

Electron Diffraction Intensities from Slightly Bent Multilayer Paraffinic Crystals

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Electron diffraction intensities from slightly bent orthorhombic paraffinic crystals are evaluated in light of the expected modulation to the Patterson function as derived by Cowley [Acta Crystallogr. **14**, 920 (1961)]. Dependence of this effect on reciprocal distance is clearly shown. Low angle intensities are best correlated to diffraction from the whole unit cell, which is a bilayer of mutually displaced monolayers, whereas high angle reflections appear to originate from a monolayer alone. This effect represents a uniform crystal bend of only 1.0° .

Introduction

The imperfection of thin paraffinic crystals is often manifested by the intensity distributions of transmission electron diffraction patterns obtained from them. Most commonly found is a situation where each monolayer in a multilamellar crystal appears to diffract independently of every other monolayer. Often the intensity distribution of the $hk0$ electron diffraction pattern is that of a monolayer alone. This effect is to be found in the electron diffraction data from paraffins used by Vainshtein et al.¹ in their crystal structure analysis, but was not recognized by them. Knoop and his co-workers^{2–4} often observed this effect with lipid materials packing in the hexagonal methylene subcell but interpreted the hexagonal symmetry of the diffraction pattern, which can only arise from monolayers⁵, to indicate an eclipsed packing of contiguous monolayers. Later studies by us on orthorhombic paraffin microcrystals⁶ in comparison to an X-ray crystal structure on larger crystals⁷, identified this peculiarity in the diffraction intensity distribution and verified its existence in other microcrystalline long chain materials^{8–10}. Using the favored energetics of interlayer packing¹¹, it was argued that the suggested eclipsed stacking of monolayers could not exist¹².

An illustration of the problem is given in Fig. 1 which shows the (001) projection of a bilayer orthorhombic paraffin crystal, needed to form one unit cell⁷. Were the diffraction to emanate from one layer alone, the intensity distribution of the $hk0$

diffraction pattern would give $|F_{200}| \cong |F_{110}|$ whereas if the whole unit cell were to diffract coherently: $|F_{200}| \cong 2|F_{110}|$. The former case is most often seen⁶.

Following a suggestion given in a correspondence from Prof. J. M. Cowley, we indicated that the effect may be due to elastic bending of the thin crystals¹². However it is very difficult to isolate the influence of bend on the diffraction pattern from perturbations due to other crystal defects. One should have a crystal which is nearly perfect and only slightly bent — a situation rarely encountered in these materials.

The purpose of this paper is to utilize some of these rare occurrences in an illustration of how elastic bends actually affect the diffraction intensities. (The effects on the diffraction intensities of crystal deformations due to other defects, which often mask the phenomenon described here, will be described in detail in a later publication.) Moreover, we will only discuss here the situation where the incident electron beam is parallel to the long chain axes.

Experimental

Sample Preparation

Two materials crystallizing with acyl chains in the 0_1 methylene subcell seen in polyethylene¹³ and with long chains axes perpendicular to the $\{001\}$ crystal face are used here. One is commercially available n-hexatriacontane (98%, Aldrich Chemical Co., Inc., Milwaukee, Wisconsin) crystallized onto carbon-Formvar covered 400-mesh electron microscope grids from a dilute solution in light petroleum. The other is DL-(1,2/3)-1,2-di-0-palmi-

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toylecyclopentane-1,2,3-triol synthesized by Dr. A. J. Hancock at the University of Missouri, Kansas City¹⁴ and crystallized onto the same type electron microscope grids from dilute warm n-pentanol solution. Previous crystal structure analysis¹⁵ indicates the chain packing to be identical to the orthorhombic n-paraffins.

Electron Diffraction and Microscopy

Electron diffraction experiments at 100 kV were carried out on a JEOL JEM-100 U electron microscope, using usual precautions against radiation damage to the sample⁶. Bright field diffraction contrast images at low magnification (2.6 K) were obtained after the diffraction pattern by isolating the incident beam with the objective aperture and rapidly focusing the intermediate lens onto the image plane of the objective lens¹⁶. Again, the beam current was low enough to cause no discernible radiation damage to the sample, as would be evidenced by migrating bend contours¹⁷.

High voltage electron diffraction experiments were done on the AEI-EM 7 instrument at the University of Wisconsin at Madison. Again, normal precautions were taken to minimize beam damage⁶.

Protocols for data analysis were those described earlier⁶. Electron scattering factor tables for carbon and hydrogen are those given by Doyle and Turner¹⁸.

Method of Analysis

A facile model for the effect of uniform crystal bending on transmission electron diffraction intensity data was given by Cowley¹⁹ and later applied by him²⁰ to layered silicate structures. In this model, the Patterson function of the crystal is modulated by the bending process according to an exponential term which increasingly diminishes the weight of Patterson vectors as their components parallel to the incident beam become large. The smearing of Patterson peaks by bending is given by the Gaussian distribution function¹⁹ which is then convoluted with the Patterson function, i.e.

$$q_i(p, r_i) = \frac{\sigma}{r_i \sqrt{\pi}} \exp(-\sigma^2 p^2 / r_i^2).$$

Here p is the distance measured along the arc, r_i is the length of the Patterson vector and σ is a constant describing the amount of bending. If the half width of the distribution is supposed to be the limit of arcing, then, since p/r_i is α , the amount of bending in radians, $\sigma = \alpha^{-1}$.

The Fourier transform of the Patterson function is the intensity of the diffraction pattern. Thus

$$I(\underline{s}) = \sum_i W_i(\underline{s}) \cdot \cos(2\pi i r_i \cdot \underline{s}) \exp - \left[\frac{\pi^2}{\sigma^2} s^2 z_i^2 \right] \quad (1)$$

describes how the diffracted intensity is modified by the bending. $W_i(\underline{s})$ is the Fourier transform of the Patterson peak $w_i(r)$, \underline{s} is the reciprocal vector and $s = d^*$ is its magnitude. The z -component (along the beam) of the Patterson vector r_i is given by $z_i = r_i \cos \alpha$.

An estimate for the maximum thickness for coherent scattering of the crystal for a given bend σ at a specified locus in reciprocal space defined by s is given by

$$z_0 = (\sigma/\pi s). \quad (2)$$

Patterson vectors with z -components beyond this value are presumed not to contribute significantly to the intensity of the zone. It should be noted especially that this z_0 is not uniform in reciprocal space for a given bend, but rather is inversely proportional to s .

Results

With the dependence of z_0 upon d^* , then, for a slightly bent crystal, one should encounter a distribution of intensities at low angle which corresponds to the whole unit cell, while that at high angle will

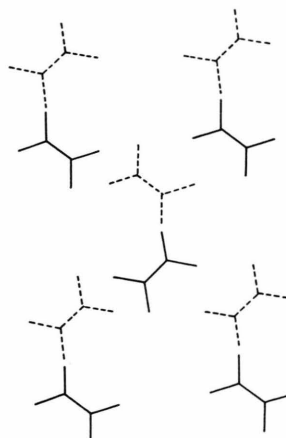


Fig. 1. The (001) projection of the n-hexatriacontane crystal structure after Teare (Reference 7). The solid line and dotted line figures represent respective monolayers of paraffin chains. In the diffraction experiments the incident beam is normal to this {001} face of the crystal or parallel to the long chain axes.

correspond to a portion (or a sum of portions) of the unit cell. The case of the orthorhombic paraffin structure (Fig. 1) provides a very simple test of this model. Most of the intensity of a given reflection is due either to the unit cell of two contiguous, displaced monolayers or to a monolayer alone, because all atoms of a chain are eclipsed in this projection. Thus, for a slightly bent crystal of this kind, the low angle data should be from the whole unit cell and the high angle data should be from the monolayer.

Because of the apparent layer rigidity imposed by a ring moiety in cyclitol analogs of diglycerides¹⁵, electron diffraction patterns from multilayer crystals, while giving the typical unit cell spacings of a 0_{\perp} subcell (001) projection, have a salient difference in the intensity distribution when compared to ($hk0$) patterns from monolayers. Here $|I_{110}| < |I_{200}|$ instead of $|I_{110}| \cong |I_{200}|$, as is illustrated in Figure 2. The same situation also was encountered occasionally when diffraction patterns were obtained in high voltage experiments on multilayer crystals of n-hexatriacontane²¹.

A test of this $\sin \theta/\lambda$ dependence of bend effects on the diffraction pattern was made with some of the diffraction patterns from the paraffin. Using an arbitrary cutoff of $s = 0.40 \text{ \AA}^{-1}$, structure factors corresponding to the whole unit cell or to the subcell

were both compared to the observed structure factors for zones below and above this cutoff point in reciprocal space. The results are shown in Figs. 3 and 4 for two accelerating voltages (400 kV and 800 kV) and are consistent with the bending model proposed by Cowley^{19,20}. Low angle data agree best with the unit cell phasing model and high angle data are most congruent with scattering from the subcell.

Discussion

Now that it is ascertained that the distribution of intensity in a bent paraffin crystal conforms to the predicted variation with $\sin \theta/\lambda$, the next task is to estimate the amount of crystal bending. In earlier determinations on silicates¹⁹, only the bending within the coherence width of the incident beam was considered. This model implies that the average change in crystal orientation is included within this region i.e. the crystal surface is undulated. However, for paraffinic materials, well-defined bend contours are often observed, denoting a uniform band of the crystal surface well outside the limits of the beam coherence width (which for our operation was about 250 \AA). The Patterson distortion must be considered for the width of this uniformly bent crystal region, and if there are sets of parallel bend contours due to the same Bragg reflection, this width is defined as the distance between them.

To estimate the amount of crystal bending, we assume the value of z_0 in (2) to be 47.6 \AA at $s = 0.40 \text{ \AA}^{-1}$, the thickness of a n-hexatriacontane monolayer. Thus, from (2) $\alpha = \sigma^{-1} = 0.02 \text{ rad} = 1.0^\circ$, which is small. If this represents a uniform curvature over a typical 5μ wide crystal, the radius of curvature would be 250μ . Diffraction contrast micrographs also confirm the crystals exhibiting these diffraction effects to be only very slightly bent (Figure 5). Thus, with only this perturbation to a crystal having a long unit cell axis parallel to the incident beam, a very significant impediment to *ab initio* crystal structure analysis is given which is independent of dynamical effects.

In this model we are making the approximation that the two Patterson functions represent a constant z_0 in the regions $s = 0 \rightarrow 0.40 \text{ \AA}^{-1}$ and $s = 0.40 \rightarrow 1.0 \text{ \AA}^{-1}$, as did Cowley and Goswani²⁰ in their assessment of electron diffraction from bent montmorillonite foils. Considering the average s for the two regions; i.e. 0.20 \AA^{-1} and 0.70 \AA^{-1} then the



Fig. 2. An $hk0$ electron diffraction pattern from a multilayer crystal of DL-(1,2/3)-1,2-di-O-palmitoylcyclopentane-1,2,3-triol. The intensity distribution of the diffraction pattern can be compared to a monolayer type pattern by reference to Fig. 2 of Reference 6. Accelerating voltage: 100 kV. Subcell axes: $a_s \cong 7.5 \text{ \AA}$, $b_s \cong 5.0 \text{ \AA}$.

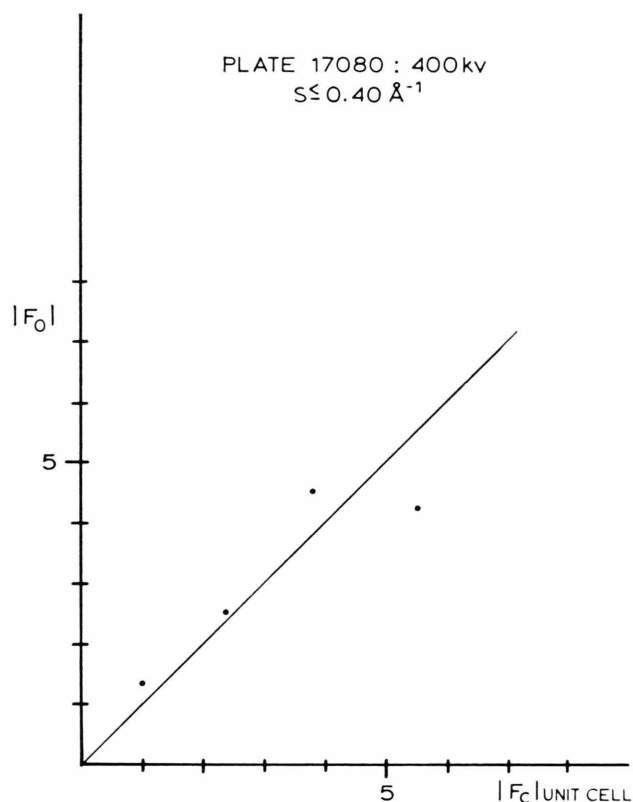


Fig. 3a

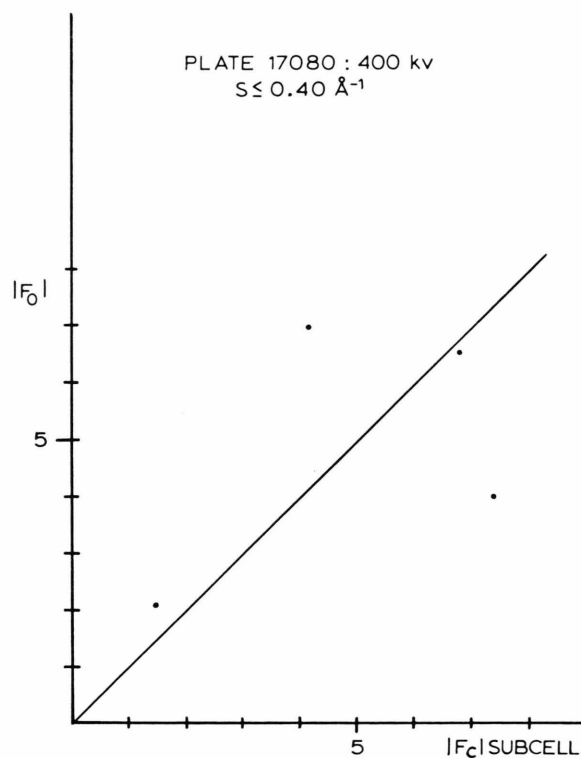


Fig. 3a

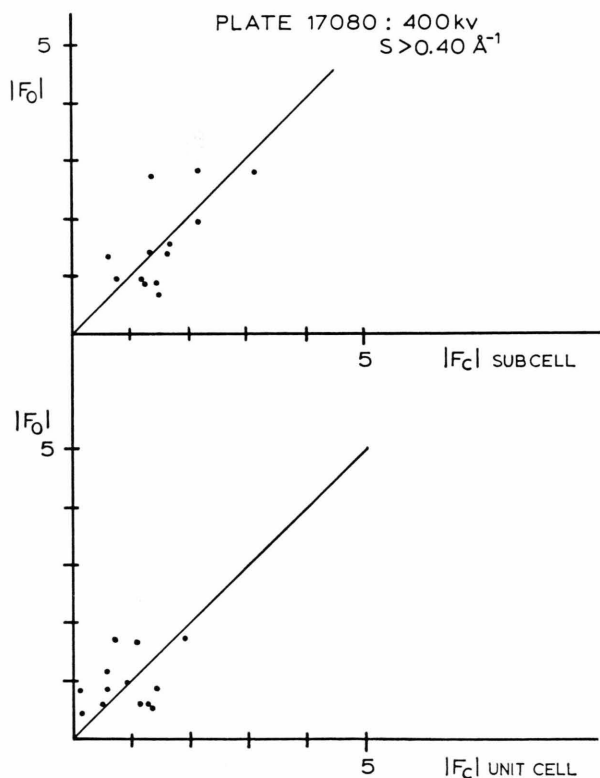


Fig. 3b

Fig. 3. (a) Cross-correlation comparison of low angle data ($s \leq 0.40 \text{ \AA}^{-1}$) from slightly bent n-hexatriacontane crystal (accelerating voltage: 400 kV) to calculated kinematical structure factors from the unit cell (bilayer of Fig. 1) or the subcell (monolayer). The best correlation is with the unit cell data.

(b) Cross correlation comparison of 400 kV high angle paraffin diffraction data ($s > 0.40 \text{ \AA}^{-1}$) to calculated kinematical structure factor from the bilayer unit cell and to the subcell. Conventional residuals $R = \frac{\sum \|F_0 - k F_c\|}{\sum |F_0|}$ are 0.52 for observed data to the unit cell and 0.29 for observed data to the subcell. In both (a) and (b) data scaled such that $\sum |F_0| = \sum |F_c|$.

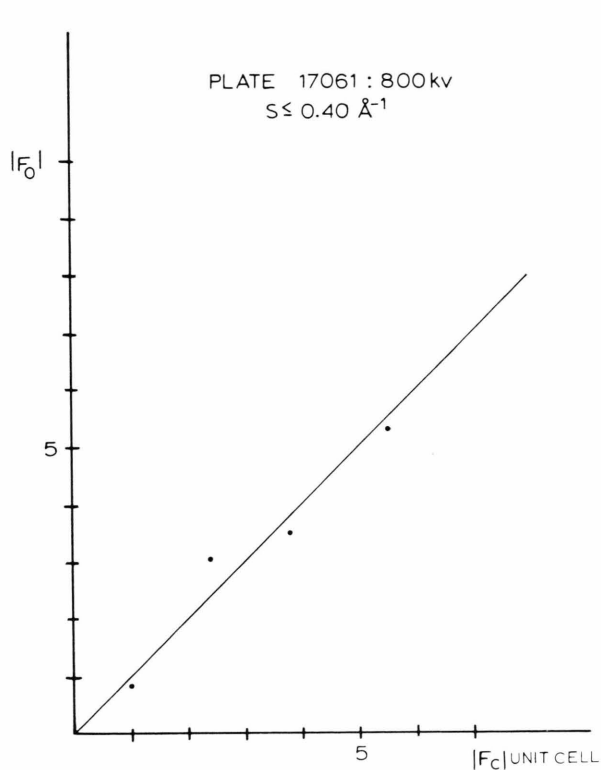


Fig. 4a

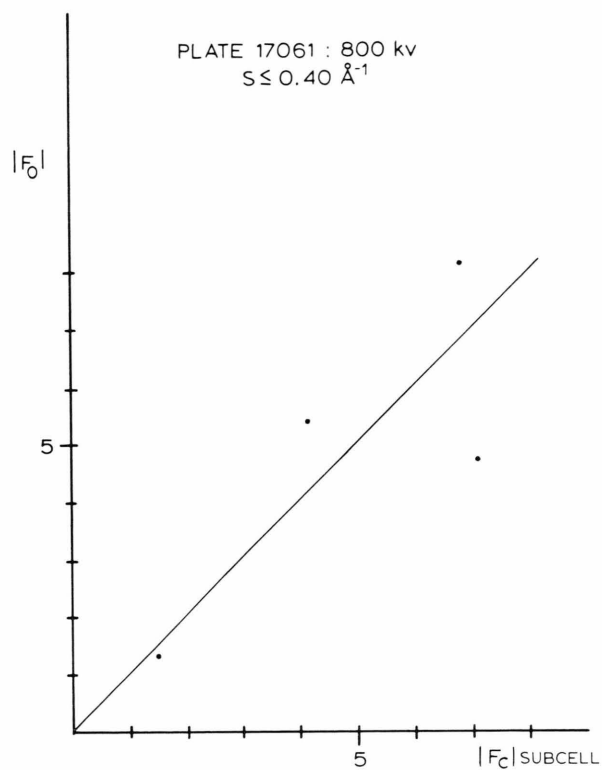


Fig. 4 a

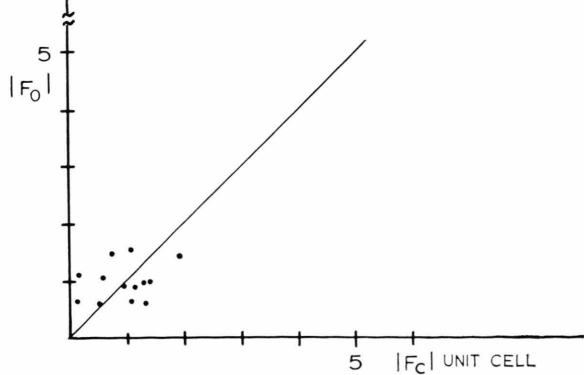
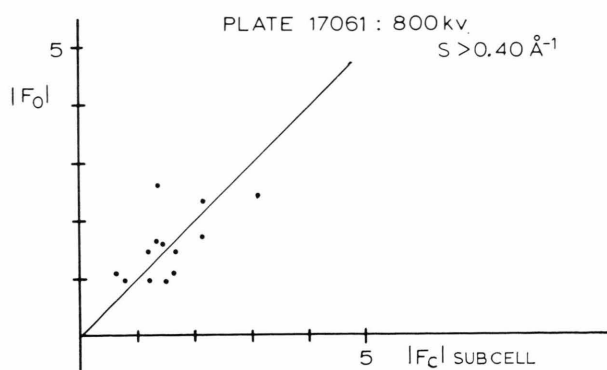


Fig. 4b

Fig. 4. Same caption as Fig. 2 except accelerating voltage is 800 kV. Also for part (b) the residuals for comparison of observed data to calculated data from the unit cell and subcell are, respectively, 0.45 and 0.27.



Fig. 5. Bright field diffraction contrast image of the crystal used to obtain the diffraction pattern in Fig. 2, the large dark area on the crystal surface, due to parts of the crystal in perfect Bragg incidence, indicate the crystal to be only slightly bent.

Patterson functions respectively represent $z_0 = 95 \text{ \AA}$, nearly the width of the whole unit cell, and $z_0 = 27.2 \text{ \AA}$, about half the length of one chain in a monolayer. These Pattersons will respectively represent the diffraction from a whole unit cell and from the subcell, as is observed.

Rigorous calculations would actually account for the strict dependence of z_0 on s as shown in Figure 6. Since the whole treatment assumes kinematical diffraction, it is probably not worth going to these lengths. We have already shown that n-beam dynamical effects are also important for thin paraffinic crystals⁶, even out to high accelerating voltages²¹. In fact, the cross-correlations of high angle data to calculated subcell structure factors in Figs. 3 and 4 reveal one observed reflection in particular to be uncorrelated to the calculated kinematical value. This is the (220) intensity which is very strongly affected by n-beam interactions^{6, 21}.

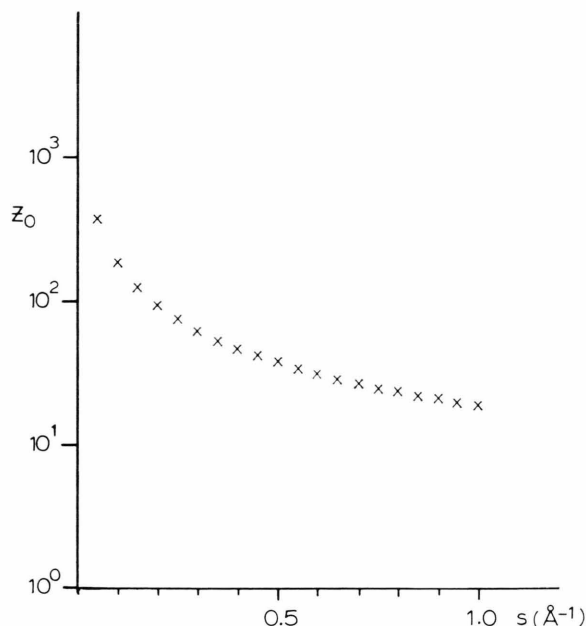


Fig. 6. The dependence of maximum contributing Patterson vector component z (Eq. (2)) on reciprocal distance s for a crystal bend of 1.0° .

Another possible error results from the fact that n-paraffin crystals grow around screw dislocations parallel to [001] and have successive layers of surface area smaller than the underlying layers²². Thus, diffraction from a bilayer may include small regions where the beam samples only the monolayer fringe. However, these experimental data do demonstrate, in fact, the expected diffraction from a slightly bent crystal.

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