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# Temperature dependence of pitch and twist elastic constant in a cholesteric to smectic A phase transition

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To understand chirality in cholesteric (Ch) liquid crystals, we performed an experimental study on the Ch–smectic A (SmA) transition of a cholesteric liquid crystal. By studying the reflection spectrum at zero field and at the critical electric field used to unwind the helical structure, we were able to measure the helical pitch  $P$  and the twist elastic constant  $K^{22}$  in the Ch phase. As the temperature was lowered toward the Ch–TGB phase transition, the helical pitch and twist elastic constant diverged. The results support the model that short range SmA forms in the Ch phase. When the results were fitted by power-law temperature dependence, the exponent for  $P$  was 0.78 and the exponent for  $K^{22}$  was 1.36.

## 1. Introduction

Cholesteric (Ch) liquid crystals possess long range orientational order but no positional order as nematic liquid crystals [1]. The molecules are locally aligned, on average, along a common direction called the director  $\mathbf{n}$ . There is, however, a spontaneous twist about an axis (helix), which is normal to the director. The distance over which the director rotates  $360^\circ$  is called the pitch  $P$ . The chirality  $q$  of a Ch liquid crystal is defined by  $q = 2\pi/P$ . Two of the factors affecting the pitch are molecular structure and temperature. The influence of temperature is more profound in Ch liquid crystals which exhibit smectic A (SmA) at lower temperatures [2–5]. The Ch to SmA phase transition is of great fundamental and practical interest. For fundamental science, the transition is analogous to the superconducting to normal transition in metals [6]. The use of cholesteric materials for laboratory exploration is convenient because of their low experimental cost and easy experimental observation. An understanding of the behaviour of the pitch in the transition also helps us to understand the effect of molecular structure on the helical structure. In practical applications, the transition is used in thermochromatic devices such as thermometers and temperature field detectors [2].

Experimentally it has been observed that the pitch increases dramatically when the temperature is lowered toward the Ch–SmA transition [3, 4]. To explain the anomalous behaviour of the pitch, Keating and Botcher

proposed microscopic models, where anharmonic rotational vibrations of molecules in the plane perpendicular to the helical axis were considered [7]. Although the theories explained the temperature dependence of pitch near the Ch–SmA transition, the proposed vibration was not verified by light scattering experimental results [8]. Nevertheless, it is commonly believed that pretransition exists in the cholesteric phase of materials which have the SmA phase at lower temperatures. At temperatures near the Ch–SmA transition, short range SmA order forms in the Ch phase. In the SmA phase, the pitch is infinitely long and it is impossible to have twist deformation because of  $\nabla \times \mathbf{n} = 0$ . Therefore the short range temporary SmA ordering causes the pitch  $P$  and the twist elastic constant  $K^{22}$  to increase dramatically as the temperature is lowered toward the Ch–SmA transition. Based on mean field theory, Alben predicted that  $K^{22}/P$  was approximately a constant near the transition temperature [9], that is,  $K^{22}$  and  $P$  were described by the same power-law.

There are several theoretical studies on the twist elastic constant in the nematic–SmA (N–SmA) transition and the nematic–SmC (N–SmC) transition. De Gennes predicted that the increment of  $K^{22}$  was governed by  $\delta K^{22} \propto (T - T^*)^{-0.5}$  in the N–SmA transition and  $\delta K^{22} \propto (T - T^*)^{-0.75}$  in the N–SmC transition [10]. Chen and Lubensky also predicted  $\delta K^{22} \propto (T - T^*)^{-0.5}$  in the N–SmA transition but  $\delta K^{22} \propto (T - T^*)^{-1.0}$  in the N–SmC transition [11]. Chu and McMillan predicted  $\delta K^{22} \propto (T - T^*)^{-0.5}$  in the N–SmC transition [12]. It would be expected that the Ch–SmA transition is similar to

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the N–SmA transition. In experimental studies, usually only  $P$  was measured as a function of temperature; its temperature behaviour was assumed to be the same as that of the elastic constant  $K^{22}$  and it was then compared with theoretical predictions [5].

To verify the existing theories, we carried out an experimental study on the Ch–SmA transition of a cholesteric liquid crystal. We used reflective optical spectroscopy to monitor the change of the helical pitch  $P$  with temperature in the cholesteric phase. The voltage threshold to unwind the helical structure at various temperatures was also measured; we could thus derive the variation of the twist elastic constant  $K^{22}$  as a function of temperature. As the temperature was lowered toward the Ch–SmA transition, both the pitch and the elastic constant increased dramatically. Our results showed that  $K^{22}$  and  $P$  had different temperature behaviour. The increment of the twist elastic constant was governed by  $\delta P \propto (T - T^*)^{-0.78 \pm 0.04}$  while the increment of the pitch was governed by  $\delta K^{22} \propto (T - T^*)^{-1.36 \pm 0.12}$ .

## 2. Experiments and results

A cholesteric mixture was prepared, composed of 54.125 wt % 8CB, 12.16 wt % TM75A, 14.88 wt % chiral dopant CB15 and 18.84 wt % chiral dopant CE1. 8CB exhibited both nematic and SmA phases with the N–SmA transition at 33.5°C. TM75A was a thermochromic liquid crystal which exhibited Ch and SmA phases with the transition at 41.3°C. The chiral dopants CB15 and CE1 were added so that the mixture exhibited both Ch and SmA phases and had a positive dielectric anisotropy. All the materials were from Merck. The mixture was filled into cells made from two parallel glass plates with indium tin oxide (ITO) film as transparent electrodes. On top of the ITO, polyimide was coated and rubbed to generate homogeneous alignment of the liquid crystal. The thickness  $h$  of the cells was controlled by 5  $\mu\text{m}$  glass fibre spacers. In the experiments the sample was placed inside a temperature controller with the accuracy of 50 mK.

We studied the phase behaviour of the mixture under a polarizing optical microscope. The mixture was in the isotropic phase above 55°C; as the temperature was decreased, the mixture exhibited the following phase sequence.

$$\text{SmA-24.0-TGB-25.0-Ch-51.5-BP-55.0-I } (^{\circ}\text{C})$$

Microphotographs of the textures of the phases are shown in figure 1. The photograph of the Ch phase was taken in reflective mode and those of the TGB and SmA were taken in transmissive mode. In the Ch phase, the colour of the reflected light changed in a sequence of green, yellow, orange, and red to infrared red.

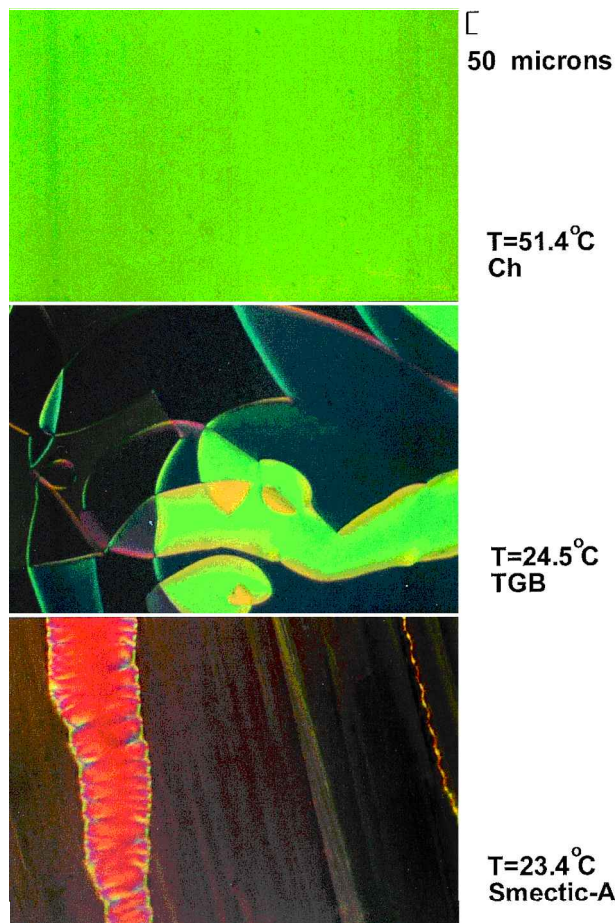


Figure 1. Microphotographs of the mesophases.

### 2.1. Temperature dependence of pitch

When the cholesteric liquid crystal was in the planar texture, it reflected coloured light. In the 5  $\mu\text{m}$  cell, there were more than 10 pitches and the reflection was saturated [13]. The central wavelength of the reflection band was  $\lambda_o = \bar{n}P = 1/2(n_e + n_o)P$ , where  $n_e$  and  $n_o$  are the extraordinary and ordinary refractive indices, respectively. The bandwidth was  $\Delta\lambda = \Delta n = (n_e - n_o)P$ . The reflection of the cholesteric liquid crystal was experimentally measured using an optical spectrometer connected to the optical microscope. Crossed polarizers were used in the measurement and thus the maximum reflectance was 25% when normalized to the incident light before the polarizer. Figure 2 shows an experimentally measured reflection spectrum where the maximum reflectance was reached.  $\Delta\lambda$  was calculated from the full width at the half maximum of the reflection peak.  $\lambda_o$  was determined by the middle point of the full width at half maximum. From the spectrum we obtained  $\Delta\lambda = 62 \text{ nm}$  and  $\lambda_o = 603 \text{ nm}$ . Assuming the average refractive index  $(n_e + n_o)/2$  to be 1.6, we obtained  $\Delta n = 0.164$  which was close to the birefringence (0.157) of

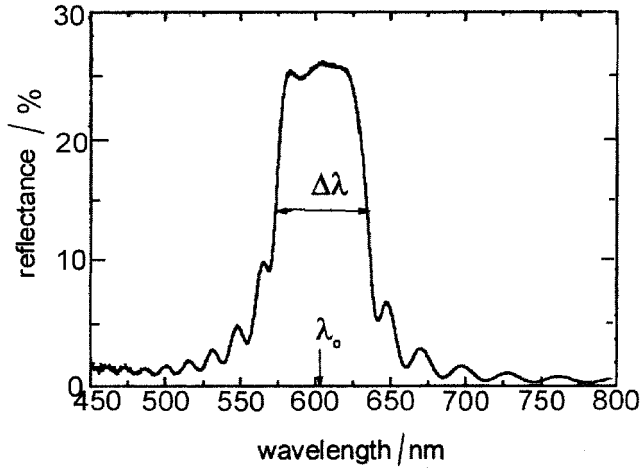


Figure 2. Experimentally measured reflection spectrum at 42°C.

8CB. Both  $n_o$  and  $n_e$  were temperature- and wavelength-dependent. The temperature dependence of  $n_o$  was smaller than that of  $n_e$ . Unfortunately we were unable to determine their values. As an approximation, we used the formula  $P = (\lambda_o - \Delta\lambda/2)/n_o$ , with  $n_o$  as a constant, to calculate the value of  $P$ .

In the Ch phase, under slow cooling (at  $-0.5^\circ\text{C min}^{-1}$ ), the colour of the reflected light of the sample varied from green to red. The measured central wavelength and bandwidth of the reflection peak of the cell are shown in figure 3. Because of the homogeneous anchoring, the pitch was quantized to satisfy the boundary condition;  $h/(P/2)$  was an integer. Thus the centre wavelength of the reflection peak remained constant over a certain temperature range and then jumped to a longer wavelength as the temperature was decreased. The calculated pitch is shown in figure 4 where  $n_o = 1.5$  was used.  $P$  increased dramatically when the temperature was lowered toward the SmA phase. The increment of the

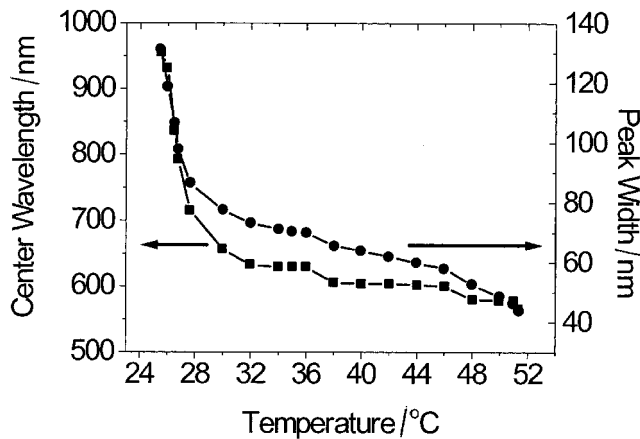


Figure 3. Central wavelength and bandwidth of the reflection peak of the material in the Ch phase vs. temperature.

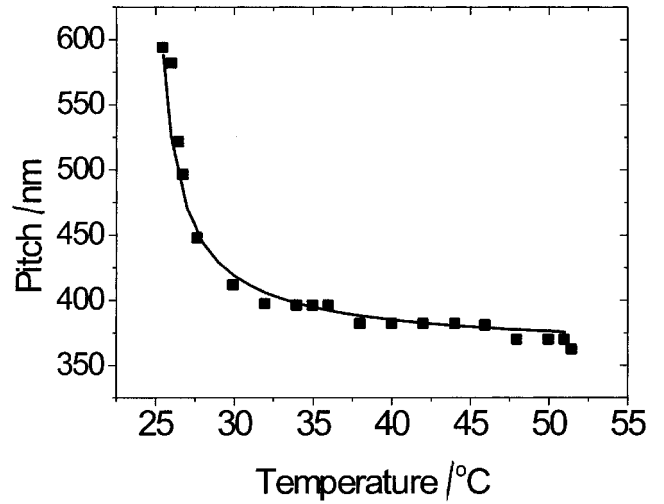


Figure 4. Pitch of the material in the Ch phase vs. temperature. Symbol: experimental data, solid line: fitting.

pitch with decreasing temperature was mainly attributed to the pretransitional SmA effect. We attempted to fit the experimental data by

$$P = P_o + \delta P = P_o + A(T^* - T)^{-\alpha} \quad (1)$$

where  $P_o$  was a constant and  $A(T - T^*)^{-\alpha}$  was the term contributed by the pretransitional effect. By  $\chi^2$  fitting, we obtained the fitting parameters:  $P_o = 358 \pm 8$  nm,  $A = 230 \pm 10$ ,  $T^* = 24.5 \pm 0.2^\circ\text{C}$  and  $\alpha = 0.78 \pm 0.04$ . This value of  $\alpha$  is close to the experimental result of Pindak [5].

## 2.2. Temperature dependence of the twist elastic constant

For a cholesteric liquid crystal with positive dielectric anisotropy ( $\Delta\epsilon > 0$ ), the helical structure can be unwound by applying an external electric field across the cell. The voltage threshold to unwind the helical structure is

$$V_c = \frac{\pi^2 h}{P} \left( \frac{K_{22}}{\epsilon_o \Delta\epsilon} \right)^{1/2} \quad (2)$$

where  $h$  is the cell thickness [1, 14].  $V_c$  can be experimentally measured and then  $K_{22}$  can be calculated. The experimentally measured voltage threshold required to unwind the helical structure is shown in figure 5. The applied voltage was an a.c. square wave with frequency 1 kHz.

We also measured  $\Delta\epsilon$ . In the experiment, we measured the capacitance  $C^P$  of the cell in the planar texture, where the liquid crystal director was parallel to the cell surface, with a low voltage applied across the cell:  $C^P = \epsilon_{\perp} A/h$ , where  $A$  was the area of the cell. We then measured the capacitance  $C^H$  of the cell in the homeotropic texture, where the liquid crystal director was

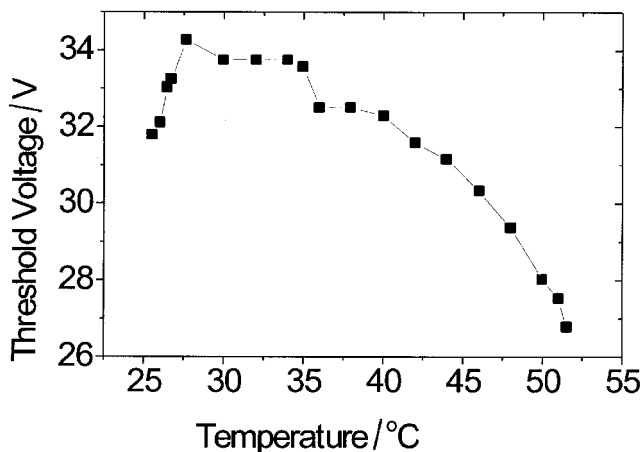


Figure 5. Threshold voltage required to unwind the helical structure vs. temperature. The solid line is a guide to the eye.

aligned perpendicular to the cell surface, with a high voltage applied across the cell:  $C^H = \epsilon_{\parallel} A/h$ . From  $C^P$  and  $C^H$ ,  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$  were calculated. In figure 6  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$  are shown as a function of temperature. In this experiment, the frequency was also 1 kHz.

Having measured the pitch  $P$  and  $\Delta\epsilon$ , we used equation (2) to calculate  $K_{22}$  from  $V_c$ . The calculated  $K_{22}$  as a function of temperature in the Ch phase is shown in figure 7. The elastic constant increased dramatically as the temperature was lowered toward the Ch–SmA transition. Figure 8 shows  $K_{22}/P$  as a function of temperature;  $K_{22}/P$  is clearly not a temperature-independent constant, in contradiction to Alben's prediction. One reason is that the changes of  $P$  and  $K_{22}$  caused by the pretransitional effect were really the ones considered in Alben's theory. In reality, the changes of  $P$  and  $K_{22}$  were not zero even where there was no SmA pretransitional effect. For  $P$ , the pretransitional effect was the dominant

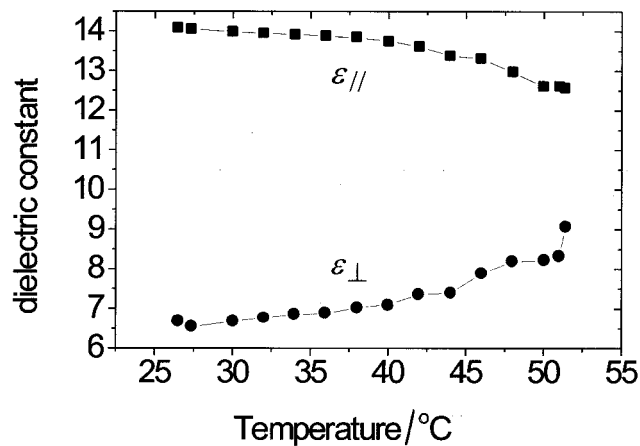


Figure 6. Dielectric constants vs. temperature. The solid lines are a guide to the eye.

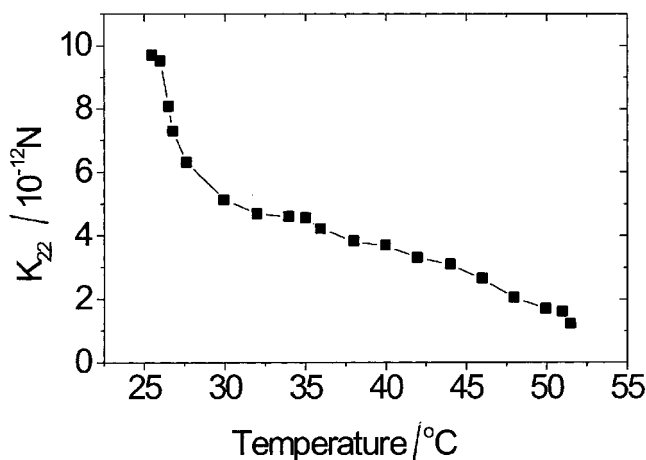


Figure 7. Twist elastic constant vs. temperature. The solid line is a guide to the eye.

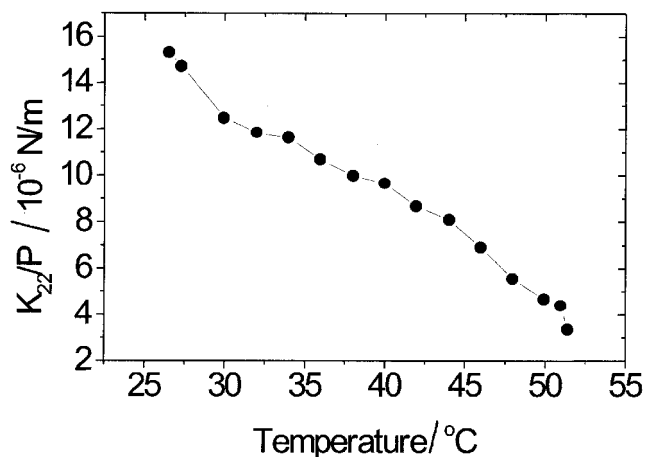


Figure 8. Ratio between  $K_{22}$  and  $P$  vs. temperature. The solid line is a guide to the eye.

factor causing the pitch to change. For  $K_{22}$ , even without the pretransitional effect, it would change with temperature because the nematic orientational order changed with temperature.

We now write  $K_{22}$  as  $K_{22} = K_{220} + \delta K_{22}$ , where  $\delta K_{22}$  is the part contributed by the pretransitional effect. Without the pretransitional effect,  $K_{22} \propto S^2$  (where  $S$  is the orientational order parameter); the temperature dependence of the elastic constant is described by [15, 16]

$$K_{220} = B(1 - \beta T)^{0.44} \quad (3)$$

where  $B$  and  $\beta$  are fitting parameters. We assume that at temperatures 12°C higher than the Ch–TGB transition, the pretransitional effect can be neglected for the reason discussed below. The experimental data and fitting by equation (3) in the temperature region from 38–52°C is shown in figure 9. The fitting parameters are  $B = 6.70$

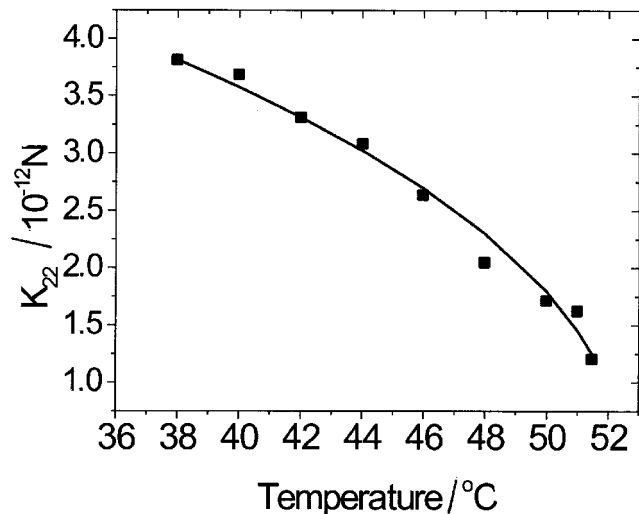


Figure 9. Twist elastic constant vs. temperature in the temperature region 38–51°C. The solid line is the fitting.

and  $\beta = 0.19 \times 10^{-1}$ . Then  $\delta K_{22}$  is obtained by subtracting  $K_{220}$  from  $K_{22}$  and is plotted as a function of temperature in figure 10. We fit  $\delta K_{22}$  by

$$\delta K_{22} = C(T^* - T)^{-\gamma} \quad (4)$$

and obtain the parameters:  $C = (6.31 \pm 0.80) \times 10^{-12}$ ,  $T^* = 24.3 \pm 0.2^\circ\text{C}$  and  $\gamma = 1.36 \pm 0.12$ . This exponent does not agree with any existing theories. Using these fitting parameters, at  $T = 38^\circ\text{C}$ ,  $\delta K_{22}$  is calculated to be  $0.18 \times 10^{-12}$  N which is very small when compared with  $K_{220}$ ; therefore the contribution to  $K_{22}$  by  $\delta K_{22}$  can be neglected when  $T \geq 38^\circ\text{C}$ . The temperature vs. pitch data shown in figure 4, where the pitch was almost a

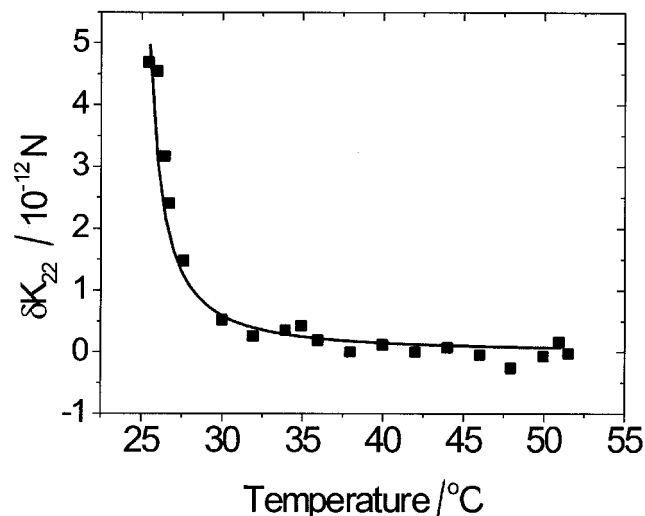


Figure 10. Increment of the elastic constant  $\delta K_{22}$  vs. temperature. The solid line is the fitting.

constant for temperatures higher than  $38^\circ\text{C}$ , also suggest that the pretransitional effect is negligible when the temperature is higher than  $38^\circ\text{C}$ .

### 3. Conclusion

We experimentally studied the cholesteric to smectic A phase transition. We measured the cholesteric pitch and the twist elastic constant  $K_{22}$  as a function of temperature near the transition. Both the pitch and the twist elastic constant increased rapidly as the temperature approached the transition temperature. This result supports the theory that strong fluctuation of SmA order exists in the cholesteric phase.  $K_{22}/P$  is, however, not a constant independent of temperature.  $P$  and  $K_{22}$  showed different behaviours when the temperature was lowered toward SmA. Their increments were governed by  $\delta P \propto (T - T^*)^{-0.78 \pm 0.04}$  and  $\delta K_{22} \propto (T - T^*)^{-1.36 \pm 0.12}$ , respectively, which did not agree with the existing theories. More theoretical work is needed in order to understand the role played by SmA fluctuations in the cholesteric phase.

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