

X-Ray Diffraction Intensities of a Smectic-A Liquid Crystal

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Higher-order diffraction from the smectic-A liquid-crystalline phase of cyanooctylbiphenyl (COB) has been measured. The dominant short-range disorder, described by the relative intensities, is in agreement with our estimate of the smectic order parameter based on McMillan's mean-field theory.

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Two striking features of the x-ray pattern of smectic-A liquid crystals are the presence of one small-angle diffraction order which reflects the layering of the smectic and the absence or extreme weakness of higher-order diffraction.¹⁻³ At moderate angular resolution, the first diffraction order has a width equal to the angular resolution of the instrument and is, therefore, not discernible from a Bragg reflection. The lack of higher-order diffraction from these complex organic molecules is in marked contrast with the relatively intense higher-order diffraction in the crystalline state.

In this Letter we report the measurement of the second-diffraction-order intensity relative to the first for cyanooctylbiphenyl (COB). The intensity is extremely small; yet the reflection's width is still determined by the instrument. The loss of intensity is attributed to large short-range disorder as described by McMillan.⁴ These measurements permit evaluating a smectic order parameter⁴ and show that the smectic-A maintains nearly perfect periodicity but is subject to large local motions. The short-range disorder is so significant that the density wave is nearly sinusoidal. However, our determination of the deviation from a sine wave form is adequately described by McMillan's theory⁴ with use of calculated structure factors.

The experiment requires the elimination of multiple scattering whose line shape we have found to be in itself novel. This shape demonstrates the relatively large component of diffuse scattering which surrounds the first small-angle reflection. Small differences of this diffuse scattering from simple thermal diffuse scattering are expected because of the one-dimensional character of the material.⁵ The line shape, for primary diffraction, has been described theoretically^{6,7} and experimentally.² Deviations from true long-range order are subtle and are not expected to dramatically alter integrated intensities. The short-range disorder which is indicated by the

loss of higher-order intensity dominates in this system, at least in the vicinity of the nematic-smectic phase transition.

COB was aligned by cooling from nematic in a 1-kV, 500-Hz alternating electric field. We chose COB because it is typical of the class of compounds which have previously been studied² and found to exhibit virtually no (less than 10^{-4} times the intensity of the first order) second-order diffraction. The samples were rectangular with thicknesses which varied from 1 mm to 1 cm along the direction of the incident x-ray beam. The electrodes were made of polished brass and coated with SiO_2 . The gap between the electrodes was 2 mm. The smectic director is aligned parallel to the field and perpendicular to the electrode surface.

X rays were obtained from a copper rotating anode with a projected source size of $(0.2 \text{ mm})^2$ operating at 50 kV and 80 mA. $\text{Cu } K\alpha$ x rays ($\lambda = 1.54 \text{ \AA}$) were selected by a quartz-crystal monochromator. The incident beam was defined by a slit so that its relevant angular resolution was 5×10^{-4} rad. Scattered x rays were detected by a stable position-sensitive proportional detector. The detector is filled with Ar-CH_4 at 100 bars and is $\approx 90\%$ efficient. A damage-resistant nichrome wire was used with charge division encoding. The position resolution of the detector corresponds to an angular resolution (for the scattering angle) of 2×10^{-3} rad. For $q_0 = 2.03 \times 10^{-1} \text{ \AA}^{-1}$ ($d = 31 \text{ \AA}$), the resolution along the detector (full width at half maximum) corresponds to $\Delta q_{\parallel} < 0.04 q_0$.

The sample was rotated about an axis orthogonal to the director and the scattering plane with use of a precision, computer-controlled rotation stage. This angle will be denoted as ω ($\omega = 0$ when the beam is perpendicular to the smectic director). The angular resolution of the experiment was therefore dominated by the definition of the incident beam. Because of the relatively poor resolution along \vec{q}_{\parallel} and the small angular region

investigated, these scans are indistinguishable from ones along \vec{q}_1 . Therefore, the resolution

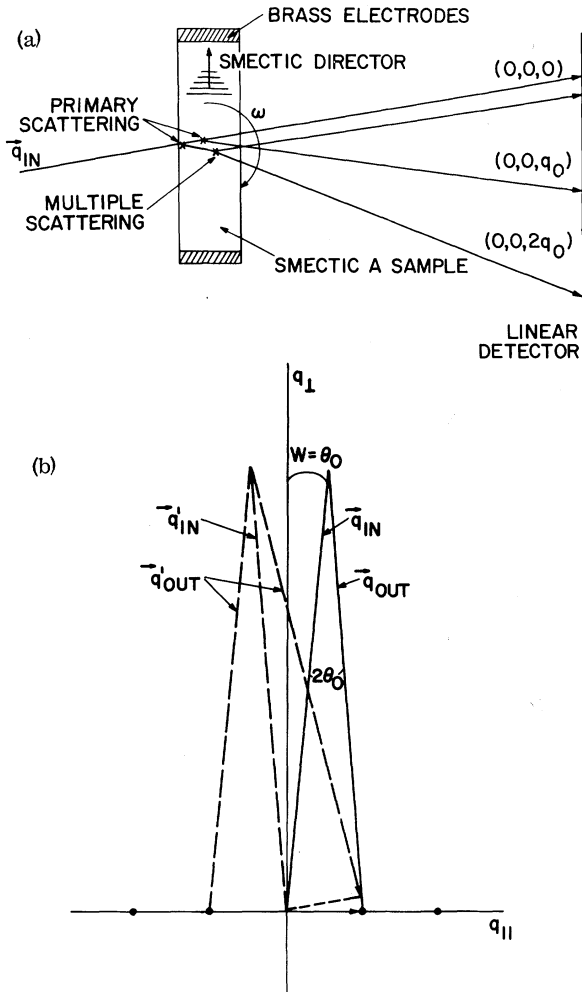


FIG. 1. (a) This schematic shows the diffraction geometry. The rays indicate primary first-order scattering and multiple scattering. Multiple scattering produces intensity which coincides with primary second-order scattering and with the transmitted beam. Sharp reflections (with both primary and secondary scattering) are integrated along the detector length and across the detector face (out of the plane of the drawing). This integrated intensity is measured as a function of the angle ω . (b) The reciprocal-space version of the same process is shown for $\omega = \theta_0$. Here $\vec{q} = \vec{q}_{in} - \vec{q}_{out}$ intersects the most intense portion of the first-order maximum. \vec{q}_{in}' is identical to \vec{q}_{out} but is translated to the center of the scattering space. Secondary diffraction from $(0, 0, q_0)$ produces a \vec{q}_{out}' which coincides in angle with primary diffraction from $(0, 0, 2q_0)$. Secondary diffraction from $(0, 0, -q_0)$ produces \vec{q}_{out}' which coincides in angle with the original \vec{q}_{in} . This diagram shows the condition producing a maximum at $\omega = \theta_0$. Rotation of the diagram so that \vec{q}_{out}' intersect the peak of the $(0, 0, q_0)$ produces another maximum at $\omega = 3\theta_0$.

along q_1 is $\approx 5 \times 10^{-4} q_0$. A schematic of the experimental arrangement is given in Fig. 1.

The experimental intensity of the second harmonic is many orders of magnitude smaller than it is for the first and their rocking curves [Figs. 2(a) and 2(b) for a 1-mm sample] are not of the same shape. To explain this, multiple scattering, where x rays undergo two first-order scattering events to produce an event at $(0, 0, 2q_0)$, must be considered [Fig. 1(b)]. With neglect of dynamical effects, at small scattering angles the integrated intensity of this multiple scattering, I_2^M , is approximated by

$$I_2^M(\omega) \propto t^2 I_1(\omega - \theta_0) I_1(\omega - 3\theta_0), \quad (1)$$

where t is the sample thickness, $2\theta_0$ is the Bragg angle for the first order, i.e., $\theta_0 = \sin^{-1}(\lambda q_0/4\pi)$, ω is as previously defined, and I_1 is the singly scattered first-order intensity at $|\vec{q}_1| = q_0$. [$I_1(x)$ has a maximum at $x = 0$.] Thus, the intensity of the second order at $|\vec{q}_2| = 2q_0$, denoted by I_2 , has two components approximated by

$$I_2(\omega) = A I_1(\omega - \theta_0) I_1(\omega - 3\theta_0) + B I_1(\omega - 2\theta_0). \quad (2)$$

B gives the fractional contribution to the second singularity, $I_2(\omega)$, of the intrinsic second-order scattering assumed to have the same line shape as the first-order scattering: $I_2^0 = B I_1(\omega - 2\theta_0)$. This is maximum at $\omega = 2\theta_0$.

For this smectic-A liquid crystal, $I_1(\omega)$ has a sharp peak determined by detector resolution and mosaic spread, and relatively intense long tails. Consequently, multiple scattering contributes to a maximum in the second-order intensity when $\omega_0 = \theta_0$ and $3\theta_0$ and *not* when $\omega = 2\theta_0$. This case is unusual and would not occur if, for example, $I_1(\omega)$ were described by a Gaussian distribution. Figure 2(c) demonstrates this phenomena for a thick sample ($t = 1$ cm) where multiple scattering dominates. The asymmetry is due to the skewed $I_1(\omega)$ distribution probably imparted by wall effects as evidenced by the fact that although all of the thick samples showed characteristic peaks at θ_0 and $3\theta_0$, the relative intensities of the two peaks varied from sample to sample.

For $t = 1$ mm, A and B of Eq. (2) were determined by a least-squares procedure. The fit is shown in Fig. 2(b). The value of $B = 1.9 \times 10^{-4}$ is the ratio of the second to the first singularity free from multiple-scattering effects. If the same fitting technique is applied to the $t = 1$ cm data, the fit is poorer but shows that essentially all the scattering is from multiple scattering. The value of B must be corrected by the Lorentz

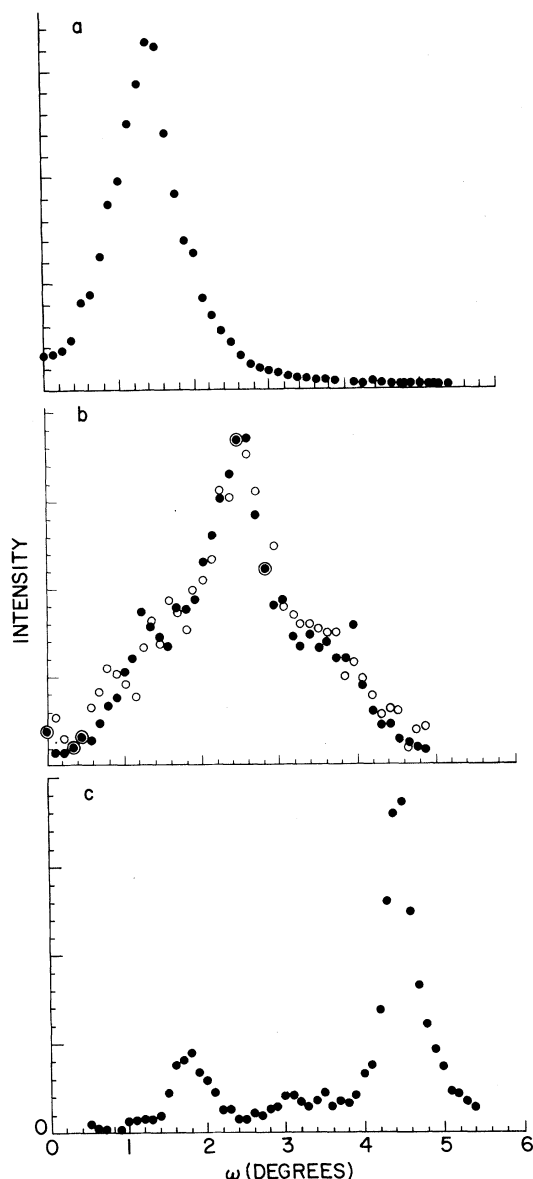


FIG. 2. The rocking curves for COB at 25°C aligned with a 1-kV, 500-Hz electric field. The thickness of the sample is 1 mm. (a) The rocking curve for the reflection at $(0, 0, q_0)$. $q_0 = 2\pi/d = 2.03 \times 10^{-1} \text{ \AA}^{-1}$. (b) The rocking curve for the $(0, 0, 2q_0)$ reflection (open circles) fitted with a curve calculated from the $(0, 0, q_0)$ rocking curve data (closed circles). The calculated intensity is given by Eq. (2). For this fit, $B = 1.9 \times 10^{-4}$ and the fraction of multiple scattering is given by $[\sum A I_1(\omega) \times I_1(\omega - 2\theta_0)] / [\sum I(\omega)] = 0.43$. The error is given by

$$\frac{\sum [I_{\text{calc}}(\omega) - I_{\text{obs}}(\omega)]^2}{\sum I_{\text{obs}}(\omega)^2} \times 100 = 2.5$$

The sums are over the data points. (c) The rocking curve at $(0, 0, 2q_0)$ for a 10-mm-thick sample.

factor due, in our case, only to the finite angular distribution about the axis perpendicular to the

scattering plane. The factor is proportional to $1/q$ therefore decreasing the intensity of the second singularity by 2. Thus, experimentally, we find the ratio of the intrinsic second-order intensity, $I_2^0(T)$, to the first-order intensity, $I_1(T)$, is $I_2^0/I_1 = 3.8 \times 10^{-4}$ for temperature $T = 25^\circ\text{C}$. Before comparing this value to a theoretical estimate, we need to factor out the “zero-temperature” structure factor of the particular molecule.

The “zero-temperature” structure factor for COB can be calculated along an axis perpendicular to the smectic planes (Z axis) from atomic coordinates derived from the recent crystal-structure determination of the similar molecule cyanobenzylidene-*p-n*-octyloxyaniline⁸ and the recently proposed model for the molecular packing of this compound into smectic- A layers.^{9,10} For the calculation, we place two opposing molecules in a bilayer arrangement such that the aromatic rings overlap. The structure factor is then real and given by

$$F(q_{\parallel}) = 2 \sum_i f_i \cos[q_{\parallel}(Z_i - \delta)], \quad (3)$$

where δ is the overlap parameter, Z_i are the atomic coordinates, and f_i are the atomic scattering factors. For $\delta = 6.5 \text{ \AA}$,^{9,10} d is $\sim 30.6 \text{ \AA}$ and I_2^0/I_1 is found to be 0.057. We can now correct the observed ratio 3.8×10^{-4} by the factor 0.057 to give as an experimental estimate for smectic layers $I_2^0/I_1 = 6.7 \times 10^{-3}$.

A theoretical estimate for this quantity can be found with use of McMillan's theory⁴ where intralayer disorder is described in terms of a smectic order parameter which decreases close to the nematic-to-smectic transition temperature, T_{NS} . With a mean-field model based on simple interatomic forces, the self-consistent potential in a multilayered system produces a density wave whose amplitude is given by the order parameter $\sigma = \langle \cos(2\pi z/d) \rangle$. Extending the calculation, it can be shown that the amplitude of the second-order component to the density wave is given by $\langle \cos(4\pi z/d) \rangle = (\frac{1}{2} + \gamma/\alpha)\sigma^2$, where $\gamma/\alpha = 0.5(\alpha/2)^3 / [1 - (\alpha/2)^3]$ and α is McMillan's parameter which may be determined from the ratio of T_{NS} to the nematic-to-isotropic transition temperature, T_{NI} . For COB, $\alpha \approx 0.935$. For point particles following these density waves, the ratio of diffracted intensities is given by

$$\frac{I_2^0}{I_1} = \frac{\langle \cos(4\pi z/d) \rangle^2}{\langle \cos(2\pi z/d) \rangle} = 0.31\sigma^2 = 18.3 \times 10^{-3}, \quad (4)$$

since $\sigma^2 = 2(1 - T/T_{\text{NS}})/(1 - 2\gamma/\alpha)$, $T_{\text{NS}} = 306 \text{ K}$, and $T \approx 2.98 \text{ K}$ for our experiment. This value

is within a factor of 3 of the experimentally determined one of 6.7×10^{-3} .

In conclusion, we find that smectic-A liquid crystals, in the vicinity of T_{NS} , are subject to an unusually large short-range disorder while maintaining well-defined long-range order. McMillan's⁴ description of the short-range disorder is useful in predicting x-ray intensities, thus relating their measurement to a smectic order parameter and phase-transition behavior. The density wave deviates only slightly from pure sinusoidal form. However, the measured deviation is predictable from McMillan's theory and the zero-temperature structure factor. Similar x-ray measurements as a function of temperature and particularly with use of liquid crystals which appear to deviate^{11,12} from McMillan's theory would be useful and may verify some points of more generalized mean-field theories.¹²

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