III. EXPERIMENTAL

The absorption spectra were measured with Cary 14 and 14 RI spectrophotometers. For the low-temperature spectra the crystals were immersed in liquid nitrogen in an optical silica cryostat.

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Theory of NMR Line Shapes in Dipolar-Broadened Spin Systems and Applications to SrF_2, CsF, and NaCl

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Detailed line-shape measurements of fluorine resonance in SrF_2 have been made and the results compared with theories of dipolar broadening and with Barnaal and Lowe's data from CaF_2. It was recognized that the theoretical results of Evans and Powles (EP) and of Lee, Tse, Goldburg, and Lowe (LTGL) were derived from the same basic expansion for the free-induction-decay function. This made it appropriate to combine their results in order to obtain an improvement in the theory. The combined result was compared with experimental data of LTGL from NaCl and with Hutchins and Day's results from CsF. In most cases, the combined result gave as good or better agreement than either the approximation of EP or that of LTGL.

I. INTRODUCTION

We have studied NMR line shapes observed in several single crystals of alkali halides and other ionic compounds. These crystals provide excellent tests of theories of dipolar broadening which have recently been developed. Our work has included a detailed analysis of line shapes in strontium fluoride which led us to consider, in detail, the theoretical development and its generalizations described in this paper. Before describing our results we will review the development of the theory.

In 1948, Bloembergen, Purcell, and Pound[1] proposed the Gaussian model for a system of spin-$\frac{1}{2}$ particles on a rigid lattice. A given spin experiences local magnetic fields due to neighboring spins. It was found by an approximate calculation that the distribution of this local field at a representative spin is essentially Gaussian in shape. Later that year, Van Vleck[2] published exact calculations of the second and fourth moments of such a spin system. Comparison of moments for a Gaussian shape with these exact results showed that the Gaussian was only a rough approximation.

The continuous-wave (cw) experimental analysis of calcium fluoride by Pake and Purcell,[3] in 1948, indicated that Van Vleck's results were correct. Bruce,[4] in 1957, using the same calcium fluoride crystal of Pake and Purcell,[3] repeated the cw experiment employing improved experimental techniques, and the new results were in excellent agreement with Van Vleck's theory.

The same calcium fluoride crystal was again used by Lowe and Norberg[5] (LN) for a free-induction-decay (FID) experiment. The beat structure exhibited by these Bloch decays clearly demonstrated the non-Gaussian character of the corresponding cw line shapes since, in the same paper, they proved that a cw line shape is the Fourier transform of the corresponding FID. They also developed an expansion of the theoretical FID which applied to a system with a single set of particles having spin $\frac{1}{2}$ such as may be found in calcium fluoride. Their FID data were in good agreement with Fourier transforms of Bruce's[4] data and both were in reasonably good agreement with their theory.

Further theoretical developments were made in 1967 by Lee, Tse, Goldburg, and Lowe[6] (LTGL) and by Evans and Powles[7] (EP). Both groups were motivated by the following criticisms of the LN procedure: that the convergence properties of their expansion are not known, that uniqueness is questioned,[8] and that the series diverges for times not much greater than those calculated by LN. Clough and McDonald[9] had developed a generalization of this method but it was subject to the same criticisms. We have noted that both groups independently developed the same basic expansion for the FID having the form

$$F(t)=F_0(t)+F_1(t)+F_2(t)+\cdots .$$

Each term in this series does not diverge for long times. EP[7] evaluated the first two terms exactly. LTGL,[6] however, utilized this expansion differently. They were able to show that the original LN expansion[5] could be uniquely obtained from this new expansion by substituting for a certain operator in F_1 and higher terms its power series in time. This substitution gave F_1, F_2, etc., each as an infinite series of terms; truncation of these series gave approximate expressions for these terms. They then evaluated, in this approximation,

$$F(t)=F_0(t)+\tilde{F}_1(t)+\tilde{F}_2(t)$$

for a system having two sets of particles each with arbitrary spin. Here $\tilde{F}_1$ and $\tilde{F}_2$ are the LTGL approximations to F_1 and F_2, respectively. They may be written as $\tilde{F}_1=F_0V_1$ and $\tilde{F}_2=F_0V_2$ so that their approximation may be written in the form $F(t)=F_0(t)\times V(t)$, where $V=1+V_1+V_2$. Gade and Lowe[10] had previously generalized the LN expansion to a single set of particles with arbitrary spin.

Now, since both F_0 and F_1 can be evaluated exactly,[7,11,12] we suggest that an appropriate theoretical expression would be the combined result given by

$$F(t)=F_0(t)+F_1(t)+\tilde{F}_2(t) .$$

We have determined $\tilde{F}_2$ to the same degree of generality as Demco's[11] evaluation of F_0 and F_1. That is, a system with any number of sets of particles each with arbitrary spin. Gibbs[12] has independently evaluated F_0+F_1 with somewhat less generality. In Sec. II, we outline the derivation of these results and describe how they may be applied to a system having less than 100% abundant spin species such as is found in strontium fluoride.

Other related theories applicable to a system of spin-$\frac{1}{2}$ particles have been developed. Tjon[13] obtained an approximate integral equation for the FID which was solved numerically using the Gaussian assumption. Borckmans and Walgraef[14] also obtained an integral equation which had to be solved numerically for the FID. Mansfield[15] used a Green's-function formalism to obtain an expression for the cw line shape involving an adjustable parameter.

Until fairly recently, detailed experimental study of dipolar line shapes was limited to the single calcium fluoride crystal used by Pake and Purcell,[3] Bruce,[4] and LN.[5] Then in 1966, Barnaal and Lowe[16] repeated these measurements on a different single crystal of calcium fluoride which they believed was more accurately oriented. In addition, it was discovered that detailed line-shape measurements obtained from FID data should be corrected to account for the finite bandwidths of the receiver and pickup coil[17] as well as the finite width of the excitation pulse.[18] Their sample was fairly free from paramagnetic impurities having a T_1 of 30 sec at room temperature. In 1967, LTGL[6] studied the sodium resonance in sodium chloride. They found quadrupole effects to be negligible in their samples. Then, recently, Hutchins and Day[19] reported FID shapes obtained from cesium fluoride. All these experimental data as well as our results from strontium fluoride will be discussed in Sec. III where we compare them with our theoretical calculations. In Sec. IV, our observations will be summarized and discussed.

II. THEORY

For a system consisting of any number of sets of particles on a rigid lattice each having arbitrary spin the Hamiltonian may be written as

$$H=H_Z+H_D ,$$

where H_Z is the Zeeman term describing their interaction with an external field $\vec{H}_0$, and H_D is the truncated dipolar term.[2,5] Let the set of particles whose resonance is observed have spin I and gyromagnetic ratio γ, remaining sets having spins S_μ and gyromagnetic ratios γ_μ where μ labels different sets. We may then write, for $\vec{H}_0 = H_0\hat{z}$,

$$H_Z = -\hbar\gamma H_0 I^z - \sum_\mu \hbar\gamma_\mu H_0 S^z_\mu$$

and $H_D = \hbar(\alpha+\beta)$,

where

$$\alpha = \sum_{i\neq j} A_{ij}\vec{\mathrm{I}}_i\cdot\vec{\mathrm{I}}_j + \sum_\mu \sum_{i(\mu)\neq j(\mu)} A_{i(\mu)j(\mu)}\vec{\mathrm{S}}_{\mu i(\mu)}\cdot\vec{\mathrm{S}}_{\mu j(\mu)}, \tag{1}$$

and

$$\beta = \sum_{i\neq j} B_{ij}I^z_i I^z_j + \sum_\mu \Big[\sum_{i(\mu)\neq j(\mu)} B_{i(\mu)j(\mu)} \times S^z_{\mu i(\mu)}S^z_{\mu j(\mu)} + \sum_i \sum_{j(\mu)} 2C_{ij(\mu)}S^z_{\mu j(\mu)}I^z_i + \sum_{\nu(\neq\mu)}\sum_{i(\mu)}\sum_{j(\nu)} 2D_{i(\mu)j(\nu)}S^z_{\mu i(\mu)}S^z_{\nu j(\nu)}\Big]. \tag{2}$$

Spin operators for particles with spin I and spin S_μ are $\vec{\mathrm{I}}_j$ and $\vec{\mathrm{S}}_{\mu j(\mu)}$, respectively; operators for, say, the z component of total spin of a set are then

$$I^z = \sum_i I^z_i \quad \text{and} \quad S^z_\mu = \sum_{j(\mu)} S^z_{\mu j(\mu)}.$$

Restricted double sums will be written as $\sum_{i\neq j}$ while corresponding single sums will appear as $\sum_{i(\neq j)}$. Coefficients in (1) and (2) have the following definitions:

$$\begin{aligned}
A_{ij} &= -\tfrac{1}{3}B_{ij},\\
B_{ij} &= \tfrac{3}{4}\gamma^2\hbar(1-3\cos^2\theta_{ij})r^{-3}_{ij},\\
A_{i(\mu)j(\mu)} &= -\tfrac{1}{3}B_{i(\mu)j(\mu)},\\
B_{i(\mu)j(\mu)} &= \tfrac{3}{4}\gamma^2_\mu\hbar(1-3\cos^2\theta_{i(\mu)j(\mu)})r^{-3}_{i(\mu)j(\mu)},\\
C_{ij(\mu)} &= \tfrac{1}{2}\gamma\gamma_\mu\hbar(1-3\cos^2\theta_{ij(\mu)})r^{-3}_{ij(\mu)},\\
D_{i(\mu)j(\nu)} &= \tfrac{1}{2}\gamma_\mu\gamma_\nu\hbar(1-3\cos^2\theta_{i(\mu)j(\nu)})r^{-3}_{i(\mu)j(\nu)}.
\end{aligned} \tag{3}$$

In each of the preceding coefficients, θ_{pq} is the angle between $\vec{\mathrm{r}}_{pq}$ and $\vec{\mathrm{H}}_0$ where r_{pq} is the distance between lattice points p and q. Although some simplification of equations is possible using (3), it is advantageous to defer this so that terms in our final results may be traced to their occurrence in (1) or (2).

The normalized FID amplitude is given by

$$F(t) = \mathrm{Tr}\{I_x I_x(t)\}/\mathrm{Tr}\{I^2_x\}, \tag{4}$$

where

$$\begin{aligned}
I_x(t) &= \exp(iH_D t/\hbar)\,I_x\exp(-iH_D t/\hbar)\\
&= \exp[i(\alpha+\beta)t]\,I_x\exp[-i(\alpha+\beta)t].
\end{aligned}$$

Following LTGL,[6] it is observed that $I_x(t)$ satisfies

$$i\frac{\partial}{\partial t}I_x(t) = [I_x(t),\ \alpha+\beta].$$

A new operator $I'_x(t)$ is defined by

$$I_x(t) = e^{+i\beta t}I'_x(t)\,e^{-i\beta t}, \tag{5}$$

and is found to satisfy the equation

$$i\frac{\partial I'_x}{\partial t}(t) = [I'_x(t),\ \alpha(t)], \tag{6}$$

where $\quad \alpha(t) = e^{-i\beta t}\alpha e^{i\beta t}$.

The integral equation corresponding to (6) is

$$I'_x(t) = I_x - i\int_0^t [I'_x(t'),\ \alpha(t')]\,dt'.$$

Solving this equation by successive iteration produces the expression[6,7]

$$I'_x(t) = I_x + \sum_{n=1}^\infty (-i)^n \int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n \times[\cdots[I_x,\ \alpha(t_n)],\ldots,\ \alpha(t_1)]. \tag{7}$$

Notice that this is an expansion in powers of α. Since α and I_x commute, α will affect $F(t)$ only through the presence of β.[7] Using (4), (5), and (7), we obtain the corresponding expansion for $F(t)$

$$F(t) = F_0(t) + F_1(t) + F_2(t) + \cdots.$$

These first three terms are written in terms of $I''_x(t) = \exp(-i\beta t)I_x\exp(i\beta t)$ as follows:

$$F_0(t) = \mathrm{Tr}\{I''_x(t)I_x\}/\mathrm{Tr}\{I^2_x\}, \tag{8}$$

$$F_1(t) = (-i)\int_0^t dt_1 \frac{\mathrm{Tr}\{I''_x(t)[I_x,\ \alpha(t_1)]\}}{\mathrm{Tr}\{I^2_x\}}, \tag{9}$$

$$F_2(t) = (-i)^2\int_0^t dt_1\int_0^{t_1}dt_2 \times\frac{\mathrm{Tr}\{I''_x(t)[[I_x,\ \alpha(t_2)],\ \alpha(t_1)]\}}{\mathrm{Tr}\{I^2_x\}}. \tag{10}$$

LTGL[6] evaluated (8) exactly and (9) and (10) approximately by expanding $\alpha(t_n)$ by its definition as a power series in t_n keeping terms through t^4 in the resulting series for F_1 and F_2. This result can be written as

$$F_{\mathrm{LTGL}} = F_0 + \tilde{F}_1 + \tilde{F}_2, \tag{11}$$

where the tildes indicate the LTGL approximation to F_1 and F_2. EP,[7] Demco,[11] and Gibbs[12] found that F_1 could also be evaluated exactly and to this approximation

$$F_{\mathrm{EPDG}} = F_0 + F_1. \tag{12}$$

One of us (R. F.) has suggested that the results of (11) and (12) be combined to give

$$F_F = F_0 + F_1 + \tilde{F}_2, \tag{13}$$

which should be a better approximation than either (11) or (12) alone. That is, rather than evaluate F_2 exactly, we may approximate it by using the expansion for $\alpha(t_n)$. When this expansion is substituted in (10) we obtain an infinite series of terms

$$F_2=\sum_{n=3}^{\infty}(t^n/n!)f_n(t).$$

However, this is just the technique used by LTGL who included terms in this series through t^4. We may therefore obtain from their work an approximate expression for F_2 which applies to a system having two sets of particles each with arbitrary spin.

In order to have a general expression for F_F the calculation of LTGL[6] has been extended to a system of any number of sets of particles each with arbitrary spin. The calculations are straightforward but tedious and they are omitted here. The appendixes of Gade and Lowe[10] are helpful in evaluating the terms below. We find

$$F_0+\tilde{F}_1+\tilde{F}_2=F_0(t)\,V(t)\,,$$

$$F_0(t)=\prod_{l(\neq k)}\left(\frac{\sin[(2I+1)B_{kl}t]}{(2I+1)\sin[B_{kl}t]}\right)\times\prod_{\mu}\prod_{l(\mu)}\left(\frac{\sin[(2S+1)C_{kl(\mu)}t]}{(2S+1)\sin[C_{kl(\mu)}t]}\right),\qquad(14)$$

and

$$\begin{aligned}V(t)={}&1+(t^2/2!)\Big[-4\sum_{j\neq l}{}'A_{jk}(B_{jl}-B_{kl})X(2B_{jk}t)X(2B_{kl}t)-2\sum_{\mu}\sum_{j,l(\mu)}{}'A_{jk}(C_{jl(\mu)}-C_{kl(\mu)})X(2B_{jk}t)\\&\times X_\mu(2C_{kl(\mu)}t)+2\sum_{j(\neq k)}A_{jk}B_{jk}\,Y(2B_{jk}t)\Big]+\frac{t^3}{3!}\Big\{-\tfrac{4}{5}(2I-1)(2I+3)\sum_{j(\neq k)}A_{jk}B_{jk}^2\,X(2B_{jk}t)\\&+\tfrac{12}{5}(2I-1)(2I+3)\sum_{j(\neq k)}A_{jk}^2B_{jk}\,X(2B_{jk}t)-\tfrac{16}{3}I(I+1)\sum_{j\neq l}{}'A_{jk}B_{kl}(B_{kl}-B_{jl})X(2B_{jk}t)+\tfrac{16}{3}(I)(I+1)\\&\times\sum_{j\neq l}{}'[2A_{jk}^2(B_{lk}-B_{jl})+A_{jk}A_{kl}(B_{jk}-B_{jl})+A_{jk}A_{jl}(B_{kl}-B_{kj})]X(2B_{kl}t)-\tfrac{16}{3}\sum_{\mu}[S_\mu(S_\mu+1)]\\&\times\sum_{j,l(\mu)}{}'A_{jk}C_{kl(\mu)}(C_{kl(\mu)}-C_{jl(\mu)})X(2B_{jk}t)+\tfrac{16}{3}I(I+1)\sum_{\mu}\sum_{j,l(\mu)}{}'A_{jk}^2(C_{kl(\mu)}-C_{jl(\mu)})\\&\times X_\mu(2C_{kl(\mu)}t)+\tfrac{16}{3}\sum_{\mu}S_\mu(S_\mu+1)\sum_{j(\mu)\neq l(\mu)}(A_{j(\mu)l(\mu)})^2(C_{kj(\mu)}-C_{kl(\mu)})X_\mu(2C_{kl(\mu)}t)\Big\}\\&+(t^4/4!)\Big\{-\tfrac{24}{5}I(I+1)(2I+3)(2I-1)\sum_{j(\neq k)}A_{jk}^2B_{jk}^2-\tfrac{32}{3}I^2(I+1)^2\sum_{j\neq l}{}'[2A_{jk}^2B_{kl}(B_{kl}-B_{jl})\\&+A_{jk}A_{jl}(B_{kl}-B_{jl})(B_{kl}-B_{jk})]-\tfrac{32}{3}I(I+1)\sum_{\mu}S_\mu(S_\mu+1)\sum_{j,l(\mu)}{}'A_{jk}^2C_{kl(\mu)}(C_{kl(\mu)}-C_{jl(\mu)})\\&-\tfrac{32}{3}\sum_{\mu}S_\mu^2(S_\mu+1)^2\sum_{j(\mu)\neq l(\mu)}(A_{j(\mu)l(\mu)})^2C_{kj(\mu)}(C_{kj(\mu)}-C_{kl(\mu)})\Big\},\end{aligned}\qquad(15)$$

where the X and Y functions are

$$\begin{aligned}X(2B_{jk}t)&=\tfrac{1}{2}\cot(B_{jk}t)-\tfrac{1}{2}(2I+1)\cot[(2I+1)B_{jk}t]\,,\\X_\mu(2C_{kl(\mu)}t)&=\tfrac{1}{2}\cot(C_{kl(\mu)}t)-\tfrac{1}{2}(2S_\mu+1)\cot[(2S_\mu+1)C_{kl(\mu)}t]\,,\\\text{and}\quad Y(2B_{jk}t)&=-2I(I+1)+3\cot(B_{jk}t)[X(2B_{jk}t)]\,.\end{aligned}\qquad(16)$$

In (14) and (15) the index k refers to a reference spin, and a primed sum in (15) means that neither j or l may equal k.

The function F_0+F_1 has been evaluated by EP,[7] Demco,[11] and Gibbs.[12] The results of EP apply to a single set of spin-$\frac{1}{2}$ particles. This calculation was extended by Demco[11] to include any number of sets of particles each with arbitrary spin. The expressions given below differ from his, both because there is an error in his published results and also because our result has been written in a somewhat different form. F_0 was given in (14). For F_1 we find

$$\begin{aligned}F_1={}&-2\sum_{j(\neq k)}A_{jk}\,t\,X(2B_{jk}t)\prod_{l(\neq k)}\left(\frac{\sin[(2I+1)B_{lk}t]}{(2I+1)\sin(B_{lk}t)}\right)\prod_{\mu}\prod_{l(\mu)}\left(\frac{\sin[(2S_\mu+1)C_{kl(\mu)}t]}{(2S_\mu+1)\sin[C_{kl(\mu)}t]}\right)+\tfrac{16}{3}I(I+1)\\&\times\sum_{j(\neq k)}A_{jk}\sin(B_{jk}t)\int_0^t dt_1\Bigg[\left(\frac{X(2B_{jk}t_1)}{\sin(B_{jk}t_1)}\;\frac{\sin[(2I+1)B_{jk}t_1]}{(2I+1)\sin(B_{jk}t_1)}\right)\left(\frac{X[2B_{jk}(t_1-t)]}{\sin[B_{jk}(t_1-t)]}\;\frac{\sin[(2I+1)B_{jk}(t_1-t)]}{(2I+1)\sin[B_{jk}(t_1-t)]}\right)\\&\times\prod_{l(\neq j,k)}\left(\frac{\sin\{(2I+1)[B_{jl}(t_1-t)-B_{kl}t_1]\}}{(2I+1)\sin[B_{jl}(t_1-t)-B_{kl}t_1]}\right)\prod_{\mu}\prod_{l(\mu)}\left(\frac{\sin\{(2S_\mu+1)[C_{jl(\mu)}(t_1-t)-C_{kl(\mu)}t_1]\}}{(2S_\mu+1)\sin[C_{jl(\mu)}(t_1-t)-C_{kl(\mu)}t_1]}\right)\Bigg]\,,\end{aligned}\qquad(17)$$

where $X(2B_{jk}t)$ is defined in (16). It is characteristic of the expansion (7) that F_0 and F_1 do not diverge for long times.

In addition to the approximations F_{LTGL} and F_{EPDG}, we have suggested the combined result $F_0+F_1+\tilde{F}_2$. Results for F_0 and F_1 were given in (14) and (17). The evaluation of $\tilde{F}_2$ was included in (15) and may be selected from it by choosing terms second order in the A_{kl} coefficients; the EP-LTGL expansion is an expansion in powers of α and F_2 involves α to second order. The result is

$$\tilde{F}_2=F_0(t)\,V_2(t)\ ,$$

where
$$\begin{aligned} V_2(t)=(t^3/3!)\{&\tfrac{12}{5}(2I-1)(2I+3)\sum_{j(\neq k)}A_{jk}^2B_{jk}X(2B_{jk}t)\\ &+\tfrac{16}{3}I(I+1)\sum_{j\neq l}{}'[2A_{jk}^2(B_{kl}-B_{jl})+A_{jk}A_{kl}(B_{jk}-B_{jl})+A_{jk}A_{jl}(B_{kl}-B_{kj})]\,X(2B_{kl}t)\\ &+\tfrac{16}{3}I(I+1)\sum_{\mu}\ \sum_{j,l(\mu)}{}'A_{jk}^2(C_{kl(\mu)}-C_{jl(\mu)})\\ &\times X_\mu(2C_{kl(\mu)}t)+\tfrac{16}{3}\sum_{\mu}[S_\mu(S_\mu+1)]\sum_{j(\mu)\neq k(\mu)}(A_{j(\mu)k(\mu)})^2(C_{kj(\mu)}-C_{kk(\mu)})X(2C_{kj(\mu)}t)\}\\ &+(t^4/4!)\{-\tfrac{24}{5}I(I+1)(2I-1)(2I+3)\sum_{j(\neq k)}A_{jk}^2B_{jk}^2-\tfrac{32}{3}I^2(I+1)^2\sum_{j\neq l}{}'[2A_{jk}^2B_{kl}(B_{kl}-B_{jl})\\ &+A_{jk}A_{jl}(B_{kl}-B_{jl})(B_{kl}-B_{kj})]-\tfrac{32}{3}I(I+1)\sum_{\mu}S_\mu(S_\mu+1)\sum_{j,l(\mu)}{}'A_{jk}^2C_{kl(\mu)}(C_{kl(\mu)}-C_{jl(\mu)})\\ &-\tfrac{32}{3}\sum_{\mu}S_\mu^2(S_\mu+1)^2\sum_{j(\mu)\neq l(\mu)}(A_{j(\mu)l(\mu)})^2C_{kj(\mu)}(C_{kj(\mu)}-C_{kl(\mu)})\}\ . \end{aligned}\tag{18}$$

One application of these generalized results might be to sodium resonance in NaCl. Na^{23} is 100% abundant, whereas Cl^{35} and Cl^{37} are 75 and 25% abundant, respectively. Both chlorine isotopes have spin $\frac{3}{2}$ but different gyromagnetic ratios. The two sets of chlorine spins share the same sublattice and have a large number of equally probable configurations on this lattice. As a result, any of the expressions given for $F(t)$ must be averaged over all possible configurations of these isotopes. Actually a simpler method[6] is justified for this problem. The magnetic moments of Cl^{35} and Cl^{37} are approximately equal so that the chlorine spins may be considered to be a single spin-$\frac{3}{2}$ system with a magnetic moment which is the average of the two. There are, however, other cases where this method cannot be justified. An example of this type of system is strontium fluoride (SrF_2). F^{19} is 100% abundant, whereas Sr^{87} is 7% abundant. The remaining isotope of strontium has spin zero so we have a system with two sets of spins where spins in one set have many possible arrangements on their sublattice. We have calculated the fluorine line shape in SrF_2 using the method described below.

Consider a system consisting of a 100% abundant observed spin species I on one sublattice, and on a second sublattice, several isotopes, say m, each having different spins S_μ. These isotopes will be assumed to be randomly distributed on the second sublattice in accordance with their relative abundances $P_1, P_2, \ldots, P_m$. The method we use to evaluate the configuration average of $F(t)$ will be illustrated for the F_0 term. Since the resonant spins occupy nonidentical sites in a sample we must first write

$$F_0=\frac{1}{N}\sum_{k=1}^{N}\prod_{l(\neq k)}\left(\frac{\sin[(2I+1)B_{lk}t]}{(2I+1)\sin(B_{lk}t)}\right)\times\prod_{\mu=1}^{m}\prod_{l(\mu)=1}^{N_\mu}\left(\frac{\sin[(2S_\mu+1)C_{kl(\mu)}t]}{(2S_\mu+1)\sin(C_{kl(\mu)}t)}\right)\ ,\tag{19}$$

where N is the number of resonant spins. Letting N_0 represent the total number of isotopes sharing a sublattice we have

$$N_0=\sum_{\mu=1}^{m}N_\mu\ ,$$

where N_μ is the number of particles with spin S_μ. Notice that N_0 is also the total number of sublattice sites available to spins S_μ (some species may have $S_\mu=0$). The relative abundance of the μth spin species may now be written as

$$P_\mu=N_\mu/N_0\ .$$

The double pi product in (19), $\Pi_\mu\Pi_{l(\mu)}$, covers each point on the sublattice and properly identifies the isotope on each of these lattice points for some prescribed configuration. The resonant spin set entirely spans its sublattice with identical atoms; hence, the pi product Π_l in (19) is independent of k so that

$$F_0 = T\frac{1}{N}\sum_{k=1}^{N}\left(\prod_{\mu=1}^{m}\prod_{l(\mu)=1}^{N_\mu}\frac{\sin[A_\mu Z^{\mu}_{kl(\mu)}]}{A_\mu\sin(Z^{\mu}_{kl(\mu)})}\right) ,$$

where $A_\mu = 2S_\mu + 1$, $Z^{\mu}_{kl(\mu)} = C_{kl(\mu)}t$, and

$$T = \prod_{l(\neq k)}\{\sin[(2I+1)B_{lk}t]/(2I+1)\sin(B_{lk}t)\} .$$

Now consider, instead of a single sample, a very large number $\mathfrak{N}$ of samples identical except for the arrangements of the S_μ spins. Each configuration is assumed equally probable so that the average of F_0 over this ensemble is given by

$$F_0 = T\frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\frac{1}{N}\sum_{k=1}^{N}\prod_{\mu=1}^{m}\prod_{l(\mu,\epsilon)}^{N_\mu}\times\left(\frac{\sin(A_\mu Z^{\mu}_{kl(\mu,\epsilon)})}{A_\mu\sin(Z^{\mu}_{kl(\mu,\epsilon)})}\right) . \tag{20}$$

The pi products in F_0 and F_1 can always be expanded in a power series. Thus, for example,

$$\prod_{k=1}^{L}\left(\frac{\sin(AX_k)}{A\sin(X_k)}\right) = 1 + C_1\sum_{k=1}^{L}X_k + C_2\sum_{k\neq l}^{L}X_kX_l + \cdots ,$$

where the coefficients C_j are constants. Using this result in (20) requires the calculation

$$Q = \frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\left[\prod_{\mu=1}^{m}\prod_{l(\mu,\epsilon)}^{N_\mu}\frac{\sin[A_\mu Z^{\mu}_{kl(\mu,\epsilon)}]}{A_\mu\sin(Z^{\mu}_{kl(\mu,\epsilon)})}\right]$$

$$= \frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\prod_{\mu=1}^{m}\left[1 + C^{\mu}_1\sum_{l(\mu,\epsilon)=1}^{N_\mu}Z^{\mu}_{kl(\mu,\epsilon)} + C^{\mu}_2 \times\sum_{l(\mu,\epsilon)\neq j(\mu,\epsilon)}^{N_\mu}Z^{\mu}_{kl(\mu,\epsilon)}Z^{\mu}_{kj(\mu,\epsilon)} + \cdots\right]$$

$$= \frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\left[1 + \sum_{\mu=1}^{m}C^{\mu}_1\sum_{l(\mu,\epsilon)}^{N_\mu}Z^{\mu}_{kl(\mu,\epsilon)} + \sum_{\mu\neq\nu}^{m}C^{\mu}_1C^{\nu}_1\sum_{l(\mu,\epsilon)}^{N_\mu}\sum_{l(\nu,\epsilon)}^{N_\nu}Z^{\mu}_{kl(\mu,\epsilon)}Z^{\nu}_{kl(\nu,\epsilon)} + \sum_{\mu=1}^{m}C^{\mu}_2\sum_{l(\mu,\epsilon)\neq j(\mu,\epsilon)}^{N_\mu}Z^{\mu}_{kl(\mu,\epsilon)}Z^{\mu}_{kj(\mu,\epsilon)} + \cdots\right] . \tag{21}$$

To proceed with the evaluation of Q we note that P_μ is the probability that a lattice site of the nonresonant spins will have an S_μ-type spin on it. That is, P_μ is the number of configurations in the ensemble for which an S_μ spin occupies the jth sublattice position divided by $\mathfrak{N}$, the total number of configurations. On evaluating (21) we find terms such as

$$Q_1 = 1,\quad Q_2 = \frac{1}{\mathrm{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\left[\sum_{\mu=1}^{m}C^{\mu}_1\sum_{l(\mu,\epsilon)}^{N_\mu}Z^{\mu}_{kl(\mu,\epsilon)}\right]$$

$$= \sum_{\mu=1}^{m}C^{\mu}_1\left[\frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\sum_{l(\mu,\epsilon)}^{N_\mu}Z^{\mu}_{kl(\mu,l)}\right]$$

$$= \sum_{\mu=1}^{m}C^{\mu}_1\left[\frac{1}{\mathfrak{N}}\sum_{\epsilon=1}\sum_{l'=1}^{N_0}Z^{\mu}_{kl'}\Theta^{\mu,\epsilon}_{l'}\right]$$

where $\Theta^{\mu,\epsilon}_{l'} = 1$ if the sublattice site l' is occupied by an S_μ spin for the ϵth configuration and is zero otherwise. Hence,

$$Q_2 = \sum_{\mu=1}^{m}C^{\mu}_1\sum_{l'=1}^{N_0}Z^{\mu}_{kl'}\left[\frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\Theta^{\mu,\epsilon}_{l'}\right]$$

$$= \sum_{\mu=1}^{m}\sum_{l'=1}^{N_0}C^{\mu}_1Z^{\mu}_{kl'}P_\mu .$$

Similarly,

$$Q_3 = \frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\left[\sum_{\mu\neq\nu}^{m}C^{\mu}_1C^{\nu}_1\sum_{l(\mu,\epsilon)}^{N_\mu}\sum_{l(\nu,\epsilon)}^{N_\nu}Z^{\mu}_{kl(\mu,\epsilon)}Z^{\nu}_{kl(\nu,\epsilon)}\right]$$

$$= \sum_{\mu\neq\nu}^{m}\sum_{l'\neq j'}^{N_0}C^{\mu}_1C^{\nu}_1Z^{\mu}_{kl'}Z^{\nu}_{kj'}\left[\frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\Theta^{\mu,\epsilon}_{l'}\Theta^{\nu,\epsilon}_{j'}\right]$$

$$= \sum_{\mu\neq\nu}^{m}\sum_{l'\neq j'}^{N_0}C^{\mu}_1C^{\nu}_1Z^{\mu}_{kl'}Z^{\nu}_{kj'}P_\mu P_\nu ,$$

where it is evident that $j'\neq l'$ for if $j'=l'$ then either $\Theta^{\mu,\epsilon}_{l'}$ or $\Theta^{\nu,\epsilon}_{l'}$ equals zero for each ϵ. As a further example consider Q_4:

$$Q_4 = \frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\left[\sum_{\mu=1}^{m}C^{\mu}_2\sum_{l(\mu,\epsilon)\neq j(\mu,\epsilon)}^{N_\mu}Z^{\mu}_{kl(\mu,\epsilon)}Z^{\mu}_{kj(\mu,\epsilon)}\right]$$

$$= \sum_{\mu=1}^{m}\sum_{l'\neq j'}^{N_0}C^{\mu}_2Z^{\mu}_{kl'}\left[\frac{1}{\mathfrak{N}}\sum_{\epsilon=1}^{\mathfrak{N}}\Theta^{\mu,\epsilon}_{l'}\Theta^{\mu,\epsilon}_{j'}\right]$$

$$= \sum_{\mu=1}^{m}\sum_{l'\neq j'}^{N_0}C^{\mu}_2Z^{\mu}_{kl'}Z^{\mu}_{jk'}[P_\mu P'_\mu] ,$$

where $P'_\mu = (N_\mu - 1)/(N'_0 - 1) = P_\mu$

since $N_0 >>> 1$. Thus

$$Q_4 = \sum_{\mu=1}^{m}\sum_{l'\neq j'}C^{\mu}_2Z^{\mu}_{kl'}Z^{\mu}_{kj'}P^2_\mu .$$

Other terms are calculated in a similar manner. We obtain, finally,

$$F_0 = \left(\prod_{l(\neq k)}\frac{\sin[(2I+1)B_{kl}t]}{(2I+1)\sin(B_{kl}t)}\right)(Q_1 + Q_2 + Q_3 + Q_4 + \cdots) .$$

The evaluation is now simplified since we sum over every point on the sublattice. We can consider each point on this sublattice to be shared by each isotope since the probabilities P_μ ensure that proper weights are assigned. As a result F_0 is independent of k, a reference spin site. Similar results have been obtained for F_1. When applied to the fluorine resonance in SrF_2 we have, for example,

$$F_0 = \prod_{l(\neq k)} \left(\frac{\sin[(2I+1)B_{kl}t]}{(2I+1)\sin(B_{kl}t)} \right) \Bigg[1 + \frac{t^2}{2!} C_1 P \times \sum_{l'=1}^{N_0} (C_{kl'})^2 + \frac{t^4}{4!} \Bigg(C_2 P \sum_{l'=1}^{N_0} (C_{kl'})^4 + 3(C_1)^2 P^2 \sum_{l' \neq j'}^{N_0} C_{kl'}^2 C_{kj'}^2 \Bigg) + \cdots \Bigg] \quad , \tag{22}$$

where $P = 0.07$ and the coefficients are

$$C_1 = \tfrac{1}{3}[1 - (2S+1)^2] = -33$$

and $C_2 = \frac{1}{5}[(2S+1)^4 - \frac{10}{3}(2S+1)^2 + \frac{7}{3}] = \frac{9669}{5}$.

In this instance terms through t^4 are sufficient because both P and (γ_{Sr}/γ_F) are small. Notice that coefficients $C_j = 0$ when $S = 0$ as required.

We could apply the averaging method just described to any system having several isotopes for one or more of its atoms. The number of terms required in expansions such as (22) will depend on the particular crystal to which the method is applied and so general results will not be given here.

III. COMPARISON OF EXPERIMENT AND THEORY

Experimental measurements were made at room temperature on a Varian DA-60 spectrometer operating at 56 MHz for F^{19}. Our sample was a cylindrically shaped Harshaw crystal $\frac{1}{2}$ in. in diam and 1 in. in length having [110] direction approximately along the axis of the cylinder. Alignment to within 1° was subsequently carried out using x-ray diffraction. Each crystal was then mounted on a shaft which allowed rotation of [110] axis perpendicular to $\vec{H}_0$. For each of the three principal orientations of a cubic crystal with respect to $\vec{H}_0$ several independent sets of runs or data sets were made. Line shapes within each set of data were averaged to a single symmetrized curve from which an FID curve was calculated by Fourier transformation. Second moments were also obtained.

Magnetic field modulation was made at 80 cps with an amplitude of about 0.4 G. For this modulation amplitude, corrections to measured second moments were less than or about equal to 1%. Using Andrew's[20] formula for the line shape observed using field modulation, we may easily obtain by Fourier transformation a relation between the FID calculated from the observed cw line shape $F'(t)$ and the true FID shape $F(t)$:

$$F(t) = F'(t)/(1 - D_2 t^2 + D_4 t^4 - \cdots) \quad .$$

Coefficients of terms through t^4 are related to the modulation amplitude H_m as follows

$$D_2 = \tfrac{1}{8}\gamma^2 H_m^2 \;, \quad D_4 = \tfrac{1}{192}\gamma^4 H_m^4 \quad .$$

For those times of interest and for values of H_m that we used, the dominant correction factor is $D_2 t^2$; in addition, $D_2 t^2 \ll 1$, so that our calculated FID shapes need not be corrected for modulation distortion. Notice that the zeros of the decay $F(t)$ are predicted to be independent of H_m. Except for this, the correction for field modulation is such that $|F| > |F'|$ for typical values of H_m and t. This is usually in the direction opposite to that correction which must be made for distortion due to finite bandwidths in an FID experiment measuring $F''(t)$; that is $|F| < |F''|$ for a major portion of the decay.[16,17]

Our sample of SrF_2 was fairly free from paramagnetic impurities having a T_1 of 600 sec. For this sample, the magnetic field was swept at a rate of 0.01 G/sec. Square roots of second moments are given in Table I. The next to last column gives theoretical values obtained from Van Vleck's theory when only fluorine nuclei are considered while the last column shows the effect of the 7% abundant Sr^{87} nuclei. Their effect is quite small being most pronounced for the [111] orientation. Figure 1 shows Fourier transforms of our cw data compared with the theoretical results F_{EPDG} and F_{LTGL}. The time axis is labeled by values of a dimensionless time τ, where the actual time is $t = (36.5\ \mu\text{sec})\tau$. Configuration averaging was carried out on F_{EPDG} as described in Sec. II. Since Sr^{87} nuclei produced noticeable effects in these calculations only for the [111] orientation, we calculated F_{LTGL} by considering only a single set of spin-$\frac{1}{2}$ particles. For this case the formula of LTGL reduces to that obtained by LN. Comparison of the two theoretical results with the data shows that although for some orientations one is in better agreement than the other neither one is

TABLE I. Square roots of experimental second moments expressed in G compared with Van Vleck theory.

Orientation	Data set 1	Data set 2	Data set 3	Theory (F only)	Theory
[100]	2.97 ± 0.04	3.01 ± 0.06	2.98 ± 0.03	3.00	3.00
[110]	1.85 ± 0.02	1.84 ± 0.02	1.86 ± 0.02	1.85	1.86
[111]	1.27 ± 0.01	1.26 ± 0.01	1.25 ± 0.02	1.25	1.27

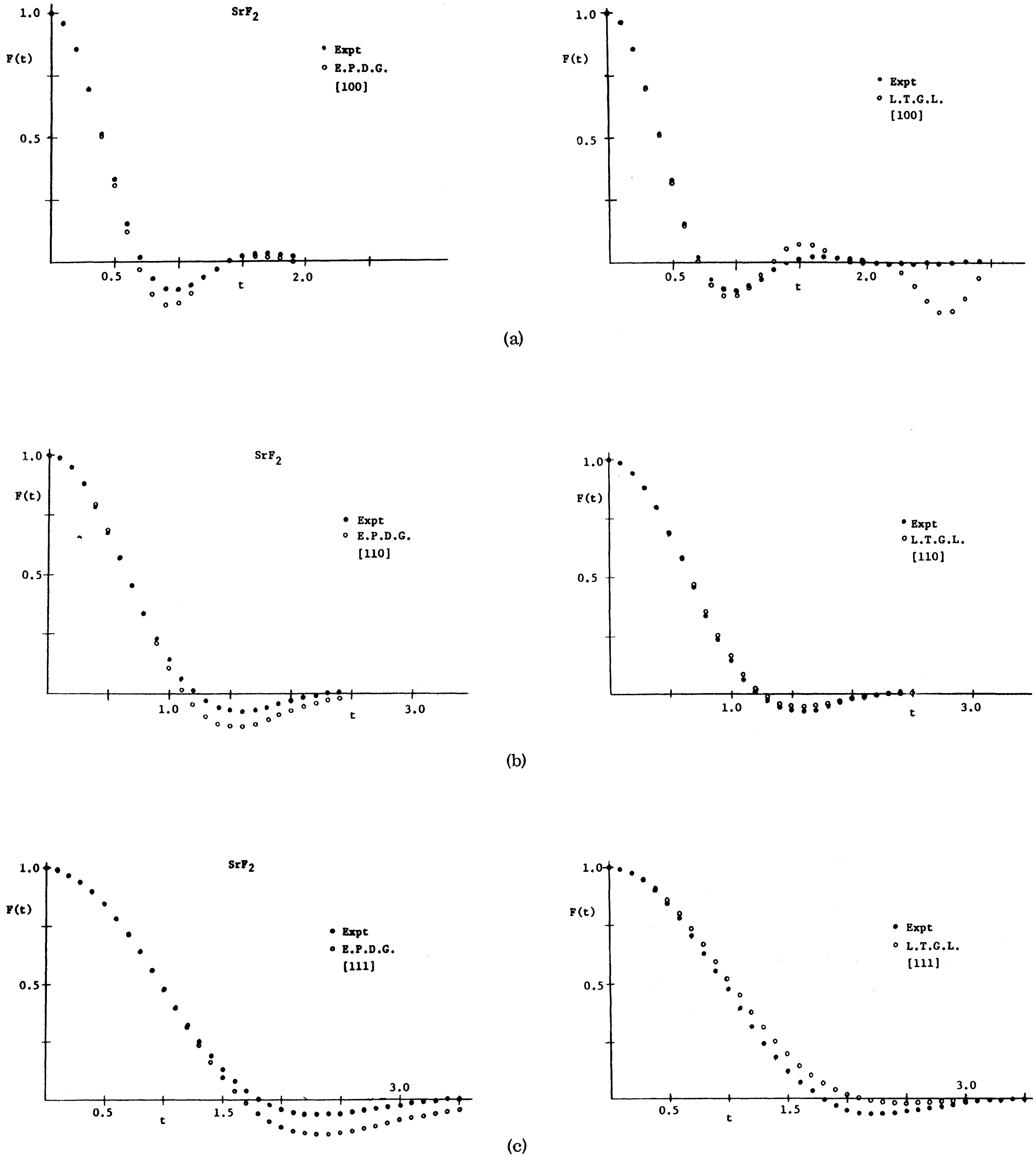


FIG. 1. Theoretical and experimental FID's of the fluorine spin system in SrF_2 where a unit of t corresponds to 36.5 μsec: (a) $\vec{H}_0 \parallel [100]$; (b) $\vec{H}_0 \parallel [110]$; (c) $\vec{H}_0 \parallel [111]$.

in better agreement for all orientations. Notice that the LTGL result begins to diverge near $\tau = 2$ for the [100] orientation. This consequence of the time expansion used by LTGL was not observed in any of our other calculations for those values of τ that were used.

These calculations have shown that the Sr^{87} nuclei produce quite small effects. If these nuclei produced negligible effects fluorine FID's from CaF_2 and SrF_2 should be identical when properly scaled. That is, in the theoretical FID formula (4), we may write $t = (a^3/\gamma^2\hbar)\tau$ where τ is a dimensionless time, γ is the fluorine gyromagnetic ratio, a is the nearest-neighbor distance, and $2\pi\hbar$ is

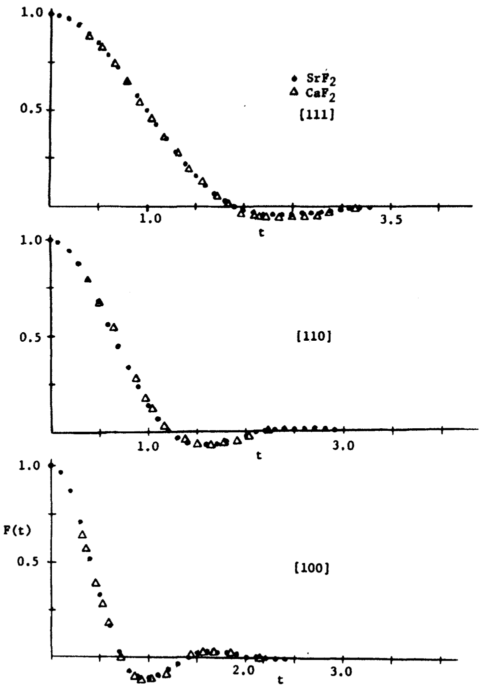


FIG. 2. FID's of CaF$_2$ and SrF$_2$ experimentally compared on a dimensionless time scale.

Planck's constant. Since SrF$_2$ and CaF$_2$ have the same crystal structure, the FID formulas, when expressed in terms of τ, predict identical decays when Sr^{87} terms are omitted. We have plotted, in this manner, the most accurate FID measurements on CaF$_2$, made by Barnaal and Lowe,[16] together with the Fourier transforms of our cw line shapes from SrF$_2$. These results are shown in Fig. 2. The scale factor $(a^3/\gamma^2\hbar)$ is 30.3 μsec for CaF$_2$ and 36.5 μsec for SrF$_2$. Consider first the [100] orientation. The two sets of data are in excellent agreement. For this orientation the theories of Van Vleck and EPDG predict negligible effects due to Sr^{87} nuclei. The data for the [110] orientation are slightly less well matched and for the [111] orientation there is a more pronounced deviation of the two line shapes which is outside the consistency limits of our data sets. These observations are consistent with the effect that Sr^{87} nuclei would have on the observed fluorine resonance. The local fields of strontium nuclei would broaden the cw line shape and hence narrow the FID. The agreement of these two sets of data suggests that a detailed comparison of experimental and theoretical line shapes is justified.

We have made such comparisons using data reported by LTGL on NaCl[6] and Hutchins and Day[19] on CsF. Theoretical calculations were made to determine the three approximations to the FID discussed in Sec. II: F_{LTGL}, and F_{EPDG}, and F_F. In our evaluation of both $\tilde{F}_2$ and F_{LTGL} we do not use the last approximation of LTGL in neglecting sums in (15) and (18) involving odd powers of coefficients like A_{kl}. Although in many cases these terms are negligibly small there are some cases in which they are not and hence our results may differ slightly from those reported by LTGL and Hutchins and Day.[19] All FID shapes are plotted as a function of the dimensionless time τ, where the real time t is given by

$$t=(a^3/\gamma^2\hbar)\tau\ .$$

For a fcc lattice it is convenient to let the distance factor a be half the nearest-neighbor distance; γ is the gyromagnetic ratio of a nucleus chosen to be F^{19} in CsF and Na^{23} in NaCl. Plotting in this fashion makes FID shapes dependent upon the lattice type, in these cases fcc-fcc, and upon the spins and the ratio (γ'/γ) where γ' and γ are the gyromagnetic ratios of the two nuclear species. In each calculation 134 resonant spins nearest the reference spin were included except in the evalua-

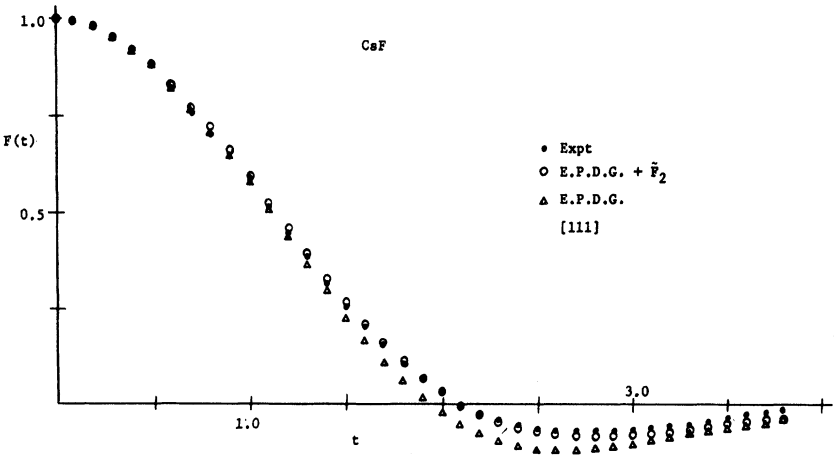


FIG. 3. Experimental FID compared with theories F_F and F_{EPDG} for the fluorine spin system of CsF with $\vec{H}_0 \parallel$ [111]. A unit of t corresponds to 40.6 μsec.

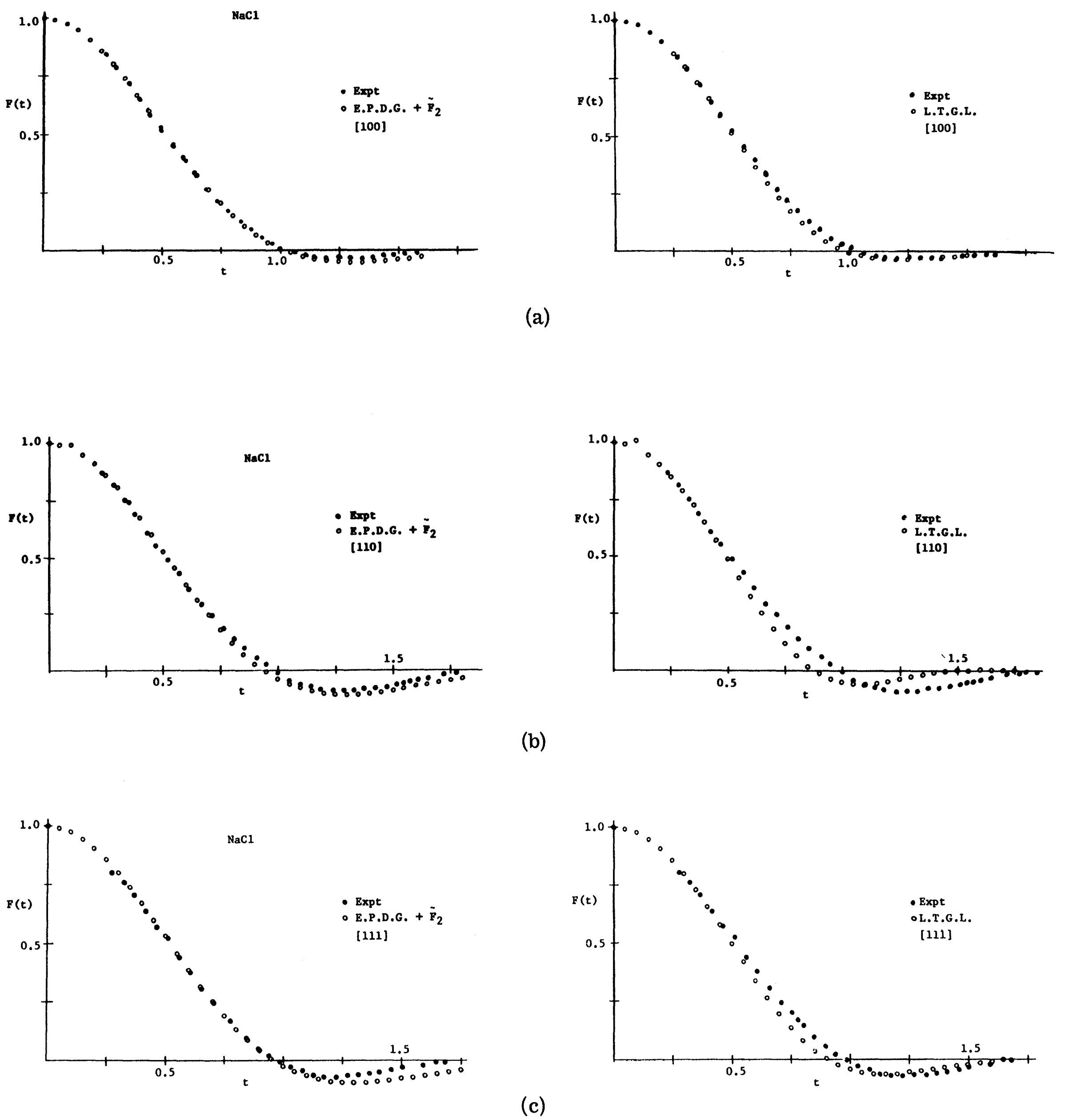


FIG. 4. Theoretical and experimental FID's of sodium spin system of NaCl where a unit of t corresponds to 425 μ sec: (a) $\vec{H}_0 \parallel [100]$; (b) $\vec{H}_0 \parallel [110]$; (c) $\vec{H}_0 \parallel [111]$.

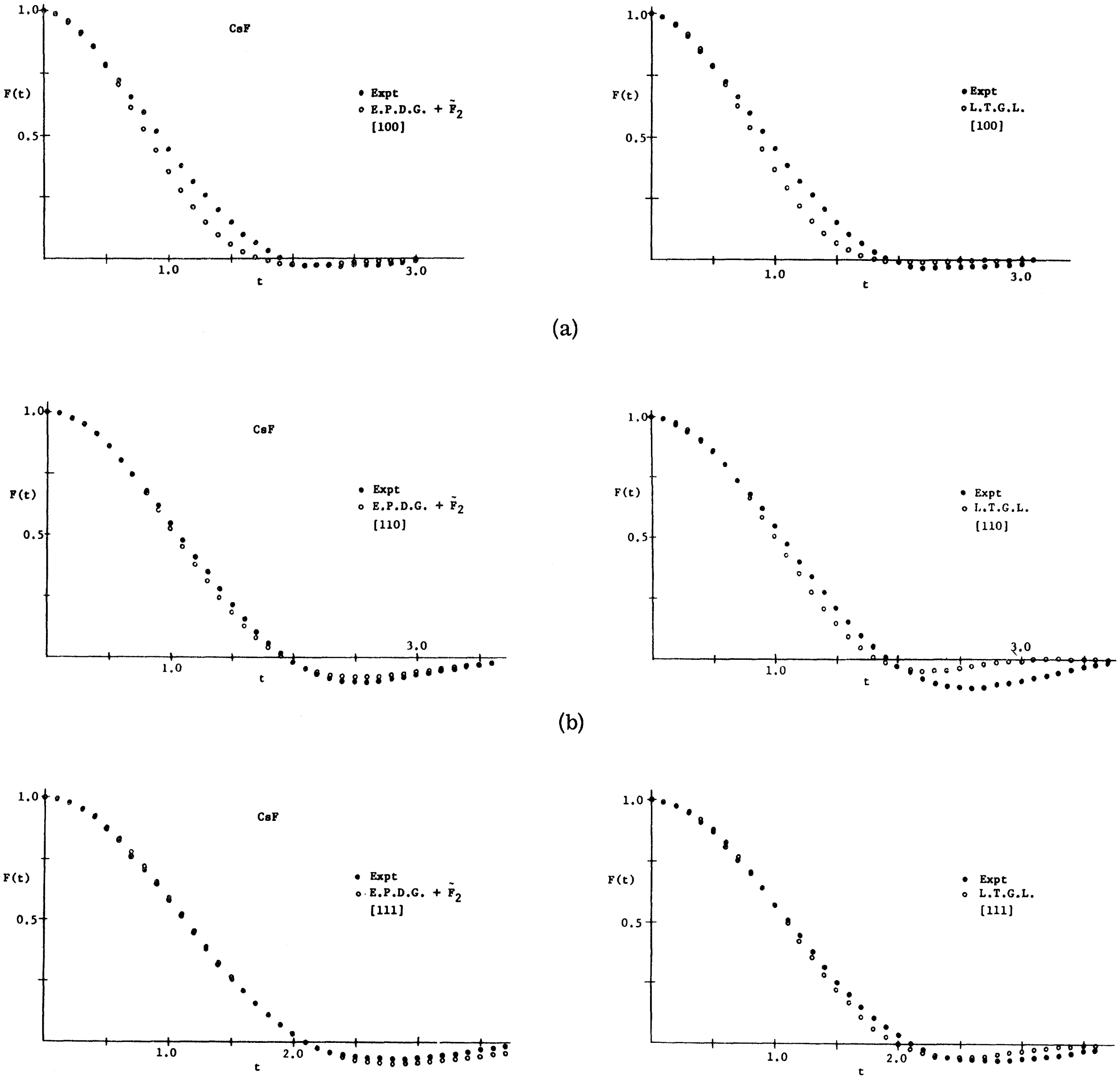
tion of the integral in (17) for which 54 spins are included. For several crystal orientations and times τ we increased these numbers to 200 and 86 spins, respectively, without finding a significant change. The number of unobserved spins included was 116 which was increased to 128 when 200 resonant spins were considered. The average computation time per τ point was about 20 sec on an IBM 360/75.

In all our comparisons we found that $F_F = F_{\text{EPDG}} + \tilde{F}_2$ was in as good or better agreement with experiment than F_{EPDG} alone. To illustrate the improvement obtained we show in Fig. 3 a comparison with the [111] fluorine resonance in CsF. Subsequent comparisons will omit F_{EPDG} both because it is consistently improved upon by F_F and because in earlier work, F_{LTGL} has been used exclusively to compare with data from two spin species crystals.

LTGL[6] studied the soduim resonance in NaCl.

In order to reduce quadrupole effects as much as possible they used a sample specially grown to be exceedingly strain free. However, they found that standard commerically available samples produced equivalent results. Their data did show significant effects, however, when these samples were subjected to strong thermal shocks. In Fig. 4, we compare their best data with F_{LTGL} and F_F. The time scale factor here is 425 μsec. In calculating the line shape, chlorine spins were assumed to form a single spin system as discussed in Sec. II. Examination of results for each orientation shows that F_F is in better agreement with the data than F_{LTGL}. The [110]orientation shows the greatest improvement. However, differences between theory and experiment occur in the same way for each orientation.

Even though quadrupole effects are evidently not significant for these sodium chloride data it would be of interest to make similar comparisons for a crystal in which they are absent. We have thus calculated line shapes for the fluorine res-



(a)

(b)

(c)

FIG. 5. Theoretical and experimental FID's of fluorine spin system of CsF where a unit of t corresponds to 40.6 μsec: (a) $\vec{H}_0 \parallel [100]$; (b) $\vec{H}_0 \parallel [110]$; (c) $\vec{H}_0 \parallel [111]$.

onance in cesium fluoride which was recently reported by Hutchins and Day.[19] Results are given in Fig. 5. Consider first the [110] and [111] orientations. Theory and experiment compare in a manner quite similar to that found for the corresponding orientations of NaCl. For the [100] orientation in CsF both theoretical curves are in substantial agreement with each other but not with the experimental data. This was surprising to us in view of the consistency of all our other comparisons.

IV. SUMMARY AND DISCUSSION

The excellent agreement of our cw data from SrF_2 with the FID data from CaF_2 has led us to make detailed comparisons between different line-shape theories and experiments on other crystals. It was recognized that the theoretical results of EP and LTGL were derived from the same basic expansion for the FID function. This made it appropriate to combine their results in the manner described earlier in order to obtain an improvement in the theory. This combined result was compared with data from crystals having two sets of spins and was found to give as good or better agreement than either the result of EPDG or that of LTGL alone.

Crystals having two or more sets of spins are of interest because of additional dipole-dipole couplings that influence the line shape: The unobserved spins produce local fields at the observed spin sites which broadens the cw line shape while the spin-flip–flop interaction between unobserved spins effectively averages this local field which tends to narrow the line.[8] Abragam and Winter[21] found that the K^{39} line shape in KF was qualitatively Lorentzian rather than Gaussian because of the large effect of F^{19}-F^{19} interactions. The magnitude of this effect is determined essentially by the ratio γ'/γ where γ' and γ are gyromagnetic ratios of the unobserved and observed spins, respectively.[8] KF represents an extreme case in which this ratio is quite large: $\gamma(F^{19})/\gamma(K^{39})$ is about 20. Thus in NaCl $\gamma(Cl^{35})/\gamma(Na^{23})$ is about the same as $\gamma(Cl^{37})/\gamma(Na^{23})$ which is approximately 0.30. In CsF we have $\gamma(Cs^{133})/\gamma(F^{19})$ approximately equal to 0.14. Thus comparisons between experiment and dipolar theory that have been made have been limited to cases in which interactions between nonresonant spins were not large. Experiments on crystals in which these interactions are large would provide a further test of theories of dipolar broadening.

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