STUDY OF A STRUCTURAL PHASE TRANSITION BY TWO DIMENSIONAL FOURIER TRANSFORM NMR METHOD

A. Trokiner, P.P. Man, H. Théveneau and P. Papon

Laboratoire de Dispositifs Infrarouge et Physique Thermique, UA CNRS 836, E.S.P.C.I., 10, rue Vauquelin 75231 Paris Cedex 05
France

(Received: May 22, 1985, by M. BALANSKI)

The fluoroperovskite RbCaF₃ undergoes a structural phase transition at 195.5 K, from a cubic phase where the $^{87}$Rb nuclei have no quadrupolar interaction ($Q = 0$) to a tetragonal phase where $Q 
eq 0$. The transition is weakly first-order. A two-dimensional FT NMR experiment has been performed on $^{87}$Rb ($I = 3/2$) in a single crystal in both phases and in the vicinity of the phase transition. Our results show the coexistence of the two phases at the phase transition.

Introduction

The study of magnetic resonance of nuclei with spin $I > 1/2$, possessing a quadrupolar electric moment, has revealed its power to investigate phase transitions, especially purely structural or ferroelectric phase transitions, because of its sensitivity to any change in the neighbouring electric field gradient (e.f.g.). For instance, in the case of the fluoroperovskite RbCaF₃, the resonance of rubidium nuclei $^{87}$Rb, with spin $I = 3/2$, was used to describe the cubic to tetragonal phase transition.

We present a two dimensional NMR experiment realized near the cubic to tetragonal phase transition of RbCaF₃ on the $^{87}$Rb nucleus and based on variation of the length of the excitation RF pulse.

Phase transitions in RbCaF₃

This perovskite undergoes an antiferrodistorsive phase transition from cubic ($O_h$) to tetragonal ($O_{h1}$) symmetry. The transition temperature $T_c$ of our crystal is 195.5 K. It has been determined by measuring the $^{87}$Rb spin-lattice relaxation time $T_1$, the transition being characterized by a decrease of $T_1$ with temperature when approaching the transition. (These results will be presented elsewhere). The phase transition is due to the softening of the zone-corner $A_25$ mode, whose eigenvectors correspond to the staggered rotations of the CaF₆ octahedra around the cubic axes $4$. This leads to a static e.f.g. arising at the resonant nucleus, $^{87}$Rb, below $T_c$. The weakly first-order character of the phase transition has been established by other techniques such as specific heat measurements $5$, X-ray $6$ and EPR $7$ measurements which show up a discontinuity of parameters related to the order-parameter of the phase transition. Pretransitional effects above $T_c$ have been reported $2$ and attributed to the existence of precursor tetragonal domains.

2-D FT NMR method

In a system of half integer spins, with quadrupolar splitting, the energy levels are not equidistant, and one must use selective excitation pulse to observe, for instance, the central transition ($+1/2 \rightarrow +1/2$). In the framework of fictitious spin $1/2$ formalism $8,9,10$, it is shown that the intensity of the NMR signal depends both on the pulse length and on the ratio $\omega_0/\omega_q$ where $\omega_0 = \gamma H_0$, $\omega_q$ is the radio frequency field amplitude, $\gamma$ is the gyromagnetic ratio of the nucleus; $\omega_0 = \frac{3e^2Q}{\hbar 2I(2I-1)}$ is the quadrupolar coupling constant where $Q$ is the e.f.g. in the case of a $3/2$ spin system submitted to a strong static magnetic field, the Hamiltonian in a coordinate frame rotating with an angular frequency $\omega$ about its $z$ axis, is:

$$H = \hbar (\omega_0 - \omega) I_z - \hbar \omega_1 I_x + \hbar \omega_0 I_y + \hbar \omega_0 I_z + H_D$$

(1)

where $H_0$ is the dipolar Hamiltonian, $H_D$ is the second-order quadrupolar interaction term respectively $11$,

$$H_D = \frac{1}{6} \hbar \omega_0^2 [3 I_z^2 - I(I+1)]$$

(2)

For our system, the asymmetry parameter of the e.f.g. is zero, so $\omega_0 = \omega_0(3cos^2 \theta - 1)/2$ is the angle between the laboratory frame and the unique axis of the e.f.g. tensor.

When the quadrupolar interaction is strong we can neglect $H_D$ in eq. 1. If the RF magnetic field is strong enough compared to the linewidth, one can neglect $\omega - \omega_0 I_z$ in eq. 1. During the RF pulse, $H_D$ can be neglected. Irradiating only the central transition ($\omega = \omega_0$), the expression of the Hamiltonian $H$ during the pulse is:

$$H = -\hbar \omega_1 I_x + H_0$$

(3)
Just after a RF pulse of length $\tau$ the density matrix $\rho(\tau)$ is given by:

$$\rho(\tau) = \exp\left(-\frac{i\tau}{\hbar}\right) \mathbf{I} \exp\left(-\frac{i\tau}{\hbar}\right)$$

After the pulse, the Hamiltonian implied in the decay of the free induction decay (FID) is:

$$H_0 = H_Q + H_Q$$

So, the time dependence of the FID, $S_2(t)$, can be expressed, in the coordinate system rotating with $\omega$, as:

$$S_2(t) = \frac{1}{2} \text{Tr} \left\{ \exp\left(-\frac{i\tau}{\hbar}\right) \rho(\tau) \exp\left(-\frac{i\tau}{\hbar}\right) \mathbf{I} \right\}$$

($\mathbf{Z}$ is a normalization constant).

It can be shown that in the case of strong RF pulses (non selective excitation), where $\omega_1 >> \omega_Q$, the NMR signal is maximum at $\omega = \pi/2$. In the case of selective excitation where only the central line, in resonance, is excited, $\omega_1 << \omega_Q$ and the NMR signal intensity is maximum for:

$$\omega_{\text{eff}} = (I + 1/2) \omega = \pi/2$$

For $I = 3/2$ the pulse duration which maximizes the signal is divided by 2: in other words the effective RF field is increased by a factor of 2.

In systems where there are coexisting sites with strong and weak quadrupolar interactions, the use of 2-D FT NMR technique may allow one to resolve NMR lines in the $F_2$ dimension (corresponding to the classical frequency shift such as a chemical shift) but it allows also to resolve the signal in the $F_1$ dimension (corresponding to the effective RF field strength). Such a technique has been used to distinguish the $^{23}$Na ($I = 3/2$) signals in a mixture of NaCl ($\omega_0 = 0$) and NaNbO$_2$ ($\omega_0 = 2$), the $^{27}$Al ($I = 5/2$) signals in a powdered sample of beryl, as well as the $^{93}$Nb ($I = 9/2$) signals in a powdered mixture of LiNbO$_3$ and NbO$_2$. We have applied this technique to study a phase transition in a crystal where the quadrupolar interaction strength increases when decreasing the temperature through the transition region.

Experimental results

We have performed our experiments on a single crystal of RbCaF$_3$ oriented with $H_0$//h, at four different temperatures 295 K, 195 K, 193 K and 183 K.

The $^{87}$Rb 2D spectra were recorded with a Bruker CXP 300 NMR spectrometer, equipped with a 7 Tesla superconducting magnet. The 2D spectra were obtained with the following acquisition parameters: resonance frequency 98.2 MHz, recycle time 600 ms, sweep width in the $F_2$ dimension 250 kHz, number of scans per increment of the pulse duration 500, number of data points 512. The length of the RF pulse was incremented in steps of 2.5 µs up to 125 µs and the strength of the RF pulse was $\omega/2\pi = 58.6$ kHz. For the spectra obtained at 183 K, the RF pulse was incremented in steps of 2.5 µs up to 65 µs. The FID's were Fourier transformed in the magnitude mode. A sinebell digital filter and zero filling were used in the $F_1$ dimension. Temperature regulation was obtained with a Bruker cryostat with evaporated nitrogen flow. Temperature calibration was better than ± 0.7 K and stability at the sample about ± 0.1 K. As we used a solenoid coil, the crystal was horizontal; this minimized thermal gradient which is mostly vertical. We checked that the thermal gradient from one part to the other part of the crystal was better than 0.2 K. These performances were obtained by waiting one hour at the temperature chosen in order to establish thermal equilibrium before starting the acquisition.

The 2D spectra for different temperatures are represented in Fig. 1 to 4.

At 295 K (Fig. 1) the symmetry is cubic. One peak arises at $\omega_1 = 58.6$ kHz in the $F_1$ dimension; this corresponds to $\tau = 4.2$ µs for the $\pi/2$ pulse duration.

At 195 K, near the transition temperature, two peaks arise, one at 58.6 kHz and the other at 107 kHz in the $F_1$ dimension. The last one...
corresponds to strong quadrupolar coupling (or selective excitation) which is compatible with the occurrence of a tetragonal phase.

At 193 K, the two peaks at 58.6 and 107 kHz still exist but their relative amplitudes have changed. It seems that the peak corresponding to the selective excitation increases compared to the peak at $\omega$. At 183 K, the intense peak is located near 117 kHz, but a small one remains at $\omega_2$ indicating the presence of few cubic domains in the tetragonal phase.

For the orientation of our sample, two tetragonal ferroelastic domains may appear in the tetragonal ferroelastic phase. Because of the high value of the static field, the second order quadrupolar shift is negligible (estimated to 2 kHz at 183 K) compared to the width of the line (equal to 6 kHz). So the two central lines, which correspond to the two domains, overlap, in the temperature range investigated.

That is why no shift in the $F_2$ dimension arises on our spectra.

The peak arising at 58.6 kHz exists at all the four temperatures investigated; it is assigned to the cubic phase. The other signal, located near 117 kHz, exists only at 195 K, 193 K and 183 K; it is assigned to spins with strong quadrupolar interactions. This signal is due to the tetragonal phase. The wings which appear near the phase transition are not yet well understood and their interpretation is on progress.

We think that this 2-D FT NMR method, applied here for the first time to phase transitions, is generally useful for the direct observation of the coexistence of different phases.

Acknowledgement

We wish to thank Professor J.S. Waugh for reading the manuscript and making useful suggestions, and Dr J.Y. Gesland (Université du Mans) for providing us with the RbCaF$_3$ crystal.

REFERENCES