4. DIFFUSE SCATTERING AND RELATED TOPICS

molecules develop long-range order in which the orientation of the director $\langle \mathbf{n} \rangle$ varies in a plane-wave-like manner that can be described as $\mathbf{x}\cos(2\pi z/\lambda) + \mathbf{y}\sin(2\pi z/\lambda)$, where $\mathbf{x}$ and $\mathbf{y}$ are unit vectors and $\lambda/2$ is the cholesteric 'pitch' that can be anywhere from 0.1 to 10 μm depending on the particular molecule. Even more interesting is that for many cholesteric systems there is a small temperature range, of the order of 1 K, between the cholesteric and isotropic phases for which there is a phase known as the 'blue phase' (Coates & Gray, 1975; Stegemeyer & Bergmann, 1981; Meiboom *et al.*, 1981; Bensimon *et al.*, 1983; Hornreich & Shtrikman, 1983; Crooker, 1983). In fact, there is more than one 'blue phase' but they all have the property that the cholesteric twist forms a three-dimensional lattice twisted network rather than the plane-wave-like twist of the cholesteric phase. Three-dimensional Bragg scattering from blue phases using laser light indicates cubic lattices; however, since the optical cholesteric interactions are much stronger than the usual interactions between X-rays and atoms, interpretation of the results is subtler.

Gray and Goodby discuss a 'smectic-D' phase that is otherwise omitted from this chapter (Gray & Goodby, 1984). Gray and co-workers first observed this phase in the homologous series of 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (Gray *et al.*, 1957). In the hexadecyloxy compound, this phase exists for a region of about 26 K between the smectic-C and smectic-A phases: smectic-C (444.2 K) smectic-D (470.4 K) smectic-A. It is optically isotropic and X-ray studies by Diele *et al.* (1972) and by Tardieu & Billard (1976) indicate a number of similarities to the 'cubic–isotropic' phase observed in lyotropic systems (Luzzati & Riess-Husson, 1966; Tardieu & Luzzati, 1970). More recently, Etherington *et al.* (1986) studied the 'smectic-D' phase of 3′-cyano-4′-*n*-octadecyloxy-biphenyl-4-carboxylic acid. Since this material appears to be more stable than some of the others that were previously studied, they were able to perform sufficient measurements to determine that the space group is cubic *P*23 or *Pm*3 with a lattice parameter of 86 Å. Etherington *et al.* suggested that the 'smectic-D' phase that they studied is a true three-dimensional cubic crystal of micelles and noted that the designation of 'smectic-D' is not accurate. Guillon & Skoulios (1987) have proposed a molecular model for this and related phases.

Fontell (1974) has reviewed the literature on the X-ray diffraction studies of lyotropic mesomorphic systems and the reader is referred there for more extensive information on those cubic systems. The mesomorphic structures of lyotropic systems are much richer than those of the thermotropic and, in addition to all structures mentioned here, there are lyotropic systems in which the smectic-A lamellae seem to break up into cylindrical rods which seem to have the same macroscopic symmetry as some of the discotic phases. On the other hand, it is also much more difficult to prepare a review for the lyotropic systems in the same type of detail as for the thermotropic. The extra complexity associated with the need to control water concentration as well as temperature has made both theoretical and experimental progress more difficult, and, since there has not been very much experimental work on well oriented samples, detailed knowledge of many of these phases is also limited. Aside from the simpler lamellae systems, which seem to have the same symmetry as the thermotropic smectic-A phase, it is not at all clear which of the other phases are three-dimensional crystals and which are true mesomorphic structures. For example, dipalmitoylphosphatidylcholine has an L_β phase that appears for temperatures and (or) water content that is lower than that of the smectic-A L_α phase (Shipley *et al.*, 1974; Small, 1967; Chapman *et al.*, 1967). The diffraction pattern for this phase contains sharp large-angle reflections that may well correspond to a phase that is like one of the crystalline phases listed in Tables 4.4.1.1 and 4.4.1.2, and Fig. 4.4.1.1. On the other hand, this phase could also be hexatic and we do not have sufficient information to decide. The interested

reader is referred to the referenced articles for further detailed information.

4.4.7. Notes added in proof to first edition

4.4.7.1. *Phases with intermediate molecular tilt: smectic-L, crystalline-M,N*

Following the completion of this manuscript, Smith and co-workers [G. S. Smith, E. B. Sirota, C. R. Safinya & N. A. Clark (1988). *Phys. Rev. Lett.* **60**, 813–816; E. B. Sirota, G. S. Smith, C. R. Safinya, R. J. Plano & N. A. Clark (1988). *Science*, **242**, 1406–1409] published an X-ray scattering study of the structure of a freely suspended multilayer film of hydrated phosphatidylcholine in which the phase that had been designated $L_{B'}$ in the literature on lipid phases [M. J. Janiak, D. M. Small & G. G. Shipley (1979). *J. Biol. Chem.* **254**, 6068–6078; V. Luzzati (1968). In *Biological Membranes: Physical Fact and Function*, Vol. 1, edited by D. Chapman, pp. 71–123; A. Tardieu, V. Luzzati & F. C. Reman (1973). *J. Mol. Biol.* **75**, 711–733] was shown to consist of three separate two-dimensional phases in which the positional order in adjacent layers is uncoupled. The three phases are distinguished by the direction of the alkane-chain tilt relative to the nearest neighbours, and in one of these phases the orientation varies continuously with increasing hydration. At the lowest hydration, they observe a phase in which the tilt is towards the second-nearest neighbour; in analogy to the smectic-F phase, they designate this phase $L_{\beta F}$. On increasing hydration, they observe a phase in which the tilt direction is intermediate between the nearest- and next-nearest-neighbour directions, and which varies continuously with hydration. This is a new phase that was not previously known and they designate it $L_{\beta L}$. On further hydration, they observe a phase in which the molecular tilt is towards a nearest neighbour and this is designated $L_{\beta I}$. At maximum hydration, they observe the phase with long-wavelength modulation that was previously designated P_β [M. J. Janiak, D. M. Small & G. G. Shipley (1979). *J. Biol. Chem.* **254**, 6068–6078]. J. V. Selinger & D. R. Nelson [*Phys. Rev. Lett.* (1988), **61**, 416–419] have subsequently developed a theory for the phase transitions between phases with varying tilt orientation and have rationalized the existence of phases with intermediate tilt. To be complete, both Fig. 4.4.1.1 and Table 4.4.1.1 should be amended to include this type of hexatic order which is now referred to as the smectic-L. Extension of the previous logic suggests that the crystalline phases with intermediate tilt should be designated M and N, where N has 'herringbone' type of intermolecular order.

4.4.7.2. *Nematic to smectic-A phase transition*

At the time this manuscript was prepared, there was a fundamental discrepancy between theoretical predictions for the details of the critical properties of the second-order nematic to smectic-A phase transition. This has been resolved. W. G. Bouwan & W. H. de Jeu [*Phys. Rev. Lett.* (1992), **68**, 800–803] reported an X-ray scattering study of the critical properties of octyloxy-phenylcyanobenzyloxybenzoate in which the data were in good agreement with predictions of the three-dimensional xy model [T. C. Lubensky (1983). *J. Chim. Phys.* **80**, 31–43; J. C. Le Guillou & J. Zinn-Justin (1985). *J. Phys. Lett.* **52**, L-137–L-141]. The differences between this experiment and others that were discussed previously, and which did not agree with theory, are firstly that this material is much further from the tricritical point that appears to be ubiquitous for most liquid-crystalline materials and, secondly, that they used the Landau–De Gennes theory to argue that the critical temperature dependence for the $\mathbf{Q}_\perp^4$ term in the differential cross section given in equation (4.4.2.7) is not that of the $c\xi_\perp^4$ term but

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rather should vary as $[(T - T_{\mathrm{NA}})/T]^{-\gamma/4}$, where γ is the exponent that describes the critical-temperature dependence of the smectic order parameter $|\Psi|^2 \simeq [(T - T_{\mathrm{NA}})/T]^{-\gamma}$. The experimental results are in good agreement with the Monte Carlo simulation of the $\mathrm{N}-\mathrm{S_A}$ transition that was reported by C. Dasgupta [*Phys. Rev. Lett.* (1985), **55**, 1771–1774; *J. Phys. (Paris)*, (1987), **48**, 957–970].

references