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Isothermal relaxation of discommensurations in K_2ZnCl_4

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Résumé. — Au voisinage de la température, T_c , de transition incommensurable-ferroélectrique, la susceptibilité de K_2ZnCl_4 présente une contribution anormale. Des mesures diélectriques quasi-statiques et la courbe d'hystérésis montrent que cette partie anormale provient de la dynamique particulière des discommensurations. En utilisant des mesures diélectriques isothermes nous avons trouvé, en accord avec les résultats obtenus dans Rb_2ZnCl_4 , que le temps caractéristique de relaxation est de l'ordre de 10^4 s dans les 2 phases. Dans une petite gamme de température au voisinage de T_c nous avons observé une relaxation non monotone liée au blocage des discommensurations par des défauts. Pour la première fois nous montrons que le temps caractéristique de cette relaxation particulière augmente à la même température au refroidissement ou au chauffage.

Abstract. — At the incommensurate-ferroelectric transition temperature T_c of K_2ZnCl_4 , the dielectric susceptibility contains an anomalous contribution both above and below T_c . Previous quasi-static dielectric measurements and hysteresis loops demonstrated that this anomalous part arises from the peculiar dynamics of discommensurations. We have used isothermal dielectric measurements to get some insight into the long time dynamics of these discommensurations. We have found that the characteristic relaxation times τ are of the order of 10^4 s in the incommensurate and in the ferroelectric phase. Even more unusual is a non-monotonous relaxation which is observed in a restricted temperature range above and below T_c . In agreement with previous results in Rb_2ZnCl_4 , this is ascribed to the pinning of discommensurations by defects. We show, for the first time, that the crossover time of this peculiar relaxation increases drastically at the same temperature under either heating or cooling conditions.

Introduction.

Among the family of A_2BX_4 compounds, K_2ZnCl_4 is the one which displays the most interesting thermodynamical properties. The temperature interval where these effects are seen lies in the vicinity of the lock-in transition temperature T_c which separates the high temperature incommensurate phase from the low temperature ferroelectric phase.

From the beginning, it was shown that the dielectric anomaly at T_c was sensitive to the temperature variation rate [1]. Starting from an as-grown sample Unruh could monitor the

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magnitude and the position of the dielectric anomaly by appropriate temperature cycling and annealing [2]. The minimum thermal hysteresis of 4 K was achieved after a cooling run at 0.007 K/min [2]. At $T_c - 100$ K, room temperature hysteresis cycles are evolving on a time scale of weeks.

It seems that the thermodynamical properties of K_2ZnCl_4 above and below T_c result from a nucleation-growth-rearrangement process of the discommensurations [2].

A clear connection of this slow dynamics with the discommensuration motion was inferred from direct TEM observations [3]. Based on the general model of the dielectric susceptibility in A_2BX_4 compounds [4] a topology of the discommensurations was proposed.

A macroscopic description of this process was given by Hamano *et al.* [5] using radio-frequency dielectric dispersion data. A Debye type relaxation was observed in the ferroelectric (C) and in the incommensurate (IC) phase. This relaxation was ascribed to the domain wall motion in the C phase and to the discommensuration dynamics in the IC phase. In the vicinity of T_c a crossover between these two relaxations was reported, giving a direct insight into the gradual transformation of ferroelectric domain wall into incommensurate discommensuration. The non-monotonous time variation of the relaxation step $\epsilon_1(1 \text{ MHz}) - \epsilon_1(100 \text{ MHz})$ was a signature of this process.

Low frequency dielectric experiments and X-ray diffraction confirmed this behaviour [6, 7]. A clear connection was found between the time evolution of the satellite line intensity and the dielectric maximum.

However, these isothermal experiments were performed only at a few temperatures. It is the aim of the present work to extend the isothermal dielectric experiments in order to get some insight into the gradual transformation of the monotonous relaxation away from T_c to the non-monotonous relaxation in the vicinity of T_c .

Sample preparation and experiments.

The K_2ZnCl_4 crystals used in this study were grown in aqueous solutions of KCl and ZnCl following the standard conditions. The impurity content of these crystals was probed by several chemical analysis. We found 130 p.p.m. at. of sodium and 500 p.p.m. at. of calcium as the major impurities, other elements being below the analysis sensibility (about 1 p.p.m. at.).

Three samples were cut from the same crystal. After polishing, gold electrodes were always evaporated on the faces perpendicular to the b axis which is the ferroelectric axis. To compare our samples with the standard low-defects K_2ZnCl_4 , we performed the same temperature run as Unruh [2]: the sample was first annealed at 450 K for 20 h, then cooled down to 350 K at a rate of 0.006 K/min and then heated again at the same rate. Under these conditions, the dielectric susceptibility that we have recorded follows approximately the results of Mashiyama *et al.* [6], showing that the amount of defects in our samples is comparable to that used in previous studies.

It was then possible to apply our experimental procedure. This procedure was two fold: under heating and under cooling conditions. Under heating conditions, the sample was heated from room temperature up to the operating temperature T_s at a rate of 0.5 K/min. While keeping T_s stable with a precision better than 0.01 K, we recorded the time evolution of ϵ_1 , the real part of the dielectric susceptibility.

Under cooling conditions, starting from room temperature, the sample was heated up to 450 K at a rate of 0.5 K/min and then immediately cooled to the operating temperature T_s with the same rate. The dielectric susceptibility ϵ_1 was recorded at T_s under the same conditions as for heating cycles. We have used a rather high thermal variation rate in order to keep the samples far from equilibrium and to test both the fast and slow isothermal relaxations.

The test signal frequency of the HP4192 bridge was 100 kHz, i.e. much below the frequency range where dispersive effects occur [5]. The signal amplitude was 1 V peak-peak and the overall connection capacitance was lower than 0.02 pF. To avoid possible irreversible ageing of our samples we ensured that the absolute value of ϵ_1 was reproducible at any temperature within 0.1 %. The operating temperatures T_c were set randomly in order to avoid any systematic and unwanted effects of the sample history.

Results.

We first describe our dielectric data under temperature cycling. At all temperatures, the absolute value of ϵ_1 is nearly the same as that reported by Mashiyama *et al.* [6]. When the temperature variation rate is high (0.5 K/min), we find a hysteresis of 24 K (curves A in Figs. 1a and 1b). Using a slow cycle, this thermal hysteresis was reduced to 5 K with a temperature variation rate of 0.006 K/min (curves B in figs. 1a and 1b).

Applying the experimental procedure described above, the starting points of all the isothermal relaxations lie on curves A. In fact, the temperature variation rate of all the temperature cycles preceding the isothermal experiments was 0.5 K/min which is the rate of curves A. At the end of the isothermal experiments, the samples were close to the dielectric curves B. We thus tested the relaxation from curves A to curves B, i.e. from an out-of-equilibrium state to a near-equilibrium state. This leads to the specific features of each temperature range that we have pointed out in figure 1.

Far from the critical regime, in region I, we have detected no isothermal relaxation. In region II, where the fast and slow cooling (heating) curves start diverging, the isothermal relaxation is an increasing function of time (curves II in Figs. 2a and 2b). We have fitted this data using the stretched exponential law proposed by Mashiyama [7]

$$\epsilon_1(t) \approx \epsilon_\infty - \Delta\epsilon \exp\left(-\sqrt{\frac{t}{\tau}}\right) \quad (1)$$

where ϵ_∞ is the near equilibrium susceptibility and τ is the relaxation time.

The same law holds for the decrease which was observed in region IV but with a plus sign preceding the exponential.

The most interesting relaxation that we actually report lies in region III. In fact, in this temperature interval, the isothermal relaxation is a non-monotonous function of time : ϵ_1 first increases, reaches a maximum at a time t_0 and finally slowly decreases for $t > t_0$ (curves III in figs. 2a and 2b). This relaxation is qualitatively sketched in figure 1 for a temperature T_c within region III. Starting from curve A, the dielectric susceptibility first increases, reaches a virtual maximum and then decreases toward the near-equilibrium susceptibility at T_c . As displayed in figure 1, the border of regions III are not well defined. This is because the regions were determined experimentally and the shortest t_0 that we could detect is of the order of 10 s. This limit was set after several tests in order to ensure thermal equilibrium within the sample. A non-monotonous variation of ϵ_1 may be observed outside of regions III for shorter time scales. We recall that the operating temperatures were set randomly. However, the non-monotonous relaxation in region III was systematically reproducible.

In particular, the relaxations are qualitatively similar under either cooling or heating conditions. The fitting of such data is not easy. In Rb_2ZnCl_4 , the monotonous relaxation was fitted using a superposition of 2 stretched exponentials as given in equation (1) [11]. These two relaxations were ascribed to the dynamics of discommensurations and ferroelectric domain walls which both decrease the dielectric susceptibility. Our non-monotonous data cannot be modelled in the same way.

Fig. 1. — Dielectric susceptibility *versus* temperature for K_2ZnCl_4 under cooling (a) and under heating (b). Curves A were recorded under the fast temperature variation rate of 0.5 K/min and curves B under the slow rate of 0.006 K/min. The border lines between the isothermal regimes I-II-III-IV have been determined experimentally. The isothermal behaviour is schematically sketched by the arrows in temperature region III. Hatched areas point out the imprecision of region limits.

This is why the only parameter that we have recorded *versus* temperature is the crossover time t_0 where the susceptibility reaches its maximum. In figure 3, we have plotted this crossover time t_0 as a function of temperature. It clearly increases at T_c under both heating or cooling conditions.

Outside this interval III, the susceptibility relaxes directly from the non-equilibrium to the near-equilibrium susceptibilities (regions IV). In these temperature ranges we fixed $t_0 = 0$.

To summarize our experimental results qualitatively, we point out that the succession of isothermal relaxations I-II-III-IV is the same under either cooling or heating conditions. This was rather unexpected since the isothermal susceptibility relaxation is generally thought to arise from discommensurations kinetics. This kinetics has not to be the same when starting from the ferroelectric phase or from the incommensurate phase. We can ascribe the reversible

Fig. 2. — (a) Isothermal relaxations under cooling conditions. The labels on each curve correspond to the temperature regions of figure 1a. (b) Isothermal relaxations under heating conditions. The labels on each curve correspond to the temperature regions of figure 1b. Note that the starting time of the experiments was taken 10 s after the temperature stabilization of the sample.

behaviour of the isothermal relaxations to our experimental procedure : at the initial stage of the relaxation, the system was in a fully non-equilibrium incommensurate state under either cooling or heating conditions (see regions III in Figs. 1a and 1b).

Discussion.

In the vicinity of T_c , the anomalous dielectric susceptibility $\varepsilon_1(T)$ is usually written as [7]

$$\varepsilon_1(T) = n(T) \exp(6 L \sqrt{v}) \quad (2)$$

where $n(T)$ is the density of discommensurations, L the average distance between the discommensurations and v an interaction term. Starting from the incommensurate phase and

Fig. 3. — Crossover time t_0 versus temperature under cooling conditions (triangles) and under heating conditions (circles). The maximum of t_0 is found to coincide for both sets of data.

cooling the sample, $n(T)$ decreases and L increases. This leads to the divergence of $\varepsilon_1(T)$ at T_c . However, in real crystals, n and L are non-monotonous functions of the temperature: discommensurations may coexist with ferroelectric domain walls just below T_c , the structural defects and the surface of the sample have a pinning effect on the discommensurations.. This has been discussed extensively in the literature for K_2ZnCl_4 [2, 6] and Rb_2ZnCl_4 [8, 9, 10].

Our starting point is that the isothermal relaxations that we have observed follow equation (2). It is the time evolution of n and L which governs the dielectric behaviour.

In a first step, we empirically compare our results with the X-ray data of Mashiyama and Kasatani [6]. In this work, it was shown that the isothermal dielectric relaxation close to T_c was related to the relative evolution of the commensurate $I(2\ 0\ 2/3)$ and incommensurate $I(2\ 0\ 2/3 + \delta)$ peaks. Either on a cooling or on a heating run, the dielectric maximum occurred under two conditions [6]

- (1) incommensurate and commensurate peaks were both detected,
- (2) the commensurate intensity was almost negligible regarding the incommensurate one.

Even if these requirements remain qualitative, we can use them to infer the temperature evolution of t_0 the time where the dielectric maximum occurs. In fact, the relaxation time of the incommensurate line increases at T_c [7]. This means that it takes a longer time for conditions (1) and (2) to be satisfied at T_c . It is thus not surprising that t_0 increases at T_c under either cooling or heating conditions.

We now turn to a description which was given by Hamano *et al.* [9]. These authors used a Landau-type model of a regular lattice of discommensurations to account for the isothermal relaxations in A_2BX_4 compounds. The free energy F_{IC} has two minima: one at 0 for the commensurate phase and one at δ which is the equilibrium misfit parameter at a given temperature. We note that in this model δ is proportional to the number of discommensurations. According to Hamano *et al.* [9], there is some equivalence between field induced and temperature induced isothermal relaxations. This is schematically depicted in figure 4.

We first focus on the C to IC transition (Fig. 4). At the early stage of the isothermal relaxation, the system is suddenly brought from curve I to curve II. During the whole isothermal relaxation on curve II, the number of discommensurations increases, thus

Fig. 4. — Theoretical variation of the free energy *versus* the number of discommensurations following Hamano [9]. Under heating conditions the isothermal relaxation proceeds from curve I to curve II. Under cooling conditions it goes from curve II to I. A' is the border point between a pure lattice of discommensurations and a mixed commensurate-incommensurate phase. A is the absolute minimum of the free energy in the incommensurate phase. Curve III is the critical free energy at T_c where the relaxation is the longest.

increasing the dielectric susceptibility (see Eq. (2)). However, when the density of discommensurations is high, the average distance between them decreases and the exponential factor dominates the prefactor n and the dielectric susceptibility decreases. This defines the observed crossover time t_0 . In agreement with the experiments [6], Hamano *et al.* infer that this crossover occurs at a particular point A' on the free energy curve II. This point is on the border between a mixed C and IC phase (to the left of A') and a pure IC phase (to the right of A'). Experimentally, this point is reached when the C line disappears from the X-ray spectrum. Geometrically, A' is the point where the tangent to the free energy curve meets the origin. Within this model, there is thus an agreement between our data and previous results from [6, 9]. What is new is that we can explain why t_0 is the highest at T_c . In fact, this temperature corresponds to the free energy curve III in figure 4. On this particular curve, A' and A are superposed and the crossover would take an infinite time to occur.

On a cooling run (IC to C transition), we can reverse the above description and find that t_0 is the time when A' is crossed between steps 2 and 3 of the relaxation (Fig. 4, curve I). During step 2, it is the exponential factor of equation (2) which allows for the increase of the dielectric susceptibility while the number of discommensurations is decreasing. Again, the maximum crossover time is found when the free energy curve has two degenerate minima at T_c .

We thus propose that the crossover time t_0 be a relevant parameter for the incommensurate-ferroelectric phase transition in K_2ZnCl_4 . The temperature variation of t_0 is reported in figure 3. Within the overall experimental error ($\Delta T = 0.1$ K), the two heating and cooling curves for t_0 merge at 403.5 K. For temperatures higher than this characteristic temperature under heating conditions, t_0 escapes our time scale (24 h maximum). The same effect occurs on cooling conditions at temperatures lower than 403.5 K. To our knowledge, it is the first time that a physical quantity displays this kind of behaviour in K_2ZnCl_4 . In fact, the other parameters which we calculated from the isothermal data, τ and ϵ_∞ have a hysteresis of more than 5 K.

The common temperature where t_0 has the same value both under cooling or heating conditions could be a very specific feature of K_2ZnCl_4 . Is this the « true » transition temperature? Even if it lies within the thermal hysteresis of the dielectric susceptibility [2], some care is required. In fact, from DC field experiments in Rb_2ZnCl_4 , it was shown that

t_0 is very sensitive to the defect content of the sample [8, 10]. It was possible to decrease t_0 by two orders of magnitude in purified Rb_2ZnCl_4 as compared to standard samples. This was a proof for a pinning of discommensurations by lattice defects, the lower the defect density, the shorter the crossover time t_0 . This pinning effect has obviously to be taken into account in K_2ZnCl_4 . The high value of t_0 that we have observed is the signature of a rather high density of defects. This is consistent with the minimum hysteresis of 5 K in our samples.

However, the pinning has no measurable effect on the temperature variation of t_0 . This variation probes the intrinsic dynamics of the discommensurations while the absolute value of t_0 is sensitive to the interaction of the discommensurations with the defects. To confirm this point, it would be interesting to apply our experimental procedure to high purity K_2ZnCl_4 and Rb_2ZnCl_4 .

To summarize, we have observed a non-monotonous isothermal relaxation of the dielectric susceptibility of K_2ZnCl_4 . This is consistent with the radio frequency dielectric data reported previously [5]. Our data are also consistent with the model proposed by Hamano *et al.* for Rb_2ZnCl_4 [8]. Moreover, we have been able to measure such anomalous relaxations starting either from the incommensurate or from the ferroelectric phases. This was possible because we did not use a DC electric field but a high thermal variation rate as the driving source for a non-equilibrium initial state. We thus confirmed that the competition between ferroelectric domain walls and incommensurate discommensurations leads to an extremum in the susceptibility relaxation. We have shown that the crossover time between both dynamics tends to diverge near T_c .

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