PHYSICAL REVIEW B VOLUME 41, NUMBER 13 1 MAY 1990

Critical behavior of the layer compressional elastic constant B at the smectic-A–nematic phase transition

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(Received 24 October 1989)

The temperature dependence of the layer compressional elastic constant B has been studied in four different compounds. Two of them, 4-cyano-4'-(n-octyl)biphenyl and 4-cyano-4'-(n-octyloxy)biphenyl, are polar and give partially bilayered smectic-A_d phases while the remaining two are nonpolar and present monolayered smectic-A_m phases. In all cases, the smectic-A–to nematic phase transition was found to be second order. A second-sound resonance technique has been used to measure Φ, the critical exponent of B on approaching the nematic phase. The values found lie in between 0.39 and 0.42, while the uncertainty is about 0.03. Although the nematic–smectic-A transition does not belong to a single universality class the Φ exponents are much less scattered than previously reported, with a mean exponent of 0.41 being consistent with the four reported values. When available, in the case of polar compounds, the set of critical exponents measured by calorimetry or x-ray scattering together with Φ, seems to be accounted for by the anisotropic model of the smectic-A–nematic phase transition.

I. INTRODUCTION

The problem of the smectic-A–nematic (Sm-A–N) phase transition remains rather controversial, as there is no universal behavior.

In fact, different kinds of smectic-A phases must be distinguished,[1] depending on the molecular arrangement inside the layers. Three main classes can be defined:[2] Sm-A_2 bilayered with dimers of polar molecules, Sm-A_d partially bilayered and made of dimers, and Sm-$A_{m(1)}$ monolayered, which can be made of monomers (dimers) depending on the polarity of the molecules.

A further complication is due to the fact that such phases are often close to each other as can be seen by studying binary mixtures[1] where one may go continuously, or across phase transitions, from one smectic-A phase to another.

Last, the study of these phase diagrams has shown that the behavior is often modified by the vicinity of other phases, such as the isotropic phase[3,4] for example, or by the proximity of triple points, critical points,[5,6] and so on.

A special attention has been paid recently to the temperature range of the nematic phase,[6,7,8] which would imply a saturated nematic order parameter ($S\sim 1$) when it is large and then would allow for a *universal saturated behavior.*

This versatility explains that even when the smectic-A–nematic phase transition is second order, one does not find in literature a universal set of critical exponents that would account for a universal behavior.

Different models for this phase transition have been proposed following de Gennes,[9] which seem to be reconciled in the general frame of the anisotropic model that will be recalled in Sec. II.

We describe in Sec. III the improvements of the experimental technique we used in order to measure the elastic constant B and its critical behavior.

We eventually report, in Secs. IV and V, on the results obtained with four different compounds representing polar and nonpolar ones.

II. THEORETICAL BACKGROUND

According to the review of Lubensky[10] on the anisotropic model of the N–Sm-A transition, three critical exponents are of interest for us: $\alpha, \nu_\perp$, and $\nu_\parallel$. The first one is measured by calorimetry,[11] the two others separately by x rays scattering in the nematic phase.[12] A linear combination of these two exponents may be measured by means of the layer compressional elastic constant B, which obeys

$$B=B_0(T_c-T)^{\Phi}, \quad \text{with } \Phi=2\nu_\perp-\nu_\parallel \; .$$

Two universality classes are proposed in this model, while the possibility of another one is not excluded.

The *"inverted xy" class of a type-*II *superconductor in three dimensions,*[13] predicts mainly $\nu_\perp=\nu_\parallel=\Phi=0.67$.

The anisotropic class [14] predicts $2\nu_\perp=\nu_\parallel$, which implies that B should be finite at the transition as $\Phi=0$.

Anyway, the anisotropic model predicts the following *hyperscaling relation* to be obeyed by the different critical exponents, in any of its two (or more) classes:

$$2-\alpha=2\nu_\perp+\nu_\parallel \; .$$

Many experimental results have been reported that do not favor definitely this partition in two universality classes. It has been shown[6] in a series of homologous compounds that the exponent α may vary continuously from tricritical to xy value. A *(noninverted) xy behavior,* which is close but not identical to the first model, has been reported recently[15] with smectic-A_1 compounds.

Apart from this, anisotropic behaviors have been found but, to our knowledge, the simple factor of 2 between $\nu_\perp$ and $\nu_\parallel$ was never found. The ratio $\nu_\parallel$ over $\nu_\perp$ lies between 1 and 2, but the *hyperscaling relation* always holds in the limit of the cumulated experimental uncertainties.

III. EXPERIMENTAL SETUP AND FITTING PROCEDURE

In the case of B measurement, two kinds of techniques have been used. First, direct determinations of B can be done by means of second-sound resonance techniques;[16,17] second, indirect measurements through K_1/B are inferred from the line width of Rayleigh scattering.[12,18]

The problem is that, independently of the nonuniversality of the transition, the values of Φ determined from thermal variations of B are not coherent in the literature between the two kinds of techniques and even between the different direct measurements.[16,17] This is the reason why we decided to carry out new investigations with a second-sound resonance experiment.

We subsequently improved the setup of Ricard and Prost, using the interdigital-electrode technique[19] to force second sound resonances.

We first designed a microcomputer-driven, three-stage oven[20] with millidegree-Kelvin accuracy and long-term stability (cf. Fig. 1). The central part contains a free surface sample which is about 500 μm thick.

The homeotropic alignment is mainly imposed by the free surface, according to Fish *et al.*,[16] with the help of a silane coating of the bottom surface on which are etched the interdigital electrodes.[19]

A 10–20-V_{pp} ac voltage is applied on a regular pattern with a 400-μm period on the bottom surface (i.e., the electrodes). At a given sample thickness D and elastic modulus B, there occurs a second-sound resonance when the pulsation of the applied field obeys

$$\omega_0^2=(B/\rho)(\pi/2D)^2 .$$

So the relative variations of B are known through ω_0 to a few percent, while the determination of the absolute value of B requires knowledge of the sample thickness, which is less accurate in a free-surface sample (D is measured with the help of a mechanical displacement to ± 20 μm).

The undulation-compression distortion of the sample induces a phase grating which scatters a He-Ne, 0.3–0.8-mW laser beam. One must notice that, even if the light power is weak, it induces a heating of the sample, inside the beam, of some millidegrees Kelvin. In order to prove this, we measured the smectic-A–nematic transition shift in one of the studied compounds as a function of the laser power (see Fig. 2), and worked at sufficiently low power.

A typical experimental scan is shown in Fig. 3.

The least-squares fit of the resonance curve is done, by Minuit software,[21] according to the law

$$I(\omega)=\left| A/(\omega^2-\omega_0^2+i\omega\omega_r)+C'+iC'' \right| ,$$

where the resonance frequency gives the elastic constant B through

$$\rho\omega_0^2=B\pi^2/4D^2 ,$$

while ω_r measures the damping.

From this fit, one determines the resonance frequency and its uncertainty $\delta\omega_0$ defined arbitrarily as the change in parameter ω_0 required to get twice the least-squares fit.

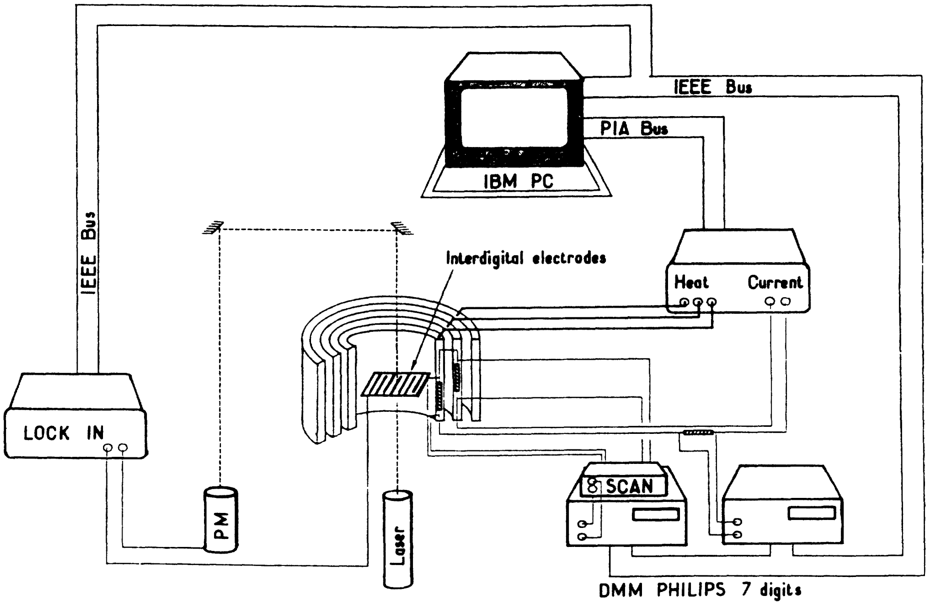


FIG. 1. Sketch of the experimental setup. The temperature gap between the central ovens is set at 0.1 K.

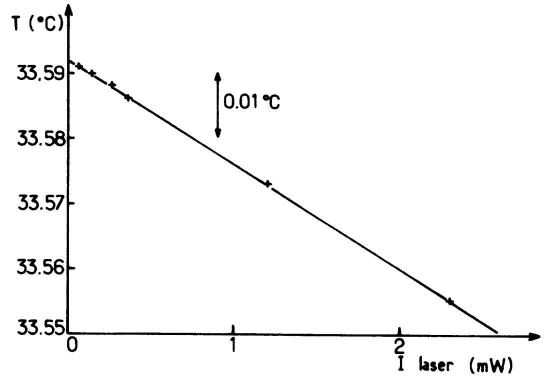


FIG. 2. Plot of the apparent transition temperature in 8CB versus beam power. The temperature is determined by the disappearance of the low-frequency (~ 1 Hz) signal in the nematic phase. The transition temperature defined this way is essentially identical to the one determined by letting it be a free parameter in the fit of $B(T)$.

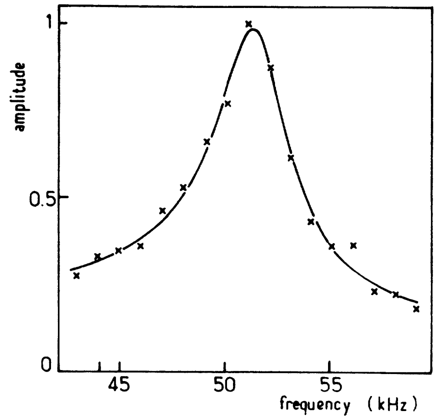


FIG. 3. Typical resonance curve: amplitude of scattered light versus frequency. The least-squares fit corresponds to the continuous curve; it gives mainly the B value through the resonance frequency and the shear viscosity η_3 through its width.

The damping frequency ω_r may be used to determine the shear viscosity η_3.[22] We found it to be essentially constant in the temperature range of the experiment, except in the last hundredth of a degree where we found an anomalous increase. This may be easily understood in the case of a second-order transition where small temperature gradients close to T_c cause large variations of B. So, this increase is due to the uncertainty on T which leads to a dispersion of ω_0 values that appears as an anomalous damping of the resonance curve.

This fact, together with the agreement between T_c values determined by the experiment and by the fit of B, leads us to state that the phase transition was effectively second order in the case of the studied compounds. It has the disadvantage of forbidding the use of experimental points in the transition region.

The last problem we have been confronted with is the thermal drift of the compounds.[23] We have chosen to study cyanobiphenyls or benzoates that allowed us to work at rather low temperature ($<80°$ C), with a drift lower than two mK per day.

This is the reason why we do not present experiments on Sm-A_1 compounds (with dimers of polar molecules): we have not yet found one obeying these criteria. This would be interesting in the future, as these compounds are good candidates to behave according to the XY model.[15]

IV. RESULTS AND DISCUSSION

A. Compounds

We used two polar compounds, namely 4-cyano-4′-(n-octyl) biphenyl (8 CB) and 4-cyano-4′-(*n*-octyloxy) biphenyl (8 OCB), representing the Sm-A_d phase, chosen because they are extremely stable—no thermal drift is measurable for 8CB—and extensively studied in the literature.

We then used two benzoates, representatives of the Sm-A_m phase, which were rather stable (2 mK per day). (See Table I.)

One of them (B1) presents a small nematic range that would render the N–Sm-A transition first order following McMillan's theory;[3,4] we found it instead to be second order. It also presents a smectic-C phase at lower temperature that influences the shape of the $B(T)$ curve [Fig. 4(c)], but it does not change appreciably the value of Φ. We have simulated this behavior with a computed

TABLE I. Studied compounds. Transition temperatures are in °C.

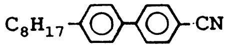
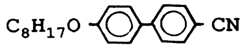
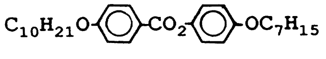
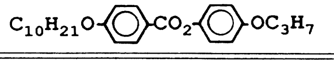
8CB	 C_8H_{17} CN	$K \underset{20}{—} \text{Sm-}A \underset{33.6}{—} N \underset{40}{—} I$
8OCB	 $C_8H_{17}O$ CN	$K \underset{54.5}{—} \text{Sm-}A \underset{67.3}{—} N \underset{80}{—} I$
B1	 $C_{10}H_{21}O$ CO_2 OC_7H_{15}	$K \underset{71}{—} \text{Sm-}C \underset{79.5}{—} \text{Sm-}A \underset{83.4}{—} N \underset{87.5}{—} I$
B2	 $C_{10}H_{21}O$ CO_2 OC_3H_7	$K \underset{60}{—} \text{Sm-}A \underset{70.3}{—} N \underset{81}{—} I$

TABLE II. Critical exponents Φ, $\nu_{\parallel}$, $\nu_{\perp}$, and α measured by different groups.

	Ref.	8CB	8OCB	B1	B2
Φ	This work	0.4 ± 0.03	0.4 ± 0.025	0.39 ± 0.03	0.42 ± 0.015
	17	0.63 ± 0.03	0.49 ± 0.03		
	16	0.36 ± 0.03	0.30 ± 0.23		
	12	0.26 ± 0.06	0.30 ± 0.05		
	18		0.29 ± 0.02		
$\nu_{\parallel}$	12	0.67 ± 0.03	0.71 ± 0.04		
$\nu_{\perp}$	12	0.51 ± 0.03	0.58 ± 0.04		
α	6	0.31 ± 0.03			
	11	0.30 ± 0.05	0.25 ± 0.05		

curve and found, after fitting, that B_0 was depressed but that Φ was only slightly changed from 0.39 to 0.38. We have not tried to fit the B dependence on the smectic-*C* side, but our data confirm the results of the Strasbourg group on terephthal-bis-*p*-*p*′-butylaniline[24,25] showing the existence of significant fluctuation effects which are incompatible with the Landau model.

In order to avoid these complications, we studied the second benzoate compound which presents a larger nematic range and no smectic-*C* phase.

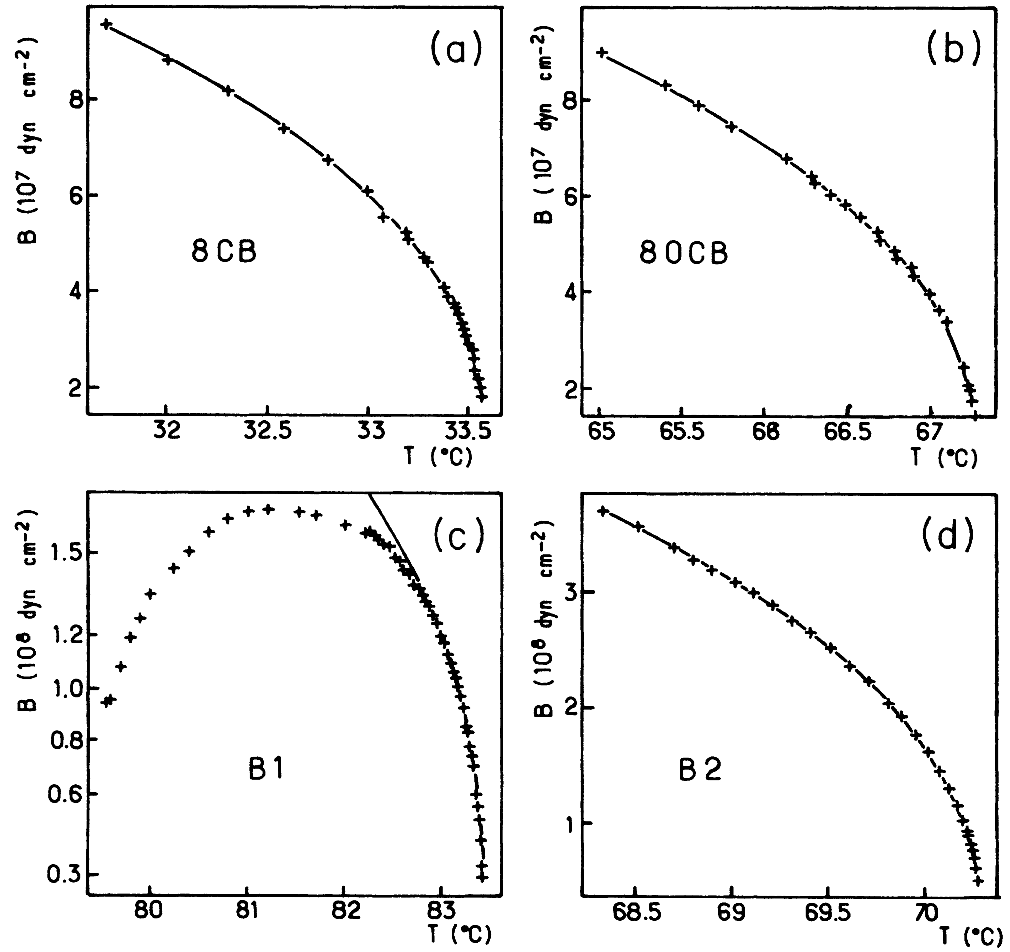


FIG. 4. Plot of the thermal variations of the layer compressional modulus B. The best χ^2 fit corresponds to the continuous line. For the B1 compound, the fit has been made in the last 400 mK below the transition. (a) for 8CB $\Phi = 0.4$, (b) for 8OCB $\Phi = 0.4$, (c) for B1 $\Phi = 0.39$, (d) for B2 $\Phi = 0.42$.

TABLE III. Hyperscaling relation in its form $\alpha+\Phi+2\nu_{\parallel}$ is verified by almost all reported experiments.

$\alpha+\Phi+2\nu_{\parallel}$	8CB	8OCB
Refs. 11, 12, this work	2.04 ±0.14	2.07 ±0.16
Refs. 11, 12, 16	2.00 ±0.14	1.97 ±0.15
Refs. 11, 12	1.90 ±0.17	1.97 ±0.18
Refs. 11, 12, 17	2.27 ±0.14	2.16 ±0.16

B. Results

The fit of the experimental curves reported in Figs. 4(a)– 4(d) is done using Minuit software[22] by minimizing a χ^2 function:[26]

$$\chi^2=\frac{1}{N-3}\sum_i [B_i-B_0(T_c-T_i)^{\Phi}]^2/\delta B_i^2 ,$$

where B_0, T_c, and Φ are adjustable parameters.

δB_i^2 is determined from $\delta\omega_0$ estimated by the procedure explained in Sec. III; it is not identical to the standard deviation σ_i of B_i, so that the best fit value does not give χ^2 close to 1 but it plays the same role when comparing different fits.

Table II summarizes the different values determined experimentally for Φ together with previous results of the literature concerning Φ, $\nu_{\perp}$, $\nu_{\parallel}$, and α for 8CB and 8OCB.

As can be seen, the Φ values are much less dispersed than previously reported.

Concerning the polar compounds, for which comparisons can be made between different techniques, we see that the direct measurements of B, such as the one we make, yield an exponent which is about 0.4, while indirect measurements through K_1/B give[12,18] a set of values about or less than 0.3.

This systematic difference, which seems not to be an artifact, as it is confirmed by different workers, arises a problem interesting by itself. It may be due to the influence of K_1, the curvature elastic constant which is not necessarily constant at the transition, or to the fact that we work on free-surface samples without mechanical stress, or due to the different domains of wave vectors in which the experiments are made.

TABLE IV. Hyperscaling relation in its original form, is verified when combining α and ν measurements.

$\alpha+2\nu_{\perp}+\nu_{\parallel}$	8CB	8OCB
Refs. 11, 12	1.99 ±0.14	2.12 ±0.17

The nonpolar compounds confirm that the effective exponent one can measure strongly depends on the proximity of other phases, but the influence of the nature of the smectic-A phase is not very important.

The next two tables (Tables III and IV) show that the hyperscaling relation, which may be expressed as $\Phi+2\nu_{\parallel}+\alpha\ =2=2\nu_{\perp}+\nu_{\parallel}+\alpha$, can hardly be used to go further as it is obeyed in all cases in the limit of cumulated uncertainties.

V. SUMMARY

We have put into order an experiment which is able to give accurately the critical behavior of the layer compressional elastic constant B in the smectic-A phase when approaching virtually any phase transition. In this paper we study the classical, even if not fully understood, smectic-A–nematic phase transition. We find that the critical exponent Φ is close to 0.4 in the studied compounds. Further studies are needed in order to assert if this particular exponent is also nonuniversal like most of the other ones for this particular phase transition.

ACKNOWLEDGMENTS

We would like to thank Professor J. Thoen for his help during the setup of our oven.

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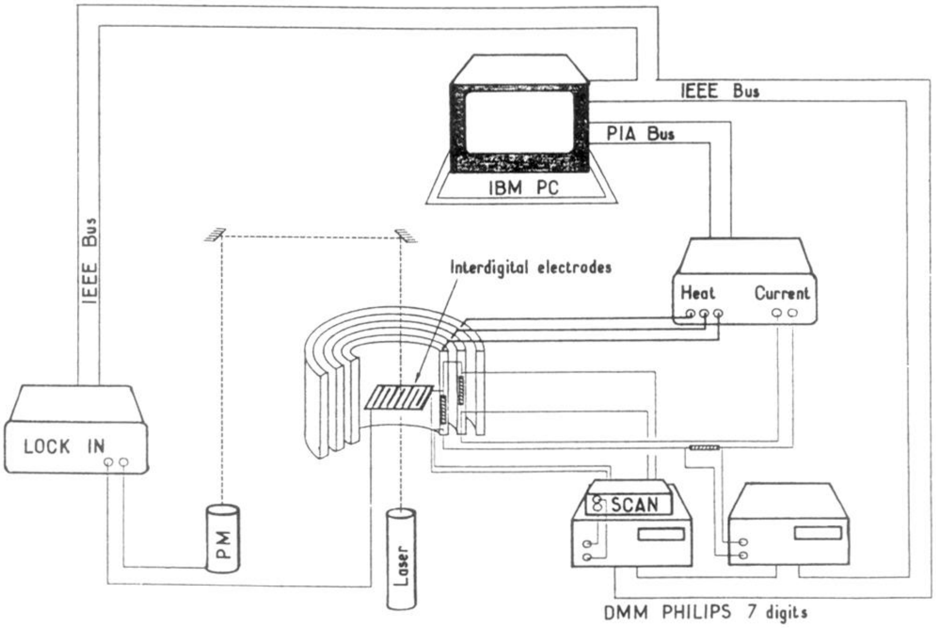

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