

TABLE I. Calculated and experimental Stark shifts in MHz/(kV/cm)².

Level	α_0 (expt)	α_2 (expt)	α_0 (calc)	α_2 (calc)
$4d\ ^2D_{3/2}$	155.3(1.7)	-38.5(7)	152.02	-35.64
$4d\ ^2D_{5/2}$	156.1(1.3)	-53.2(5)	151.97	-51.06
$5s\ S_{1/2}$	5.2(3)		5.81	

expressed in terms of integrals of the radial wave functions as follows:

$$\alpha_0(\frac{5}{2}) = -\frac{2}{15}(P + \frac{3}{2}F), \quad \alpha_2(\frac{5}{2}) = \frac{2}{15}(P + \frac{3}{7}F), \quad (5)$$

where the notation is that of Ref. 6 and we have let $P(\frac{3}{2}) = P(\frac{5}{2}) = P$ and $F(\frac{3}{2}) = F(\frac{5}{2}) = F$. It has been assumed that the spin-orbit interaction does not affect these radial integrals. Using the same assumption we find $\alpha_0(\frac{3}{2}) = \alpha_0(\frac{5}{2})$ and $\alpha_2(\frac{3}{2}) = \frac{7}{10}\alpha_2(\frac{5}{2})$. The experimental values agree with these expressions to within 3.5%. One may solve Eq. (5) for P and F by using the measured polarizabilities. Thus, in units of MHz/(kV/cm)², we obtain $F = 711.2(9.1)$ and $P = 101.0(10.6)$. In the Coulomb calculation, 98% of the $4d$ level shifts come from interaction with $5p$ and $4f$. Thus the measured P and F are very nearly the radial integrals for the nearest states only. Then the experimentally determined P and F can be used to evaluate the oscillator strengths, giving $f_{4d \rightarrow 5p} = 0.274(29)$ and $f_{4d \rightarrow 4f} = 0.018\ 85(24)$.

Two-photon spectroscopy has provided a convenient means to study Stark shifts in highly excited states with high resolution. Further im-

provements, such as the use of laser frequency locking and heterodyne techniques, should increase this resolution even more.

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Orientalional Order Measurements near a Possible Nematic-Smectic-A Tricritical Point*

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We have measured a proton NMR dipolar splitting, ΔH , proportional to the "nematic order parameter," in the nematic and smectic-A phases of *p*-cyanobenzylidene-*p*-nonyl-aniline, at pressures up to 3.5 kbar. The discontinuity in ΔH at the nematic-smectic-A phase transition decreases from a relatively large value at 1 atm to an unobservably small value at higher pressures. We tentatively identify a tricritical point for this transition at $t_i = 140 \pm 4^\circ\text{C}$ and $P_i = 2.89 \pm 0.23$ kbar.

There has been considerable interest recently in the nature of the nematic-smectic-A liquid-crystal phase transition, since mean-field theo-

ries¹⁻³ indicate that this transition is allowed to be second order. Although clearly first order in most compounds,⁴ possible second-order behav-

ior has been observed, most notably in *p*-cyanobenzylidene-*p*-octyloxyaniline.⁵ Recently, however, independent investigators using three different experimental techniques have reported strong evidence that the transition in CBOOA is very weakly first order.⁶ Indeed, the assertion that the nematic-smectic-*A* phase transition is *always* at least weakly first order has been made on purely theoretical grounds.⁷ Nevertheless, there is much experimental evidence to support at least qualitatively the ideas expressed by the mean-field theories. Although the various mean-field theories differ in detail, a common prediction is that, as the reduced temperature t_r ($\equiv T_{NA}/T_{NI}$, the ratio of nematic-smectic-*A* to nematic-isotropic transition temperatures) decreases, a first-order nematic-smectic-*A* transition should become weaker and finally second order. This prediction seems to be borne out in studies of homologous series of compounds,⁴ where the variation in t_r is effected by varying the length of molecular alkyl end chains. This type of study suffers two serious restrictions: t_r is not continuously variable, and it is not clear that results on different compounds are strictly comparable. The use of hydrostatic pressure appears to be a feasible technique for varying t_r continuously, allowing, in principle, observation of both first- and second-order behavior in a single compound on opposite sides of a tricritical point. Recently, Keyes, Weston, and Daniels,⁸ measuring turbidity in cholesteryl oleyl carbonate, reported evidence of a change in the nature of the cholesteric-smectic-*A* phase transition under pressure suggestive of a tricritical point. Their result has been confirmed by others in calorimetric experiments under pressure.⁹ In this Letter, we examine the effects of pressure on the nematic-smectic-*A* transition in *p*-cyanobenzylidene-*p*-nonylaniline (CBNA) by measuring a quantity proportional to the nematic order parameter, a splitting ΔH in the proton dipolar NMR spectrum, at pressures up to 3.5 kbar. In qualitative agreement with mean-field-theory predictions, as t_r decreases with increasing pressure, the discontinuity in ΔH at the nematic-smectic-*A* transition is observed to decrease from a value 15 times our experimental resolution of 0.3% of ΔH to a value undetectable within this resolution.

Descriptions of the smectic-*A* phase contain a parameter σ (ψ , in de Gennes's treatment), proportional to the smectic-layer density-wave amplitude, which measures the strength of the smectic order. In the context of the theory of

tricritical phenomena,¹⁰ σ would be called an ordering density. Also involved in the theory of tricritical phenomena is a nonordering density; this nonordering density may be chosen to be the nematic order parameter $\eta = \langle 3 \cos^2 \theta - 1 \rangle / 2$, where θ is the angle between the long axis of a molecule and the optic axis (which is normal to the smectic layers in smectic-*A* phases). Both σ and η should change discontinuously in a first-order nematic-smectic-*A* transition, and continuously in a second-order transition. Although the ordering density is the observable of choice in general, measurements of σ in smectic liquid crystals are extremely difficult in practice. By contrast, our measurements of η are rather simple and precise.

The sample of CBNA was kindly provided by G. N. Taylor and was recrystallized from *n*-hexane until T_{NI} did not change. The sample was degassed by repeated melt-freeze-thaw cycles *in vacuo*, then introduced into 6-mm Pyrex NMR tube in an atmosphere of dry nitrogen. The sample was isolated from the pressure-transmitting fluid by the method of Brooks, Stejskal, and Weiss,¹¹ and an NMR coil potted in Teflon was fitted tightly over the NMR tube. The temperature was regulated to $\pm 0.05^\circ\text{C}$, and was homogeneous over the sample volume to 0.2°C . The pressure was constant to ± 0.5 bar up to 700 bar and to ± 3 bar at higher pressure. Pressure was measured with Heise gauges calibrated against dead-weight testers. The NMR detector was of the cw hybrid-tee¹² type operating at 28 MHz. A typical NMR signal in the absence of the pressure-generating fluid is shown in the inset of Fig. 1, which also defines the splitting ΔH . The splitting ΔH was measured to an accuracy of ± 0.004 Oe. In experiments under pressure, an extremely narrow NMR signal from the pressure-transmitting fluid is superimposed on the CBNA NMR signal, but this does not in any way affect the measurement of ΔH .

The splitting ΔH was measured for nine temperatures between 79 and 140°C over a range of pressures large enough to incorporate the whole nematic range and a large part of the smectic-*A* range. Alignment of the smectic-*A* layers normal to the field was assured by inducing the phase change from the nematic in the presence of the operating field of 6.7 kOe. That this field is sufficient to produce alignment was checked by inducing the phase change from the nematic in fields up to 14.5 kOe, with no change in the results for ΔH ; we performed this check both at

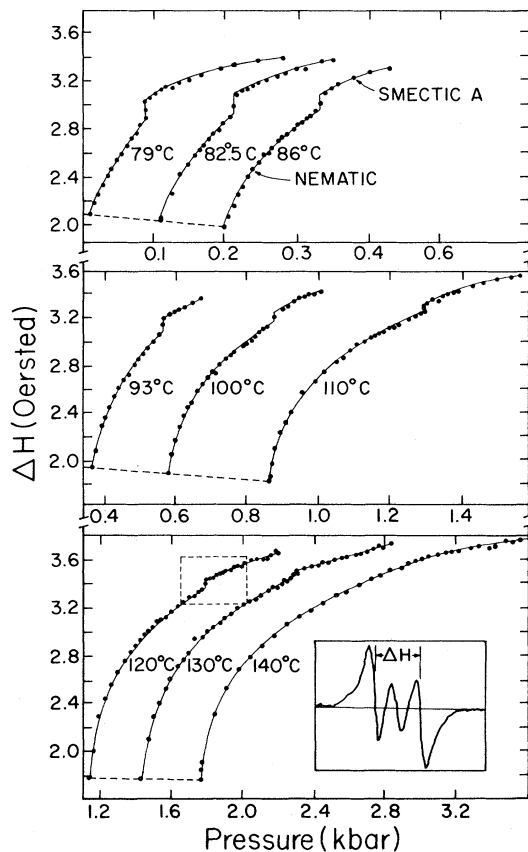


FIG. 1. Dependence of NMR dipolar splitting ΔH on pressure at nine temperatures for CBNA. The inset shows a typical derivative NMR spectrum for CBNA and defines the splitting ΔH . The solid curves are to aid the eye. The discontinuity in ΔH separates the nematic and smectic-A phases, as labeled on the 86°C curve. The dashed box on the 120°C curve is expanded in Fig. 2.

high pressure (2.2 kbar) and at 1 atm.

The data on ΔH versus pressure are shown in Fig. 1. In the lower-temperature runs, the discontinuity in ΔH (and, thus, the discontinuity in the order parameter η) at the nematic-smectic-A transition is relatively large. This is expected since the thermal range of the nematic phase of CBNA at 1 atm is small (2°C) and the latent heat for the nematic-smectic-A transition is relatively large (0.43 cal/g) at 1 atm.¹³ As the temperature is increased, the nematic-smectic-A transition occurs at larger values of ΔH , and the discontinuity in ΔH decreases. Finally, at 140°C, no first-order-transition effects are observed to a maximum pressure of 3.5 kbar [$\delta(\Delta H) > 0.01$ G] although, by extrapolation of the nematic-smectic-A coexistence curve, the transition is

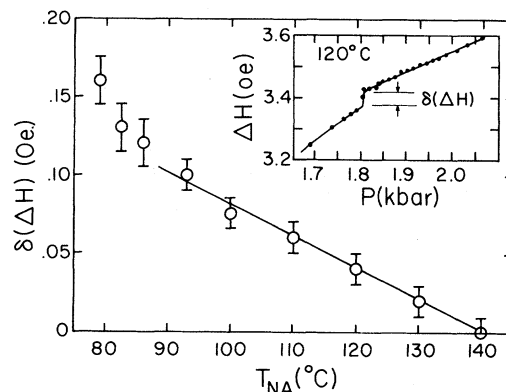
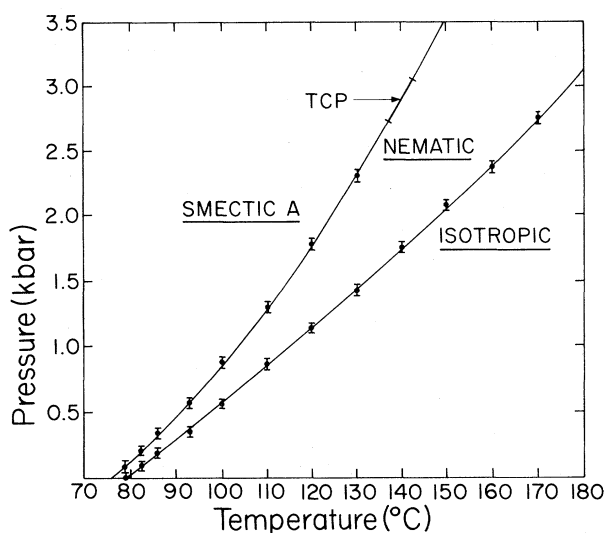


FIG. 2. The discontinuity $\delta(\Delta H)$ in H at the nematic-smectic-A transition in CBNA versus the transition temperature T_{NA} . The solid line is a least-squares fit as discussed in the text. The inset shows ΔH versus pressure at 120°C, near the nematic-smectic-A transition, illustrating how the value of $\delta(\Delta H)$ is obtained.

predicted at 2.89 kbar at 140°C.

The discontinuity in ΔH at the nematic-smectic-A transition, $\delta(\Delta H) = \Delta H_{\text{smectic}} - \Delta H_{\text{nematic}}$, is presented in Fig. 2 as a function of T_{NA} . In classical tricritical theory, the discontinuity in the nonordering density decreases along the line of first-order transitions as $(T_t - T_{NA})^{\beta_u}$, where T_t is the tricritical temperature, and β_u is 1. The value of β_u pertaining to nematic-smectic-A transitions is unknown, and our data are not of sufficient precision to determine this number, but it is at least reasonable to fit a straight line to the data on $\delta(\Delta H)$. The solid line in Fig. 2 represents a least-squares linear fit to the data points at 93°C and above. The T intercept yields a tentative tricritical temperature $T_t = 140 \pm 4^\circ\text{C}$ and equivalent tricritical pressure $P_t = 2.89 \pm 0.23$ kbar. The error estimates for T_t and P_t are determined from our estimated error limits of ± 0.01 Oe for $\delta(\Delta H)$, which represents a conservative estimate of the limit of detectability for a discontinuity in ΔH , rather than a standard error.

The P - T phase diagram for CBNA is shown in Fig. 3. The solid curves are a least-squares fit of a quadratic function of temperature to the data points, with extrapolation to higher pressures as shown. The nematic-isotropic coexistence curve is nearly linear, while the nematic-smectic-A coexistence curve is rather nonlinear. Thus, the temperature range of the nematic phase increases rather strongly with increasing pressure. The value of reduced temperature t_r is 0.92 ± 0.01 at the tricritical pressure of 2.89 kbar, compared to the theoretical prediction of

FIG. 3. P - T phase diagram of CBNA.

0.87 in McMillan's theory¹ and 0.88 in a more refined calculation by Lee *et al.*,² and an experimental value of 0.88 for a *cholesteric-smectic-A* tricritical point.⁸

One unfortunate aspect of the compound CBNA concerns the relationship of ΔH to η . Theoretically, there is a simple linear relationship, but the proportionality constant cannot be calculated because the conformation and motion of the nonyl chain are unknown. Although knowledge of the proportionality constant would be of interest, it is not essential in the present context.

Previous experimental studies under pressure have indicated that the value of η along the nematic-*isotropic* coexistence curve is nearly constant,¹⁴ as predicted by mean-field theories.¹⁵ Since ΔH at this transition is clearly decreasing in CBNA, we postulate that this decrease may be due to the close proximity of the smectic-A phase, inasmuch as this decrease is most pronounced in the region of small nematic range. The possibility that ΔH is not strictly proportional to η could also explain this behavior; even if this is the case, we feel justified in assuming that ΔH is a monotonically increasing function of η at constant temperature, so that a discontinuity in ΔH at the nematic-*smectic-A* transition implies a discontinuity in η , and *vice versa*.

At the end of the experiment, decomposition effects were checked by repeating the 110°C run. The character of the curve of ΔH versus pressure and the value of $\delta(\Delta H)$ were unchanged, but the nematic-*smectic-A* transition pressure increased

very slightly, by 0.02 kbar. This is evidence of some decomposition, but the quantities of principal interest, ΔH and $\delta(\Delta H)$ at the transition, were clearly not affected.

In conclusion, from our measurements of the NMR splitting ΔH near the nematic-*smectic-A* transition in CBNA, we tentatively identify a tricritical point at 2.89 kbar. The temperature variation of the discontinuity in ΔH is in qualitative agreement with currently accepted ideas about tricritical phenomena and mean-field theories of the nematic-*smectic-A* phase transition. The possibility that the transition merely becomes very weakly first order cannot of course be ruled out. Further experiments on this compound are clearly indicated; suggested are measurements of σ , turbidity, latent heat, volume change, and elastic constants. The authors are currently engaged in the last of these.

Finally, we point out that the confirmation of a nematic-*smectic-A* tricritical point at elevated pressure would suggest the existence of compounds with a second-order transition at 1 atm. If so, then similar tricritical points should exist in appropriate mixtures.¹⁶

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Tricritical Slowing Down of Superfluid Dynamics in ^3He - ^4He Mixtures

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Measurements of the Rayleigh scattering by concentration fluctuations in the coexisting superfluid in ^3He - ^4He mixtures near the tricritical temperature T_t show a single Lorentzian line of width such that $\Gamma/q^2 = D_{\text{eff}} = 1.5 \times 10^{-4} \epsilon^{0.95 \pm 0.07} \text{ cm}^2 \text{ sec}^{-1}$ for $9 \times 10^{-4} \leq 1 - T/T_t \leq \epsilon \leq 7 \times 10^{-3}$. Thus the effective diffusion coefficient D_{eff} is proportional to ϵ^{+1} and, since the concentration susceptibility $(\partial x / \partial \Delta)_{PT}$ is proportional to ϵ^{-1} , the effective kinetic coefficient $L_{D,\text{eff}} = D_{\text{eff}} / (\partial \Delta / \partial x)_{PT}$ is proportional to $\epsilon^{+1} \epsilon^{-1} \sim \epsilon^0$.

Dynamics close to conventional critical points features a phenomenon known as "critical slowing down" which is due to a singularity in the relaxation time for fluctuations of the appropriate order parameter.¹ In the case of binary fluid mixtures at a consolute critical point, slowing down of the relaxation of concentration fluctuations (typically by a factor of $\sim 10^{-4}$) narrows part of the undisplaced (or Rayleigh) line in the light-scattering spectrum, providing a manifestation ideally measured with the help of lasers and optical homodyne spectroscopy.^{2,3} These effects are now understood in terms of dynamical-scaling and mode-mode-coupling theories.⁴⁻⁶

Here we report that the first measurements of dynamical properties at a *tricritical* point⁷⁻⁹ show critical slowing down of concentration fluctuations in the *superfluid* phase of mixtures of ^3He and ^4He . We find that the central linewidth Γ of the coexisting superfluid in the hydrodynamic regime vanishes as $(1 - T/T_t)^1 = \epsilon^1$ as the tricritical temperature T_t is approached. This result should provide a fundamental test for tricritical-dynamical-scaling theory in a superfluid.

The thermodynamic properties of ^3He - ^4He mixtures in the tricritical region have been rather completely characterized and static tricritical exponents have been determined.¹⁰⁻¹² Scattering-intensity measurements of Leiderer, Watts, and

Webb,¹³ for example, recently yielded tricritical exponents¹³ $\beta = \gamma_{\pm}' = \nu_{\pm}' = \eta_{\pm}' = 1.0$ consistent with static tricritical scaling theory.⁷⁻⁹ The experiments generally confirm the theory of static tricritical scaling.

Light-scattering measurements in tricritical ^3He - ^4He mixtures reflect only concentration fluctuations because the concentration dependence of the refractive index overshadows its temperature and pressure dependence. Consequently the divergence of the scattered intensity on approaching the tricritical point (T_t, x_t) is due primarily to concentration fluctuations and reflects the divergence of the concentration susceptibility $(\partial x / \partial \Delta)_{PT} \sim \epsilon^{-1}$, and effects of the correlation length $\xi \sim \epsilon^{-1}$. The corresponding *spectrum* of the tricritical light scattering thus reflects the dynamics of the decay of concentration fluctuations.

The theory of the spectrum of critical light scattering in ^3He - ^4He mixtures has been discussed by Gor'kov and Pitaevskii¹⁴ and more recently by Griffin¹⁵ on the basis of two-fluid hydrodynamics.¹⁶ They predict a Lorentzian Rayleigh line in the superfluid phase of width $\Gamma = D_{\text{eff}} q^2$ determined by an "effective" diffusion coefficient D_{eff} and the scattering vector $q = (4\pi/\lambda)\sin\theta/2$, where λ is the scattered-radiation wavelength and θ is the scattering angle. We can identify a corresponding symmetrical kinetic coefficient