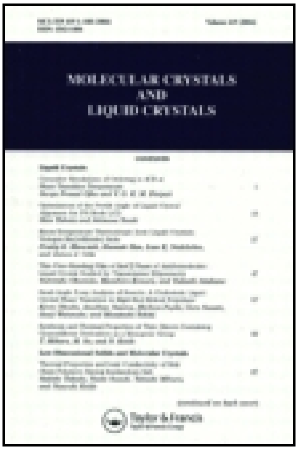

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High-Resolution X-ray Study of the Smectic A-Smectic B Phase Transition and the Smectic B Phase in Butyloxybenzylidene Octylaniline

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We have carried out a high resolution X-ray study of the smectic phases of Butyloxybenzylidene Octylaniline. We find that the phase previously identified as Smectic-B in this material is crystalline with in-plane order extending over at least 1.4 μm. The in-plane Bragg peaks are accompanied by anomalously strong diffuse scattering that can be described by a form $1/(q_\perp^2 + \gamma^2 q_z^2)$. Unless the elastic constant C_{44} is more than an order of magnitude smaller than previously reported values of $\sim 10^8$ ergs/cm^3 the diffuse scattering can not be due to acoustic phonons. The crystalline-B to Smectic-A melting transition is strongly first order with no observable pre-transition effects on either side of the transition.

In spite of extensive research, the well-ordered smectic phases such as B, E, F and H are still only poorly understood. A variety of theoretical models have been proposed for these phases, beginning with the stacked two dimensional harmonic crystal model of de Gennes and Sarma.[1] Very recently, important progress has occurred in the theory of two dimensional melting. The relevance of two dimensional (2d) dislocation-mediated melting, proposed by Kosterlitz and Thouless,[2] to liquid crystals was first realized by Huberman *et al.*[3] Recently the theory of 2d melting has been advanced by Halperin and Nelson and Young.[4] Helperin and Nelson have suggested that a 2d solid may first melt into a 2d "hexatic phase" characterized by very long range bond orientational order but short range positional order and this hexatic phase

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will then melt into an isotropic fluid. Two of us (RJB and JDL) have proposed a model for smectic B's which is, in essence, an amalgam of the de Gennes–Sarma and Halperin–Nelson ideas.[5] In this model a SmA liquid crystal may transform on cooling either into a 3d solid with positional long range order or into a 3d "stacked hexatic phase" with 3d bond orientational long range order and positional short range order. The former transition would be strongly first order whereas the latter could be second order. Only the stacked hexatic phase would be a true liquid crystal.

Previous low resolution X-ray experiments[6–11] have suggested that Butyloxybenzylidene Octylaniline (40.8) has a B-phase exhibiting the characteristics expected for the stacked hexatic model. Therefore, we have carried out a high resolution X-ray study of the B-phase and the B–A transition in this material. Concurrent with this work Moncton and Pindak[12] have carried out X-ray studies of freely suspended films of the B-phase of 40.8. Other workers have searched for pre-transition effects in the viscosity,[13] linear optical properties,[14] and heat capacity of 40.8 at the smectic A to smectic B transition.[15] We will show below that this transition is strongly first order, and that the phase, previously identified as smectic B, has 3d long range crystalline order in this material. Henceforth we will refer to this phase as *B-type lamellar solid* to distinguish it from a true smectic B.[5] Finally we will describe the results of our study on the anomalously strong diffuse scattering that accompanies the Bragg peaks.

The transition temperatures of our 40.8 as received from CPAC-Organics were slightly lower than accepted values for pure 40.8. However, after pumping on the material for eight hours at 75°C the following transition temperatures were obtained: isotropic → nematic 78.8°C, nematic → smectic A 63.6°C, and smectic A → B-solid 49.6°C. The sample cell consisted of a 2 mm × 1 cm × 1 cm beryllium can sealed by a teflon plug held in the mouth of the can by a brass fixture. We filled the cell with 40.8 and placed it onto a heated (~80°C) vacuum stage for approximately eight hours. After that the cell was brought down to room temperature under vacuum and sealed in dry nitrogen. With the sample prepared in this way and held below 49°C, the smectic A to B-solid transition temperature was virtually unchanged for approximately four weeks.

An oriented B-solid sample was prepared by heating the sample into the isotropic phase and then slowly cooling it down to 45°C in the presence of a magnetic field of approximately 5000 Gauss. Cooling rates varied from ~1°C per hour to as low as ~0.01°C per hour near the smectic A to B transition. Since the magnetic field was not necessary for maintaining orientational order in the smectic phases, the samples could be grown in a large electromagnet and then moved to the X-ray spectrometer. Our samples were oriented in the sense that all of the smectic layers were parallel to one another with cooling-rate dependent angular mosaicities that varied from ±0.3°C to ±2°C. Within the layers, however, the single crystal grain size was much less than the overall cell dimension and the sample appeared as a two-dimensional powder.

The X-ray spectrometer was similar to the one described by Als-Nielsen *et al.*[16] We discuss first the results for the B-solid phase below 49°C. In agreement with others[11,12] we observe a series of Bragg peaks superposed on a very strong diffuse background. Figure 1 illustrates the results for one $(1, 0, q_z)$ scan through the Bragg peaks. For CuKα radiation ($\lambda = 1.542$ Å) the (1, 0, 0) peak occurs at a $2\theta = 20.35°$ corresponding to a lattice spacing of 4.36 Å. Successive peaks imply a periodicity normal to the layer of 57.4 Å, two times longer than the layer spacing as determined from the Bragg peak indexed as (0, 0, 1). This is consistent with a hexagonal close packed, ABAB, structure[11,12] in which the lowest order (0, 0, 1/2) reflection is missing by virtue of the structure factor. That is, the unit cell is actually two layers thick

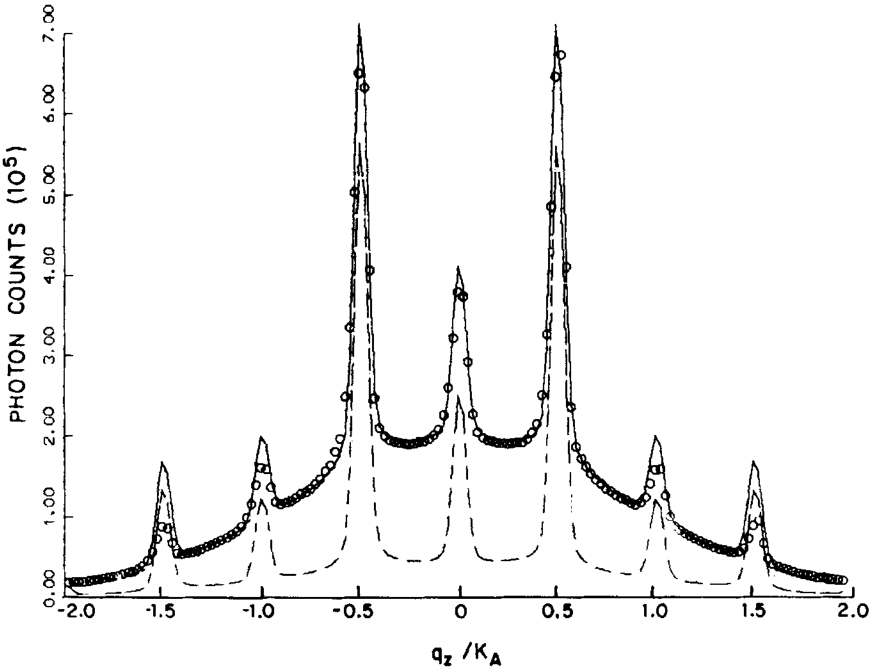
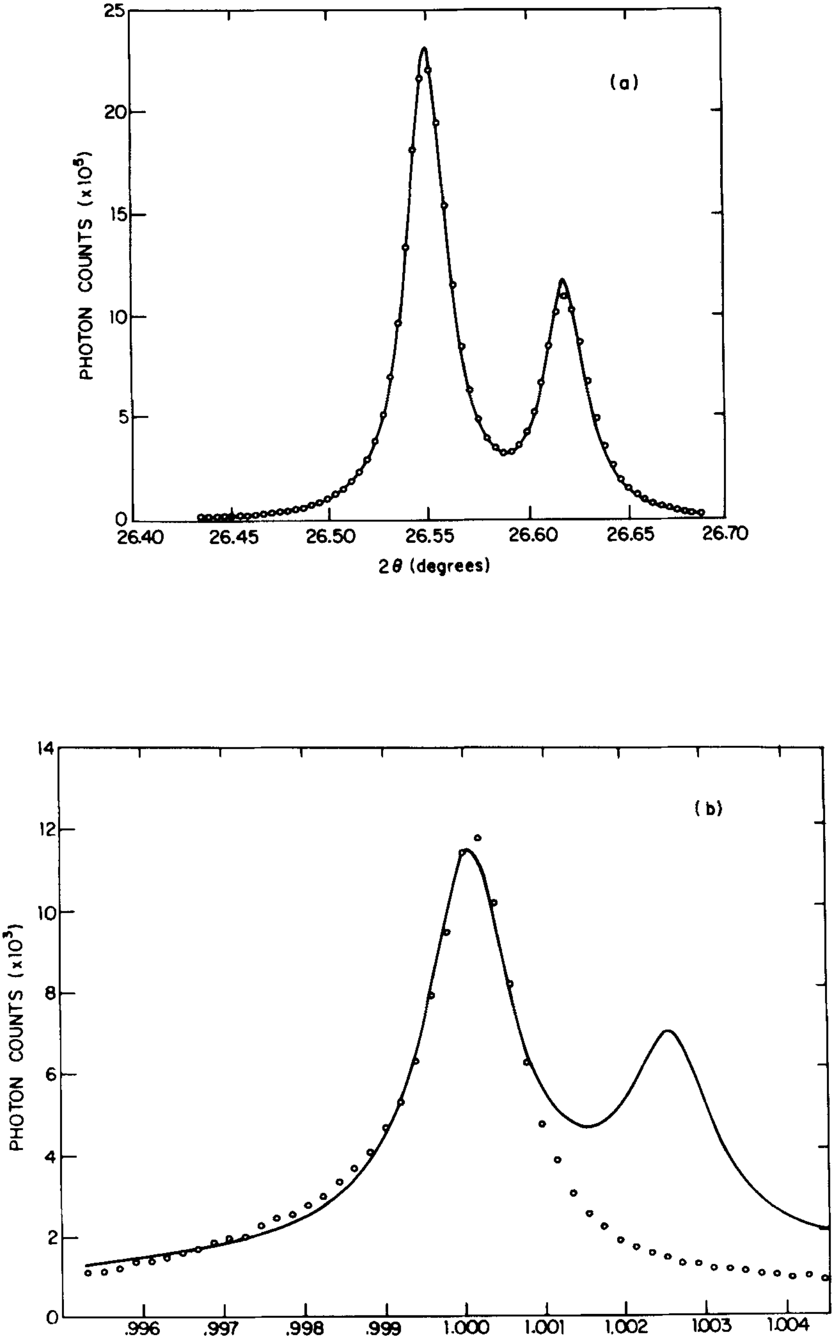


FIGURE 1 $(1, 0, q_z/K_A)$ scan showing the anamalously intense diffuse scattering and the $(1, 0, n/2)$ Bragg peaks. The circles represent experimental data, the full line the 2d powder average of the theoretical $S_{th}(1, 0, q_z/K_A)$, and dashed line the phonon and Bragg contributions to $S_{th}(1, 0, q_z/K_A)$, assuming $C_{44} \sim 5 \times 10^7$ ergs/cm^3. S_{th} accounts for the acoustic phonons, Bragg peaks, additional q^{-2} singularities at peaks, and form- and Debye–Waller factors. $K_A = 2\pi/L$ where $L = 28.7$ Å is the layer spacing in the solid-B phase.


(a)
PHOTON COUNTS (x10^5)
0
5
10
15
20
25
26.40
26.45
26.50
26.55
26.60
26.65
26.70
2θ (degrees)
(b)
PHOTON COUNTS (x10^3)
0
2
4
6
8
10
12
14
.996
.997
.998
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1.000
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1.004

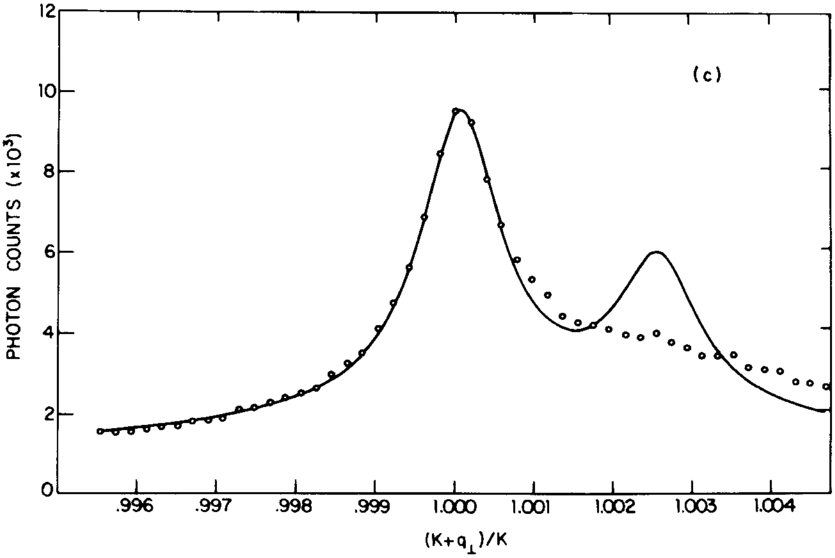

FIGURE 2a Resolution function derived from (0, 0, 2) reflection of graphite. The two peaks correspond to the CuKα_1 and CuKα_2 lines. b) $1 - q_{\perp}/K$ scan through the (1, 0, 1/2) peak. c) $1 - q_{\perp}/K$ scan through the (1, 0, 0) peak. As the result of geometric factors the CuKα_2 peaks were partially obscured (see text).

and correct crystallographic notation would assign the small angle ($2\theta = 3.09°$) peak corresponding to the lowest observed order of Bragg reflection to (0, 0, 2). We will adhere to the common practice of calling this the (0, 0, 1) peak and assigning the larger angle peaks to (1, 0, m/2).

In order to determine the extent ξ_x of the positional correlations within the layers we installed Ge crystals as monochromator and analyzer and carried out longitudinal scans through the (1, 0, 0) and (1, 0, 1/2) Bragg peaks. The resolution function for these scans was measured by observing the (0, 0, 2) Bragg reflection from graphite in the reflection or Bragg configuration. The result, shown in Figure 2a, corresponds to a Lorentzian resolution function with a half width at half maximum of 0.01155°. This translates to a half width at half maximum of 0.0008165 Å^{-1} when applied to the (1, 0, 0) peak of 40.8. Figures 2b and 2c display the results of scans through the (1, 0, 0) and (1, 0, 1/2) peaks, respectively. The sample geometry dictated that these were taken in the Laue configuration. For our spectrometer aligned on the CuKα_1 line with an entrance slit less than 1 mm wide immediately in front of the analyzer crystal, and approximately 1.5 m between analyzer and monochromator, the CuKα_2 line is not passed in the transmission configuration. The solid line is the sum of the resolution function shown in Figure 2a and a diffuse scattering signal that is calculated as the convolution of the resolution function with a form $[q_x^2 + q_y^2 + \gamma^2 q_z^2]^{-1}$. This is then averaged over the x–y plane as is appropriate to a two-dimensional powder. Both Bragg and diffuse terms were averaged over the measured mosaic distribution for this sample. We will discuss the suitability of the above form of the diffuse background signal below. The principal result that the (1, 0, 0) and (1, 0, 1/2) Bragg peaks are resolution-limited does not depend on how we represent the diffuse background. A non-linear least square fit of the data to the above theoretical form, allowing the intensities of the peak, of the background, and the width of the resolution function to be free parameters yields a half width at half maximum for both the (1, 0, 0) and (1, 0, 1/2) scans of $\Delta q_\perp = 0.79 \pm 0.05 \times 10^{-3}$ Å^{-1}; the measured width of the resolution function is $0.82 \pm 0.014 \times 10^{-3}$ Å^{-1}. By taking the extreme limits of both error bars we conclude that the in-plane correlation length ξ_x is greater than 1.4 μm. A straightforward geometrical analysis applied to the (1, 0, 1/2) scan demonstrates that the between-plane correlation length ξ_z is greater than 0.14 μm. Thus, our bulk samples of (40.8) in the B-solid phase have positional correlations at 45.5°C extending at least 1.4 μm within the layer plane and 0.14 μm normal to it. We next discuss the first order character of the smectic A to B-solid transition and the absence of any observed pretransition phenomena.

The (0, 0, 1) and (1, 0, m/2) peaks and the broad background intensities of an oriented sample of 40.8 were monitored as the sample temperature was increased from 45.5°C over a period of approximately two weeks. Aside from the subjective observation that certain features of the mosaic distribution function smoothed out slightly between 47°C and 48°C there was no observable change in *any detail* of the X-ray spectra until the temperature reached 49.1°C. Between 49.1°C and 49.3°C the intensities of the (1, 0, m/2) peaks decreased to zero linearly with temperature. Beyond 49.3°C, the only observable feature in (θ, 2θ) scans around the position of the (1, 0, m/2) peaks was a broad maximum characteristic of a liquid with a temperature-independent width corresponding to an in-plane correlation length of ~20 Å. There was absolutely no indication of anything interpretable as a pretransition increase in the positional correlations.

The above data were taken with a moderate resolution X-ray spectrometer. At a later stage (by then the sample had become less pure), we monitored the A, B coexistence by measuring the (0, 0, 1) peaks of the A and B phases. The planar spacings in the A and B phases differ by 1.3% so that the A and B peaks may be readily separated using the high resolution configuration described previously. We show in Figure 3a a set of scans just above, in the middle, and just below the coexistence region. The results are just those expected from a strongly first order transition that is broadened by a small impurity concentration. If I_B and I_A are the intensities of the (1, 0, 0) peaks

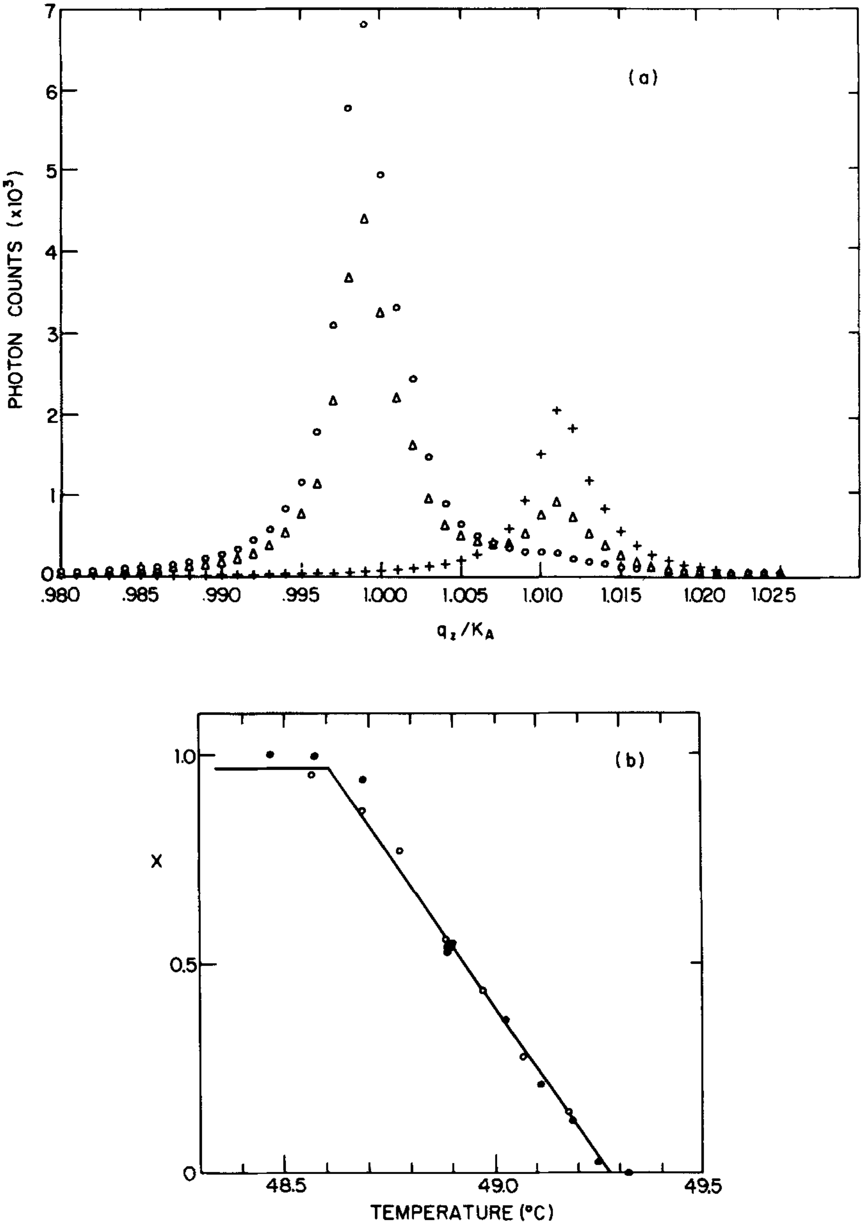

FIGURE 3a (0, 0, 1 − q_z/K_A) scans at temperatures $T = 49.3$°C (Smectic A phase) (+), T = 48.9°C (coexistence region) Δ, and $T = 48.7$°C (solid-B phase) 0. b) Relative concentration $\chi = I_B/(I_B + 4I_A)$ of A to B phases are plotted against the temperature T. Filled circles are for heating and open circles for cooling.

in the B and A phases respectively the relative concentration of B to A is given by $\chi = I_B/(I_B + 4I_A)$ where the factor 4 arises from the larger intensity of the (0, 0, 1) peak in the B phase. Figure 3b is a plot of χ vs. T on heating and then on cooling through the transition; the linear behavior is evident. These data are consistent with the low resolution results on the purer sample which had a correspondingly narrower coexistence regime. Although it is conceivable that impurities can convert an otherwise second order transition into a first order transition there is absolutely no reason to believe that this effect is occurring here. For example, the complete absence of pretransition phenomena expected for second or weakly first order transitions weighs heavily against any such hypothesis.

It is evident, therefore, that 40.8 exhibits the less interesting of the two possibilities suggested by Birgeneau and Litster,[5] viz., a first order transition from the A phase into a 3d positionally ordered solid. The label "smectic B" is incorrect since in 40.8 that phase is not liquid crystalline at all; we suggest instead *B-type lamellar solid.* It remains to be proven whether or not the "stacked hexatic phase" does indeed exist in Nature.

The B-solid is unusual since the in-plane Bragg peaks are accompanied by extraordinarily strong diffuse scattering. We have carried out a detailed analysis of this scattering which will be the subject of a future publication. The chief results are as follows.

When we represented the diffuse background for the high resolution data near the Bragg peaks as a two dimensional powder average of the sum of anisotropic Lorentzians

$$S(\mathbf{q}) \sim (\xi_\perp^2 q_\perp^2 + \xi_z^2 q_z^2 + 1)^{-1} \tag{1}$$

with $q_\perp^2 = q_x^2 + q_y^2$, each centered at the Bragg positions, a least squares analysis yielded $3000\ \text{Å} < \xi_\perp < \infty$. This implies that the diffuse scattering is dominated by q^{-2} singularities as could arise for example from acoustic phonons. We therefore attempted to analyze the low resolution data, shown in Figures 1 and 4, with the background signal represented by a form that approximates the contributions of transverse acoustic phonons with anisotropies and polarization factors comparable to previously reported values.[17,18] Although this could describe the data very well for $|q_\perp - K| \gtrsim 0.05$, where K is the reciprocal lattice vector for the (1, 0, 0) peak, it seriously underestimated the intensities close to the Bragg peaks. The solid lines in Figures 1 and 4 are the results of fitting the data with a background signal that is the superposition of the polarized transverse phonons and an additional sharp ridge that is approximately of the form $1/q_\perp^2$, independent of q_z. The difference between the solid and dashed lines in Figure 1 represents the contribution from this term. On the other hand, in contrast with previously reported values of $C_{44} \sim 10^8$ ergs/cm^3 values as low as 10^6 ergs/cm^3 were reported at

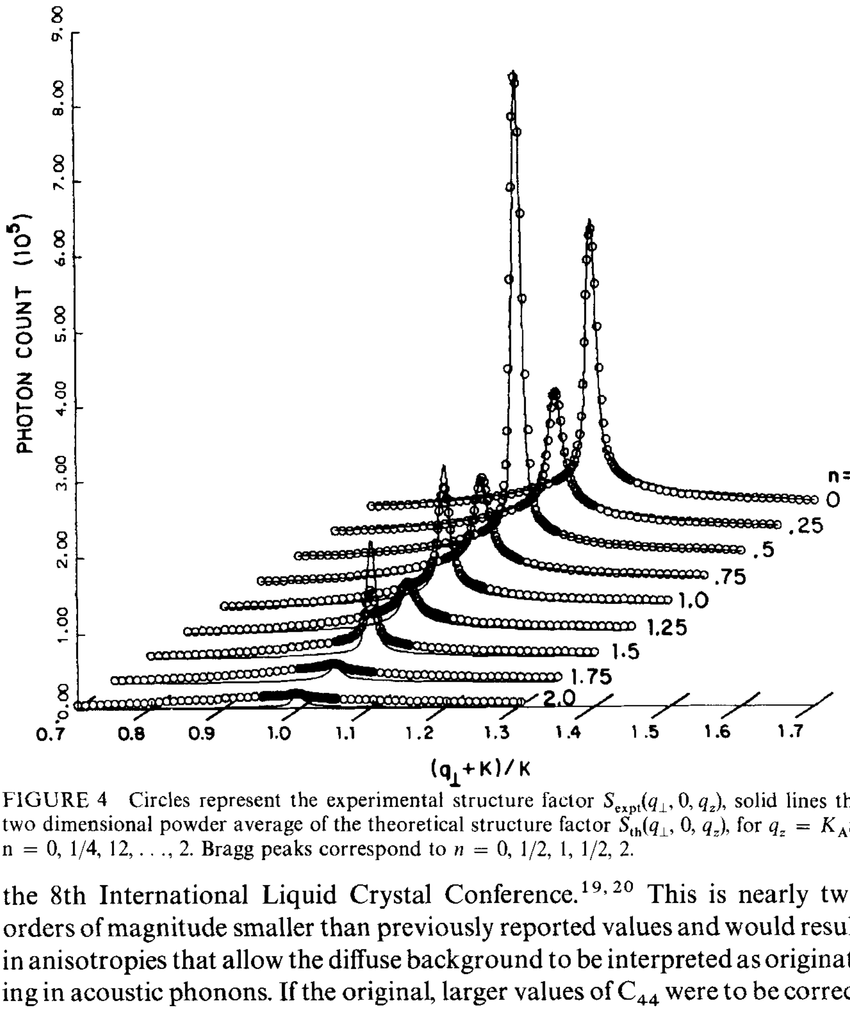

FIGURE 4 Circles represent the experimental structure factor $S_{expt}(q_\perp, 0, q_z)$, solid lines the two dimensional powder average of the theoretical structure factor $S_{th}(q_\perp, 0, q_z)$, for $q_z = K_A n$, n = 0, 1/4, 12, . . ., 2. Bragg peaks correspond to n = 0, 1/2, 1, 1/2, 2.

the 8th International Liquid Crystal Conference.[19,20] This is nearly two orders of magnitude smaller than previously reported values and would result in anisotropies that allow the diffuse background to be interpreted as originating in acoustic phonons. If the original, larger values of C_{44} were to be correct the origin of the diffuse scattering would have to be some other long range, nearly two dimensional fluctuations including, for example, either static or dynamic correlations of the aliphatic tails. The explicit origin of this strong 2d diffuse scattering would then remain an open question.

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