

High-Pressure Investigation of the Reentrant Nematic – Bilayer-Smectic-A Transition

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We find that certain cyano Schiff bases and cyanobiphenyls with alkyl or alkoxy end groups exhibiting a bilayer smectic-A phase also exhibit a reentrant nematic phase at high pressure. A tentative model of the bilayer smectic phase held in place via the attractive interaction of the alkyl or alkoxy chains accounts for most of our experimental results.

Recently, it was discovered¹ that mixtures obtained by doping CBOOA with HBAB (Table I) exhibited upon cooling the sequence of phases nematic, smectic, and again nematic. We refer to the lower-temperature transition as reentrant. We present here, for the first time, experimental evidence that such a reentrant transition can also be induced under pressure. The data suggest a model of the bilayer smectic-A phase which accounts for the main features observed both under pressure and by means of the addition of suitable impurities and supercooling.¹

Starting from the hypothesis¹ that the unusual reentrant property is linked to the bilayer nature

of the smectic-A phase, we chose those compounds shown in Table I which were known (or suspected) to possess a bilayer smectic-A phase. In addition to the pure compounds with smectic phases, we studied mixtures of CBOOA with HBAB and CBNA with CBHA. We observed the transitions visually using a temperature-controlled, high-pressure optical microscope stage. The temperature could be read with a precision of 0.02°C and the stability of the temperature controller was better than 0.1°C. The precision and stability of the pressure measurements were better than 10 bars. The maximum observation pressure is approximately 10 kbar.²

Figure 1 shows the complete phase diagram for COOB which has a typical reentrant nematic-smectic-A transition.³ The main features of these reentrant phases are these: (1) They occur only in the supercooled region of the liquid; (2) P_m , the pressure at which these bilayers cease to exist, depends upon the average number of hydrocarbons interacting within a layer; and (3) P_m increases with increasing latent heat of the nematic-smectic-A transition measured at 1 atm. We observed similar reentrant nematic phases for CBOOA⁴ and mixtures of CBOOA with HBAB. Pure CBNA, CBOA, and COB did not exhibit this property for pressures under 10 kbar—even though they, too, possess a bilayer smectic-A phase.^{5,6}

A fundamental feature of molecules exhibiting layered phases is that they are *amphiphilic*, i.e., they have both a polar and a nonpolar part (e.g., lipid bilayers).⁷ Here, we refer to the cyano-

TABLE I. Materials used in the experiments.

ACRONYM	NAME	STRUCTURE
CBOOA	N-p-cyanobenzylidene-p-octyloxyaniline	
CBOA	N-p-cyanobenzylidene-p-octylaniline	
CBNA	N-p-cyanobenzylidene-p-nonylaniline	
CBHA	N-p-cyanobenzylidene-p-heptylaniline	
HBAB	p-hexyloxybenzylidene-p-aminobenzonitrile	
COOB	4-cyano-4'-octyloxy biphenyl	
COB	4-cyano-4'-octylbiphenyl	

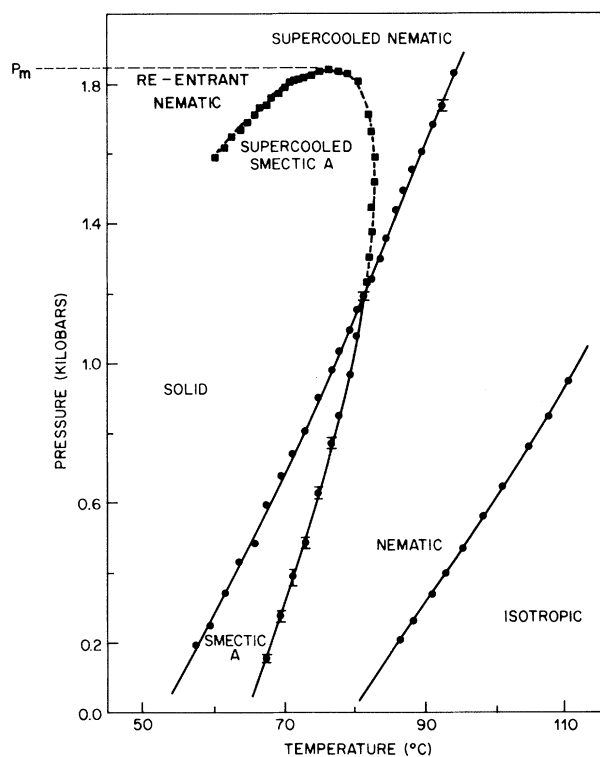


FIG. 1. Pressure-temperature (P - T) phase diagram for COOB. Data taken on the reentrant nematic-smectic-A transition in the supercooled liquid are shown as squares. P_m is the maximum pressure at which the smectic exists for this compound.

aromatic rings as the polar part and the aliphatic chains as the nonpolar part. The enhanced affinity for the polar parts of the molecules to interact preferentially with other polar groups via fairly long-range electrostatic forces and for the nonpolar parts to interact with similar groups via fairly short-range forces is the *key* to smectic layering.⁷ In most liquid crystals, the polar segments of the molecules are in the middle with hydrocarbon chains extending outward. These kinds of molecules tend to form *monolayer* smectic-A phases. In our case, a large polar contribution comes from the cyano group at one end so that some kind of dimerization is likely. The rest of the molecule is relatively nonpolar except for the alkoxy compounds in which case the oxygen adds to the dipole moment of the polar head. Consequently, bilayer, but incommensurate, smectic-A phases are probable.

Our model of the bilayer smectic-A phase is shown in Fig. 2. This model fits the measured layer spacings^{5,6,8} which are never commensurate with the molecular length. There are often two

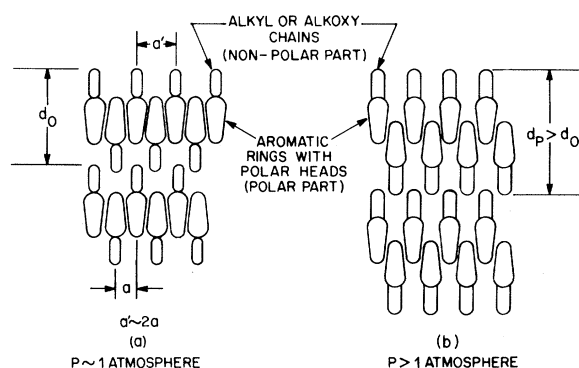


FIG. 2. Schematic of a bilayer smectic-A phase at (a) 1 atm and (b) under pressure. The two parts of the molecule are assumed to be immiscible. The molecules move freely within each layer and with difficulty between layers. There is no correlation between molecules in different layers (see text).

diffuse outer rings in their x-ray patterns (up to now not accounted for) which correspond to repeat distances of 4.3 and 8.6 Å.⁶ It may well be the *preference* of like groups to interact which prevents the bilayer from being driven towards the more dense, monolayer smectic-A arrangement under pressure. We visualize instead the configuration shown in Fig. 2(b). By drawing the molecules with a smaller head, we symbolize the preference even under compression of the polar parts to remain in a polar milieu rather than extrude into the nonpolar hydrocarbon region. The increase in layer spacing under pressure (shown grossly exaggerated) is offset by a slight compacting of the flexible nonpolar part. This occurs under pressure as a background scale effect in all smectics⁹ and weakens the efficiency of the nonpolar segments to hold the layer together. It further accounts for the rarity of pressure-induced smectic-A phases for compounds possessing only a nematic phase at 1 atm.

It is proposed that the short-range attractive interactions of the nonpolar tails stabilizes the smectic layers. The strength of this interaction is proportional to the number of methylene groups composing the tail.¹⁰ When this number is seven or less there is no smectic-A phase. Interjecting molecules with only a six-unit hydrocarbon tail (e.g., HBAB) into a layer composed mostly of molecules with the eight-unit tail (e.g., CBOOA) renders the smectic layer more susceptible to rupture upon application of stress (pressure).

Since decreasing the temperature is physically equivalent to a slight application of pressure, the CBOOA-HBAB mixtures¹ exhibiting the reentrant

transition at 1 atm are compatible with a layer spacing which is observed in pure CBOOA to *increase* with decreasing temperature.¹¹ The decreasing strength of the bilayer with increasing concentration of HBAB accounts for the increase of the reentrant temperature at 1 atm and the positive slope of the P - T curve for the reentrant transitions. For the alkoxy compounds the layer-spacing increase—whether this be with increased pressure or decreased temperature—is more dramatic than for the alkyl homologs because of their enhanced dipolar nature (supported by the larger dielectric anisotropies of the alkoxy cyanobiphenyls versus the alkyl homologs¹²). Thus, both CBOOA and COOB exhibit the reentrant nematic phase when $P_m < 2$ kbar, but CBOA and COB (the alkyl homologs) do not for pressures under 10 kbar (or before crystallization).

In order to test quantitatively the reduction of P_m as the average number of methylene groups interacting in a layer decreases, we doped CBNA (no reentrant nematic phase observed below 10 kbar or before crystallization) with CBHA (which has no smectic phase). Our results are shown in Figs. 3(a) and 3(b) where clearly P_m decreases with increasing concentration of CBHA ($c \cong$ mole fraction of CBHA) and linearly with the ratio of the volume of CBNA to CBHA. A linear best fit to the data shows $P_m = 0$ when this ratio is 0.07. In agreement with this, our mixture of 7% CBNA in CBHA showed no smectic phase above 20°C. It is to be noted that the amount of both materials in these mixtures is significantly greater than the unknown impurities. The points marked with a cross indicate that crystallization occurred rapidly at these pressures and temperatures.

In summary, assuming that the polar-polar and nonpolar-nonpolar interactions *must* be maintained to ensure the stability of the bilayer smectic-A phase under pressure, we propose that the layer spacing *expands* with increasing pressure. This enables us to account for the transitions between less-dense smectic and more-dense nematic characteristic of the high-pressure side of the reentrant phase diagrams [Figs. 1 and 3(a)]. The forces stabilizing the layers are the short-range attractive hydrocarbon (nonpolar-nonpolar) interactions. These forces are proportional to the length of the hydrocarbon chains. The origin of the forces driving the layers apart is the increasingly repulsive interaction of the aromatic rings with increasing pressure. The alkoxy homologs are initially ($P \approx 0$) closer together than their alkyl counterparts because of their larger dipole

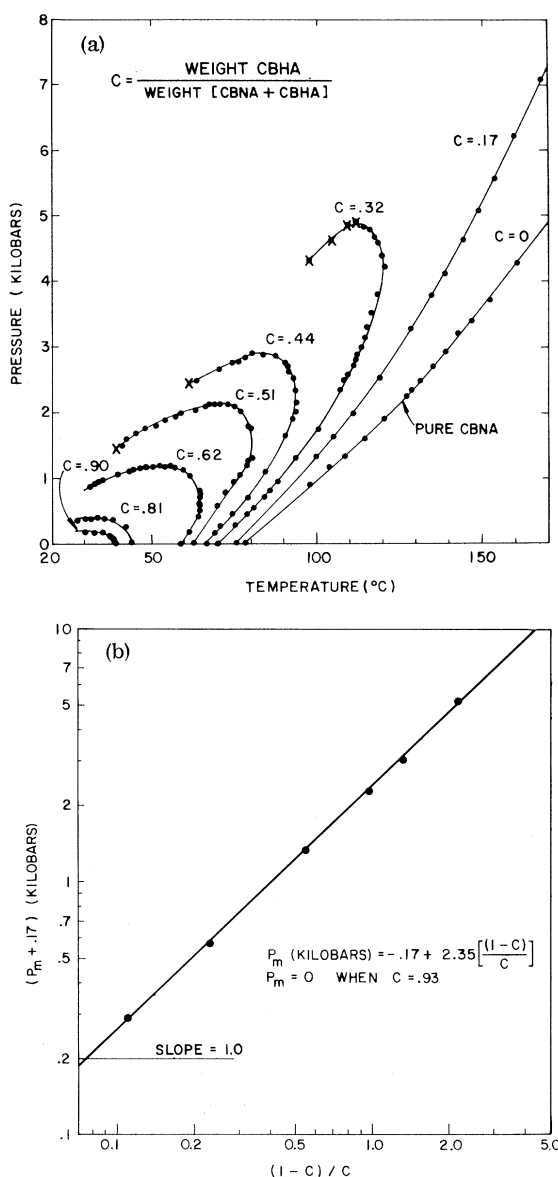


FIG. 3. (a) P - T phase diagram for the nematic-smectic-A transition (only) of CBNA and mixtures of CBNA with CBHA showing reduction of P_m with increasing concentration, c , of CBHA (see text). (b) P_m vs the ratio of the volume of CBNA to that of CBHA $[(1-c)/c]$ shown as a log-log plot. $P_m = 0$ for $c = 0.93$. c is the ratio of the weight of CBHA to the weight of CBHA + CBNA.

moment. For them we observe P_m to be relatively small ($P_m \approx 2$ kbar) (Fig. 1). P_m for the pure alkyl homologs we suppose to be greater than 10 kbar or pressures required to induce crystallization. However, we were able to induce the reentrant nematic phase in CBNA (an alkyl homolog) by adding to it its homologous, shorter counter-

part, CBHA, and $P_m = 0$ when $c = 0.93$ [Figs. 3(a) and 3(b)]. Our model (Fig. 2) is not compatible with monolayer smectics exhibiting the reentrant nematic phase.

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Observation of Electronic Band-Structure Effects on Impact Ionization by Temperature Tuning

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Impact ionization in semiconductors is shown to be strongly affected by temperature-tuning the band structure. In $\langle 100 \rangle$ GaAs between 25 and 150°C the hole ionization rate β is greater than the electron rate α , whereas above this temperature α becomes greater than β . This effect is attributed to the sudden lowering of the electron threshold ionization energy close to 200°C and is shown to be evidence for the existence of the pseudogap between the Γ_6 - X_6 and Γ_7 - X_7 conduction bands.

We demonstrate for the first time that the relative magnitudes of impact-ionization rates for electrons and holes in semiconductors can be reversed by temperature tuning. In $\langle 100 \rangle$ GaAs at room temperature, the ionization rate for holes, β , is greater than that for electrons, α , whereas at 200°C and above the opposite occurs. The main features of this effect may be explained in terms of a simple model based on the band structure, which predicts an abrupt change in the electron threshold ionization energy near 200°C. These results shed new light on the relationship of impact ionization to electronic band structure, and at the same time provide a new method of probing high-energy-band regions not previously explored. In particular, we present the first experimental evidence for the existence of the theo-

retically predicted pseudogap in $\langle 100 \rangle$ GaAs between the Γ_6 - X_6 and Γ_7 - X_7 conduction bands.

Measurements were made in the field region of GaAs p - n homojunctions grown by liquid-phase epitaxy on $\langle 100 \rangle$ Sn-doped GaAs substrates. These samples were one-sided, abrupt junctions with n -side and p -side dopings of $n \approx 2.6 \times 10^{16} \text{ cm}^{-3}$ and $p \approx 2 \times 10^{18} \text{ cm}^{-3}$, respectively, and had a maximum electric field at breakdown of $E_m \approx 5 \times 10^5 \text{ V cm}^{-1}$. Avalanche multiplication was measured by optically exciting free carriers and monitoring the photocurrent as a function of reverse bias voltage for several ambient temperatures, with the diodes mounted on a heater in a dry nitrogen atmosphere. The samples were processed photolithographically into the configuration illustrated in the inset of Fig. 1 so that low-intensity ($\approx 10^{-5}$