Critical point on the smectic *A*-smectic *B* phase-transition line in MBMBAC

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The thermal expansion of MBMBAC (β-methylbutyl-methoxybenzylidene amino cinnamate) near the S_A–S_B phase transition has been studied at high pressure. This is a first-order phase transition at low pressures but becomes a continuous one above 1 kbar. The coordinates of the critical point have been established: $T_c \approx 358$ K and $P_c \approx 1$ kbar. The behavior of the density jump $\Delta\rho$ at the S_A–S_B transition in the region of the first-order phase transition is described by $\Delta\rho \sim (T - T_c)^x$ with $x \approx 0.35$.

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High-precision x-ray measurements[1,2] have shown that among liquid-crystal phases which had previously been identified as smectics B there are phases which have an extremely extended, three-dimensional, positional order and which are apparently not true liquid crystals. On the other hand, there is at least one known case[3] of a true liquid-crystal smectic B, a three-dimensional analog of Nelson and Halperin's hexatic phase.[4]

The relationship between the two S_B forms, like the existence of other intermediate S_B forms, remains an open question.

It would seem that the S_A-S_B phase transition would have to be sensitive to the interparticle correlations in the smectic B. In the few cases that have been resolved,, this in fact is the situation. The S_A-S_B transition in the material 4O.8 [or BBOA: *N*-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline], which has an extended positional order, is a first-order phase transition,[2,5] whereas the transition from a hexatic, orientationally ordered S_B phase to a S_A phase in the material 65OBC [*n*-hexyl-4^1-*n*-pentyloxybiphenyl-4-carboxylate] occurs through a continuous phase transition.[5] These isolated observations do not, however, rule out the possibility that the S_A-S_B phase transition may depend on the temperature and pressure in some manner. It is therefore worthwhile to study the evolution of the S_A-S_B phase transition along the phase-equilibrium curve.

In this letter we are reporting *P-V-T* measurements along the S_A-S_B phase line at a high pressure in MBMBAC. This material has been studied previously in Refs. 6 and 7.

The material itself was obtained from the US company "Organix" and was used both in the form as furnished and after an additional purification.2) The additional purification had essentially no effect on the temperatures of the phase transitions in MBMBAC, which turned out to be as follows (see also Refs. 6 and 7):

$$C - 48.5\,^\circ\mathrm{C} - S_B - 60.1\,^\circ\mathrm{C} - S_A - 80.7\,^\circ\mathrm{C} - N - 100.4\,^\circ\mathrm{C} - I.$$

The measurements were taken with a piston pressure gauge with an intermediate liquid (mercury).[8] To calculate the zero volume of the pressure gauge, we used the molar volume found by us for MBMBAC in a separate experiment: $V = 1.76 \pm 0.01$ cm^3/mole at $T = 96.98\,^\circ$C and $P = 1$ atm. The accuracy of the high-pressure volume measurements was ~0.01%. The absolute errors in the temperature and pressure measurements were no worse than ±0.01 K and ±10 bar. The errors in the measurement of the corresponding quantities on the scales of the thermocouple and the pressure gauge do not exceed ±0.001 K and ±2 bar.

All the measurements were taken during thermal expansion at a constant pressure. The pressure was held constant within 0.1 bar. The temperature was varied continuously at ~0.05-0.1 K/h. All the measurements were taken with an automatic data-collection and processing system based on a Solartron digital voltmeter.

The experimental results are summarized in Fig. 1 and Table I.

It can be seen in Fig. 1 that the S_A-S_B phase transition in MBMBAC at atmospheric pressure is a slightly blurred, first-order phase transition. The blurring is over a short interval, ~0.15 K. As the pressure is raised, the difference between the phase volumes of the S_A and S_B decreases rapidly, and at the maximum pressure used in these experiments the temperature dependence of the volume shows nothing more than a barely discernible anomaly at the S_A-S_B transition. The entire effect was reproduced several times with different portions of the material and under various ex-

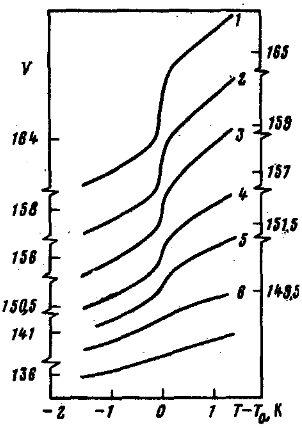

FIG. 1. Temperature dependence of the molar volume V (in cubic centimeters per mole) of MBMBAC near the S_A–S_B phase transition. 1–1 bar; 2–674; 3–967; 4–1502; 5–2202; 6–4058; 7–5601 bar.

perimental conditions. There can thus be no doubt regarding the existence of a critical point on the curve of the S_A–S_B transition in MBMBAC.

To pursue the analysis of the effect, it is convenient to work with the isobars of the thermal expansion of the material in the phase-transition region, found through a numerical differentiation of the raw data (Fig. 2).

At low pressures the derivatives $(\partial V/\partial T)_p$ have the shape typical of impurity-blurred, first-order phase transitions (the δ-function transforms into something resembling a trapezoid). As the pressure is raised, the maximum value of the function $(\partial V/\partial T)_p(T)$ initially remains essentially constant, but the width of this function de-

TABLE I. Thermodynamics of the S_A–S_B phase transition in MBMBAC key: 1–$^{1)}$The error in these values of ΔV does not exceed 5%. $^{2)}$The error in this value of ΔV can be as high as 100%.

T, K	P, kbar	V_{S_B}, cm^3/mole	$\Delta V^{1)}$, cm^3/mole	$\Delta V/V_{S_B}$ %	$\Delta S/R$
333.25	0.001	164.20	0.50	0.3	0.21
340.17	0.269	162.00	0.42	0.26	0.18
343.64	0.404	160.8	0.43	0.27	0.19
350.36	0.674	158.80	0.34	0.21	0.16
354.79	0.854	157.30	0.23	0.15	0.11
357.42	0.967	156.50	0.05$^{2)}$	0.03	0.02
359.62	1.055	156.00	–	–	–
365.52	1.309	154.30	–	–	–
370.20	1.502	153.20	–	–	–
385.55	2.202	149.40	–	–	–
398.05	2.810	146.60	–	–	–
409.50	3.401	144.20	–	–	–
421.60	4.058	141.60	–	–	–
432.90	4.647	139.40	–	–	–
447.00	5.601	136.20	–	–	–

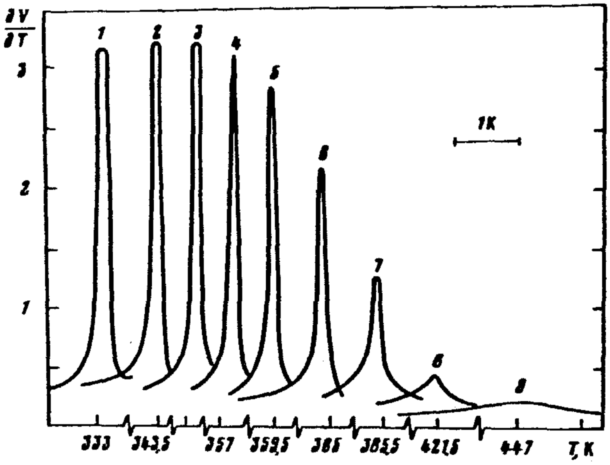

FIG. 2. Temperature dependence of $(\partial V/\partial T)_p$ (in cubic centimeters per mole per kelvin) near the S_A–S_B phase transition for MBMBAC. 1–1 bar; 2–404; 3–674; 4–967; 5–1055; 6–1309; 7–2202; 8–4058; 9–5601 bar.

creases; this width determines the transition interval ΔT and ultimately the volume change ΔV upon the transition. At a pressure ~1 kbar there is a sharp change in the shape of the function $(\partial V/\partial T)_p(T)$; the curves of $(\partial V/\partial T)_p$ become peaked, and the maximum values of $(\partial V/\partial T)_p(T)$ begin to decrease sharply. The coordinates of the critical point can evidently be identified with the beginning of the sharp decrease in the maximum value of the derivative $(\partial V/\partial T)_p$ near the phase transition.

On the other hand, by defining the interval ΔT of the first-order phase transition as the distance between the inflection points of the function $(\partial V/\partial T)_p(T)$ and using the curves of $V(T)$ in Fig. 1, we can determine the volume change ΔV at the transition. By extrapolating ΔV to zero, we can easily determine the critical parameters.

The values found for ΔV at the S_A–S_B transition, the calculated values of the entropy change ΔS, and the coordinates of the S_A–S_B transition curve in MBMBAC are all listed in Table I. Since ΔV or $\Delta\rho$ behaves in a critical manner at the S_A–S_B transition (Fig. 3), we analyzed the functional dependences ΔV, $\Delta\rho = f(T - T_c)$ with

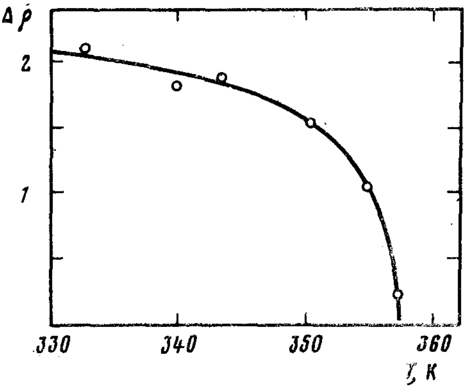

FIG. 3. Temperature dependence of the density jump $\Delta\rho$ (in kilograms per cubic meter) at the S_A–S_B transition in MBMBAC.

the help of expressions of the type ΔV, $\Delta\rho \sim (T - T_c)^x$, treating T_c as a free parameter. We found the following values for the critical parameters:

$$T_c = 357.4\,\mathrm{K}(353 \div 361.3),$$

$$P_c = 0.95 \text{ kbar } (0.77 \div 1.10).$$

$$V_c = 156.5 \pm 1 \text{ cm}^3/\text{mole},$$

$$x = 0.35\ (0.23 \div 0.54).$$

The confidence intervals of the corresponding quantities at a 0.9 confidence level are given in parentheses.

Although the error in the determination of the exponent x is not small, we do see that its most probable value is extremely close to the value which corresponds to the behavior of ΔV and $\Delta\rho$ near a liquid–vapor critical point ($\beta = 0.33$). We wish to emphasize that, according to the Landau theory, the volume change is linear in the difference $T - T_c$ in the case of a tricritical point.

The general behavior of the derivatives $(\partial V/\partial T)_p$ also implies that the observed effects are similar to those which occur near a liquid–vapor critical point (there is no jump in the regular parts of the thermal expansion, and the anomalies are smeared over rapidly with distance from the critical point).

Since the existence of a critical point on the S_A–S_B transition line apparently rules out the identification of the S_B phase of MBMBAC with the crystalline smectic B, it is reasonable to assume that the S_B phase of this material has an orientational order. If so, the critical point on S_A–S_B phase line may be a) a true critical point, in which case the orientational order parameter is not zero in the S_A phase, or b) a polycritical point of a special type whose similarity to a liquid-vapor critical point is a consequence of the general weakness of the orientational transition.[4]

Alternative b seems more likely to us, but a detailed analysis of this phenomenon should be postponed until more comprehensive data are available on the nature of the S_A and S_B phases and on the properties of the S_A–S_B phase transition in MBMBAC.

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