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## Kinetics of the lock-in phase transition in $\text{Rb}_2\text{ZnCl}_4$

A Gibaud†§, S M Shapiro† and J Y Gesland‡

† Brookhaven National Laboratory, Department of Physics, Building 510, Upton, LI, NY 11973, USA

‡ Université du Maine, Faculté des Sciences, URA No 807 CNRS, Avenue Olivier Messiaen, 72017, Le Mans Cédex, France

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**Abstract.** High-resolution x-ray scattering experiments have been performed on single crystals of the incommensurate system  $\text{Rb}_2\text{ZnCl}_4$  with emphasis on the kinetics of the lock-in phase transition. The nearly perfect single crystal (mosaic spread  $\approx 0.6$  min) displayed a large hysteresis of 20 K. As the sample was cooled quickly from the paraelectric phase into the commensurate phase, via the incommensurate phase, the time evolution of the disappearance of the incommensurate peak intensity was monitored. The time becomes longer when the sample is quenched to lower than the lock-in temperature, which is contrary to the expected kinetic behaviour of nucleation and growth. The characteristic time of decay exhibits an Arrhenius-like behaviour with an energetic barrier  $E_b$  to overcome of the order of 0.37 eV. The origin of the energetic barrier is interpreted in terms of an order–disorder process of the  $\text{ZnCl}_4$  tetrahedra network.

### 1. Introduction

Among the materials that undergo the series of commensurate–incommensurate–lock-in phase transitions, the compounds of the  $\text{A}_2\text{BX}_4$  family with ( $\text{A} = \text{Rb}, \text{K}, \dots$ ;  $\text{B} = \text{Zn}, \text{Se}, \dots$ ;  $\text{X} = \text{Cl}, \text{O}, \text{Br}$ ) are probably the most widely investigated examples [1, 2] (for a recent detailed review of structurally incommensurate crystal phases see [3]). In  $\text{Rb}_2\text{ZnCl}_4$ , the incommensurate phase arises from small rotations of  $\text{ZnCl}_4$  tetrahedra about the  $c$  axis of the high-temperature orthorhombic phase (space group  $Pm\bar{c}n$ ,  $a = 7.2859 \text{ \AA}$ ,  $b = 12.719 \text{ \AA}$ ,  $c = 9.263 \text{ \AA}$  [4]) together with shifts of the  $\text{Rb}^+$  ions along the  $a$  axis [1, 5]. The modulation wave-vector of the order parameter has only one temperature-dependent component  $q(T) = (\frac{1}{3} - \delta(T))c^*$  which develops at  $T_1 = 298 \text{ K}$  along the  $c^*$  axis.

At  $T_1$ ,  $\delta$  is reported to be 0.03; on further cooling it remains nearly constant over a large temperature range and eventually vanishes at  $T_L = 190 \text{ K}$  [6]. At this temperature the crystal suddenly transforms into a ferroelectric phase with a spontaneous polarization developing along the  $a$  axis of the high-temperature phase. The space group becomes  $P2_1cn$  and the wave-vector of the order parameter is locked at the commensurate value  $q_L = \frac{1}{3}c^*$ . The lock-in transition is first order and usually exhibits some hysteresis, which has been reported to be sample dependent and therefore attributed to defects [7].

§ Permanent address: Université du Maine, Faculté des Sciences, URA 807 CNRS, Avenue Olivier Messiaen, 72017 Le Mans Cédex, France.

Although this material has been extensively studied, very little is known about the kinetics of the first-order lock-in phase transition. In this paper, we report high-resolution x-ray scattering experiments performed on single crystals of  $\text{Rb}_2\text{ZnCl}_4$  with emphasis on the kinetics of the lock-in transition. As the sample was rapidly cooled from the paraelectric phase into the ferroelectric one, via the incommensurate phase, the time evolution of the commensurate and incommensurate peak intensities and their positions were monitored. It is shown that the kinetics is not consistent with the usual behaviour of nucleation and growth at a first-order phase transition and that the very long time required for the crystal to leave the incommensurate state is probably related to order-disorder processes of the  $\text{ZnCl}_4$  tetrahedra.

## 2. Experimental details

A nearly perfect single crystal of  $\text{Rb}_2\text{ZnCl}_4$  (mosaic spread less than  $0.6'$ ) was grown by one of us (JYG) by the Czochralski technique with the growth axis along the [001] direction. A search for contamination by cations such as  $\text{K}^+$  by x-ray fluorescence showed no contamination greater than 0.1%. The crystal was 12 cm long and a few cm wide with a natural trend for cleavage perpendicular to the [010] direction. Let us emphasize that  $\text{Rb}_2\text{ZnCl}_4$  crystals grown by this technique are very massive and may be extremely sensitive to strain release. Indeed, the first crystal that was grown exploded into several pieces during a sawing procedure and the others are extremely fragile and difficult to preserve uncracked when they are manipulated.

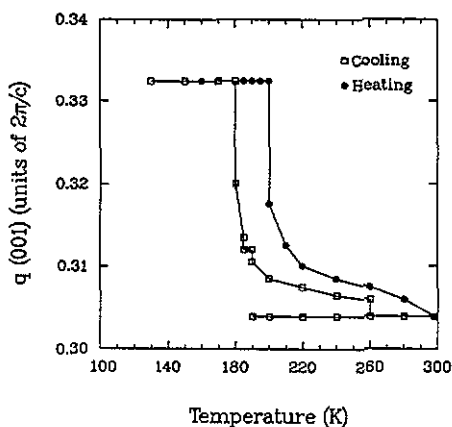
A small piece ( $9 \times 9 \times 2 \text{ mm}^3$ ) of the crystal boule was cleaved for the x-ray scattering experiments and was mounted free of strain by partially wrapping in a metal foil and then gluing the foil to a Cu holder. To ensure a good thermal contact the sample was inserted in a Be can filled with He gas. The can was attached to the cold finger of a closed-cycle cryogenerator. The crystal was mounted in the [100] zone with the [010] direction perpendicular to the crystal face. The system has been extensively studied and the atomic displacements are well known. In the chosen scattering plane, the results are only sensitive to the libration motion of  $\text{ZnCl}_4$  tetrahedra and not to the displacement of  $\text{Rb}^+$  ions since the displacements of these ions are perpendicular to the scattering plane.

$\text{Cu K}\alpha_1$  radiation was produced by a Rigaku rotating-anode generator operating at 8 kW (40 kV, 200 mA). The incident and (sometimes) scattered beams were collimated by reflection of the (111) planes of Si crystals. The experimental resolution thus achieved was typically  $1.5 \times 10^{-3} RLU$  in both directions of the scattering plane.

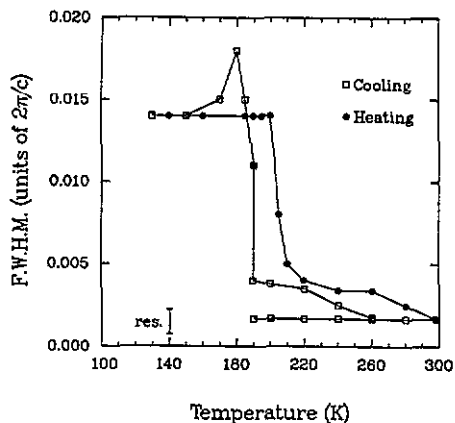
## 3. Results

### 3.1. Temperature dependence of the modulation wavevector

The first part of the experiment was devoted to the measurement of the temperature dependence of the modulation wavevector. Experiments were performed around the  $(0, 8, 2(\frac{1}{2} - \delta))$  reflection which was found to be the most intense accessible incommensurate satellite in this scattering plane. As shown in figure 1, we observe above  $T_L$  a somewhat similar behaviour to that already reported for  $q(T)$ . However, when approaching  $T_L$  from above some marked differences arise:



**Figure 1.** Evolution of the modulation wave-vector on cooling (open squares) and on warming (full circles) showing the pinning effect and the large hysteresis present in this crystal (lines are guides to the eyes).



**Figure 2.** Evolution of the FWHM (in reciprocal lattice units) of the satellite along the  $c^*$  direction on cooling (open squares) and on heating (full circles) (the FWHM of the resolution function is shown in the bottom left corner).

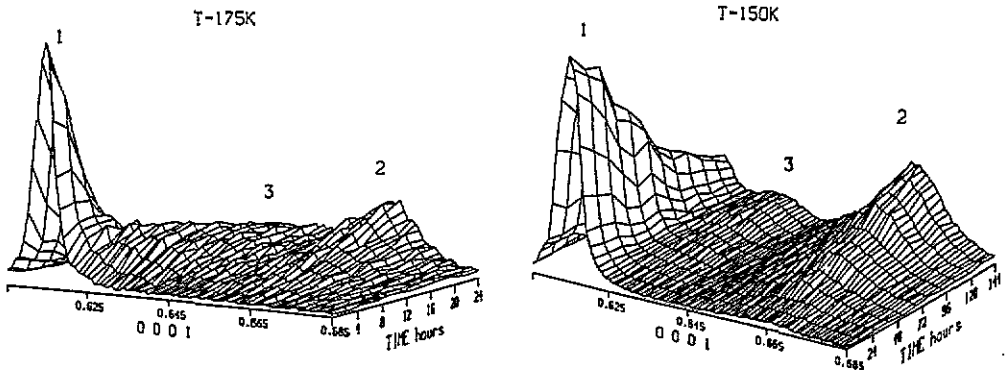
- (i) a pinning of the modulation wave-vector to the initial value together with the appearance of a second satellite, which is broad (see figure 2);
- (ii) a very large hysteresis (nearly 20 K) characterized by  $T_L = 180$  K on cooling and  $T_L = 200$  K on warming;
- (iii) a long time to achieve equilibrium at each temperature close to  $T_L$ , giving rise to steps in the modulation wave-vector.

In addition, it was observed that, below  $T_L$ , the final value  $q = 0.3325 c^*$  of the modulation wave-vector did not correspond to a commensurate value since  $\delta$  remained locked at  $\delta = 0.0008 \pm 0.0005$ . In addition, the FWHM of the satellite was always broader than the resolution.

Similar results have been already encountered for  $\text{Rb}_2\text{ZnCl}_4$  crystals containing substitutional impurities such as  $\text{K}^+$  ions [8], but are rather surprising for a nominally pure sample in which, as already mentioned above, a systematical search for contaminated cations did not reveal anything. However, it must be pointed out that even in nominally pure compounds such effects are sometimes observed, as was seen for  $\text{K}_2\text{ZnCl}_4$  [9]. These are usually attributed to some unknown defects. In this case, a possible explanation might lie in the growth technique; indeed, most of the  $\text{Rb}_2\text{ZnCl}_4$  crystals so far investigated by others were grown by slow evaporation from purified starting materials in solution. Such methods are extremely slow (a few weeks) and are likely to provide crystals that are more free of strain than ones grown by the Czochralski technique. It is possible that Czochralski-grown crystals might contain a higher concentration of intrinsic defects or strains, which would be responsible for the above observations.

### 3.2. Kinetics of the lock-in transformation

The second part of this experiment was devoted to a study of the kinetics of the lock-in transformation. The sample was cooled from  $T = 310$  K at a rate of  $4 \text{ K min}^{-1}$  to various temperatures below  $T_L$ . Once the sample was at the expected temperature, the intensity



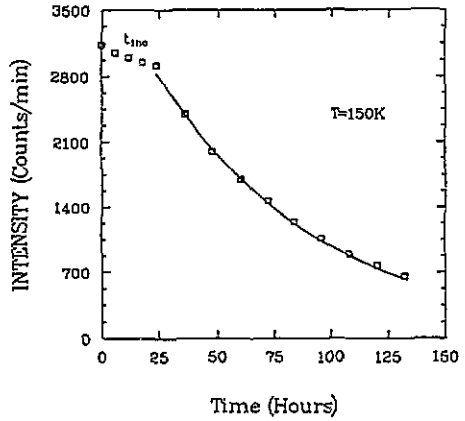
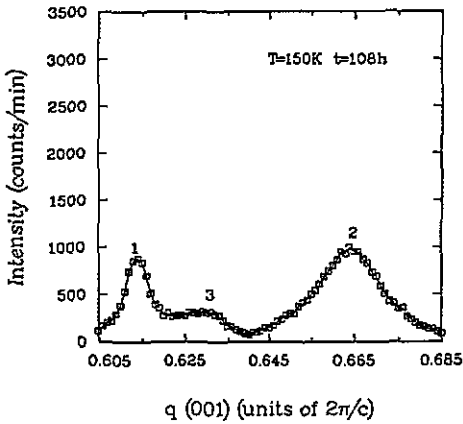
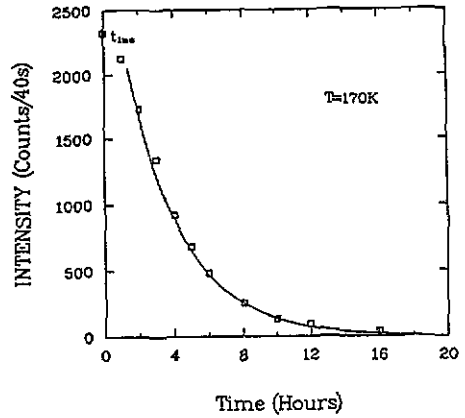
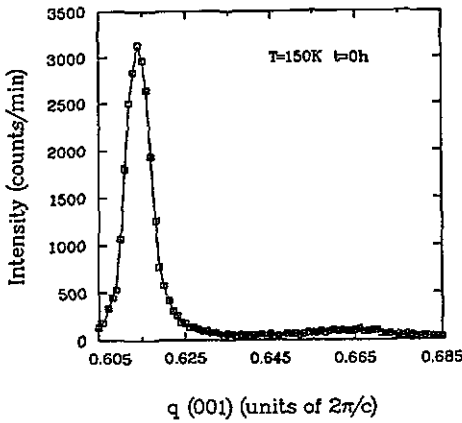
**Figure 3.** Evolution with time and  $q$ -dependence along  $\{001\}$  of the incommensurate satellite intensity (at  $q = 0.614$ ; peak 1) showing the appearance of the nearly commensurate broad peak (at  $q = 0.665$ ; peak 2) and an additional broad peak (at  $q = 0.628$ , peak 3) for quenched temperatures  $T_L - 5\text{ K} = 175\text{ K}$  and  $T_L - 30\text{ K} = 150\text{ K}$ .

and the location of the satellite reflection were measured as functions of time. Figure 3 shows the evolution of the peak intensities at  $T_L - 30\text{ K} = 150\text{ K}$  and  $T_L - 5\text{ K} = 175\text{ K}$ . It is clearly seen that the further the temperature to which the crystal was cooled was from  $T_L$ , the longer it took for the crystal to transform into the ferroelectric phase. Whatever the quenched temperature below  $T_L$ , the satellite (peak 1) was located at a constant starting position  $q = 0.307c^*$  and remained at this position until it completely disappeared. The width along the  $[001]$  direction was also constant (FWHM =  $6 \times 10^{-3}$  RLU which is larger than the resolution of the instrument). Its intensity steadily decreased as a function of time while a very broad peak (peak 2) grew around the expected lock-in position (see figures 3 and 4). This latter peak never reached a commensurate state, and even for the longest time and the lowest temperature remained locked at  $\delta = 0.008 \pm 0.005$ . A third peak (peak 3) was observed with a modulation wave-vector intermediate between the incommensurate and the nearly commensurate ones.

It can be observed from figure 5 that the kinetics of disappearance of peak 1 occurs on two time scales. The early stages of the decay process reveal the presence of an 'incubation' time  $t_{\text{inc}}$  during which the rate of decay is much smaller than observed for later times. For  $t > t_{\text{inc}}$ , the rate of decay is quicker and, since the FWHM of the incommensurate peak (peak 1) is constant during the decay, it is possible to characterize the kinetics by estimating how the peak intensity is decreasing as a function of time. This was successfully achieved by a fitting of the peak intensity at the different quenched temperatures to an exponential form:

$$I(t, T) = I_0 \exp - \frac{(t - t_{\text{inc}})}{\tau(T)}$$

with  $I_0$  being the peak intensity at  $t - t_{\text{inc}} = 0$  and  $\tau(T)$  the characteristic time of decay (see figure 5). The incubation time was adjusted visually at each temperature. Let us point out that a similar exponential decay has been observed in  $\text{K}_2\text{ZnCl}_4$ , although the temperature path to reach the ferroelectric state was different; similarly such a decay was only observed when the commensurate state was coexisting with the incommensurate one.



**Figure 4.**  $q$ -scans showing the presence of a peak (peak 1 at  $q = 0.614$ ) with a constant FWHM (top). The development with time of two broad peaks (peak 2 at  $q = 0.665$  and peak 3 at  $q = 0.628$ ) (bottom).

**Figure 5.** Evolution with time of peak 1 when sample is quenched from  $T = 300$  K to  $T_1 > T = 170$  K (top) and  $T = 150$  K (bottom). The presence of an incubation time is indicated in the figure. The full curve is an exponential fit to the data for  $t > t_{inc}$ .

In order to define how the characteristic time is evolving as a function of  $T$ , we have plotted in figure 6  $\tau$  as a function of the inverse temperature. A very good agreement is obtained when the characteristic time is fitted to the following analytical function:

$$\tau(T) = \tau_0 \exp(E_b/k_B T)$$

with  $\tau_0 = (3.1 \pm 2) \times 10^{-11}$  h and  $E_b = 0.37 \pm 0.020$  eV.

This illustrates conclusively that the characteristic time increases exponentially as  $1/T$  and is clear evidence that the kinetics of the lock-in transformation is governed by an Arrhenius-like energy-activated process in which the energetic barrier to overcome is proportional to a constant height  $E_b$ . In addition, this shows that it is possible to freeze the incommensurate phase if the crystal is quenched at a sufficiently low temperature. Indeed from the above coefficients one can infer that  $\tau$  will be nearly 1900 years at  $T = 105$  K!

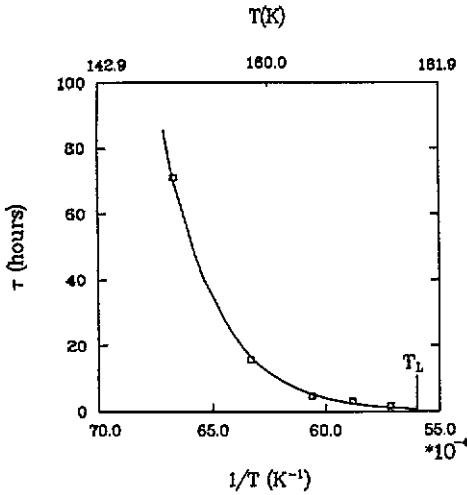


Figure 6. The temperature dependence of the observed decay time  $\tau$  as a function of inverse temperature. The full curve is a fit to an exponential dependence, described in the text. The lock-in temperature  $T_L$  is indicated.

It is also seen in figure 5 that the incubation time is also strongly dependent on  $1/T$ . As is evident in figure 5, this time also becomes longer as  $T$  is decreased. In fact, the incubation time follows a similar law to the characteristic time, such as:

$$t_{\text{inc}}(T) = t_{\text{inc}0} \exp(E'_b/k_B T)$$

with  $t_{\text{inc}0} = (3.1 \pm 2) \times 10^{-11}$  h and  $E'_b = 0.36 \pm 0.04$  eV.

#### 4. Discussion

Except for the coexistence of phases which, at a first-order transition, is commonly the signature of a non-equilibrium process, these results are rather surprising from a thermodynamical point of view. In particular, the temperature dependence of  $\tau$  is contrary to the expected kinetic behaviour of a nucleation and growth encountered in various materials that undergo first-order phase transformations. In these systems, the expected behaviour is that the growth time will be quicker the further the temperature is from  $T_c$ . This is easily seen from free-energy considerations since, far below  $T_c$ , the low-temperature phase is the preferred one and only a slight perturbation will transform it. Very near  $T_c$ , the high- and the low-temperature states can coexist with equal probability and a long relaxation time is expected. This has been evident for several well-known materials undergoing first-order phase transformations, such as the ordering in  $\text{Cu}_3\text{Au}$  [10] and the FCC-BCC transition in Rb [11].

In our case, a marked difference arises from the fact that when the crystal is quenched below  $T_L$  it has first to overcome an energetic barrier to transform from the incommensurate state (high-energy state) to the commensurate one (low-energy state). This leads us to the obvious question of what the origin of the energetic barrier is.

Since, in this scattering plane, the intensity that is measured at the incommensurate position is only related to the libration motion of the  $\text{ZnCl}_4$  tetrahedra, one can infer that the energetic barrier might be related to an order-disorder process of the  $\text{ZnCl}_4$  tetrahedra network which is more and more difficult to establish once  $T_L$  has been reached. Indeed, as shown by Katkanant *et al* [12] in an *ab initio* calculation of the

$Rb_2ZnCl_4$  dynamics, the very reason for observing an incommensurate behaviour lies in the presence in this structure of imperfect and structurally unstable helices of  $ZnCl_4$  tetrahedra. Along the helices, large libration movements involving ångström-size displacements of the  $Cl^-$  ions are possible with little change in energy in the incommensurate phase. A similar statement was made by Quilichini and Pannetier [5] in their neutron scattering study of the different phases of  $Rb_2ZnCl_4$ ; measuring the Debye–Waller factor they have stressed the likely existence of an order–disorder network of  $ZnCl_4$  tetrahedra.

Our work indicates that when the crystal is quenched below  $T_L$ , tetrahedra are frozen in an incommensurate position during the incubation time with a mean modulation wave-vector  $q = 0.307 c^*$  which is very close to the modulation wave-vector observed immediately below  $T_1$  on slow cooling. This state is periodic over a correlation length of 150 Å and slowly evolves towards a commensurate one with an energetic barrier to overcome equal to  $E_b$ . The evolution occurs in two simultaneous steps characterized by the appearance of an intermediate incommensurate state (peak 3) together with the nearly commensurate reflection (peak 2). As is evident from the large FWHM of these two reflections, it is clear that the ordering is spatially limited to regions less than 50 Å wide. Furthermore, the presence of three peaks demonstrates that in order to evolve from an incommensurate phase with  $q_{inc} = 0.307 c^*$  at  $t = 0$  h to a commensurate state at  $t = \infty$ , the system has to go through a disordered regime in which the modulation can take any values between  $q_{inc}$  and  $q_L$ . As in this scattering plane, the diffracted intensity is only related to the chlorine movements, i.e. to the angle of libration of the  $ZnCl_4$  tetrahedra around the  $c$ -axis, one can conclude that, in the intermediate stage, this angle is not spatially well defined, which implies that the  $ZnCl_4$  tetrahedra network is disordered. Let us note that our experiment does not provide any information about the  $Rb^+$ -ion motion; however, the libration motion of the  $ZnCl_4$  tetrahedra is intimately coupled to the translation motion of the  $Rb^+$  ions and there is little doubt that these ions are also involved in the order–disorder process.

In the framework of incommensurate phase transitions, this kinetic behaviour also suggests that domain walls that separate commensurate regions from discommensurations cannot move rapidly once the crystal is quenched below  $T_L$ . The kinetics of the domain walls at the lock-in phase transition is not well documented in the literature. However, following the EM experiments of Fung *et al* [13] in  $2Ha-TaSe_2$ , the formation of domain walls or discommensurations, and its evolution close to  $T_L$ , has been studied in  $Rb_2ZnCl_4$  by several authors [14], [15]). These studies show that the domain wall density goes to zero at  $T_L$  and that above  $T_L$  the incommensurate phase has a stripe structure which collapses along a deperiodization line. In the lock-in phase, walls are a relic of the incommensurate phase. It is clear that the crystal quench, together with the presence of defects in this crystal, has a strong influence on the mobility of the domain walls. However, it is not yet clear whether the real cause for such a slow kinetics is intrinsic or extrinsic. The observation in this crystal of an unusually large hysteresis (20 K) might be a good indication of the presence of some defects or strain, which could slow down the kinetics of the domain walls. It is possible that the presence of defects can raise the energy barrier separating the incommensurate state from the commensurate one. It turns out that the kinetics of the lock-in phase transition certainly deserved further study, especially for single crystals which do not exhibit such a large hysteresis, and that additional theoretical studies of the kinetics are needed to clarify the understanding of these phenomena.



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