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Studies of Thermal Expansion and Diffuse Scatterings in the Successive Phase Transitions of Cholesteryl 2, 2, 3, 3-Tetrafluoropropionate(CTFP) by X-ray Diffraction Method

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The thermal expansion measurements for a cholesteryl 2, 2, 3, 3-tetrafluoropropionate(CTFP) single crystal were made over a wide temperature range from 88K to room temperature by X-ray diffraction method. The results indicated that the CTFP crystals undergo successive phase transitions at about 123, 143, 167, 178 and 198K and that the existence of another phase transition at about 156K is suggested: The phase transitions near 123, 143, 167 and 178K correspond to the commensurate-incommensurate(IC), IC-IC, IC-IC and IC-normal phase transitions respectively, and the transition near 198K is a phase transition in normal phase. The existence of two types of X-ray diffuse scatterings associated with the phase transitions were found in this work. The molecular arrangement in the crystal and the mechanism for the successive phase transitions are discussed from the thermal expansion and diffuse scatterings data.

KEY WORDS: Cholesteryl 2, 2, 3, 3-tetrafluoropropionate(CTFP)/ Successive Phase Transition/ Thermal Expansion/

I. INTRODUCTION

Our recent X-ray diffraction and dielectric studies revealed that cholesteryl 2, 2, 3, 3-tetrafluoropropionate(CTFP) single crystal showed the successive phase transitions near 178, 143 and 123K[1~3], which originate in normal-incommensurate(IC), IC-IC and IC-commensurate phase changes, respectively. Furthermore, the existence of the transition near 167K was suggested[2]. The 143K transition is found to be a first order one from the discontinuous change in the modulation wave number-temperature plots[2] and the 178K transition is inferred to be a second order one from Curie-Weise plots of reciprocal of dielectric constant versus temperature[4].

The purpose of the present work is to investigate phase transitions and the mechanism in the CTFP crystals from the thermal expansion measurements of the lattice constants by X-ray diffraction method. A few coments on the crystal structure and the thermal motion associated with the modulated structures are presented from the X-ray diffuse scattering studies.

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II. EXPERIMENTAL

The untwinned and transparent CTFP single crystal was obtained by a very slow evaporation method from acetone solution[1]. The sample size used in this X-ray experiments was about 0.7×0.7×1.0mm.

The precession photographs were taken with Ni-filtered CuKα radiation generated by RU-200 of Rigaku Denki Company. The Laue photographs were taken with LiF-monochromated CuKα radiation. After the as-grown specimens were once cooled to about 88K within about 10 minutes, X-ray photographs were taken at various temperatures on heating. During taking the photographs, the temperature of the specimen was held within ±1K at the respective temperatures by the cold nitrogen gas flow system designed previously[5].

The lattice constants were determined by a travelling microscope with the accuracy of ±0.005mm directly from the precession photographs. Here, the reciprocal monoclinic angle, β^* is the angle between the a*- and c*-axes. Where, a* and c* mean the reciprocal lattice constants of a and c, respectively.

III. RESULTS AND DISCUSSION

The crystal structure of CTFP at room temperature is monoclinic, $P2_1$ or $P2_1/m$ with a=12.44(1), b=9.27(1), c=13.30(1)Å and β=106.0(1)° and contains two mole-

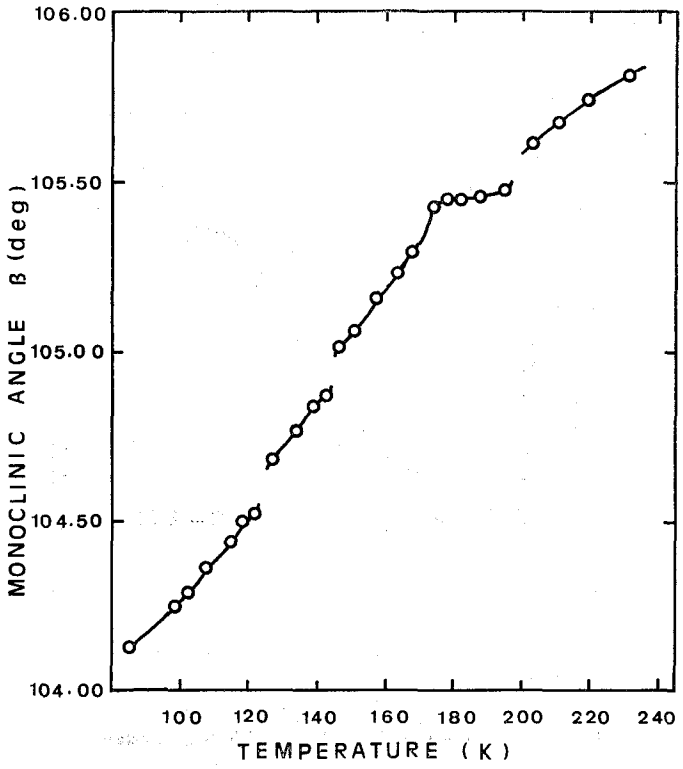

Fig. 1. Temperature dependence of monoclinic angle β.

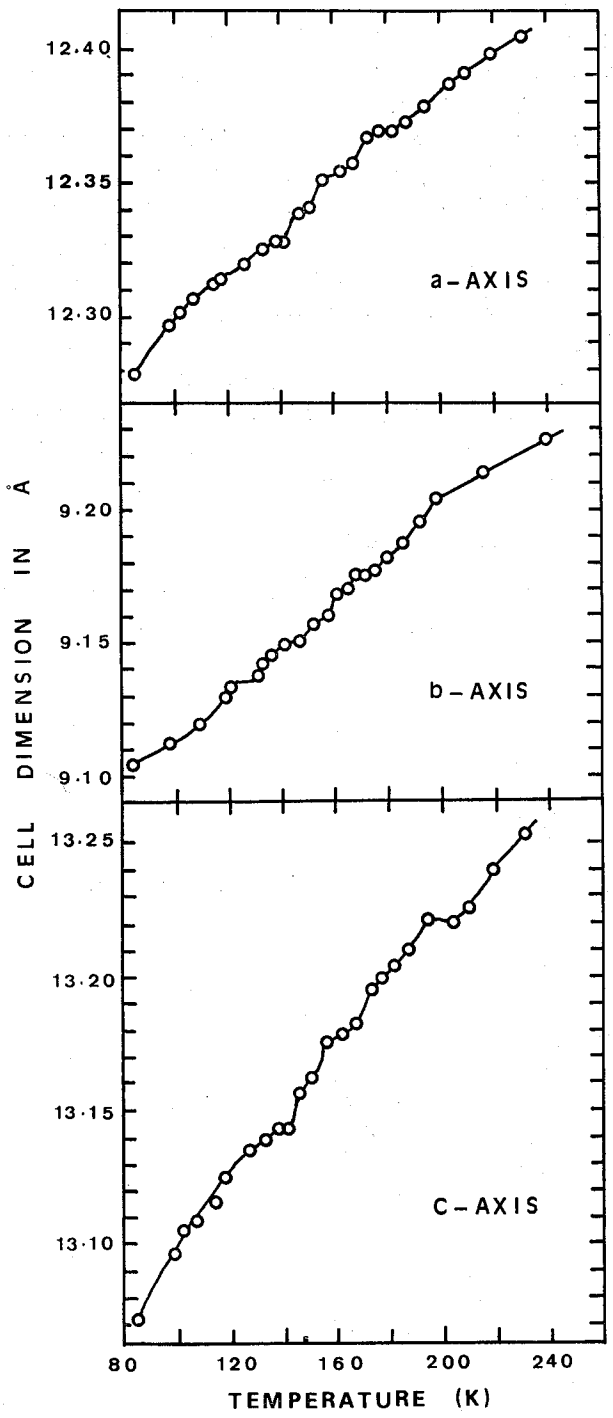

Fig. 2. Temperature dependence of lattice constants.

cules per unit cell[2].

Figures 1 and 2 show temperature dependences of lattice constants, β, and, a, b and c, in the CTFP single crystal, respectively. Here, the lattice constants at 88K are a=12.28(1), b=9.10(1), c=13.07(1)Å and β=104.1(1)°, which are of course smaller than those at room temperature. The β-temperature plots (Fig. 1) indicate clearly the existence of four phase transitions near 123, 143, 178 and 198K. These transitions except 198K correspond to the successive phase transitions reported in the previous paper[2]. The three transitions near 123, 143 and 198K are first order phase changes, while the 178K transition seems to be of a second order, since the former three transitions are seen as the discontinuous changes and the 178K transition is observed as a bend. On the other hand, in the plots of a, b and c versus temperature (Fig. 2), the changes corresponding to the four transitions near 123, 143, 178 and 198K are not so distinct as those in the β-temperature plots, but two bends appear at about 156 and 167K, which are not visualized in the β-temperature plots. In the modulation wave number-temperature plots in our previous study[2], the existence of the 167K transition was suggested, but the change near 156K was first observed in this work. The change may be phase transition point and it is of interest that the modulation wave number at 156K is approximately 1/6, which means that the crystal indicates just a commensurate phase near 156K.

Consequently, the six phase transitions found here are classified into the two groups, the transitions near 123, 143, 178 and 198K, and the transitions near 156 and 167K. The former transitions show the large change in the β-temperature plots and the latter ones are observed in the plots of a, b and c versus temperature. This finding, therefore, suggests that the transitions near 123, 143, 178 and 198K are mainly related to an intermolecular displacement of CTFP molecules in the a-c plane with changing temperature, and that the transitions near 156 and 167K occur as a result of an intermolecular change perpendicular to the a-c plane.

Thermal expansion of the lattice constants may be closely related to the crystal structure. The crystal structure of the CTFP has not been analyzed yet. However, the crystal structures of some cholesteryl alkanoates have been determined by several workers[6]. Molecular shapes of these compounds are regarded as rod-like ones which is associated with steroid ring and alkyl chain. The molecules arranged to form monolayers and crystal structures consist of the monolayers. Refering to the crystal structures of cholesteryl alkanoates, some molecular arrangement in the CTFP crystal is postulated from the diffuse scattering studies in the following paragraph.

Figure 3 shows Laue photographs of the CTFP crystal at room temperature. There are observed two types of the diffuse scatterings, spots and streaks. The diffuse spots are observed as large ellipsoids on the b*-axis (Fig. 3(a) and (b)), and this indicates that the CTFP crystal is constructed of layers perpendicular to the b-axis[7,8]. Furthermore, the narrow diffuse streaks intersect the a*-axis (Fig. 3 (a) and (c)), and the diffuse scatterings distribute as sheets in the reciprocal space. Therefore, the CTFP molecules would be rod-like ones and may orient perpendicular to the streaks[7,8]. In other words, the rod-like CTFP molecules are arranged parallel to each other in the layers. Here, the angle between the long axis of the molecule and the a-axis was esti-

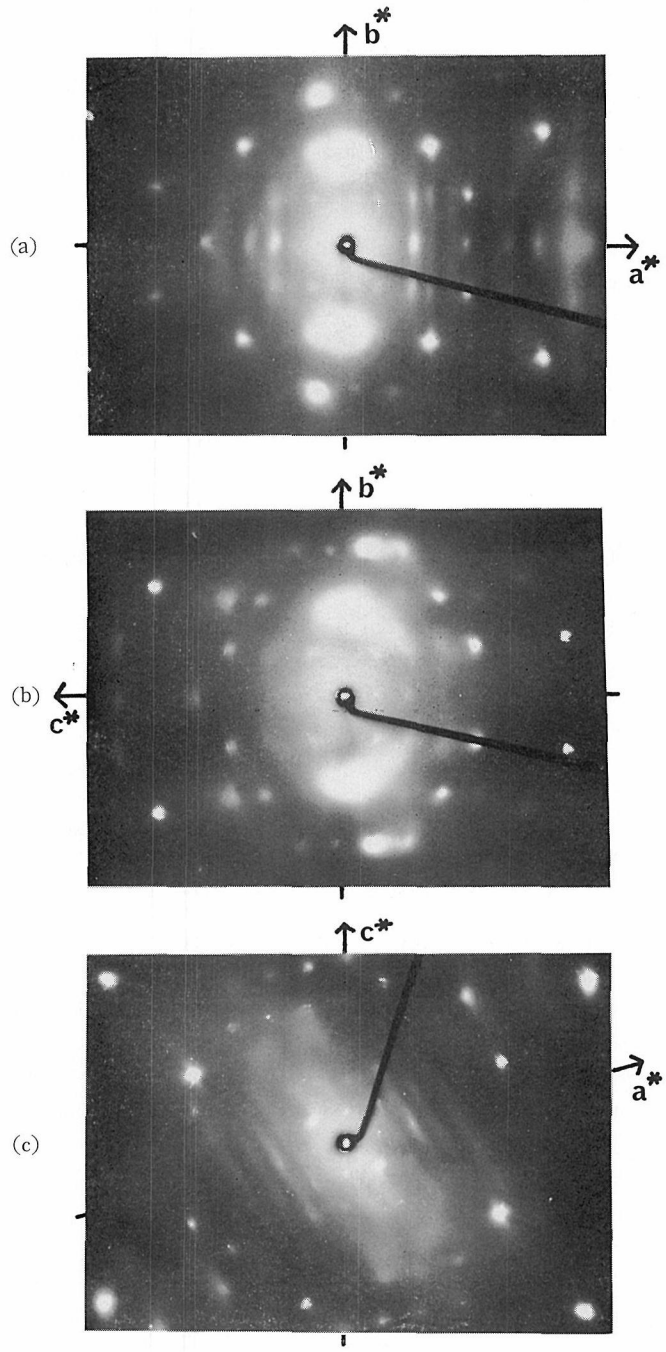

Fig. 3. Laue photographs taken by LiF-monochromated CuKα radiation at room temperature (positive prints). Incident X-ray beam is parallel to c-, a- and b-axes for (a), (b) and (c), respectively.

mated to be about 30°. Since the thermal vibration of the rod-like rigid CTFP molecules in the layer can take in the normal direction to the long molecular axis, two types of the thermal vibrations can exist, one in the parallel direction to the b-axis and the other in the a-c plane. The former may be reflected in the thermal expansion along the b-axis, and so may be related to the modulated structures. On the other hand, the latter should affect most strongly the change of monoclinic angle, β. Here, it is noted that the change of β with temperature is attributable to a movement of the a-axis going away from the c-axis.

The present diffuse scattering data indicate the existence of the thermal motion which may be closely connected with the modulated structures in the CTFP crystal. More detailed studies of the diffuse scatterings should serve to elucidate the mechanism of the successive phase transitions and to help crystal structure analysis.

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