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 *n*O.*m* series that only differ by one or two —CH$_2$— groups have different sequences of mesomorphic phases, we learn that within any one molecule the difference in chemical potentials between the different meso-morphic 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
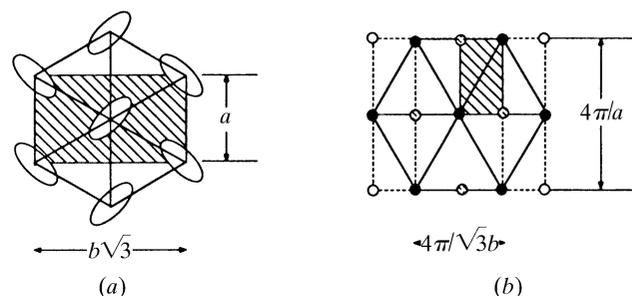
Fig. 4.4.4.7. (*a*) The 'herringbone' stacking suggested for the crystalline-E phase in which molecular rotation is partially restricted. The primitive rectangular unit cell containing two molecules is illustrated by the shaded region. The lattice has rectangular symmetry and $a \neq b$. (*b*) The position 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*).