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X-ray scattering by the phases of 4-methoxybenzylidene-4'-*n*-butylaniline quenched under a magnetic field

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X-ray scattering by the phases of 4-methoxybenzylidene-4′-*n*-butylaniline quenched under a magnetic field

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Normally 4-methoxybenzylidene-4′-*n*-butylaniline exhibits only one liquid-crystalline phase; it is nematic at room temperature. However, after quenching it at liquid nitrogen temperature it is possible to reach four new phases by successive annealing. We report here an experiment aimed at providing a better understanding of these phases by studying their texture after quenching in a magnetic field large enough to orient the sample in the nematic phase.

1. Introduction

The well-known 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) molecule consists of only 33 atoms and is nematic in the temperature range 19 to 36°C. After quenching at liquid nitrogen temperature it is possible, by gradual annealing, to reach new phases [1]. The initial quenched C_0 phase has a structure very similar to the nematic phase, with a somewhat improved short range order. The first two phases, C_1 and C_2, look like bilayer smectic phases, the two higher temperature phases are crystalline. Two more crystalline phases, C_5 and C_6, may be obtained by slow cooling from the nematic state.

Recently we have reported an X-ray study with a detailed description of the spectra obtained from an unaligned sample [2]. This allowed a clear identification of the phases, nevertheless the information was somewhat too limited to permit the development of a model for these observations. On the other hand it was of interest to check whether the same structures were obtained when the quenching was performed under a magnetic field, which aligns the nematic phase fully. Furthermore, we expected to create a texture which might help to index the peaks, thanks to the modulation of the Debye–Scherrer rings as a function of the field strength.

2. Experimental

We have used the same spectrometer as described in detail in [2]. The incoming X-ray CuKα beam (λ = 1·541 Å) was monochromated by the [002] reflection of a pyrolitic graphite monochromator. The scattered photons were detected by a

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curved linear position sensitive multidetector (INEL–CSP 120), which covers 120°, symmetrically relative to the main beam. A hollow beam-catcher absorbs the main beam, to prevent it hitting the middle of the detector.

The liquid crystal sample was introduced into a 0·5 mm Lindeman glass capillary tube, 10 mm long, placed vertically in a goniometer head which allows it to be set exactly on the X-ray beam at the point which is the centre of curvature of the detector. As before the quenching and cooling of the sample was provided by a nitrogen gas flow cryostat, placed immediately above the sample. The precision of the temperature control is 0·5°C. This kind of cooling device, out of the scattering horizontal plane, allowed us to avoid the use of windows on the X-ray beam, and most important for this experiment to place an electromagnet around the sample. This provided a horizontal magnetic field perpendicular to the incoming X-ray beam. The field could reach 0·8 T. The field was applied during the quenching and annealing processes. To quench into the C_0 phase was easy. Nevertheless it was very difficult afterwards to reach the C_1 phase through the first annealing. While the strength of the field and the annealing temperature were varied, they looked to be relevant parameters and the C_3 phase was generally found. Instead the C_1 phase could only be reliably obtained after a long period of alignment in the nematic phase. Several hours seem to be necessary, although the liquid crystal appears to be fully aligned after a few minutes. This feature will be explored systematically in a further experiment. Finally the experiment protocol was as follows. The field value was kept at 0·2 T. The sample was aligned for at least 5 hours in the nematic phase, before quenching. Then, with the field applied, the sample was annealed stepwise until the phase transition appeared and was complete. The temperature was decreased down to 100 K and the field removed. The sample was then rotated around the vertical axis, and an X-ray diffraction pattern was registered for each value of the sample angle ω; this allowed us to make a 'rocking curve' for the whole diffraction pattern. This was performed successfully for the phases C_1, C_2 and C_3 (see figures 1, 2 and 3), but for the phase C_4, which always crystallized with large grains, the nice continuous texture observed for the C_1–C_3 phases was broken.

On each of the diffraction patterns we show the zero position ω_0, which corresponds to the original setting, when the sample was quenched with the field horizontal and perpendicular to the incoming X-ray beam. Consider now a peak, the Bragg vector of which is along the magnetic field, as for a smectic A phase. It is clear that its intensity will be maximal at the zero position and minimal once the sample is rotated by 90°. On the contrary, the intensity of purely transverse peaks would be a minimum at ω_0 and a maximum at $\omega_0 + 90°$. An oblique Bragg vector with respect to the field direction would give rise to a maximum of the intensity at an intermediate angle. Therefore the arrays shown in figures 1 to 3 are derived from the diffraction patterns found for the unaligned sample through the modulation (the texture) due to the alignment. The shape of the Bragg peaks as a function of ω describes how the orientation of the crystallites of the sample is modulated by the alignment field. The angular width is analogous to the mosaic spread of an imperfect crystal. It should be noted that this is an approximation valid mostly for the Bragg peaks whose reciprocal space vector is close to the field (the explanation of this is not within the scope of this paper and will be given in a geometrical analysis of this type of modulation [3]).

The peak shape versus the angle ω can be approximated by a periodic function of gaussian or lorentzian type. Two functions were tried to analyse single peaks

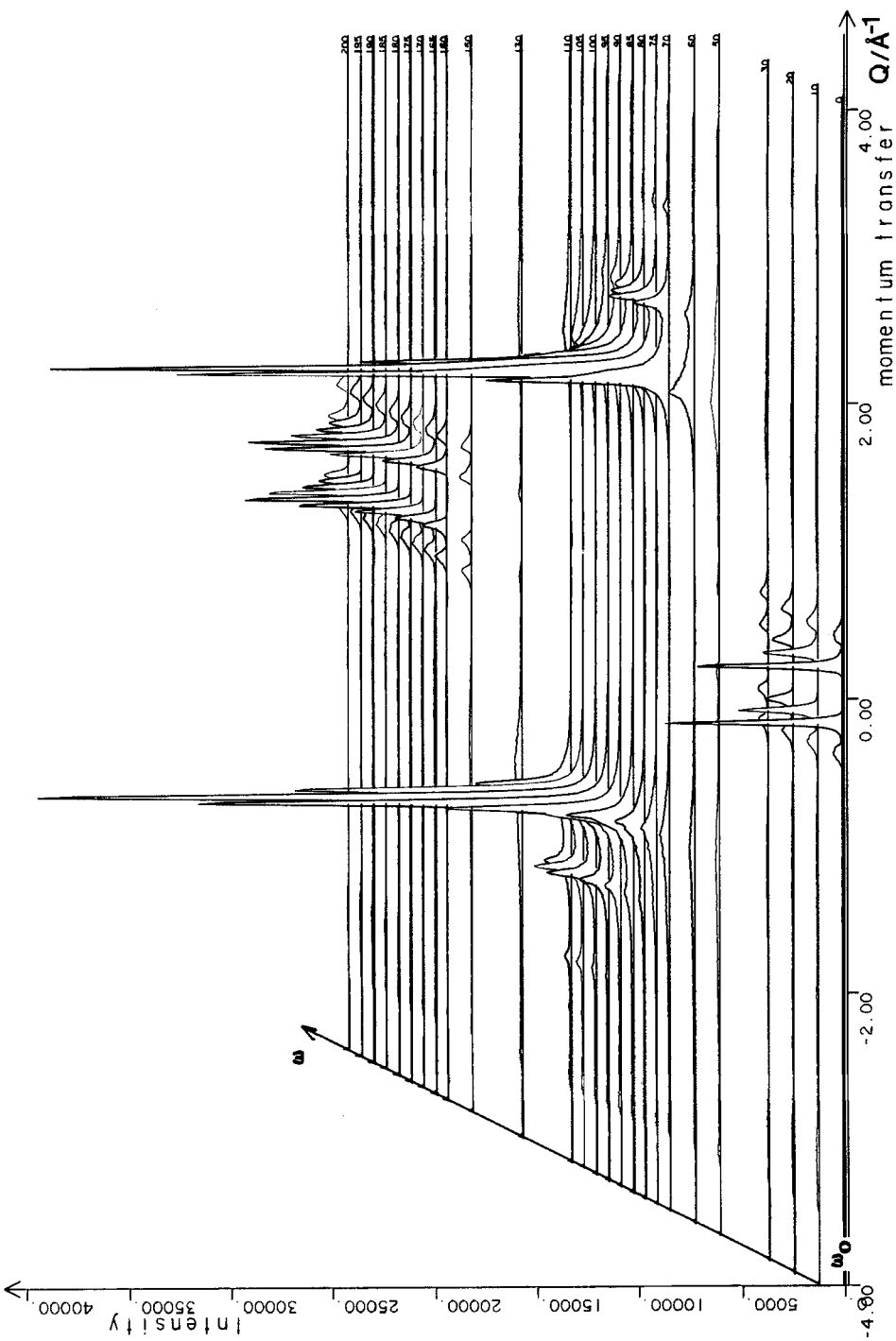

Figure 1. Phase C_1. Array of X-ray diffraction patterns (λ = 1·5418 Å) scattered in the horizontal plane, displayed for various positions of the aligned sample, rotated through an angle ω around the vertical axis. ω_0 marks the position of the sample quenched with a horizontal aligning magnetic field and perpendicular to the incoming X-ray beam.

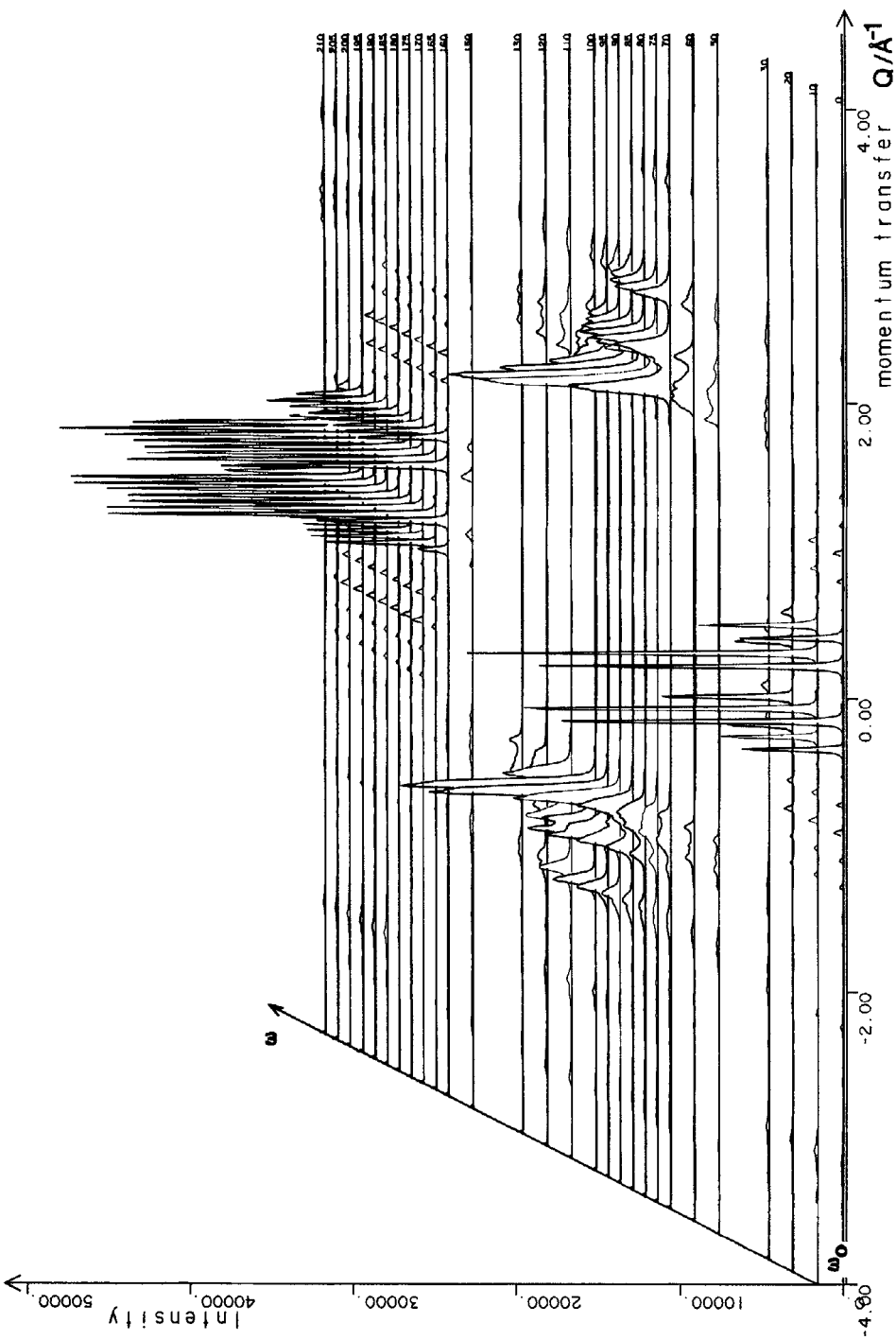

Figure 2. Phase C_2. Array of X-ray diffraction patterns (λ = 1·5418 Å) scattered in the horizontal plane, displayed for various positions of the aligned sample, rotated through an angle ω around the vertical axis, ω_0 marks the position of the sample quenched with a horizontal aligning magnetic field perpendicular to the incoming X-ray beam.

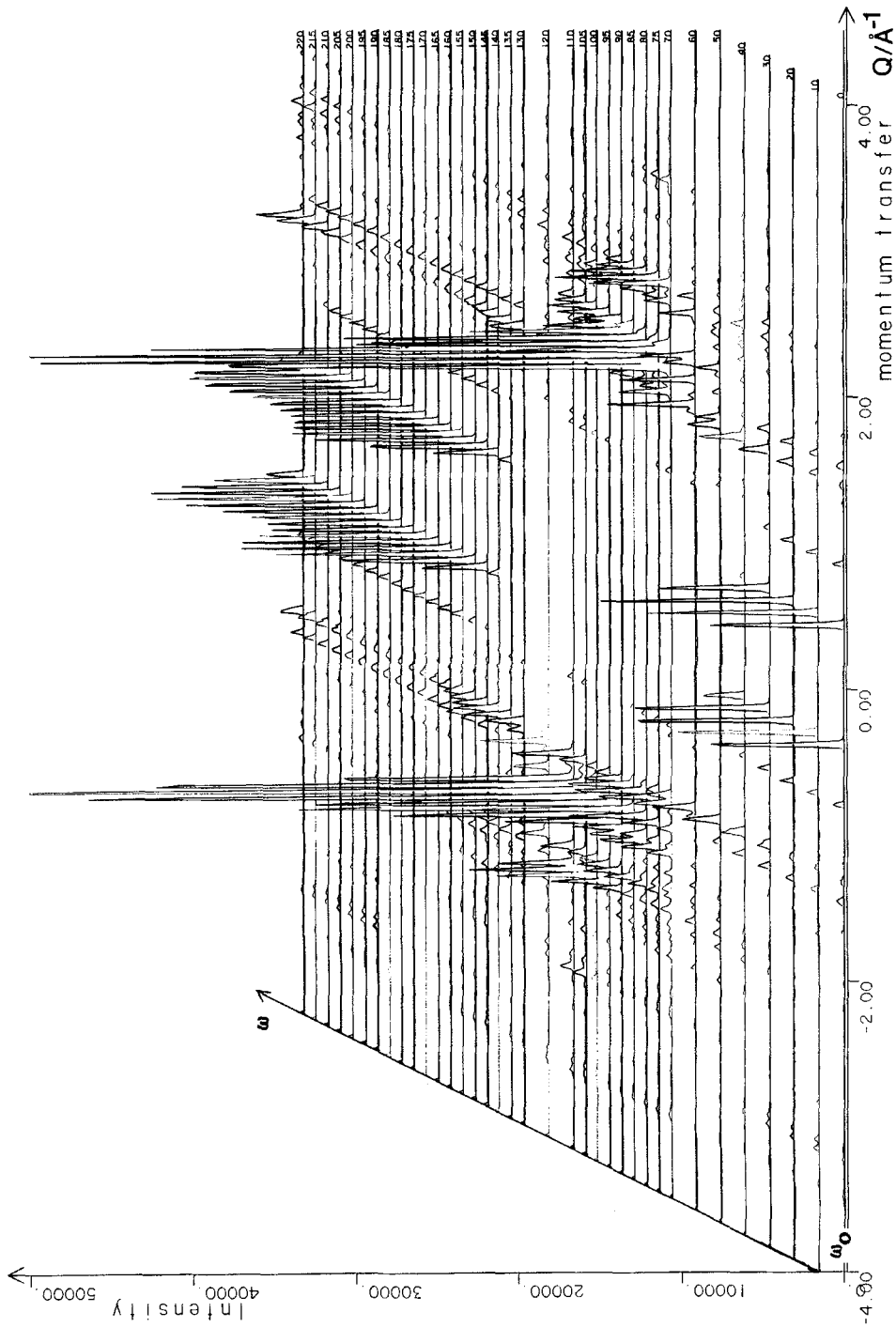

Figure 3. Phase C_3. Array of X-ray diffraction patterns ($\lambda = 1{\cdot}5418$ Å) scattered in the horizontal plane, displayed for various positions of the aligned sample, rotated through an angle ω around the vertical axis, ω_0 marks the position of the sample quenched with a horizontal aligning magnetic field perpendicular to the incoming X-ray beam.

(assuming $\omega_0 = 0$)

$$I(\omega) = \frac{I_0}{1 + \left|\frac{\sin(\omega - \omega_1)}{\Delta\omega}\right|^2} \tag{1}$$

and

$$I(\omega) = I_0 \exp\left\{-\left|\frac{\sin(\omega - \omega_1)}{\Delta\omega}\right|^2\right\}, \tag{2}$$

where ω is the angular position of the sample, ω_1 is the peak position, $\Delta\omega$ is the width, and I_0 is a scaling factor.

3. Discussion

The features described here are at once found in figure 1 for the phase C_1. The low angle gaussian peak at $Q = 0{\cdot}2\,\text{Å}^{-1}$ considered as due to smectic layers appears at ω_0, while the lorentzian large angle peaks appear at $\omega_0 + 90°$. This proves that they are due to a transverse correlation. It is interesting to note that the low angle peak is maximum at exactly ω_0, which means that the layers are perpendicular to the aligning field. We may also remark that the large angle peaks are not maximum at exactly $\omega_0 + 90°$; a given peak on the $+Q$ side is a maximum at $\omega_0 + 90° - \varepsilon$; the same peak on the $-Q$ side is a maximum at $\omega_0 + 90° + \varepsilon$. Indeed since the geometry of the aligned sample is no longer symmetric with respect to the incoming and outcoming beam there is no reason why the scattering should be symmetric [3]. This means that such peaks are not purely transverse.

The characteristics of the most significant peaks analysed with the function in equation (1) are listed in table 1.

Table 1. A fit the the two dominant peaks to equation (1).

Q position/Å^{-1}	ω position/°	$\Delta\omega$ width/°
0·2	0	8·9
1·5	80·6	4·4

Figure 2 shows the results for phase C_2. The low angle smectic peaks appear now up to the seventh harmonic (to be compared with the zero field experiment, when only two orders could be seen), and a splitting is clearly visible. This confirms the results of a previous neutron scattering experiment [1]. A possible explanation is the following, the molecules keep more or less parallel to the magnetic field, nevertheless they are tilted in the smectic layers. Consider now the normal to the layers of a smectic region. The set of these layer normals builds a cone around the field direction. The 2ω angle between the split low angle pair is then equal to the top cone angle. The low angle peaks and the first large angle peak have been analysed with the function (1), the results are summarized in table 2.

Table 2. The dominant peaks for phase C_2 fitted to equation (1).

Q position/Å^{-1}	ω position/°	$\Delta\omega$ width/°
0·2	8·25	5
1·5	79·4	11

Finally, the corresponding pattern for phase C_3 is shown in figure 3. Here the splitting is still larger. There is no other feature with respect to the zero field experiment. Nevertheless the fitting of the shape versus ω shows that a gaussian function is now required. The characteristics of two peaks are listed in table 3.

Table 3. The dominant peaks for phase C_3 fitted to equation (2).

Q position/Å^{-1}	ω position/°	$\Delta\omega$ width/°
0·41	17·5	14
1·53	81·5	12

4. Conclusion

After being quenched with an applied magnetic field, MBBA goes through the same phase sequence as without the field, provided it is kept for a very long time in the nematic phase with the field on. The modulation of the Debye–Scherrer rings confirms the analysis proposed for the zero field experiments. In particular the C_1 phase looks similar to a smectic A phase (no tilt), while the C_2 phase looks rather like a tilted smectic phase. (Considering the ω width of the first smectic Bragg peak at 0·2 Å^{-1} we cannot rule out the possibility of a small tilt for the phase C_1, which would explain the apparent larger width for C_1 than for C_2.) For these phases the analysis of the ω shape must be made with a lorentzian-like function, which is consistent with the liquid-crystalline character of these structures. The C_3 phase, while crystalline, probably keeps a molecular packing close to that of the smectic phases, however the fact that the modulation must be analysed with a gaussian-like function, confirms its crystalline character. On the other hand, the C_4 phase has a completely different crystalline and textural behaviour.

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