

TABLE I. Results for Cu, Al, and KCl:CN⁻. c is the concentration in parts per million, N the number of defects in units of $10^{18}/\text{cm}^3$, η is dimensionless, and $\Delta\nu = \Delta\Omega/2\pi$ is in THz.

	c	N	η	$\Delta\nu$
Cu	3700	310	-30 ^a	0.40
	600	50		0.16
	60	5		0.05
Al	3700	230	-27 ^a	0.37
	800	50		0.17
	80	5		0.05
KCl:CN ⁻	3700	6	-32 ^b	0.16

^a η related to C_{44} .

^b η related to $C_{11}-C_{12}$.

mentioned, Eq. (13) appears to be a good approximation in KCl:CN⁻, but in Cu and Al it appears to overestimate the splitting. However, since we are not certain of the experimental value of Ω_0 it is not yet possible to evaluate the accuracy in these cases.

The principle question of interest here, of course, is whether or not the internal modes can be observed directly by neutron scattering via their coupling to the lattice modes. Table I clearly shows the problem. Whereas it is relatively easy to obtain a concentration of $c = 0.0037$ CN⁻ ions in KCl it is not likely that this concentration of interstitials in fcc metals can be obtained. With present experimental techniques in neutron scattering, splittings, shifts, and broadenings of the order of 0.05 THz can be observed. Table I suggests that a concentration of 0.00006

in Cu gives at best a marginal chance for observing the effects due to internal modes. At a concentration of 0.0006 on the other hand, both Table I and our calculations of S_{coh} indicate that the hybridization effects should be observable in a carefully controlled experiment. We believe that the direct observation of the internal modes of the split interstitial in fcc metals awaits only the attainment of the proper concentration in the near future.

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New Liquid-Crystal Phase Diagram

P. E. Cladis

Bell Laboratories, Murray Hill, New Jersey

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The nematic-smectic-A transition temperature of mixtures of HBAB {*p*-[(*p*-hexyloxybenzylidene)-amino] benzonitrile} and CBOOA [N-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline] becomes multivalued with increasing concentration of HBAB. The nematic phase occurs at both a higher and a lower temperature than the smectic phase. Measurements of the bend elastic constant as a function of concentration are presented.

By mixing HBAB¹ {*p*-[(*p*-hexyloxybenzylidene)-amino] benzonitrile} in CBOOA² (N-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline) (Fig. 1), I have found that a smectic phase may be formed which

reverts to the nematic phase at still *lower* temperatures. As far as I can ascertain, this is the first time such an effect has been observed. Measurements of the bend elastic constant, K_3/χ_a , on

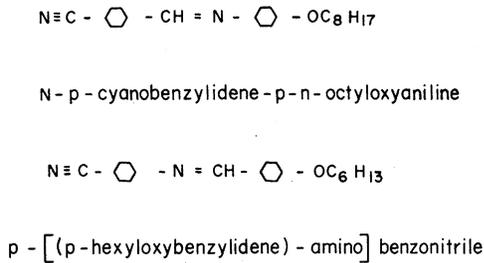


FIG. 1. CBOOA (top) and HBAB.

both sides of the smectic phase are presented.

HBAB has only a nematic liquid-crystal phase between ~ 101 and 35°C , whereas CBOOA has both a nematic phase for temperatures T between ~ 83 and $\sim 108^\circ\text{C}$ and a smectic-A phase when T lies between ~ 83 and $\sim 44^\circ\text{C}$. The lowest temperatures refer to the crystallization temperature of both compounds. The melting temperatures are about 30°C higher. These molecules are similar in shape; however, the Schiff base of the two molecules is inverted with respect to the nitrile bond (Fig. 1).

According to the x-ray data of McMillan,³ CBOOA forms a smectic phase whose interlayer spacing is $\sim 35 \text{ \AA}$. Fully extended, the molecule is about 27 \AA . Thus, as Gray and Lydon⁴ point out, "some form of double-layer structure is clearly mandatory." According to Lin, Keyes, and Daniels,⁵ this bilayered smectic (without impurities) becomes unstable with respect to a more dense nematic phase above a certain pressure but at constant temperature. Here, one will see that for a fixed amount of impurity, the smectic phase becomes unstable below a certain temperature ($T_{\text{NS}}^{(2)}$) which depends upon the concentration of impurity. It is possible that these two effects are due to the bilayered nature of the smectic phase of CBOOA.

Quantities of HBAB and CBOOA were weighed and mixed together under vacuum at a temperature of 120°C for a period of 24 h. The transition temperatures were deduced by light-microscopic observations using a Mettler hot stage. The molar fraction, c , of HBAB ranged between 0 and 1; however, most of the samples were characterized by $c < 0.16$. Figure 2 shows the variation of the nematic-isotropic, T_{NI} , the nematic-smectic, T_{NS} , the melting, T_{M} , and crystallization temperatures, T_{cryst} , as a function of concentration of HBAB.

From Fig. 2, we see that the solute molecule

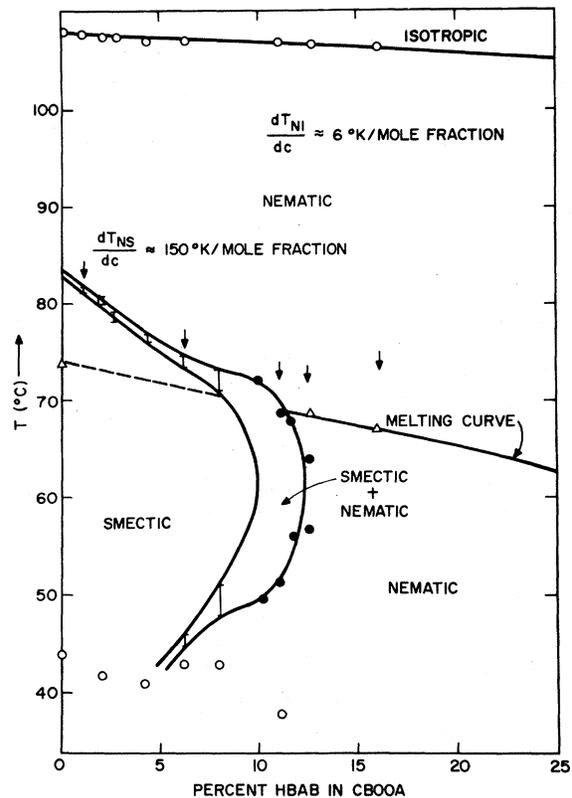


FIG. 2. The phase diagram (T, c) for mixtures of CBOOA and HBAB. T is in degrees centigrade and c in weight percent (approximately the mole fraction). The nematic-isotropic transition temperature of HBAB was $\sim 101^\circ\text{C}$. The arrows indicate the selected concentrations whose bend elastic constant is shown in Fig. 3. In the smectic-nematic region of the phase diagram, the solid circles indicate the temperature where stripes were first observed to appear (or disappear) *somewhere* in the sample (heterogeneous smectic phase). For those samples not marked by solid circles, the stripes were observed to form throughout the sample at a given temperature (apparently homogeneous samples). The open circles at $\sim 40^\circ\text{C}$ refer to crystallization temperatures.

has very little effect on T_{NI} , whereas T_{NS} is shown to be dramatically changed so that the smectic phase is bounded by the curve

$$c \leq c_0 + \beta(T_{\text{NS}} - T_0)^2, \quad (1)$$

where

$$T_0 \sim 61^\circ\text{C}, \quad c_0 \sim 0.09$$

and

$$\beta \sim -5.4 \times 10^3 / ^\circ\text{K}^2.$$

Although there is, in principle,⁶ no *a priori* rea-

son for a phase of lower symmetry to be the higher-temperature phase rather than the lower-temperature phase, one expects it to be one or the other. Thus, this is the first time the smectic phase has been observed to occur both at a higher and a lower temperature than the nematic phase.

For example, for $c = 0.08$ upon cooling towards the smectic phase, one can observe an apparently ordinary nematic to smectic-A transition when $T \sim 72^\circ\text{C}$. At 73°C , if one has applied a large magnetic field, one can observe "stripes"⁷ beginning to appear throughout the sample. At 71°C , these stripes turn into the familiar "honeycomb texture." This honeycomb texture remains upon further cooling until $T \sim 51^\circ\text{C}$. At this temperature it relaxes back through the "virgule" and "stripe texture" so that at 49°C , the sample is once more apparently completely nematic. One can repeat this whole sequence of events on samples made in thin capillaries to obtain all the familiar results⁸ except that again at $T \sim 49^\circ\text{C}$ one recovers results that are familiar upon *warming* a smectic sample rather than *cooling* it through to the nematic phase. Even without a magnetic field one can follow the appearance of the smectic phase and its subsequent disappearance by observing the fluctuations of the director in the nematic phase. These fluctuations are absent while the sample is smectic and present when the sample is nematic. All of these results can be removed in the inverse order if one warms from the lower-temperature nematic-smectic-A transition to the higher one.

We also see that for $c > 0.09$ no single phase is observed in the smectic range of the phase diagram until $c > 0.12$, where only an apparently homogeneous nematic phase is observed. For $0.09 \leq c \leq 0.12$ the sample is composed of coexisting regions of nematic and smectic. The temperature range over which the sample was observed to be heterogeneous are indicated by the filled circles of Fig. 2. Hence, in this concentration range ($0.09 \leq c \leq 0.12$), the nematic to smectic-A transition is of first order.

The transition width of the nematic-smectic-A transition in Fig. 2 is taken to be where stripes occur. This is in keeping with the hypothesis⁷ (which was required to explain their existence) that the stripes are a manifestation of a nematic-smectic-A phase-coexistence region. In contrast to the case $0.09 \leq c \leq 0.12$, no large-scale phase coexistence has been observed for $c < 0.09$ in the absence of bend (or twist) deformations.

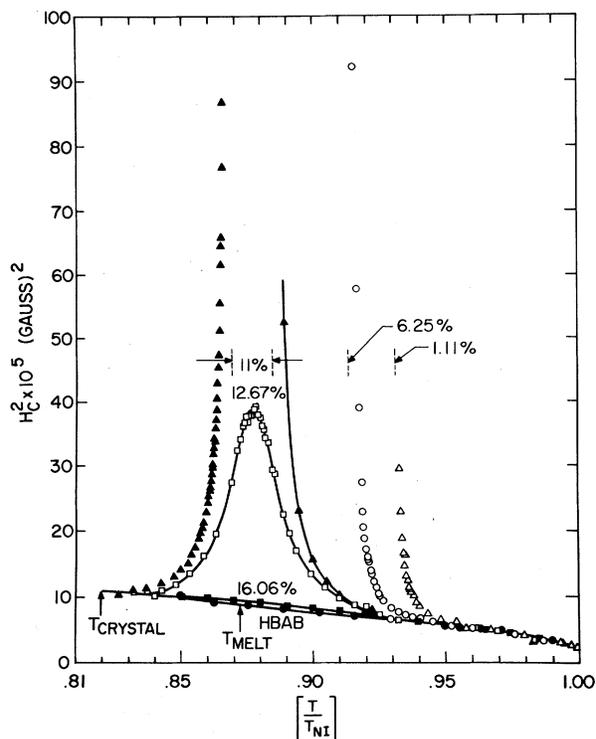


FIG. 3. The bend elastic constant $\propto H_c^2$ as a function of reduced temperature. The percent by weight of HBAB in CBOOA is indicated for each sample. The "base line" is pure HBAB. This is a qualitative plot. It is quantitatively correct for pure HBAB and the 1.1% and 6.25% mixtures whose sample thicknesses were ~ 122 , 122 , and $128 \mu\text{m}$, respectively. H_c^2 has been scaled for the 11% mixture by 0.89, the 12.67% by 0.86, and the 16.06% by 0.73. Their thicknesses were measured to be 120 , 127 , and $125 \mu\text{m}$, respectively.

However, without bend deformations, it is not possible to observe small regions of smectic coexisting with the nematic particularly if these smectic regions are localized on the surface of the microscope slides. Consequently, the width of the phase-coexistence region in the absence of bend deformations is not known when $c < 0.09$.

In the region marked smectic, the phase appears to be homogeneous as far as one can tell from light-microscope observations, with no macroscopic phase separation. The nematic phase appears to be homogeneous for all temperatures.

Figure 3 shows the square of the critical magnetic field (H_c^2), for the Freedericksz transition⁹ for a nematic with homoeotropic boundary condition. As is well known, $(H_c^2) \propto K_3/\chi_a$, where K_3 is the bend elastic constant and $\chi_a = \chi_{\parallel} - \chi_{\perp}$ the difference between the magnetic susceptibility paral-

lel and perpendicular to the symmetry axis of the molecule. As can be seen, the pretransitional rise in $K_3(T)$ as one approaches the smectic phase transition is observed both above and below the smectic phase. We can even see a small rise in K_3 when there is no smectic transition but when one is close to c_0 , i.e., $c_0 < c \cong 0.12$.

We also note that this new smectic transition is reversible. On Fig. 3 the solid triangles represent data taken both upon increasing temperature and upon decreasing temperature.

In similar experiments with mixtures of CBOOA and ortho-MBBA (N-[*p*-methoxybenzylidene]-*p*-butylaniline)¹⁰ I did not notice such an effect. I have since checked these same samples and they do *not* show an intermediate nematic phase between the smectic and crystal transition.

In conclusion, Fig. 2 is a new kind of liquid-crystal phase diagram. Further experiments of a different nature (e.g., x rays) will be required to determine how homogeneous the smectic phase really is for this system. It looks very homogeneous with the light microscope. The bend elastic constant is found to behave similarly when approaching the smectic phase both from above and from below.

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Ground Vibronic Levels of Titanium Alum*

A. Jesion, Y. H. Shing, and D. Walsh

Eaton Electronics Laboratory, McGill University, Montreal, Canada

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The excited Γ_7 state of Ti^{3+} in CsAl alum has been determined by spin-lattice relaxation measurements in the temperature range of 2.63–1.27°K to be $7 \pm 1 \text{ cm}^{-1}$ above the quasi- Γ_8 ground state. The agreement with theoretical predictions confirms the strong coupling of the Γ_{5g} electronic state to the Γ_{3g} vibrational mode.

The unusual electron paramagnetic resonance (EPR) of Ti^{3+} as a dilute substitutional impurity for Al in CsAl alum has been successfully interpreted in terms of a quasi- Γ_8 ground state.¹ This ground state arises from the dynamic Jahn-Teller coupling of the Γ_{5g} electronic state to the Γ_{3g} vibrational mode which leads to an almost complete cancelation of the trigonal crystal field. The vibronic reduction factor² $\gamma \cong 0.03$ calculated from the quasi- Γ_8 ground state predicted the first excited Γ_7 state to be at 6 cm^{-1} above the ground

state. This Letter reports accurate measurements of the spin-lattice relaxation rate of Ti^{3+} in CsAl alum using pulse-saturation techniques in the temperature interval 2.63 to 1.27°K. The temperature dependence of the spin-lattice relaxation rate is described by both a Raman non-resonant two-phonon process and an Orbach process³ via the excited Γ_7 state. The Orbach process confirms the predicted splitting between the Γ_7 and the quasi- Γ_8 states.

The spin-lattice relaxation measurements were