4.4. SCATTERING FROM MESOMORPHIC STRUCTURES
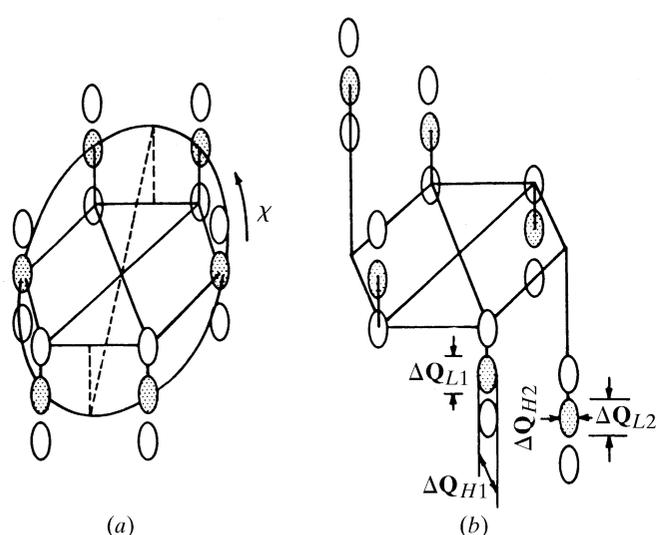

Fig. 4.4.4.4. Scattering intensities in reciprocal space from three-dimensional tilted hexatic phases: (*a*) the smectic-I and (*b*) the smectic-F. The variation of the intensity along the Q_L direction indicates interlayer correlations that are absent in Figs. 4.4.4.1(*d*) and (*e*). The peak widths $\Delta Q_{L1,2}$ and $\Delta Q_{H1,2}$ correspond to the four inequivalent widths in the smectic-F phase. Similar inequivalent widths exist for the smectic-I phase. The circle through the shaded points in (*a*) indicates the reciprocal-space scan that directly measures the hexatic order. A similar scan in the smectic-C phase would have intensity independent of χ.

Fig. 4.4.4.5. The phase diagram for free films of 7O.7 as a function of thickness and temperature. The phases *ABAB*, *AAA*, OR_{m1}, OR_{m2}, OR'_{m1}, *M* and *ABAB* are all crystalline-B with varying interlayer stacking, or long-wavelength modulations; CrG, SmF and SmI are crystalline-G, smectic-F and smectic-I, respectively (Sirota *et al.*, 1985; Sirota, Pershan & Deutsch, 1987; Sirota, Pershan, Sorensen & Collett, 1987).

Leadbetter, 1981) and by Benattar and co-workers (Benattar *et al.*, 1978, 1980, 1983; Guillon *et al.*, 1986) showed it to have the reciprocal-space structure illustrated in Fig. 4.4.4.4(*b*). There are interlayer correlations in the three-dimensional smectic-F phases, and as a consequence the reciprocal-space structure has maxima along the diffuse rods. Benattar *et al.* (1979) obtained monodomain smectic-F samples of the liquid crystal *N,N'*-(1,4-phenylenedimethylene)bis(4-*n*-pentylaniline) by melting a single crystal that was previously precipitated from solution. One of the more surprising results of this work was the demonstration that the near-neighbour packing was very close to what would be expected from a model in which rigid closely packed rods were simply tilted away from the layer normal. In view of the facts that the molecules are clearly not cylindrical, and that the molecular tilt indicates that the macroscopic symmetry has been broken, it would have been reasonable to expect significant deviations from local hexagonal symmetry when the system is viewed along the molecular axis. The fact that this is not the case indicates that this phase has a considerable amount of rotational disorder around the long axis of the molecules.

Other important features of the smectic-F phase are, firstly, that the local molecular packing is identical to that of the tilted crystalline-G phase (Benattar *et al.*, 1979; Sirota *et al.*, 1985; Guillon *et al.*, 1986). Secondly, there is considerable temperature dependence of the widths of the various diffuse peaks. Fig. 4.4.4.4(*b*) indicates the four inequivalent line widths that Sirota and co-workers measured in freely suspended films of the liquid crystal *N*-[4-(*n*-heptyloxy)benzylidene]-4-*n*-heptyl aniline (7O.7). Parenthetically, bulk samples of this material do not have a smectic-F phase; however, the smectic-F is observed in freely suspended films as thick as ~200 layers. Fig. 4.4.4.5 illustrates the thickness–temperature phase diagram of 7O.7 between 325 and 342 K (Sirota *et al.*, 1985; Sirota, Pershan & Deutsch, 1987). Bulk samples and thick films have a first-order transition from the crystalline-B to the smectic-C at 342 K. Thinner films indicate a surface phase above
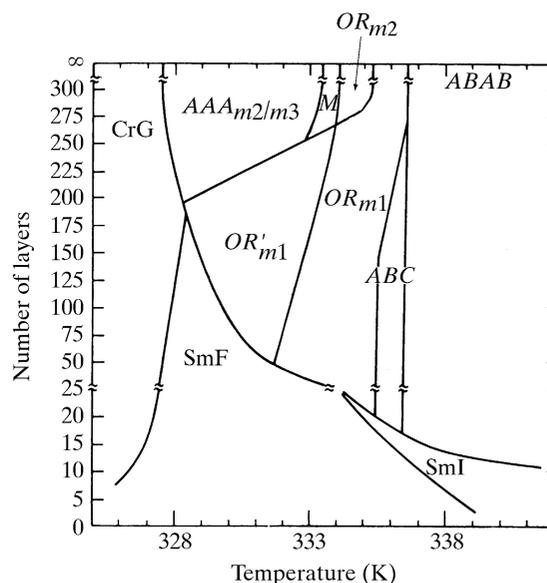
342 K that will be discussed below. Furthermore, although there is a strong temperature dependence of the widths of the diffuse scattering peaks, the widths are independent of film thickness. This demonstrates that, although the free film boundary conditions have stabilized the smectic-F phase, the properties of the phase are not affected by the boundaries. Finally, the fact that the widths ΔQ_{L1} and ΔQ_{L2} along the **L** direction and ΔQ_{H1} and ΔQ_{H2} along the in-plane directions are not equal indicates that the correlations are very anisotropic (Brock *et al.*, 1986; Sirota *et al.*, 1985). We will discuss one possible model for these properties after presenting other data on thick films of 7O.7. From the fact that the positions of the intensity maxima for the diffuse spots of the smectic-F phase of 7O.7 correspond exactly to the positions of the Bragg peaks in the crystalline-G phase, we learn that the local molecular packing must be identical in the two phases. The major difference between the crystalline-G and the tilted hexatic smectic-F phase is that, in the latter, defects destroy the long-range positional order of the former (Benattar *et al.*, 1979; Sirota *et al.*, 1985). Although this is consistent with the existing theoretical model that attributes hexatic order to a proliferation of unbounded dislocations, it is not obvious that the proliferation is attributable to the same Kosterlitz–Thouless mechanism that Halperin & Nelson and Young discussed for the transition from the two-dimensional crystal to the hexatic phase. We will say more on this point below.

The only identified difference between the two tilted hexatic phases, the smectic-F and the smectic-I, is the direction of the molecular tilt relative to the near-neighbour positions. For the smectic-I, the molecules tilt towards one of the near neighbours, while for the smectic-F they tilt between the neighbours (Gane & Leadbetter, 1983). There are a number of systems that have both smectic-I and smectic-F phases, and in all cases of which we are aware the smectic-I is the higher-temperature phase (Gray & Goodby, 1984; Sirota *et al.*, 1985; Sirota, Pershan, Sorensen & Collett, 1987).

Optical studies of freely suspended films of materials in the *n*O.*m* series indicated tilted surface phases at temperatures for which the bulk had uniaxial phases (Farber, 1985). As mentioned above,

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