

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

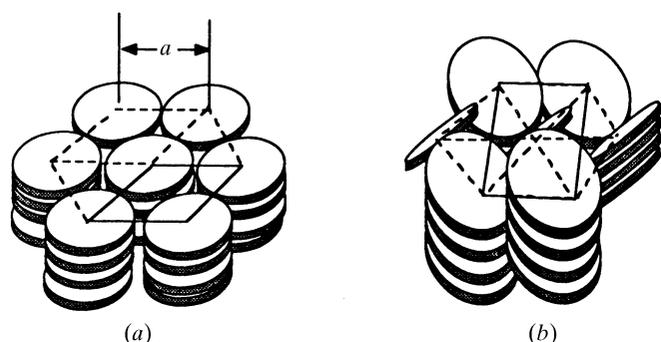


Fig. 4.4.5.1. Schematic illustration of the molecular stacking for the discotic (a) D_2 and (b) D_1 phases. In neither of these two phases is there any indication of long-range positional order along the columns. The hexagonal symmetry of the D_1 phase is broken by 'herringbone-like' correlations in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

on cooling the sequence of phases with the same relative orientation of tilt to near-neighbour position is $F \rightarrow G \rightarrow H$. 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 $I \rightarrow J \rightarrow K$. 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 (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 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*-octadecyloxybiphenyl-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 $P23$ or $Pm3$ 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