# Continuous Diffuse Electron Scattering from Polymethylene Compounds
## II. Oblique Layer Crystals

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The positions of continuous diffuse scattering streaks in electron diffraction patterns from oblique layer crystals isostructural to monoclinic paraffins are predicted using the kinematical difference Fourier transform (DFT) model of Amorós and Amorós. However, indications of correlated chain motions are found as was seen in a bimolecular rectangular layer structure. This correlated chain "motion" and the large temperature factors used for the DFT calculation (which are inconsistent with X-ray crystal structure results) suggest the presence of point defects in the long chains proposed earlier by other workers.

Continuous bands of diffusely scattered electrons are sometimes observed in transmission electron diffraction experiments on organic microcrystals. Charlesby et al. [1] interpreted the dispositions of such scattering from anthracene crystals as being related somehow to the Fourier transform of the repeating molecule in the crystal, consistent with its orientation in a particular crystal projection. Using X-ray diffraction information from many molecular crystals, Amorós and Amorós [2] described this continuous scattering in terms of the autocorrelation function ("$Q$-function"), for thermally agitated molecules in the crystal, i.e.

$$Q(\boldsymbol{r}) = P_{\mathrm{T}}(\boldsymbol{r}) + Q_{\mathrm{mole}}(\boldsymbol{r}) - \overline{Q}_{\mathrm{mole_T}}(\boldsymbol{r}) \,. \qquad (1)$$

The $Q$-function of a thermally agitated crystal $Q(\boldsymbol{r})$ is related to the Patterson function of the average crystal $P_{\mathrm{T}}(\boldsymbol{r})$ as well as the difference of molecular $Q$-functions for a molecule which is, respectively, at rest and thermally agitated. Fourier transforming the sceond part of (1) gives the difference Fourier transform (DFT):

$$\begin{aligned} I_{\mathrm{DFT}} &= I_{\mathrm{mole}}(\boldsymbol{r}^*) \cdot (1 - |D|^2) \\ &= |F_{\mathrm{mole}}|^2 \{1 - \exp(-\tfrac{1}{2} B |\boldsymbol{r}^*|^2)\} \,, \end{aligned}$$

where $D$ is the Debye-Waller temperature factor. This description of continuous scatter holds for a crystal with one molecule per unit cell. For multimolecular unit cells, the $I_{\mathrm{DFT}}$ is a sum of individual molecular contributions, because the motions of the molecules are assumed to be uncorrelated.

We reported earlier [3] an application of this methodology to rectangular layer paraffinic crystals (i.e. those with long chain axes perpendicular to the crystal surface or parallel to the incident electron beam). In these studies, the diffuse scatter from paraffinic chains in the hexagonal methylene subcell (for which one chain is found per unit cell) is well explained by the DFT calculation. However, for a "bimolecular" crystal such as an orthorhombic paraffin monolayer packing in the $\mathrm{O}_{\perp}$

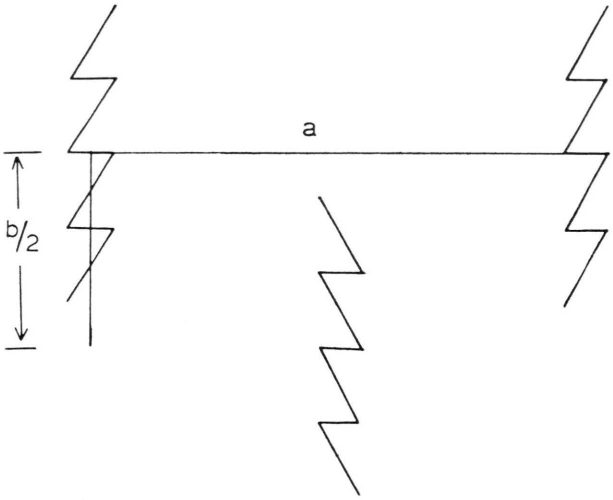

Fig. 1. Projection of eight carbon zig-zag chain used for DFT calculations. The model has the same chain packing found for monoclinic even chain n-paraffins [8] with unit cell constants $a \simeq 5.6$ Å, $b \simeq 7.4$ Å. In this oblique layer structure the chain axes are tilted around the $\mathrm{O}_{\perp}$ methylene subcell $a_{\mathrm{s}}$ axis (equivalent to unit cell b axis) by about 30°. For DFT calculations for uncorrelated molecular motions, one molecule was placed in the unit cell. For DFT calculations considering correlated chain motions the transform was made for the whole unit cell in pgg symmetry.

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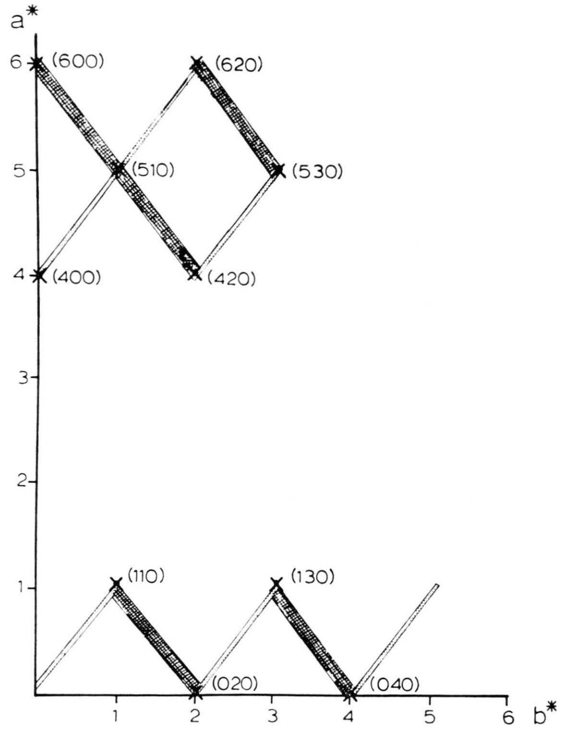

Fig. 2. Representation of diffuse scattering from the oblique layer structure shown in Figure 1. This composite drawing is taken from representative $hk0$ electron diffraction patterns of untilted microcrystals of stearic acid (B-form), behenic acid (B-form) and cetyl palmitate (monoclinic form). Positions of Bragg peaks indicated by "X". (Continuous diffuse scattering from actual diffraction patterns is of too low contrast for adequate photographic reproduction).

methylene subcell [4], the DFT calculation was less satisfactory as long as the condition of uncorrelated motion was imposed. $I_{\mathrm{DFT}}$ calculated with $I_{\mathrm{mole}}$ replaced by the intensity from the whole bimolecular unit cell gave a better account of the observed diffuse scatter.

Continuous bands have also been observed in untilted oblique layer paraffinic crystals (i.e. with long chain axes inclined to the crystal surface) such as the B-form of fatty acids and the monoclinic polymorph of the wax, cetyl palmitate. A representation of this chain packing in (001) projection is given in Figure 1. Diffraction from this zone has been discussed in greater detail elsewhere [5–7]. It is sufficient to note here that the $hk0$ electron diffraction from this projection (projected molecules in Fig. 1 packing with plane group symmetry pgg) is a band pattern sampled by the reciprocal lattice and representing the Fourier transform of the diffraction grating made up of rows of carbon atoms spaced at 0.20 of the short unit cell length ($a \simeq 5.6$ Å). Hence the corresponding intense diffraction bands appear at $h = 0.5$.

The diffuse diffraction is superimposed on the spot electron diffraction pattern as represented schematically by Figure 2. The most intense diffuse streaks pass through the strongest reflections of the diffraction pattern i.e. (020), (040), (510) and (530). Less intense diffuse streaks are sometimes observed which are perpendicular to these.

Using the atomic coordinates given by Shearer and Vand [8] for a monoclinic paraffin monolayer, the DFT of the (001) projection was calculated for an eight carbon chain model. If independently agitated molecules are assumed, the resulting DFT (Fig. 3) has no resemblance to Figure 2. Calculation of a DFT with correlated molecular motions (hence using the whole unit cell) gives a diffuse pattern (Fig. 4) which is very similar to Figure 2. This result is entirely consistent with our findings for rectangular layer structures.

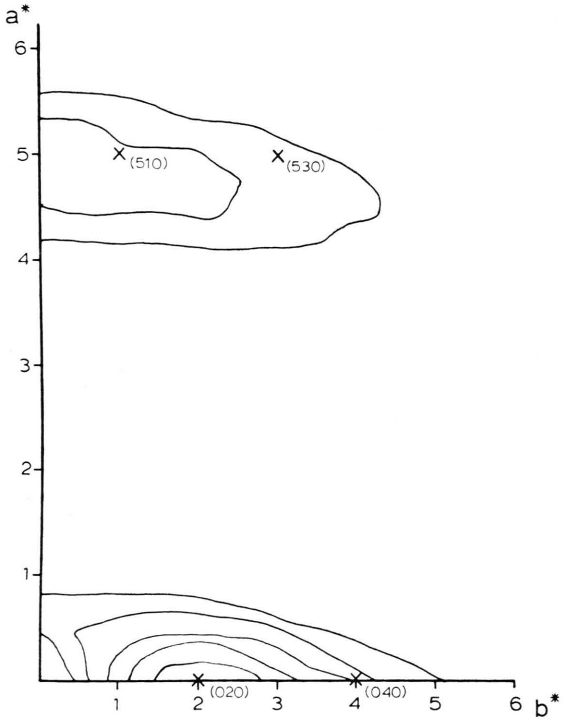

Fig. 3. Difference Fourier transform (DFT) calculated using a unimolecular crystal model (see Figure 1). $B = 10$ Å. Positions of major Bragg peaks indicated by "X".

Why are these results at variance with the DFT model which assumes independent thermal vibrations of individual molecules? Other experiments on the electron diffraction of paraffiic chain structures may give the answer to this. It is often found that multilayer crystals of long chain materials do not give diffraction intensities from the true unit cell — e.g. if this unit cell is composed of a bilayer instead of a molecular monolayer. This phenomenon is explained very well by observed crystal bending [7, 9] as originally proposed by Cowley [10] for silicates. However, bending does not explain why coherent scattering is *not* commonly seen from functional groups in the paraffinic chain (e.g. in carboxylic acids, glycerides, phospholipids etc.). This incoherence was attributed to the presence of point defects in the long chains [7], as originally proposed for linear polymers [11]. Such point defects or "kinks" in one chain would slightly disturb the arrangement of atoms in adjacent chains. In concert, over the whole crystal, this would be expressed as an apparent temperature factor involving concerted "motions" of adjacent acyl chains. Since virtual thermal motions of the magnitude used for DFT calculations are not otherwise justified for these materials (e.g. by comparison to X-ray single crystal studies), the presence of such point defects seems to be particularly important for thin paraffinic microcrystals rapidly grown from solvent.

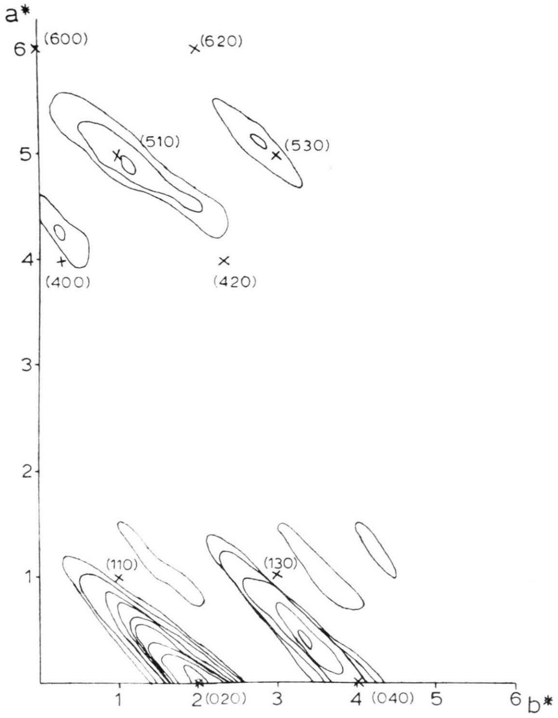

Fig. 4. Difference Fourier transform (DFT) calculated using a bimolecular crystal model (see Figure 1). $B = 10 \text{Å}^2$. Positions of major Bragg peaks indicated by "X".

*Acknowledgements*

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[1] A. Charlesby, G. I. Finch, and H. Wilman, Proc. Phys. Soc. London **51**, 479 (1939).
[2] J. L. Amorós and M. Amorós, Molecular Crystals: Their Transforms and Diffuse Scattering, Wiley, New York (1968).
[3] D. L. Dorset, Z. Naturforsch. **32a**, 1161 (1977).
[4] D. L. Dorset, Acta Crystallogr. **A32**, 207 (1976).
[5] D. L. Dorset, J. Appl. Crystallogr. **9**, 142 (1976).
[6] D. L. Dorset, Bioorg. Khim. **2**, 781 (1976).
[7] D. L. Dorset, Z. Naturforsch. in press.
[8] H. M. M. Shearer and V. Vand, Acta Crystallogr. **9**, 379 (1956).
[9] D. L. Dorset, Z. Naturforsch. **32a**, 1166 (1977).
[10] J. M. Cowley, Acta Crystallogr. **14**, 920 (1961).
[11] D. H. Reneker, B. M. Fanconi, and J. Mazur, J. Appl. Phys. **48**, 4032 (1977).