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A study of the relaxation of discommensurations in K_2ZnCl_4 : III. Measurements of the complex dielectric constant

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Abstract. Dynamics of discommensurations (DC) in the incommensurate–commensurate (I–C) transition at T_C in K_2ZnCl_4 were studied. Slow relaxation processes are revealed by an investigation of the frequency-dependent complex dielectric constant. The occurrence of a polydispersion indicates that in the vicinity of T_C there exists a transient chaotic state with an inhomogeneous distribution of DC. By fitting the experimental data, we found that there exist two characteristic relaxation frequencies during the C–I transition. One corresponds to the regions of the frozen-in state of the C phase, the other to the regions with DC newly created from the C domains of the crystal. This indicates the coexistence of the C and I phases near T_C . The results reveal that the phase transformation proceeds through the nucleation of DC stripples and through the rearrangement of both the newly created DC and the ‘frozen-in’ ones.

1. Introduction

In two previous papers (Pan and Unruh 1990, 1992) we presented results of experimental studies on discommensurations (DC) and on their relaxation properties in K_2ZnCl_4 , by means of transmission electron microscopy (TEM), measurements of the quasi-static dielectric constant, and measurements of the ferroelectric hysteresis. TEM observations have shown that in the commensurate (C) phase of K_2ZnCl_4 there exist some regions with a high density of regularly distributed DC, which are considered as the frozen-in state of the incommensurate (I) phase during the I–C transition on cooling, and that rearrangements or relaxations of the DC configuration occur when the DC density changes. These relaxational processes are expected to persist at higher temperatures, in particular during the C–I transition at $T_C \simeq 403$ K, as indicated by the measurements of the quasi-static dielectric constant. The study of the ferroelectric hysteresis has also shown that the density of DC in the C phase decreases exponentially with time, which leads to an increase of the coercive field with time and to relaxational dielectric properties. The different shapes of the curves of the dielectric constant versus temperature were interpreted by assuming different nucleation probabilities of DC stripples, each consisting of six DC terminated by two vortices in the case of K_2ZnCl_4 , in the virgin crystals and in those which had been heated to above T_C .

In the present work we present experimental results on dynamical properties related to DC during the C–I transition in K_2ZnCl_4 , by means of measurements of the frequency-dependent complex dielectric constant $\epsilon^*(\omega) = \epsilon' - i\epsilon''$. In section 2

the experimental method is briefly described. In section 3 we present the measured data of $\epsilon^*(\omega)$, which are fitted by means of a least-squares method using a double Cole–Cole formula. The results will be discussed in section 4, which, in considering the previous studies (Pan and Unruh 1990, 1992, Sakata *et al* 1990), gives insight into the kinetics and dynamics of the DC during the I–C transition in K_2ZnCl_4 .

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 313 K. Cylindrical *b*-cut samples of about 3 mm in diameter and 0.5 mm in thickness were provided with evaporated gold electrodes. The dielectric measurements in the frequency range from 1 MHz to 1 GHz were performed by means of a coaxial reflectometer set-up (HP-4191A RF impedance analyser). The sample was placed at the end of a radial transmission line in the sample holder as termination of the coaxial line. The complex dielectric constant was determined from the measured reflection coefficient. Heating within the temperature range of 290–500 K was achieved by using an electric furnace. The temperature was stabilized to within ± 0.01 K. In order to reduce the influence of the time dependence of the dielectric constant on the measured dispersion curves, every measurement commenced 30 min after a change of the temperature, which was lowered at a rate of about 0.5 K min^{-1} .

3. Experimental results

3.1. Temperature dependence of the dielectric dispersion

With the first heating run the virgin crystal of K_2ZnCl_4 exhibited a broad and small maximum of the quasi-static dielectric constant and hardly showed a dielectric dispersion. In subsequent thermal cycles the strength of the dispersion gradually increased, and the Cole–Cole plots of ϵ^* approached the form of semicircles except in the vicinity of T_C . After annealing at 450 K, a relaxation of the Debye type was obtained during subsequent cooling. Figure 1 shows some examples of the Cole–Cole plots on cooling from 450 to 390 K, after annealing at 450 K for 18 h. In the high-temperature region of the I phase ($T \gtrsim T_C + 3 \text{ K}$, $T_C = 401.5 \text{ K}$ on cooling), the Cole–Cole plots are semicircles and can thus be well approximated by the Debye formula with a single relaxation time (figure 1(a)). With a further decrease of temperature the dispersion deviated from the Debye type, and became polydispersive. The plots can be well fitted by the Cole–Cole formula with a characteristic relaxation time τ . In the vicinity of T_C the dispersion could no longer be described by a single Cole–Cole formula, so that the double Cole–Cole formula

$$\epsilon(\omega) - \epsilon_\infty = A(\epsilon_s - \epsilon_\infty)/[1 + (i\omega\tau_1)^{1-h_1}] + (1 - A)(\epsilon_s - \epsilon_\infty)/[1 + (i\omega\tau_2)^{1-h_2}] \quad (1)$$

is used for the fitting of the experimental data, where ϵ_s and ϵ_∞ are, respectively, the dielectric constant at the low-frequency and at the high-frequency limit of the dispersion, τ_1 and τ_2 the characteristic relaxation times, h_1 and h_2 the dispersion parameters, which represent a measure of the distribution of the relaxation times,

and A the relative portion of the first dispersion step. In the studied crystal ϵ_∞ is about 11.5 and practically temperature-independent. The points and the full curves in figure 1 represent, respectively, the measured data and the fits of the data with equation (1) by means of the least-squares method.

As seen in figure 1(a), above 401.5 K the plots of the measured data can be fitted by a single Cole-Cole formula, although the value of h increases on approaching T_C . However, below 401.5 K the experimental values deviated from a simple Cole-Cole behaviour (figure 1(b)). Two relaxation regions might be distinguished, which became clear on further cooling. Finally, a single Cole-Cole relaxation was found below 400.3 K (figure 1(c)). With further cooling from about 400 K the dispersion vanished gradually. It should be noted that the dispersion below T_C gradually diminishes also with time at constant temperature. The time dependence of the dielectric dispersion will be studied later.

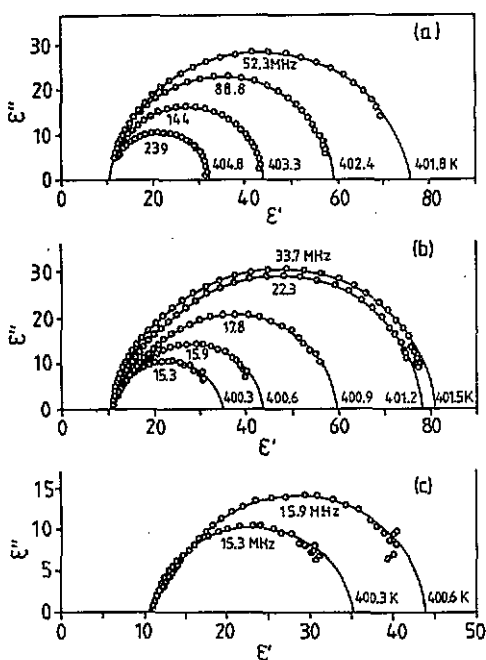


Figure 1. Cole-Cole plots of the dielectric dispersion of K_2ZnCl_4 on cooling (a) in the I phase, (b) in the transient region and (c) in the C phase. Frequencies designate $1/2\pi\tau_1$.

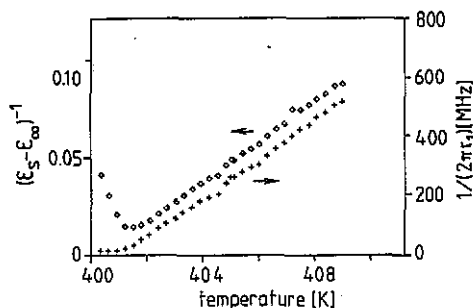


Figure 2. The temperature dependences of $(\epsilon_s - \epsilon_\infty)^{-1}$ (diamonds) and $1/2\pi\tau_1$ (crosses), obtained from fitting the data with the double Cole-Cole formula.

In figure 2 $(\epsilon_s - \epsilon_\infty)^{-1}$ and the characteristic relaxation frequency $(1/2\pi\tau_1)$ are plotted against temperature on the cooling run, where ϵ_s and τ_1 are according to the fitted values of the experimental data. One notes that near T_C both the static dielectric constant and the characteristic relaxation time obey well the Curie-Weiss law, showing a significant critical slowing down on approaching the I-C transition temperature. This result is in agreement with the results of other I phases, such as Rb_2ZnCl_4 and K_2SeO_4 (Horioka *et al* 1981, Deguchi *et al* 1984, Montnacher 1986). However, it should be pointed out that we did not find the gradual development of

a low-frequency dispersion in the I phase. Instead, we found that the low-frequency dispersion part in the Cole-Cole diagrams, characterized by τ_1 , is dominant in the whole temperature range.

Figure 3 shows the temperature dependence of the dispersion parameter h for the same cooling run as in figure 1. We see that the inhomogeneity of the crystal increases on approaching T_C . We would like to point out that the value of h is significantly reduced by stabilizing the temperature for several hours, as will be seen in the following section.

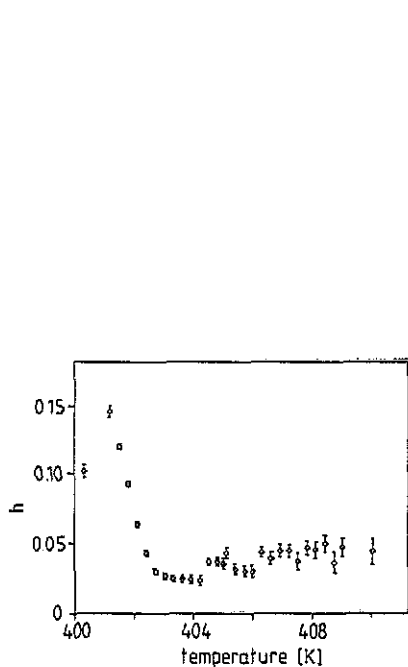


Figure 3. Temperature dependence of the dispersion parameter h . Note the increase of h on approaching the I-C transition temperature 401.5 K (cooling run).

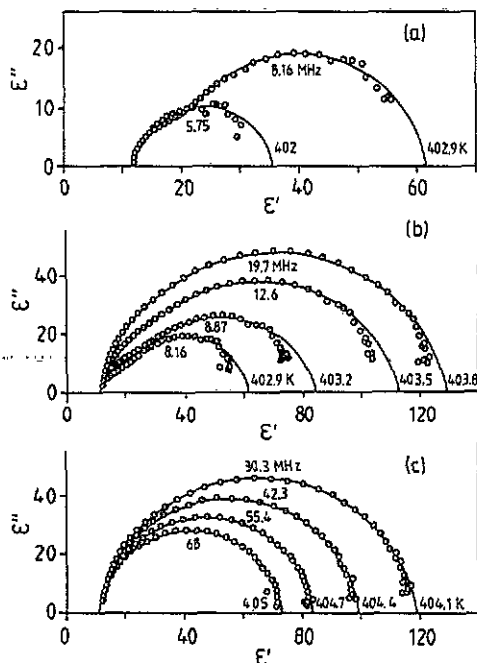


Figure 4. Cole-Cole plots of the dielectric dispersion of K_2ZnCl_4 on heating (a) and (b) in the C phase and (c) in the I phase. The points and the full curves represent, respectively, the experimental data and the curves fitted by means of the least-squares method.

Figure 4 shows the Cole-Cole diagrams of the dielectric dispersion of K_2ZnCl_4 during the C-I transition on heating. Similarly to the results obtained on cooling, the relaxation showed a characteristic change at the C-I transition temperature. Below 402.5 K the relaxations were monodispersive of Debye type, with a large relaxation time τ_1 of about 0.02 μs . On approaching the C-I transition temperature ($T_C \approx 404$ K on heating), a second characteristic relaxation with a time constant τ_2 of the order of several nanoseconds developed at the high-frequency side as seen in figure 4, the portion of which increased on heating. Surprisingly the second relaxation time τ_2 increased with increasing temperature, whereas the first one τ_1 decreased, as seen in figure 5. During the occurrence of the second relaxation, its strength increased rapidly, i.e. the static dielectric constant increased. At about 404 K, where the static dielectric constant ϵ_s reaches a maximum, the two characteristic relaxation times

approached the same value, and the Cole–Cole diagrams could therefore again be approximated by a single Cole–Cole formula (equation (1) with $A = 1$), as shown in figure 4(c). Afterwards, the strength and the relaxation time decreased with increasing temperature. These results indicate that the I phase develops from the C phase when ϵ_s rises and that the C phase disappears when ϵ_s reaches its maximum.

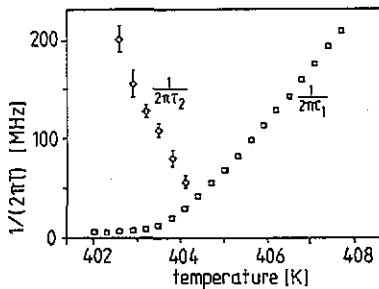


Figure 5. Temperature dependence of the characteristic relaxation times τ_1 and τ_2 . Note that $1/\tau_1$ increases, whereas $1/\tau_2$ decreases with increasing temperature.

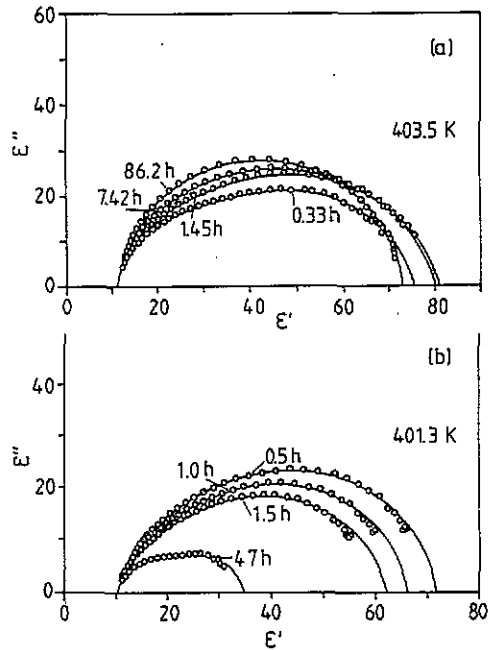


Figure 6. Time dependence of Cole–Cole plots of the complex dielectric constant measured (a) at 403.5 K on heating and (b) at 401.3 K on cooling, showing the transformation of the crystal between the C phase and the I phase.

It has also been found that not only the static dielectric constant but also the dynamic relaxation time of the I phase exhibits thermal hysteresis. We do not plot it here because there are no significant differences with the results of Ema *et al* (1984).

3.2. Time dependence of the dielectric dispersion

Figure 6(a) shows the time dependence of the dielectric dispersion during the C–I phase transition on cooling. The sample was previously stabilized at 399 K for 13 h, with a residual value of $(\epsilon_s - \epsilon_\infty)$ of 10. It was then heated to 403.5 K at a rate of 0.5 K min^{-1} . The first measurement was carried out when the temperature was stabilized for about 20 min, as shown in figure 6(a). The dispersion was found to be approximated by equation (1), with two characteristic relaxation times similar to that of figure 4(b). The static dielectric constant, ϵ_s , increased during the first few hours and then decreased with time as shown in figure 7. However, the relaxation frequency $f_1 = 1/2\pi\tau_1$ at the low-frequency side increased monotonically with time, while $f_2 = 1/2\pi\tau_2$ at the high-frequency side decreased, as shown in figure 8. Simultaneously,

the portion of the second relaxation increased with time. In about 60 h the two relaxation times approached the same value. After 86 h the sample exhibited a relaxation of nearly Debye type with a relaxation frequency of about 60 MHz, as seen in figures 6(a) and 8. This means that the crystal became homogeneous. It was noticed again that the second relaxation (τ_2) developed when ϵ_s showed a rapid increase.

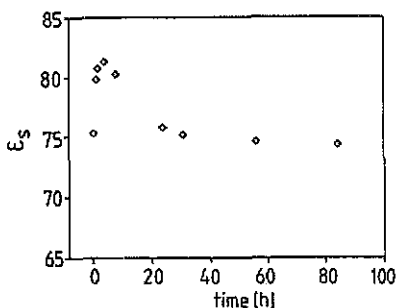


Figure 7. Time dependence of the static dielectric constant ϵ_s at 403.5 K, from the fitting of measured dispersion curves.

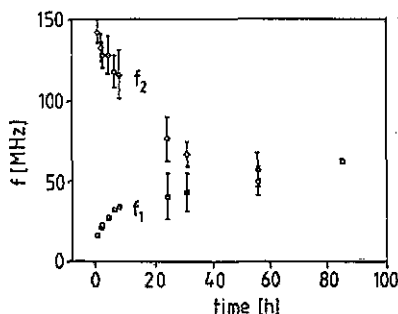


Figure 8. Time dependence of the relaxation frequencies f_1 and f_2 , obtained from the fitting of the experimental data taken at 403.5 K. Bars represent the errors of f_1 and f_2 .

Similar studies were performed during the I-C transition on cooling (figure 6(b)). The sample was cooled from 410 to 401.3 K (about 0.2 K below $T_C \approx 401.5$ K on cooling). In the beginning, ϵ_s increased and then decreased with time after the temperature had been stabilized at 401.3 K for 0.5 h. Again, the data could be fitted by assuming two Cole-Cole type dispersions according to equation (1).

In conclusion, the following results were obtained by three different techniques. The DC in the C phase of K_2ZnCl_4 were directly observed by TEM. They tend to form pairs and belong predominantly to regions in which a DC lattice exists. The decomposition of DC pairs and the rearrangement of DC after electron beam irradiation were revealed by dark-field micrographs using the satellite reflections. The detailed analysis of the configuration of DC pointed to an attractive interaction between isolated DC and a repulsive one between pairs of DC (Pan and Unruh 1990). The dielectric constant of K_2ZnCl_4 has been studied near T_C with repeated temperature cycling and annealing at a temperature above T_C . The increase of the coercive field of the ferroelectric hysteresis with time has been noted in the C phase of the annealed sample, which was attributed to a decrease of the DC density. The process of the I-C transition has been studied through the time and temperature evolutions of the dielectric dispersion in the radio frequency (RF) range. The coexistence of the C and I phases between 401.5 and 404.1 K has been revealed by the occurrence of a dispersion of a double Cole-Cole type. The mechanism of these phenomena will be discussed in the following.

4. Discussion

The relaxation frequencies of several incommensurate materials, such as K_2SeO_4 and Rb_2ZnCl_4 (Horioka *et al* 1980, 1981, Deguchi *et al* 1984, Montnacher 1986),

$[N(CH_3)_4]_2ZnCl_4$ (Horioka 1983) and K_2ZnCl_4 (Ema *et al* 1984), are known to exhibit a critical slowing down at T_C . The low-frequency relaxation occurs predominantly in the DC regime. From this point of view, Horioka *et al* (1980, 1981) attributed the relaxation to the domain-wall-like motion of DC. In accordance with this, the results presented above reveal characteristic processes of the I-C transition and the dynamics of DC.

Figure 1 shows the process of the transformation of K_2ZnCl_4 from the I phase to the C phase possessing a certain density of frozen-in DC. The monodispersion of Debye type in the high-temperature range of the multi-DC regime indicates a homogeneous distribution of DC in the entire crystal. With a further decrease of temperature, the deviation from the Debye-type relaxation indicates an inhomogeneity of the spatial distribution of DC, which corresponds to the increase of the distribution parameter h in figure 3. This inhomogeneity may be explained by the fact that the DC lattice has not reached a state of thermal equilibrium because of nucleation and pinning effects. One should note from figures 1(b) and (c) that the sample begins to exhibit two characteristic relaxations when the static dielectric constant ϵ_s reaches a maximum, indicating the coexistence of the C phase and the I phase. The relaxation with the lower characteristic frequency results from the C phase developing from the I phase at T_C . The dispersion at the high-frequency side is due to the regions that have not been transformed into the C phase. With further decreasing temperature, the former relaxation frequency continuously decreases while the latter (about 44 MHz) shows hardly any change. However, the portion of the latter decreases and vanishes at about 400 K. This process of the I-C transformation has also been demonstrated by the time dependence of the dispersion after cooling the sample down to 401.3 K from above, as shown in figure 6(b).

We would like to point out that the C phase of K_2ZnCl_4 still contains many DC or even a perfect DC lattice in some regions of the sample, as directly observed by electron microscopy (Pan and Unruh 1990). These DC may be pinned by crystal defects and correspond to the existence of the dispersion below T_C .

However, the situation on heating is quite different. Below about 402.5 K only the Debye-type dispersion ($f_1 \approx 8$ MHz) due to frozen-in DC is observed (figure 4(a)). At about 402.9 K the second relaxation develops at the high-frequency side of the dispersion (figure 4(a)), indicating the appearance of the I phase. Both relaxations coexist in the crystal up to about 404 K. The crystal completely transforms into the I phase at 404.1 K, indicated by a single Cole-Cole-type dispersion. This means that the C and I phases coexist between 402.5 and 404.1 K on heating (figures 4(b) and (c)). It is also noticed from figure 4 that on the heating run the occurrence of the I structure corresponds to a rapid increase of ϵ_s , while the vanishing of the C phase is associated with ϵ_s being maximal.

We would like to point out that our results are in accordance with the results reported by Mashiyama and Kasatani (1987). They studied the I-C transition of K_2ZnCl_4 by dielectric measurements and simultaneously by x-ray scattering. They observed that with increasing temperature the I satellites appear and coexist with the C satellites when ϵ begins to rise, and that the C satellites disappear when ϵ becomes maximum. On the cooling run, they observed that the peak of ϵ corresponds to the appearance of the C reflections.

In these investigations it is astonishing to find that with increasing temperature from 402.5 to 404.1 K the relaxation frequency, $1/2\pi\tau_1$, of the dispersion at the low-frequency side increases, whereas the other one, $1/2\pi\tau_2$, decreases rapidly. On

approaching 404.1 K the two relaxation frequencies become the same, as shown in figure 5. This is also revealed in the time dependence of the relaxation frequencies, as shown in figure 8. That the relaxation of the I structure is due to the motion of DC means that, in the early stage of the C-I transition, the I regions, which are directly nucleated from the C phase, have a smaller DC spacing than that of the equilibrium state. These processes of the C-I transition can be understood as nucleation and growth of stripples of DC. As seen from the electron micrographs (Pan and Unruh 1990), the regions with a high density of DC are often observed in the C phase. Most DC in the C phase do not appear as isolated domain walls but belong to regions with an almost perfect DC lattice. Of course, the inter-DC distance may be somewhat larger than that of the equilibrium state at T_C because of the slow rearrangement of DC. When the temperature is raised to a temperature (403.5 K) above T_C^0 , which is defined as the C-I transition temperature with an extremely slow heating rate, the nucleation of stripples occurs in the C regions. Just after generation, these stripples of lenticular shape have a small spacing of adjacent DC and small radial dimension. As schematically shown in figure 9(b), these stripples of DC coexist with regions of the frozen-in state.

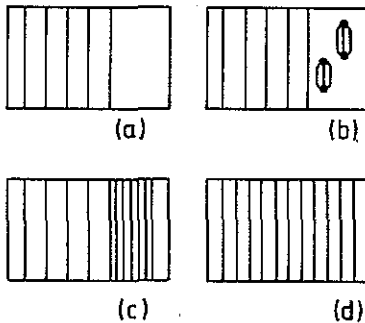


Figure 9. Schematic plot of the successive processes of the C-I transition of K_2ZnCl_4 . (a) Before the transition... Note the coexistence of a large C domain and the region of the frozen-in state of the I phase. (b) Two stripples nucleate from the C domain, the DC spacing of which is smaller than that of frozen-in DC. (c) The stripples grow by extension perpendicular to the modulation direction. (d) Rearrangements of both the frozen-in DC and newly created DC approaching the equilibrium state with a homogeneous distribution of DC.

As known from the TEM studies, the motions of DC are usually parallel to the c plane but negligible perpendicular to it. Accordingly, the newly generated stripples extend dominantly parallel to the c plane and form clusters of DC which have smaller spacing than the equilibrium state because of the very slow motion of DC parallel to the modulation wavevector (figures 9(b) and (c)). In accordance with this, these regions of the system exhibit a high value of the relaxation frequency of the dielectric dispersion. Furthermore, the homogeneous DC lattice develops by slow relaxational processes and approaches the equilibrium state. As a consequence, the relaxation frequency f_2 shows a slow decrease. Simultaneously, DC in a frozen-in region, where the spacing of adjacent DC is too large with respect to the equilibrium one at the same temperature, are rearranged by similar processes (see figures 9(a) to (d)). Consequently the relaxation frequency f_1 of these regions exhibits an increase. When the processes of rearrangement in both kinds of regions are completed, the distribution of DC in the crystal eventually becomes homogeneous (see figure 9(d)), giving rise to a relaxation of the Debye type.

We may assume that there is no qualitative difference between the region of the frozen-in state and the newly created region from the C domains. When all the C domains are filled by the nucleated DC or stripples, one can say that the C phase has disappeared and therefore the crystal has transformed into the I phase. At this stage,

however, there exists a wide range of the distribution of the inter-DC distance, which results in a dielectric dispersion of the single Cole–Cole type with a rather high value of h .

We would like to point out that the present conclusions are not consistent with that reported by Ema *et al* (1985). In their experiments only a monodispersive relaxation was observed, and the relaxation frequency exhibited a monotonic increase with time even after ϵ_s had reached its maximum. On the contrary, they explained these results on the assumption that in the early stage of the C–I transition the DC possess a larger spacing than that in the equilibrium state. When the DC fill all the C regions ϵ_s reaches a maximum. With increase in time the spacing of DC becomes more and more narrow on approaching the equilibrium state, owing to further nucleation of DC. Accordingly, the relaxation frequency increases with time. However, ϵ_s exhibits a decrease due to the increasing strength of the repulsive interaction of DC. One should note that the time dependence of the relaxation frequency obtained by Ema *et al* (1985) is very similar to that of f_1 , as plotted in figure 8, and that their crystals had lower impurity than our crystals, indicated by a small thermal hysteresis of about 0.7 K (2.5 K in our sample). Therefore, the contradiction may be understood as follows. The motion of DC along the c direction in their crystal may be much faster *due to the low density of impurities in the crystal*, and thus the spacing of the newly created DC is not far from that of the regions of the frozen-in state. Consequently, the relaxation frequencies in both kinds of regions are not far from each other, and therefore only one characteristic relaxation of a single Cole–Cole type is observed.

5. Conclusions

In conclusion, the present study shows that the C–I transition in K_2ZnCl_4 is characteristic of first order and proceeds through the successive processes of nucleation and growth of stripples made up of six DC, respectively, bound by a pair of vortices. The coexistence of the C and I phases has been found in the vicinity of T_C within a temperature range of about 2.5 K in K_2ZnCl_4 . It has also been found that, in the early stage of the C–I transition of K_2ZnCl_4 , the DC created from the C regions possess a smaller inter-DC distance than those in the equilibrium state at the same temperature, owing to the strong anisotropic motions of DC along the direction parallel to the modulation wavevector and perpendicular to it. We have also found that the pinning effects of DC by crystal defects play an important role in both the I and C phases, which enhance the thermal hysteresis and stabilize the DC in the C phase. From the time and temperature dependences of the relaxation frequencies, and taking into account the results of TEM observations (Pan and Unruh 1990), the mechanism of the C–I transition could be largely elucidated.

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