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Electron microscopy study of discommensurations in K_2ZnCl_4

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Abstract. Discommensurations have been studied by transmission electron microscopy in the ferroelectric commensurate phase of K_2ZnCl_4. Characteristic patterns show regularly arranged pairs of discommensurations and vortices where three pairs or six isolated discommensurations terminate. The results point to an attractive interaction between isolated discommensurations and to a repulsive interaction between pairs of discommensurations.

1. Introduction

Although various theoretical and experimental investigations on incommensurate–commensurate (IC–C) transitions in insulators exist (e.g. Blinc and Levanyuk 1986) the real structure of the soliton lattice and its rearrangements on changes of temperature or electromechanical fields is unknown for most systems with IC phases. In particular, this holds true for nucleation and annihilation processes of discommensurations (DCs) in the IC as well as in the C phases. Here we are concerned with A_2BX_4-type crystals showing ferroelectric C phases, in which phase solitons with a shift of the order parameter phase of $2\pi/6$ represent walls between oppositely polarised ferroelectric domains. In the case of Rb_2ZnCl_4 the static patterns of DCs and some information about their kinematic behaviour have been revealed by transmission electron microscopy (TEM) (Bestgen 1986, Tsuda *et al* 1988). In this paper corresponding investigations are applied to K_2ZnCl_4 which undergoes a similar sequence of phase transformations as Rb_2ZnCl_4, that is from a paraelectric (N) phase (space group Pcmn) to an IC phase at $T_I \simeq 553$ K and then to a ferroelectric C phase (space group $Pc2_1n$) at $T_C \simeq 403$ K.

2. Experimental methods

Single crystals of K_2ZnCl_4 were grown from a stoichiometric mixture of aqueous solutions of KCl and $ZnCl_2$ at about 40 °C. Thin crystal plates of about $4 \times 4 \times 0.5$ mm^3 were cut using a wet thread. For dielectric measurements these platelets were provided with evaporated gold electrodes. For electron microscopic investigations the plates were thinned to about 100 nm by ion beam bombardment at an operating voltage of 6 kV and

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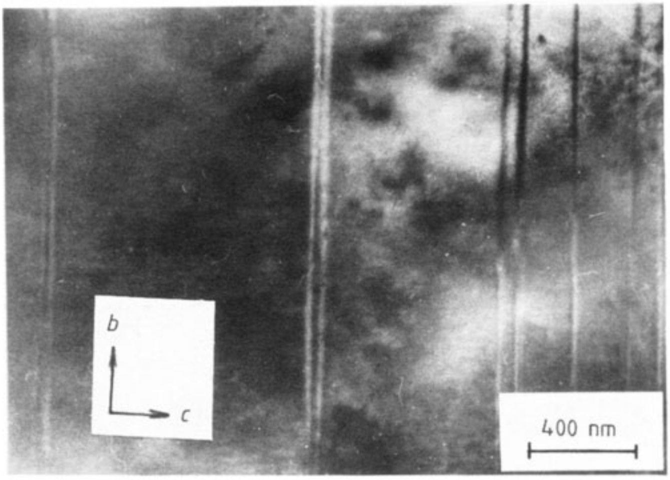

Figure 1. A dark-field image from satellite reflections of K_2ZnCl_4, (100) plane, taken at 205 K. The sample had been prepared on a cold stage at liquid nitrogen temperature during the ion etching process.

an incident angle of about 12°, a process which took about six hours. Observations were achieved with a JEOL-200CX electron microscope at an accelerating voltage of 200 kV, using a side-entry cold stage. To reduce the damage to the crystals by the electron irradiation, beam intensities were reduced to 1 mA cm^{-2} during observations. The ferroelectric hysteresis loops of several crystal plates were recorded on a digital oscilloscope in order to compare samples which had been subjected to different methods of preparation.

3. Results

The electron diffraction pattern of K_2ZnCl_4 in the C phase exhibits the same characteristics as that of Rb_2ZnCl_4 (Bestgen 1986), but the intensities of the satellite reflections at room temperature are much stronger than those of Rb_2ZnCl_4 at the same relative temperature. This is due to the differences of roughly 200 K between the respective C–IC and IC–N transition temperatures. Dark-field images were taken at different temperatures by selecting satellite reflections in TEM during several cycles from ambient temperature down to 110 K on every sample, and were recorded on a video camera connected to the electron microscope. Unfortunately, the damage to the crystal structure was so severe at and above room temperature that no investigations could be performed in the vicinity of the transition points. However, discommensurations, which were recognised as similar to those in Rb_2ZnCl_4 (Bestgen 1986, Tsuda *et al* 1988), have been observed in all plates at lower temperatures.

Two different groups of samples were studied in our experiments. One group was prepared on a cold stage which was at liquid nitrogen temperature during the ion thinning process, another one was prepared on a stage at room temperature. The difference between the two groups is as follows: the density of DCs in the former case is low, only a few DCs, which might be induced during the thinning process, exist in the area of observation at the thin edge of the specimen (figure 1). The thicker parts of these samples

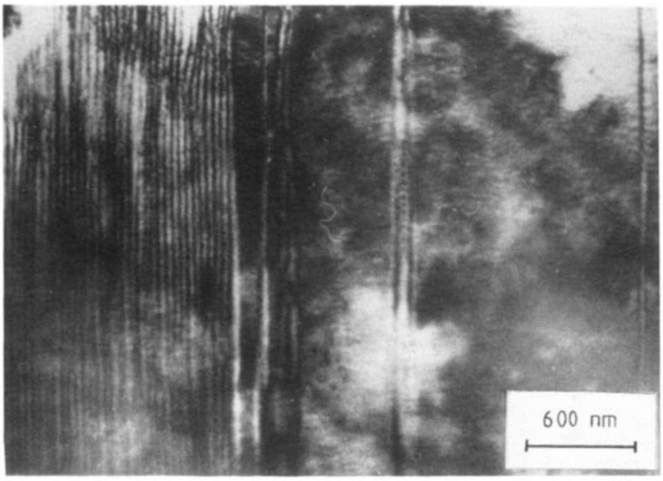

Figure 2. An image from a sample prepared in a normal stage. Note that the density of DCs is inhomogeneous and much higher than in the case of figure 1.

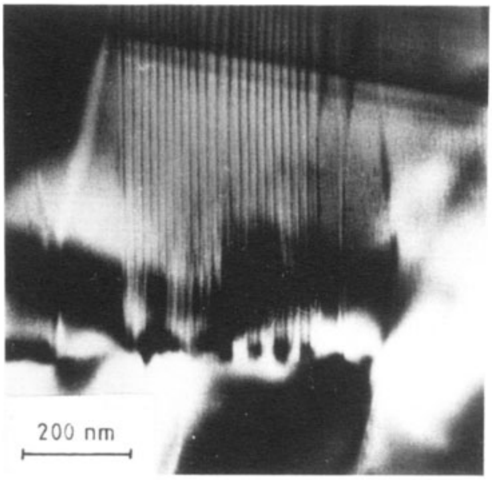

Figure 3. The dark-field image showing an array of vortices at 193 K.

are in general completely free of DCs. On the contrary the density of DCs in the latter case is high and inhomogeneous (figure 2). Regions with a high density of regularly arranged DCs are seen in all the samples prepared with the normal stage (figures 2, 3, 4). From a consideration of the case of barium sodium niobate where a high density of DCs results in superlattice reflections at irrational positions in the electron diffraction patterns of the C phase (Pan *et al* 1985), a similar phenomenon is expected to exist in K_2ZnCl_4.

Another notable fact is that DCs occasionally terminate at a vortex (figures 5 and 6). A vortex array is seen in figure 3. Similar to the case of Rb_2ZnCl_4 (Tsuda *et al* 1988), the configurations of DCs at vortices show that DCs repel each other (see figures 5, 6) as the

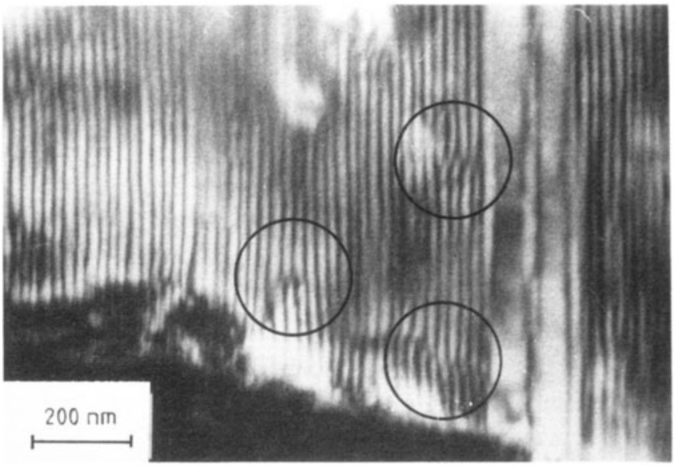

Figure 4. A dark field micrograph taken at 208 K. Within the indicated circles DCs frequently change their respective partners, thus giving evidence of the existence of pairs and of an attractive interaction.

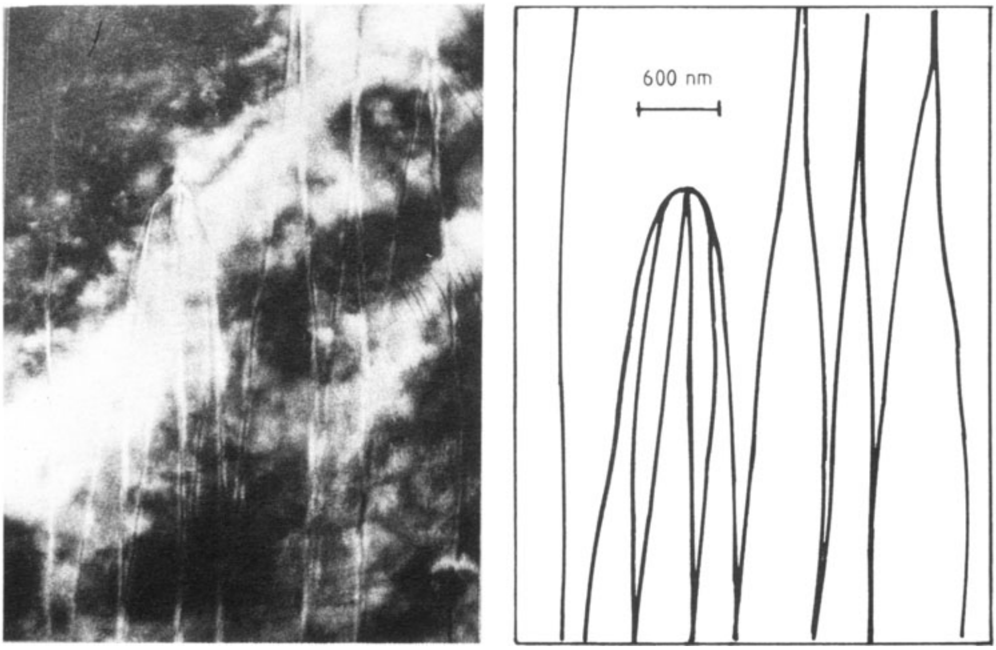

Figure 5. A pattern of DCs showing split pairs and a vortex. The line drawing is given for clarity.

angle, at which the DCs meet there, is not far from $\frac{1}{2}\pi$†. Strictly speaking this behaviour applies to pairs of DCs, as isolated neighbouring DCs seem to experience an attractive interaction and are consequently bound to pairs. This can be concluded from the

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† Similar patterns have also been observed recently by Sakata and Hamano (1989) using a replica technique.

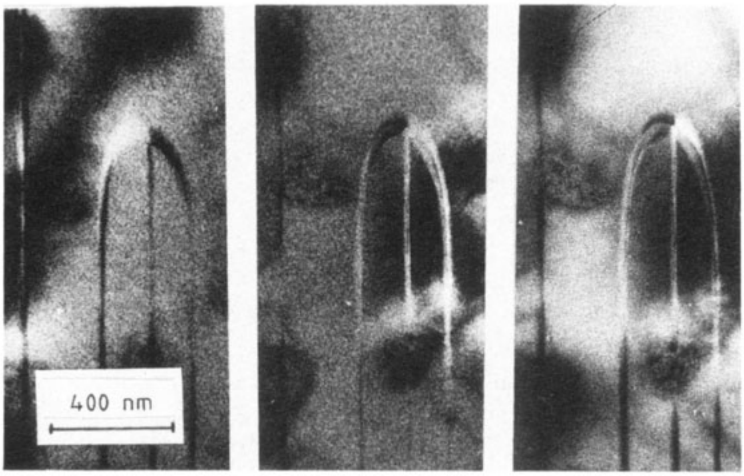

Figure 6. A vortex consisting of three pairs of DCs. A splitting of the outer pairs occurs with continued electron irradiation increasing from left to right.

observation that pairs often split up into single DCs, which form new pairs with adjacent DCs, where the angle between meeting DCs is almost zero. These features have been observed particularly near the crystal edge as shown in the lower part of figure 4 and in figure 5.

In-situ observations prove that in general the configurations of DCs are stable from ambient temperature down to 110 K, the lowest temperature used in our investigations. However, motions and rearrangements of DCs can be observed during prolonged or enhanced irradiation by the electron beam. It has been found that in some regions pairs of vortices were formed by collapses of six DCs (or three pairs of DCs) which move in opposite directions along the *b*-axis. These processes complete in a short time so that it was not possible to take micrographs. Motions of an isolated vortex along *b* can also easily be observed and controlled by focusing or defocusing the electron beam, but motions perpendicular to the *c*-plane are scarce. At the boundary of regions with high and low densities of DCs, respectively, a rearrangement of DCs by motions perpendicular to the *c*-plane could sometimes be observed. Another fact is that an isolated pair of DCs can gradually decompose and form isolated DCs under the influence of the electron beam. The initial stages of such a process taking place at a vortex are shown in figure 6. More details will be reported elsewhere (Sakata *et al* 1990).

Usually, DCs in the high-density region do not collapse to form pairs of vortices, that is anti-stripples, although they frequently exchange their partners as shown in figure 4. This means that some repulsive interaction has to be assumed between pairs of DCs, and that these pairs are relatively stable in the C phase even at temperatures rather far below the C–IC transition temperature.

Dielectric measurements may reveal the average behaviour of DCs because DCs act as ferroelectric domain walls within the C phase of K_2ZnCl_4. Thus the mobility of DCs can be probed in an approximate way by investigating the ferroelectric hysteresis. Doing this we found a considerable increase of the coercive field strength, E_c, with time at room temperature when the samples had been annealed at about 420 K for several hours. Furthermore, as-grown samples could not be repolarised by fields of 15 kV cm^{-1} and a frequency of 0.1 Hz while the values of E_c of freshly quenched crystals were about 0.5 kV cm^{-1}. One may conclude, therefore, that the density and/or mobility of DCs decreases steadily at room temperature and eventually becomes practically zero.

4. Discussion

According to the experimental results mentioned above, there exist substantially less DCs in the samples that were thinned in a cold stage. One may assume that ion beam bombardment will increase the temperature of the sample considerably, so that samples thinned in the normal stage had been heated very probably to a temperature above the C–IC transition ($T_C \simeq 403$ K). During the process of thinning, which lasted for hours, the samples were annealed at a temperature above T_C and quenched to ambient temperature when the ion beam was switched off. Furthermore, it cannot be discounted that defects have been induced in the crystals by the bombardment ions, which may act as pinning centres on DCs. As a result, the formation of anti-stripples of DCs does not take place in some areas of the crystals and regions with high densities of DCs are left in the C phase. Due to the smaller influence of thermal fluctuations at low temperatures, the boundaries of such regions are rather sharp, but the regular patterns of pairs of DCs with an average 'lattice' distance of the order of 15 nm in regions with high densities of DCs remain noteworthy.

Rearrangements of DCs are expected to take place more easily at temperatures near the C–IC transition temperature. As the anomalous part of the permittivity, $\varepsilon - \varepsilon_\infty$, is a sensitive measure of the density of DCs, n_s, several investigations deal with the time dependence of ε after the crystals had been quenched from the IC phase to just below T_C (Zhang *et al* 1985, Mashiyama and Kasatani 1987, Sakata *et al* 1988). Zhang *et al* (1985) deduced from their dielectric measurements that the relation $dn_s/dt = -Cn_s^2$ holds for a certain period of time. They inferred from this result that the decay of the 'dielectric tails' in the ferroelectric phase is mediated by pair annihilation of DCs, whereas another mechanism should contribute to the decay immediately after quenching, when n_s is large. Although our electron microscopic results refer to much lower temperatures it is tempting to relate the occurrence of pairs of DCs to the apparent 'pair annihilation' derived from the dielectric behaviour by Zhang *et al* (1985). Indeed, DCs are dielectrically inactive if an attractive interaction between isolated DCs results in bound pairs. In the case of Rb_2ZnCl_4 a definite temperature of about 160 K has been deduced from the dielectric behaviour, below which pairs of DCs are assumed to be formed (Levstik *et al* 1987). A corresponding temperature cannot be given for K_2ZnCl_4 as no dielectric anomaly, comparable with those found in the case of Rb_2ZnCl_4, could be traced below T_C with our crystals. On the other hand, the dielectric results point out that the formation of pairs is relevant, at least up to T_C, in this case. Finally we would like to remark that the strong dependence of E_C on the history of the samples indicates that nucleations of DCs cannot be of importance during the repolarisation processes. This can be inferred from our observation that E_C increases with time to values above the dielectric breakdown field, whereas the threshold field of nucleation may be assumed to be independent of time. This is in accordance with the occurrence of extremely high values of E_C (Gesi 1978) that are observed in virgin crystals.

Acknowledgments

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