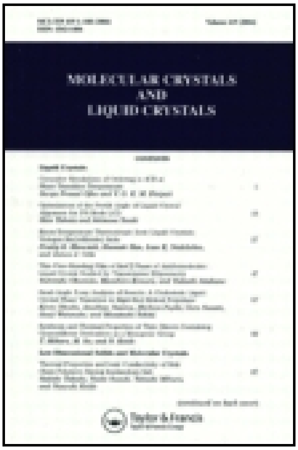

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The Use of X-Ray Diffraction in the Study of Thermotropic Liquid Crystals With Rod-Like Molecules

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The Use of X-Ray Diffraction in the Study of Thermotropic Liquid Crystals With Rod-Like Molecules

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The paper first reviews briefly the various kinds of information that can be obtained from x-ray diffraction studies. Next, specific examples are given from the literature of determinations of each of the different kinds of data.

I. INTRODUCTION

In the study of liquid crystals, as in the study of liquids and in the study of crystals, x-ray diffraction is a very useful tool because the wavelength of the x-rays is of the same order of magnitude as the interatomic and intermolecular distances in the material investigated. Thus, from x-ray diffraction data, it is possible to gather information about the local molecular arrangement (conformation and packing), and about the existence and range of order in the molecular orientations and/or positions.

In discussing the positions of x-ray diffraction maxima in the diffraction pattern in a plane perpendicular to the incident x-ray beam, we will use the terms "radial position" and "azimuthal position" (see Figure 1). "Radial position" will refer to the distance of the maximum from the center of the x-ray diffraction pattern, "azimuthal position" will refer to the angle which a line from the maximum to the center would make with a reference line through the center. Similarly, we will use the terms "radial width" and "azimuthal width" to describe the size of the maxima (see Figure 1).

We will limit our discussion to *thermotropic* liquid crystals, but

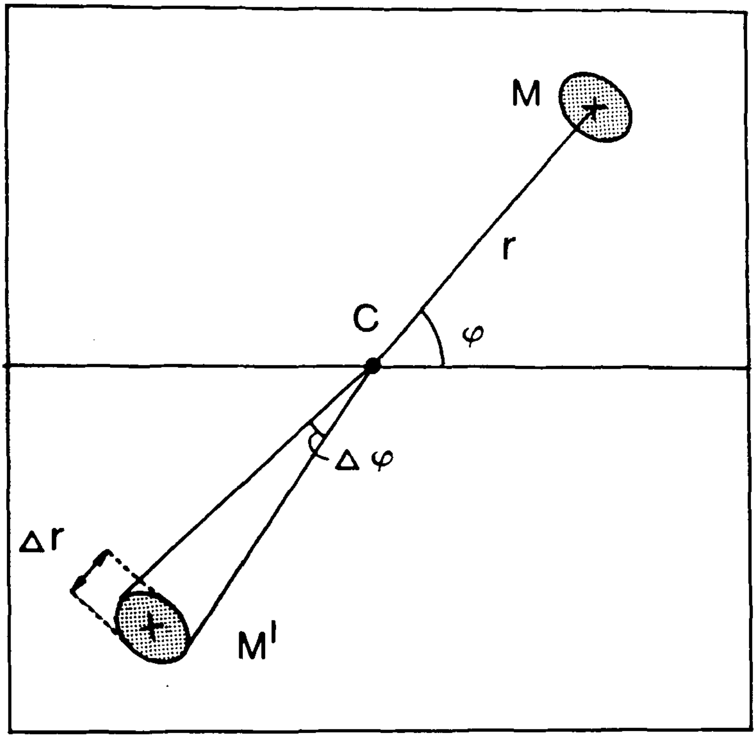

FIGURE 1 Illustration of the definition of the "radial position" *r*, the "azimuthal position" ϕ, the "radial width" Δr, and the "azimuthal width" $\Delta\phi$ of a diffraction maximum. The horizontal line is the "reference line," *C* is the center of the diffraction pattern, and *M* and *M'* are two maxima.

most statements would also apply, occasionally with some minor modifications, to *lyotropic* liquid crystals. The two main sections of this paper, on "What can be learned" and "What has been learned," are divided into rather small sub-sections. To facilitate cross-referencing, each sub-section under "What can be learned" corresponds with an identically marked sub-section under "What has been learned."

II. WHAT CAN BE LEARNED

1. Molecular orientation

In a first approximation, the molecules in a thermotropic liquid crystal can be thought of as cylindrical rods.† If one would have infinitely-

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†Mesophases of disc-like molecules will not be discussed in this article.

long rods, perpendicular to the incident x-ray beam, the diffraction pattern of these rods would be confined to a plane that is perpendicular to the rods and that contains the incident beam.[1] Liquid crystal molecules are not *infinitely* long, of course, but they are long, and, consequently, the diffraction pattern associated with the packing of molecules aligned perpendicular to the x-ray beam will be concentrated around the above-mentioned plane, and the diffraction maxima will lie in this plane. Because of this, the azimuthal *positions* of these diffraction maxima will give information about the average direction of the molecules. The azimuthal *width* of the maxima will be related to the extent to which the directions of the individual molecules differ from the average. Thus, the azimuthal width of the maxima will give information about the degree of overall orientational order in the sample.

2. Molecular packing

The x-ray diffraction pattern from an assembly of parallel rods does not only depend on the orientation of these rods (see *1* above), but also on the manner in which the rods are packed together.

a. Average distance

From the radial *position* of the diffraction maxima, one can obtain the angle between the diffracted beam and the incident beam. This angle is related to the average distance between the long axes of adjacent rods. Thus, the radial position of the maxima gives information on the average distance between the molecules (see also Section *d*, below).

b. Regularity of packing

The radial *width* of the diffraction maxima is related to the *regularity* of the molecular packing: the more constant the distance between adjacent molecules, the narrower the diffraction maximum. Thus, a sharp maximum indicates an ordered packing and a broad maximum indicates a disordered packing (see also Section 6, below).

c. Type of packing

If the molecules form a hexagonal close-packing of cylinders, all distances between neighboring molecules are equal, and there is only *one* sharp diffraction maximum corresponding to nearest-neighbor distances. If there is more than one such maximum, then there must also be more than one value for these distances, and the packing can no longer be hexagonal. Thus, the *number* of maxima gives information about the *type* of the molecular packing.

d. Lattice dimensions

The radial *positions* of the diffraction maxima discussed in Section

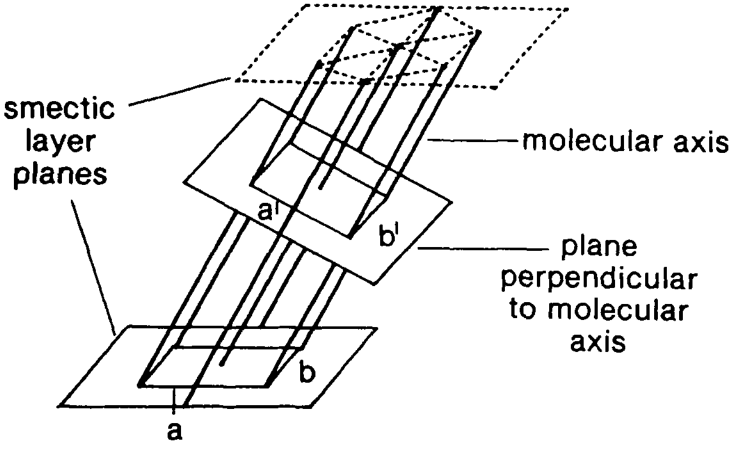

FIGURE 2 Schematic representation of a regular arrangement of parallel tilted molecules in a smectic layer. The two-dimensional lattice in the plane of the smectic layer is indicated by *a* and *b*, that in the plane perpendicular to the long molecular axis by *a'* and *b'*.

2.c (above) give information on the *lattice dimensions* related to the packing of the molecules. These lattice dimensions can be obtained for all smectic phases that give sharp outer diffraction maxima. For orthogonal phases, the radial positions of these maxima directly yield the dimensions of the two-dimensional lattice in the plane of the smectic layer.[2] For tilted phases, the radial positions of the maxima give the dimensions of the two-dimensional lattice in the plane perpendicular to the long axis of the unit cell of the structure.[3,4] Generally, one assumes that the long axes of the molecules are parallel to the long axis of this unit cell.[3,4] In that case, the two-dimensional lattice determined from the radial positions of the outer maxima is the lattice in the plane perpendicular to the long molecular axis (the a'b' lattice in Figure 2). One should not confuse this two-dimensional lattice, however, with the two-dimensional lattice defined by the two short axes of the unit cell (*a* and *b* in Figure 2): these axes are located in the plane of the smectic layer,[3,4] not in the plane perpendicular to the long molecular axis.

3. Molecular length

In addition to the diffraction effects discussed in *1* and *2* above, rod-like molecules also produce diffraction maxima related to their length.[5,6]

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†We disregard here the smectic *D* phase which appears to have a structure without layers.[7]

From the radial positions of these maxima, one can calculate the average effective molecular length.

4. Smectic layers

In smectic phases, there are certain diffraction effects specifically associated with the smectic layer structure.† A stack of identical flat smectic layers, parallel to each other, as in a smectic monodomain, gives these diffraction maxima only in special directions, and only for certain orientations of the stack relative to the incident x-ray beam. Various kinds of information can be obtained from these data.

a. Orientation

From the position of the layer diffraction maxima, one can determine the orientation of the smectic layers (see Figure 3). Since one

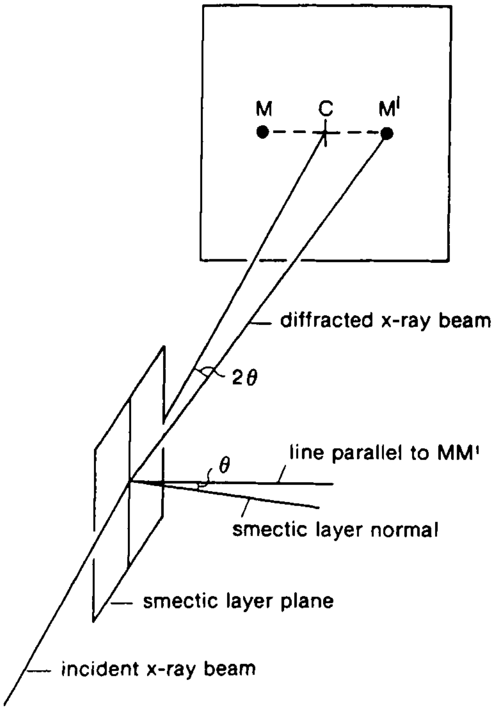

FIGURE 3 Illustration of the relationship between the orientation of the smectic layers and the position of the smectic layer reflections. The cross labeled *C* marks the center of the diffraction pattern, *M* and *M'* are smectic layer reflections. The figure shows the orientation of the smectic layers corresponding to the reflection *M'*. The angle θ is always small (only a few degrees) and can, for a first approximation, be set equal to zero. Thus, the smectic layers for both *M* and *M'* are approximately perpendicular to the line *MM'*.

can also determine the average direction of the molecules (see *1* above), one can, by combining these two pieces of information, find the angle between the director and the plane of the layers.

b. Layer thickness

The diffraction angle of the smectic layer diffraction maxima is determined by the thickness of the smectic layers. Thus, one can calculate this layer *thickness* from the radial *positions* of these maxima.

c. Regularity of stacking

The *regularity* of the stacking of the smectic layers can be determined from the *width* and the relative intensities of the corresponding diffraction maxima. For instance, one can obtain information on how flat the layers are and how well-defined, and how constant is the layer thickness (see also Section 6, below).

5. Three-dimensional lattices

Even though one- and two-dimensional lattices do give x-ray diffraction maxima, there are certain maxima that only occur when the lattice is *three*-dimensional.[8] A study of these maxima can give information on the existence and extent of a three-dimensional lattice.

6. Correlation lengths

It frequently happens that a particular kind of order only exists over limited distances (e.g., smectic layer structures in nematic phases). A careful study of the x-ray diffraction pattern, in particular of the width of the corresponding diffraction maxima, can then yield the correlation lengths which are a measure of the average distances over which the order is maintained.

7. Other aspects

Studies of the diffraction pattern can give information on a variety of other things. Some examples will be given in Section III.7.

III WHAT HAS BEEN LEARNED

1. Molecular orientation

Depending on the material and on the external conditions, one can obtain samples of nematic and smectic phases that are without preferred orientation ("random samples") (Figure 4a), samples with

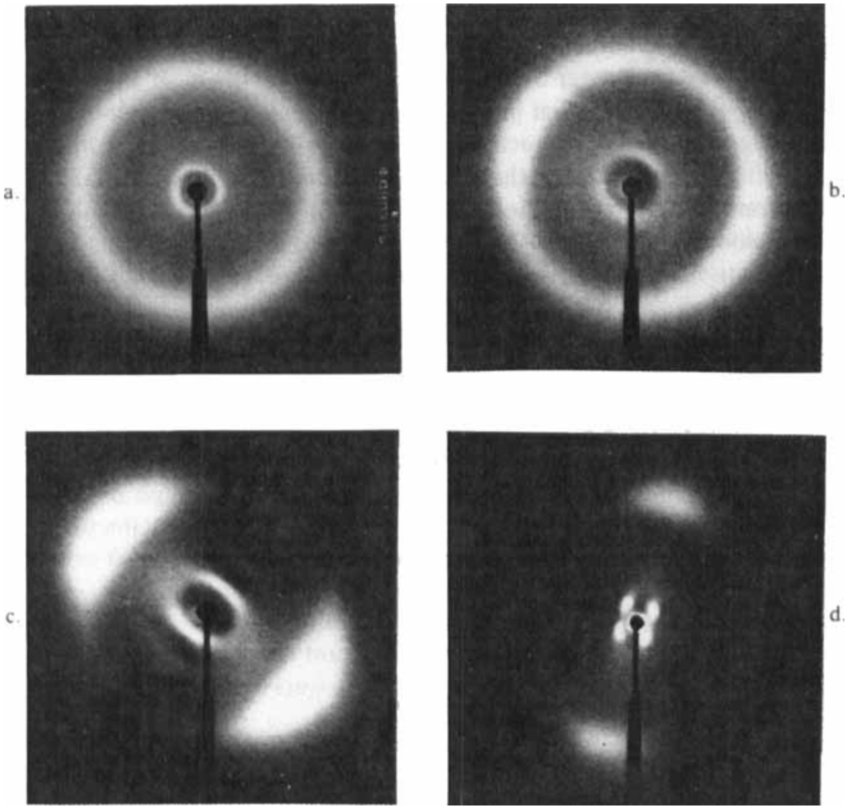

FIGURE 4 X-ray diffraction photographs of nematic phases: (a) ordinary nematic without preferred orientation, (b) ordinary nematic with moderate preferred orientation, (c) ordinary nematic with strong preferred orientation, and (d) skewed cybotactic nematic with strong preferred orientation [from Ref. 9].

moderate preferred orientation (Figure 4b), or samples with strong preferred orientation ("monodomains") (Figures 4c and 4d).

In all cases, the two main diffraction effects usually observed on x-ray diffraction patterns are (see Figure 4): the "inner ring" or "inner maxima" (close to the center of the diffraction pattern, and corresponding to a diffraction angle† of only a few degrees), and the "outer ring" or "outer maxima" (much farther out in the diffraction pattern, and corresponding to a diffraction angle of about 10°).[10]

In the case of a monodomain, the extent of the outer-ring maxima,

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†The diffraction angle (θ) is equal to one-half of the angle (2θ) between the diffracted x-ray beam and the incident x-ray beam (see Figure 3).

measured along a circle around the center of the diffraction pattern (i.e., the azimuthal width), allows one to calculate[11-15] the orientational order parameter S. Qualitatively, a comparison of Figure 4c with Figure 4d shows that in Figure 4d (a skewed cybotactic nematic) the degree of order is much greater than in Figure 4c (an ordinary nematic). Quantitatively, the S values obtained agree well with those determined by other methods (Figure 5). In all cases (i.e., random, monodomain, or otherwise; Figure 4), the outer-ring maxima give information on the orientation of the director (see, e.g., Section III.4.a).

2. Molecular packing

a. Average distance

A considerable amount of work has been done on calculations of the average intermolecular distance D (i.e., the average distance between the long axes of adjacent molecules) from the diameter of the outer ring of the x-ray diffraction pattern.[9,14,15,19-23] Most of the work through 1973 is summarized and referenced in Ref. 9; the data are graphically displayed in Figure 6. As may be seen from Figure 6, the average value of D in common liquid crystal phases is about 5 Å. An example of some recent data[20] is Figure 7; the D values here

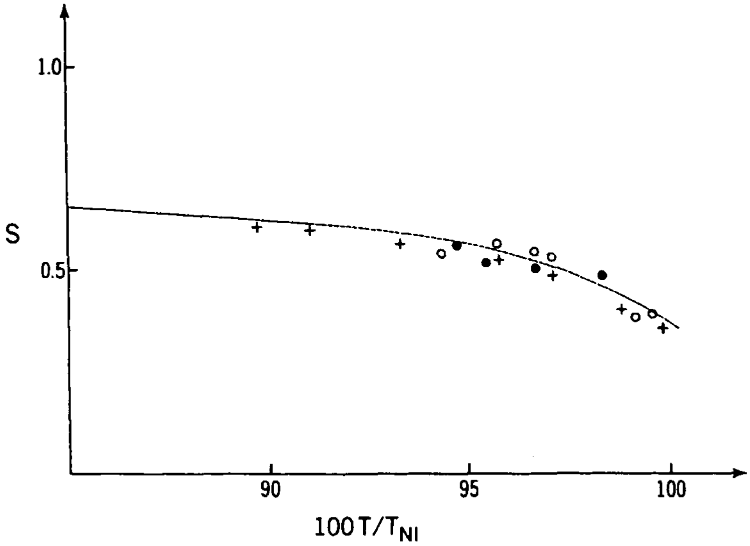

FIGURE 5 Temperature dependence of the orientational order parameter S in the nematic phase of p-azoxyanisole. + : optical studies;[16] ●: x-ray diffraction;[17] o: nuclear magnetic resonance spectroscopy[18] [from Ref. 11].

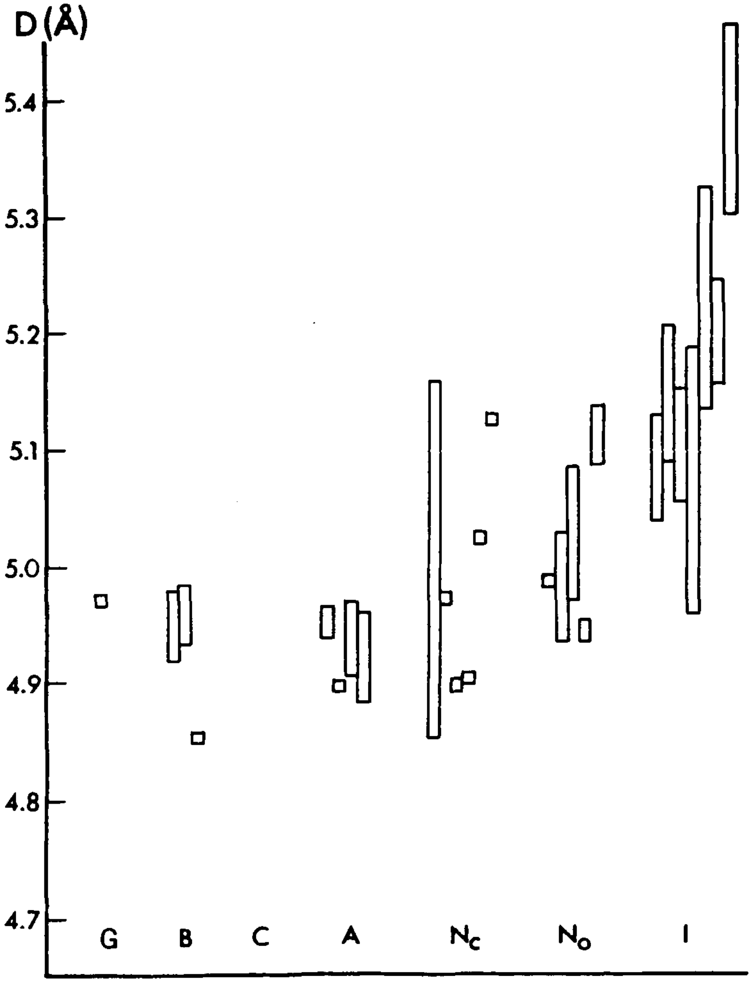

FIGURE 6 Plot of the intermolecular distance *D* according to phase-type and compound. Squares generally represent single measurements, rectangles represent the range of *D* for the temperature range investigated [from Ref. 9].

are significantly greater than the corresponding values from Figure 6, because the compound used contained a bulky group in the center of the molecule. Figure 7 shows that the relative precision of the data can be quite high ($\sigma \approx 0.003$ Å), but the unexpected *decrease* of *D* at the *B*-*C* transition probably indicates that there is still considerable uncertainty about the absolute accuracy of the data. The *D* values in the *B* and *F* phases of Figure 7 were calculated from the diffraction angle θ with the formula $2D \sin\theta = 1.1547\lambda$, based on the assumption of a hexagonal lattice, and the *D* values in the *C* and *A* phases were

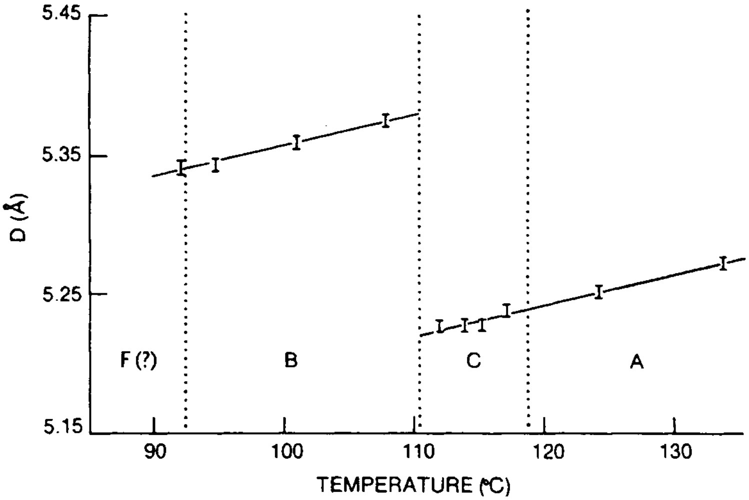

FIGURE 7 Intermolecular distance D as a function of temperature. The data points are marked by error bars with a length of 4σ [from Ref. 20].

calculated with the formula 2D sinθ = 1.117λ, based on the assumption of a disordered packing of the molecules.[20] Thus, the apparent change in D at the B-C transition depends on the validity of these assumptions. We are now inclined to believe (Ref. 23, p. 16) that even in the A and C phases there is enough short-range order to justify using the formula 2D sinθ = 1.1547λ. Thus, this formula should have been used for *all* phases in Figure 7. If this would have been done, there would have been a small *increase* in D at the B-C transition, rather than a decrease. This appears to be much more reasonable.

b. Regularity of packing

The least-ordered liquid crystal phase is the nematic phase. The outer diffraction ring of this phase (Figure 8b) is, therefore, broader than that of any other liquid crystal phase. In the smectic A phase we still have a disordered arrangement of the molecules, within the layers, and the outer ring is still a broad ring (Figure 8a), although somewhat less so than in the nematic phase. The smectic B phase has an ordered arrangement of the molecules, and, as a consequence, the outer ring is fairly sharp (Figure 9b).

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†We believe, though, that this only applies to the *appearance* of the *average* molecular packing, and that locally, at a given moment, the molecules are arranged in a herringbone packing.[8,24,25]

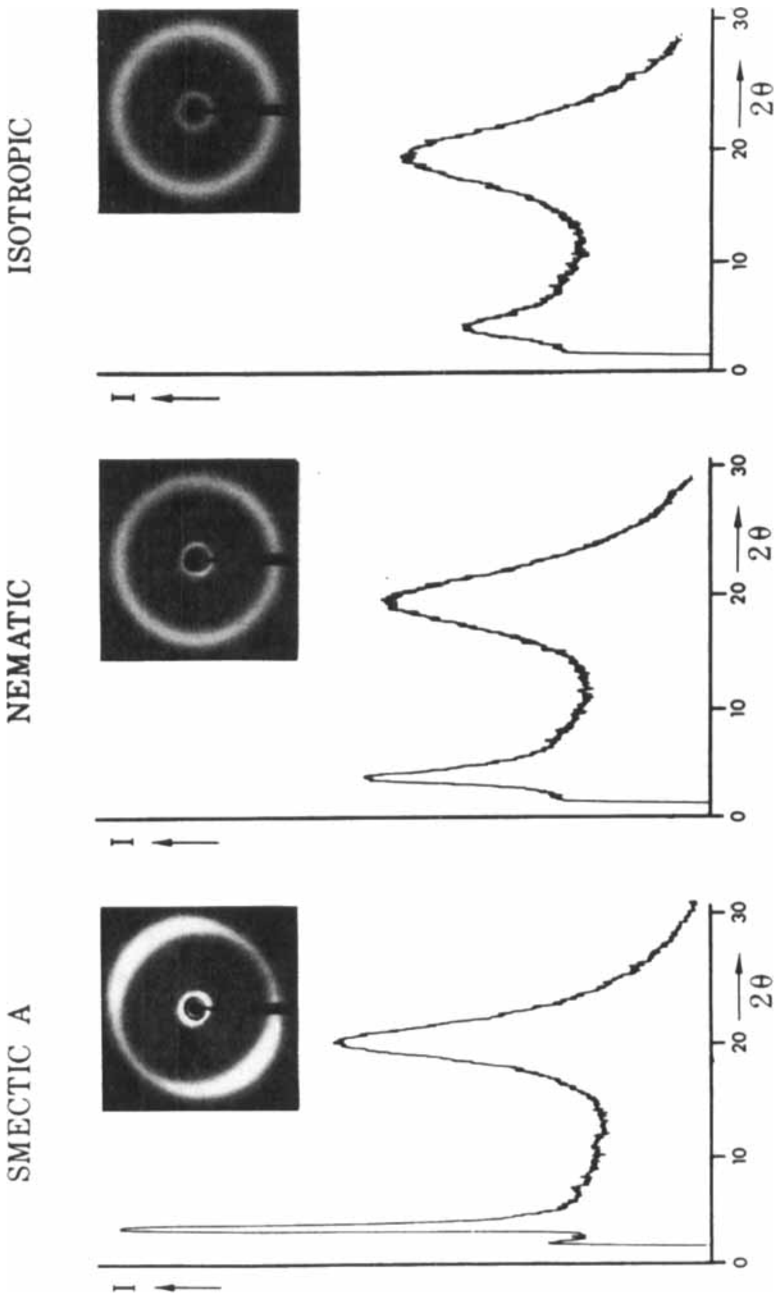

FIGURE 8 Diffraction patterns and densitometer traces of the (a) smectic *A*, (b) nematic, and (c) isotropic phases of one compound.

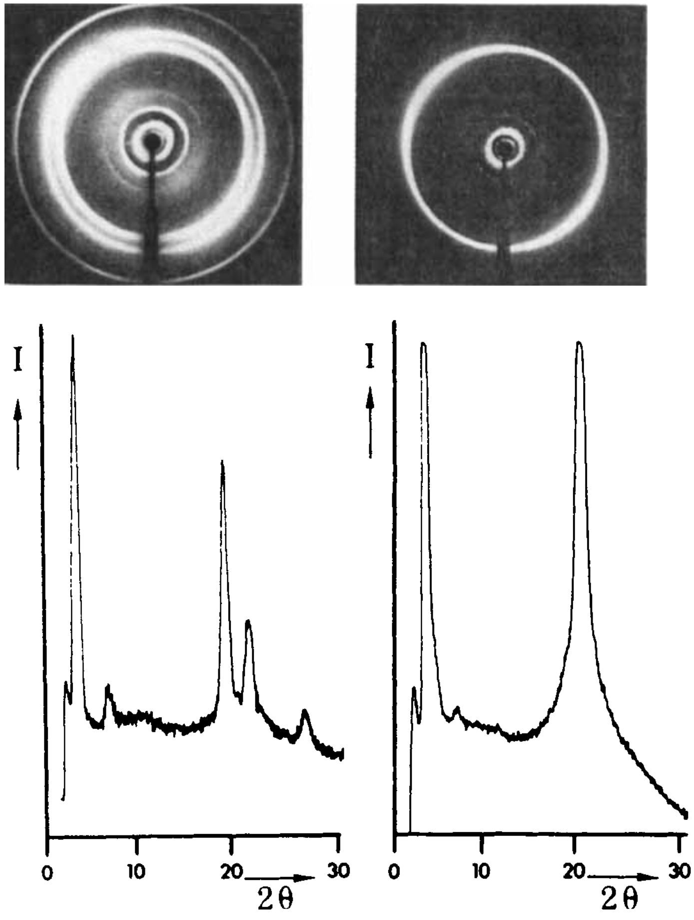

FIGURE 9 Diffraction patterns and densitometer traces of (a) a smectic *E* phase and (b) a smectic *B* phase [from Ref. 9].

c. Type of packing

In the smectic *B* phase, there is only *one* sharp outer ring (Figure 9b), and the molecular packing appears to be a close-packing of cylinders† in which all nearest-neighbor distances are equal. In the smectic *E* phase, however, the molecules are arranged in a herringbone packing,$^{26-28}$ there are *two* different nearest-neighbor distances, and there are *two* sharp outer rings corresponding to these distances (Figure 9a). The outermost ring in Figure 9a does not correspond to a nearest-neighbor distance, but is evidence of the fact that the layer lattice in the *E* phase is much better developed than that in the *B* phase (Figure 9b), where this ring is absent.

d. Lattice dimensions

The lattice dimensions corresponding to the packing of parallel molecules have been determined for the ordered smectic phases of many compounds. Some examples are: smectic B,[2,20,29,30] smectic E,[26-29] smectic F,[31,32] smectic G,[3,4,30,33,34] smectic H,[33] and smectic I.[32,35]

3. Molecular length

The information about the molecular length that can be obtained from the x-ray diffraction pattern depends on the phase the sample is in. If the sample is in the *isotropic* phase, the diffraction pattern is like that of a random sample of the nematic phase (Figure 8b), only both rings will be weaker and more diffuse (Figure 8c). From the diffraction angle θ of the inner ring, the molecular length ℓ can then be calculated with the formula[5,6] $2\ell \sin\theta = 1.229\lambda$. The variation of ℓ with temperature, given in Figure 10, is typical of our experience:[5,36] starting at the N-Is point, the value of ℓ decreases with increasing temperature, but this decrease tapers off, and at higher temperatures ℓ may increase again. Extrapolated to the N-Is point, the value of ℓ is generally quite close to ℓ_c, the length of the molecule calculated from standard bond lengths and angles under the assumption of a planar, all-trans conformation of the molecule.[5,36] We have

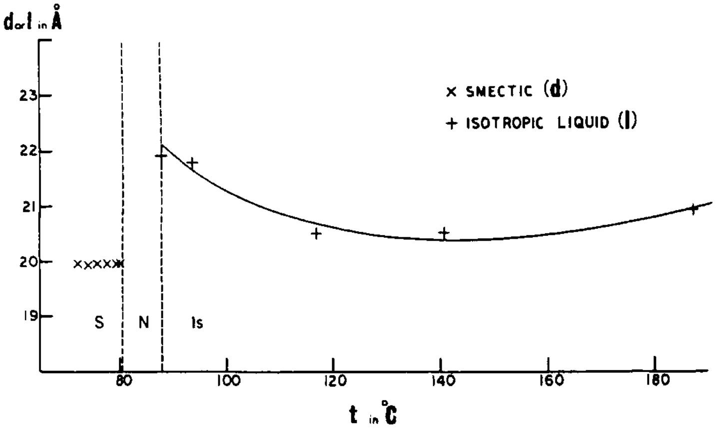

FIGURE 10 The layer thickness *d* in the smectic phase and the molecular length ℓ in the isotropic phase, as a function of temperature [data from Ref. 5].

interpreted the agreement between ℓ and ℓ_c to mean that in the isotropic phase, close to the N-Is point, the molecules are predominantly in the fully extended conformation. The variation of ℓ with temperature (Figure 10) can then be explained as indicating that the effective length of the molecule first decreases because of an increase in the numbers of molecules with other conformations[36] and then increases because of thermal expansion.

In the *nematic* phase, even though the inner diffraction ring (Figure 8b) is stronger and less diffuse than in the isotropic phase (Figure 8c), it is more difficult to determine ℓ, because the relationship between ℓ and θ now depends on the alignment of the molecules in the sample.[5] For a random sample, the formula is $2\ell \sin\theta = 1.229\lambda$, as for the isotropic phase. If all molecules were strictly parallel to the incident beam, the formula would be $\ell(1 - \cos 2\theta) = \lambda$. If all molecules were strictly parallel to each other but perpendicular to the incident beam, the formula would be $\ell \sin 2\theta = \lambda$. Thus, to be able to calculate ℓ, one would need to know both the direction and the degree of the alignment in the sample.[37]

In *smectic* phases, the inner diffraction maxima (Figure 8a; Figure 9) are related to the spacing of the smectic layers rather than to the length of the molecules. For this reason, the inner maxima do not provide any direct information about the molecular length in the smectic phase. In a number of cases, however, there are diffuse diffraction maxima that are related to the molecular length (Ref. 2, Ref. 3, and Ref. 38, pp.24–26), and then it may be possible to obtain direct information about ℓ from those.

4. Smectic layers

a. Orientation

Figure 11 is the diffraction pattern of an aligned sample of a smectic *A* phase. The smectic layers, which give the *inner* maxima, are essentially perpendicular to the imaginary line connecting the centers of the inner maxima (see Figure 3). The azimuthal positions of the *outer* maxima indicate[10] that the director (i.e., the average direction of the long axes of the molecules) is parallel to the plane of the photograph and perpendicular to the imaginary line connecting the centers of the outer maxima. Thus, Figure 11 gives us the orientation of the smectic layers and of the director, and it confirms that in a smectic *A* phase the director is perpendicular to the layers. In a similar manner it is possible to obtain direct measurements of the tilt angle

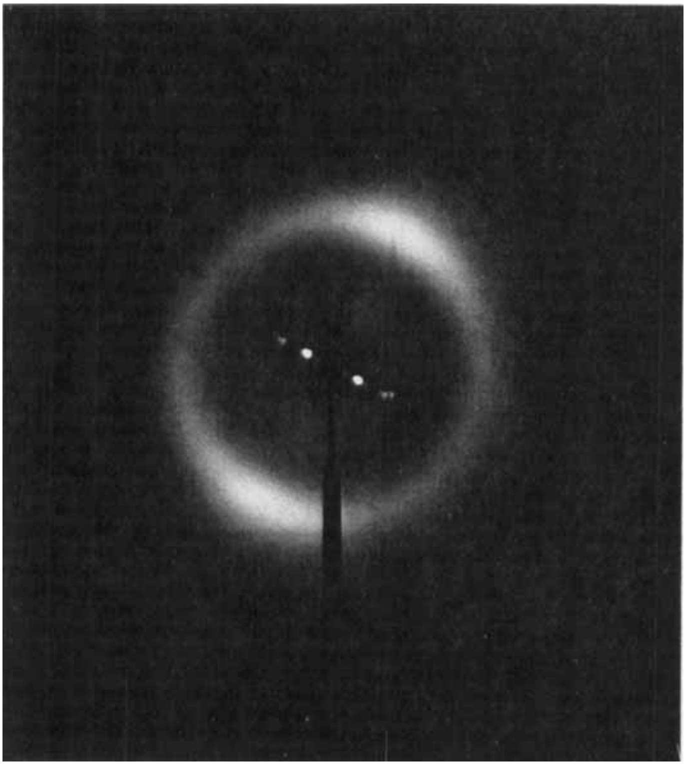

FIGURE 11 X-ray diffraction photograph of an aligned smectic *A* phase [from Ref. 9].

in smectic *C* phases[9,13,35,39–46] and in other tilted smectic phases, and also in skewed cybotactic nematic phases.[10,47–52]

b. Layer thickness

From the diffraction angle θ of the inner maxima, one obtains the smectic layer thickness *d* with the Bragg formula: $2d \sin\theta = n\lambda$ ($n = 1$ for the first-order inner ring, $n = 2$ for the second-order, etc.). An example of some recent data is given in Figure 12, and many more data[†] can be found in the literature.[2,3,5,13,19,20,22,23, 26–29, 31,33,35,36,54–62]

For *orthogonal* phases, i.e., phases in which the director is per-

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[†] Of the various ways in which x-rays are used in the study of liquid crystals, the determination of *d* appears to be the most common one.

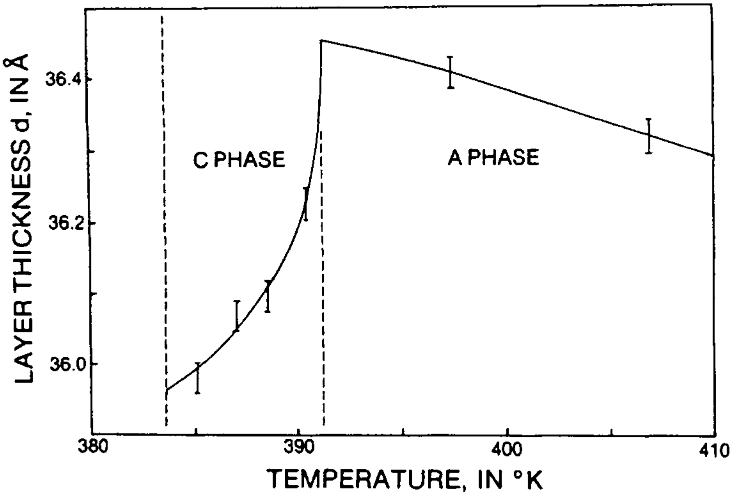

FIGURE 12 Layer thickness *d* as a function of temperature. The data points are marked by error bars with a length of 2σ; the full line is obtained by fitting a model [from Ref. 53].

pendicular to the smectic layer, one might expect that *d* would be equal to the molecular length ℓ. It has been generally found, however, that *d* is less† than ℓ, and various explanations had been proposed for this.[5,54–56,63] It now appears, however, that these explanations are not necessary, and that the differences between *d* and ℓ can be adequately explained by taking account of the orientational disorder of the molecular long axis, which is present in all smectic phases.[37,64,65]

For *tilted* phases, the differences between *d* and ℓ, or between the *d* in the tilted phase (d_t) and the *d* in the corresponding orthogonal phase (d_0), have been used to calculate "tilted angles" α with the formulas $d = \ell\cos\alpha$[4,13,34,58,60] or $d_t = d_0\cos\alpha$,[20,35,44–46,57,60] respectively, and this has also been done for skewed cybotactic nematic phases.[10,52,66] It should be noted, however, that none of these calculations have taken into account the effect of orientational disorder, and that, since this disorder is quite large, all these calculations should be re-done with models incorporating the orientational disorder.[53,67,68]

c. Regularity of stacking

Since a stack of identical flat smectic layers, parallel to each other, gives layer diffraction maxima only in certain directions (Section II.4),

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†We exclude here from the discussion smectic phases with bilayers.

one can judge the distribution of the orientations of the layers within a sample from the azimuthal spread in the diffraction directions (this is similar to the determination of the orientational order parameter S from the azimuthal extent of the outer ring maxima; see Section III.1). In a good monodomain sample, the layers should, of course, be very closely parallel to each other. For smectic A layers on glass or mica a spread of 0.05°–0.16° has been reported,[69] and for freely-suspended smectic B films a spread of less than 0.01° has been reported.[70]

The concept of paracrystallinity[71] allows the calculation of several parameters, describing different kinds of distortions in the smectic layer stacking, from the width and intensity of the smectic layer reflections.[69] X-ray diffraction data obtained from the lamellar structure of myelin have also been found to be consistent with a paracrystalline model.[72] Other measurements of intensity and width of the smectic layer reflections have been interpreted as showing that the smectic A phase maintains nearly perfect periodicity but is subject to large local motions[73] (see also Section III.7).

5. Three-dimensional lattices

Many smectic phases with an ordered arrangement of the molecules within the layer are now believed to have a three-dimensional lattice. An important criterion in deciding whether a given phase has a three-dimensional lattice is the existence of x-ray reflections for which all three indices are non-zero[8] (see Table 1). This criterion has been used in assigning a three-dimensional lattice to a smectic G phase,[3]† to smectic E phases,[9,26–28] and to smectic B phases.[75,76] Liquid crystal phases with a three-dimensional lattice have often been called "crystalline," but it has been pointed out that there are significant differences between such "crystalline" liquid crystals ("liquid-crystalline solids") and ordinary crystals ("crystalline solids").[77–79]

6. Correlation lengths

From an analysis of the x-ray diffraction pattern, correlation lengths have been obtained for a number of different situations: smectic B order in an isotropic phase,[80] smectic A order in nematic phases,[46,81,82] smectic C order in nematic phases,[47,83,93] layer correlations in smectic A,[46,84] B,[2,85] and G[2,4,85] phases, and positional order in smectic A,[46] B,[86] C,[87] F,[87,88] and G[87] phases.

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†At that time this phase was called smectic H, but now it has been reclassified as G.[74]

TABLE I

Indices and observed 2θ values for x-ray reflections from the smectic *G* phase of 4-butyloxybenzal-4′-ethylaniline (from Ref. 3).

hkℓ	2θ[a]	hkℓ	2θ[a]
001	4.9	$20\overline{5}$	22.1
2	10.2	$\overline{4}$	19.3
3	15.4	$\overline{3}$	17.7
4	20.3	$\overline{2}$	17.4
5	25.7	$\overline{1}$	18.5
$0\overline{21}$	36.5	0	20.7
0	36.1	1	23.5
1	36.0	$3\overline{12}$	32.0
$1\overline{13}$	21.8	$\overline{1}$	33.8
$\overline{2}$	20.4	0	36.1
$\overline{1}$	19.8	1	38.7
0	20.5	$31\overline{2}$	32.0
1	22.6	$\overline{1}$	33.9
2	25.3	0	-
3	29.6	1	38.9
4	33.1	$40\overline{4}$	34.4
$11\overline{4}$	24.6	$\overline{3}$	35.7
$\overline{3}$	22.5	$\overline{2}$	-
$\overline{2}$	20.0	$\overline{1}$	39.2
$\overline{1}$	19.5	0	42.1
0	20.5		
1	22.7		

[a] Calculated from the data in Ref. 3 with a sample-to-film distance of 50.87 mm.

7. Other aspects

a. The structure of liquid crystal phases

X-ray diffraction has played a major, and often crucial, role in the determination of the structures of the many different types of liquid crystal phases. A discussion of this, however, falls outside the scope of this paper.

b. Phase transitions

Recently, high-resolution x-ray diffraction studies have contributed significantly to the study of the nature of the various phase transitions between liquid crystal phases. Again, however, this falls outside the scope of the present paper.

c. Free-standing smectic films

A special technique for studying the structure of smectic liquid crystals is the use of free-standing smectic films. It has been found that this method yields extremely good monodomains (see Section

III.4.c, above). Using such monodomain samples, it was shown that there are two different kinds of smectic B phases: those with 3-D positional order ("crystal B"), and those without ("hexatic B").[70,75,89] It should be kept in mind, however, that free-standing film samples can be much more ordered than other samples of the same compound at the same temperature.

d. High-intensity x-ray sources

Most of the x-ray work discussed in this paper can be and has been done using conventional sealed x-ray tubes (0.5–1 kW). For high-resolution studies,[44-46,73,81,83,84,86] however, and for studies on free-standing smectic films,[70,75,89] one often needs more powerful x-ray sources, like rotating anodes (4–50 kW). A few studies have even used synchrotron[90,91] or plasma[92] radiation.

References

1. R. W. James, *The Optical Principles of the Diffraction of X-rays* (Bell and Sons, London, 1958).
2. A. M. Levelut and M. Lambert, *C.R. Acad. Sci.*, Paris, Ser. A.B. **B272**, 1018 (1971).
3. A. de Vries and D. L. Fishel, *Mol. Cryst. Liq. Cryst.* **16**, 311 (1972).
4. J. Doucet, A. M. Levelut and M. Lambert, *Mol. Cryst. Liq. Cryst.* **24**, 317 (1973).
5. A. de Vries, *Mol. Cryst. Liq. Cryst.* **11**, 361 (1970).
6. A. de Vries, *Acta Crystallogr.* **31A**, S158 (1975).
7. S. Diele, P. Brand and H. Sackmann, *Mol. Cryst. Liq. Cryst.* **17**, 163 (1972).
8. A. de Vries, *Mol. Cryst. Liq. Cryst.* **63**, 215 (1981).
9. A. de Vries, *Pramana*, Suppl. No. 1, 93 (1975).
10. A. de Vries, *Mol. Cryst. Liq. Cryst.* **10**, 219 (1970).
11. J. Falgueirettes and P. Delord, in *Liquid Crystals and Plastic Crystals*, Vol. 2, edited by G. W. Gray and P. A. Winsor (Horwood, Chichester, 1974), pp. 62–79.
12. A. de Vries, *J. Chem. Phys.* **56**, 4489 (1972).
13. A. J. Leadbetter and E. K. Norris, *Mol. Phys.* **38**, 669 (1979).
14. B. Bhattacharjee, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.* **89**, 181 (1982).
15. B. Jha, B. Bhattacharjee, S. Paul and R. Paul, *Phys. Status Solidi A* **76**, 461 (1983).
16. P. Chatelain, *Bull. Soc. Fr. Mineral. Cristallogr.* **78**, 262 (1955).
17. J. Falgueirettes, *Bull. Soc. Fr. Mineral. Cristallogr.* **82**, 171 (1959).
18. A. Saupe, *Angew. Chem. Internat. Edn.* **7**, 97 (1968).
19. B. K. Vainshtein, I. G. Chistyakov, B. N. Makarov, G. G. Maidachenko, L. A. Gusakova, V. M. Chaikovskii, L. A. Mineev, V. D. Belilovskii, L. K. Vistin and S. P. Chumakova, *Sov. Phys. Crystallogr.* **22**, 337 (1977).
20. A. de Vries, A. Ekachai and N. Spielberg, *J. Phys.* (France) **40**, Colloque C3, 147 (1979).
21. A. J. Leadbetter and A. I. Mehta, *Mol. Cryst. Liq. Cryst. Lett.* **72**, 51 (1981).
22. A. Ekachai, A. de Vries, M. E. Neubert and N. Spielberg, *J. Chem. Phys.* **74**, 4048 (1981).
23. A. Ekachai, Ph.D. dissertation, Kent State University, Ohio, USA (1980).
24. A. M. Levelut, *J. Phys.* (France) **37**, Colloque C3, 51 (1976).
25. A. de Vries, *J. Chem. Phys.* **70**, 2705 (1979).

26. S. Diele, *Phys. Status Solidi* **A25**, K183 (1974).
27. D. B. Chung, Ph.D. dissertation, Kent State University, Ohio, USA (1974).
28. J. Doucet, A. M. Levelut, M. Lambert, L. Liebert and L. Strzelecki, *J. Phys.* (France) **36**, Colloque C1, 13 (1975).
29. S. Diele, D. Jaeckel, D. Demus and H. Sackmann, *Crystal Res. Techn.* **17**, 1591 (1982).
30. P. A. C. Gane, A. J. Leadbetter, P. A. Tucker, G. W. Gray and A. R. Tajbakhsh, *J. Chem. Phys.* **77**, 6215 (1982).
31. A. J. Leadbetter, J. P. Gaughan, B. Kelly, G. W. Gray and J. Goodby, *J. Phys.* (France) **40**, Colloque C3, 178 (1979).
32. J. J. Benattar, F. Moussa, M. Lambert and C. Germain, *J. Phys. Lett.* (France) **42**, 67 (1981).
33. J. Doucet, A. M. Levelut and M. Lambert, *Phys. Rev. Lett.* **32**, 301 (1974).
34. K. Usha Deniz and A. I. Mehta, *Phys. Lett.* **89A**, 411 (1982).
35. S. Diele, D. Demus and H. Sackmann, *Mol. Cryst. Liq. Cryst. Lett.* **56**, 217 (1980).
36. A. de Vries, *Mol. Cryst. Liq. Cryst.* **20**, 119 (1973).
37. A. J. Leadbetter, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press, London, 1979) pp. 285–316.
38. A. de Vries, in *Liquid Crystals: The Fourth State of Matter*, edited by F. D. Saeva (Dekker, New York, 1979) pp. 1–72.
39. I. G. Chistyakov and W. M. Chaikowsky, *Mol. Cryst. Liq. Cryst.* **7**, 269 (1969).
40. I. G. Chistyakov, L. S. Schabischev, R. I. Jarenov and L. A. Gusakova, *Mol. Cryst. Liq. Cryst.* **7**, 279 (1969).
41. A. de Vries, *Acta Crystallogr.* **A25**, S135 (1969).
42. A. de Vries, *J. Phys.* (France) **36**, Colloque C1, 1 (1975).
43. H. Hervet, S. Lagomarsino, F. Rustichelli and F. Volino, *Solid State Comm.* **17**, 1533 (1975).
44. C. R. Safinya, M. Kaplan, J. Als-Nielsen, R. J. Birgeneau, D. Davidov, J. D. Litster, D. L. Johnson and M. E. Neubert, *Phys. Rev.* B **21**, 4149 (1980).
45. R. J. Birgeneau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu and J. Goodby, *Phys. Rev.* A **27**, 1251 (1983).
46. B. M. Ocko, A. R. Kortan, R. J. Birgeneau and J. W. Goodby, *J. Phys.* (France) **45**, 113 (1984).
47. W. L. McMillan, *Phys. Rev.* A **8**, 328 (1973).
48. K. Usha Deniz, A. S. Paranjpe, E. B. Mirza, P. S. Parvathanathan and K. S. Patel, *J. Phys.* (France) **40**, Colloque C3, 136 (1979).
49. K. Usha Deniz, A. S. Paranjpe, V. A. Amrithalingam and K. V. Muralidharan, *Mol. Cryst. Liq. Cryst. Lett.* **49**, 265 (1979).
50. K. Usha Deniz, A. S. Paranjpe, V. Amirthalingam and K. V. Muralidharan, in *Liquid Crystals*, edited by S. Chandrasekhar (Heyden, London, 1980) pp. 185–190.
51. A. de Vries and S. B. Qadri, in *Liquid Crystals*, edited by S. Chandrasekhar (Heyden, London, 1980) pp. 179–184.
52. V. M. Sethna, A. de Vries and N. Spielberg, *Mol. Cryst. Liq. Cryst.* **62**, 141 (1980).
53. A. de Vries, *J. Chem. Phys.* **71**, 25 (1979).
54. S. Diele, P. Brand and H. Sackmann, *Mol. Cryst. Liq. Cryst.* **16**, 105 (1972).
55. J. Doucet and A. M. Levelut, *J. Phys.* (France) **38**, 1163 (1977).
56. W. H. de Jeu and J. A. de Poorter, *Phys. Lett.* **61A**, 114 (1977).
57. R. Bartolino, J. Doucet and G. Durand, *Ann. Phys.* (Paris) **3**, 389 (1978).
58. A. Blumstein and L. Patel, *Mol. Cryst. Liq. Cryst.* **48**, 151 (1978).
59. F. Hardouin and A. M. Levelut, *J. Phys.* (France) **41**, 41 (1980).
60. S. Diele, H. Hartung, P. Ebeling, D. Vetters, H. Krüger and D. Demus, in *Advances in Liquid Crystal Research and Applications*, edited by L. Bata (Pergamon, New York, 1981) pp. 39–49.

61. F. Hardouin, A. M. Levelut and G. Sigaud, *J. Phys.* (France) **42**, 71 (1981).
62. S. Kumar, J. D. LeGrange, W. L. McMillan and J. M. Mochel, *Phys. Rev.* A **25**, 2258 (1982).
63. A. de Vries, *Mol. Cryst. Liq. Cryst. Lett.* **41**, 27 (1977).
64. A. J. Leadbetter and R. M. Richardson, *Mol. Phys.* **35**, 1191 (1978).
65. A. de Vries, A. Ekachai and N. Spielberg, *Mol. Cryst. Liq. Cryst. Lett.* **49**, 143 (1979).
66. K. A. Suresh and S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.* **40**, 133 (1977).
67. V. M. Sethna, Ph.D. dissertation, Kent State University, Ohio, USA (1980).
68. A. de Vries, in *Liquid Crystals and Ordered Fluids*, Vol. 4, edited by A. C. Griffin and J. F. Johnson (Plenum, New York, 1984) pp. 137–153.
69. W. R. Krigbaum, J. C. Poirier and M. J. Costello, *Mol. Cryst. Liq. Cryst.* **20**, 133 (1973).
70. D. E. Moncton and R. Pindak, in *Ordering in Two Dimensions*, edited by S. K. Sinha (Elsevier North Holland, New York, 1980) pp. 83–90.
71. R. Bonart, R. Hosemann and R. McCullough, Polymer **4**, 199 (1963).
72. A. Hybl, *Mol. Cryst. Liq. Cryst.* **36**, 271 (1976).
73. J. Stamatoff, P. E. Cladis, D. Guillon, M. C. Cross, T. Bilash and P. Finn, *Phys. Rev. Lett.* **44**, 1509 (1980).
74. H. Sackmann, *J. Phys.* (France) **40**, Colloque C3, 5 (1979).
75. D. E. Moncton and R. Pindak, *Phys. Rev. Lett.* **43**, 701 (1979).
76. A. J. Leadbetter, J. C. Frost and M. A. Mazid, *J. Phys. Lett.* (France) **40**, 325 (1979).
77. A. de Vries, *Mol. Cryst. Liq. Cryst. Lett.* **49**, 19 (1978).
78. H. Kresse, S. Diele, A. Wiegeleben, D. Demus and B. Gajewska, *Phys. Status Solidi* **A67**, K21 (1981).
79. R. Y. Dong, H. Schmiedel, N. A. P. Vaz, Z. Yaniv, M. E. Neubert and J. W. Doane, *Mol. Cryst. Liq. Cryst.* **98**, 411 (1983).
80. B. Pura and J. Przedmojski, *Phys. Lett.* **96A**, 98 (1983).
81. A. R. Kortan, H. V. Känel, R. J. Birgeneau and J. D. Litster, *Phys. Rev. Lett.* **47**, 1206 (1981).
82. A. Rajewska, B. Pura, J. Przedmojski and R. Dabrowski, *Phys. Status Solidi* **A76**, 127 (1983).
83. C. R. Safinya, L. J. Martinez-Miranda, M. Kaplan, J. D. Litster and R. J. Birgeneau, *Phys. Rev. Lett.* **50**, 56 (1983).
84. J. Als-Nielsen, J. D. Litster, R. J. Birgeneau, M. Kaplan, C. R. Safinya, A. Lindegaard-Andersen and S. Mathiesen, *Phys. Rev. B* **22**, 312 (1980).
85. A. M. Levelut, J. Doucet and M. Lambert, *J. Phys.*, (France) **35**, 773 (1974).
86. P. S. Pershan, G. Aeppli, J. D. Litster and R. J. Birgeneau, *Mol. Cryst. Liq. Cryst.* **67**, 205 (1981).
87. S. Kumar, *J. Phys.* (France) **44**, 123 (1983).
88. J. J. Benattar, F. Moussa, M. Lambert and A. M. Levelut, *Springer Ser. Chem. Phys.* **11**, 49 (1980).
89. R. Pindak, D. E. Moncton, S. D. Davey and J. W. Goodby, *Phys. Rev. Lett.* **46**, 1135 (1981).
90. J. Als-Nielsen, F. Christensen and P. S. Pershan, *Phys. Rev. Lett.* **48**, 1107 (1982).
91. D. E. Moncton, R. Pindak, S. C. Davey and G. S. Brown, *Phys. Rev. Lett.* **49**, 1865 (1982).
92. R. D. Frankel and J. M. Forsyth, Science **204**, 622 (1979).
93. H. -C. Liu, Ph.D. dissertation, Kent State University, Ohio, USA (1985).