

## 4. DIFFUSE SCATTERING AND RELATED TOPICS

other degrees of freedom, have considerable thermal motions that make it possible for the conflicting packing requirements to be simultaneously reconciled by one or another compromise. On the other hand, with decreasing temperature, some of the thermal motions become frozen out, and the energy cost of the reconciliation that was possible at higher temperatures becomes too great. At this point, the system must find another solution, and the various modulated phases represent the different compromises. Finally, all of the compromises involving inhomogeneities, like the modulations or grain boundaries, become impossible and the system transforms into a homogeneous crystalline-G phase.

If this type of argument could be made more specific, it would also provide a possible explanation for the molecular origin of the three-dimensional hexatic phases. The original suggestion for the existence of hexatic phases in two dimensions was based on the fact that the interaction energy between dislocations in two dimensions was logarithmic, such that the entropy and the enthalpy had the same functional dependence on the density of dislocations. This gave rise to the observation that above a certain temperature two-dimensional crystals would be unstable against thermally generated dislocations. Although Litster and Birgeneau's suggestion that some of the observed smectic phases might be stacks of two-dimensional hexatics is certainly correct, it is not necessary that the observed three-dimensional hexatics originate from entropy-driven thermally excited dislocations. For example, the temperature–layer-number phase diagram for 7O.7 that is shown in Fig. 4.4.4.5 has the interesting property that the temperature region over which the tilted hexatic phases exist in thin films is almost the same as the temperature region for which the modulated phases exist in thick films and in bulk samples.

From the fact that molecules in the *nO.m* series that only differ by one or two  $-\text{CH}_2-$  groups have different sequences of mesomorphic phases, we learn that within any one molecule the difference in chemical potentials between the different mesomorphic phases must be very small (Leadbetter, Mazid & Kelly, 1979; Doucet & Levelut, 1977; Leadbetter, Frost & Mazid, 1979; Leadbetter, Mazid & Richardson, 1980; Smith *et al.*, 1973; Smith & Garland, 1973). For example, although in 7O.7 the smectic-F phase is only observed in finite-thickness films, both 5O.6 and 9O.4 have smectic-F phase in bulk. Thus, in bulk 7O.7 the chemical potential for the smectic-F phase must be only slightly larger than that of the modulated crystalline-B phases, and the effect of the surfaces must be sufficient to reverse the order in samples of finite thickness.

As far as the appearance of the smectic-F phase in 7O.7 is concerned, it is well known that the interaction energy between dislocation pairs is very different near a free surface from that in the bulk (Pershan, 1974; Pershan & Prost, 1975). The origin of this is that the elastic properties of the surface will usually cause the stress field of a dislocation near to the surface either to vanish or to be considerably smaller than it would in the bulk. Since the interaction energy between dislocations depends on this stress field, the surface significantly modifies the dislocation–dislocation interaction. This is a long-range effect, and it would not be surprising if the interactions that stabilized the dislocation arrays to produce the long-wavelength modulations in the thick samples were sufficiently weaker in the samples of finite thickness that the dislocation arrays are disordered. Alternatively, there is evidence that specific surface interactions favour a finite molecular tilt at temperatures where the bulk phases are uniaxial (Farber, 1985). Incommensurability between the period of the tilted surface molecules and the crystalline-B phases below the surface would increase the density of dislocations, and this would also modify the dislocation–dislocation interactions in the bulk.

Sirota *et al.* (1985) and Sirota, Pershan, Sorensen & Collett (1987) demonstrated that, while the correlation lengths of the smectic-F phase have a significant temperature dependence, the

lengths are independent of film thickness, and this supports the argument that although the effects of the surface are important in stabilizing the smectic-F phase in 7O.7, once the phase is established it is essentially no different from the smectic-F phases observed in bulk samples of other materials. Brock *et al.* (1986) observed anisotropies in the correlation lengths of thick samples of 8OSI that are similar to those observed by Sirota.

These observations motivate the hypothesis that the dislocation densities in the smectic-F phases are determined by the same incommensurability that gives rise to the modulated crystalline-B structures. Although all of the experimental evidence supporting this hypothesis was obtained from the smectic-F tilted hexatic phase, there is no reason why this speculation could not apply to both the tilted smectic-I and the untilted hexatic-B phase.

4.4.4.3.2. *Crystal-G, crystal-J*

The crystalline-G and crystalline-J phases are the ordered versions of the smectic-F and smectic-I phases, respectively. The positions of the principal peaks illustrated in Fig. 4.4.4.4 for the smectic-F(I) are identical to the positions in the smectic-G(J) phase if small thermal shifts are discounted. In both the hexatic and the crystalline phases, the molecules are tilted with respect to the layer normals by approximately 25 to 30° with nearly hexagonal packing around the tilted axis (Doucet & Levelut, 1977; Levelut *et al.*, 1974; Levelut, 1976; Leadbetter, Mazid & Kelly, 1979; Sirota, Pershan, Sorensen & Collett, 1987). The interlayer molecular packing appears to be end to end, in an AAA type of stacking (Benattar *et al.*, 1983; Benattar *et al.*, 1981; Levelut, 1976; Gane *et al.*, 1983). There is only one molecule per unit cell and there is no evidence for the long-wavelength modulations that are so prevalent in the crystalline-B phase that is the next higher temperature phase above the crystalline-G in 7O.7.

4.4.4.4. *Crystalline phases with herringbone packing*4.4.4.4.1. *Crystal-E*

Fig. 4.4.4.7 illustrates the intralayer molecular packing proposed for the crystalline-E phase (Levelut, 1976; Doucet, 1979; Levelut *et al.*, 1974; Doucet *et al.*, 1975; Leadbetter *et al.*, 1976; Richardson *et al.*, 1978; Leadbetter, Frost, Gaughan & Mazid, 1979; Leadbetter, Frost & Mazid, 1979). The molecules are, on average, normal to the

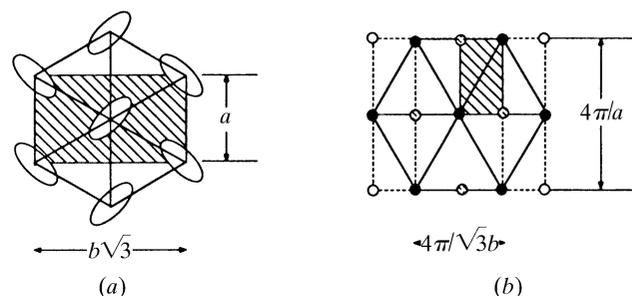


Fig. 4.4.4.7. (a) The 'herringbone' stacking suggested for the crystalline-E phase in which molecular rotation is partially restricted. The primitive rectangular unit cell containing two molecules is illustrated by the shaded region. The lattice has rectangular symmetry and  $a \neq b$ . (b) The position of the Bragg peaks in the plane in reciprocal space that is parallel to the layers. The dark circles indicate the principal Bragg peaks that would be the only ones present if all molecules were equivalent. The open circles indicate additional peaks that are observed for the model illustrated in (a). The cross-hatched circles indicate peaks that are missing because of the glide plane in (a).

#### 4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

layers; however, from the optical birefringence it is apparent that the site symmetry is not uniaxial. X-ray diffraction studies on single crystals by Doucet and co-workers demonstrated that the biaxiality was not attributable to molecular tilt and subsequent work by a number of others resulted in the arrangement shown in Fig. 4.4.4.7(a). The most important distinguishing reciprocal-space feature associated with the intralayer 'herringbone' packing is the appearance of Bragg peaks at  $\sin(\theta)$  equal to  $\sqrt{7}/2$  times the value for the lowest-order in-plane Bragg peak for the triangular lattice (Pindak *et al.*, 1981). These are illustrated by the open circles in Fig. 4.4.4.7(b). The shaded circles correspond to peaks that are missing because of the glide plane that relates the two molecules in the rectangular cell.

Leadbetter, Mazid & Malik (1980) carried out detailed studies on both the crystalline-E phase of isobutyl 4-(4-phenylbenzylidene-amino)cinnamate (IBPBAC) and the crystalline phase immediately below the crystalline-E phase. Partially ordered samples of the crystalline-E phase were obtained by melting the lower-temperature crystalline phase. Although the data for the crystalline-E phase left some ambiguity, they argued that the phase they were studying might well have had molecular tilts of the order of 5 or 6°. This is an important distinction, since the crystalline-H and crystalline-J phases are essentially tilted versions of the crystalline-E. Thus, one important symmetry difference that might distinguish the crystalline-E from the others is the presence of a mirror plane parallel to the layers. In view of the low symmetry of the individual molecules, the existence of such a mirror plane would imply residual molecular motions. In fact, using neutron diffraction Leadbetter *et al.* (1976) demonstrated for a different liquid crystal that, even though the site symmetry is not axially symmetric, there is considerable residual rotational motion in the crystalline-E phase about the long axis of the molecules. Since the in-plane spacing is too small for neighbouring molecules to be rotating independently of each other, they proposed what might be interpreted as large partially hindered rotations.

##### 4.4.4.4.2. Crystal-H, crystal-K

The crystalline-H and crystalline-K phases are tilted versions of the crystalline-E. The crystalline-H is tilted in the direction between the near neighbours, with the convenient mnemonic that on cooling the sequence of phases with the same relative orientation of tilt to near-neighbour position is F → G → H. Similarly, the tilt direction for the crystalline-K phase is similar to that of the smectic-I and crystalline-J so that the expected phase sequence on cooling might be I → J → K. In fact, both of these sequences are only intended to indicate the progression in lower symmetry; the actual transitions vary from material to material.

#### 4.4.5. Discotic phases

In contrast to the long thin rod-like molecules that formed most of the other phases discussed in this chapter, the discotic phases are formed by molecules that are more disc-like [see Fig. 4.4.1.3(f), for example]. There was evidence that mesomorphic phases were formed from disc-like molecules as far back as 1960 (Brooks & Taylor, 1968); however, the first identification of a discotic phase was by Chandrasekhar *et al.* (1977) with benzenehexyl hexa-*n*-alkanoate compounds. Disc-like molecules can form either a fluid nematic phase in which the disc normals are aligned, without any particular long-range order at the molecular centre of mass, or more-ordered 'columnar' (Helfrich, 1979) or 'discotic' (Billard *et al.*, 1981) phases in which the molecular positions are correlated such that the discs stack on top of one another to form columns. Some of the literature designates this nematic phase as  $N_D$  to distinguish it from the phase formed by 'rod-like' molecules

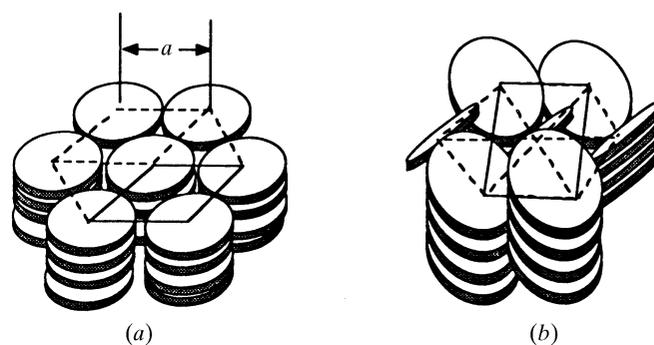


Fig. 4.4.5.1. Schematic illustration of the molecular stacking for the discotic (a)  $D_2$  and (b)  $D_1$  phases. In neither of these two phases is there any indication of long-range positional order along the columns. The hexagonal symmetry of the  $D_1$  phase is broken by 'herringbone-like' correlations in the molecular tilt from column to column.

(Destrade *et al.*, 1983). In the same way that the appearance of layers characterizes order in smectic phases, the order for the discotic phases is characterized by the appearance of columns. Chandrasekhar (1982, 1983) and Destrade *et al.* (1983) have reviewed this area and have summarized the several notations for various phases that appear in the literature. Levelut (1983) has also written a review and presented a table listing the space groups for columnar phases formed by 18 different molecules. Unfortunately, it is not absolutely clear which of these are mesomorphic phases and which are crystals with true long-range positional order.

Fig. 4.4.5.1 illustrates the molecular packing in two of the well identified discotic phases that are designated as  $D_1$  and  $D_2$  (Chandrasekhar, 1982). The phase  $D_2$  consists of a hexagonal array of columns for which there is no intracolumnar order. The system is uniaxial and, as originally proposed, the molecular normals were supposed to be along the column axis. However, recent X-ray scattering studies on oriented free-standing fibres of the  $D_2$  phase of triphenylene hexa-*n*-dodecanoate indicate that the molecules are tilted with respect to the layer normal (Safinya *et al.*, 1985, 1984). The  $D_1$  phase is definitely a tilted phase, and consequently the columns are packed in a rectangular cell. According to Safinya *et al.*, the  $D_1$  to  $D_2$  transition corresponds to an order-disorder transition in which the molecular tilt orientation is ordered about the column axis in the  $D_1$  phase and disordered in the  $D_2$  phase. The reciprocal-space structure of the  $D_1$  phase is similar to that of the crystalline-E phase shown in Fig. 4.4.4.7(b).

Other discotic phases that have been proposed would have the molecules arranged periodically along the column, but disordered between columns. This does not seem physically realistic since it is well known that thermal fluctuations rule out the possibility of a one-dimensional periodic structure even more strongly than for the two-dimensional lattice that was discussed above (Landau, 1965; Peierls, 1934). On the other hand, in the absence of either more high-resolution studies on oriented fibres or further theoretical studies, we prefer not to speculate on the variety of possible true discotic or discotic-like crystalline phases that might exist. This is a subject for future research.

#### 4.4.6. Other phases

We have deliberately chosen not to discuss the properties of the cholesteric phase in this chapter because the length scales that characterize the long-range order are of the order of micrometres and are more easily studied by optical scattering than by X-rays (De Gennes, 1974; De Vries, 1951). Nematic phases formed from chiral