X-ray Study on the Successive Phase Transition in Cholesteryl 2,2,3,3-Tetrafluoropropanoate (CTFP)

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Abstract
These studies on phase transition and crystal structure in a single crystal of CTFP by X-ray diffraction in the temperature range 88 to 293 K show that CTFP undergoes successive phase transitions at about 123, 143 and 178 K and that the existence of another phase transition at about 168 K is possible. In the lowest-temperature phase, various commensurate and incommensurate structures were found. The appearance of the structure depends on storage duration at 293 K after undergoing the successive phase transitions. The original crystal, just crystallized from acetone solution, showed commensurate structure of which the modulation wave number, \( \delta \), is 0.20. The samples stored for a week and a month were both incommensurate. However, the crystals stored for two months were commensurate (\( \delta = 0.20 \)). Therefore, the storage duration of two months is a relaxation time long enough to recover the genuine structure. In the other temperature phases below 178 K, the crystals were all incommensurate. Consequently, the complicated structural change of CTFP crystals during storage is now well understood as a thermal relaxation phenomenon.

Introduction
From earlier dielectric measurements (Yano, Nabata & Aoki, 1982) in a polycrystalline state of CTFP (\( \text{C}_{27}\text{H}_{45}\text{OCOCF}_{2}\text{CF}_{2}\text{H} \)), it was found that CTFP crystals undergo an unusual phase transition near 173 K. Recently, the present authors clarified (Nakamura, Yoshimura, Shimaoka & Yano, 1982) by the preliminary X-ray diffraction studies of a single crystal that this transition at 179 K was an incommensurate-paraelectric phase transition; the CTFP crystal was monoclinic and the space group was either \( P2_1 \) or \( P2_1/m \) at 298 K; at 88 K many satellite reflections were observed along the \( b^* \) direction and the wave number of modulation, \( \delta \), was about 0.17.

The purpose of this paper is to report the results of a detailed X-ray study in the temperature region 88 to 293 K in CTFP single crystals. The existence of four transitions, so-called successive phase transitions, and the influence of the thermal history of the single crystal on these transitions are discussed.

Experimental
Specimen
CTFP was synthesized by an esterification of cholesterol and 2,2,3,3-tetrafluoropropanoic acid. Details of the synthesis are described in the previous paper (Nakamura, Yoshimura, Shimaoka & Yano, 1982). Single crystals of CTFP were grown by a very slow evaporation method from acetone solution.

Apparatus
X-ray measurements were performed by taking precession photographs with Ni-filtered Cu \( K\alpha \) radiation generated by RU-200 of Rigaku Denki Company. For the measurements in the lower temperature region, the sample was cooled and held at the necessary temperature within \( \pm 1 \) K by the newly designed cold-nitrogen gas-flow system (Yoshimura, Tsuda & Shimaoka, 1982).

Measurements
The X-ray studies of the CTFP crystal were serially carried out as follows: the virgin sample just crystallized from acetone solution was cooled to 88 K...
within about 10 min, and the X-ray diffraction photographs were taken on heating at temperatures between 88 and 293 K. This is the first running cycle and is denoted by run I. After run I, the sample was stored for a week at room temperature, 293 K. Thenceforth the sample was cooled again to 88 K within about 10 min, and run II was executed in the same way as run I. Runs III and IV were conducted in turn. The difference between runs II, III and IV is only in storage durations at 293 K after run I was performed, that is, a week, a month and two months for runs II, III and IV, respectively.

Results and discussion

As reported in our previous paper (Nakamura, Yoshimura, Shimaoka & Yano, 1982), the CTFP crystal was monoclinic and exhibited many satellite reflections at \((h k \pm \delta l)\) in the reciprocal lattice in the precession photographs taken at 88 K. In the present work, we also observed many similar satellite reflections in the reciprocal lattice at temperatures below 178 K. However, the value of \(\delta\) changes considerably depending on the temperature and the thermal history of the crystal. Fig. 1 shows the temperature dependence of \(\delta\) for the CTFP crystal for the four runs.

In run I, \(\delta\) is 0.20 in the temperature range 88 to 123 K, and decreases very gradually to about 0.195 with increasing temperatures from 123 to about 143 K. Then, after the value of \(\delta\) falls abruptly to about 0.18 at 143 K, it descends almost continuously to 0.14 at about 178 K. However, the \(\delta\)-temperature plots seem to indicate a small bend around 168 K, which indicates the possibility of the existence of another phase transition. The discontinuous change of \(\delta\) at 143 K suggests that the transition is first order, although the 178 K transition may be second order as described in the previous paper (Nakamura, Yoshimura, Shimaoka & Yano, 1982).

On the other hand, the intensities of the satellite reflections are weaker with increasing temperature, and the reflections disappeared at 178 K. Above 178 K, however, very weak diffuse scattering was still observed. This diffuse scattering becomes gradually weaker with further temperature increase from 178 K, but still remains faintly even at room temperature, 293 K. Consequently, in run I, the \(\delta\)-temperature relationships indicate that the CTFP crystal undergoes successively commensurate–incommensurate (123 K), incommensurate–incommensurate (143 K) and incommensurate–paraelectric (178 K) phase transitions with increasing temperature from 88 K. The transition at 178 K corresponds to that reported previously.

In runs II and III, the \(\delta\)-temperature plots in Fig. 1 indicate the existence of successive phase transitions at about 123, 143, 178 and presumably 168 K, similar to those in run I. However, there are apparently some difference in the values of \(\delta\) below 143 K among runs; the values of \(\delta\) at 88 K are approximately 0.20, 0.18 and 0.19 for runs I, II and III, respectively, and at 143 K, 0.195, 0.18 and 0.19. The existence of the 123 K transition is shown by a small peak in the \(\delta\)-temperature curve and the maximum of \(\delta\) at the peak was estimated to be about 0.19 for run II. On the other hand, above 143 K, temperature dependences of \(\delta\) for runs II and III are the same as those for run I, as is seen in Fig. 1. Thus, the successive phase transitions in runs II and III consist of incommensurate–incommensurate (123 K), incommensurate–incommensurate (143 K) and incommensurate–paraelectric (178 K) phase transitions, although the values of \(\delta\) below 143 K in runs II and III are appreciably different.

Plots of \(\delta\) versus temperature for run IV are also shown in Fig. 1; the dependence of \(\delta\) on temperature is almost the same as that for run I in a wide temperature range, 88 to 178 K. This means that the crystal structure of each phase in run IV is the same as that of run I, the original crystal, and that the crystal in run IV undergoes successive phase transitions in the same way as in run I.

Thus, the successive phase transitions of CTFP crystals were affected by the thermal history of samples. In spite of the fact that all samples undergo the successive phase transition at the same temperatures, 123, 143 and 198 K, the differences in the wave number of modulation are clearly observed in the lower temperature phases below 143 K. These differences can be considered as the result of the duration stored at room temperature, after the original sample undergoes the successive phase transitions. For example, the value of \(\delta\) at 88 K changes from 0.20, that of run I, to 0.18 for a week’s storage and to 0.19 for a month’s, and returns to 0.20 for two months’. These changes of \(\delta\) by the storage duration should

![Fig. 1. Temperature dependence of modulation wave number, \(\delta\).](image-url)
be reflected by those of the crystal structure at 293 K. Moreover, the lattice dimensions change with the storage duration, although the crystal system is monoclinic for all crystals. For instance, the lattice dimensions at room temperature were $a = 12.44(1)$, $b = 9.27(1)$, $c = 13.30(1)$ Å and $\beta = 106.0(1)^\circ$ for the original crystal, and $a = 12.45(1)$, $b = 9.33(3)$, $c = 13.32(1)$ Å and $\beta = 106.2(1)^\circ$ for a week's storage sample (type II). The relation between phase transition, crystal structure and thermal process is schematically shown in Fig. 2. Here, types I, II, III and IV signify the types of crystal corresponding to run numbers, although type I is actually equal to type IV. According to the above results, the mechanism of the thermal history of the crystal structure is considered to be as follows. The original crystal is stable and changes to a metastable structure by undergoing the successive phase transitions on heating from 88 K. The stable state of the original crystal can be regarded as a strain-free state, but these metastable crystals hold strain. The strain can be considered to be small deviations of the lattice constants from those of the original crystal and these deviations were observed mainly in the $b$ axis and in the monoclinic angle, $\beta$. The metastable structures shift gradually to the original stable ones by storing the crystals at 293 K. Thus, the above process indicates that the sample recovers the strain-free stable state. Furthermore, CTFP is a macro-molecule, and closely resembles cholesteryl propionate ($C_{27}H_{45}OCOCH_2CH_3$) which is a typical material to exhibit a liquid-crystal phase. However, it had already been reported that CTFP exhibits no liquid-crystal phase (Yano, Nabata & Aoki, 1981). This fact suggests that the intermolecular interaction of CTFP should be larger than that of cholesteryl propionate. Therefore, considerably longer time is necessary for the sample to recover the strain-free stable state. Indeed, the metastable structures are transformed almost completely into the original crystal structure by storage for two months and the relaxation time for this thermal process is considered to be about two months at room temperature. The existence of a thermal relaxation process in the structural transformation is of course connected with the successive phase transition of CTFP, as already described in this paper.

For a more accurate understanding of this complicated phenomenon, the following are now in progress: structure analysis of type I, measurement of the temperature dependence of the lattice parameters, measurement of specific heat, observation of diffuse scattering and dielectric measurements. Some results already obtained support the above considerations and will be published elsewhere in the near future.

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References