

TWO SMECTIC-A PHASES

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In the smectic-A phase of octyloxycyanobiphenyl and octylcyanobiphenyl, the heat capacities observed in heating from the crystalline phase and in cooling from the isotropic phase are found to have large and small values, respectively. The state with large heat capacity is clarified to be stable.

1. Introduction

The phase transition of liquid crystals with the sequence of phases, crystalline(K), smectic-A(SmA), nematic(N) and isotropic(I) phases, has been studied intensively. From the viewpoint of critical phenomena, the transition from the smectic-A to the nematic phase has attracted considerable attention. A simple three-dimensional XY model expected from the theoretical treatment by de Gennes [1] is not applicable to this phase transition in the strict sense. Letting $t = |T/T_{NA} - 1|$ where T_{NA} is the nematic-smectic-A transition temperature, the correlation lengths diverge as $\xi_{||} = \xi_{||}^0 t^{-\nu_{||}}$ and $\xi_{\perp} = \xi_{\perp}^0 t^{-\nu_{\perp}}$ with the different values of $\nu_{||}$ and ν_{\perp} , where the subscripts, $||$ and \perp , mean parallel and perpendicular to the nematic director, respectively. Typical experimental results show $\nu_{||} - \nu_{\perp}$ is about 0.13 and $\nu_{||}$ ranges from 0.66 to 0.83 [2]. The critical exponent α of heat capacity also depends on materials. For octyloxycyanobiphenyl(80CB) [3-6] and octylcyanobiphenyl(8CB) [5,7], these critical exponents have been found to satisfy an extended hyperscaling relation, $\nu_{||} + 2\nu_{\perp} = 2 - \alpha$ [8]. The problem of the non-universal behavior has been attacked by many researchers but is still left open. On the other hand, in the phase diagram of these liquid crystals the reentrant nematic phase has been found under high pressure [9] and in the mixture of the liquid crystal and the other one [10,11]. At present it is not clear whether the non-universal behavior is related to the appearance of the reentrant nematic phase. In the present paper we will exhibit that the unstable smectic-A phase appears under a certain condition.

2. Experimental Results

The heat capacity of 80CB and 8CB was measured by ac calorimetry. The schematic view of the sample cell is shown in Fig. 1. The bottom of the cell is composed of three layers, a phosphor-bronze plate, liquid crystal, and a phosphor-bronze plate. Each thickness of the layers was about 100 μm . The ac heat was applied on the lower face of the bottom by alternately chopped light. Then, the temperature around the center of the bottom plate rised and falled uniformly. The inverse of this ac temperature amplitude was proportional to the total heat capacity of the two metal plates and the liquid crystal sample per unit area. The details of the ac calorimetry for liquid materials will be published elsewhere.

Figure 2 shows the temperature dependence of heat capacity of 80CB observed in cooling run. On the other hand, Fig. 3 shows the heat capacity in heating obtained under the same conditions with the former cooling run. By

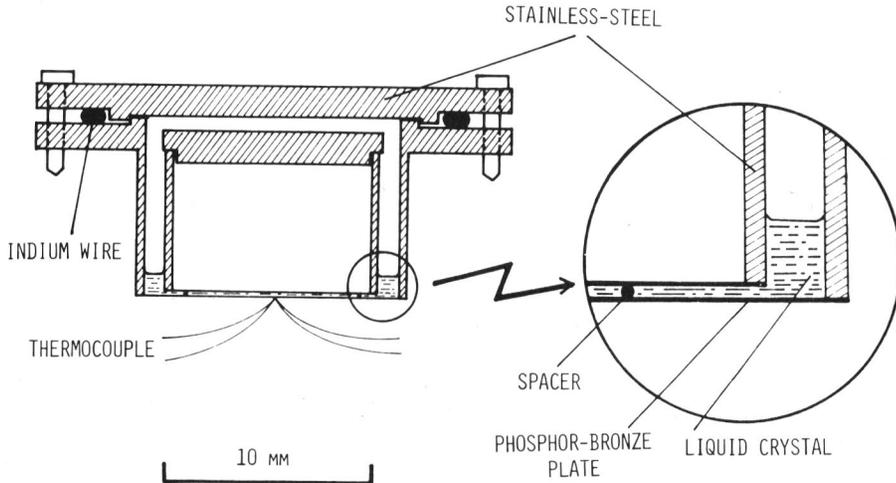


Fig. 1. Sample cell for the ac calorimetry. The cell was composed of two sets of can and cover. For the principle of the experiment, see text.

comparing between the both results, it is clear that the heat capacities in the smectic-A phase are quite different from each other, i.e., there are two states; one has large heat capacity; another has small heat capacity. So far the results which correspond to the large heat capacity has been reported [3-6]. The fact that this state appears frequently seems to indicate that it is stable. In order to test the stability, we carried out the following experiment. The sample was heated and cooled repeatedly in the sequence denoted by the number enclosed by circle in Fig. 4: In process 1 it was heated from the crystalline phase to 340.24 K just below T_{NA} with the rate of 1 K/h, in process 2 cooled down to 339 K in the smectic-A phase with 3 K/h, in process 3 heated up to 340.31 K just below T_{NA} with 1 K/h, in process 4 cooled to 339 K with 3 K/h, in process 5 heated to 341 K above T_{NA} with 4 K/h, in process 6 cooled to 339 K with 4 K/h, in process 7 heated to 341 K with 4 K/h, and in process 8 cooled to 339.7 K with 4 K/h. As seen from process 2, in this cooling run the sample no longer stays in the same state with process 1 and however, in the next heating run of process 3 the sample remains in the almost same state with process 2. Once the sample was heated above T_{NA} , the heat capacity has the saturated largest value. Then, it can be concluded that the state with large heat capacity is more stable than that with small heat capacity.

The similar temperature hysteresis of the heat capacity was also observed in 8CB. Therefore, this behavior appears to be general phenomena.

3. Discussion

When we consider the two states in the smectic-A phase, we should pay attention to the pressure effect. In the present sample cell, the sample was held between a pair of the hard metals, which were kept in a fixed distance during the experiment. Owing to the large thermal expansion of liquid crystals, the sample will become dense in cooling and might remain in a compressed condition in heating. From the measurement of the pressure dependence of heat capacity for 80CB by Kasting *et al.* [4], at 4 K lower than T_{NA} , the heat capacity can be estimated to be about 80R at 1 bar and about 60R at 2000 bar, where R is the gas constant. Above about 2300 bar the smectic-A phase disappears and the reentrant nematic phase comes out [9]. In order to calibrate the absolute value, we fitted our data in the range $-5 \text{ K} < T - T_{NA} < 0 \text{ K}$ to the heat capacity obtained at 1 bar by Kasting *et al.* [4]. Thus obtained heat capacity for our small value in the smectic-A phase is about 30R. The magnitude is extremely small in comparison with the value observed at 2000 bar and then, the smectic-A phase with such small heat capacity no longer exists. For this reason, the pressure effect seems to be not the case for the origin of the state with small heat capacity. However, there still remains a

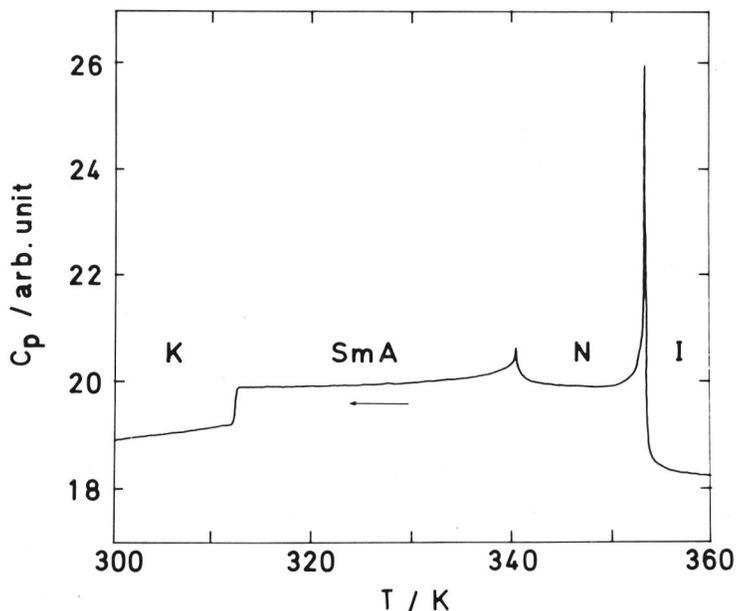


Fig. 2. Temperature dependence of heat capacity of 80CB in the cooling run from the isotropic phase.

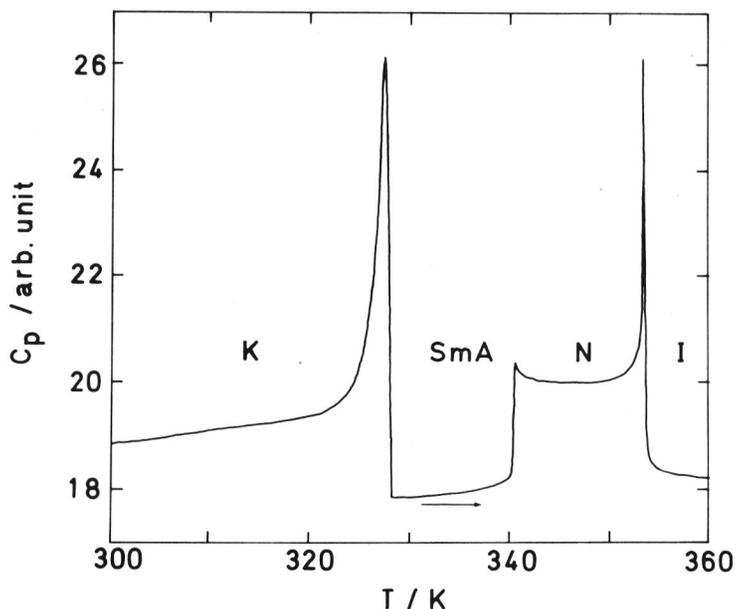


Fig. 3. Temperature dependence of heat capacity of 80CB in the heating run from the crystalline phase.

problem in comparing between our data and the result by Kasting *et al.* [4]. We observed a big jump of heat capacity at the isotropic-nematic transition temperature except for a sharp anomaly and on the other hand, Kasting *et al.* [4] have not found such a jump. At present it is not clear why this discrepancy takes place.

As seen in Figs. 2 and 3, in spite of the difference of the heat capacity in the smectic-A phase, T_{NA} in the cooling run is nearly identical to that in the heating run. This fact, together with the test of the stability of the smectic-A phase done in the experiment of Fig. 4, very near T_{NA} the liquid crystal recovers quickly from the unstable state and changes into the stable state. It is very likely that the change of the structure near T_{NA} holds the key to the stabilization of the smectic-A phase.

The drop of the heat capacity in the smectic-A phase of 80CB did not

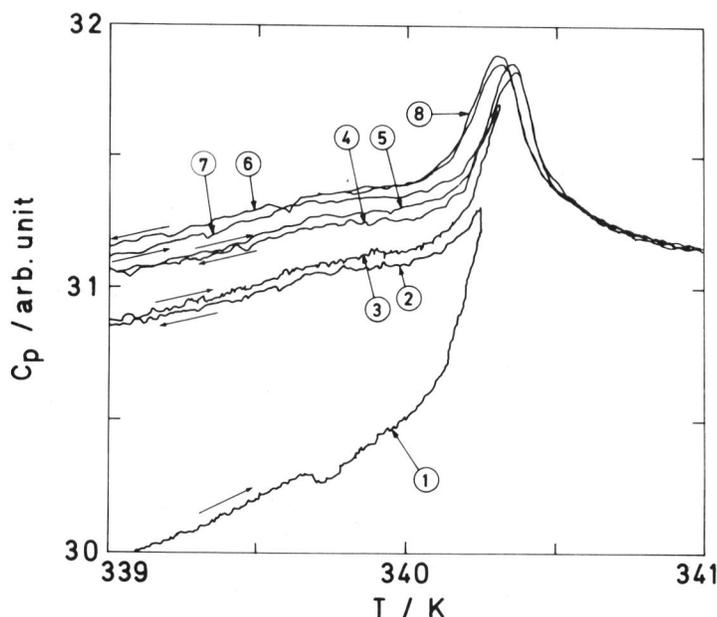


Fig. 4. Examination of the stability of the smectic-A phase. For the details, see text.

depend on the heating rate and was almost constant. Its magnitude was the near same with that of the isotropic phase. The above facts were very similar in 8CB. On the other hand, the heat capacity with large value which appeared in cooling is the same magnitude with that of the nematic phase in both 80CB and 8CB. From these results, the state with small heat capacity seems to be not simply unstable but metastable.

In the present experiment, care was not taken for the surface of the liquid crystals with the thickness of about 100 μm , which were put between a pair of the metal plates. It is well-known that the nematic liquid crystals are oriented by the effect of the boundary surface. In a further study, the present phenomena should be considered from this respect.

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Note added— A precise measurement of the heat capacity of 8CB for the large bulk of 22 g has been carried out by J. Thoen *et al.* [to be published in *Phys. Rev. A* 26 [5] (1982)]. It gives a quite different result from this result.