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Anomalous Temperature Dependence of the Elastic Constant B at the Smectic-to-Nematic Phase Transition in Binary Mixtures of Hexyloxycyanobiphenyl-Octyloxycyanobiphenyl (6OCB-8OCB)

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(Received 10 December 1981)

In hexyloxycyanobiphenyl-octyloxycyanobiphenyl (6OCB-8OCB) binary mixtures displaying reentrant behavior, the smectic elastic constant, B, deviates from a simple power law of the form $B = B_1(T_{NA} - T)^{\varphi}$ and levels off as $T \to T_{NA}$. This behavior is consistent with the Nelson-Toner dislocation-unbinding model of the transition.

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The nematic to smectic-A (N-A) phase transition is one of the major unsolved problems in statistical physics. Following de Gennes's proposal[1] of an analogy between the smectic-A and superconducting phases there have been numerous experiments demonstrating the apparently continuous nature of the N-A transition. Unfortunately, the critical exponents extracted from these experiments are not consistent with the hypothesis of a universal transition.[2-6] Nelson and Toner[7] have recently argued that the N-A transition occurs through the spontaneous generation of free dislocations. They predict that although the correlation lengths $\xi_{\parallel}$ and $\xi_{\perp}$ diverge as the transition temperature, T_{NA}, is approached the ratio $\xi_{\parallel}/\xi_{\perp}^2$ becomes a nonzero constant. Since anisotropic scaling[7,8] predicts that the smectic elastic constant $B \sim \xi_{\parallel}/\xi_{\perp}^2$, Nelson and Toner argue that it should vanish discontinuously at the N-A transition. Analogous effects have been observed as a result of vortex unbinding in two-dimensional[9,10] films of superfluid ^{4}He and have been searched for at the melting transition of two-dimensional liquid-crystalline films.[11] Confirmation of this effect in a three-dimensional system for which the lower marginal dimensionality is three would be particularly interesting. Unfortunately, the expected jump discontinuity in B has not been observed in previous experiments. In this Letter we present experimental results for the critical behavior of B in binary mixtures of octyloxycyanobiphenol (8OCB) and hexyloxycyanobiphenol (6OCB) that show this jump discontinuity and are consistent with the Nelson-Toner proposal.

For a range of concentrations mixtures of 8OCB and 6OCB exhibit sequentially (on lowering the temperature) a nematic, a smectic-A, and a "reentrant" nematic phase.[12-16] The width of the smectic-A phase in temperature, $\delta T(y)$, is given by $\delta T(y) = A(y_0 - y)^{1/2}$, where y is the fractional molar concentration of 6OCB, $y_0 = 0.4254$, and $A = 87.22$ K. In all previous studies of these mixtures the N-A transition appears to be continuous at a temperature resolution of 10 mK.

The experimental technique used here has been described previously.[17] The elastic constant, B, was determined from the light scattered by bulk second-sound modes at the free surface (i.e., air–liquid-crystal interface) of 300–500-μm-thick oriented samples. The materials were obtained from British Drug House and were used without further purification. The mole fractions were determined to better than 1% and the transition temperatures agree with those in the literature.[14] The measured $B(\Delta T = T_{NA} - T)$ for four mixtures are shown in Fig. 1. In each case, T_{NA} was directly determined on both heating and cooling to ±5 mK. It is clear for $y \geq 0.37$ that the $B(\Delta T)$ curves level off [$\partial B/\partial(\Delta T)$ becomes small-

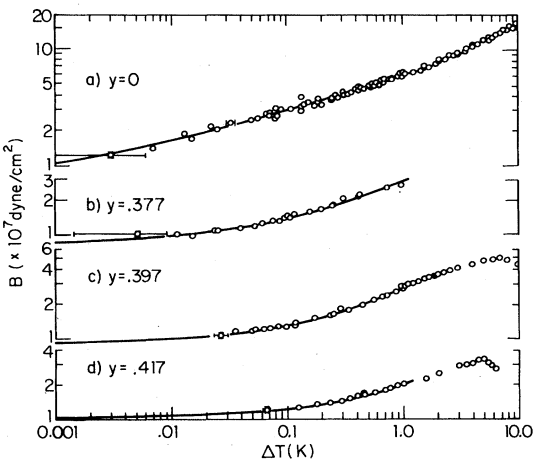


FIG. 1. $B(\Delta T)$ for pure 8OCB and three different binary mixtures of 8OCB-6OCB. The solid line represents the result of nonlinear least-squares fits to the data for $\Delta T \leq 1.0$ K.

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er] as $\Delta T \to 0$.

Possible artifacts that might produce the observed leveling off of $B(\Delta T)$ are (1) phase separation of the binary mixture, (2) vertical inhomogeneities of the samples, (3) nonhydrodynamic behavior, or (4) temperature inhomogeneities within the oven. Phase separation has never been observed in 8OCB-6OCB mixtures and the phase diagram that we obtain is essentially identical to those in the literature.[12-16] In addition, absolutely no hysteresis was observed: The transition temperatures obtained on heating and cooling are identical to ±5 mK.

To check experimentally for the presence of either a vertical inhomogeneity or nonhydrodynamic behavior the response of the first two modes was measured. The results are shown in Fig. 2 for the most sensitive case ($y = 0.417$) and three temperatures. In all cases the ratio of the resonant frequencies of the two modes is independent of temperature and is equal to the value predicted for a homogeneous sample. The observed leveling off of $B(\Delta T)$ cannot be due to either effect. To check for the presence of temperature gradients, B was determined for different positions on samples with $y = 0$ and $y = 0.42$ with $\Delta T \approx 10$ mK. The measured gradient was smaller than 5 mK.

The results of the least-squares fits of the data with $\Delta T \lesssim 1.0$ K by the Nelson-Toner form, $B(T) = B(T_{NA}) + B_1(\Delta T)^{\varphi}$, are shown by the solid lines in Fig. 1 and are given in Table I, fit I. Except for $y = 0$ (pure 8OCB), $B(T_{NA}) = 0$ is not allowed by the fits. The results of fitting the data by the form of a weakly first-order transition, $B(T) = B_1[T^*(y) - T]^{\varphi}$, are shown as fit II in Table I. The temperatures $T^*(y)$ at which $B(T)$ would extrapolate to zero are 50, 120, and 300 mK higher than the observed transition temperatures for $y = 0.377$, 0.397, and 0.417, respectively. However, the absence of a peak in the specific heat argues against a first-order transition.[15] The

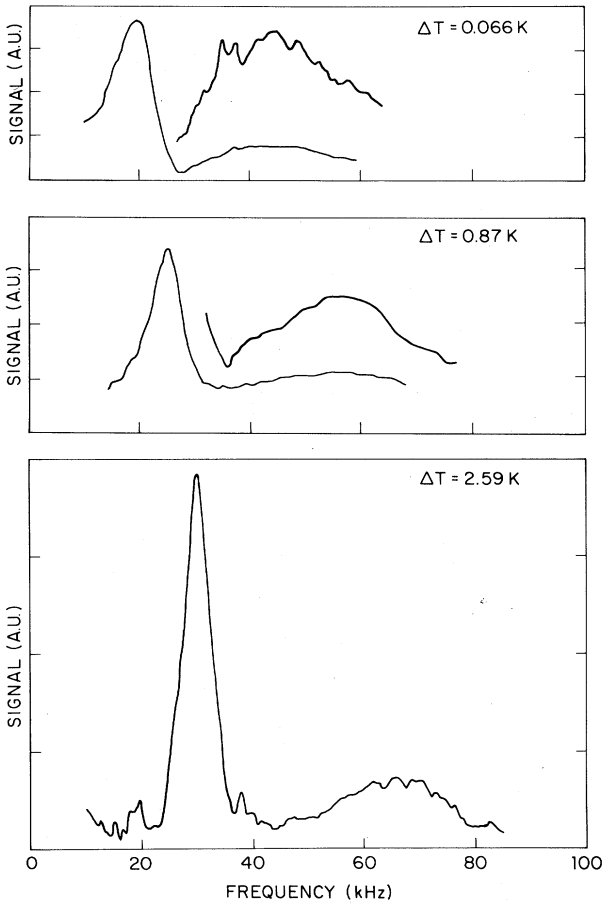


FIG. 2. The observed response as a function of frequency at three different temperatures for the sample with $y = 0.417$.

TABLE I. Results of nonlinear least-squares fits with $\chi^2 \leq 1.0$. Fit I is with the form $B(T) = B(T_{NA}) + B_1(\Delta T)^{\varphi}$ for $\Delta T \leq 1.0$ K. Fit II is with the form $B(T) = B_1[T^*(y) - T]^{\varphi}$ for $\Delta T \leq 1.0$ K. Values for $T^*(y) - T_{NA}$ are given in the text.

Fit	y	$10^{-7}B(T_{NA})$ (dyn cm^{-2})	$10^{-7}B_1$ (dyn cm^{-2} K$^{-\varphi}$)	φ	$B_p(y)$ (dyn cm^{-2} K$^{-0.636}$)
I	0.417	1.03 ± 0.07	1.01 ± 0.07	0.69 ± 0.07	1.26
	0.397	0.90 ± 0.07	1.81 ± 0.11	0.64 ± 0.04	1.72
	0.377	0.86 ± 0.07	2.07 ± 0.13	0.56 ± 0.04	2.11
	0	0.15 ± 0.43	5.9 ± 0.45	0.33 ± 0.04	4.17
II	0.417		1.83 ± 0.07	0.42 ± 0.05	
	0.397		2.59 ± 0.02	0.45 ± 0.03	
	0.377		2.81 ± 0.05	0.36 ± 0.02	

results of fitting with a continuous transition with a critical region ≤ 100 mK, $B(T) = B_1(\Delta T)^{\varphi}$, are $\varphi \simeq 0.13 \pm 0.05$ with $\chi^2 \approx 3$.

An independent test of the present experimental method derives from the concentration dependence of B_1. Recent x-ray measurements on 8OCB-6OCB mixtures by Kortan *et al.*[14] have shown that the correlation lengths in both the nematic and the reentrant nematic phases are described very well by a generalized Pershan-Prost model.[18] Within the smectic-*A* phase, the model predicts $B(T) = B(T_{NA}) + B_2[\delta T(y)\Delta T + (\Delta T)^2]^{\varphi}$. For $\Delta T \leq \delta T(y)$, $B(T) = B(T_{NA}) + B_p(y) \times (\Delta T)^{\varphi}$, where $B_p(y) = B_2[\delta T(y)]^{\varphi}$. Treating $B(T_{NA})$, B_2, and φ as free parameters, the data within $\Delta T \leq 1$ K for the three samples with $y > 0.37$ were simultaneously fitted by this form. The resulting values are $B(T_{NA}) = (0.89 \pm 0.06) \times 10^7$ dyn cm^{-2}, $B_2 = (0.317 \pm 0.04) \times 10^7$ dyn cm^{-2} K$^{-\varphi}$, and $\varphi = 0.636 \pm 0.04$. For $y > 0$, good agreement is found between these values of $B(T_{NA})$ and φ and the values obtained in the individual fits. The calculated values for $B_p(y)$, displayed in the last column of Table I, fit I, also agree well with the values of B_1. For $y = 0$, the model slightly underestimates B_1 and overestimates $B(T_{NA})$. Although the values for $B(T_{NA})$ decrease with decreasing y, the quantity that is expected to have a universal value at the transition is $\eta_{\rm crit} \propto [B(T_{NA})K_1]^{-1/2}$ rather than $B(T_{NA})$. Our results suggest that the Frank constant, $K_1(T_{NA})$, should increase with decreasing concentration. Since $K_1(T)$ does not display critical behavior at the *N*-*A* transition, a measurement of its concentration dependence would provide an excellent test of the universality of $\eta_{\rm crit}$. For a typical K_1 [$(1.5-6) \times 10^{-7}$ dyn] and $B(T_{NA}) = 0.89 \times 10^7$ dyn cm^{-2} we find very reasonable values for $\eta_{\rm crit}$ (0.29–0.58). The largest experimentally measured η is 0.38 ± 0.06.[19]

Nelson and Toner[20] have argued from the anisotropic scaling results that a necessary condition for observing true critical behavior on the nematic side of the transition is that the dimensionless parameter $\zeta = \xi_\perp^2 q_0/\xi_\parallel$ [where $q_0 = 2\pi/$(layer spacing)] be roughly equal to $\zeta_M = k_B q_0^3/B(T_{NA})$. Using our measured values of $B(T_{NA})$ (0.89×10^7 dyn cm^{-2} for $y \gtrsim 0.37$ and $\leq 0.58 \times 10^7$ dyn cm^{-2} for $y = 0$) we find $\zeta_M = 42$ for $y \gtrsim 0.37$ and $\zeta_M \geq 0.62$ for $y = 0$. Table II presents a comparison of the largest observed values, $\zeta_{\rm exp}$, with the estimated maximum values, ζ_M, for the nematic critical scattering measurements.[2,14] Extrapolating ζ to smaller $\Delta T = T - T_{NA}$ using the measured temperature dependence of $\xi_{\perp,\parallel}$, we display in Table II ΔT_M, which is the value at which $\zeta \simeq \zeta_M$. The smallest value of ΔT for which a measurement was made is $\Delta T_{\rm exp}$. Similar estimates for octylcyanobiphenyl[2] (8CB) and butyloxybenzylidene octylaniline[6] (4O.8) demonstrate that *by this criterion* none of the previous x-ray measurements have been in the true critical regime.

TABLE II. Comparison of the predicted critical region with critical x-ray scattering measurements for $T > T_{NA}$.

Material	ζ_M	$\zeta_{\rm exp}$	$\Delta T_{\rm exp}$ (K)	ΔT_M (K)	Refs.
8OCB-6OCB:					
$y = 0$	≥ 62	6.5	0.03	$\leq 2.3 \times 10^{-4}$	2
$y = 0.330$	42	12.1	0.045	3.5×10^{-3}	14
$y = 0.413$	42	8.7	0.215	5.5×10^{-3}	14
$y = 0.420$	42	15.4	0.13	2.6×10^{-2}	14
8CB	≥ 79	6	0.01	$\leq 7.9 \times 10^{-6}$	2,21
4O.8	≥ 50	11.7	0.003	$\leq 1.2 \times 10^{-4}$	6,21

In conclusion, we have found that in 8OCB-6OCB binary mixtures the smectic elastic constant deviates from a simple power law and levels off at $T \to T_{NA}$. This behavior is consistent with the Nelson-Toner model of the transition in which B goes to zero discontinuously even though the transition is second order. However, it is not possible to distinguish this result from either a weakly first-order transition or a transition with a very small critical region.

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Solitons in Quasi One-Dimensional Spin- and Charge-Density-Wave Systems

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The solitons of spin-density-wave and charge-density-wave systems of arbitrary commensurability are discussed. Spin-density-wave systems can have both "scalar" (i.e., phase and amplitude) solitons as well as "polarization" solitons. A simple picture is presented to account for the various charge and spin states of the scalar solitons of both systems. Localized states are also found in polarization solitons. Unlike those of the scalar solitons, they are in general nondegenerate.

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Most quasi one-dimensional materials (at ambient pressures) are either charge-density-wave (CDW) or spin-density-wave (SDW) systems. Recently, there has been much interest in the solitons in CDW systems and the associated electronic excitations.[1-3] These excitations are expected to have unusual spin-charge relations[1,2] and are fractionally charged in general.

There have been few studies on the solitons in SDW systems. Unlike CDW's, SDW's are pseudovectors rather than scalars. As a result, there is a greater variety of SDW solitons. It is natural to ask whether localized electronic states similar to those in CDW systems[1,2] also exist in SDW solitons, and what are their spin-charge relations if they do. Furthermore, since the charges of CDW solitons result from nonintegral depletions on states from both the valence and the conduction band,[1,2] it is interesting to find out whether there can be depletion mechanisms leading to fractional spins in SDW solitons.[4]

Returning to the CDW solitons, I note that although some of the earlier phenomenological theories on CDW's[5,6] already anticipate the possibility of fractional charges, their predictions are not identical to the recent microscopic calculations.[1,2] References 1 and 2 predict more charged states than Refs. 5 and 6. Apart from these differences, there is also the question about the generality of these results. While Refs. 5 and 6 consider only solitons with slowly varying phase, Refs. 1 and 2 have ignored the interactions between electrons and the quantum fluctuations of phonons. It would be useful to know how the predictions of these theories are affected by the relaxations of these restrictions.

In the following, I shall present a simple picture for the charge and spin of the solitons in both CDW and SDW systems. It enables us to answer the previous questions. I also present a study on the "polarization" solitons—a kind of soliton special to SDW's.

Formation of a single CDW (SDW) corresponds to the appearance of a new Fourier component

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