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X-RAY INVESTIGATION ON TEMPERATURE DEPENDENCE OF THE TILT ANGLE IN FERROELECTRIC LIQUID CRYSTALS*

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The temperature dependence of the molecular tilt angle in a series of ferroelectric liquid crystals is deduced from X-ray diffraction measurement. The critical exponent β has been estimated from the experimental data. The non-classical value of β for the compounds lies in the range 0.36–0.41.

In recent years many researches on the smectic C^* phase and the smectic A – smectic C^* phase transition have been carried out both experimentally and theoretically.[1,2] This $A - C^*$ phase transition is considered as second order, and the order parameter in the smectic C^* phase can be written in the form

$$\theta = \theta_0 e^{i\varphi}, \tag{1}$$

where θ is the tilt angle of molecules with respect to the normal and the smectic layer, and φ characterizes the azimuthal direction of tilt. Such a form of the order parameter brings in a remarkable analogy to the wave function of superfluid helium – the order parameter of the transition to the superfluid phase. The helium analogy predicts that the tilt angle θ will vary according to the law $\theta \sim (T_c - T)^\beta$ with the critical exponent $\beta = 0.35$, while in mean field theory $\beta = 0.5$. Some works have been presented to explain the non-classical behavior of the tilt angle,[2,3] however, this property has not been well understood yet. In this paper we report the temperature dependence of the tilt angle measured by X-ray diffraction in a series of chiral liquid crystals, and discuss the non-classical character of the critical exponent β.

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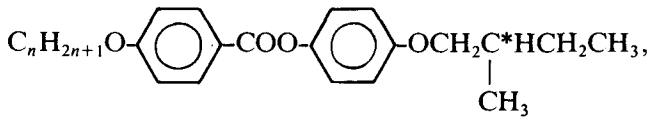
The compounds used in this experiment are optically active esters of (+)-*p*-2-methylbutyloxy-phenyl-*p*-alkyloxy benzoic acid. The molecular formula of this series of compounds is as follows[4]



where n represents the number of carbon atoms in the alkyloxy chain (here $n = 10, 11, 12$). Note that the compounds $C_{11}(n=11)$ and $C_{12}(n=12)$ are new synthesized ferroelectric liquid crystals. These three compounds all exhibit the following phase transitions

$$C — S_{C^*} — S_A — I,$$

where C – crystal, S_{C^*} – smectic C^* phase, S_A – smectic A phase and I – isotropic liquid. The $S_A - S_{C^*}$ phase transition temperatures for three compounds lie in the range 46 – 50°C measured by DSC technique and optical observation under the polarizing microscope.

The experiment was performed on the unoriented sample. The powder material was placed in a mylar cell with the thickness of 1 mm. The sample cell was positioned at the centre of a goniometer and enclosed by a cylindrical heater. The temperature of the sample was stabilized and controlled automatically within ±0.1°C. The incident parallel X-ray beam (CuKα) was generated by a D/Max γA X-ray generator (RICAGU) operating at 40 kV and 100 mA. The powder diffraction patterns were recorded by a diffractometer.

The method we used here is based on the rigid rod model to describe the molecules using the convenient equation

$$\theta = \cos^{-1}(d_{C^*}/d_A), \tag{2}$$

where d_A and d_{C^*} are the smectic interlayer distance in A and C^* phases respectively. These two spatial periods can be obtained from X-ray diffraction patterns, through the Bragg relation $\lambda = 2d\sin(\alpha/2)$, where λ is the wavelength of the radiation ($\lambda = 0.15418$ nm) and α the Bragg reflection angle.

The measurement of temperature dependence of the tilt angle has been conducted for three compounds. The experimental results are shown in Fig. 1. We notice that for three compounds θ shows the same temperature dependence, with the close absolute values. This can be easily understood because they are chemically similar. The large tilt angle is $\theta \sim 15°$, for $T - T_c \sim -8$°C, which is comparable with that for the compound DOBAMBC.[5] We have tried a power law fit $\theta = \theta_0(T_c - T)^\beta$ to estimate the critical exponent β from the experimental data.

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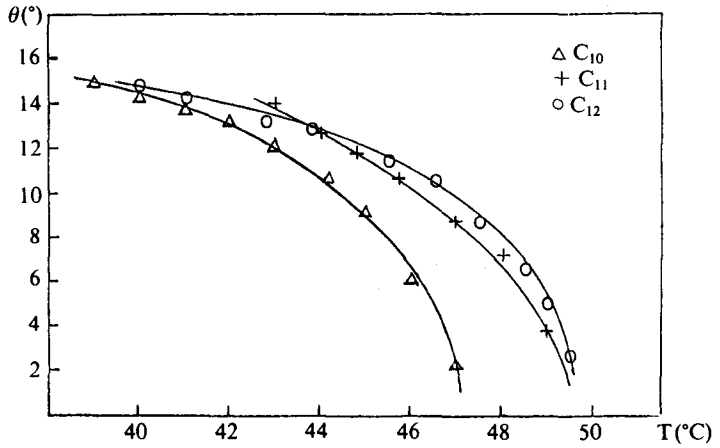

Fig. 1. The tilt angle as a function of temperature in smectic C^* phase in a series of chiral compounds.

Such fit needs to determine T_c precisely, otherwise, a small shift in T_c will lead strong change of the value of β. However, it is very difficult to measure T_c directly by X-ray diffraction. Therefore we adopt a new data-processing method. For each compound the data are processed to determine the three parameters θ_0, T_c and β, which can be adjusted in calculation. The fit results are shown in Table 1. The value of β is between 0.36–0.41, which is consistent with the experimental results obtained by other authors.[5,6]

The critical exponent β is of importance in the theory of phase transition. It describes the behavior of order parameter at the critical point. The experimental results presented in this letter confirm once again that the critical exponent β has the non-classical character, no matter what the material is, and its value usually lies in the range 0.3–0.5 for individual material.[1] This is not comformable to the prediction of mean-field theory. On the other hand, we note the certain spread in the value of β. The reason of such non-classical character of β and spread in its value has not yet been clear, although some theories were presented.[2,3] We suggest that in these phenomenological theories it is not suitable to assume that all the expansion coefficients are temperature independent. In fact, the susceptibility χ,

Table 1. The fit results of three parameters.

	θ_0	T_c	β
C_{10}	6.9	46.9	0.39
C_{11}	6.2	49.4	0.41
C_{12}	6.2	49.6	0.36

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flexoelectric coefficient μ_f and wave vector of the helix q_0 are all dependent on temperature. Strictly speaking, when one deduces the temperature dependence of the tilt angle from Landau theory, the temperature effects of these coefficients should be taken into account, but this is too complex to be solved. Besides, note that the values of χ, μ_f and q_0 are different for various materials, which will affect the temperature dependence of the tilt angle. Maybe this is the origin of a considerable spread in the value of the critical exponent. Therefore, more theoretical work and more precise high-resolution experiments have to be done.

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