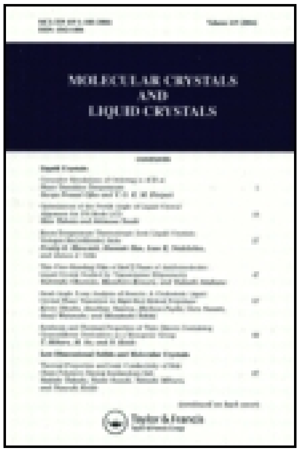

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Dielectric Studies of the Successive Phase Transitions in Cholesteryl 2,2,3,3-Tetrafluoropropionate (CTFP)

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The successive phase transitions and the thermal hysteresis in CTFP crystals were studied by measuring the dielectric constant, ϵ', and the loss, ϵ'', as a function of temperature along the three principal axes of a monoclinic single crystal. The two anisotropic peaks of ϵ' were observed near −120 and −94 °C. The value of ϵ' indicated a maximum of about 21 at −94 °C along the c^*-axis. The former peak was explained by a dielectric relaxation through modulation wave motion including polar groups in an incommensurate (INC) phase (Phase II), and the latter peak was related to a Phase I (normal phase)—Phase II transition. In Phase III/III* (INC phase) and Phase IV (commensurate phase)/IV* (INC phase) below −130 °C, the molecular motion associated with the phase transition was dielectrically inactive, and one dielectric relaxation was observed near −150 °C, which is not related to the phase transition phenomenon. In this work, two transitions near −80 and 0 °C were found in the normal phase (Phase I) as peaks of ϵ''. The peak near −80 °C appeared only in the crystals which had undergone a cooling run from room temperature. From these dielectric results, the mechanism for the thermal hysteresis of the successive phase transitions was discussed and compared with our previous X-ray diffraction work.

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INTRODUCTION

Various types of successive phase transitions including commensurate (C) and incommensurate (INC) phases have been found in many inorganic and organic crystals.[1] Recently, we have found by our X-ray diffraction and dielectric measurements[2-4] that CTFP ($C_{27}H_{45}OC$-OCF_2CF_2H) crystals showed the successive phase transitions at −150, −130 and −95 °C in the crystals produced by a very slow evaporation method from acetone solution (see Table I).

The purpose of this paper is to report dielectric properties of CTFP single crystals and to discuss the mechanism of the successive phase transitions with regard to our X-ray diffraction work.

EXPERIMENTAL

CTFP was synthesized and purified in the same procedure described previously (mp = 150 °C).[2,3] The single crystal was prepared by a very slow evaporation method from acetone solution. The crystal is colorless and transparent, and shows a long and slender shape like a sword (the size is about $3 \times 3 \times 10$ mm^3). The crystals are monoclinic (possible space group is $P2_1$ or $P2_1/m$), with lattice dimensions $a = 12.44(1)$A, $b = 9.27(1)$A, $c = 13.30(1)$A and $\beta = 106.0(1)°$ at 20 °C,[4] containing two molecules per unit cell.

The dielectric constant, ϵ', and dielectric loss, ϵ'', for the single crystal were measured along the a, b and c^*-axes (c^*-axis is normal to the a-b plane), respectively, with a transformer bridge at several frequencies between 110 Hz and 100 kHz in the following thermal processes; a-axis: room temperature → −190 °C (the first cooling) →

TABLE I

The successive phase transitions of CTFP crystals

Temperature, 0 °C		−150	−130	−95
as-grown crystals	Phase IV C	Phase III INC	Phase II INC	Phase I N
crystals which underwent once the successive phase transitions[a]	Phase IV* INC	Phase III* INC	Phase II INC	Phase I* N

C: commensurate, INC: incommensurate, N: normal

[a] These crystals gradually became like the as-grown crystals during storage at room temperature.

room temperature (the first heating), *b*-axis: room temperature → −190 °C (the first cooling → room temperature (the first heating) → −190 °C (the second cooling), c^*-axis: room temperature → −70 °C (the first cooling) → room temperature (the first heating) → −190 °C (the second cooling) → room temperature (the second heating). Here, the heating/cooling rate is about 0.2 °C/min. Electrodes were made by depositing silver in vacuum on a surface of the single crystal, and to this surface a pair of thin gold wires were connected with silver paste as leading wires. Then the whole electrode system was mounted in an electrically shielded box to avoid stray capacitance.[5]

Spontaneous polarization was measured by the conventional Sawer–Tower circuit method[6] up to an applied electric field of 100 kV/m at 60 Hz, and pyroelectric current measurements were made with an electrometer (Keithley, Type 610C).

RESULTS AND DISCUSSION

Phase transitions and crystal structures of CTFP crystals have been studied in our laboratories (see Table I).[3,4] CTFP crystals are monoclinic and modulation periods are observed along the *b*-axis. The modulation wave number, δ, is 0.20 in Phase IV below −150 °C, and as the temperature is increased from −150 °C, it decreases gradually down to 0.195 at −130 °C, then falls discontinuously to 0.18 at −130 °C and decreases continuously again to 0.14 at −95 °C. The modulation periods of the two phases below −130 °C change with the thermal history of the crystals, although the transition temperatures show no dependence with the thermal history. CTFP crystals which underwent successive phase transitions on the heating process from −185 °C are metastable crystals (Phase I* above −95 °C) and showed Phase IV* ($\delta = 0.18$ at −185 °C) below −150 °C and Phase III* ($\delta = 0.185$ at −150 °C) between −150 and −130 °C, which differ in the values of δ from the respective phases in the as-grown crystals. Furthermore, the metastable crystals recover gradually the as-grown crystals with storing the crystals at room temperature, and the storage duration for recovering was about two months.

Figures 1(a) and 1(b) show temperature dependences of ϵ' and ϵ'' on the second cooling process along the c^*-axis of a CTFP single crystal at several frequencies, respectively. The values of ϵ' exhibit a steep peak at about −94 °C and a bumpy peak near −120 °C, which apparently correspond to the respective transitions at −95 and

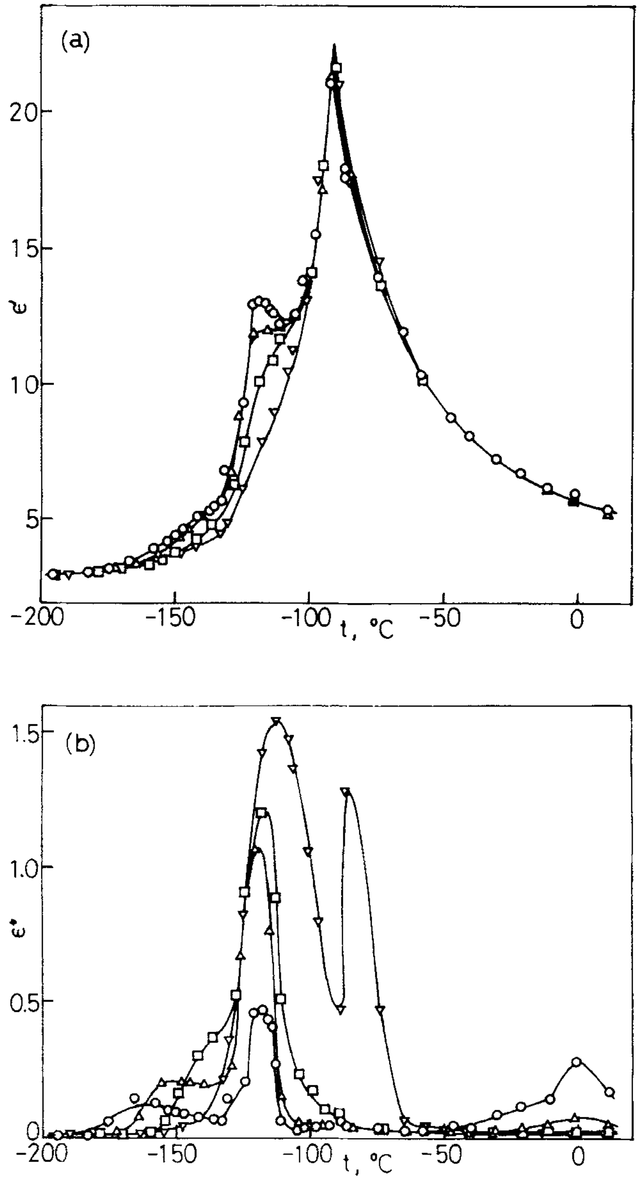

FIGURE 1 Temperature dependences of dielectric constant, ε', (a) and the loss, ε", (b) along c^*-axis in a CTFP single crystal on the second cooling process at several frequencies. ○: 110 Hz, Δ: 1 kHz, □: 10 kHz, ∇: 100 kHz.

$-130\,^\circ$C.[4] Plots of $1/\epsilon'$ versus temperature for the peak at $-94\,^\circ$C are fairly well fitted to the Curie-Weiss law for a second order ferroelectric phase transition (the Curie constant in the lower temperature side and that in the higher temperature side were about 4.1×10^2 and 9.0×10^2, respectively), in spite of the fact that neither spontaneous polarization nor pyroelectric current was observed. The bumpy peak near $-120\,^\circ$C is clearly observed in the lower frequencies, and the value of ϵ' falls discontinuously near $-130\,^\circ$C with decreasing temperature. This result suggests that the $-130\,^\circ$C transition is a first order one. Our recent results on thermal expansion of lattice dimensions along the three principal axes[7] and on the dependence of modulation wave number on temperature[4] also support the above dielectric results that the transitions at -95 and $-130\,^\circ$C obey a second order phase change and a first order one, respectively. In the ϵ''-temperature curve, three peaks are observed near 0, -80 and $-120\,^\circ$C, and one dielectric relaxation around $-150\,^\circ$C, at 110 Hz. The peak near $-120\,^\circ$C shifts very gradually to lower temperatures with decreasing frequency, and disappears abruptly near $-130\,^\circ$C. Therefore, this peak is considered to be a dielectric relaxation in Phase II. The remarkable peak near $-80\,^\circ$C is observed only in a high frequency of 100 kHz, but does not exist on the first cooling process (see Figure 5(b)). In another run, the thermal processes are repeated up to the third cooling process in the temperature range from $-185\,^\circ$C to room temperature, and the absence of the peak at $-80\,^\circ$C in the first cooling process from room temperature to $-185\,^\circ$C is confirmed. This peak suggests that a phase transition exists near $-80\,^\circ$C in Phase I*. The peak near $0\,^\circ$C suggests the existence of a phase transition near $0\,^\circ$C in the normal phase.

Dependences of ϵ' and ϵ'' on temperature in the first cooling process along the *a*-axis at several frequencies are shown in Figure 2. The two phase transitions at -130 and $-95\,^\circ$C are also seen in the ϵ'-temperature plots. The changes of ϵ', however, are much depressed, compared with those of the c^*-axis. In the ϵ''-temperature curve, no change is observed which is associated with the phase transitions, but one relaxation is observed near $-150\,^\circ$C at 110 Hz.

Figure 3 shows the temperature dependences of ϵ' and ϵ'' on the first cooling process along the *b*-axis. In the ϵ'-temperature plots, only a very small peak near $-94\,^\circ$C is observed, although the values of ϵ'' show some changes around -130, -95 and $0\,^\circ$C which may be related to the transitions at -130, -95 and $0\,^\circ$C, respectively.

Thus the ϵ'-temperature plots along the three principal axes of the CTFP single crystal show the existence of the two phase transitions at

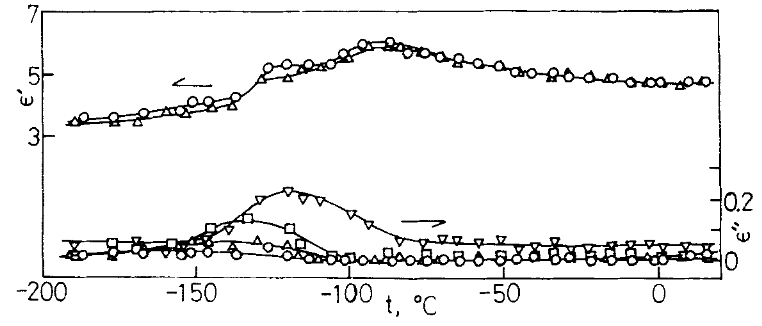

FIGURE 2 Temperature dependences of dielectric constant, ϵ', and the loss, ϵ'', along *a*-axis in a CTFP single crystal on the first cooling process at several frequencies. ○: 110 Hz, △: 1 kHz, □: 10 kHz, ▽: 100 kHz.

-95 and $-130\,^{\circ}$C as the characteristic peaks of ϵ'. The transition at $-150\,^{\circ}$C, however, was not seen from the above dielectric results, which was found as a small change in modulation wave number-temperature plots in the previous X-ray work.[4] The peaks of ϵ' corresponding to the two transitions at -95 and $-130\,^{\circ}$C appear most strongly along the c^*-axis and weakly along the *a*-axis, but are much depressed along the *b*-axis. This anisotropy of ϵ' should be closely connected with the oriented direction of dipole moments in CTFP

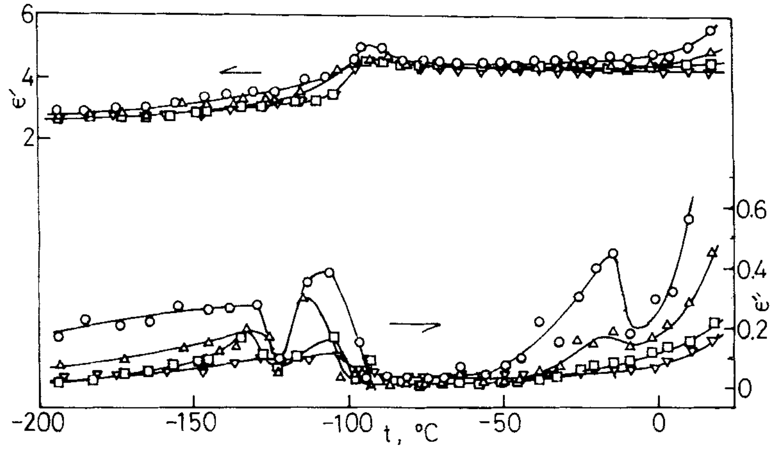

FIGURE 3 Temperature dependences of dielectric constant, ϵ', and the loss, ϵ'', along *b*-axis in a CTFP single crystal on the first cooling process, at several frequencies. ○: 110 Hz, △: 1 kHz, □: 10 kHz, ▽: 100 kHz.

crystals by an applied electric field. CTFP molecules have mainly two dipole moments in carbonyl and terminal (CF_2H) groups. Our preliminary X-ray diffraction studies suggest that the lathlike CTFP molecules in the unit cell arrange antiparallel each other, and that the angle between the long molecular axis and the *a*-axis is estimated to be about 30°. Since the dipole vectors of the two polar groups make an angle with the long molecular axis, we can confidently presume that the dipole moments orient predominantly towards the *c**-axis through the modulation wave motion by an applied electric field. Thus the dielectric behavior of CTFP crystal can be understood as follows: The transition at −150°C was not dielectrically observed, and this suggests that the polar groups are not associated with the structural change at the transition. The dielectric relaxation, however, is observed around −150°C at 110 Hz along both the *a*- and *c**-axis. The activation enthalpy and entropy were estimated to be 25 kJ/mol and 39 J/mol · deg, respectively from the Arrehenius plots in Figure 4. So,

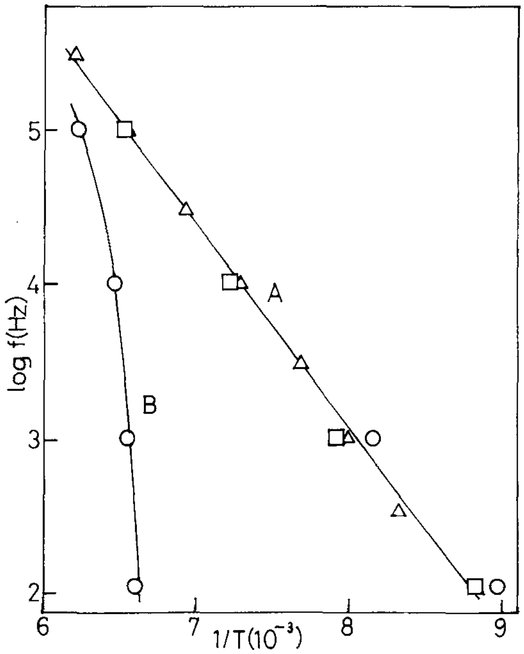

FIGURE 4 Arrhenius plots for the two dielectric relaxations. A: for the dielectric relaxation in the lower temperature range. B: for the dielectric relaxation in Phase II. ○: *c**-axis in the single crystal on the second cooling process, □: *a*-axis in the single crystal on the first cooling, Δ: in polycrystalline state (Ref. 2).

a local molecular motion of the small polar groups, possibly including the $-CF_2H$ group, may be responsible for the relaxation. This local molecular motion might not be concerned with the transition, since the relaxation behavior shows no change at the transition temperature. Recently, using differential scanning calorimetry from room temperature to $-70\,^\circ C$,[8] X-ray diffraction measurements at room temperature[8] and dielectric measurements from room temperature to $-190\,^\circ C$,[9] we studied phase transitions of a homologous series of cholesteryl ω-monohydrofluoroalkanoates $[C_{27}H_{45}OCO(CF_2)_n CF_2H$, where $n = 1, 3, 5, 7$ and $n = 1$ is CTFP]. The crystal systems are monoclinic for $n = 1, 5, 7$ and orthorhombic for $n = 3$ at room temperature, and the lattice dimensions are considerably different among the samples. Furthermore, no phase transition was observed for $n = 3$ and 7 in the crystalline state, and one phase transition existed in $n = 5$, so far as we knew from the studies. In all the sample, nevertheless, similar dielectric relaxations were observed in almost the same temperature range. This finding supports the hypothesis that the relaxation is due to a local molecular motion of polar groups and is independent of the phase transitions.

In phase II, the characteristic peaks of ϵ' and ϵ'' appear near $-120\,^\circ C$ as described already, and may be caused by a dielectric relaxation, since the peaks shift very gradually to higher temperatures with increasing frequency (see Figures 1(a) and (b)). Arrhenius plots for the dielectric relaxation are shown in Figure 4. Clearly the plots are non-linear, and become steeper as temperature decreases and approaches the $-130\,^\circ C$ transition temperature. These results suggest that the molecular motion responsible for the relaxation in phase II begins to be frozen near the $-130\,^\circ C$ transition temperature and disappears at $-130\,^\circ C$. Therefore, the dielectric relaxation is inferred to be closely related to the incommensurate wave motion in phase II. When the temperature is increased to $-94\,^\circ C$, the dipole moments begin to align with the applied electric field, especially along the c^*-axis, and the value of ϵ' indicates a maximum of about 21 along the c^*-axis at $-94\,^\circ C$, the INC–N phase transition temperature. As the temperature is increased above $-94\,^\circ C$, the value of ϵ' decreases, since the arrangement of dipole moments is distributed by thermal fluctuation of the molecules in the paraelectric phase. Accordingly, the peak of ϵ' behaves seemingly as a second order ferroelectric transition on the Curie–Weiss plots. But no evidence for ferroelectricity was found at all from spontaneous polarization and pyroelectric current measurements. This finding is of course reasonable, since the transition is an INC–N phase transition. It seems to be valid that the dipole

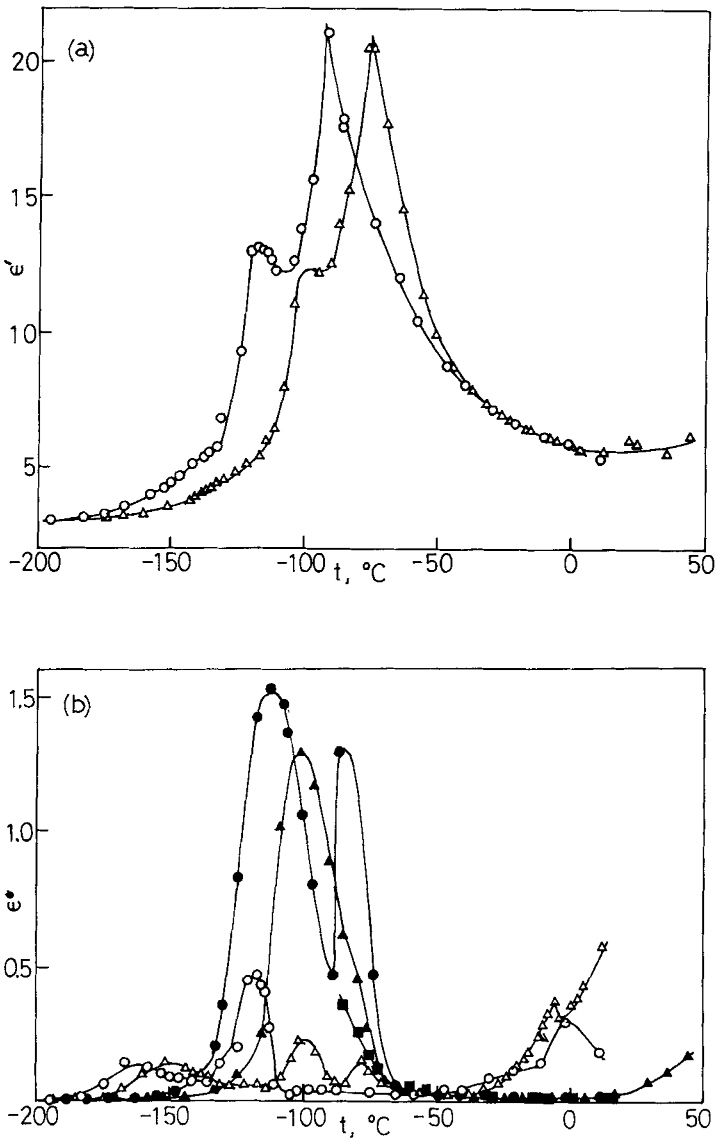

FIGURE 5 Temperature dependences of dielectric constant, ε', (a) and the loss, ε'', (b) along c^*-axis in a CTFP single crystal on a few thermal processes at 110 Hz. ○: the second cooling, Δ: the second heating, at 100 kHz, ■: the first cooling, ●: the second cooling, ▲: the second heating.

vectors connected with the −130 and −95 °C transitions are mainly in the direction of c^*-axis. More detailed discussion of course must wait the determination of more detailed crystal structure of CTFP by X-ray diffraction. This work is in progress in our laboratory.

The successive phase transitions in CTFP crystals change by thermal history of the crystals, as already described. Changes of the temperature dependences of ϵ' and ϵ'' along the three principal axes with thermal history are shown in Figures 5, 6 and 7, respectively. Along the c^*-axis, the two transitions at −130 and −95 °C are observed in the ϵ'-temperature curve (Figure 5(a)), although the transition temperatures in the heating process shift by about 18 °C to higher temperatures than those in the cooling process. In the ϵ''-temperature plots (Figure 5(b)), noticeable differences are observed in the −80 °C transition between thermal processes. The value of ϵ'' undergoes no change at −80 °C on the first cooling process, but shows a distinct peak at high frequencies in the crystal which has undergone the first cooling run once. Namely, the peak of ϵ'' at −80 °C occurs on every thermal processes except for the first cooling process. The dielectric behavior in the three phases below −95 °C was almost the same in all thermal processes. This behavior is consistent with the fact that the incommensurate structure in phase II undergoes no change in the thermal history and that molecular motions related to the crystal

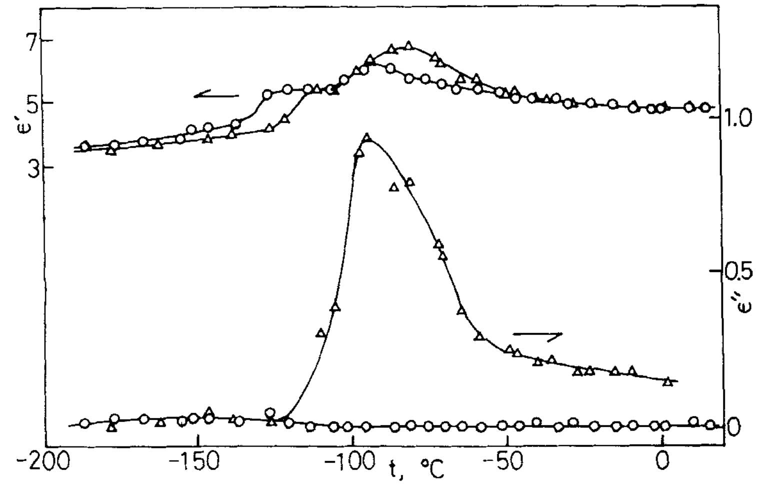

FIGURE 6 Temperature dependences of dielectric constant, ϵ', and the loss, ϵ'', along a-axis in a CTFP single crystal on two thermal processes at 110 Hz. ○: the first cooling, △: the first heating.

structure are dielectrically inactive in the two phases below −130 °C. Therefore, the transformation from the as-grown crystals to the metastable crystals is dielectrically visualized only by the transition at −80 °C, and seems to occur even in the normal phase (Phase I) during increasing temperature after the first cooling process was run up to −70 °C.

Along the *a*-axis, there are also observed two peaks of ϵ' corresponding to the transitions at −130 and −95 °C on the two thermal processes (see Figure 6). The peaks of ϵ' undergo thermal hysteresis

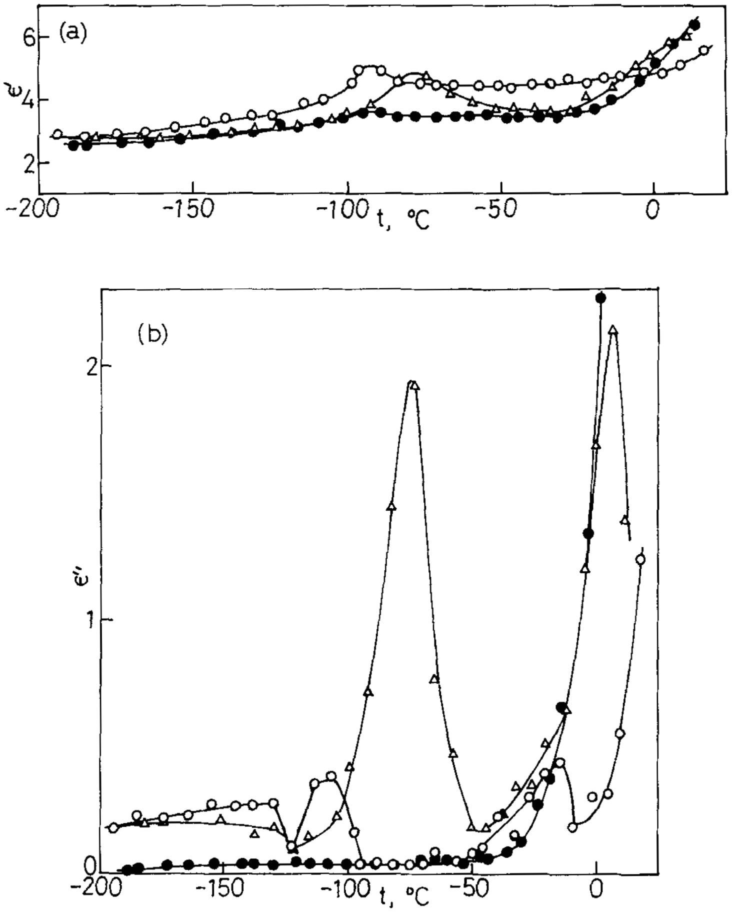

FIGURE 7 Temperature dependences of dielectric constant, ϵ', (a) and the loss, ϵ'', (b) along *b*-axis in a CTFP single crystal on three thermal processes at 110 Hz. ○: the first cooling, Δ: the first heating, ●: the second cooling.

with the temperatures exhibiting the peaks in the cooling process being lower by about 18 °C than those in the heating process, similar to that along the c^*-axis. In the ϵ''-temperature plots (Figure 6), the dielectric relaxations around −150 °C undergo no change with the thermal process, but a large peak of ϵ'' is observed near −95 °C on the first heating process. This peak may not be inherent and may originate in an ionic conduction by impurities near the transition, since the peak of ϵ'' decreases with increasing frequency. Along the b-axis, one very small peak of ϵ' is also observed, which corresponds to the transition at −95 °C, and has a similar thermal hysteresis to that of the c^*- and a-axes (Figure 7(a)).

Recently the existence of thermal hysteresis in the incommensurate-commensurate phase transition has been found in several inorganic compounds: rubidium tetrahalozincate crystals (Rb_2ZnX_4, X = Br, Cl),[10-12] barium sodium niobate ($Ba_2NaNb_5O_{15}$)[13] and potassium lead copper nitrite ($K_2PbCu(NO_2)$)).[14] In Rb_2ZnX_4 crystals, the thermal hysteresis has been studied mainly by dielectric measurements. The INC-C transition was observed as the peak of ϵ' in the ϵ'-temperature curve, and the transition temperature in the heating process is higher than that in the cooling process. Hamano *et al.*[11,12] indicated that the thermal hysteresis exists even in the INC phase which had no experience of a C–INC phase transition, and so that the thermal hysteresis is caused by crystal defects such as impurities which pin the incommensurate wave and hinder the crystals from reaching thermal equilibrium. This thermal hysteresis of Rb_2ZnX_4 crystals is seemingly analogous to that of the two peaks of ϵ' at −120 and −95 °C in the incommensurate phase (Phase II) of CTFP crystals, although the mechanism for the latter thermal hysteresis is not clarified yet. Schneck and Denoyer[13] found the existence of thermal hysteresis in the incommensurate phase of $Ba_2NaNb_5O_{15}$ crystals from X-ray diffraction studies. In this case, the values of the modulation wave, δ, in the INC phase were much larger in the cooling process, compared with those in the heating process. The change of phase transition with the thermal history in CTFP crystals seems to be rather similar to the thermal hysteresis in the incommensurate phase of $Ba_2NaNb_5O_{15}$ crystals. However, the change of the phase transition by the thermal history in CTFP crystals has two important features: The crystal transformation depend on the thermal history, and the metastable crystals revert to as-grown crystals by storing the metastable crystals at room temperature. CTFP is a macromolecular organic molecule and this is considered to cause the characteristic thermal hysteresis in the successive phase transitions.

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