

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

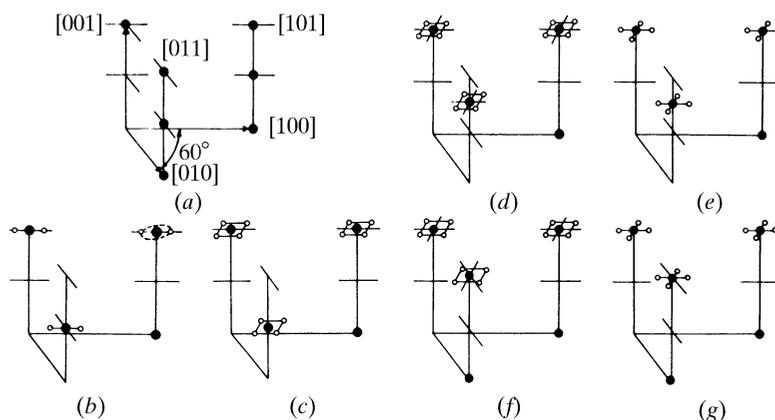


Fig. 4.4.4.6. Location of the Bragg peaks in one 60° section of reciprocal space for the three-dimensional crystalline-B phases observed in thick films of 7O.7. (a) The normal hexagonal crystalline-B phase with *ABAB* stacking. (b) The one-dimensional modulated phase with orthorhombic symmetry. The closed circles are the principal Bragg peaks and the open circles indicate side bands associated with the long-wavelength modulation. (c) The two-dimensional modulated phase with orthorhombic symmetry. Only the lowest-order side bands are shown. They are situated on the corners of squares surrounding the Bragg peak. The squares are oriented as shown and the amplitude of the square diagonal is equal to the distance between the two side bands illustrated in (b). (d) The two-dimensional modulated phase with monoclinic symmetry. Note that the *L* position of one of the peaks has shifted relative to (c). (e) A two-dimensional modulated phase with orthorhombic symmetry that is only observed on heating the quenched phase illustrated in (g). (f) The two-dimensional modulated phase with hexagonal symmetry and *AAA* layer stacking. (g) A two-dimensional hexagonal phase with *AAA* layer stacking that is only observed on rapid cooling from the phase shown in (c).

phase; (2) the period of the modulation; (3) the polarization of the modulation; and (4) the size of the observed deviations of the reciprocal-space structure from the hexagonal symmetry of the *ABAB* phase and suggests a microscopic driving mechanism that we will discuss below.

On further cooling, there is a first-order transition in which the one-dimensional modulation that appeared at the transition to orthorhombic symmetry is replaced by a two-dimensional modulation as shown in Fig. 4.4.4.6(c). On further cooling, there is another first-order transition in which the positions of the principal Bragg spots change from having orthorhombic to monoclinic symmetry as illustrated in Fig. 4.4.4.6(d). On further cooling, the Bragg peaks shift continually until there is one more first-order transition to a phase with hexagonal *AAA* positions as illustrated in Fig. 4.4.4.6(f). On further cooling, the *AAA* symmetry remains unchanged, and the modulation period is only slightly dependent on temperature, but the modulation amplitude increases dramatically. Eventually, as indicated in the phase diagram shown in Fig. 4.4.4.5, the system undergoes another first-order transition to the tilted crystalline-G phase. The patterns in Figs. 4.4.4.6(e) and (g) are observed by rapid quenching from the temperatures at which the patterns in Fig. 4.4.4.6(b) are observed.

Although there is not yet an established theoretical explanation for the origin of the 'restacking-modulation' effects, there are a number of experimental facts that we can summarize, and which indicate a probable direction for future research. Firstly, if one ignores the long wavelength modulation, the hexagonal *ABAB* phase is the only phase in the diagram for 7O.7 for which there are two molecules per unit cell. There must be some basic molecular effect that determines this particular coupling between every other layer. In addition, it is particularly interesting that it only manifests itself for a small temperature range and then vanishes as the sample is cooled. Secondly, any explanation for the driving force of the restacking transition must also explain the modulations that accompany it. In particular, unless one cools rapidly, the same modulation structures with the same amplitudes always appear at the same temperature, regardless of the sample history, *i.e.* whether heating or cooling. No significant hysteresis is observed and Sirota argued that the structures are in thermal equilibrium.

There are a number of physical systems for which the development of long-wavelength modulations is understood, and

in each case they are the result of two or more competing interaction energies that cannot be simultaneously minimized (Blinic & Levanyuk, 1986; Safinya, Varady *et al.*, 1986; Lubensky & Ingersent, 1986; Winkor & Clarke, 1986; Moncton *et al.*, 1981; Fleming *et al.*, 1980; Villain, 1980; Frank & van der Merwe, 1949; Bak *et al.*, 1979; Pokrovsky & Talapov, 1979). The easiest to visualize is epitaxial growth of one crystalline phase on the surface of another when the two lattice vectors are slightly incommensurate. The first atomic row of adsorbate molecules can be positioned to minimize the attractive interactions with the substrate. This is slightly more difficult for the second row, since the distance that minimizes the interaction energy between the first and second rows of adsorbate molecules is not necessarily the same as the distance that would minimize the interaction energy between the first row and the substrate. As more and more rows are added, the energy price of this incommensurability builds up, and one possible configuration that minimizes the global energy is a modulated structure.

In all known cases, the very existence of modulated structures implies that there must be competing interactions, and the only real question about the modulated structures in the crystalline-B phases is the identification of the competing interactions. It appears that one of the more likely possibilities is the difficulty in packing the 7O.7 molecules within a triangular lattice while simultaneously optimizing the area per molecule of the alkane tails and the conjugated rings in the core (Carlson & Sethna, 1987; Sadoc & Charvolin, 1986). Typically, the mean cross-sectional area for a straight alkane in the all-*trans* configuration is between 18 and 19 Å², while the mean area per molecule in the crystalline-B phase is closer to 24 Å². While these two could be reconciled by assuming that the alkanes are tilted with respect to the conjugated core, there is no reason why the angle that reconciles the two should also be the same angle that minimizes the internal energy of the molecule. Even if it were the correct angle at some temperature by accident, the average area per chain is certainly temperature dependent. Even without attempting to include the rotational dynamics that are necessary to understanding the axial site symmetry, it is obvious that there can be a conflict in the packing requirements of the two different parts of the molecule.

A possible explanation of these various structures might be as follows: at high temperatures, both the alkane chain, as well as the