PROC. JSSF-2, KYOTO, 1980
J. PHYS. SOC. JPN. **49** (1980) SUPPL. B, pp. 10–12.

Effect of Impurity on the Incommensurate-Commensurate Phase Transition in Rb_2ZnCl_4

Katsumi HAMANO, Yoshito IKEDA*, Takayuki FUJIMOTO, Kenji EMA and Shunsuke HIROTSU

Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo 152

The dielectric constant along the ferroelectric axis, ε_a, of Rb_2ZnCl_4 shows a pronounced thermal hysteresis over a wide temperature range including the incommensurate-commensurate transition point (−80°C). The observed thermal hysteresis is explained on the basis of the model that defects such as impurities pin the discommensurations and hinder the crystal from reaching a thermal equilibrium. The results obtained on a mixed crystal system $(Rb_{1-x}K_x)_2ZnCl_4$ are also reported.

Rubidium tetrachlorozincate Rb_2ZnCl_4 undergoes three successive phase transitions. With decreasing temperature it transforms from a normal phase (D_{2h}^{16}−Pmcn) to an incommensurate phase at about 30°C (T_i), to a ferroelectric commensurate phase ($C_{2v}^{9}-P2_1cn$, $P_s//a$) at about −80°C (T_c),[1, 2] and finally to the fourth phase at about −200°C[3] (the space group of the fourth phase has not yet been determined). In the commensurate phase, the lattice parameter is tripled along the c-axis compared with that of the normal phase, c_0, and in the incommensurate phase the modulation period is nearly but not precisely equal to $3c_0$.

The dielectric constant along the ferroelectric axis, ε_a, of a Rb_2ZnCl_4 crystal prepared from reagents of 99.9% purity by an aqueous solution method exhibits an anomaly around T_c as shown in Fig. 1(a). The anomaly is accompanied by a marked thermal hysteresis. The tail appearing in a cooling run is not observed at all in a heating run. In the incommensurate phase, the heating curve goes above the cooling curve. If we turn at a point A from a cooling run to a heating run, ε_a goes along the dashed line AB. Therefore the thermal hysteresis is seen even when heating and cooling runs are cycled only within the incommensurate phase. If we turn at a point C from a cooling run to a heating run, ε_a goes almost horizontally along the dashed line CD, then it goes along the heating curve (solid line). If we turn from C′, ε_a goes along C′D′. Therefore the tail indicates that some irreversible process is taking place with the decrease in temperature.

Figure 1(b) shows the behavior of ε_a around T_i. It has a shallow minimum around 0°C. Starting from this minimum, it begins to increase toward low temperatures. It should be noted that the thermal hysteresis is observable below the temperature of this minimum.

Our explanation of this thermal hysteresis is based on the following picture of the incommensurate phase. The incommensurate structure can be regarded as a modulated structure of the commensurate structure, the modulation period λ being

$$\lambda = 2\pi/(k_c - k_i) = c_0/\delta,$$

where k_c and k_i are the wave numbers of the commensurate and incommensurate phases, respectively. Just below T_c, the modulation is sinusoidal. When the temperature is decreased and T_c is approached nearer, λ becomes longer and the content of the higher harmonics increases, and finally the structure becomes "domain-like". The boundaries of these microscopic domains have been termed "discommensurations" (hereafter abbreviated as DC's) by McMillan.[4] According to the theory of Shiba and Ishibashi,[5] the increase of the higher harmonics is responsible for the increase of the dielectric constant toward T_c. As we noted, the thermal hysteresis begins to appear simultaneously with the increase of ε_a. This fact suggests, therefore, that the thermal hysteresis is closely connected with the appearance of harmonics.

McMillan[4,6] has discussed the pinning effect of impurities on the incommensurate charge density wave. It is reasonable to assume that similar pinning by defects occurs also for the

* Present address: Sony Magnetic Products Inc., Tagajo-city, Miyagi 985

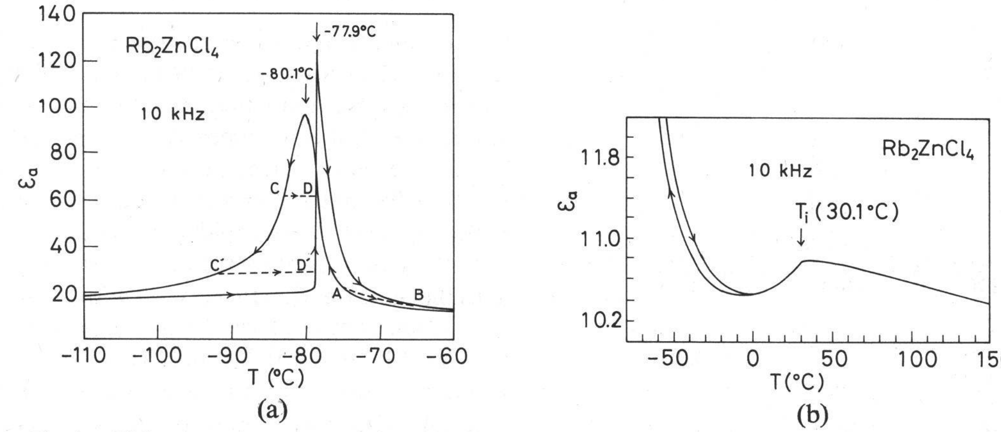

Fig. 1. Dielectric constant ε_a as a function of temperature, (a): near the incommensurate-commensurate transition point T_c, (b): near the normal-incommensuate transition point T_i.

incommensurate wave in dielectrics. We assume further that the pinning occurs more effectively when the incommensurate wave becomes domain-like and DC's are formed in the crystal. Due to the pinning by defects, the regular array of DC's is disturbed and the distance between two adjacent DC's will fluctuate around its average value, though on the whole the DC's are arrayed coherently in the crystal.

When the temperature is varied in the incommensurate phase, the modulation period λ must be changed to a new value corresponding to the new temperature. This must be done through production, annihilation, and diffusion of DC's. However such processes do not proceed smoothly due to the pinning by defects. As a result, the modulation can not follow the change in temperature immediately; it will take fairly long time to reach a thermal equilibrium.

Let the thin lines in Fig. 2(a) and (b) represent the thermal equilibrium values of δ and ε_a, respectively. Since the establishment of thermal equilibrium is hindered by the pinning, the state realized at a certain temperature in a cooling run will be the one which would be realized at somewhat higher temperatures in a defect-free crystal. By contrast, in the heating run, the actually realized state will be the one which would be realized at somewhat lower temperatures in a defect-free crystal. Thus the thermal hysteresis as shown by the thick lines is expected to occur. Figure 2(b) accounts for the observed thermal hysteresis of ε_a in the incommensurate phase. The tail appearing in the commensurate phase [Fig. 1(a)] is possibly due to the presence of remaining DC's, which are gradually removed out of the crystal with the decrease in temperature.*

If our assumption about the pinning effect of defects is right, crystals containing more defects are expected to show more pronounced thermal hysteresis. In order to test this idea, we studied a mixed crystal system $(Rb_{1-x}K_x)_2ZnCl_4$.** For small values of x, K ions may be looked as impurities. As x was increased, T_i was shifted

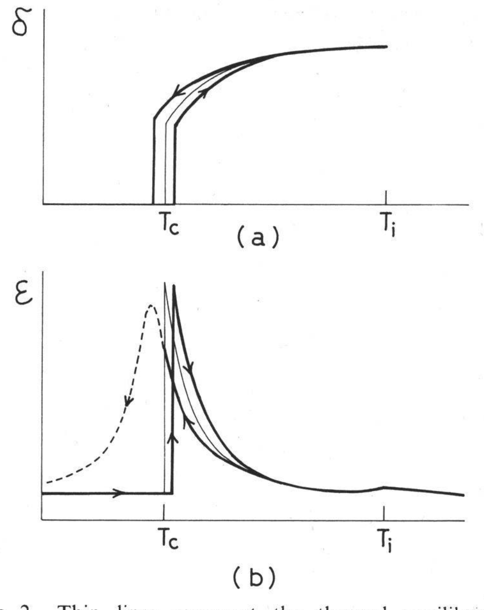

Fig. 2. Thin lines represent the thermal equilibrium values of δ and ε_a in a defect-free crystal. Thick lines represent the expected thermal hysteresis of these quantities of a real crystal containing defects.

* In order to know whether the thermal hysteresis of δ as shown in Fig. 2(a) really occurs or not, we asked Dr. H. Mashiyama of Yamaguchi University to carry out an X-ray diffraction experiment. Recently he got the result which confirmed the above expectation.

** Determination of x was made by a fluorescent X-ray analysis in AGNE GIJUTSU CENTER.

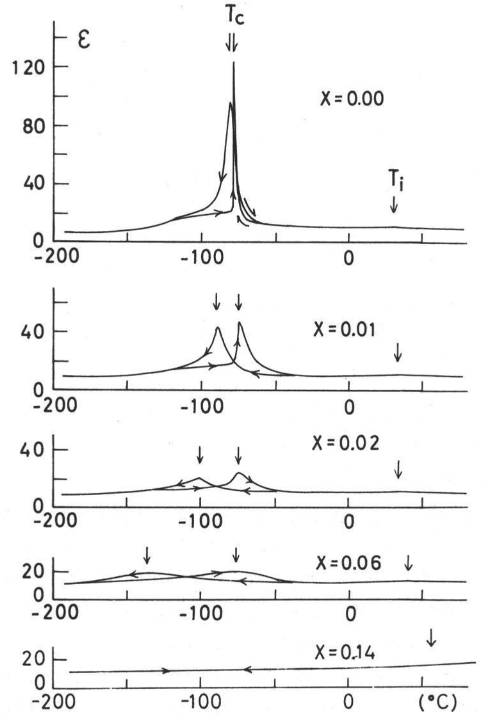

Fig. 3. Thermal hysteresis of ε_a observed in mixed crystals $(Rb_{1-x}K_x)_2ZnCl_4$.

toward high temperatures as expected from the fact that T_i of K_2ZnCl_4 is located at 280°C,[7] which is higher than that of Rb_2ZnCl_4. The anomaly at T_i was not smeared even in crystals containing fairly large amount of K ions ($x \sim 0.3$). By contrast, as seen in Fig. 3, the peaks appearing at T_c were rapidly smeared and the thermal hysteresis became more exaggerated with the increase of x. In a crystal with $x=0.14$, the commensurate phase did not appear down to −200°C. These results support strongly our assumption that impurities are the cause of the thermal hysteresis observed in the incommensurate and commensurate phases of Rb_2ZnCl_4.

References

1) S. Sawada, Y. Shiroishi, A. Yamamoto, M. Takashige and M. Matsuo: J. Phys. Soc. Jpn. **43** (1977) 2099.
2) K. Gesi and M. Iizumi: J. Phys. Soc. Jpn. **46** (1979) 697.
3) E. Francke, M. Le Postollec, J. P. Mathieu and H. Poulet: Solid State Commun. **33** (1980) 155.
4) W. L. McMillan: Phys. Rev. **B14** (1976) 1496.
5) H. Shiba and Y. Ishibashi: J. Phys. Soc. Jpn. **44** (1978) 1592.
6) W. L. McMillan: Phys. Rev. **B12** (1975) 1187.
7) K. Gesi and M. Iizumi: J. Phys. Soc. Jpn. **46** (1979) 697.