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Experimental and Theoretical Investigations of the NMR Line Shapes of LiF and NaF Single Crystals

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Experimental cw line shapes have been obtained for Li^7, Na^{23}, and F^{19} nuclei in NaF and LiF single crystals, and compared with several line-shape theories. A new line-shape theory is described which gives better results than previous ones for these two crystal systems.

INTRODUCTION

Ever since the discovery of nuclear magnetic resonance (NMR) by Purcell *et al.*[1] and Bloch *et al.*,[2] considerable effort has been devoted to the theoretical description of dipolar broadened line shapes in crystals. Until 1967, most experimental and theoretical studies of single crystals, such as those by Pake and Purcell,[3] Bruce,[4] Lowe and Norberg,[5] and others,[6–9] centered largely around the calcium fluoride crystal, which has a single magnetic ingredient of spin $\frac{1}{2}$ on a simple cubic lattice.

Lee, Tse, Goldburg, and Lowe[10] (LTGL) generalized existing theory to include more complex systems and presented the experimental results for the sodium resonance in the two-spin face-centered cubic (fcc) NaCl crystal, where both nuclei have spins of $\frac{3}{2}$.

Hutchins and Day[11] have reported the results of experiments on the two-spin fcc CsF crystal where the cesium and fluorine nuclei have spins of $\frac{7}{2}$ and $\frac{1}{2}$, respectively. Their results showed poor agreement with the LTGL theory generally, and attempts to establish cesium quadrupole-moment effects were indeterminate, leading the authors to the conclusion that dipolar broadening theory was inadequate for the cesium resonance.

In a recently published paper, Fornes, Parker, and Memory[12] (FPM) have extended the theory of LTGL and that of Evans and Powles[9] as generalized by Demco,[13] and applied their results to the previous work on NaCl and CsF, with better results.

This paper presents the results of theoretical and experimental investigations of the NMR line shapes in NaF and LiF. Fourier transforms of continuous-wave (cw) data are compared with line shapes from the theories of LTGL and FPM. Experimental moments are compared with theoretical moments from Van Vleck,[14] and a line-shape theory based on the Gram-Charlier expansion is presented.

EXPERIMENTAL PROCEDURE

Single crystals of LiF and NaF grown along the [110] axis were obtained from the Harshaw Chemical Company, and were determined to be within 1° of the axis by x-ray diffraction. All spectra were cw derivative curves taken on a Varian DA-60 spectrometer operating at 56.4 MHz for F^{19} and 15.1 MHz for Li^7 and Na^{23}. Fourier transforms of the spectra were obtained by computer for comparison with theoretical free-induction decay (FID) curves.

TABLE I. Experimental and theoretical values of $(M_2)^{1/2}$ and $(M_4)^{1/4}$ of NMR absorption line in NaF and LiF. (All moments are expressed in units of gauss.)

H_0 parallel to	Nucleus	$(M_2)^{1/2}$ Theor	$(M_2)^{1/2}$ Expt	$(M_4)^{1/4}$ Theor	$(M_4)^{1/4}$ Expt
(111)	Na *IN* NaF	1.56	1.60	2.05	2.07
(110)		2.38	2.33	3.25	3.12
(100)		3.91	3.82	5.36	4.94
(111)	F *IN* NaF	2.16	2.14	2.70	2.65
(110)		2.37	2.35	2.93	2.90
(100)		2.90	2.83	3.72	3.59
(111)	$Li^{(7)}$ *IN* LiF	3.10	3.00	3.93	3.79
(110)		4.09	4.04	5.30	5.24
(100)		6.17	5.92	8.19	7.63
(111)	F *IN* LiF	3.38	3.30	4.25	4.12
(110)		4.09	3.95	5.14	4.94
(100)		5.70	5.55	7.38	7.08

MOMENTS

Theoretical second and fourth moments of the absorption line were calculated by applying the results of Van Vleck[14] to a two-spin fcc lattice. In addition, the contributions from the two isotopes of lithium were included with weighted sums described by Abragam[15] and Fornes.[16]

The final form of the second and fourth moments for a system consisting of two spins, each with two isotopes, is

$$\frac{\langle\Delta H^2\rangle}{(8\hbar/a_0^3)^2}=(\tfrac{3}{4}\gamma_{11}^2Z_{11}P_{11}+\tfrac{1}{3}\gamma_{12}^2Z_{12}P_{12})\Big(\sum_k B_{jk}^2\Big)+\tfrac{1}{3}(\gamma_{21}^2Z_{21}P_{21}+\gamma_{22}^2Z_{22}P_{22})\Big(\sum_k C_{jk}^2\Big)\ , \tag{1}$$

$$\begin{aligned}\frac{\langle\Delta H^4\rangle}{(8\hbar/a_0^3)^4}=&\tfrac{27}{16}\gamma_{11}^4Z_{11}^2P_{11}^2\Big(\sum_k B_{jk}^2\Big)^2-\tfrac{3}{16}\gamma_{11}^4Z_{11}^2P_{11}^2\Big(\sum_{k,l}{}' B_{jk}^2(B_{jl}-B_{kl})^2\Big)\\&-\tfrac{9}{160}\gamma_{11}^4(16Z_{11}^2P_{11}+3Z_{11}P_{11})\Big(\sum_k B_{jk}^4\Big)+\tfrac{3}{4}\gamma_{11}^2Z_{11}P_{11}(\gamma_{21}^2Z_{21}P_{21}+\gamma_{22}^2Z_{22}P_{22})\Big(\sum_{kl'} B_{jk}^2(C_{jl'}^2+C_{kl'}^2)\Big)\\&+\tfrac{3}{4}\gamma_{11}^2Z_{11}P_{11}\gamma_{12}^2Z_{12}P_{12}\Big(\sum_{k,l}{}' B_{jk}^2(B_{jl}^2+B_{kl}^2)\Big)-\tfrac{5}{36}\gamma_{11}^2Z_{11}P_{11}(\gamma_{21}^2Z_{21}P_{21}+\gamma_{22}^2Z_{22}P_{22})\Big(\sum_{kl'} B_{jk}^2(C_{jl'}-C_{kl'})^2\Big)\\&-\tfrac{5}{36}\gamma_{11}^2Z_{11}P_{11}\gamma_{12}^2Z_{12}P_{12}\Big(\sum_{k\neq l} B_{jk}^2(B_{jl}-B_{kl})^2\Big)+\frac{1}{36}\frac{1}{\gamma_{11}^2}(\gamma_{21}^6Z_{21}^2P_{21}^2+\gamma_{22}^6Z_{22}^2P_{22}^2)\Big(\sum_{k',l'}{}' B_{k'l'}^2(C_{jk'}-C_{jl'})^2\Big)\\&+\frac{1}{36}\frac{1}{\gamma_{11}^2}\gamma_{12}^6Z_{12}^2P_{12}^2\Big(\sum_{k,l}{}' B_{kl}^2(B_{jk}-B_{jl})^2\Big)+\tfrac{1}{3}\gamma_{12}^4Z_{12}^2P_{12}^2\Big(\sum_k B_{jk}^2\Big)^2+\tfrac{1}{3}\Big(\gamma_{21}^4Z_{21}^2P_{21}^2+\gamma_{22}^4Z_{22}^2P_{22}^2\Big)\Big(\sum_{k'} C_{jk'}^2\Big)^2\\&+\tfrac{1}{15}\gamma_{12}^2P_{12}(3Z_{12}^2-Z_{12})\Big(\sum_k B_{jk}^4\Big)+\tfrac{1}{15}[\gamma_{21}^2P_{21}(3Z_{21}^2-Z_{21})+\gamma_{22}^2P_{22}(3Z_{22}^2-Z_{22})]\Big(\sum_{k'} C_{jk'}^4\Big)\ ,\end{aligned} \tag{2}$$

where γ_{ab} is the gyromagnetic ratio of nucleus a, isotope b (γ_{11} represents the nucleus being probed); $Z_{ab}=S_{ab}(S_{ab}+1)$, where S_{ab} is the spin of nucleus a, isotope b; P_{ab} is the fractional abundance of nucleus a, isotope b; a prime on a summation indicates that the point at the origin, labeled j, is omitted from the sum.

The geometry factors B_{jk} and C_{jk} are defined as

$$\begin{aligned}B_{jk}&=(1-3\cos\theta_{jk'}^2)R_{jk}^{-3}\ ,\\C_{jk'}&=(1-\cos\theta_{jk'}^2)R_{jk'}^{-3}\ ,\end{aligned} \tag{3}$$

where θ_{jk} is the angle between R_{jk} and the static field $H=H_0k$. The vector R_{jk} comes from the vector between lattice points

$$r_{jk}=\tfrac{1}{2}[(n+l)i+(l+m)j+(m+n)k]\,a_0=\tfrac{1}{2}R_{jk}a_0$$

or

$$r_{jk'}=\tfrac{1}{2}[(n+l+1)i+(l+m+1)j+(m+n+1)k]\,a_0$$

$$=\tfrac{1}{2}R_{jk'}a_0\ ,$$

where n, l, m are integers used to generate the points on a fcc lattice, and a_0 is the unit-cell dimension.

The second-moment values $(M_2)^{1/2}=(\langle\Delta H^2\rangle)^{1/2}$ in units of gauss were calculated on the IBM 1130 computer with sums taken over all like neighbors within a cube of dimension $16a_0$, and unlike neigh-

TABLE II. Lattice sums for a fcc crystal.

$$S_1=\sum_k B_{jk}^2$$

$$S_2=\sum_k C_{jk}^2$$

$$S_3=\sum_{k,l}{}' B_{jk}^2(B_{jl}-B_{kl})^2$$

$$S_4=\sum_{k,l}{}' B_{jk}^2(B_{jl}^2+B_{kl}^2)$$

$$S_5=\sum_{k,l}{}' B_{kl}^2(B_{jk}-B_{jl})^2$$

$$S_6=\tfrac{3}{4}\sum_{kl'} B_{jk}^2(C_{jl'}^2+C_{kl'}^2)-\tfrac{5}{36}\sum_{kl'} B_{jk}^2(C_{jl'}-C_{kl'})^2$$

$$S_7=\sum_{k',l'}{}'(C_{jk'}-C_{jl'})^2$$

$$S_8=\sum_k B_{jk}^4$$

$$S_9=\sum_k C_{jk}^4$$

Values for lattice sums as a function of crystal direction

	[111]	[110]	[100]
S_1	1.686	1.531	1.072
S_2	0.601	3.518	12.274
S_3	4.033	3.903	3.032
S_4	4.039	3.615	2.893
S_5	2.838	3.895	3.853
S_6	1.421	7.066	17.178
S_7	0.511	5.248	31.049
S_8	0.189	0.533	0.079
S_9	0.046	2.263	36.003

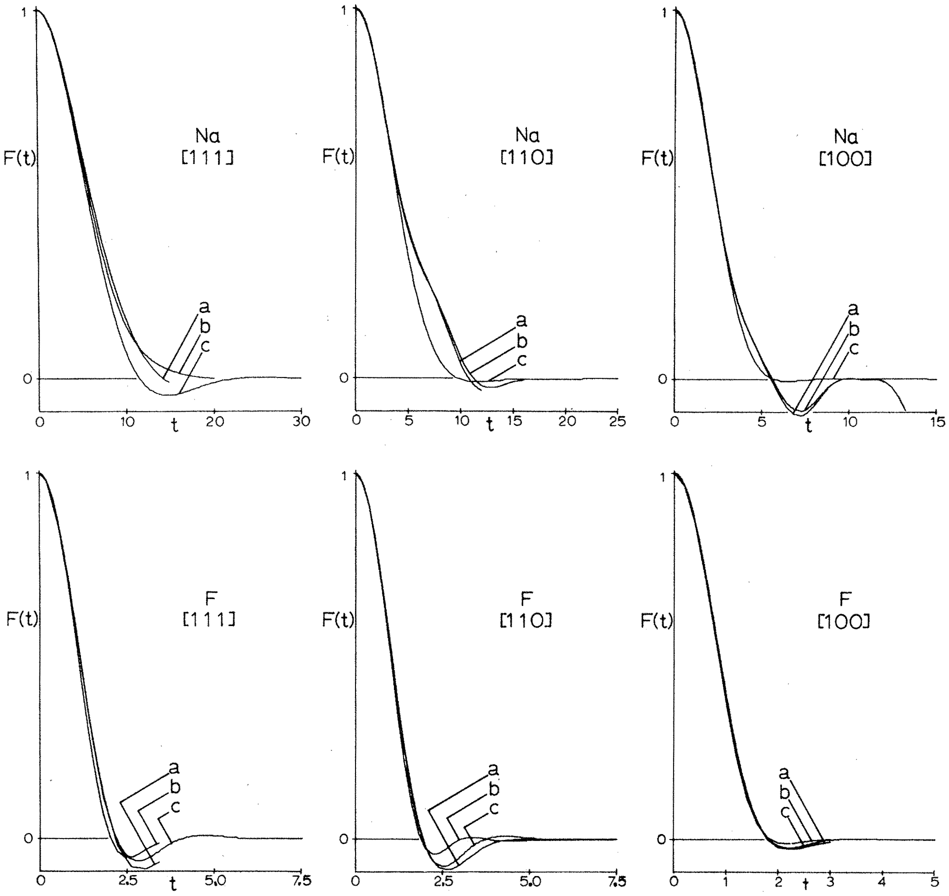

FIG. 1. Free-induction decay curves for NaF. Curves a and b were calculated from the theories of FPM and LTGL, respectively. Curve c is a typical experimental curve. The time scale is in units of 18.46 μsec.

bors within a cube of dimension $17a_0$. Fourth-moment values $(M_4)^{1/4} = (\langle \Delta H^4 \rangle)^{1/4}$ were calculated on an IBM 360/75 computer over like and unlike neighbors within cubes of dimensions $8a_0$ and $9a_0$, respectively. The theoretical and experimental values of second moment $(M_2)^{1/2}$, and fourth root of fourth moment $(M_4)^{1/4}$ are shown in Table I for NaF and LiF crystals with H_0 parallel to (111), (110), and (100). The lattice sums for a fcc lattice are shown in Table II. The quantitative agreement between theoretical and experimental moments seems to confirm the dipole-dipole interaction as the dominant broadening agent for the NMR lines in these crystals.

THEORY

The equation of motion of the x component of the magnetization vector, $M_x = \gamma \hbar I_x$, in an FID experiment has the normalized envelope function[5]

$$F(t) = \mathrm{Tr}(I_x e^{iH_d' t/\hbar} I_x e^{-H_d' t/\hbar}) / \mathrm{Tr}(I_x^2) , \tag{4}$$

where H_d' is the dipolar Hamiltonian, truncated to contain only those terms which commute with the Zeeman energy terms. Solution of this equation is made difficult by the fact that H_d' does not commute with I_x.

LTGL simplified the problem by separating H_d' into two terms

$$H_d' = \hbar(x + \beta) ,$$

where x commutes with I_x, but β does not commute with I_x or x. From an iterative procedure, $F(t)$ can be written in the form of a Dyson series expansion. The first term in the series can be written explicitly, but succeeding terms were approximated, giving the form

$$F(t) = F_0(t) + \tilde{F}_1(t) + \tilde{F}_2(t) + \cdots , \tag{5}$$

where the tilde indicates that the terms were approximated.

Evans and Powles[9] approached the problem in a slightly different way by dividing x and β into parts corresponding to interactions between the resonant spins, nonresonant spins, and mixed spins. They were then able to evaluate two terms explicitly, with the form

$$F(t)=F_0(t)+F_1(t)\ . \tag{6}$$

The result was later generalized by Demco[13] to a broader range of crystal structures. FPM[12] took the generalized equation of Demco and showed that it could be combined with the LTGL theory to give the form

$$F(t)=F_0(t)+F_1(t)+\tilde{F}_2(t)\ . \tag{7}$$

Theoretical curves obtained from the equation of FPM and LTGL are shown with the experimental curves in Figs. 1 and 2. The agreement between the theories and experiment is in general not impressive and in several cases rather poor.

In view of the great difficulty involved in extending the theories presented, and their limited success in describing the experimental results, another theoretical approach has been pursued with promising results.

It is well known that any symmetric, normalizable function which vanishes at infinity can be expanded in the complete set of Hermite polynomials. If the function is approximately Gaussian, as in the case of NMR line shapes in solids, then it is convenient to write

$$f(\omega)=e^{-\omega^2a^2/2}\sum_0^\infty C_nH_n(\omega a)\ . \tag{8}$$

Choosing $a^2=1/\gamma^2M_2$ makes the series a Gram-Charlier expansion[17,18] and causes the coefficient C_2 to vanish. Other coefficients may be made to vanish with proper choices of a^2. The Fourier transform FID function is thus

$$F(t)=e^{-t^4/2a^4}(1+B_4t^4/a^4-B_6t^6/a^6+\cdots)\ , \tag{9}$$

where

$$B_4=\frac{1}{4\,!}\left(\frac{M_4}{M_2^2}-3\right)\ ,$$

$$B_6=\frac{1}{6\,!}\left(\frac{M_6}{M_2^3}-\frac{15M_4}{M_2^2}+30\right)\ .$$

This expansion is seen to be the sum of a Gaussian curve and correction terms. Its value lies both in making use of the fact that the line shape is approxi-

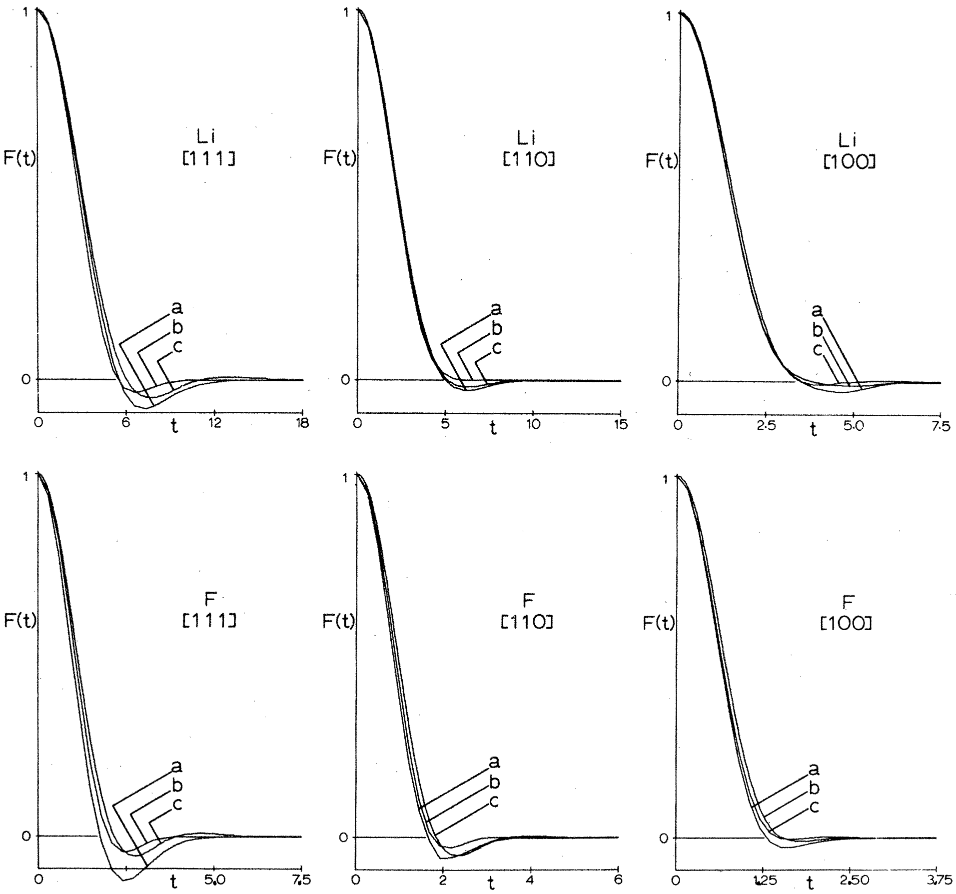

FIG. 2. Free-induction-decay curves for LiF. Curves a and b were calculated from the theories of FPM and LTGL, respectively. Curve c is a typical experimental curve. The time scale curve is in units of 12.13 μsec.

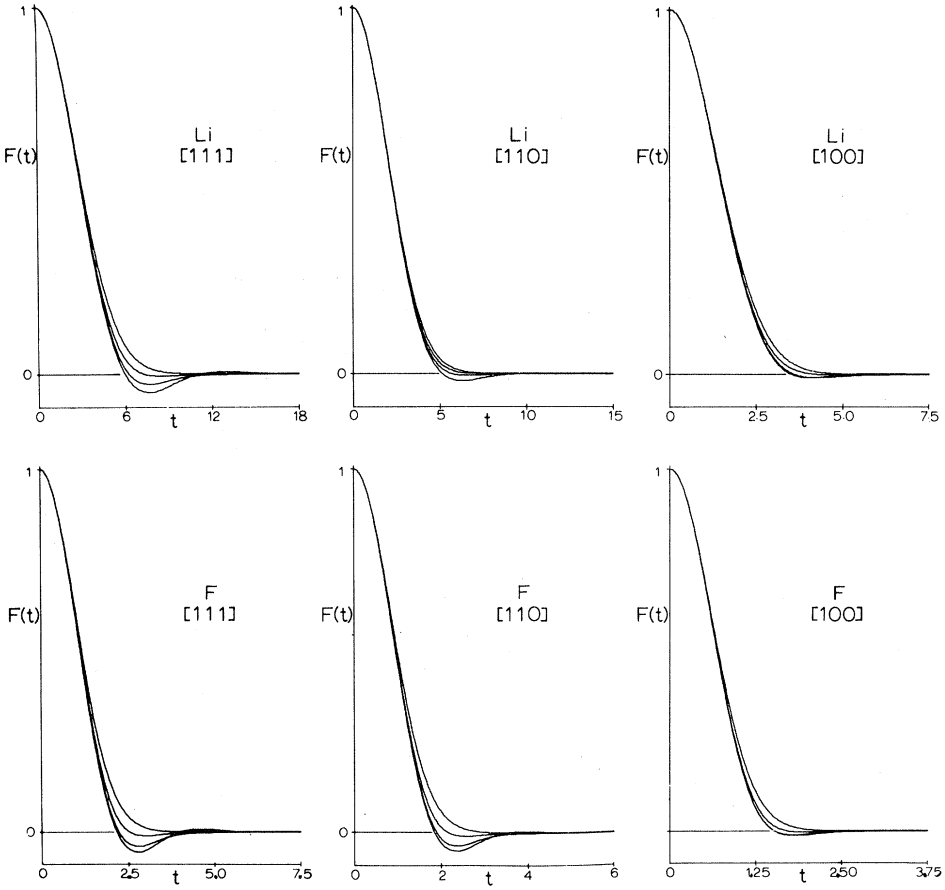

FIG. 3. Free-induction-decay curves for NaF from the Gram-Charlier expansion. The top curve is a Gaussian; the second is a Gaussian plus one correction term; the third is a Gaussian plus two correction terms; and the bottom is the experimental curve. The time scale is in units of 18.46 μsec.

mately Gaussian and in the use of the accurate Van Vleck moment formulas. The result for one, two, and three terms in the expansion are shown in Figs. 3 and 4. Some of the graphs show two of the curves superimposed, as in the case of Na[111] in Fig. 3. This occurs because the B_4 or B_6 coefficients in these cases are almost zero.

CONCLUSIONS

The Gram-Charlier three-moment expansion agrees rather well with the experimental results in the case of NaF and LiF, but is not uniquely successful. For example, a similar series expansion proposed by Bersohn and Das[19] does not give as satisfactory a fit to experimental data as does the theory of Borckmans and Walgraef.[6]

On the other hand, an empirical function using two moments,

$$F(t) = e^{-at^2/2} \sin bt/bt$$

has been presented by Abragam, with good results.[15] It has now been found that Abragam's function can be derived explicitly as the first term in an expansion of spherical Bessel functions with a Gaussian premultiplier. This and other expansions containing various multipliers and polynomial sets are discussed in a paper by Parker.[20] The Gram-Charlier three-moment expansion is therefore seen to be a special case of a set of moment expansions which appear to be one of the more accurate theoretical descriptions of dipolar broadened line shapes in single crystals.

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The moments used in the expansion are the experimental values; experimental moments were used in the expansion for two reasons: The theoretical sixth moments have not been calculated yet, and the good agreement between the theoretical and experimental moments indicates that reasonable accuracy can be obtained with the use of experimental moments.

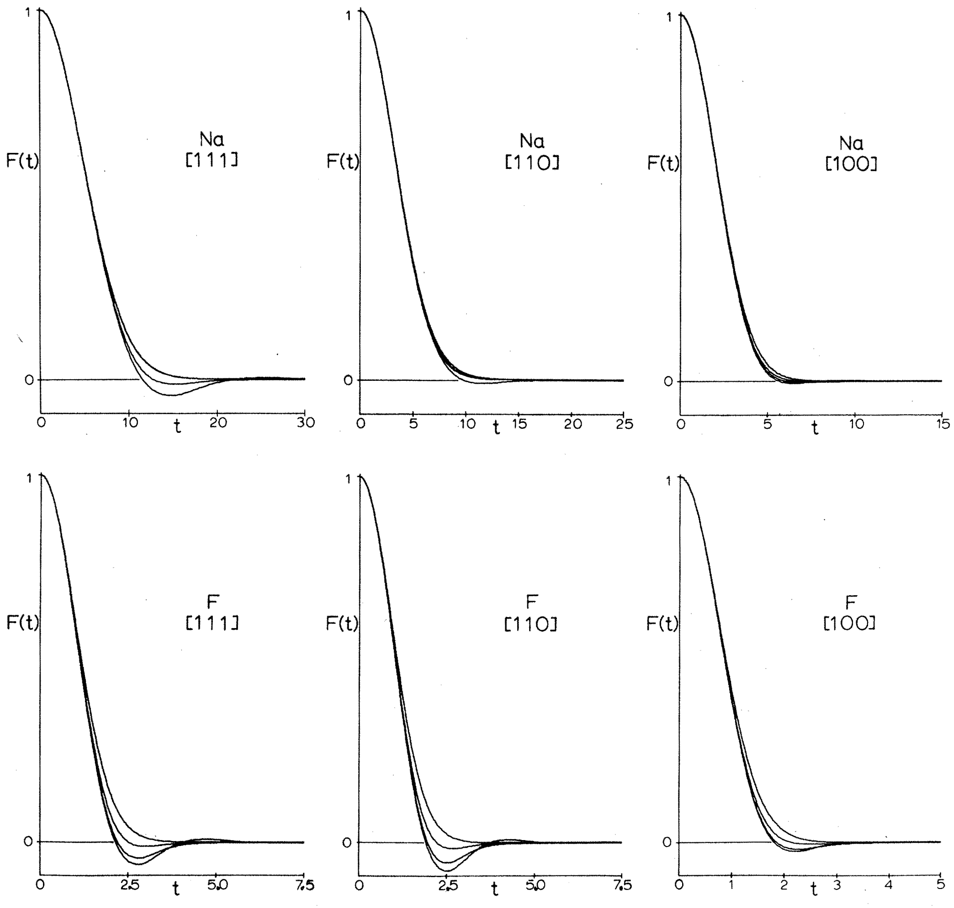

FIG. 4. Free-induction-decay curves of LiF from the Gram-Charlier expansion. The top curve is a Gaussian; the second is a Gaussian plus one correction term; the third is a Gaussian and the bottom is the experimental curve. The time scale is in units of 12.13 μsec.

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[1] E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev. 69, 37 (1946).

[2] F. Bloch, W. W. Hansen, and M. Packard, Phys. Rev. 70, 474 (1946).

[3] G. E. Pake and E. M. Purcell, Phys. Rev. 74, 1184 (1948).

[4] C. R. Bruce, Phys. Rev. 107, 43 (1957).

[5] I. J. Lowe and N. E. Norberg, Phys. Rev. 107, 46 (1957).

[6] P. Borckmans and D. Walgraef, Phys. Rev. 167, 282 (1968); Phys. Rev. Letters 21, 1516 (1968).

[7] S. Clough and J. R. McDonald, Proc. Phys. Soc. (London) 86, 833 (1965).

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

[9] W. A. B. Evans and J. G. Powles, Phys. Letters 24, 218 (1967).

[10] M. Lee, D. Tse, W. I. Goldburg, and I. J. Lowe, Phys. Rev. 158, 246 (1967).

[11] D. K. Hutchins and S. M. Day, Phys. Rev. 180, 432 (1969).

[12] R. E. Fornes, G. W. Parker, and J. D. Memory, Phys. Rev. B 1, 4228 (1970).

[13] D. Demco, Phys. Letters 27A, 702 (1968).

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

[15] A. Abragam, *The Principles of Nuclear Magnetism*, (Oxford, U. P., Oxford, 1961).

[16] R. E. Fornes, Ph.D. thesis (unpublished).

[17] D. Jackson, *Fourier Series and Orthogonal Polynomials* (Mathematical Association of America, Oberlin, Ohio, 1957), pp. 176–179.

[18] H. Cramer, *Mathematical Methods of Statistics*, (Princeton, U. P., Princeton, N. J., 1954), pp. 222–223.

[19] R. Bersohn and T. P. Das, Phys. Rev. 130, 98 (1963).

[20] G. W. Parker, Phys. Rev. B 2, 2453 (1970).