Measured Nuclear Magnetic Resonance Free-Induction-Decay Shapes and Moments for F^{19} in CaF_2†*

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The results of NMR free-induction-decay–shape measurements for F^{19} in single crystals of CaF_2 and polycrystalline CaF_2 are reported. The second and fourth moments of the corresponding absorption line are derived by empirical fits of the decay shapes. The probable errors for our results are smaller than those reported by earlier workers, and the results agree more closely with theoretical predictions for spins in a rigid lattice.

INTRODUCTION

CALCIUM fluoride (CaF_2) is an excellent material for testing theories for nuclear-magnetic-resonance line shapes and moments because; Ca^{43} is the only isotope of calcium that has a spin different from zero, and it is 0.14% abundant and has a very small magnetic moment; the only stable isotope of fluorine (F^{19}) has an angular momentum of $\hbar/2$ and thus no quadrupolar moment; and the fluorine nuclei form a simple cubic lattice which may be considered rigid. Several authors[1–3] have reported line-shape measurements for F^{19} in CaF_2. Since the free-induction-decay (fid)–shape measurements of Lowe and Norberg were reported[3] however, there have been papers published about corrections of measured fid shapes for effects due to the finite width of the excitation pulse[4] and the finite bandwidth of the pickup coil and receiver.[5] Lowe and Norberg did not correct for either of these effects, but were lucky because the results of these effects almost cancelled for their measurements. Reports on the effects of lattice vibrations on NMR second moments have also been made.[6,7] For these reasons, we repeated the fid shape measurements of F^{19} in CaF_2, using a crystal that we believe was more accurately oriented than those used in previous experiments.

EXPERIMENTAL TECHNIQUE

The free-induction-decay-shape measurements were carried out using a phase-coherent, pulsed nuclear-magnetic-resonance spectrometer with phase-sensitive detection. Parts of this apparatus are described elsewhere.[5,8,9] The apparatus was operated at 10 Mc/sec. The detected fid signal was displayed on a Tektronix 543 oscilloscope[10] and recorded photographically. The oscilloscope sweep speed was calibrated with a Tektronix 181 time mark generator and corrected for parallax error. The origin for the time axis[4] for the fid shape was taken to be the center of the 90° radio-frequency excitation pulse, which had a normal width of 1 μsec. The signal to noise ratio was improved by superimposing a number of free-induction-decay traces on one photograph. The fid-shape data on the photograph were measured, plotted onto graph paper, and then corrected for bandwidth distortions by the procedure described in Ref. 5.

The single crystal fid-shape measurements were carried out on a cylindrical sample cut from a natural crystal with a T_1 of 30 sec at 10 Mc/sec. The cylindrical axis of the sample was along the [0$\bar{1}$1] crystal axis so that rotation of the sample about this axis permitted the applied static magnetic field to be along the [100], [110], or the [111] axes. The axis of rotation of the sample was aligned along the [0$\bar{1}$1] crystal axis to within $\pm\frac{3}{4}°$ using an optical goniometer and reflections from the (111) cleaved faces of the sample. Alignment of the [100] axis along the magnetic field was done experimentally to within 1° using the fid shapes, since the [100] and [111] directions are extrema with respect to their first "beat" nulls. All single-crystal measurements were made at room temperature.

A second fid-shape measurement for the [100] and [110] directions was also made in a single crystal grown by the Harshaw Chemical Company.[11] The shapes agreed with those of the natural crystal to within the limits set by the signal to noise ratio which was about 30 to 1 at maximum signal amplitude.

The polycrystalline fid-shape measurements were made on a pellet compressed from reagent grade powder[12] having a T_1 of 0.3 sec. The fid shape of this sample was checked at 5 temperatures (20, 5, −35, −88 and −160°C). There was no observed change in

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[10] Tektronix, Inc., P. O. Box 500, Beaverton, Oregon.
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[12] Fisher Scientific Company, Pittsburgh, Pennsylvania.

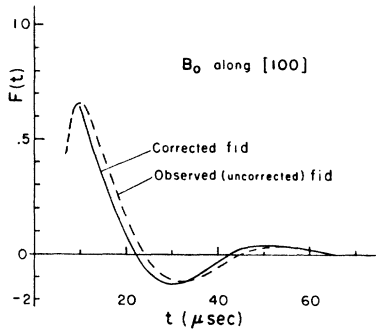

FIG. 1. Observed (uncorrected) fid shape, and the distortion-corrected fid shape for a single crystal of CaF_2 with B_0 along the [100] axis.

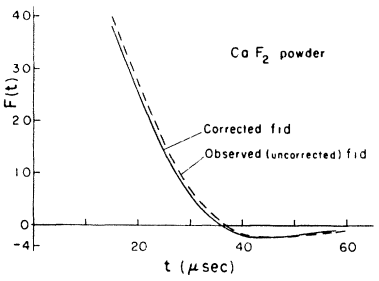

FIG. 2. Observed (uncorrected) fid shape, and the distortion-corrected fid shape for a polycrystalline sample of CaF_2 at 47°K.

line shape to within the 3% experimental error of a point by point comparison. The measurement reported here is for a temperature of −226°C to improve the signal to noise ratio.

We also made an NMR-absorption-line-shape measurement on a reagent-grade CaF_2 powder pellet using a Varian spectrometer operating at 56 Mc/sec. The magnetic field modulation was 1 G peak to peak at 80 cps. The scanning field was calibrated by means of sideband modulation, and the modulation frequency was calibrated by a frequency counter. Although the T_1 of the sample was only 0.3 sec, saturation distortion had to be carefully guarded against. For the run reported here the rf power was reduced 15 dB below the lowest level that showed a detectable change in shape.

EXPERIMENTAL RESULTS

Figure 1 shows the observed (detected) fid shape and the distortion-corrected shape for the static magnetic field along the [100] crystalline axis. Figure 2 shows the observed fid shape and the distortion-corrected shape for the polycrystalline sample. The initially increasing signal is due to recovery of the signal after the damping pulse,[9] and the distortion-correcting procedure helps minimize this effect.[5] It is clear that the amount of correction for a high-Q pickup coil is not negligible.

The crosses in Fig. 3 show the experimental distortion-corrected fid amplitudes for the [100], [110], and [111] directions in CaF_2. For comparison, the Fourier transform of continuous wave-absorption measurements by Bruce[2] are indicated by open circles. The theoretical CaF_2 fid shapes as computed from the rigid lattice parameters by Lowe and Norberg[3] are indicated by the solid lines. The amplitudes of the experimental points were normalized to 1 at zero time by the curve-fitting procedure to be described below.

It is well known that the fid shape following a 90° rf pulse of infinitesimal length may be expanded in the following power series:[3,13]

$$G(t) \propto M_0 - M_2 t^2/2! + M_4 t^4/4! - M_6 t^6/6! + \cdots, \quad (1)$$

where t is time and M_n is the nth moment of the NMR absorption line relative to its center. The second and fourth moments can be taken directly from the coefficients of t^2 and t^4 in a power series fit, or a functional fit to the fid shape.

Attempts were made to carry out a least-squares fit of a polynomial to the experimental curves using a digital computer, but the results were not completely satisfactory. Although moments within 2% of the theoretically predicted values were obtained, further improvement appeared to be hampered by the large numbers of terms required in the polynomial.

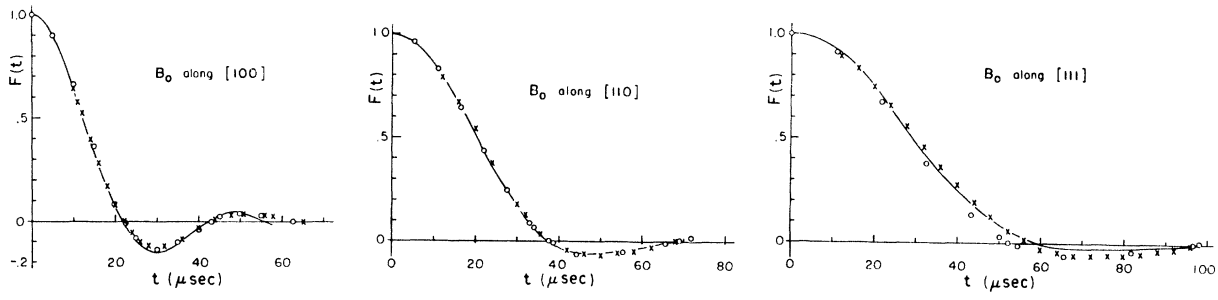

FIG. 3. Free induction decay shapes for F^{19} in CaF_2. (a) B_0 along the [100] axis, (b) B_0 along the [110] axis, (c) B_0 along the [111] axis. The crosses represent our corrected measured fid shape. The circles represent the Fourier transform of Bruce's data (Ref. 2). The solid line is the theoretical shape predicted by Lowe and Norberg (Ref. 3).

[13] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961).

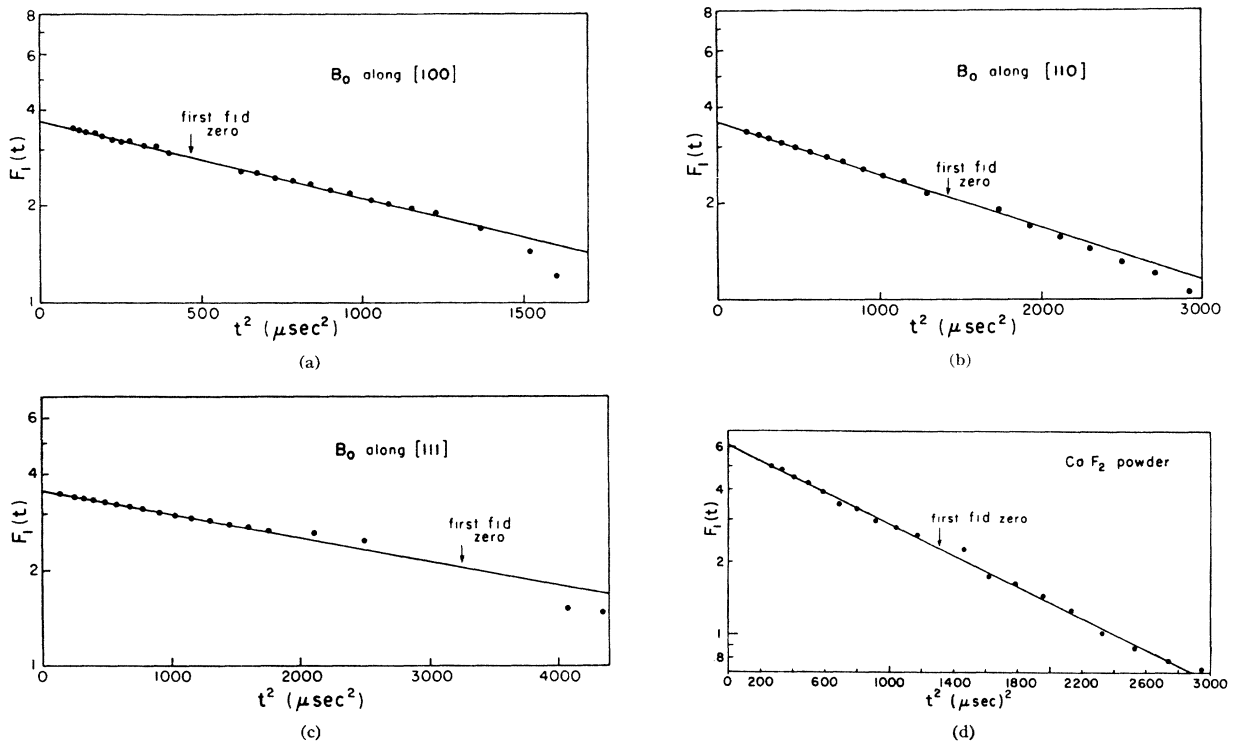

FIG. 4. Semilogarithmic plot of corrected measured fid shapes divided by $(\sin bt)/bt$ and plotted versus t^2. (a) B_0 along the [100] axis, (b) B_0 along the [110] axis, (c) B_0 along the [111] axis, (d) polycrystalline sample.

Abragam[13] has pointed out that the single-crystal fid shapes for CaF_2 are fitted rather well by the function

$$G_A(t)=[(\sin bt)/bt]\exp(-a^2t^2/2), \quad (2)$$

where

$$M_2=(a^2+\tfrac{1}{3}b^2), \quad M_4=(3a^4+2a^2b^2+\tfrac{1}{5}b^4). \quad (3)$$

In fitting this function to the experimental data, b was determined by the first node or crossing point. The experimental fid shape $F(t)$ was then divided by $(\sin bt)/bt$ yielding a function $F_1(t)$ which would be Gaussian if $G_A(t)$ were an exact fit. The $\log F_1(t)$ was therefore plotted versus t^2 to determine the quality of fit and the value of a. Actually, the fid-shape zeros were not found to be precisely periodic, and therefore as t approaches the second zero the plot of $\log F_1(t)$ versus t^2 begins to deviate markedly from a straight line. However $\log F_1(t)$ is straight over a considerable part of the fid duration, giving one confidence in the fit and the second moment derived from it.

Plots of $\log F_1(t)$ versus t^2 are shown in Fig. 4 for the applied magnetic field along the [100], [110] and [111] directions in CaF_2, as well as polycrystalline CaF_2. The experimental values for $(M_2)^{1/2}$ and $(M_4)^{1/4}$ from these fits of $G_A(t)$ to the single crystal data are presented in Table I. The averages of the moments reported by Bruce,[2] and the theoretical moments calculated from the rigid lattice parameters by O'Reilly and Tsang[6] are also given.

Table II gives the moments computed from fid shapes

TABLE I. $(M_2)^{1/2}$ and $(M_4)^{1/4}$ in gauss, for F^{19} in CaF_2 for B_0 along the [100], [110] and [111] directions.

Direction of B_0	Pulse NMR results of this work using Eq. (2)	Av. of Bruce data[a]	Theory[b]
		$(M_2)^{1/2}$(G)	
[100]	3.54±0.07	3.49±0.2	3.59
[110]	2.18±0.04	2.2 ±0.1	2.21
[111]	1.47±0.03	1.55±0.06	1.49
		$(M_4)^{1/4}$(G)	
[100]	4.27±0.08	4.16±0.16	4.29
[110]	2.69±0.05	2.70±0.08	2.68
[111]	1.81±0.04	1.90±0.07	1.82

[a] See Ref. 2.
[b] See Ref. 6.

TABLE II. $(M_2)^{1/2}$ and $(M_4)^{1/4}$ in gauss, for F^{19} in polycrystalline CaF_2.

Moment (G)	Pulse NMR results of this work using Eq. (2)	C. W. NMR results of this work	C. W. NMR results O'Reilly[a]	Theory[a]
$(M_2)^{1/2}$	2.51±0.05	2.53±0.06	2.65±0.03	2.55
$(M_4)^{1/4}$	3.17±0.06	···	3.37±0.08	3.22

[a] See Ref. 6.

for the polycrystalline sample, as well as moments from the absorption measurement performed by ourselves and an absorption measurement by O'Reilly and Tsang.[6]

The errors listed with our fid-moment data are due principally to three factors: signal-to-noise ratio of the fid shape, inaccuracy of correction for distortion, and inaccuracy of positioning the time origin. In curve fitting using Eq. (2), one finds roughly 80% of the moment is due to b in the $(\sin bt)/bt$ term. Since the root second moment is proportional to b, the percentage accuracy of b is a reasonable measure of the accuracy of the root moments. The first crossing point was judged to be known to approximately ± 0.4 μsec, resulting in approximately 1.5% to 2% accuracy in the root moments.

DISCUSSION

The agreement of the predicted theoretical shape[3] with the measured fid shape in the [111] direction is better than previous measurements. The fid shape in the [111] direction is quite orientation-sensitive, with any misalignment resulting in an earlier first crossing point. It is believed that the crystal orientation is better for our data than that used by Lowe and by Bruce (the same crystal was used by both authors at that time). The moment results appear to bear this out.

Our experimental moment results for the single-crystal case agree well with the theoretical predictions for a rigid lattice. The data verify the conclusion of Ref. 7 (revised over that of Ref. 6) that the effect of lattice vibrations on the second moment in CaF_2 is not significant.

Moments may also be obtained from the experimental fid-shape data by fitting the data with other functions besides $G_A(t)$ of Eq. (2). Equation (1) shows that the fitting of the curve for small t is most critical for the determination of the second and fourth moments. Another trial function that should fit the experimental fid-shape data down to the first zero is

$$G_c(t)=e^{-a^2t^2/2}\cos ct. \tag{4}$$

TABLE III. Values of $(M_2)^{1/2}$ and $(M_4)^{1/4}$ for F^{19} in CaF_2, derived by fitting Eq. (4) to fid shape data. Data are only for comparison with Tables I and II.

Direction of B_0	$(M_2)^{1/2}$ (G)	$(M_4)^{1/4}$ (G)
[100]	3.57±0.07	4.36±0.08
[110]	2.18±0.04	2.70±0.05
[111]	1.46±0.03	1.81±0.04
polycryst.	2.56±0.05	3.26±0.06

The second and fourth moments obtained by fitting Eq. (4) to the experimental fid shapes is given in Table III. There is good agreement between the moments listed in Table I and III. The moments listed in Table I are regarded as more accurate because of the quality of the fit over the observable part of the fid shape.

It appears that pulsed NMR techniques are a quite good way of measuring second and fourth moments of line shapes. There are no saturation problems, and the effects due to the finite width of the excitation rf pulse, and the distortions due to the finite bandwidth of the receiver can be corrected for by a relatively straightforward procedure. The finite recovery time of the apparatus following an rf pulse increases the difficulty of obtaining rf information about the free induction decay shape near the origin. However, this does not seem to prevent the accurate extraction of second and fourth moments from the observed part of the free induction decay if one can fit a well-behaved function to the observed part of the fid shape.

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