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A high resolution X-ray scattering study of the phases and phase transitions in N-(4-n-butyloxybenzylidene)-4-n-heptylaniline (40.7)

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Abstract. We report high resolution X-ray scattering measurements of the smectic phases and phase transitions in the material N-(4-n-butyloxy-benzylidene)-4-n-heptylaniline (40.7) (I → N → Sm A → Sm C → Sm B). For the nematic to smectic A transition we have measured the critical exponents $\gamma = 1.45 \pm 0.03$, $\nu_{||} = 0.78 \pm 0.02$ et $\nu_{\perp} = 0.65 \pm 0.02$. Les corrélations de position dans les plans de la phase smectique A sont décrites par une lorentzienne presque bidimensionnelle et moyennée dans la direction azimuthale avec une longueur de corrélation de 15.8 Å. En plus de mesures antérieures de la capacité calorifique et de diffusion de lumière, des mesures de l’angle d’inclinaison moléculaire et de la séparation des couches dans la phase smectique C indiquent que la transition smectique A-smectique C est correctement décrite par une théorie du type champ moyen Landau-Ginsburg avec un terme de sixième ordre anormalement grand. La transition smectique C-smectique B est du premier ordre avec une région de coexistence d’approximativement 0.5 °C. À l’intérieur de cette région la phase smectique B peut coexister avec une phase soit smectique A soit smectique C. Dans la phase smectique B les couches passent par transition continue d’une séquence d’empilement ABAB à ABCABC quand la température décroît de 35 °C à 31 °C.

1. Introduction.

Liquid crystals exhibit a rich variety of phases intermediate between normal liquids and solids [1, 2]. X-ray scattering experiments directly probe the molecular order by measuring the Fourier transform of the instantaneous positional correlation function. Computer controlled, high resolution, triple axis spectrometers have greatly facilitated X-ray scattering studies of liquid crystal materials during the past decade. These advances rest both on the high resolution provided by perfect silicon X-ray spectrometers and the implementation of quantitative instrumental deconvolution techniques in the lineshape analysis. These improved techniques are extremely useful in probing subtle changes in the neighbourhood of phase transitions [3, 4].

Since Smith and Gardlund [5] published an extensive survey of N-4-n-(p-alkoxybenzylidene)-4-n-alkylaniline compounds ($m0.m$) ten years ago, these
compounds have been studied extensively because of their diverse phase behaviour close to room-temperature [6-11]. We initially began studying N-(4-n-butoxybenzylidene)-4-n-heptylaniline (40.7) because of the possibility that it might exhibit a smectic F phase [5]. An additional motivation was provided by a heat capacity study of Bloemen and Garland [12] which suggested that the N → Sm A transition differed from that in materials such as 4-n-octyloxy-4-cyanobiphenyl (8OCB) [13] and N-(4-n-butoxybenzylidene)-4-n-octylaniline (40.8) [4]. Further, a heat capacity anomaly was observed just before the transition to the Sm B phase suggesting interesting precursive behaviour. Finally, rather complete information is available from a number of different studies on the phases and phase transitions in 40.8 [4, 6, 7]. Therefore, a detailed comparison with the nearby homolog 40.7, which exhibits a number of curious differences in behaviour, seemed to be quite useful. We felt that it would be especially valuable to carry out a complete high resolution study of all of the smectic phases and phase transitions in one single material. The results of this study are reported in this paper. Detailed comparisons with theory and other experiments both on 40.7 and other materials are also given here. As we shall see, a number of very interesting new features do indeed emerge from each of the smectic phases in 40.7.

We begin our discussion with a cursory review of previous experiments and theory relevant to the phases observed in 40.7.

The nematic to smectic A transition, corresponding to the development of a one dimensional density wave in a three dimensional fluid, has been studied extensively [14]. McMillan’s mean field theory (MFT) [15] calculation predicted that the transition should be second-order if the McMillan ratio \( T_{NA}/T_{NI} \), that is the ratio of the N → Sm A transition temperature, \( T_{NA} \), to the N → I transition temperature, \( T_{NI} \), was less than 0.87. Early experiments erroneously suggested that the nematic to smectic A transition was usually first order. However, recent, more precise X-ray, light scattering and calorimetric measurements indicate that the transition is nearly always continuous to within \( \pm 0.5 \) °C centigrade for \( T_{NA}/T_{NI} \) as high as 0.97 [14, 16]. The discrepancy with the McMillan prediction [15] is most certainly due to the inadequacies of MFT in three-dimensions since the lower critical dimensionality of the Sm A phase is also three [1, 17, 18].

Measurements of the N to Sm A transition in 40.8 [4], 8OCB [13], 4-n-octyl(1-4-cyanobiphenyl) (8CB) [18], N-(4-cyanobenzylidene)-4-n-octylaniline (CBOOA) [13, 19] and 4-n-pentylphenyl 4-n-octyloxybenzoate (85S) [20] indicate that the correlation length exponent along the density wave, \( \nu_\parallel \), is not equal to the perpendicular correlation length exponent, \( \nu_\perp \), and that these exponents are non-universal. The degree of anisotropy, \( \nu_\perp/\nu_\parallel \), appears to assume the universal value of 0.13 ± 0.03 for all systems although \( \nu_\parallel \) ranges from 0.67 to 0.83. Lubensky and co-workers [21] have argued, within the context of the de Gennes model [15], that to all orders of perturbation theory for finite values of the splay elastic constant \( K_{1} \), that the nematic to smectic A transition must either be isotropic with \( \nu_\parallel = \nu_\perp = \nu_{xy} \) or anisotropic with \( \nu_\parallel = 2 \nu_\perp \). The isotropic fixed point is that of the inverted XY model [22] whereas the anisotropic fixed point may be the dislocation fixed point [23]; no quantitative values for the exponents have been calculated for the latter critical point.

Toner and Nelson [23] argue that the Sm A free energy with dislocations is analogous to the nematic free energy. Therefore, as is the case in the Kosterlitz-Thouless theory of two-dimensional (2D) melting [24], dislocations might provide the mechanism for the melting of the Sm A phase to a nematic phase. Unlike the 2D case, where the transition is mediated by the unbinding of bound dislocations, the mechanism for the melting of the Sm A phase is the divergence of the size of dislocation loops. The region of maximum strain generated by these dislocation loops is anisotropic [25]; thus, the correlation length, which is the distance between dislocation loops, must also grow anisotropically. Close to the transition, on the smectic side [23], Toner and Nelson predict that \( \nu_\parallel = 2 \nu_\perp \). Estimates of the dislocation critical region by Fisch et al. [26] on 40.8 and 8OCB indicate that it must be within \( t = T/T_{NA} - 1 = 10^{-5} \). Recent experimental findings [4, 14] which measure correlation lengths to within \( t = 10^{-5} \) on the nematic side give no indication of crossover behaviour. Therefore, the crossover to \( \nu_\parallel = 2 \nu_\perp \) behaviour would have to occur within \( t = 10^{-7} \). Thus, to be useful, the theory must be extended to predict the experimentally observable regime of \( 10^{-5} < t < 10^{-2} \).

Lubensky et al. [21, 27] argue that the smectic correlation function is most easily determined using a set of non-physical variables which restores long range order in the Sm A phase. This model yields inverted 3D XY behaviour in the transformed frame. It is predicted that thermodynamic quantities such as the heat capacity and the nematic elastic constants should exhibit transformation-independent divergences so that they should be characterized by 3D XY exponents. However, the physical mass density fluctuations which are directly probed with X-rays should manifest different behaviour. Using an anisotropic momentum shell renormalization technique, Lubensky and co-workers [21] predict for the « laboratory gauge » mass density fluctuations an explicit crossover from \( v_\parallel = v_\perp = v_{xy} \) to \( v_\parallel = 2 \nu_\perp = v_{xy} \) close to the transition. Toner [28] has also carried out a renormalization calculation where the core dislocation energy has been included; he predicts that \( v_\parallel = 6/5 v_{xy} \); \( v_\parallel = 4/5 v_{xy} \). In section 3 these predictions will be compared with our measurements on 40.7. X-ray experiments on 40.8, CBOOA, and 8OCB yield values for \( \nu_\parallel \approx 0.7 \) and \( \gamma \approx 1.31 \) which are in good agreement with the 3D XY
prediction [29]. As noted earlier, \( v_{ij} \), on the other hand is typically 0.13 less than \( v_{ij} \), in disagreement with all theories. Experiments on 8OCB/6OCB mixtures [30] and 8S5 [22] report exponents which are larger. The results pertaining to the N \( \rightarrow \) Sm A transition in 40.7 will be presented in section 3.

In the Sm A phase the molecules are fluid-like within the plane of the layers with a correlation length of \( \sim 16 \) Å in contrast to the smectic density wave correlations which extend over distances greater than 30,000 Å. However, the smectic density wave does not have true long-range order due to the Landau-Peierls instability and its concomitant power law decay of the correlation function [17]. These properties have been verified by previous X-ray studies but a detailed line-shape analysis in the plane perpendicular to the molecular axis is lacking. We have found that the in-plane scattering in the smectic A phase of 40.7 is well described by a temperature independent 2D azimuthally-averaged Lorentzian. These results will be discussed in section 4.

The smectic A phase in thermotropic liquid crystals is unusual in that only the lowest order reflection \((0,0,1)\) is readily observable. This is in sharp contrast to lyotropic liquid crystals [31] and solids where higher harmonics may be quite intense. Indeed, the absence of higher harmonics in the Sm A phase is precisely why the density modulation is written with only one sinusoidal component. Previous X-ray studies on 8CB, 8OCB, and CBOOA allow for a ratio of the \((0,0,2)\) to the \((0,0,1)\) intensity as high as \(10^{-4}\) [32]. Measurements on 40.7, to be presented in section 4, show that this ratio is less than \(2 \times 10^{-7}\).

The smectic C phase differs from the smectic A phase in that in the smectic C phase the nematic director is oriented at an angle to the direction of the mass density wave. Liquid crystals with both Sm A and Sm C phases can have a second-order transition between the two phases [1]. De Gennes has proposed a simple model which places this transition in the universality class of the 3D XY model [33]. Recently Grinstein and Pelcovits [34] have included elastic and director fluctuations; their results are consistent with the XY classification. Safinya et al. [35], using a Landau-Ginzburg model, have argued that the bare length characterizing the tilt fluctuations is generally large so that the true critical region should be observably small. Huang and Viner [36] also favour the mean-field model; however, they made the important additional observation that in order to understand the heat capacity anomaly associated with the Sm A \( \rightarrow \) Sm C transition in some materials, one must postulate the existence of unusually large higher order terms in a Landau free energy expansion. Within the context of this model the tilt order parameter exponent, \( \beta \), crosses over from 1/2 near the transition to the tricritical value of 1/4 at lower temperature. It is very difficult to distinguish this behaviour from a single power law with an intermediate \( \beta \). Indeed, as we shall show, X-ray measurements on 40.7 are consistent with the XY value of \( \beta \) or mean field behaviour with an unusually large sixth order term. However by considering light scattering and calorimetric data along with our X-ray results one can arrive at a unique description [37]. The results pertaining to the Sm A \( \rightarrow \) Sm C transition will be presented in section 5.

The liquid crystal B phase is characterized by hexagonal order within each layer. Recent experiments clearly demonstrate that Sm B phases fall within two classes: a crystalline B phase with long range 3D positional order and a hexatic phase with long-range bond orientational order but with short-range in-plane positional order [38, 6-11, 39]. Orientationally-ordered phases have attracted particular attention since it was proposed that in two dimensions a hexatic phase could exist as an intermediate structure between an isotropic fluid and a well-ordered solid [40]. Subsequently it was suggested that if the layer coupling was sufficiently weak the Sm B phase could exhibit a "stacked hexatic" phase [38]. Our observations in 40.7 reveal that the Sm B phase is not a hexatic phase but rather a crystal phase as are the Sm B phases in the homologs 40.4, 40.8 and 70.7 [6-11].

In going from a Sm C to a crystalline Sm B phase the molecules must return to zero tilt in addition to developing long-range order within the plane of the layers. Like the Sm A to Sm B transition in 40.8 [7], the transition to a Sm B phase in 40.7 is characterized by a first order transition with an impurity-induced two phase coexistence region. We find the novel result that the Sm B phase coexists with a Sm A phase in one sample, whereas it coexists with a Sm C phase in another. Microscope [41] and X-ray results pertaining to the Sm C to Sm B transition will be discussed in section 6.

Recent free-standing liquid crystal film experiments by Collett et al. [42] and Moncton et al. [6] as well as bulk measurements by Leadbetter et al. [8] have shown that the stacking sequence between adjacent layers can undergo a series of restacking transitions. These transitions have no associated latent heat or thermal anomaly leaving their detailed nature a mystery. In section 7, we report our measurements on 40.7 in which an ABAB(hcp) stacking continuously restacks to an ABCABC stacking upon cooling between 35°C and 31°C. High resolution measurements of the layer spacing do not indicate any anomaly at the transition. These results will be presented in section 7. Conclusions of this whole study are summarized in the final section.

2. Experimental.

The X-ray measurements reported here utilize three spectrometer configurations, two with very high resolution, the other with low resolution. All configurations use a 12 kW Rigaku rotating anode generator operated with a copper target at 40 kV and 200 mA.
as an X-ray source. The two high resolution spectrometers are capable of probing correlation lengths in the micron range; this is ideal for smectic density wave studies. The low resolution configuration provides considerably more intensity which is necessary for measurements of the in-plane liquid structure in the smectic A phase.

The monochromator and analyser for the high resolution spectrometer use perfect Si(111) wafers, with a Darwin width of approximately 4 s. The monochromator angles \( \theta \) and \( 2 \theta \) are defined by vertical slits to select the CuK\( _{\alpha 1} (\lambda = 1.5405 \text{ Å}) \) and CuK\( _{\alpha 2} (\lambda = 1.544 \text{ Å}) \) lines. Both slits are adjusted to be slightly larger than the filament spot size. This provides an in-plane resolution of \( 1.5 \times 10^{-4} \text{ Å}^{-1} \) half-width-at-half-maximum (HWHM) and a background of 0.2 counts per second. For the nematic to smectic A measurements the vertical divergence of the beam is matched to the vertical acceptance of the detector. After the monochromator yielding a vertical resolution of 0.065 \( \text{ Å}^{-1} \) HWHM. To achieve better vertical resolution for the smectic A to smectic C experiment, the horizontal slit after the monochromator is matched to Soller slits before the detector providing a vertical resolution of 0.012 \( \text{ Å}^{-1} \) HWHM.

The low resolution configuration utilizes a slit-limited graphite (002) crystal as a monochromator and vertical Soller slits for collimation after the sample. This spectrometer provides longitudinal in-plane resolution of 0.025 \( \text{ Å}^{-1} \) HWHM which is much better than required to study in-plane correlations of the smectic A phase and adequate to study the stacking sequences in the Sm B phase.

We performed studies on two samples of 40.7. Sample 1 was prepared commercially (CPAC Organix), sample 2 was synthesized from 4-n-butyloxybenzaldehyde and 4-n-heptylaniline (Frinton) by the following technique. The benzaldehyde is purified by fractional distillation under reduced pressure, the fraction boiling at 110 °C/1 mm Hg being collected. Similarly, the aniline is purified initially by fractional distillation under reduced pressure from powdered zinc. The aniline is redistilled twice more until it appears as a very pale yellow liquid boiling at 107 °C/1 mm Hg. The purified starting materials are mixed together in equimolar amounts (0.05 mol) at room temperature and then distilled with light-petrol (40-60 °C) (200 ml). The reaction mixture is stirred in the dark for a further 18 h. The solution is dried over anhydrous magnesium sulphate and decolourizing charcoal to remove water from the reaction and unreacted starting material. The solution is filtered and cooled in dry ice, the precipitate is rapidly filtered in the cold and the product desiccated under reduced pressure over calcium chloride. The recrystallization procedure is repeated until the white product had constant transition temperature (five times). The final yield is 40 % pure product.

Extensive studies have been conducted on Schiff-base liquid crystal compounds because of their diverse phase behaviour. Unfortunately, they tend to degrade when exposed to moisture. These fragments, together with other impurities, renormalize the interactions resulting in lower transition temperatures. Thus, detailed studies of phase transitions in these compounds can be complicated by drifting transition temperatures and possible impurity inhomogeneities.

Our findings show that 40.7 degrades much more rapidly in the nematic phase than in the smectic phases. Therefore, decomposition presents the greatest difficulty in measuring the N \( \rightarrow \) Sm A critical behaviour close to the transition. In sample 1, before we took measures to reduce decomposition, the critical temperature drifted by over 0.1 °C per day. To prevent further deterioration, we permanently sealed the sample with a low vapour pressure epoxy (Torr seal). This reduced the drift of \( T_{\text{NA}} \) to 0.002 °C per day. A second sample was kept in an oven incorporating flowing argon (1 l/h); this also reduced the drift to 0.002 °C per day; because appropriate precautions were taken from the beginning, \( T_{\text{NA}} \) for the second sample was 1 °C higher than that for sample 1. Nevertheless, our results, to be presented in section 3, indicate that the N \( \rightarrow \) Sm A critical behaviour is identical in both samples.

As noted above, impurities tend to decrease the transition temperature but not all the transitions are affected equally. For example, \( T_{\text{AC}} \) for sample 2 (purer sample) is 0.5 °C higher than sample 1. However, there is only a 0.1 °C difference in \( T_{\text{CB}} \). Therefore, impurities decrease the size of the Sm C range.

Temperature control of about 0.002 °C is provided by a two stage servo-controlled oven with kapton windows. Flowing argon through the outer stage approximately doubles the temperature fluctuations. The temperature of the sample is measured with a calibrated silicon thermistor with a resolution of 0.001 °C. The absolute temperature is known to \( \pm 0.2 \) °C. The sample dimensions were typically \( 1 \times 1 \times 0.2 \) cm\(^3\) with an illuminated area of \( 0.2 \times 0.5 \) cm\(^2\). Varied sample cell configurations were used but in all cases the windows were either kapton or beryllium.

All of our experiments on 40.7 rely on magnetic fields to obtain alignment of the director and hence the smectic layers. The measurements of the N \( \rightarrow \) Sm A and Sm A \( \rightarrow \) Sm C critical behaviour use a 0.4 T electromagnet which rotates with the sample on the goniometer. This provides alignment of the liquid crystal molecules along the field direction. In the smectic A phase, where the average molecular tilt is zero, the layers are perpendicular to the field. As the molecules tilt with respect to the field in the smectic C phase, the layers must tilt in order to keep the molecules aligned along the field direction. Geometrical factors did not permit measurements of the in-plane structure with the field arrangement described above.
Since the magnetic field is not necessary for maintaining orientational order in the smectic phases, the sample could be grown in a magnet and then moved to the X-ray spectrometer.

3. Nematic to smectic A transition.

Using the high resolution configuration with open vertical resolution described in section 2, we have measured the wave vector dependent susceptibility of smectic fluctuations in the nematic phase of 40.7. These fluctuations are centred about the $q$-vector for the smectic layers $(0, 0, q_0^s)$ where $q_0^s = 0.233 3 \text{ Å}^{-1}$ for sample 1 and $0.233 9 \text{ Å}^{-1}$ for sample 2, as shown in figure 1. In order to map out the critical scattering we carried out longitudinal scans $(q_L = 0, q_\parallel$ varied) and transverse scans $(q_\parallel = q_0^s, q_L$ varied) for a series of reduced temperatures $t = T/T_{NA} - 1$.

The nematic to smectic A transition temperature, $T_{NA}$, could be determined by longitudinal and transverse scans through the $(0, 0, q_0^s)$ peak in the immediate neighbourhood of $T_{NA}$. As the transition is approached from the nematic side both scans continuously narrow due to the diverging correlation lengths. The longitudinal width continues to narrow until at $T_{NA}$ the width is comparable to the spectrometer resolution. As may be seen in figure 2, subtle changes in the longitudinal width manifest themselves in the depth of the dip between the $a_1$ and $a_2$ peaks. Since the integrated intensity of the $(0, 0, q_0^s)$ peak increases dramatically at the transition, this provides a second measure of the transition temperature.

Fig. 1. — Smectic A $q$-vector corresponding to smectic layering $(q_0^s)$ versus temperature in 40.7. The two samples are described in section 2.

Fig. 2. — Longitudinal and transverse scans at a series of temperatures in the vicinity of nematic to smectic A transition for sample 2. The transition temperature $(T_{NA})$ is $56.331 \pm 0.003$ °C. The two peaks in the longitudinal scans correspond to $K_{a_1}$ and $K_{a_2}$ X-rays.
The behaviour of the transverse width with temperature provides the most sensitive determination of T_{NA}. At the transition, the width of the transverse scan changes abruptly, sometimes by as much as a factor of five over a few millidegrees Kelvin. Since the transverse in-plane resolution of the spectrometer is less than 10^{-5} \text{Å}^{-1}, the perpendicular width at T_{NA} is controlled by the mosaicity of the sample. The sample mosaicity, in turn, depends on the strength and homogeneity of the aligning magnetic field and the anchoring of the liquid crystal molecules to the walls of the sample cell. As might be expected, the mosaicity depends on the orientation of the sample cell with respect to the direction of the magnetic field.

The transverse width is determined by measuring the X-ray scattering as a function of the sample angle $\phi$ at the detector angle corresponding to the (0, 0, $q_0^0$) peak. In order to minimize wall effects, the oven containing the sample is rotated with respect to the magnetic field to obtain the best mosaic. Misalignment causes the peak position of the $\phi$ scan to shift and the width to increase as the temperature is lowered further into the smectic phase. The transition temperature, determined in this fashion, showed no hysteresis effects to within two millidegrees.

The nematic to smectic A transition in sample 1 was deduced using this technique. The critical temperature could be determined to within 0.002 °C. The mosaicity was better than 0.050 HWHM.

In figure 2 we present typical longitudinal and transverse scans, above and below the transition, through the (0, 0, $q_0^0$) peak for sample 2. The transition temperature is taken as 56.332 ± 0.003 °C which clearly brackets both phases. The uncertainty in T_{NA} may include a small coexistence region; in fact we believe that this arises from a small temperature gradient across the sample.

As mentioned earlier, we took steps to reduce the drift in the transition temperature. Since the shift is linear with time the actual critical temperature could be interpolated accurately. The uncertainty in this correction always represents a negligible error in the reduced temperature. Impurities could have the effect of smoothing an otherwise first order transition into a continuous transition if the impurities are quenched. Since the Sm A phase is fluid within the plane it is likely that all impurities would anneal.

Previous studies of the N → Sm A transition in other systems [3] indicate that the X-ray cross-section in the nematic phase may be expressed as

$$S(q) = \frac{\sigma_0}{1 + \frac{2}{\xi_{\parallel}}(q_{\parallel} - q_{0,\parallel}^0)^2 + \frac{2}{\xi_{\perp}} q_{\perp}^2 (1 + c \xi_{\parallel}^2 q_{\parallel}^2)}$$

where $\sigma_0$ is the susceptibility at (0, 0, $q_{0,\parallel}^0$), $\xi_{\parallel}$ is the parallel correlation length and $\xi_{\perp}$ is the transverse correlation length. We note that $q_{\perp}$ has components in and out of the scattering plane. The longitudinal and transverse scans through the (0, 0, $q_{0,\parallel}^0$) peak are simultaneously fit to the convolution of the X-ray cross-section with the experimental resolution with a correction for the sample absorption. For a discussion of the spectrometer resolution function see the appendix. As is evident from figure 3, the fit gives an excellent description of the critical scattering data with a goodness-of-fit parameter $\chi^2$ typically around 2.

We note that the fourth order term must be included in order to describe accurately the transverse scan. In equation 1, the coefficient of the fourth order term is dimensionless; thus when $c$ is zero the scattering cross-section is Lorentzian in the transverse direction, whereas when $c$ is 0.25 the scattering has the form of a Lorentzian squared. In figure 5b the coefficient of the fourth order term is plotted as a function of reduced temperature. Close to the transition $c$ is small indicating that a pure Lorentzian is adequate; however far from the transition $c$ approaches 0.25 implying that a Lorentzian squared is a better description. There is no theory for this evolution from Lorentzian squared to Lorentzian profiles.

Although equation 1 provides an excellent description of the N → Sm A cross-section when fit to the
Fig. 4. — Susceptibility ($\sigma_0$) and the longitudinal and transverse correlation lengths versus reduced temperature. The solid lines are single power law fits as described in the text. The dotted line is the Lubensky cross-over form as described in section 3.

The fitted parameters, $\sigma_0$, $\xi_{||}$, and $\xi_\perp$ are plotted on a logarithmic scale in figure 4 for both samples. Although the transition temperatures differ by 1.4°C for the two samples, there are no significant differences in the critical behaviour. This important result supports our hypothesis that the impurities are benign. Using perfect silicon scattering techniques, it is possible to measure $\sigma_0$, $\xi_{||}$ and $\xi_\perp$ over the range $3 \times 10^{-5} < t < 2.5 \times 10^{-2}$ in reduced temperature. From figure 5a, it is apparent that the parallel and perpendicular correlation lengths are diverging at slightly different rates. The ratio, $\xi_{||}/\xi_\perp$, varies by a factor of two over the range measured, as shown in figure 5a. Thus, as found previously in other materials, a single length scale is not adequate to describe the $N \rightarrow$ Sm A transition in 40.7.

In figure 4 we show the results of fits to a simple power law for the susceptibility, the parallel correlation length and the perpendicular correlation length (solid lines).

$$\sigma_0 \sim t^{-1.45 \pm 0.03}$$  
$$\xi_{||} q_0^0 = 1.55 t^{-0.78 \pm 0.02}$$  
$$\xi_\perp q_0^0 = 0.25 t^{-0.65 \pm 0.02}$$

where $q_0^0 = 0.2377 \text{ Å}^{-1}$. It is evident from these fits that mean-field theory $v_{||} = 0.5$, anisotropic dislocation behaviour $v_{||} = 2 v_\perp$, and non-transformed 3D XY behaviour do not provide a suitable explanation of the critical region in 40.7.

Lubensky et al. [21] have proposed that at the $N \rightarrow$ Sm A transition the liquid crystal correlation lengths may exhibit cross-over from 3D isotropic XY behaviour $v_{||} = v_\perp = v_\text{XY}$ to 3D anisotropic XY behaviour $v_{||} = 2 v_\perp = v_\text{XY}$. In an attempt to describe our measured data we have preserved the essential cross-over feature but with $v_{||}$ fixed at 0.78 rather than at $v_\text{XY} = 0.66$. The theory predicts no crossover for $\xi_{||}$ in the experimental accessible regime, however, $\xi_\perp$ should exhibit a crossover when the rescaled bend and splay elastic constants are equal, that is, when $K_{||}/K_3 = S^2$ where $S$ is the length anisotropy. We have fit $\xi_{||}$ to the crossover form [21] with $S = 7$, $K_1 = 8 \times 10^{-7}$ dyne, and $K_3 = (k_B T/24 \pi) q_0^{02} \xi_{||}$. The best fit, shown as a dotted line in figure 4, with just the amplitude adjusted, is slightly worse than a single power law shown as the solid line in figure 4.
Toner [28] has shown that the dislocation loop model may also exhibit the critical properties of the inverted 3D XY model. The behaviour of the correlation lengths is calculated using the anisotropic decorrelating effects of dislocations. He concludes that $v_\parallel = 6/5 v_{xy} = 0.8$ and $v_\perp = 4/5 v_{xy} = 0.533$ in the laboratory frame. This prediction for $v_\parallel$ is in good agreement with the measured value; however, the prediction for $v_\perp$ differs considerably from the measured value in 40.7. There is, as yet, no prediction for $v_y$.

According to the theories proposed by Toner [18] and Lubensky et al. [21], thermodynamic quantities such as heat capacity and elastic constants should exhibit transformation-independent divergences. Both theories predict that $K_3$ should diverge with an exponent $x_{xy}$. However, light scattering experiments [14] show that $K_3$ diverges with the x-ray exponent $v_\parallel = 0.78$ and indeed the absolute lengths for $\xi_{xy}$ determined using light scattering agree well with those measured directly with X-rays. Heat capacity results [14] on 40.7 indicate that the critical exponent $x$ is consistent with the $XY$ result of $-0.02$, whereas in 40.8, $x = 0.16$ [4]. The anisotropic scaling relation $v_\parallel + 2v_\perp + x = 2$, is satisfied to within the experimental errors in 40.7.

The above results for the N $\rightarrow$ Sm A transition in 40.7 together with those in a variety of other materials have recently been discussed by Garland et al. [14]. It is clear that no current theory adequately accounts for the observed critical behaviour at the N $\rightarrow$ Sm A transition. There is an interesting dependence of the exponents on the McMillan ratio, $T_{NA}/T_{N\phi}$ which deserves further attention both theoretically and experimentally.

4. Smectic A phase.

4.1 In-plane Structure. — The smectic A phase can be described as a one-dimensional mass density wave in a three dimensional fluid [1]. The mass density wave is related to the smectic order parameter through the relation

$$\rho = \rho_0 [1 + \frac{1}{2} \{ \sigma_1 e^{\phi(r)} e^{i\phi_{\rho}} + \phi \}]$$  \hspace{1cm} (3)

where $\rho_0$ is the average density. Our high resolution studies conclusively show that the correlation length along the direction of the mass density wave is greater than 30,000 Å. In this section, we discuss the liquid structure factor perpendicular to the density wave direction. In the course of our experiments we have accurately measured the smectic wave vector $q_0^2 = 0.233 4 \pm 0.000 1 \text{ Å}^{-1}$ and the $q$-vector for the first peak in the in-plane liquid structure factor $q_1^2 = 1.43 \pm 0.01 \text{ Å}^{-1}$ for sample 1; we find for sample 2: $q_2^2 = 0.233 9 \pm 0.000 1 \text{ Å}^{-1}$. In contrast to other liquid crystal systems, the lattice constant in the Sm A phase is quite insensitive to temperature, being constant to within our experimental resolution over the entire range. The slight decrease in $q_2^2$ with increasing impurities, corresponding to an increase in the layer spacing by 0.25 %, between the two samples, is consistent with the impurities preferentially dissolving in the tail region.

Utilizing the low resolution configuration we have conducted detailed studies of the in-plane correlations in the smectic A phase in sample 1. With the molecular director in the scattering plane, longitudinal scans $(1 - q_1/q_0^2, 0, 0)$ probe the structure within the smectic layers; transverse scans $(1, 0, q_2/q_0^2)$ probe the molecular correlations between layers. Typical longitudinal and transverse scans are shown in figure 6. A 360° sample cell permitted us to measure the mosaicity of the sample at the $(0, 0, 1)$ position which is less than $5^\circ$ HWHM.

In order to describe the scattering in the smectic A phase, we use a simple theory relevant to 2D hexatic fluids [43]. Specifically, the positional correlations are assumed to decay with a Yukawa form

$$g(r) \sim e^{-\sigma r}/r^{1/2}.$$  \hspace{1cm} (4)

Fourier transforming in the plane yields a Lorentzian, which must be powder averaged in the azimuthal

![Fig. 6. — Transverse (a) and longitudinal (b) scans through the in-plane liquid scattering in the smectic A phase. The solid line is the result of a least-squares fit to a quasi two dimensional circularly averaged Lorentzian. The dashed line is the best fit without circularly averaging.](image-url)
direction to average over all local orientations; this yields the scattering function $S(q)$

$$S(q) = C\left[\kappa^2 + (q_{\perp} - q_{\perp}^0)^2\right]^{-1/2} \left[\kappa^2 + (q_{\perp} + q_{\perp}^0)^2\right]^{-1/2}$$ (5)

which is nearly the square root of a Lorentzian. However, the term proportional to $q_{\perp} + q_{\perp}^0$ provides a slight asymmetry to $S(q)$ in such a way that the high-$q$ wing is less intense than the low-$q$ wing. As may be seen in figure 6b, this is, in fact, the reverse of the measured scattering profile. Thus, in order to fit the far wings of the longitudinal scan it is necessary to include a smoothly varying prefactor, $1 + b(q_{\perp}/q_{\perp}^0)^2$, to equation 5. This does not change the value of $\kappa$ obtained by fitting the central region without the prefactor; however, it does result in a considerable improvement in the fit to the wings. The best fit to this form yields $\kappa^{-1} = 15.8 \text{ Å}$ and $b = 1$ and is shown as the solid line in figure 6b. We have also fit the same data to a Lorentzian (not powder averaged) which yields a goodness of fit $\chi^2$ worse by a factor of ten and a correlation length smaller by a factor of two; this is shown as a dashed line in figure 6b. Convolutions with the instrumental resolution function have not been performed since the resolution ellipse is much narrower than the scattering; however, a correction has been made for the sample absorption.

If the in-plane positional correlations are truly 2D, longitudinal scans through $q_{\parallel} = 0$, $q_{\perp}^0$, and $2 q_{\perp}^0$ should all be identical except for a scale factor due to the molecular structure factor. However, these scans broaden slightly as $|q_{\parallel}|$ increases although the overall shape remains the same as can be seen from figure 6b. To incorporate this feature, we have included a correlation length, albeit small, along the layering direction. Specifically, in (5) $\kappa^2$ is replaced by $\kappa^2 + c^2 q_{\parallel}^2$ which has the effect of broadening the longitudinal scans as $|q_{\parallel}|$ increases. This converts a two dimensional Lorentzian into an anisotropic, three dimensional Lorentzian, powder-averaged in-plane. In addition, we find empirically that for $q_{\parallel} \neq 0$ the peak occurs at $q_{\perp} = q_{\perp}^0 \left[1 + \left(\frac{q_{\parallel}}{q_{\perp}^0}\right)^2\right]^{1/2}$ rather than $q_{\perp} = q_{\perp}^0$; accordingly for fits with $q_{\parallel} \neq 0$ we have replaced $q_{\perp}$ by this expression. This effect is commonly observed in liquid crystal materials including nematics and presumably originates from short range director fluctuations. Simultaneous fits to $q_{\perp}$-scans through $q_{\perp}^0 = 0$, $q_{\perp}^0$, and $2 q_{\perp}^0$ shown as the solid line in figure 6b yield an inter-layer correlation length of 4 Å. This distance corresponds to a small fraction of the layer separation whereas the in-plane correlations extend over several molecules. We emphasize that the 3D Lorentzian is so anisotropic that it is nearly two dimensional. The inter-layer correlation length, derived from the above analysis, accounts for some of the decrease in scattering intensity with increasing $|q_{\perp}|$ for the transverse scan through the liquid structure peak. To accommodate a faster fall-off, we have included a Gaussian form factor $e^{-1/2(q_{\parallel}/q_{\parallel}^0)^2}$ along the layering direction. The best fit, shown as the solid line in figure 6a, yields $f = 3$ Å. From the transverse scan alone it is very difficult to distinguish effects of a molecular X-ray form factor from those of between layer correlations. However, by simultaneously fitting longitudinal scans through $q_{\parallel} \neq 0$ we have been able to separate the two effects.

In summary, an anisotropic three dimensional Lorentzian, powder-averaged in the plane, gives a good description of the measured transverse liquid structure in the smectic A phase of 40.7. However, subtle systematic deviations are observed from this form. To accommodate these differences we have included as empirical corrections a sloping prefactor, a form factor along the layering direction and a shift in the peak position with $q_{\parallel}$. These slight corrections do not alter our conclusion that the Sm A phase is well described by weakly coupled stacks of 2D fluids with well-developed in-plane order.

4.2 Higher order reflections of the smectic A density wave. — The smectic A density wave modulation can be expanded [44] in terms of a Fourier series of $q_{\parallel}^0 = 2\pi/\ell$

$$\rho = \rho_0 \left[1 + \sum_{s=1}^{\infty} \{ \sigma_s e^{i(\ell \varphi)} e^{in\theta_s} + cc \}\right]$$ (6)

where the first coefficient $\sigma_1$ is the smectic order parameter. However, previous experimental studies have shown that the scattering intensity from higher harmonics is quite weak in comparison to the $(0, 0, 1)$ reflection [32]. It is precisely this novel feature of the smectic A phase that provides the justification for defining the first coefficient in the Fourier expansion as the smectic order parameter.

The study of higher order reflections can be complicated by multiple scattering effects. A single X-ray can scatter from a smectic layer with a momentum transfer $q_{\parallel}^0$ and re-scatter a second time also by $q_{\parallel}$ before emerging from the sample. Depending on the sample alignment, this event may be undistinguishable from scattering off the second harmonic of the smectic density wave with momentum transfer $2 q_{\parallel}^0$. In well aligned samples with flat structureless tails, such as it occurs naturally in the Sm A Landau-Peierls state [17], multiple scattering is manifested by peaks at $\phi = \phi_0$ and $3 \phi_0$. Therefore, in principle, multiple scattering events are distinguishable from the intrinsic $(0, 0, 2)$ reflection which is at $\phi = 2 \phi_0$. However, in samples with mosaicities of the order $\phi_0$, the two multiple scattering peaks merge into a single peak centred about $2 \phi_0$ which masks the observation of the intrinsic $(0, 0, 2)$ reflection. Such mosaicity effects have limited the precision of previous experiments.

In order to optimize the scattering intensity we utilized the low resolution configuration described in section 2 with an 0.8 T magnetic field to improve...
the alignment. With this configuration the width of the (0, 0, 1) rocking curve is determined by the transverse spectrometer resolution, whereas the tails of the rocking curve are due to either Landau-Peierls or mosaicity effects. In figure 7 we show the (0, 0, 1) and (0, 0, 2) rocking curves at 0.5 °C below T_{NA}. It is clear that multiple scattering is manifested by peaks with the line-shape of the (0, 0, 1) reflection but at $\phi = \phi_0$ and 3 $\phi_0$.

The peak intensity of the (0, 0, 1) rocking curve is $2 \times 10^6$ counts/second with a resolution-limited HWHM = 0.1°. The relative intensity of the multiple scattering peaks to the primary reflection is approximately 0.000 1 after background subtraction. From figure 7 we see that there is no evidence of the (0, 0, 2) reflection at the noise level of 5 counts/second. Reduction of the random noise is accomplished by adding many scans through $\phi = 2 \phi_0$ yielding a counting noise level of 0.8 counts/second. Since the precise form and position of the (0, 0, 2) peak is known, we have fit the data to this form assuming a flat background. The best fit reduces the upper bound for the (0, 0, 2) peak intensity to 0.4 counts/second. Therefore, our best estimate of the ratio of the second harmonic scattered intensity to the primary intensity is less than $2 \times 10^{-5}$. This upper bound is three orders of magnitude lower than measures of the same ratio in the bilayer smectics 8CB and 80CB.

5. Smectic A to smectic C transition.

The smectic A to C transition corresponds to the tilting of the molecular direction with respect to the smectic layers. In the limit that the director is held fixed by the magnetic field, the Sm A peak which is at (0, 0, q') spreads out into a ring of scattering in the Sm C phase. The ring, which is centred about the point (0, 0, q' cos $\phi$) with a radius $q' \sin \phi$, intersects the scattering plane at (± $q' \sin \phi$, 0, $q' \cos \phi$) where the tilt angle, $\phi$, is the Sm C order parameter. Since the layers must continually break and reform as the layers tilt with respect to the molecules, the mosaicity in the Sm C phase is somewhat worse than the corresponding mosaicity in the Sm A phase. Unlike the N → Sm A experiments where we intentionally chose the vertical resolution to be large, it is necessary to improve the vertical resolution so as not to integrate over the entire ring.

The experiment is carried out by performing longitudinal and $\phi$ scans through the scattering ring (Fig. 8). The high resolution configuration enabled us to measure changes in the scattering wave vector $q'_1$ to within $5 \times 10^{-5}$ Å⁻¹. The sample mosaicity limited the tilt angle measurement to an accuracy of 0.1°. For a well-aligned sample there should be two peaks at $\pm \phi$ from the ring of scattering; however, the raw data shown in figure 8 indicate a central peak as well. This effect has been observed previously in the Sm C phase of 8S5 [35]. Longitudinal scans through this peak reveal the same scattering wave vector as the peaks at $\pm \phi$, ruling out coexistence with the A phase. Therefore, this peak is due to layers which did not tilt with respect to the field. Presumably this effect is related to the strong coupling between the walls of the sample cell and the liquid crystal.

We have performed Sm A-Sm C measurements on both samples; in sample 2 the Sm A → Sm C transition temperature is higher and the C range larger than in sample 1 (Fig. 10). The tilt angle, $\phi$, has the same behaviour for both samples, and is shown for sample 2 in figure 9b (open circles). Galerne [45] has noted that...
Fig. 8. — Scattering profiles of scans exhibiting symmetrical splitting of the Sm A phase into a ring in reciprocal space as the Sm C phase is entered at a series of temperatures.

Fig. 9. — (a) Difference between the calculated tilt for fits to equation 11 and a single power law with $\beta = 0.37$ as a function of temperature. (b) Temperature dependence of the tilt angle (open circles) and $\cos^{-1}(d_c/d_A)$ (closed circles) in the Sm C phase.

Fig. 10. — Smectic q-vector corresponding to smectic layering versus temperature for the Sm A, Sm C and Sm B phases. For sample 1 $T_{AC} = 49.30$ °C and $T_{BC} = 48.7$ °C whereas for sample 2 $T_{AC} = 49.680$ °C and $T_{BC} = 48.8$ °C.

In his measurements the apparent critical behaviour of the Sm A $\rightarrow$ Sm C transition depends on the strength of the magnetic field. To study the effects of the aligning field we performed experiments with fields as weak as 0.01 T. In this latter case only the layer spacing can be measured directly; we find that the critical behaviour is independent of the magnitude of the field for all fields and reduced temperatures. Consequently, the local strains inherent in a polydomain sample do not affect the phase transition behaviour.

If the molecules are considered as rods the layer spacing is simply related to the tilt by

$$d_c = d_A \cos \phi$$

where $d_A$ is the separation between the smectic layers in the Sm A phase and $\phi$ is the tilt angle. The tilt angle, determined independently from $\phi$ scans (Fig. 9b : open circles) and from $\cos^{-1}(d_c/d_A)$ (Fig. 9b : closed circles) agree absolutely. Wulf has proposed a model [46] in which the molecules are already tilted in the Sm A phase and the Sm A $\rightarrow$ Sm C transition simply involves the development of long range order of the local tilt. Clearly 40.7 is considered as a rod rather than in the « Wulf » limit.

The free energy in a Landau model is given by a power series in the order parameter $\phi$

$$F = \frac{at}{2} \phi^2 + \frac{b}{4} \phi^4 + \frac{c}{6} \phi^6 + \frac{1}{2 M} |\nabla \phi|^2 + \frac{1}{2 M} |\nabla \phi|^2 + \ldots$$

where we have explicitly included terms up to sixth order. In mean field theory all fluctuations are ignored; therefore, with $t_0 = b^2/ac$ standard calculations yield

$$\phi = \left( \frac{b}{3c} \right)^{1/2} \left[ \left( 1 - \frac{3t}{t_0} \right)^{1/2} - 1 \right]^{1/2}.$$
This form exhibits a crossover from $\beta = 1/2$ to $\beta = 1/4$ at approximately $t_t = 1/3$. As noted by de Gennes [1,33], if the fluctuations terms are included, the Sm A $\rightarrow$ Sm C transition is in the universality class of the 3D XY model; in that case, power law behaviour is expected with $\phi = |t|^{-0.35}$. As discussed by Safinya et al. [35] the critical region estimated from the Ginzburg criterion [47] is expected to be within $10^{-3}$ in reduced temperature; therefore mean field behaviour should apply throughout the accessible experimental region.

The mean field result works extremely well in describing the tilt in 40.7 where the best fit gives a crossover temperature $t_t$ of $1.3 \times 10^{-3}$ (solid line, Fig. 9b). A single power law fit with $\beta = 0.37 \pm 0.02$ is indistinguishable from the crossover function, the maximum deviation from the two functions being only $0.05$ which is less than our $\phi$ resolution (Fig. 9a). Clearly it is impossible to ascertain whether the Sm A $\rightarrow$ Sm C transition is critical or mean field from the X-ray data alone.

Heat capacity and light scattering measurements on the Sm A $\rightarrow$ Sm C phase transition in 40.7 are capable of distinguishing mean field behaviour from critical behaviour. Evaluation of the heat capacity data, including the precursor effects of the nearby B phase, clearly supports the mean field picture with $|t_0| = 1.3 \times 10^{-3}$ in agreement with our X-ray results [37]. Light scattering measurements of the correlation lengths associated with Sm C fluctuations yield values which are large, $20 \AA$. Combining this with the heat capacity jump one finds that the critical region should be inside of $|t| = 10^{-5}$. Therefore current experiments in 40.7 do not access the true critical region. The susceptibility for Sm C fluctuations on the Sm A side also favour the mean field description [48].

In conclusion, we find that in 40.7, even though the order parameter is consistent with the 3D XY model over the reduced temperature range

$$5 \times 10^{-5} < |t| < 3 \times 10^{-3}$$

the data as a whole are uniquely described by a mean field model with an unusually large sixth order term. The early crossover from the usual mean field behaviour seen in many other transitions such as ferroelectrics and superconductivity seems to be caused by an anomalously large sixth order term, $c$, in the Landau free energy. This means physically that the liquid crystal resists large tilts. It might be noted that the relative displacement of the molecules is only $0.3 \AA$ at the maximum observed tilt (8°). We do not have a reasonable physical explanation for the appearance of saturation effects at such small displacements.

Finally, it should be emphasized that the mean field behaviour we have observed in 40.7 may not be universal. The majority of A-C transitions studied to-date with adequate precision are mean field in character [35-37, 49]. However, evidence for helium-like critical behaviour has been obtained in p-nonyloxybenzoate-p-butyloxyphenol [50] and possibly azoxy-4, 4'-di'undecyl-x-methylcinnamate [45] although the interpretation of the results in this latter system is still controversial [37].


The smectic C $\rightarrow$ smectic B transition involves the development of in-plane order and relaxation of the tilt. Therefore, the transition must be first order unless there is a precursive return of the tilt to zero. Indeed, our results conclusively show that in 40.7 the transition is strongly first order to a crystalline B phase. However, we observe quite novel coexistence behaviour at the transition. In sample 1 the Sm C phase disappears completely and is replaced by a re-entrant Sm A phase coexisting with the Sm B phase. In sample 2 the Sm B phase coexists with the Sm C phase. Such diverse behaviour between two samples of the same system with only slightly different transition temperatures is highly unusual. High resolution X-ray measurements can easily separate the scattering from the Sm B and Sm A phases since the layer spacing is different in the two phases (Fig. 10). The differences can also be distinguished by microscopy.

Typically the nematic, Sm A and Sm C phases of 40.7 exhibit their paramorphic microscopic textures. However, the crystal B phase which succeeds a Sm C phase can exhibit an additional texture to its more usual truncated fan and homeotropic textures. In sample 2, some of the areas which are homeotropic in the Sm A phase and schlieren in the Sm C phase become mosaic in the crystal B phase (Fig. 11).

This is unusual because normally the Sm B phase would return to the homeotropic texture. These mosaic areas are usually observed around the edges of focal-conic domains. The formation of this texture suggests that the molecules which are perpendicular to the glass supports in the Sm A phase must be tilted with respect to this axis in the Sm B phase. Consequently, the layers that are parallel to the glass supports must now be tilted with respect to them. Hence the transition from the A phase through the Sm C phase to the Sm B phase must take place with the molecules first tilting and then the layers breaking and reforming at a different angle so that the tilt angle of the Sm C phase becomes the normal to the new layers in the Sm B phase. When this occurs a mosaic texture is observed, as is the case for sample 2.

As the Sm C phase disappears in sample 1 due to the entry into the two-phase coexistence region with the Sm B, a phase appears with the smectic layer wave vector of $0.233 \AA^{-1}$; this is identical to the Sm A phase smectic layer wave vector. Unlike the Sm C phase which showed a splitting in the $\phi$ scan, no such splitting appears in this phase. This demonstrates convincingly that this is a re-entrant Sm A phase. At the transition the smectic layers must break and reform since in the Sm C phase the layers are tilted.
Surprisingly, the mosaicity as determined from the \( \phi \) scans of the re-entrant Sm A and the coexisting Sm B phases are identical to the mosaicity of the high temperature Sm A phase. Thus the director in the Sm B phase is always along the applied magnetic field.

Sample 2 differs from sample 1 in that the Sm B phase coexists with a Sm C phase. The smectic layer wave vector corresponding to the Sm C phase is continuous across the Sm C to Sm B transition suggesting that the coexisting phase is a tilted phase. This is confirmed by \( \phi \) scans which clearly indicate the same splitting as in the pure Sm C phase. More surprisingly, \( \phi \) scans through the Sm B phase peak are identical to those through the Sm C phase peak except for a scale factor. This might lead one to conclude that the Sm B phase is in fact a tilted phase such as a Sm G or a Sm H type. However, comparison of the smectic layer wave vector for sample 1 and sample 2 shows clearly that this is not the case. It may be seen from figure 10 that the changes in the lattice constant between the Sm A phase and the low temperature phase are identical for both samples. This would not occur if the Sm B phase of sample 2 was, in fact, a tilted phase. Thus the fundamental difference in the two samples is in the mosaicity pattern and the concomitant geometry of the directors in the two coexisting phases with respect to the applied field direction.

As stated above, in sample 1 on entry into the coexistence region, the layers reform so that the Sm B director is along the field direction. This geometry apparently stabilizes the higher temperature Sm A phase in favour of the Sm C phase. The Sm A phase director is also along the field so that in this configuration both the diamagnetic anisotropy and the interfacial energies are minimized at the cost of retaining the Sm A phase for about 0.6 °C below its unconstrained stability limit. In sample 2, on the other hand, one obtains conventional coexistence behaviour. In that case, however, the Sm B phase director is tilted with respect to the applied field. Thus the diamagnetic anisotropy energy is minimized for the Sm C phase but not for the coexisting Sm B phase.

Clearly, these novel effects arise because of the subtle balance between interfacial energies, wall pinning effects, magnetic field energies and the small difference in free energy between the Sm A and Sm C phases at the temperatures where the transition into the Sm B phase begins. Slight differences in this balance for different samples can produce dramatic differences in the coexisting states and in the macroscopic domain patterns.

### 7. Smectic B phase.

Using the low resolution spectrometer configuration and the field cooled sample described in section 2, we have measured the crystal structure of the Sm B phase. Although the layers are well ordered, within the layers the crystallites form with random orientations, thereby creating a two dimensional powder. The scattering is consistent with a triangular lattice within the plane with a nearest neighbour separation of 5.03 ± 0.01 Å. Longitudinal scans through the lowest order in-plane peak (1, 0, 0) indicate an intense resolution-limited peak with a very large diffuse background. The essential details of the scattering are identical to those in 40.8 as discussed extensively by Moncton et al. [6] and Pershan et al. [7].

Very recently, Pindak and Moncton [51] observed an additional peak in 14S5 at \( q_{1}/q_{0} = 1.32 \) which corresponds to herringbone ordering within the planes. The scattering around the (1, 0, 0) position is asymmetric in 40.7 with considerably more scattering on the high-\( q \) side as shown in figure 12. This may be due to herringbone short-range order although the large diffuse background makes this identification difficult. The only other identifiable peak corresponds to the (1, 1, 0) position which is at \( q_{1}/q_{0} = \sqrt{3} = 1.73 \).

Above 35 °C the molecules pack in an ABAB structure (hcp), as observed previously in other materials and undergo a continuous restacking transition to ABC stacking upon cooling. This is shown by transverse scans through the (1, 0, 0) peak along the layer normal as shown in figure 13. Although the
restacking transition starts at 35 °C, the ABC sequencing is not completed until 31 °C. The coexistence region may contain domains with both AB and ABC stacking, stacking sequences which repeat after more than three layers, or random stacking sequences. Our measurements cannot distinguish between these three possibilities.

Concurrent with the in-plane measurements, we have also performed detailed measurements of the layer lattice constant. There is absolutely no indication of the restacking transition from these data as shown in figure 1. This demonstrates clearly that the layer spacing is quite insensitive to the molecular re-arrangement in going from AB to ABC stacking. The change in heat capacity in going from these two stacking sequences is also unobservably small.

8. Summary.

Our experiments have demonstrated that in 40.7:

(1) the nematic to smectic A transition is second order with exponents $\gamma = 1.45 \pm 0.03$, $\nu_L = 0.78 \pm 0.02$ and $\nu_I = 0.65 \pm 0.02$. The correlation length and heat capacity exponents combine to give $\nu_L + 2 \nu_I + \alpha - 2 = 0.05 \pm 0.10$ thus satisfying anisotropic hyperscaling to within the combined errors. Our longitudinal correlation lengths measured directly with X-rays agree absolutely with those deduced in reference 14 from a dynamical scaling analysis of light scattering studies of $K_3$. The experimental data thus are all internally consistent. However, no current theory is able to account for the measured exponents; thus we conclude that the N → Sm A problem remains unsolved;

(2) we have analysed quantitatively the in-plane fluid positional correlation function in the Sm A phase. The first peak in the in-plane fluid structure factor is reasonably well-described by a circularly-averaged two dimensional Lorentzian with a correlation length of 15.8 Å. Successive layers are found to be at best poorly correlated. The second harmonic of the order parameter is shown to be at least $10^{-3}$ less than the primary sine-wave order parameter;

(3) the smectic A to smectic C phase transition is second order. The Sm C phase lattice constant $d_c$ is simply related to the tilt by $d_c = d_A \cos \phi$ as predicted by the most naive hard rod model. This precludes more exotic models for the Sm A → Sm C transition in 40.7. The X-ray data alone for the tilt are consistent with a power law with $\beta = 0.37 \pm 0.02$ or with a tricritical mean field theory with a crossover from $\beta = \frac{1}{2}$ to $\beta = \frac{1}{4}$ at $t_0 = 1.3 \times 10^{-5}$. Heat capacity, light scattering and susceptibility data all support the mean field description albeit with an anomalously large sixth order term in the Landau expansion for the free energy. This is consistent with the Ginsburg criterion which predicts that the critical region is inside of $10^{-5}$;

(4) the Sm C → Sm B transition is first order with an impurity-induced coexistence region of about 0.5 °C. Within this region, depending on the geometry
of the domains with respect to the applied magnetic field, the Sm B phase may co-exist either with the Sm C or a re-entrant Sm A phase;

(5) the Sm B phase is crystalline with hexagonal close packed structure. Between $35^\circ C$ and $31^\circ C$ there is a restacking transition from the ABAB (hcp) sequence to ABCABC stacking. The layer spacing is remarkably insensitive to this restacking with no change on a scale of 1 part in $10^{-4}$.

Clearly 40.7, like other materials in the $n0.m$ family, exhibits rich behaviour. Detailed studies on other homologs similar to those reported here would be quite valuable in further elucidating the smectic phases and phase transitions in liquid crystals. Studies of the N $\rightarrow$ Sm A are particularly important since that transition remains one of the major unsolved problems in the theory of equilibrium critical phenomena.

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Appendix.

The resolution of the spectrometer, in reciprocal space, is best described by a three dimensional ellipse. By far the longest axis of the ellipse is the out-of-plane component which corresponds to the vertical resolution which is approximately $0.05^{-1} \text{Å}$. This effectively integrates over the component of $q$ perpendicular to the scattering plane. The longitudinal in-plane resolution of $1.5 \times 10^{-4} \text{Å}^{-1}$ HWHM results primarily from the Darwin width of the monochromator and analyser crystals with a small correction from the intrinsic energy width of the copper $K\alpha$ lines. Since there is no energy broadening of the $2\theta$ in-plane resolution when $2\theta = 0$, the Darwin width contribution to the resolution function is found directly by measuring the angular divergence of the main beam. The actual $2\theta$ resolution is found by convoluting the energy distribution of the CuK$_\alpha$ lines with the $2\theta$ resolution for the appropriate scattering angles. As discussed by Safinya [52], the $2\theta$ resolution is best described by a Lorentzian modified by a fourth order correction. This correction becomes significant when the width from the parallel correlation length is comparable to the width of the $2\theta$ in-plane resolution. The transverse in-plane resolution of the spectrometer is less than $10^{-5} \text{Å}^{-1}$ HWHM, which is effectively a $\delta$-function. Thus the actual transverse in-plane resolution is effectively determined by the sample mosaicity which in turn originates from wall effects and the divergence of the magnetic field in the sample. Both the vertical resolution and the transverse in-plane resolution may usually be taken as Gaussians.

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