

(1979).

<sup>4</sup>Y.-K. M. Peng *et al.*, Bull. Am. Phys. Soc. **24**, 947 (1979) [Engineering Test Facility (ETF)].<sup>5</sup>P. H. Rutherford, Bull. Am. Phys. Soc. **24**, 1010 (1979) [International Tokamak Reactor (INTOR)].<sup>6</sup>L. C. Bernard *et al.*, Nucl. Fusion **20**, 1199 (1980).<sup>7</sup>W. Kerner *et al.*, in *Proceedings of the Ninth European Conference on Controlled Fusion and Plasma Physics, Oxford, England, 1979*, edited by R. J. Bickerton (Culham Laboratory, Oxford, England, 1979), Vol. I, p. 9.<sup>8</sup>A. M. M. Todd *et al.*, Phys. Rev. Lett. **38**, 826 (1977).<sup>9</sup>D. Berger, Ph.D. thesis, Lausanne, 1977 (unpublished).<sup>10</sup>A. M. M. Todd *et al.*, Nucl. Fusion **19**, 743 (1979).<sup>11</sup>L. E. Zakharov and V. D. Shafranov, Zh. Tech. Fiz. **43**, 225 (1973) [Sov. Phys. Tech. Phys. **18**, 151 (1973)].<sup>12</sup>D. R. Dobrott *et al.*, Phys. Rev. Lett. **39**, 943 (1977).<sup>13</sup>J. W. Connor *et al.*, Phys. Rev. Lett. **40**, 396 (1978).<sup>14</sup>C. Mercier, Nucl. Fusion **1**, 47 (1970).<sup>15</sup>R. Gruber *et al.*, to be published.

## Heat-Capacity Study of the Transition from a Stacked-Hexatic-*B* Phase to a Smectic-*A* Phase

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High-resolution ac calorimetry measurements have been performed on a liquid-crystal material exhibiting a stacked-hexatic-*B*-smectic-*A* phase transition. The transition appears to be second order with a pronounced, symmetric heat capacity peak and no observable thermal hysteresis. The data can be fitted by a power law divergence with critical exponents  $\alpha = \alpha' = 0.64 \pm 0.04$  and a ratio of critical amplitudes  $A/A' = 0.83$ . Measurements have also been carried out on a crystalline-*B*-smectic-*A* transition which is found to be first order.

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It is well known that some liquid-crystal materials exhibit a layered phase with hexagonal in-plane ordering.<sup>1</sup> This phase is referred to as a smectic *B* or, simply, *B* phase. Recent experiments<sup>2-8</sup> have established that, among the *B* phases in different materials, there are two microscopically distinct types. The first type is a crystalline phase. X-ray measurements<sup>2</sup> demonstrated that this *B* phase has long-range, three-dimensional (3D) positional order. Its crystalline nature was confirmed by mechanical measurements which showed that this phase supports a shear both within<sup>3,4</sup> and between<sup>5</sup> its layers. The second type of *B* phase was first identified by its lack of interlayer correlations.<sup>6</sup> A detailed x-ray study<sup>7</sup> demonstrated that the second *B* phase has only short-range in-plane positional order but long-range 3D sixfold bond-orientational order. The mechanical measurements<sup>8</sup> demonstrated that the second *B* phase does not support an in-plane shear.

The possibility of a phase characterized by bond-orientational order was first discussed in the context of two-dimensional (2D) melting.<sup>9,10</sup> A bond-orientationally ordered phase (a hexatic phase)

was predicted to occur between the 2D solid and liquid if 2D melting was a dislocation-mediated second-order phase transition. Subsequently, a 3D liquid-crystal phase was proposed which consisted of stacked, interacting 2D hexatic layers.<sup>11</sup> The structural and mechanical properties of the second *B* phase are those expected for this 3D stacked hexatic phase. We, therefore, refer to the first type of *B* phase as a crystalline *B* and the second as a hexatic *B*. Both *B* phases can melt into a higher temperature smectic-*A* (*A*) phase with fluidlike layers.

In this paper we report detailed heat-capacity measurements on the hexatic-*B*-*A* transition. This transition is important to study because the liquid-crystal hexatic *B* phase is the only system in which the existence of hexatic ordering has been proven. We will also report measurements on the crystalline-*B*-*A* transition which we find to be first order. In contrast, the hexatic-*B*-*A* transition is second order exhibiting a symmetric heat-capacity peak with no observable thermal hysteresis.

The liquid-crystal compounds that we chose to study were *N*-(4-*n*-butyloxybenzylidene)-4-*n*-

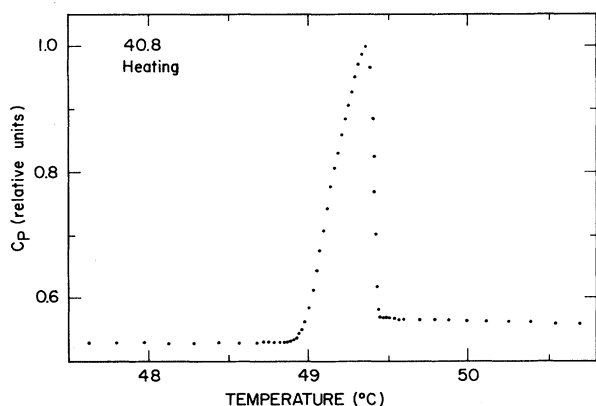


FIG. 1. Temperature dependence of the heat capacity at the crystalline-*B*-*A* transition in 4O.8. The data were taken in a heating run.

octylaniline (4O.8) which has a crystalline *B* phase and *n*-hexyl-4'-*n*-pentyloxybiphenyl-4-carboxylate (65OBC)<sup>12</sup> which has a hexatic *B* phase. The *B* phases in both compounds have been identified and characterized by x-ray<sup>2,7</sup> and mechanical<sup>3,4,5,8</sup> techniques.

Our heat-capacity data were taken with use of an ac calorimeter<sup>13</sup> operated at 0.63 Hz. The liquid-crystal samples were contained between a pair of microscope cover slides in a chemically etched cavity 1.1 cm diam  $\times$  0.02 mm deep (inset Fig. 2). Both dc and ac sample temperatures

were measured directly by two electrically isolated 0.001-in. flattened Chromel-Constantan thermocouple junctions which were attached to the top cover slide by using a minute amount of GE 7031 varnish. The resistance heater was a 90-Å-thick gold film covering the entire bottom surface of the lower cover slide. The sample was maintained in a dry nitrogen atmosphere.

In order to achieve optimum resolution the amplitude of the ac temperature oscillation was 2 mK (peak-to-peak) in the vicinity of the transition. On the inverse heat capacity versus frequency curve the thermal relaxation time of the sample resulted in a 3-dB high-frequency cutoff at 34 Hz, well above the 0.63 Hz operating frequency. This ensured that the sample was in thermal equilibrium throughout the measured temperature range. The accuracy of the absolute temperature scale was better than 0.2 K and the accuracy of the relative scale was better than 3 mK.

The temperature dependence of the heat capacity for the crystalline-*B*-*A* transition in 4O.8 is shown in Fig. 1. The asymmetry on both sides of the transition is evident. Data taken on heating and cooling exhibited a 50-mK difference in the temperature of the peak position as well as different peak heights. This indicates the existence of superheating and supercooling. These observations demonstrate that the crystalline-*B*-

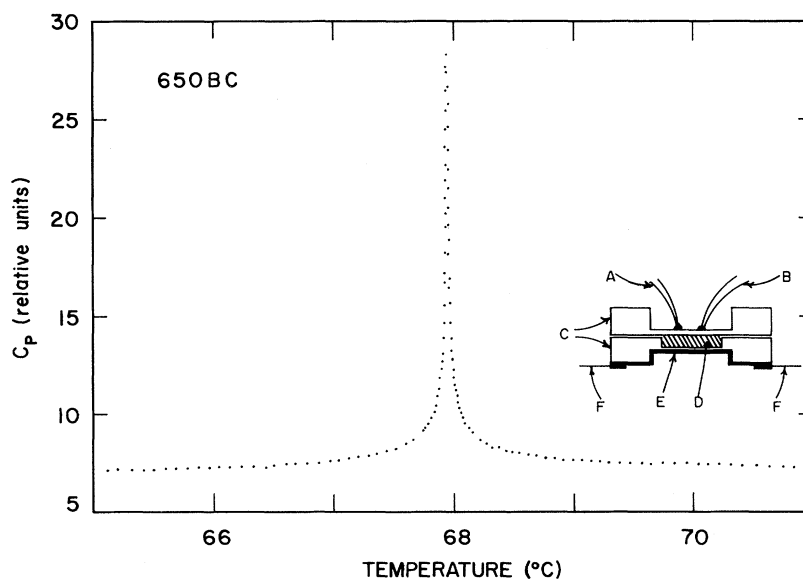


FIG. 2. The temperature dependence of the heat capacity at the hexatic-*B*-*A* transition in 65OBC. The inset describes the sample cell which contains two thermocouple junctions (*A* and *B*) to measure the ac and dc temperatures, a pair of chemically etched microscope cover slides (*C*), a liquid-crystal sample (*D*), and gold-film resistance heater (*E*).

A transition in 4O.8 is a first-order transition.

The temperature dependence of the heat capacity for the hexatic- $B$ - $A$  transition in 65OBC is shown in Fig. 2. For clarity only part of the data have been plotted. The addendum heat-capacity contribution from the sample cell was estimated to be 4.7 in relative units which is approximately two-thirds of the total background and is much smaller than that of the divergent part of the heat capacity. In contrast to the 4O.8 data, this transition appeared to be second order with a pronounced symmetric peak. There was no observable thermal hysteresis within our relative temperature resolution between successive runs ( $\pm 4$  mK) and  $T_c$  was stable through repetitions of the experiment.

The heat-capacity data were fitted with the power law form

$$C_p^+ = At^{-\alpha} + B + DT,$$

$$C_p^- = A' t^{-\alpha'} + B' + DT$$

in the reduced temperature range  $2 \times 10^{-5} < t = |(T - T_c)/T_c| < 1.6 \times 10^{-2}$ . The transition temperature and linear background slope were assumed to be the same on both sides of the transition. The optimum least-squares fitting parameters were  $\alpha = 0.65 \pm 0.02$ ,  $\alpha' = 0.61 \pm 0.02$ ,  $A/A' = 0.83$ ,  $B = 5.30$ ,  $B' = 5.15$ , and  $T_c = (67.930 \pm 0.003)^\circ\text{C}$ . The quality of fitting was insensitive to the fitting range. A log-log plot of the divergent part of the heat capacity versus reduced temperature is shown in Fig. 3 for data above and below  $T_c$ . We believe that the difference between  $\alpha$  and  $\alpha'$  is insignificant. This is corroborated by the observation that requiring  $B = B'$  resulted in a best fit with  $\alpha = \alpha' = 0.64 \pm 0.04$ .

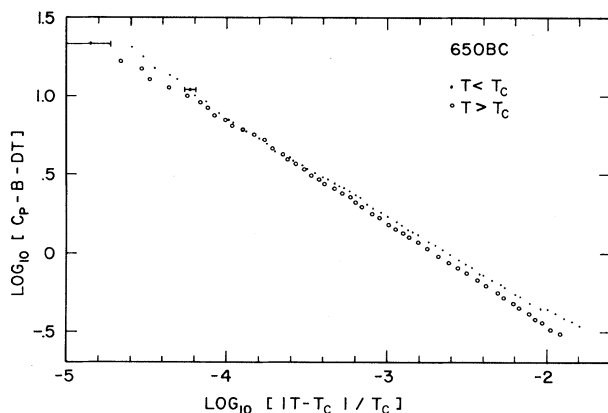


FIG. 3.  $\log_{10}(C_p - B - DT)$  vs  $\log_{10}(|T - T_c|/T_c)$  for the hexatic- $B$ - $A$  transition in 65OBC.

An x-ray study<sup>7</sup> of the hexatic  $B$  phase in 65OBC identified bond-orientational order as the order parameter for the hexatic- $B$ - $A$  transition. If this is the case, then the anisotropic 3D  $XY$  model should apply to this transition. The heat capacity exponent for this model is slightly negative which clearly disagrees with our measurement. In fact, most 3D models predict an  $\alpha \approx 0$ . To our knowledge the only model system which predicts a heat-capacity exponent consistent with our result is the 2D four-state Potts model in which  $\alpha = 0.67$ . In principle, a four-state Potts-like orientational ordering of the molecules about their long axes is possible (Fig. 4);<sup>14</sup> however, x-ray results<sup>7</sup> rule out this structure in favor of a local herringbone molecular orientational ordering. Another possibility is that the hexatic- $B$ - $A$  transition in 65OBC is in the vicinity of a multicritical point with the interlayer interaction strength acting as the second relevant thermodynamic parameter. An increase in the strength of this coupling results in a first-order phase transition. We have qualitatively observed this by studying mixtures of 4O.8 and 65OBC. As a small concentration of 4O.8 ( $\sim 10\%$  by weight) is added to 65OBC, the hexatic- $B$ - $A$  transition begins to take on the characteristics of a first-order transition. Extensive measurements on such mixtures are currently in progress.

In conclusion, we have established that, unlike the first-order crystalline- $B$ - $A$  transition in 4O.8, the hexatic- $B$ - $A$  transition in 65OBC is second order. The measured heat-capacity exponents  $\alpha = \alpha' = 0.64$  cannot be explained by any current theory. The anisotropic  $XY$  model, which

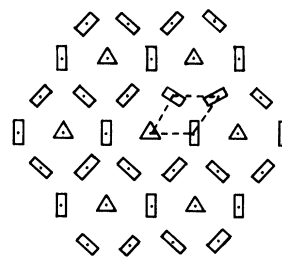


FIG. 4. A view down the long molecular axes of the lath-shaped 65OBC molecules describing a possible orientational ordering of the molecules about their long axes. This ordering has the symmetry of the four-state Potts model. The triangles indicate molecules which, within a single domain, orient in the same direction parallel to one of the three directions of the surrounding molecules. The dashed lines indicate the unit cell.

should apply to this system, may be incomplete without a consideration of couplings between the bond-orientational order parameter and other ordering fields, such as the local herringbone molecular orientational order. We note that a possible check of our measured value for the exponent  $\alpha$  is contained in the temperature dependence of the in-plane positional correlation length. Since this quantity is a function of the free energy it should exhibit a  $(1 - \alpha)$  singularity.<sup>15</sup> X-ray measurements of the positional correlation length<sup>7</sup> are consistent with a  $(1 - 0.64)$  singularity although more detailed data are required.

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<sup>1</sup>P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

<sup>2</sup>D. E. Moncton and R. Pindak, *Phys. Rev. Lett.* **43**,

701 (1979); A. J. Leadbetter, M. A. Mazid, B. A. Kelley, J. Goodby, and G. W. Gray, *Phys. Rev. Lett.* **43**, 630 (1979); P. S. Pershan, G. Aeppli, J. D. Litster, and R. J. Birgeneau, in Proceedings of the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 1980 (to be published).

<sup>3</sup>R. Pindak, D. J. Bishop, and W. O. Sprenger, *Phys. Rev. Lett.* **44**, 1461 (1980).

<sup>4</sup>J. C. Tarczon and K. Miyano, *Phys. Rev. Lett.* **46**, 119 (1981).

<sup>5</sup>M. Cagnon and G. Durand, *Phys. Rev. Lett.* **45**, 1418 (1980).

<sup>6</sup>A. J. Leadbetter, J. C. Frost, and M. A. Mazid, *J. Phys. (Paris) Lett.* **40**, L325 (1979).

<sup>7</sup>R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, *Phys. Rev. Lett.* **46**, 1135 (1981).

<sup>8</sup>R. Pindak, D. J. Bishop, W. O. Sprenger, and D. D. Osheroff, to be published.

<sup>9</sup>P. G. de Gennes and G. Sarma, *Phys. Lett.* **38A**, 219 (1972).

<sup>10</sup>B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978).

<sup>11</sup>R. J. Birgeneau and J. D. Litster, *J. Phys. (Paris) Lett.* **39**, 399 (1978).

<sup>12</sup>J. W. Goodby and R. Pindak, to be published.

<sup>13</sup>J. M. Viner and C. C. Huang, to be published.

<sup>14</sup>M. Schick, private communication.

<sup>15</sup>An experimental example of a  $(1 - \alpha)$  singularity is the behavior of the electrical resistivity near an order-disorder transition. See, for example, D. S. Simons and M. B. Salamon, *Phys. Rev. Lett.* **26**, 750 (1971).

## Measurements of Second Sound in Partially Spin-Polarized <sup>3</sup>He-<sup>4</sup>He Solutions

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The second-sound velocity of three dilute <sup>3</sup>He-<sup>4</sup>He mixtures was measured with high precision down to a temperature of 10 mK and in a magnetic field of 93 kOe. For the most dilute sample, which had a molar concentration of 0.001, the maximum spin polarization of the <sup>3</sup>He atoms was estimated to be 36%. The measured relative change in the second-sound velocity was 3%. This is considerably larger than the change predicted recently by Bashkin and Meyerovich. An explanation for this discrepancy is presented.

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There is currently significant interest in spin-polarized quantum systems. In addition to the work on atomic hydrogen and on pure liquid <sup>3</sup>He, there have also been theoretical studies on <sup>3</sup>He-<sup>4</sup>He mixtures.<sup>1</sup> However, the effects of large magnetic fields on the properties of dilute <sup>3</sup>He-<sup>4</sup>He solutions have not previously been experimentally measured. In this Letter we report results for second-sound propagation in solutions with nominal <sup>3</sup>He molar concentrations  $X$  of 0.001, 0.003, and 0.010 in a magnetic field  $H$  of 93 kOe.

The data extend down to a temperature of 10 mK and clearly show the effects of a partial polarization of the nuclear spins.

The design of the second-sound resonator (length, 1.4 cm; diameter, 1.3 cm) was similar to that described in Ref. 2. However, the resonator used for the present study was constructed mainly of silver rather than copper in order to avoid a large heat capacity of the empty cell at high fields and at low temperatures. In addition, the cylindrical surface of the resonance cavity