# Time Resolved Studies on a Millisecond Time Scale: Transient Properties of the Ferroelectric Phase Transition in $Rb_2ZnCl_4$

U.Steigenberger[1], G.Eckold [2,3] and M.Hagen[1,4]

[1]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OXON OX11 0QX, UK

[2]Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

[3]Institut für Kristallographie, RWTH Aachen, 52056 Aachen, Germany

[4]Department of Physics, Keele University, Keele, UK

## Abstract

Using time resolved neutron scattering, the evolution of the phase transition between the paraelectric incommensurate (IC) phase and the ferroelectric commensurate (C) phase in $Rb_2ZnCl_4$ has been observed on a microscopic scale. The transformation was driven by a strong rapidly cycling electric field of 8kV/cm applied along the ferroelectric a-axis of the crystal. The response of the sample was monitored by measuring satellite reflections corresponding to the IC- and the C-phase respectively. Synchronization of the electric field to the time structure of the ISIS pulsed neutron source allowed us to observe field induced structural changes on a time scale of **milliseconds**. Characteristic relaxation times were found to depend strongly on temperature.

## 1 Introduction

Studying the evolution of a phase transition as a function of real time provides unique information on possible driving mechanisms. Different intermediate non-equilibrium phases can be passed through and knowledge of these may shed light on the questions **why** and **how** a particular final state is reached. An area of particular interest are transitions between modulated phases where one of the phases is ferroelectric and can be stimulated by an externally applied electric field.

Neutron scattering is a very powerful tool which provides unique information on the properties of condensed matter on a microscopic scale. The wavelengths of thermal neutrons are of the same order of magnitude as interatomic distances and their energies are comparable to those of the elementary lattice vibrations. The measurement of structures and excitations in crystals under equilibrium conditions has therefore been a mainstay of neutron scattering for many years now. However the inherently more difficult measurement of crystal structures under non-equilibrium (time-varying) conditions is a relatively new avenue of investigation. Recently Eck-

old [1] reported the first measurements of processes with typical relaxation times between one to several hundred seconds, using a triple-axis spectrometer at a reactor neutron source. At a pulsed neutron source it is possible to take advantage of the fact that the neutrons are time stamped, to develop special techniques for time resolved studies on shorter time scales.

In this paper we describe a technique for measuring processes with relaxation time scales of order milliseconds at pulsed neutron sources and present some of the results which we have obtained on the ferroelectric phase transition in $Rb_2ZnCl_4$ using this technique.

In section 2 we briefly outline some of the features of $Rb_2ZnCl_4$ relevant to our measurements and then describe in section 3 our technique for time resolved measurements on the millisecond scale which we have developed at the ISIS pulsed neutron facility using the PRISMA spectrometer.

## 2 The ferroelectric phase transition in $Rb_2ZnCl_4$

$Rb_2ZnCl_4$ undergoes two phase transitions [2, 3]. In the normal, high temperature, phase the crystal symmetry is orthorhombic with space group Pmcn. Below 303K the crystal enters an intermediate phase which is characterised by an incommensurate modulation wavevector $q_{IC}=(\frac{1}{3}-\delta)c^*$ where $\delta$, the misfit parameter, is a function of temperature. At $T_c(E=0)=193K$, $Rb_2ZnCl_4$ becomes ferroelectric with the spontaneous polarisation along the a-axis and at the same time the modulation wavevector locks into the commensurate value $q_C=\frac{1}{3}c^*$. The crystal structure of the ferroelectric phase remains orthorhombic, but the space group is now $P2_1cn$.

In the vicinity of the transition temperature $T_c$ (for $T>T_c$) the phase transition from the high temperature IC-phase to the low temperature C-phase can also be driven by applying a strong electric field along the a-axis [4], (cf. figure 1). The electric field induced IC-C transition has been experimentally determined to be first order. The IC and C (for $\delta = 0$) phases give rise to fundamental satellite peaks at $(h,0,l\pm(\frac{1}{3}-\delta))$ satellite positions (for l=odd) and also to higher order harmonics. We have chosen for our investigation of $Rb_2ZnCl_4$ to study the $(2,0,1+(\frac{1}{3}-\delta))$ satellite.

The size of the $Rb_2ZnCl_4$ single crystal used was $4.7 \times 8 \times 9mm^3$ and the crystal was of nearly optical quality resulting in a thermal hysteresis of the ferroelectric transition of less than 0.2 K. The sample was mounted with the b*-axis perpendicular to the scattering plane on a boron nitride support inside a closed cycle refrigerator. A thin aluminium container, diameter 40mm, was positioned around the crystal in order to minimize thermal fluctuations. A platinum resistor was mounted very close to the sample to measure the temperature which was controlled to better than 0.1° and measured to 0.01° with a high sensitivity digital voltmeter. The two opposite a-faces of the crystal were coated with silver paint in order to act as electrodes and a high voltage generator was used to produce an electric field of up to 8kV/cm along

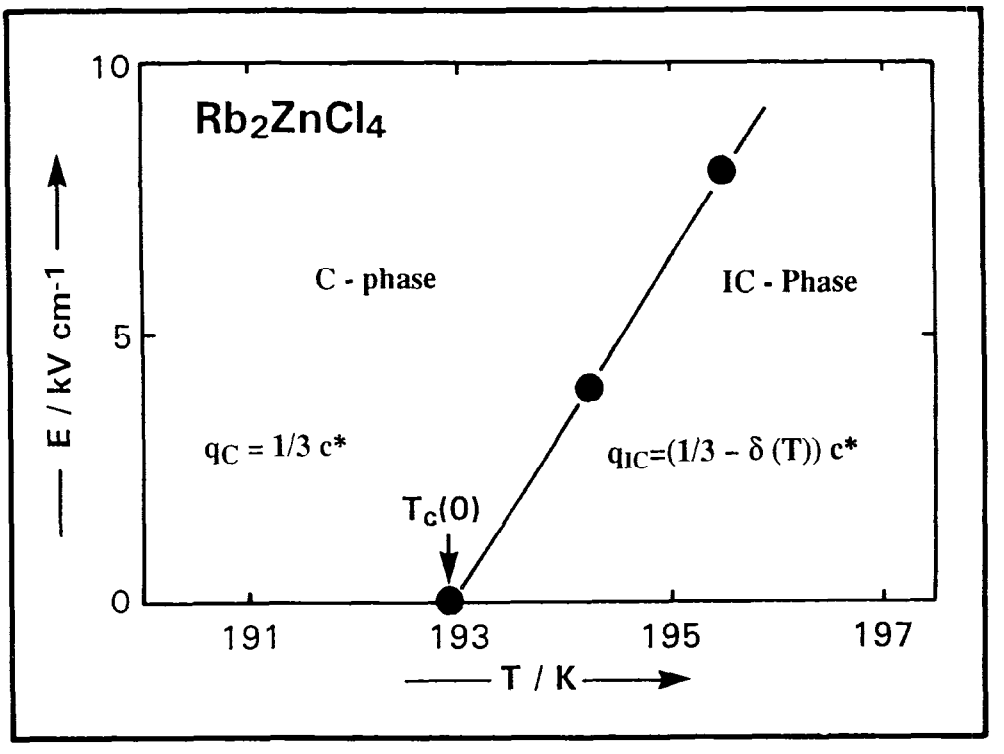


Figure 1: The phase diagram of $Rb_2ZnCl_4$ in the presence of an electric field along the ferroelectric a-axis. The regions of the commensurate C-phase and the incommensurate IC-phase are marked.

the ferroelectric a-axis. This field could be applied either statically or cycled at various frequencies up to 25Hz.

## 3 Time resolved measuring technique

The type of approach to a real time neutron scattering experiment at a pulsed neutron source depends upon whether the relaxation time ( $t_S$ ) of the sample is comparable or not to the frame length ( $\tau$ ) of the source.

Relaxation processes where $t_S$ is of the order of $\tau$ can be studied if the process is reversible and can be triggered by an external perturbation. Instruments at pulsed neutron sources can be used for such measurements by synchronising the external trigger to the production of the neutron pulse. If the relaxation process is contained within one frame, then the real time dependence can be scanned by varying a time delay between the production of the neutron pulse and triggering the external field. If the relaxation process is longer than one frame, of order a few frames, then it is possible to "daisy-chain" frames together to perform a measurement. We have developed this technique at ISIS as described below.

The time resolved neutron scattering measurements reported here were performed at the ISIS spallation neutron source at the SERC Rutherford Appleton Laboratory, U.K., using the PRISMA spectrometer. At a spallation source, sharp pulses of

neutrons are produced with a high peak intensity, separated by a time which is given by the frequency of the proton accelerator. At ISIS this frequency is 50Hz and hence the separation time between two pulses, $\tau$, is 20 milliseconds. This time structure of the neutron source means that the energies of the elastically scattered neutrons can be determined from the time-of-flight they take to travel a distance L from the moderator to the detector. For a single crystal aligned with a scattering plane (h,k,l) in a ($\Theta$,2$\Theta$) configuration with respect to the detector, the corresponding Bragg peaks will be measured at times

$$t_{B,hkl} = \frac{d_{hkl} \cdot m_N \cdot L \cdot sin\Theta}{\pi \cdot \hbar}$$

where 2$\Theta$ is the scattering angle, $m_N$ is the mass of the neutron and $d_{hkl}$ is the d-spacing between the (h,k,l) planes. By rotating the crystal in small steps the rocking curve can be measured.

In a standard pulsed neutron diffraction experiment the scattered neutrons are recorded within the entire time frame of 20 ms and stored in channels of 1 $\mu$s width in the memory of the data acquisition electronics. Subsequent frames are added together until sufficient counting statistics are achieved. For the time resolved measurements an electronic system was installed between the master pulse input and the data acquisition electronics which allowed us to create "superframes" consisting of n standard ISIS frames (the superframe being 20·n ms long), with n=2,4,6,8,10 etc. The electronic system did this by preventing the data acquisition electronics from being reset to t=0 for the subsequent n-1 frames after the first pulse.

The first ISIS master pulse is used to trigger the electric field which is switched on at $t_{on}$ for a length of time $t_{E,on} = \frac{1}{2} \cdot n \cdot 20$ ms ( ie. $\frac{1}{2}$ of the length of the superframe) and then switched off at $t_{off}$. In the first subframe the Bragg peak is measured at a time $t_B$ after the field has been switched on, in the second subframe the Bragg peak is recorded at a time $t_B + 20$ ms and so on.

The starting time $t_{on}$ can be electronically delayed with respect to the ISIS pulse in units of 1 millisecond, thus allowing a coarse tuning of the measurement of the relaxation times. The delay can also be varied by changing the scattering angle 2$\Theta$, shifting the diffraction pattern to a different time which allows for a finer tuning. For example a change in scattering angle by 2° produces a shift in $t_B$ of $\approx$ 0.12 ms at a scattering angle of 2$\Theta \approx 90°$ and a wavelength of 2.83 Å.

The rise time of the electric field was determined to be about 2ms. The time $t_B$ was corrected for the time the neutrons took to travel from the sample to the detector, using the relation $t'_B = t_B L_i/(L_i + L_f)$ where $L_i$ is the moderator to sample distance of 9.03m and $L_f$ is the sample to detector distance of 0.76m. We used different cycling frequencies of the electric field, ranging from 5Hz to 25Hz, resulting in superframes of different lengths, from 200ms to 40ms respectively.

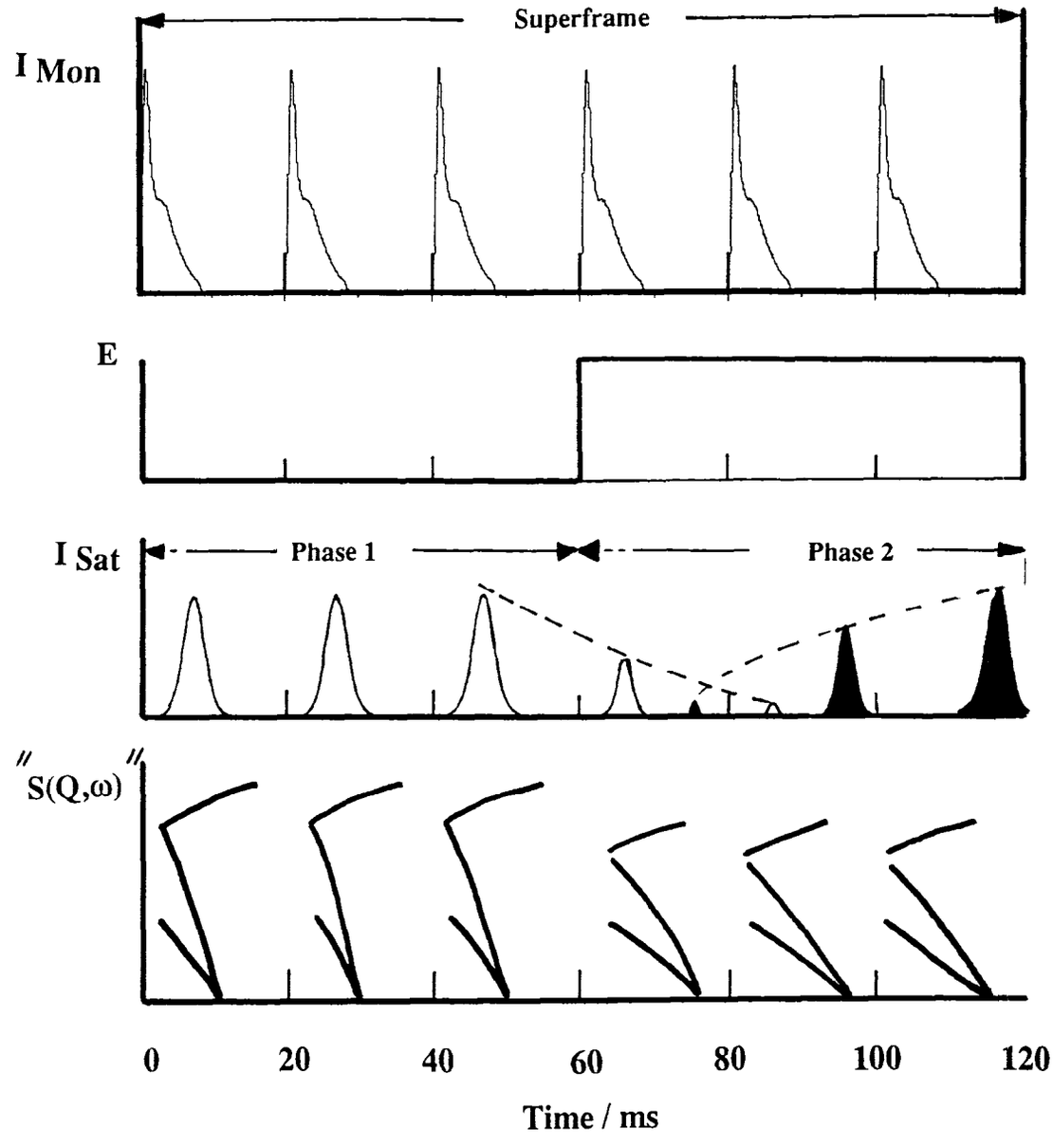


Figure 2: Schematic representation of the measuring technique illustrated for a superframe consisting of six standard frames. In the first line the six individual monitor spectra of the superframe are plotted. The next line shows the variation with time of the electric field. In line 3 the intensity of the satellite peaks is indicated schematically. When the electric field is switched on, the satellites of phase 1 gradually disappear and the satellites of phase 2 (black peaks) appear at a *different* time and their intensity increases as a function of time in the subframes 4 to 6. The last line indicates schematically how the kinetics of phonons can be measured using an inverted geometry PRISMA-type spectrometer at a pulsed neutron source.

Figure 2 shows schematically the variation with time of the various signals: 2a) the incident monitor spectra for 6 ISIS pulses which constitute a superframe in this example, 2b) the time dependence of the electric field, and 2c) the variation in time of the intensity of two sets of Bragg peaks characteristic for two different phases of the system.

Although the primary role for the PRISMA spectrometer at ISIS is to measure excitations in single crystals [5], the presence of horizontal and vertical Soller collimation makes it well suited for single crystal diffraction studies with good Q-resolution. In this diffraction mode the instrument is used without the analyser crystals in place. On PRISMA the moderator to detector distance is 9.79m and therefore at a scattering angle of 20° the commensurate $(2,0,1+\frac{1}{3})$ peak in $Rb_2ZnCl_4$ appears at 2766 $\mu$s and the $(2,0,1+(\frac{1}{3}-\delta))$ satellite peak at 2781 $\mu$s. The angular separation of the two peaks is 0.25° and their rocking curve widths are each 0.24°, which is essentially determined by the instrumental collimation.

## 4 Experimental results

A detailed description of the experimental results will be published elsewhere. Here we present some selected data to illustrate the measuring technique and the wealth of information that the results can provide.

Figure 4 shows the rocking curve of the $(2,0,1+(\frac{1}{3}$ - $\delta)$ satellite at three different times after the electric field has been switched on. The sample temperature was $T=T_c(E=0)$-0.3K, i.e. 0.3K below the phase transition temperature in zero electric field. At t=0 the incommensurate phase is fully developed, 0.2ms after the field has been switched on, a significant part of the crystal has already transformed into the commensurate phase and another 0.5ms later no trace is left of the incommensurate phase. After the electric field has been switched off, the back transformation takes place and hence at the beginning of the next cycle the sample is again in the well defined incommensurate state. For these measurements the electric field was cycled at 25 Hz. We found that on cooling through $T_c$ in an electric field cycled at 25Hz the incommensurate phase is preserved in a small temperature range even below $T_c(E=0)$ and it is therefore still possible to switch between the two phases. A detailed discussion of this unexpected behaviour will be given elsewhere.

Figure 4 summarizes our results for two different temperatures $T=T_c(0)+1.3K$ and $T=T_c(0)+1.1K$. Here we have plotted the relative volume fraction of the commensurate phase (the integrated intensity of the IC satellite divided by the sum of the total intensities of the IC and the C satellites) as a function of time. The time dependence of the electric field is also plotted for the cycling frequency of 6.25Hz which we used for these measurements. The relaxation time into the incommensurate phase increases with decreasing temperature suggesting a slowing down behaviour. On the other hand, there appears to be almost no change of the time constant for the transition into the commensurate phase. Here the volume fraction of the C-phase

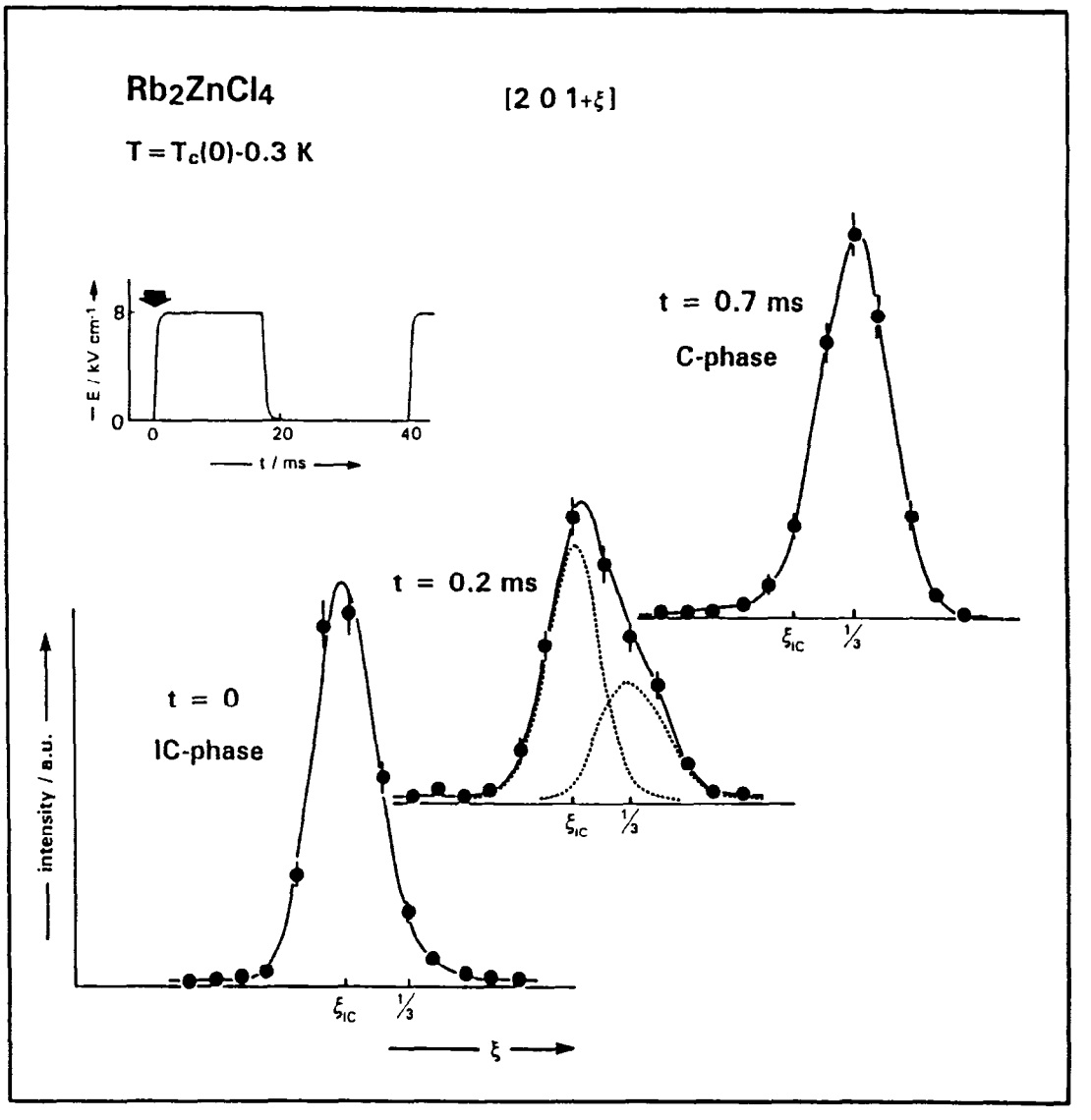


Figure 3: At T=$T_c$(E=0)-0.3K $Rb_2ZnCl_4$ is in the incommensurate phase and the satellite reflection is centred at $\xi=\xi_{IC}$. When the electric field is applied the intensity of the commensurate satellite builds up at $\xi=\frac{1}{3}$ as a function of time. For these measurements the electric field was cycled at 25Hz.

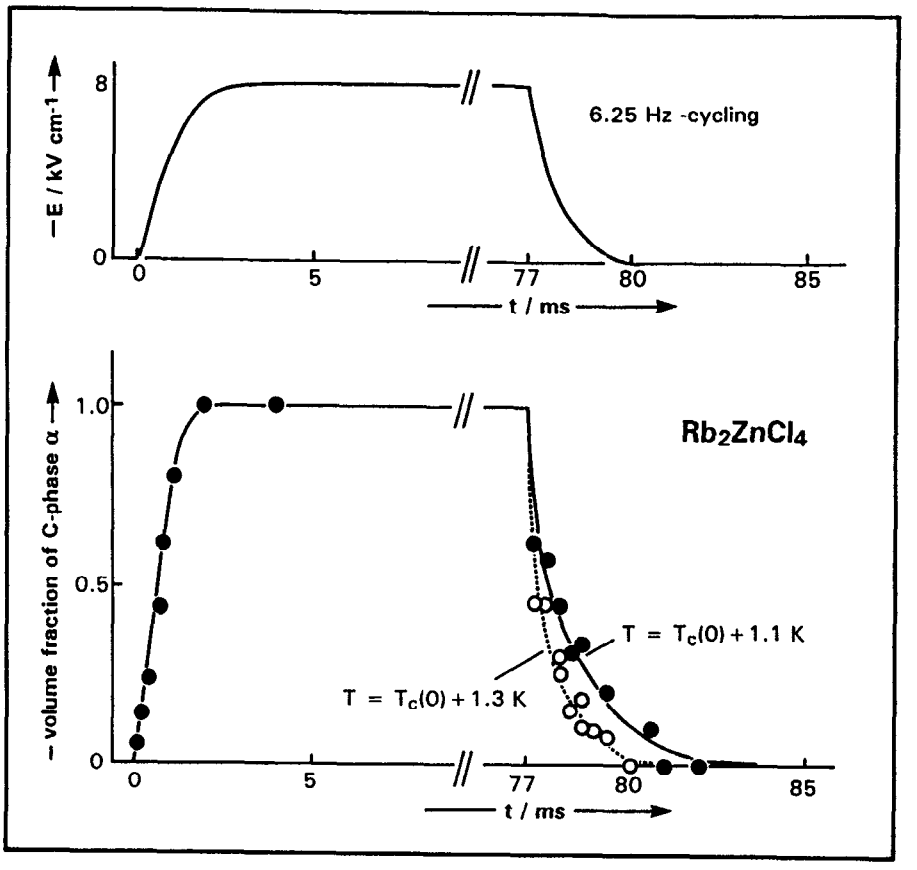


Figure 4: The volume fraction of the commensurate phase is plotted as a function of time for two different temperatures above $T_c(E = 0)$. Here the electric field was cycled at 6.25Hz.

develops with the rise time of the electric field. Within the resolution of the present experiment there are no indications for the existence of intermediate states.

## 5 Conclusion and Outlook

We have developed a technique which allows us to exploit the characteristics of a pulsed neutron source for time resolved measurements on a millisecond time scale. We have demonstrated this technique in an investigation of the ferroelectric phase transition in $Rb_2ZnCl_4$. We found that the IC-C phase transformation occurs spontaneously, whereas the reverse transformation from the C to the IC phase is clearly delayed. The relaxation times vary significantly with temperature and increase when $T_c$(E=0) is approached.

These experiments were performed using the PRISMA spectrometer as a single crystal diffractometer. However, PRISMA is designed for *inelastic* measurements in single crystals and its capability to measure in one instrumental setting a whole phonon dispersion curve will be exploited in future experiments to investigate the *kinetic behaviour of the dynamic properties* of a system in conjunction with a phase transition (see also figure 2, last line). Each subframe will record the phonon dispersion curve at a particular time during a phase transition and these measurements will provide new insight into the real time behaviour. At present pulsed sources such experiments are time consuming, since the creation of superframes does not

only yield time dependent information but also proportionately increases the total counting time of a measurement (eg. for a superframe 160ms long the counting time is increased by a factor of 8). The advent of new, more powerful spallation sources, such as the planned ESS, will make these time resolved inelastic experiments more manageable and it is therefore timely to develop these techniques.

## 6 Acknowledgements

We would like to thank Professor H.G.Unruh for providing us with the $Rb_2ZnCl_4$ crystal and H. Mitlacher, K. Gascoyne, J. Norris and K. Knowles for technical assistance with the experiment.

## References

[1] G.Eckold, Nuc.Inst. and Meth., **A289**, p221, 1990 ; G.Eckold Jül-2675, Jülich 1992

[2] S Sawada et al., J.Phys.Soc.Jpn. **43**, p2099, 1977

[3] K.Gesi et al., J.Phys.Soc.Jpn. **46**, p697, 1979

[4] K.Deguchi et al., J.Phys.Soc.Jpn. **56**, p208, 1987

[5] U.Steigenberger et al., Nuc.Inst. and Meth., **B53**, p87, 1991