DETERMINATION OF THE ELECTRIC FIELD GRADIENT IN RbCaF₃ NEAR THE PHASE TRANSITION

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The fluoroperovskite, RbCaF₃ undergoes a phase transition at 195.5K from a cubic to a tetragonal phase. The order parameter for this transition is directly related to the electric field gradient which arises in the tetragonal phase. In this work, we have used three NMR methods to measure the electric field gradient at the Rb site in a single crystal of RbCaF₃, very near this transition. These experiments are based on recent theoretical developments which allow the measurement of quadrupole parameters even for nuclei in a weak electric field gradient.

Introduction

The perovskite, RbCaF₃ undergoes a structural phase transition from a cubic phase (space group Pm 3 m) to a tetragonal phase (I 4/mmm). Nuclei with spin I > 1/2 are sensitive probes of such phase transitions since, in the cubic phase, there is no electric field gradient (EFG) whereas in the tetragonal phase the EFG is no longer zero and the nuclei experience a static quadrupolar interaction. With the arise of this interaction, one is able to study the cubic phase, there is no electric field gradient (EFG)

The temperature dependence of the EFG has already been measured at low magnetic field from the second order quadrupolar shift is too small to be observed. The three methods, nutation, twodimensional Fourier transform NMR experiment at high field. 3 With this

method it was possible to show evidence of phase coexistence at and near Tc, but the determination of \( \omega_Q \) is not straightforward.

A great deal of insight has recently been gained in understanding the dynamics of half-integer, quadrupolar spins in a radio frequency (rf) field. These calculations predict the amplitude of the free induction decay (FID) as a function of the pulse width by numerical or analytical methods. For spins-3/2, quadrupolar parameters can now be obtained by fitting FID or echo amplitudes, as a function of the pulse width, to an expression specific to the experiment being performed.

We present here results based on these recent theoretical calculations of NMR signal intensities for spins-3/2. We show how these methods enable one to rapidly measure \( \omega_Q \) very near the phase transition, and at high static fields where the second order quadrupolar shift is too small to be observed. The three methods, nutation, twodimensional Fourier transform NMR experiment at high field. 3 With this

Experimental

A single crystal of RbCaF₃, with dimensions of 3 mm x 4 mm x 18 mm, was aligned in the magnetic field such that \( H_0 \) was along the (110) axis of the unit cell. In the tetragonal phase, there are three types of domains. Each domain corresponds to an elongation of the cubic unit cell along the (100), (010) or (001) axis. Because of the angular dependence of the quadrupole interaction, these domains are magnetically distinct. In the orientation we have chosen, two of the three possible domains are equivalent and correspond to \( \theta = 45^\circ \); the third corresponds to \( \theta = 90^\circ \).
The spectrometer. The temperature was maintained at TC=4K by the B-VTI000 temperature controller. The probehead contained a 10 mm diameter solenoid coil. The experiments were performed with an rf amplitude of 16 kHz as determined with a saturated aqueous solution of RbCl; this corresponds to a $\pi/2$ pulse length of 15 $\mu$s. For $^{87}$Rb in RbCaF$_3$, the lifetime of the free induction decay is approximately 200 $\mu$s and the linewidth is 5700 Hz. The acquisition parameters are listed in Table I.

Table I. The acquisition parameters used in the three experiments performed on RbCaF$_3$. The variable pulse width in each case was varied in steps of 2 $\mu$s. Here, $t_1$ and $t_3$ are the duration of the first and second pulse and $\tau_2$ and $\tau_4$ are the delays following $t_1$ and $t_3$.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Recovery</th>
<th>$t_1/\mu$s</th>
<th>$\tau_2/\mu$s</th>
<th>$t_3/\mu$s</th>
<th>$\tau_4/\mu$s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nutation</td>
<td>500</td>
<td>2-34</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two-Pulse</td>
<td>500</td>
<td>7</td>
<td>10</td>
<td>2-34</td>
<td>10</td>
</tr>
<tr>
<td>Echo</td>
<td>500</td>
<td>7</td>
<td>200</td>
<td>2-34</td>
<td>200</td>
</tr>
</tbody>
</table>

The nutation experiment employs one variable length pulse, followed by acquisition. In the two-pulse nutation experiment, a $\pi/2$ pulse is followed by a variable

Results and Discussion

It has been known for many years that the magnitude of the quadrupolar interaction will influence the evolution of the magnetic moment in an rf field. Abragam has shown long ago that in the limit of small and large $\omega_Q$, a $\pi/2$ pulse is given by

$$\pi/2 = \frac{\omega_r}{2} t_p$$

where $t_p$ is the pulse duration. These limiting cases are reached for values of $\omega_Q$ less than 0.3 $\omega_r$ and greater than 10 $\omega_r$ and until recently the behavior of the spin system in the intermediate region was not well understood.

Recent calculations using the fictitious spin-1/2 formalism have been used to calculate the response of a spin-3/2 system to each of these three experiments. In that work, analytical expressions were derived for the signal amplitudes as a function of the pulse width for any value of $\omega_Q$ and $\omega_r$ (see appendix). Figure 1 has been derived from those results and shows the behavior of the central transition for $\omega_rX = 18$ kHz and several values of $\omega_Q$ for the nutation, two-pulse nutation and the echo experiments.

In the nutation experiment, the oscillation of the magnetic moment increases and the maximum signal amplitude decreases rather monotonically as $\omega_Q$ increases. For the two-pulse nutation experiment, the oscillations are completely changed when $\omega_Q$ is increased from 2 to 200 kHz, whereas the rough shape of the curves are not changed for the nutation experiment, as can be seen in Figure 1. For these two experiments, the curves do not change for $\omega_Q$ greater than 200 kHz ($\approx 10 \omega_r$).

The echo experiment behaves differently. For very small $\omega_Q$, the central transition gives two maxima as a function of the second pulse length; one when $\omega_r t_2$ is approximately $\pi/4$ and the other at $\pi$. As $\omega_Q$ increases, the second maximum begins to loose intensity and shift to shorter times until there is only one maximum at $\pi/2$ (7.5 $\mu$s) for all $\omega_Q$ greater than 85 kHz. In this regard the echo experiment has about half the range as the two nutation experiments for determining $\omega_Q$.

Figure 2 shows the frequency domain response of $^{87}$Rb in RbCaF$_3$, at TC=4K, to each of the experiments discussed above. An expanded plot of one of these spectra shows a single resonance which may be attributed to the
central transition of $^{87}$Rb. The satellite transitions lie outside the filter width of this experiment. By comparison with Figure 1, it can immediately be seen that, for the rf power available, we are very near the large $\omega_Q$ limit. Figure 3 shows a plot of the integrated signal intensity of the spectra displayed in Figure 2, as a function of the pulse width, for each experiment. These data are represented by diamonds in the figure. The curves are the result of calculations based on the theoretical response of a spin-3/2 system to the specific pulse experiment performed.\textsuperscript{7,9,10} (see appendix) They are identical to the calculations used in Figure 1 but, $\omega_Q$ and $\omega_{Qf}$ were optimized to fit the data. Also, these curves were calculated taking into account the contributions from each of the two magnetically distinct domains. The two contributions are weighted 2:1, and are derived from a statistical distribution of the three types of domains in the tetragonal phase. This distribution was verified by recording a spectrum at $T_c-30$K, where the signals for the two domains were separated by the second order shift, and yield an intensity ratio of 2:1.

The solid curve represents the best fit of the expressions to the signal intensities by independently varying the rf amplitude and the quadrupolar frequency. These fits have been calculated using $t_1$, $t_2$, $t_3$, the experimental values listed in Table I. In each case (nutation, two-pulse and echo experiments), the best fit was obtained with $\omega_Q^{90}/2\pi = 95$ kHz and $\omega_{Qf}/2\pi = 18$ kHz. Here, $\omega_Q^{90}$ represents the quadrupole frequency of the $\theta = 90^\circ$ domain. The difference in $\omega_{Qf}$ from the value determined with the RbCl solution may be attributed to a difference in susceptibility of the crystal and the aqueous solution, or to a slight change in the inductance of the rf coil due to the presence of the salt solution.

To illustrate the uncertainty of our fit, we have calculated the same theoretical curves but, with $\omega_Q^{90}/2\pi = 95 \pm 20$ kHz for the nutation and the two-pulse nutation experiments and $\omega_Q^{90}/2\pi = 95 \pm 40$ kHz for the echo experiment. These calculations are represented by the broken curves in Figure 3.

Two general comments can be made about the graphs in Figure 3. First, there is very good agreement between the curve of the best fit and the points for all three experiments. Second, all three experiments give consistent results for both the rf amplitude and the quadrupole frequency.

For the nutation experiment, the quality of the fit is good. However, because the data are near the limit of large

![Figure 2](image-url)

**Figure 2.** The frequency domain response of the central transition of $^{87}$Rb in RbCaF$_3$ as a function of the detection pulse width for a) the nutation, b) the two-pulse nutation and c) the echo experiments. The spectra are displayed from 2 to 34 $\mu$sec, in steps of 2 $\mu$sec. All experimental parameters are as in Table I.

![Figure 3](image-url)

**Figure 3.** The quality of fit of the data ($\circ$) to the calculated response for the three experiments. The solid line represents the best fit with $\omega_Q^{90} = 95$ kHz; the dashed lines indicate the uncertainty in $\omega_Q$. For the nutation and two-pulse experiments; (-- -- --) 75 kHz and (-- -- --) 115 kHz; for the echo experiment (-- -- --) 55 kHz and (-- -- --) 135 kHz.
Central line intensity in nutation experiment

\[ F^c(t_1) = \frac{1}{10} \{ C_{23} C_p \sin \omega_{23t_1} + C_{14} C_m \sin \omega_{14t_1} \}
+ S_{12} S_p \sin \omega_{12t_1} + S_{34} S_m \sin \omega_{34t_1} \]

Central line intensity in two x pulses of the same phase experiment

\[ 5F^c(t_1, t_2, t_3) = \xi \Delta t \{ p(t_1) \} (I_{y2,3} + I_{y4,1}) \]
+ \[ \xi \Delta \tau \{ p(t_1) \} (I_{y2,3} - I_{y4,1}) \]
+ \[ \xi \Delta t \{ p(t_1) \} (I_{y1,4} - I_{y2,3}) \]
+ \[ \xi \Delta \tau \{ p(t_1) \} (I_{y1,4} + I_{y2,3}) \]
+ \[ \{ \xi \Delta \cos 2\omega_{Qt_2} - \xi \Delta \sin 2\omega_{Qt_2} \} \{ p(t_1) \} (I_{x3,4} + I_{x1,2}) \]
+ \[ \{ \xi \Delta \cos 2\omega_{Qt_2} + \xi \Delta \sin 2\omega_{Qt_2} \} \{ p(t_1) \} (I_{x3,4} - I_{x1,2}) \]
+ \[ \{ \xi \Delta \cos 2\omega_{Qt_2} - \xi \Delta \sin 2\omega_{Qt_2} \} \{ p(t_1) \} (I_{x3,4} + I_{x1,2}) \]
+ \[ \{ \xi \Delta \cos 2\omega_{Qt_2} + \xi \Delta \sin 2\omega_{Qt_2} \} \{ p(t_1) \} (I_{x3,4} - I_{x1,2}) \]

Central line intensity in echo experiment

\[ \theta_{13} = \sqrt{(2\omega_0 - \omega_{rf})^2 + 3\omega_{rf}^2} \]
\[ \theta_{24} = \sqrt{(2\omega_0 + \omega_{rf})^2 + 3\omega_{rf}^2} \]
\[ \omega_{12} = -\omega_{rf} + \omega_{rf} - \omega_{13}/2, \] \[ \omega_{23} = -\omega_{rf} + \omega_{rf} + \omega_{13}/2 \]
\[ \omega_{34} = -\omega_{rf} - \omega_{rf} + \omega_{13}/2, \] \[ \omega_{14} = -\omega_{rf} - \omega_{rf} - \omega_{13}/2 \]

C_{14} = \cos \theta_{14} + 2\cos \theta_{23} \]
\[ C_{23} = \cos \theta_{23} + 2\cos \theta_{14} \]
\[ S_{12} = \sin \theta_{12}, \quad S_{34} = \sin \theta_{34} + 2\sin \theta_{12} \]

Appendix

We report here the analytical expressions derived for the line intensity based on the theoretical response of a spin-3/2 system to each of the three pulse experiments performed:

(a) Central line intensity in nutation experiment

(b) Central line intensity in two x pulses of the same phase experiment

(c) Central line intensity in echo experiment

with the following parameters:

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References

- $S_{12}\cos\theta_1 \cos\omega_{23} t_3 - S_{34}\cos\theta_1 \cos\omega_{34} t_4$,

$4\text{Tr}[\rho(t_1)I_y^{1,2}] = C_{23}\sin\theta_1 \sin\omega_{23} t_3 - C_{14}\sin\theta_1 \sin\omega_{14} t_4$
- $- S_{12}\cos\theta_1 \sin\omega_{12} t_2 + S_{34}\cos\theta_1 \sin\omega_{34} t_4$,

$4\text{Tr}[\rho(t_1)I_y^{1,3}] = C_{23}\sin\theta_1 \sin\omega_{23} t_3 + C_{14}\sin\theta_1 \sin\omega_{14} t_4$
- $- S_{12}\cos\theta_1 \sin\omega_{12} t_2 - S_{34}\cos\theta_1 \sin\omega_{34} t_4$,

$4\text{Tr}[\rho(t_1)I_y^{1,3}] = - C_{23}\sin\theta_1 \cos\omega_{23} t_3 + C_{14}\sin\theta_1 \cos\omega_{14} t_4$
+ $S_{12}\cos\theta_1 \cos\omega_{12} t_2 - S_{34}\cos\theta_1 \cos\omega_{34} t_4$,

$- \text{cos}\theta_1 (S_m \sin\omega_{34} t_3 - S_p \sin\omega_{12} t_3)$,

$2\xi \Delta d = \cos\theta_1 (C_p \cos\omega_{23} t_3 + C_m \cos\omega_{14} t_4)$
+ $\sin\theta_1 (S_m \cos\omega_{34} t_3 + S_p \cos\omega_{12} t_3)$,

$2\xi \Delta e = \cos\theta_1 (C_p \cos\omega_{23} t_3 - C_m \cos\omega_{14} t_4)$
- $\sin\theta_1 (S_m \cos\omega_{34} t_3 - S_p \cos\omega_{12} t_3)$,

$2\xi \Delta f = \sin\theta_1 (C_p \cos\omega_{23} t_3 + C_m \cos\omega_{14} t_4)$
- $\cos\theta_1 (S_m \cos\omega_{34} t_3 + S_p \cos\omega_{12} t_3)$,

$2\xi \Delta g = \sin\theta_1 (C_p \cos\omega_{23} t_3 - C_m \cos\omega_{14} t_4)$
+ $\cos\theta_1 (S_m \cos\omega_{34} t_3 - S_p \cos\omega_{12} t_3)$,

$2\Delta (e_2 + d_2) = (\sin2\theta_1)^2 \cos\omega_{13} t_3 + (\sin2\theta_2)^2 \cos\omega_{24} t_3$
+ $(\cos2\theta_1)^2 + (\cos2\theta_2)^2 + 2$,

The acquisition delays $\tau_2$ and $\tau_4$ in the nutation and the two-pulse experiments, respectively, do not appear explicitly in the expressions of the central line intensity because the spin-spin relaxation was not taken into account.