X-ray study of the sharpness of the smectic A layer structure

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The intensity ratio of the second order to the first order Bragg reflection resulting from smectic A layering is reported for two compounds. In one case this ratio is small ($\sim 10^{-3}$), which is of the same order as commonly reported. The second compound shows an intensity ratio which is two orders of magnitude higher. In the latter case, the spatial distribution function of the molecular centres of gravity cannot be taken as sinusoidal.

1. Introduction

In smectic A (S_A) liquid crystals, elongated molecules have their centres, on average, arranged in liquid-like layers that are perpendicular to the preferred direction of the long molecular axes. The layering of the smectic phase is reflected by the X-ray pattern, which, in most cases, is characterized by a clear first order diffraction peak and a very weak second order peak [1–4]. The loss of second order intensity can be attributed to important short range disorder, which makes the density wave describing the layering nearly sinusoidal. This observation is basic for McMillans description of the smectic A-nematic phase transition in terms of a single order parameter, τ_1, which is the first harmonic in a Fourier expansion of the density wave [5]. Exceptions are bilayer (S_{A2}) phases which are not considered here.

We report the measurement of the intensity I_{002} of the second order (quasi) Bragg reflection relative to the first order one I_{001}, for the compounds 4,4'-di-n-heptylazoxybenzene (A) and 4-n-butyloxybenzylidene-4'-aminopropiophenone (B). Structural formulas and phase transition temperatures are given in table 1. Compound A has a 20 K wide S_A temperature interval ending in a second order S_A-N phase transition at 53·5°C [6]. The 002-reflection is very weak as usual. Compound B [7] has a 56 K wide S_A interval between a smectic B [8] and a nematic phase; the S_A-N transition is first order. The ratio I_{002}/I_{001} is over one 100 times higher than for compound A. The results are interpreted in terms of the ratio of the order parameters τ_2/τ_1, where
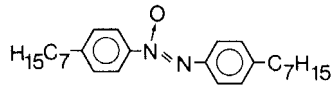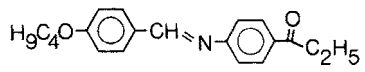
$$\tau_k = \int_{-d/2}^{d/2} f(z) \cos{(2\pi kz/d)}\,dz; \tag{1}$$

here $f(z)$ is the spatial distribution function of the molecular centres of gravity and d is the layer thickness. The first harmonic τ_1, usually referred to as the order

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Table 1. Structural formulas and transition temperatures of the compounds investigated.

Compound formula	Phases (temperatures in °C)
A $H_{15}C_7$—⬡—N≋N—⬡—C_7H_{15} (with O)	K 34 S_A 53·5 N 70·4 I
B H_9C_4O—⬡—CH≋N—⬡—C_2H_5 (with O)	K 79 S_B 87 S_A 143 N 146 I

parameter τ, is a measure of the *strength* of the smectic layering, to be distinguished from the *sharpness* of the layering. The latter quantity indicates the deviation of $f(z)$ from a sinusoidal shape into a more peaked one, and reflects itself in a non-zero ratio τ_2/τ_1. In the extreme case of an ideal solid, $f(z)$ is an array of delta functions and $\tau_2/\tau_1 = 1$. The relation between the order parameters and the scattering intensity is given by

$$\frac{I_{002}}{I_{001}} = \frac{1}{2}\left|\frac{S(2q_0)}{S(q_0)}\frac{\tau_2}{\tau_1}\right|^2, \qquad (2)$$

where $S(q)$ is the molecular structure factor and $q_0 = 2\pi/d$ is the position of the first order Bragg reflection. The factor $\frac{1}{2}$ is the Lorentz factor resulting from mosaic spread in the sample. Once $S(q)$ is known from molecular models, τ_2/τ_1 can be calculated.

2. Experimental

The measurements were performed at the Risø National Laboratory (Roskilde, Denmark) with a triple axis spectrometer. X-rays are obtained from a rotating copper anode operating at 50 kV and 180 mA. After a beam defining slit an Si(111) mono-chromator single crystal selects the CuK_α doublet ($\lambda = 1.54$ Å). A second slit placed just before the sample oven eliminates the $K_{\alpha2}$ component. The sample oven is placed on a rotation stage and the angle of rotation is denoted by ω. The detector arm can be turned through an angle 2θ relative to the direct beam. When the spectrometer is tuned to a Bragg reflection, $\theta = \theta_B$. The analyser is another Si(111) single crystal, placed behind a set of slits for further reduction of the background scattering. The analyser and monochromator crystals are placed such that they reflect in opposite directions (non-dispersive mode). The resolution obtained with this set-up is approximately 0·003° FWHM in θ, with the angles of interest between 1·5 and 4°. The liquid crystal is held in a sample holder with Be windows; the cell thickness is between 1·6 and 2·5 mm and the lateral dimensions are 13 × 13 mm. The cell is placed in a two-stage oven which achieves a temperature stabilization better than 0·05°C. Built-in permanent magnets provide a field of 0·4 T for alignment of the director in the sample.

The small intensity of the 002 reflection requires elimination of possible multiple scattering. Because the mosaicity of the samples can be of the same order of magnitude as the 001 Bragg angle, it is possible that X-rays are diffracted by two successive 001 scattering processes. The emerging X-rays then coincide either with the direct beam or with the 002-diffracted radiation. In principle, the effect of multiple scattering could be eliminated by measuring at various cell thicknesses and extrapolating to zero thickness. Practical considerations, such as the limited amount of material and the

large beam intensity needed for thin samples, led us to another approach, based on the rocking curves of the 001 and 002 peaks [4]. By analysing the shape of the 002 rocking curve with the mosaicity known from the 001 curve, multiple scattering from intrinsic 002 scattering can be separated.

3. Results and discussion

Each compound was investigated at three temperatures. In the $(\theta, 2\theta)$ scans (sample rotation $\omega = \theta$, analyser arm rotation 2θ), first and second order Bragg reflections were observed with widths close to the experimental resolution of $0.003°$ FWHM. The first order reflection occurred at a Bragg angle θ_0 of respectively $1.53°$ for compound A and $2.00°$ for B. Corresponding repeat distances are listed in table 2 and found to be close to the length of a stretched molecule as obtained from space-filling models (29.5 Å for A, 22.1 Å for B). The rocking curves of the 001 reflections are shown in figure 1. Mosaicities are typically a few degrees (see also table 2). For compound A, the rocking curves of the 002 reflection are significantly different in shape from the 001 rocking curves, as can be seen in figure 2 (*a*). The difference is attributed to multiple scattering. Separate contributions of intrinsic 002 and multiple 001 scattering to the signal are also indicated in the figure, with their relative proportions determined by a least-square fit to the experimental data. The slight asymmetry present in the mosaicity (001 rocking curve) is strongly enhanced in the theoretical multiple scattering curve. Multiple scattering amounts to approximately half of the second order signal at high temperatures, and 17 per cent at 35°C because of the smaller mosaicity of the sample at this temperature. For compound B, multiple scattering resulted in only a minor contribution to the second order intensity (see figure 2 (*b*) and table 2). Rocking curves of the 002 Bragg peak were therefore only measured at the two lower temperatures.

Table 2. Layer thickness d, mosaicity M (FWHM of 001), intensity ratio I_{002}/I_{001} with and without correction for multiple scattering, and the order parameter ratio τ_2/τ_1 for compounds A and B at different temperatures. The errors in τ_2/τ_1 are due mainly to uncertainties in the calculated structure factors.

| Compound | $T/°C$ | $d/\text{Å}$ | M/deg | $I_{002}/I_{001} \times 10^4$ | | τ_2/τ_1 |
				Measured	Corrected	
A	35	28·76	1·4	2·95	2·45	0·092 ⎫
	45	28·76	2·2	2·62	1·50	0·072 ⎬ ± 30%
	50	28·74	2·2	1·31	0·63	0·047 ⎭
B	90	22·11	4·2	584	566	0·49 ⎫
	110	22·10	4·5	372	361	0·39 ⎬ ± 15%
	130	21·99	4·6	95	92	0·20 ⎭

In the calculation of the structure factor $S(q)$, the molecules are assumed to be in their most stretched configuration, with bond angles and lengths taken from space-filling models. Taking the origin in the middle of a smectic layer, the imaginary part of $S(q)$ cancels due to the random updown distribution of the molecules in the smectic A phase. The electrons are treated as point charges located on the atomic nuclei; electrons of hydrogen atoms are located on their neighbouring carbon atoms. These simplifications have very little influence on $S(q)$ as long as $2\pi/q$ is large compared to the interatomic distances. Careful evaluation of $S(q)$ requires inclusion of the effect
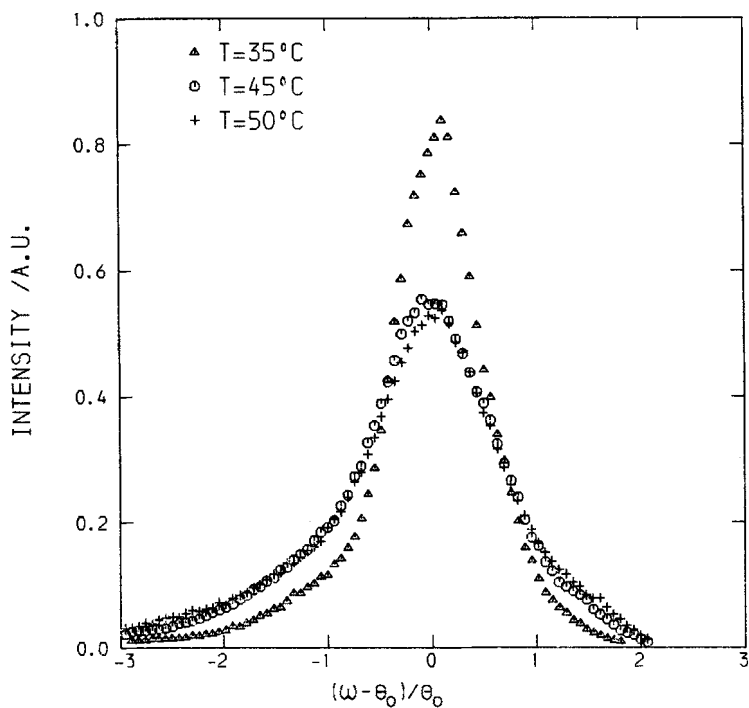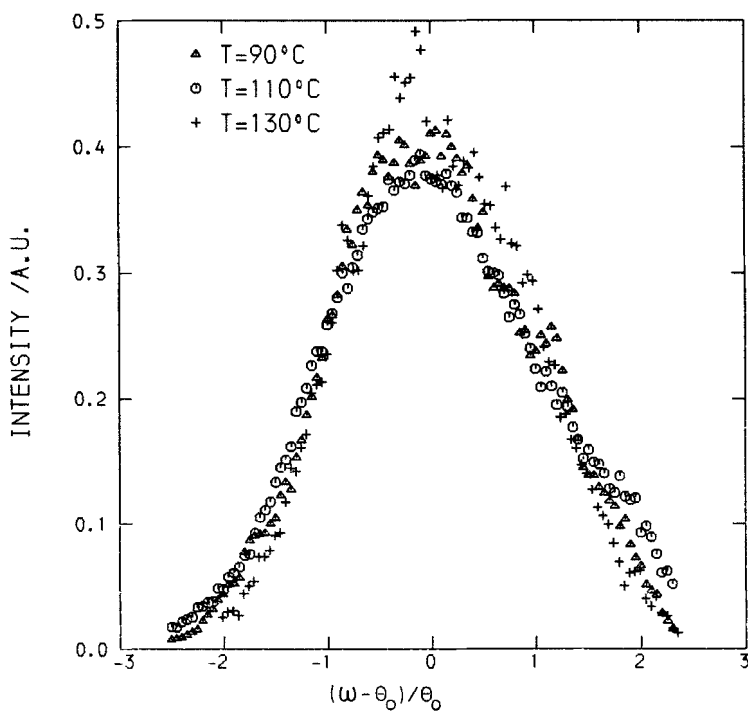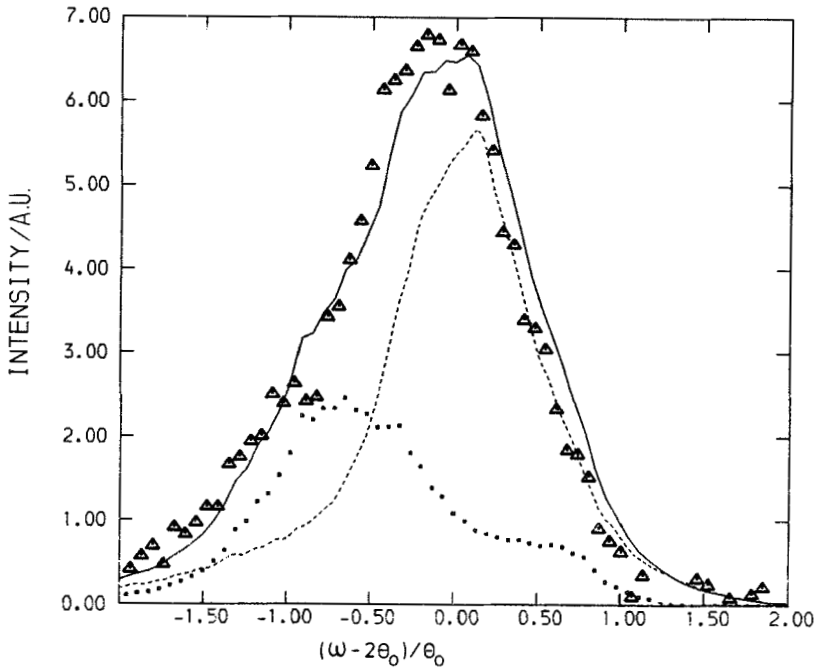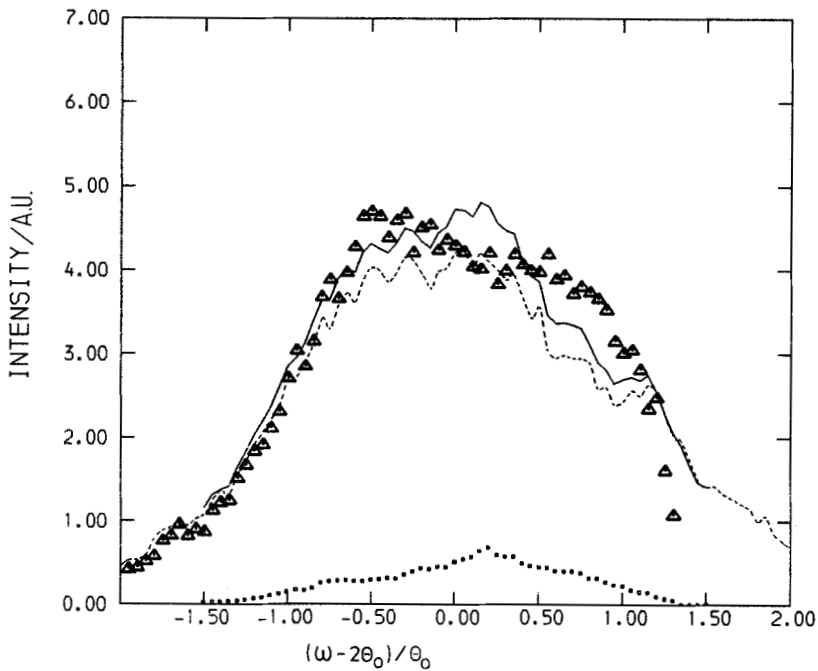
Figure 1.   Rocking curve of the first order Bragg reflection at different temperatures;
(a) compound A, (b) compound B.

Figure 2. Rocking curves of the second order Bragg reflections; (*a*) compound *A* at 35°C, (*b*) compound *B* at 90°C. Solid lines: least-square fit made up of contributions from intrinsic 002 scattering (broken lines) and multiple 001 scattering (dotted lines).

of orientational disorder [9], since the orientational order parameter is known to be not yet saturated in the S_A phase. Approximating the orientational distribution function by a gaussian of the appropriate width to obtain an order parameter between 0·7 and 0·8 [2, 10], we find $S(2q_0)/S(q_0) = -0.24 \pm 0.06$ for compound A and $S(2q_0)/S(q_0) = -0.69 \pm 0.06$ for compound B. The resulting values of τ_2/τ_1 are listed in table 2. Although part of the difference in the second order intensity between the two compounds is due to the structure factor, there is still almost an order of magnitude difference in the ratio of order parameters τ_2/τ_1.

From our observations it follows that the weak 002 reflection usually observed in smectic A phases is mainly due to multiple scattering. This is also true for compound A in this work, and similar cases have been reported [3, 4]. Though few data have been carefully analysed, compound B seems to be the first exception to this behaviour, with τ_2/τ_1 an order of magnitude higher. This anomalous smectic order could also be at the origin of the absence of texture changes at the $S_A S_B$ phase transition, which lead the original authors to the (now known to be incorrect) conclusion of two S_A phases [7]. It suggests that the S_A ordering in this case might be of an unusual kind, although it is still classical in the sense that there are no X-ray reflections or diffuse spots corresponding to $d \approx 2l$ (l is the molecular length). In-plane correlations via the terminal $-CO-C_2H_5$ moiety might play a role. Any mechanism, however, which leads to an anomaly in I_{002}/I_{001}, is likely to lead to anomalies in other properties as well. In this context, it is worth noting that the S_A–N phase transition in compound B is first order with a transition heat $\sim 0.4\,\mathrm{kJ/mol}$ [7], whereas most S_A–N transitions, including that of compound A, are second order. Powder photographs of the next higher homologue of A, which has a first order S_A–N transition [6], however, show the usual weak 002 reflection. Thus there seems to be no straightforward connection between the value of τ_2/τ_1 and the order of the transition.

We conclude that in compound B the ratio of order parameters τ_2/τ_1 has an exceptionally high value. It is clear that the usual concept of a sinusoidal distribution function to describe the smectic density wave [5] cannot be applied in such a case. This observation could well be relevant to many more smectics where this point has not been investigated experimentally.

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