments, have a quadrupole moment which couples with strain-induced field gradients in the sample and contribute to shortening of the FID (or broadening of the NMR absorption line). Fortunately no appreciable quadrupole broadening was observed except in those crystals which were intentionally subjected to severe strain by rapid quenching from just below the melting point to room temperature.

In the unstrained samples, agreement between theory and experiment was as satisfactory as in CaF_2. This good agreement was obtained even though the complexity of the calculation required dropping certain higher-order terms, which were kept by LN, and by Gade and Lowe.[5] The latter authors have calculated the FID in single-ingredient spin systems in which the nucleus has arbitrary spin.

The measurements to be described were made at three crystal orientations for which the static applied field $\mathbf{B}_0$ was parallel to the [100], [110], and [111] directions in the crystal. (We will use the notation, $\mathbf{B}_0 \parallel [100]$, $\mathbf{B}_0 \parallel [110]$, etc.) When $\mathbf{B}_0 \parallel [111]$, the effect of the chlorine nuclei on the sodium resonance is predicted to be negligibly small and therefore NaCl should behave like a face-centered-cubic one-ingredient spin-$\frac{3}{2}$ system treated by Gade and Lowe. Their results are in slightly better agreement with our measurements than the theoretical calculation described here (see Fig. 4), presumably because they were able to retain the above-mentioned high-order terms in the time expansion of the FID function. At orientations other than $\mathbf{B}_0 \parallel [111]$, the results of Gade and Lowe could, of course, not be tested in NaCl.

The next section of this paper contains our calculations of the free-induction-decay function $F(t)$ for the two-ingredient system in which the nuclei of an arbitrary spin are coupled by dipolar and scalar exchange interactions. In Sec. III the NaCl measurements are described in some detail and a comparison is made with the theory of Sec. II. Strictly speaking NaCl is a three-ingredient system, since there are two chlorine isotopes present in appreciable abundance. Both of these isotopes however have the same spin ($\frac{3}{2}$) and almost equal magnetogyric ratios; therefore, little error is introduced by treating the chlorine nuclei as a single-spin system whose magnetic moment is the average of that of the Cl^{35} and Cl^{37} isotopes. The results of this study are discussed in Sec. IV.

II. THEORY

We start with the general formula for the free-induction-decay function given by LN and by Anderson.[6] This formula, which is also derived in Abragam's book,[4] is as follows:

$$F(t)=\mathrm{Tr}\{I_x I_x(t)\}/\mathrm{Tr}\{I_x^2\}, \tag{1}$$

where I_x is the x component of the total angular momentum of the spin system I whose resonance is being observed, i.e.,

$$I_x=\sum_{i=1}^{N} I_{xi}$$

and

$$I_x(t)=\exp(i\mathcal{H}t/\hbar)\,I_x\exp(-i\mathcal{H}t/\hbar). \tag{2}$$

The operator $\mathcal{H}$ is the truncated dipolar and scalar interaction term, i.e., that part of the interaction which commutes with the Zeeman energy operator,

$$\mathcal{H}_Z \equiv -\gamma\hbar\mathbf{B}_0\cdot\sum_{i=1}^{N}\mathbf{I}_i-\gamma'\hbar\mathbf{B}_0\cdot\sum_{i'=1}^{N'}\mathbf{S}_{i'}, \tag{3}$$

where B_0 is the magnitude of the applied static magnetic field (taken to be in the z direction), and γ is the magnetogyric ratio of the resonant spin system consisting of N nuclei, each of spin I. The corresponding quantities for the unobserved spin system, whose nuclei have spin S, are γ' and N'. The terms in the truncated interaction Hamiltonian are

$$\mathcal{H}=\hbar(\alpha+\beta), \tag{4}$$

where

$$\alpha=\sum_{i<j} a_{ij}\mathbf{I}_i\cdot\mathbf{I}_j+\sum_{i'<j'} a'_{i'j'}\mathbf{S}_{i'}\cdot\mathbf{S}_{j'}, \tag{5}$$

$$\beta=\sum_{i<j} b_{ij}I_{iz}I_{jz}+\sum_{i'<j'} b'_{i'j'}S_{i'z}S_{j'z}+\sum_{i,j'} c_{ij'}I_{iz}S_{j'z}, \tag{6}$$

and

$$\begin{aligned} a_{ij}&=\tilde{A}_{ij}-\tfrac{1}{3}b_{ij},\\ b_{ij}&=\tfrac{3}{2}\gamma^2\hbar[(1-3\cos^2\theta_{ij})/r_{ij}^3], \end{aligned} \tag{7}$$

$$\begin{aligned} a_{i'j'}'&=\tilde{A}_{i'j'}-\tfrac{1}{3}b_{i'j'}',\\ b_{i'j'}'&=\tfrac{3}{2}\gamma'^2\hbar[(1-3\cos^2\theta_{i'j'})/r_{i'j'}^3],\\ c_{ij'}&=\tilde{A}_{ij'}+\gamma\gamma'\hbar[(1-3\cos^2\theta_{ij'})/r_{ij'}^3]. \end{aligned} \tag{8}$$

The exchange-interaction coefficients $\tilde{A}_{ij}$, $\tilde{A}_{i'j'}'$, and $\tilde{A}_{ij'}$ are in units of angular frequency. The unprimed and the primed indices will always be used to denote summations over the I and S spin systems respectively.

The FID function $F(t)$ of Eq. (1) is evaluated as follows: We note that the operator $I_x(t)$ satisfies the equation

$$i\hbar(\partial/\partial t)I_x(t)=[I_x(t),\mathcal{H}]. \tag{9}$$

It is convenient to introduce a new operator $I_x'(t)$ by the equation

$$I_x(t)=e^{i\beta t}I_x'(t)e^{-i\beta t} \tag{10}$$

which in turn satisfies the equation

$$i(\partial/\partial t)I_x'(t)=[I_x'(t),\alpha(t)], \tag{11}$$

with

$$\alpha(t)=e^{-i\beta t}\alpha e^{i\beta t}. \tag{12}$$

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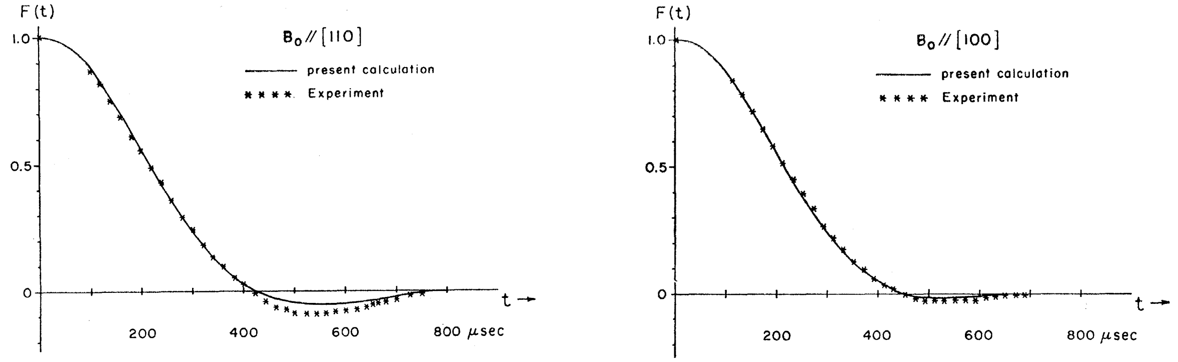
[5] S. Gade and I. J. Lowe, Phys. Rev. **148,** 382 (1966).

[6] P. W. Anderson, J. Phys. Soc. Japan **9,** 316 (1954).



(a) (b)

FIG. 1. Theoretical and experimental FID's of the Na spin system in the Melpar NaCl crystal. (a) $\mathbf{B}_0 \parallel [110]$; (b) $\mathbf{B}_0 \parallel [100]$.

The formal solution of Eq. (11), as derived by an iteration process, is given by

$$I_x'(t)=I_x+\sum_{n=1}^{\infty}(-i)^n\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n[\cdots[I_x,\alpha(t_n)],\cdots],\alpha(t_1)]. \tag{13}$$

After substitution of Eqs. (10) and (13) into Eq. (1) and rearrangement of the order of terms, Eq. (1) becomes

$$F(t)=\frac{\mathrm{Tr}\{I_x''(t)I_x'(t)\}}{\mathrm{Tr}\{I_x^2\}}=\sum_{n=0}^{\infty}G_n(t), \tag{14}$$

where

$$I_x''(t)=e^{-i\beta t}I_x e^{i\beta t}, \tag{15}$$

and

$$G_0(t)=\mathrm{Tr}\{I_x''(t)I_x\}/\mathrm{Tr}\{I_x^2\},$$

$$G_n(t)=(-i)^n\int_0^t dt_1\cdots\int_0^{t_{n-1}}dt_n\,\frac{\mathrm{Tr}\{I_x''(t)[\cdots[I_x,\alpha(t_n)],\cdots],\alpha(t_1)]\}}{\mathrm{Tr}\{I_x^2\}}.$$

The first approximation of the present calculation is to expand the operator $\alpha(t_n)$ into a power series in time t_n and, after performing integration over times t_n, t_{n-1}, $\cdots$, t_1, to cut off at t^4 the resulting power series

$$G_n(t)=\sum_{m=n+1}^{4}\frac{t^m}{m!}g_n^{(m)}(t), \qquad 3\geq n\geq 1,$$

$$G_n(t)=0, \qquad n\geq 4. \tag{16}$$

This approximation is exactly identical to the LN method, and the FID function $F(t)$ is given by the first four terms in the perturbation expansion, i.e.,

$$F(t)=G_0+G_1+G_2+G_3.$$

The coefficients $g_n^{(m)}(t)$ in Eq. (16) are polynomials of the functions $T_L(\phi)$ $(L=1,2,\cdots)$ defined as

$$T_L(\phi)=(-i)^L\frac{\{\mathrm{Tr}t_L^0\exp(i\phi I_Z)\}}{\{\mathrm{Tr}t_0^0\exp(i\phi I_Z)\}}, \tag{17}$$

where $\phi=b_{jk}t$, etc. The operators t_L^M appearing in the above definition are $t_0^0=1$, $t_1^0=I_Z$, $t_2^0=3I_Z^2-I(I+1)$, $t_3^0=5I_Z^3-3I_ZI(I+1)+I_Z$, $\cdots$ and in general the operator t_L^M $(M=L, L-1, \cdots, -L;\ L=0, 1, 2\cdots)$ is proportional to the statistical tensor T_L^M (or irreducible angular-momentum tensor) given by Fano and Racah,[7] Ambler, Eisenstein and Schooley[8] and Rose.[9] That is, $T_L^M=a_L^M\cdot t_L^M$, where a_L^M is a constant and is given in Ambler, Eisenstein, and Schooley's paper.[8] The functions $T_L'(\phi)$ for spin S are similarly defined.

The important properties of these functions $T_L(\phi)$ are (i) $T_L(\phi)\equiv 0$ for $L>2I$ and (ii) when expanded in power series in ϕ, $T_L(\phi)$ takes the form $T_L(\phi)=\phi^L(b_0+b_1\phi^2+b_2\phi^4+b_3\phi^6+\cdots)$. The lowest-order term in ϕ in $T_L(\phi)$ is ϕ^L.

In order to reduce the labor of calculation further than in the LN method, we make a second approximation of omitting from $g_n^{(m)}(t)$ all terms containing products of the form $T_{L_1}(\phi_1)T_{L_2}(\phi_2)T_{L_3}(\phi_3)\cdots T_{L_p}(\phi_p)$ for which $L_1+L_2+\cdots+L_p>4-m$. When the second approximation is made, the FID function $F(t)$ differs from the LN formula in terms corresponding to the sixth or higher moments and is simplified to the first

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[7] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

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three terms in the iteration expansion of $F(t)$, i.e.,

$$F(t)=G_0+G_1+G_2.$$

As will be seen in Sec. III, this second approximation turned out to be an oversimplification. Nevertheless it allowed considerable reduction in the labor of calculation.

The intermediate steps of the calculation are sufficiently involved that only the final result will be presented below. Writing

$$F(t)\equiv U(t)\,V(t), \tag{18}$$

one obtains the result

$$U(t)=\prod_{l}\left\{\frac{\sin[(I+\frac{1}{2})b_{kl}t]}{(2I+1)\ \sin(\frac{1}{2}b_{kl}t)}\right\}\prod_{l'}\left\{\frac{\sin[(S+\frac{1}{2})c_{kl'}t]}{(2S+1)\ \sin(\frac{1}{2}c_{kl'}t)}\right\}, \tag{19}$$

$$\begin{aligned}
V(t)=1&+(t^2/2!)\{-\sum_{j\neq l}{}'a_{jk}(b_{jl}-b_{kl})X(b_{jk}t)X(b_{kl}t)-\sum_{j,l'}{}'a_{jk}(c_{jl'}-c_{kl'})X(b_{jk}t)X'(c_{kl'}t)+\tfrac{1}{2}\sum_{j}{}'a_{jk}b_{jk}Y(b_{jk}t)\}\\
&+(t^3/3!)\{-\tfrac{1}{10}(2I-1)(2I+3)\sum_{j}{}'a_{jk}b_{jk}^2X(b_{jk}t)+[3(2I-1)(2I+3)/10]\sum_{j}{}'a_{jk}^2b_{jk}X(b_{jk}t)\\
&-\tfrac{1}{3}[I(I+1)]\sum_{j\neq l}{}'a_{jk}(b_{jl}-b_{kl})^2X(b_{jk}t)+\tfrac{1}{3}[I(I+1)]\sum_{j\neq l}{}'[2a_{jk}^2(b_{kl}-b_{jl})+2a_{jl}^2(b_{kl}-b_{kj})\\
&+a_{jk}a_{kl}(b_{jk}-b_{jl})+a_{jk}a_{jl}(b_{kl}-b_{kj})+a_{jl}a_{kl}(b_{jl}-b_{jk})+a_{jl}a_{jk}(b_{kl}-b_{jl})]X(b_{kl}t)\\
&-\tfrac{1}{3}[S(S+1)]\sum_{j,l'}{}'a_{jk}(c_{jl'}-c_{kl'})^2X(b_{jk}t)+\tfrac{1}{3}[2I(I+1)]\sum_{j,l'}{}'a_{jk}^2(c_{kl'}-c_{jl'})X'(c_{kl'}t)\\
&+\tfrac{1}{3}[S(S+1)]\sum_{j\neq k'}{}'(a_{j'k'}{}')^2(c_{kj'}-c_{kk'})[X'(c_{kj'}t)-X'(c_{kk'}t)]\}\\
&+(t^4/4!)\{-\tfrac{3}{10}I(I+1)(2I-1)(2I+3)\sum_{j}{}'a_{jk}^2b_{jk}^2\\
&-\tfrac{1}{3}I^2(I+1)^2\sum_{j\neq l}{}'[a_{jk}^2(b_{kl}-b_{jl})^2+a_{jl}^2(b_{kl}-b_{kj})^2+2a_{jk}a_{jl}(b_{kl}-b_{jl})(b_{kl}-b_{kj})]\\
&-\tfrac{1}{3}I(I+1)S(S+1)\sum_{j,l'}{}'a_{jk}^2(c_{kl'}-c_{jl'})^2-\tfrac{1}{3}S^2(S+1)^2\sum_{j'\neq k'}(a_{j'k'}{}')^2(c_{kj'}-c_{kk'})^2\},
\end{aligned} \tag{20}$$

where

$$\begin{aligned}
X(\phi)&\equiv T_1(\phi)=\tfrac{1}{2}\ \cot(\tfrac{1}{2}\phi)-(I+\tfrac{1}{2})\ \cot[(I+\tfrac{1}{2})\phi],\\
X'(\phi)&\equiv T_1'(\phi)=\tfrac{1}{2}\ \cot(\tfrac{1}{2}\phi)-(S+\tfrac{1}{2})\ \cot[(S+\tfrac{1}{2})\phi],\\
Y(\phi)&\equiv T_2(\phi)=-2I(I+1)+\tfrac{3}{2}\ \cot^2(\tfrac{1}{2}\phi)-3(I+\tfrac{1}{2})\ \cot[(I+\tfrac{1}{2})\phi]\ \cot(\tfrac{1}{2}\phi).
\end{aligned}$$

The prime above the summation notation $\sum'$ implies that the unprimed indices j and l should not take value of index k.

The function $F(t)$ given by Eq. (20) gives the correct second and fourth moments of the absorption line shape for the spin system with two ingredients as calculated by Van Vleck.[10]

Consider now the special case relevant to our experiments in which the spin-spin interaction is purely dipolar, so that

$$a_{ij}=-\tfrac{1}{3}b_{ij}\quad\text{and}\quad a_{i'j'}{}'=-\tfrac{1}{3}b_{i'j'}{}'.$$

In computing $F(t)$ we follow LN in making a third approximation which consists of omitting terms containing odd powers of the coefficients b_{ij}, $b_{i'j'}{}'$, $c_{ij'}$, etc. in Eq. (20). To justify the dropping of these terms, we note that these coefficients will take positive and negative values of almost equal magnitude with almost equal probability when the indices i, j, i', j' span the lattice sites. Clough and McDonald[11] have found that retaining these terms would only result in a slight correction to the FID function $F(t)$.

The FID function thus simplified is $F(t)=U(t)\,V(t)$, where $U(t)$ is the same as Eq. (19) and

$$\begin{aligned}
V(t)=1&-\tfrac{1}{6}t^2\{(Z_1)^2-Z_4+Z_1Z_5+\tfrac{1}{2}Z_3\}\\
&+\tfrac{1}{27}t^3\{[3(2I-1)(2I+3)/10]Z_2+2I(I+1)(AZ_1-Z_2)\\
&+S(S+1)CZ_1+\tfrac{1}{3}[I(I+1)]AZ_5+\tfrac{1}{3}[S(S+1)]DZ_5\}\\
&-(t^4/324)\{\tfrac{9}{20}I(I+1)(2I-1)(2I+3)B\\
&+3I^2(I+1)^2(A^2-B)\\
&+I(I+1)S(S+1)AC+S^2(S+1)^2CD\},
\end{aligned} \tag{21}$$

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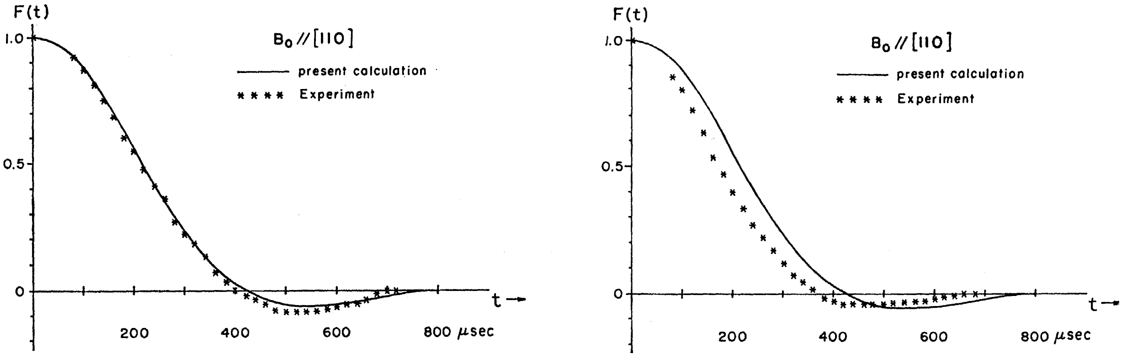
[10] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[11] S. Clough and I. R. McDonald, Proc. Phys. Soc. (London) **86**, 833 (1965).



(a) (b)

FIG. 2. Theoretical and experimental FID's of the Na spin system in Harshaw crystal I at $B_0 \parallel [110]$. (a) Before thermal quench; (b) after thermal quench.

where

$$Z_1 = {\sum_j}' b_{jk} X(b_{jk}t),$$

$$Z_2 = {\sum_j}' b_{jk}^3 X(b_{jk}t),$$

$$Z_3 = {\sum_j}' b_{jk}^2 Y(b_{jk}t),$$

$$Z_4 = {\sum_j}' b_{jk}^2 X(b_{jk}t)^2,$$

$$Z_5 = {\sum_l}' c_{kl'} X'(c_{kl'}t),$$

$$A = {\sum_j}' b_{jk}^2,$$

$$B = {\sum_j}' b_{jk}^4,$$

$$C = \sum_{l'} C_{kl'}^2,$$

$$D = \sum_{j'} (b_{j'k'}')^2.$$

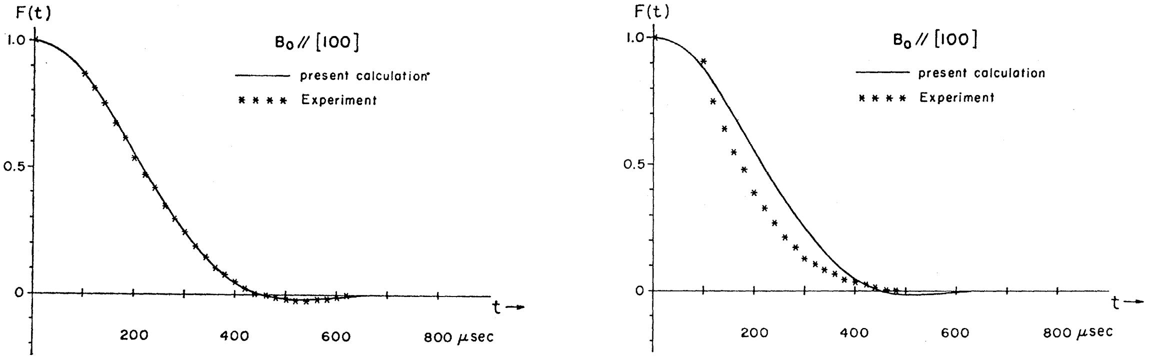
III. THE EXPERIMENTS

A. Procedure

All the measurements to be described consisted of the oscilloscope observation of the coherently detected free-induction-decay signal $F(t)$ produced by the sodium spin system in NaCl, following a $\pi/2$ pulse of approximately 10-μsec duration. All experiments were done at room temperature.

In the initial phases of this work it was thought necessary to use only exceedingly strain-free crystals to minimize quadrupole broadening effects. Toward this end we obtained from Dr. N. Fuschillo of Melpar,[12] a very carefully grown and annealed crystal, which probably contained less than 10^5 dislocation lines/cm².[13] The dimensions of the crystal are $\frac{1}{2}\times\frac{1}{2}\times1\frac{1}{2}$ in.

All measurements were made with an 8.0-Mc/sec crossed-coil spectrometer which followed a design of Clark.[14] The electromagnet used in these measurements had a field gradient of less than 3 mG across the sample and was negligible for our purpose. For the measurements at $B_0 \parallel [111]$, a Harshaw crystal (Harshaw II) was ground to cylindrical shape with its cylindrical axis perpendicular to the [111] direction. Another Harshaw crystal (Harshaw I) was used for those measurements at $B_0 \parallel [110]$ and $B_0 \parallel [100]$. The shape and size of the Melpar crystal made it impossible to take data at $B_0 \parallel [111]$ in the crossed-coil apparatus, so experiments with this crystal were done only at the



(a) (b)

FIG. 3. Theoretical and experimental FID's of the Na spin system in Harshaw crystal II at $B_0 \parallel [100]$. (a) Before thermal quench; (b) after thermal quench.

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[12] Melpar, Inc., Falls Church, Virginia.

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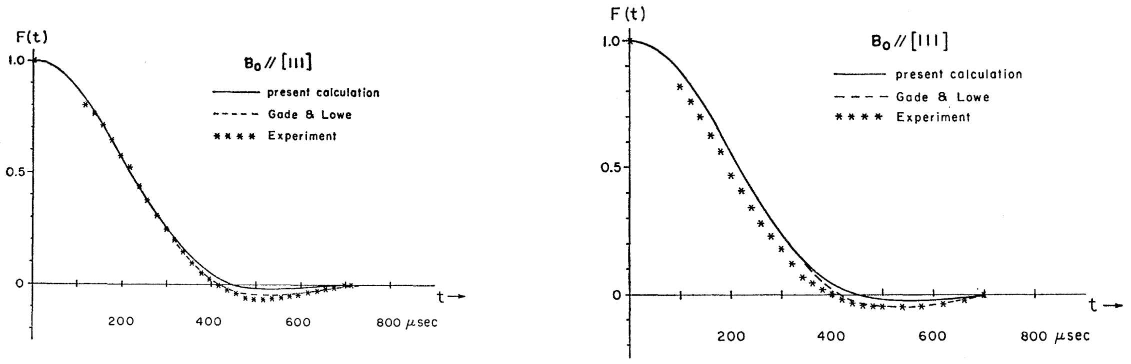
[14] W. G. Clark, Rev. Sci. Instr. **35**, 316 (1964).



(a) (b)

Fig. 4. Theoretical and experimental FID's of the Na spin system in Harshaw crystal II at $B_0 \parallel [111]$. (a) Before thermal quench; (b) after thermal quench.

orientations $B_0 \parallel [110]$ and $B_0 \parallel [100]$. After these measurements Harshaw crystal I was thermally quenched by heating it to just below the melting point and then cooling it immediately in a stream of cool air until cracks developed throughout. Harshaw crystal II was quenched in an oil bath. Free-induction-decay measurements were then made on the two quenched crystals.

B. Data Analysis

All FID lines were recorded on high-speed polaroid films. The decays were assumed to start at the center of the 10μ-sec $\pi/2$ pulse. The magnetization at $t=0$ could not be observed (because of the finite recovery time of the receiver) and therefore had to be obtained by extrapolation, using analytical functions to which the experimental points were best fitted. For comparison with the theory, these extrapolated values were normalized to unity and the normalized experimental points were plotted alongside the corresponding theoretical curves. These curves represent a computed evaluation of Eq. (21) in which γ' was taken as the average value of the Cl^{35} and Cl^{37} magnetogyric ratios weighted by the natural abundance of these isotopes.

It was found that before the thermal-quenching process the unnormalized FID functions could be satisfactorily described by the empirical function

$$S(t)=M_0\exp[-(a^2/2)t^2]\,(\sin bt/bt). \tag{22}$$

After thermal quench, the FID lines were so markedly changed that large portions (up to the first 300 μsec or more) of the lines were much better fitted to a Gaussian function

$$S(t)=M_0\exp[-(a^2/2)t^2]. \tag{23}$$

Figures 1(a) and 1(b) give the experimental points (denoted by an asterisk) using the Melpar crystal for $B_0 \parallel [110]$ and $B_0 \parallel [100]$ together with the theoretical curves based on Eqs. (18)–(21). Figures 2(a) and 3(a) show the FID's of Harshaw I for $B_0 \parallel [110]$ and $B_0 \parallel [100]$ before the thermal quench. Figures 2(b) and 3(b) are the corresponding data after the thermal quench. Figures 4(a) and 4(b) are the FID's of Harshaw II for $\mathbf{B}_0 \parallel [111]$ before and after the thermal quench, respectively. In addition to the theoretical curves (solid lines), Figs. 4(a) and 4(b) also display the theoretical lines based on Gade and Lowe's calculations[5] corresponding to $\mathbf{B}_0 \parallel [111]$. At this crystal orientation the Na-Cl interaction makes a negligible contribution to $F(t)$, and the work of Ref. 5 is applicable. To reveal the ineffectiveness of the Na-Cl interaction for $\mathbf{B}_0 \parallel [111]$, Eq. (21) was plotted with and without these terms and the two resulting graphs of $F(t)$ were found to coincide throughout the FID.

For second-moment extraction when the oscillatory-type function, Eq. (22), is used, the value of the parameter b is determined from the measurement of t_{cross}, the time at which the FID first crosses the base line. Thus, from Eq. (22),

$$b=\pi/t_{\text{cross}}. \tag{24}$$

By plotting $S(t)/[(\sin bt)/bt]$ as a function of t^2 on a

Table I. Second moments M_2 of the free-induction-decay lines in various samples of NaCl.

Sample	Field direction	M_2 in units of 10^5 (cps)^2 before thermal quench	M_2 in units of 10^5 (cps)^2 after thermal quench	M_2 in units of 10^5 (cps)^2 Theory[a]
Melpar	[110]	6.86±0.1		
Harshaw I	[110]	6.95±0.1	11.7±0.1	6.83
Melpar	[100]	7.05±0.1		
Harshaw I	[100]	6.93±0.1	11.4±0.1	6.90
Harshaw II	[111]	6.63±0.1	9.5±0.1	6.82

[a] See Ref. 16.

semilog scale, a straight line is obtained from which the value of a^2 may then be calculated. The second moment in this case is given in angular-frequency units by

$$M_2 = a^2 + \tfrac{1}{3}b^2. \qquad (25)$$

All second moments before thermal quench were calculated this way. The plots were good at least to the first crossing points. After thermal quenching the M_2 values were extracted from a Gaussian fit.

IV. DISCUSSION

Our FID measurements in NaCl before thermal quench indicate that the Lowe–Norberg theory, as extended in Sec. II, successfully describes the experimental observations through most of the decay time. However, at the crystal orientations $\mathbf{B}_0 \parallel [111]$ and $\mathbf{B}_0 \parallel [110]$, where the beat structure is more pronounced, the theoretical curves at large t consistently deviate from the experimental curves. This discrepancy is due to our second approximation explained in Sec. II in which certain higher-order terms are omitted from the formula of the LN method. At the crystal orientation $\mathbf{B}_0 \parallel [111]$, the one-ingredient theory of Gade and Lowe[5] is applicable and, as can be seen in Fig. 4(a), their formula yields a better fit to the data than the present calculation of Sec. II. This indicates the desirability of calculating $F(t)$ rigorously according to the LN method without making the further simplifications to which we have resorted in Sec. II. For the two-ingredient case, however, the full LN calculation becomes unreasonably lengthy.

Our measurements of M_2 show extremely good agreement with the theoretical values in all the samples used. Furthermore, the FID shapes and the corresponding second moments for both the Melpar and the Harshaw crystals are identical to within experimental uncertainty. It is interesting to note that in these measurements the Melpar crystal was handled with extreme care while the Harshaw crystals were deliberately subjected to stress so that visible patterns showed up when the crystals were viewed between crossed polaroids. In fact, even the rough machining (by an ordinary sandpaper-type grinder) apparently did not change the second moment for $\mathbf{B}_0 \parallel [111]$. These observations seem to contradict the common belief that strains induced in NaCl through careless handling will give rise to appreciable quadrupole broadening of the NMR line.[15] However, appreciable changes both in $S(t)$ and M_2 were observed after the Harshaw crystals were subjected to severe thermal shock. The reasonable conclusion would be that the mechanical strains were either too few or too long ranged to produce numerous or large field gradients on an atomic scale, while the thermal-quenching process produces point defects and dislocations of such proportion that the effect shows up in both the free induction decays and in the second moments. The fact that after severe thermal quench the FID lines are better described by a Gaussian function also suggests that the additional quadrupole broadening is Gaussian in nature.

Table I lists the measured second moments in our NaCl samples together with the calculated values.[16] All quantities are expressed in units of $(\text{cps})^2$. The theoretical values include contributions from both the Na-Na and Na-Cl dipolar interactions and have been calculated using the Van Vleck formula.[10]

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Stress-Induced Trigonal Crystal-Field Parameters in Some Oxide Lattices*

R. M. MACFARLANE
Department of Physics, Stanford University, Stanford, California

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Numerical perturbation methods are used to express trigonal stress splittings in terms of two phenomenological parameters, v_s and v_s', for many levels of Cr^{3+}, V^{2+}, Ni^{2+} in MgO, and Cr^{3+} in ruby and emerald. Values of v_s and v_s' for ruby and for Cr^{3+} and V^{2+} in MgO have been determined from published data. Point-charge calculations using Hartree-Fock free-ion radial wave functions give useful estimates of the stress-induced crystal-field parameters.

INTRODUCTION

WHEN an external stress is applied to a crystal containing an impurity ion, a splitting and shift of its sharp-line spectrum may be observed. There are two reasons for this. (i) If the impurity ion occupies rotationally inequivalent sites, its energy levels can suffer different shifts and give rise to an apparent splitting.[1,2] In other words, orientational degeneracy

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