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

<table>
<thead>
<tr>
<th></th>
<th>(c)</th>
<th>(N)</th>
<th>(\eta)</th>
<th>(\Delta\nu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3700</td>
<td>310</td>
<td>-30\textsuperscript{a}</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>50</td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Al</td>
<td>3700</td>
<td>230</td>
<td>-27\textsuperscript{a}</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>50</td>
<td></td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>5</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>KCl:CN\textsuperscript{−}</td>
<td>3700</td>
<td>6</td>
<td>-32\textsuperscript{b}</td>
<td>0.16</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \(\eta\) related to \(C_{44}\).
\textsuperscript{b} \(\eta\) related to \(C_{11}-C_{12}\).

mentioned, Eq. (13) appears to be a good approximation in KCl:CN\textsuperscript{−}, but in Cu and Al it appears to overestimate the splitting. However, since we are not certain of the experimental value of \(\Omega_0\) 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\textsuperscript{−} 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 \(S_{e\phi}\) 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.

The authors are grateful to F. W. Young, R. M. Nicklow, R. R. Colman, G. Leibfried, and especially T. Kaplan for helpful discussions.

\textsuperscript{*}Research sponsored by the U. S. Energy Research and Development Administration under contract with Union Carbide Corporation.


\textsuperscript{4} D. Walton, H. A. Mook, and R. M. Nicklow, Phys. Rev. Lett. 33, 412 (1974). The mechanism for the mixing in KCl:CN\textsuperscript{−} is somewhat different than in the metals but the formulation of the problem is essentially the same at low temperatures.


\textsuperscript{7} K. Lakatos and J. A. Krumhansl, Phys. Rev. 180, 729 (1969), and 175, 841 (1968).


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New Liquid-Crystal Phase Diagram

P. E. Cladis

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The nematic–smectic-A transition temperature of mixtures of HBAB \{\textit{p}-(\textit{p}-hexyloxybenzylidene)-amino\} benzonitrile and CBOOA \{\textit{N}-\textit{p}-cyanobenzylidene-\textit{p}-\textit{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 HBAB\textsuperscript{1} \{\textit{p}-(\textit{p}-hexyloxybenzylidene)-amino\} benzonitrile in CBOOA\textsuperscript{3} \{\textit{N}-\textit{p}-cyanobenzylidene-\textit{p}-\textit{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, \(K_3/\chi_3\), on
both sides of the smectic phase are presented.

HBAB has only a nematic liquid-crystal phase between \( \sim 101 \) and 35°C, whereas CBOOA has both a nematic phase for temperatures \( T \) between \( \sim 83 \) and \( \sim 108^\circ \)C and a smectic-A phase when \( T \) lies between \( \sim 83 \) and \( \sim 44^\circ \)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, CBOOA forms a smectic phase whose interlayer spacing is \( \sim 35 \) Å. Fully extended, the molecule is about 27 Å. Thus, as Gray and Lydon point out, "some form of double-layer structure is clearly mandatory." According to Lin, Keyes, and Daniels, 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 \( (T_{NS}^{(2)}) \) 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 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

\[
c = c_0 + \beta (T_{NS} - T_0)^2 \tag{1}
\]

where

\[
T_0 = 61^\circ \text{C}, \quad c_0 = 0.09
\]

and

\[
\beta = -5.4 \times 10^3 / \text{K}^2
\]

Although there is, in principle, 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 \( T \approx 72^\circ C \). At \( 73^\circ C \), if one has applied a large magnetic field, one can observe "stripes" beginning to appear throughout the sample. At \( 71^\circ C \), these stripes turn into the familiar "honeycomb texture." This honeycomb texture remains upon further cooling until \( T \approx 51^\circ C \). At this temperature it relaxes back through the "virgule" and "stripe texture" so that at \( 49^\circ C \), 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 results except that again at \( T \approx 49^\circ C \) 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 hypothesis (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.

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 transition for a nematic with homoeotropic boundary condition. As is well known, \( (H_c)^2 \propto K_3/X_\alpha \), where \( K_3 \) is the bend elastic constant and \( \chi_\alpha = \chi_\delta - \chi_\lambda \) the difference between the magnetic susceptibility paral-
iel 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 $c_5$, i.e., $c_5 < c \approx 0.12$.

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) 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.

I would like to thank F. Stillinger, B. Halperin, and S. Melboom for interesting discussions.

1 Supplied by Princeton Materials Science, Inc., Princeton, N. J.
2 Supplied by Eastman Kodak, Rochester, N. Y. and recrystallized by J. Van Meter.
4 G. W. Gray and J. E. Lydon, Nature (London) 252, 221 (1974). That such a bilayered smectic phase existed was first pointed out by these authors from x-ray measurements on 4-cyano-4'-octylbiphenyl. By constructing the molecule CBOOA, J. E. Lydon has also shown that a similar discrepancy existed between McMillan's layer spacing and the extended length of CBOOA. More evidence of the bilayered nature of the smectic phase of CBOOA has been found by B. Deleche and J. Charvolin, in Proceedings of the Fifth International Liquid Crystal Conference, Stockholm, Sweden, 1974 (to be published).

Ground Vibronic Levels of Titanium Alum*

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The excited $\Gamma_5$ 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 $7 \pm 1$ cm$^{-1}$ above the quasi-$\Gamma_3$ ground state. The agreement with theoretical predictions confirms the strong coupling of the $\Gamma_5$ electronic state to the $\Gamma_2$ 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-$\Gamma_3$ ground state. This ground state arises from the dynamic Jahn-Teller coupling of the $\Gamma_5$ electronic state to the $\Gamma_3$ vibrational mode which leads to an almost complete cancelation of the trigonal crystal field. The vibronic reduction factor $\gamma \approx 0.03$ calculated from the quasi-$\Gamma_3$ ground state predicted the first excited $\Gamma_5$ 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 process via the excited $\Gamma_5$ state. The Orbach process confirms the predicted splitting between the $\Gamma_5$ and the quasi-$\Gamma_3$ states.

The spin-lattice relaxation measurements were