

Crossover between two- and three-dimensional melting in a smectic- B -smectic- A phase transition in BBOA

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It is established that the curve of the first-order of phase transition smectic- B (S_B)-smectic- A (S_A) in N -(4- n -butyloxybenzylidene)-4- n -octylaniline (BBOA or 40.8) terminates at the end critical point (ECP), coalescing with the curve of the second-order phase transition smectic- A -nematic (N). An increase in the volume ΔV and entropy ΔS jumps on the S_B - S_A transition line with an increase in pressure is attributed to the crossover between two- and three-dimensional melting.

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As has recently become clear,¹⁻⁴ part of the most ordered smectic B phases are actually true crystals with three-dimensional, long range, positional order. The layered structure of these crystals and the extreme weakness of the interlayer interaction¹⁻⁴ permits classifying them as distinct quasi-two-dimensional solids. When heated, the crystal-line smectic- B (S_B) transforms into the liquid crystalline smectic- A (S_A) and at the same time the long-range positional order inside the smectic layers is destroyed, while the smectic one-dimensional order remains.

If we ignore the fact that the smectic one-dimensional order strictly speaking is not long range⁵ (actually it is not clear whether or not this has any meaning), then the phase transition of crystalline S_B into S_A is nothing more than two-dimensional melting in a three-dimensional system. It is clear that at least the quantitative characteristics of this phenomenon must differ from three-dimensional melting, but its relation to true two-dimensional melting is not clear. The problem lies in the fact that the two-dimensional crystalline layer in the three dimensional system even with an infinitely weak interaction between layers differs fundamentally from a two-dimensional solid in the sense that in the latter there is no long-range positional order. This may be unimportant if melting in the two-dimensional case is a first-order phase transition; but, if two-dimensional melting is a continuous phase transition, then the difference indicated may be decisive.

In any case, we think that it is interesting to follow the evolution of the phase transition crystalline smectic B -smectic A under high pressure, in view of the possible change in the nature of the transition according to the change in the "three-dimensionality" of the specimen.

In this paper, we report the results of an investigation of the S_B - S_A phase transition in N -(4- n -butyloxybenzylidene)-4- n -octylaniline (BBOA or 40.8) under high pressures. The crystalline nature of the S_B phase of BBOA was established in Refs. 1-4. A BBOA specimen was obtained from the Printon Laboratories (USA) and was cleaned by recrystallization from an absolute standard. After cleaning, the temperatures of the phase transitions in BBOA at atmospheric pressure were as follows:

$$Cr \xrightarrow{38.3^\circ C} S_B \xrightarrow{50.0^\circ C} S_A \xrightarrow{63.8^\circ C} N \xrightarrow{78.9^\circ C} I.$$

The experiments were performed with the help of a piston pressure gauge⁶ and a more sensitive bellows pressure gauge with use of a capacitive displacement sensor.⁷ The pressure in the system was stable to within ± 0.1 bar. The error in the measurements of the absolute values of pressure and temperature were, respectively, ± 10 bar and ± 0.1 K. The absolute error in the measurements of the specific volume did not exceed $0.2 \text{ cm}^3/\text{mole}$, while the relative random error in determining the volume jumps accompanying the phase transitions was of the order of 1%. The entropy jumps ΔS accompanying the S_B-S_A and S_B-N phase transitions were calculated using the Clausius-Clapeyron equation. The relative random error in the values of the entropy of the transition was of the order of 1–1.5%.

Figure 1 shows a phase diagram of BBOA, constructed from the results of our work. Figure 2 illustrates the behavior of the specific volume of BBOA in the region of S_B-S_A and S_A-N phase transitions at atmospheric pressure. Figure 3 shows the dependence of the relative volume $\Delta V/V$ and entropy jumps ΔS in the transition along the S_B-S_A and S_B-N phase transition lines as a function of pressure.

As can be seen from the phase diagram of BBOA (Fig. 1), the S_B-S_A equilibrium curve does not have an infinite extent, but terminates at the end critical point (ECP), where the S_B-S_A line coalesces with the second-order S_A-N phase-transition line. Further on the first-order phase-transition line continues as the S_B-N equilibrium. The shape of the BBOA phase diagram itself indicates that the smectic one-dimensional order in the phase S_A decreases along the S_B-S_A transition line from some finite value at atmospheric pressure to zero at the ECP; therefore, beginning at the ECP, the

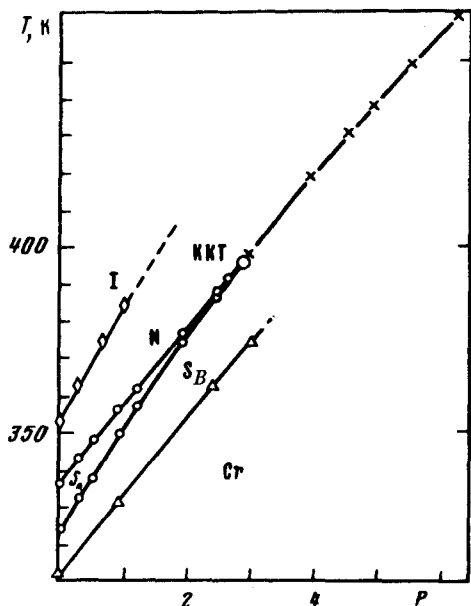


FIG. 1. Phase diagram of the liquid crystal BBOA (40.8).

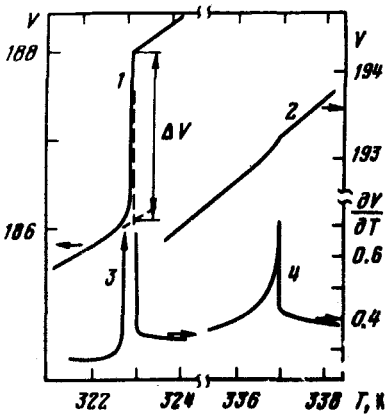


FIG. 2. Behavior of the specific volume V (cm^3/mole) of BBOA and the derivative dV/dT ($\text{cm}^3/\text{mole/K}$) in the region of the phase transitions $S_B - S_A$ (1,3) and $S_A - N$ (2,4) at atmospheric pressure. The method for determining the volume jump ΔV accompanying the first-order phase transition is shown on curve 1.

S_B phase melts directly into the positionally disordered liquid. In other words, the longitudinal (corresponding to ordering along the director) and transverse (in a plane perpendicular to the director) positional order parameters near ECP interact so strongly that the existence of the S_A phase becomes impossible and melting is already completely three-dimensional. Thus, in this specific case, the pressure increases the interlayer interaction with all of the concomitant consequences for the $S_B - S_A$ phase transition.

We shall now consider the behavior of the relative jumps in volume $\Delta V/V$ and entropy ΔS accompanying the phase transition $S_B - S_A$ (Fig. 3). It is evident from this figure that both of these quantities increase with increasing pressure. We can assert

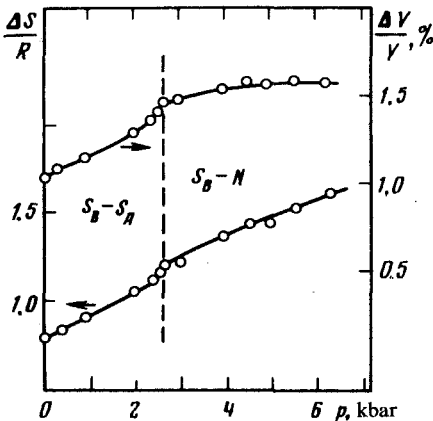


FIG. 3. The pressure dependence of the relative jump in volume $\Delta V/V$ and entropy of the transition ΔS along the $S_B - S_A$ and $S_B - N$ phase transition curves in BBOA.

that this behavior is impossible for melting of simple systems with any reasonable interparticle interactions and the given dimensionality of the space (see, for example, Ref. 8). This leads to the conclusion that the unusual behavior of ΔS and $\Delta V/V$ along the S_B-S_A phase transition line is related to the interaction of the transverse and longitudinal order parameters, whose intensity determines the degree of the "three-dimensionality" of the phase transition. The sharp increase in ΔS and $\Delta V/V$ near the ECP is evident from the sharp increase of this interaction and from the increase in the "three-dimensionality." The anomalous behavior of the quantities ΔS and $\Delta V/V$ along the S_B-N phase transition curve, where melting is already three dimensional, is explained naturally by the decomposition of the smectic fluctuations in the nematic phase. In this connection, we note that apparently three-dimensional melting is "normal," in the sense of the correspondence between the short-range order in the liquid phase (S_A) and the structure of the crystal (S_B), only at the end critical point.

Comparing the numerical values of the quantities ΔS and $\Delta V/V$, which characterize the melting of S_B at atmospheric pressure and at the ECP, we see that, as could be expected, "three-dimensional" jumps are greater than the corresponding quasi-two-dimensional jumps. We emphasize that it follows from data generated by computer experiments⁹ that the jumps in the thermodynamic quantities accompanying melting of two-dimensional systems are always smaller than those for melting of equivalent (in the sense of interparticle interactions) three-dimensional systems.

Unfortunately, pure positional contributions to the entropy of the S_B-S_A transition in BBOA are strongly masked by contributions from other degrees of freedom. For example, the entropy of the S_B-S_A phase transition at the ECP, where the corresponding transition is "normal" three-dimensional melting, is equal to 1.2 R, which greatly exceeds the entropy of melting of simple three-dimensional systems with the corresponding change in volume [~ 0.7 R (Ref. 8)]. For this reason, direct comparison of thermodynamic parameters of the S_B-S_A transition in BBOA with the melting parameter of simple systems is impossible. However, we should point out the fact that the relation of the entropies of the transition S_B-S_A at points corresponding to atmospheric pressure (maximum two-dimensionality) and ECP ("normal" three-dimensional melting) is nearly equal to 2/3 (0.79/1.2). Although the probability for a simple coincidence cannot be excluded, we nevertheless note that the value 2/3 for the ratio of the magnitudes of the entropies of melting of two-dimensional and three-dimensional systems, in the case when two-dimensional melting is a strong first-order transition, appears quite likely.

It would be interesting to estimate the purely positional part of the entropy of melting in BBOA at atmospheric pressure, when the interaction between layers is minimum. For this purpose, it is necessary to include in some manner the "incidental" contributions to the entropy of the transition along the S_B-S_A equilibrium line. We shall start from two different assumptions: a) additivity and b) multiplicativeness of "incidental" contributions. We shall normalize the entropy of the transition along the S_B-S_A curve in such a manner that the quantity ΔS at the ECP would be equal to 0.7 R. We then obtain two estimates of the probable value of the entropy of two-dimensional melting in a three-dimensional system ranging from 0.3 R to 0.45 R. It is interesting that these estimates agree well with the results of computer experiments for purely two-dimensional systems.⁹

Thus, it appears that the investigation of crystalline smectic *B* phases can be a new source of information on two-dimensional systems.

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