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Critical Behaviour in Ferroelectric Liquid Crystal

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Anomalous specific heat and optical rotatory power near the chiral smectic A-C* phase transition in ferroelectric liquid crystal DOBAMBC are measured, and constants describing the critical behaviour are estimated as $0 \leq \alpha < 0.17$ and $\beta = 0.24 \pm 0.01$.

The initial dielectric constants measured by thermal noise method show the characteristic low frequency (10^2Hz) dielectric dispersion suggesting the critical slowing down.

Many experimental and theoretical studies have been made in recent years to elucidate the critical properties of the smectic A-C phase transition in particular for the analogical aspects with the superfluid transition in helium and also with the ferroelectric phase transitions in solid.

Chiral smectic liquid crystals, in which the electric permanent dipoles are strongly coupled to the chiral part of the constituent molecules, show the ferroelectric properties in smectic C* and H* phases. DOBAMBC (p′-decyloxy-benzilidene p-amino-2methyle butyle cinnamate) is ferroelectric for the optical active (+) molecule and nonferroelectric for the racemic mixture (±).[1)]

Both substances were synthesized simultaneously with great care. The purification of samples was made by the chromatography and recrystallization methods. The difference of the transition temperature of the chiral and racemic version of our synthesized samples is less than 0.7°K, by means of the direct comparison of both samples in the differencial thermal analysis measurement. The smectic A-C* phase transition of (+) DOBAMBC (Curie temperature T_c) is $T_c = 96.75$°C.

The anomalous heat capacity in the vicinity of T_c is very small.[2)] The transition enthalpy is 1.47 kJ/mol in our vacuum adiabatic calorimetry measurement, used 7.0 g weight sample. In order to clarify the details of the critical properties of the heat capacity near T_c, an AC temperature calorimetry method[3)] was applied to the single liquid crystal sample of 25 μm thick. Figure 1 gives the temperature dependence of the anomalous specific heat C_p of (+) DOBAMBC near the Curie point T_c and the data by the form of

$$C_p = A(T - T_c)^{-\alpha}, \; T > T_c,$$
$$= A'(T_c - T)^{-\alpha'}, \; T < T_c.$$

With the use of only the data points within the interval of $0.1 \text{ K} < T - T_c < 0.7$ K in smectic A phase and $0.1 \text{ K} < T_c - T < 2.8$ K in chiral smectic C* phase, the critical exponents are $0 \leq \alpha$ and $\alpha' < 0.17$. As the temperature interval is expanded, the quality of the fit of the value decreases and the exponents have no physical meanings. The second-order phase transition in (+) DOBAMBC is confirmed with the continuous change of entropy at T_c.

In the chiral smectic liquid crystals the order parameter is the tilt angle θ of the director (the long axis of the molecule). The optical rotatory power in smectic C* phase is the direct response of the birefringence resulting from the helical structure of the director. Figure 2 shows the temperature dependence of the optical rotatory power ϱ in the vicinity of T_c. The critical

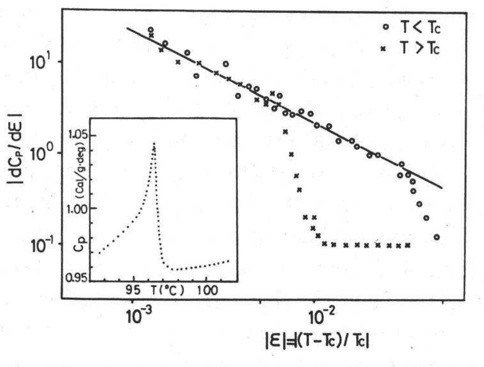

Fig. 1. The temperature dependence of the anomalous specific heat data of (+)DOBAMBC near the smectic A-C* phase transition. The solid line shows the zero indices of the critical exponents ($\alpha = \alpha' = 0$) for reference.

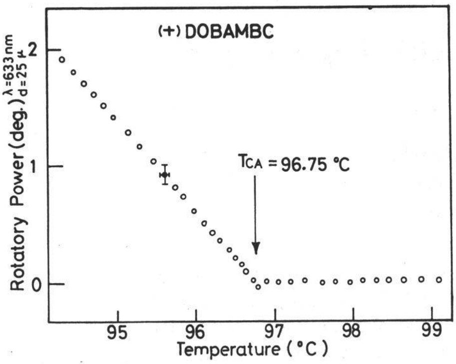

Fig. 2. Optical rotatory power data in smectic C* phase of (+)DOBAMBC near the Curie point as a function of temperature.

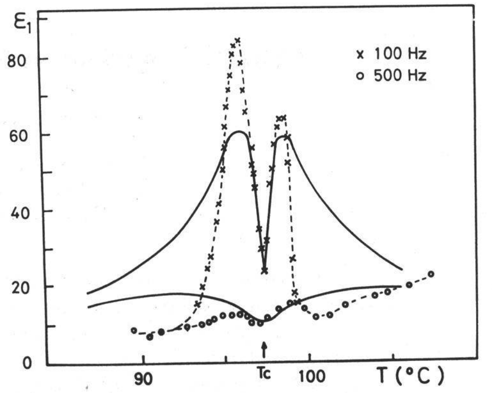

Fig. 3. The temperature dependence of the initial dielectric constant ε_1 of (+) DOBAMBC at 100 Hz (×) and 500 Hz (○) by the thermal noise method. The solid curves are culculated on the base of the Matsubara and Yoshimitsu theory (14) by putting $C_+=165$, $C_-=166$, $\tau_0=10^{-4}$, and $\beta=0.9$, in the equations: $\varepsilon_1=\varepsilon_\infty+\{(\varepsilon_0-\varepsilon_\infty)(1+aZ)\}/\{1+2aZ+Z^2\}$, $a=\cos(\pi/2)\beta$, $Z=(\tau_0\omega)^\beta(\varepsilon_0+2)(\varepsilon_\infty+2)^{-1}$ and $\varepsilon_0=C_+|T-T_c|^{-1}$.

exponent β of the order parameter θ of the form $\theta\propto(T_c-T)^\beta$ is estimated as $\beta=0.24\pm0.01$ from the vest fit of the data by using the relation of the simple form $\varrho\propto\theta^4$, which was introduced by Pieranski et al.,[4] in the case of the temperature independent pitch in the vicinity of T_c. The recent data of the measurement of the helical pitch[5] indicate that the pitch is nealy constant value of 3 μm in the temperature range of 0.1 K$<T_c-T<$2 K. Although in the present study the small corrections have not been made for the lack of the exact data about the density and the optical biaxiality near the Curie point, the β from the optical rotatory power is fairly smaller than those from the spontaneous polarization measurements by D-E hysteresis loop. The contributions of the field induced tilt of the flexoelectric[6] and the electro-clinic[7] effects may be included in the larger values of $\beta=0.3\sim0.4$ obtained from the observation of D-E hysteresis loop.[8,9]

The temperature dependence of the initial dielectric constants of (+) DOBAMBC was measured by the thermal noise method[10] based upon the Nyquist's theorem. The results of the frequencies of 100 Hz and 500 Hz are shown in Fig. 3. The dielectric critical slowing down phenomena near the Curie point in solid ferroelectrics have been understood by a phenomenological theory of Matsubara and Yoshimitsu.[11] There is clear inconsistency between the experimental results and the theoretical predictions in contrast with the case of the solid ferroelectrics. This may come from a reason[1] that the smectic A-C* phase transition is driven by the intermolecular short range forces producing the tilt, and not by the long range ferroelectric coupling, as pointed out by the fact that the transition temperature difference of the chiral and racemic version is negligibly small. There are also numerous discrepancies between the experimental results of dielectric measurements in the vicinity of the smectic A-C* phase transition of DOBAMBC.[12,13] Our preliminary measurements of the dielectric constant ε_1 by the lock-in amp method indicate that there is a threshold value of less the 2 V/cm to the impressed voltage on the sample. Additional precise dielectric experiments would be usefull to clarify the critical behaviours of soft and Goldstone modes[13] in ferroelectric liquid crystals, because the true critical region should be unobservably small for most A-C transitions[14] on the base of Ginzburg-criterion argument.

To summarize as the conclusion, we have presented the first experiment of the dielectric critical slowing down of the ferroelectric liquid crystal. The static critical exponent for specific heat was determined by AC temperature calorimetry. The critical index α is very close to zero (logarithmically). The order-parameter critical exponent β by optical rotatory power is approximately estimated as 0.24 ± 0.01, although there will be the possibility of further advanced study on β.

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