lem of finding whether and how atoms in the more complex structures can shift without interchange to their sites in the product structure, although rather complex, is fundamentally mathematical.

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On the extension of the crystal lattice along the chain direction in polyethylene single crystals from X-ray line widths

The breadth of the 002 X-ray reflection of polyethylene should provide a measure of the extension of the crystal lattice along the chain direction. Once in possession of this information, the total layer thickness of a chain-folded single crystal lamella provided by low-angle scattering data should be subdivisible into a crystalline core and fold surface region, information much required in polymer crystal studies. Earlier work in this field relating to drawn fibres [1] and single crystals [2] established a correlation between the low-angle X-ray spacing and the crystal size deduced from the 002 reflection where the latter was somewhat smaller than the full periodicity. Some years ago we embarked on a programme of work along these lines in aid of wide ranging studies on the nature of the fold surface. One byproduct, the detection of a small negative thermal expansion coefficient along the chain direction has already been reported [3]. The main body of the work, while unpublished, has formed the basis of further investigations commenced in these laboratories by Windle [4]. As because of this the reporting of the original work is no longer opportune at this date, there is nevertheless, one remaining aspect which may have noteworthy implications and is not included elsewhere. The purpose of the present note is to place this on record.

The X-ray work was performed on mats of single crystals obtained at 70° C from xylene with a long spacing of 109 Å. The mats were exceptionally well oriented, on the standards normally achievable on such samples, with the chains perpendicular to the mat surface (Fig. 1). This degree of orientation was achieved through forming very thin layers at a time by sedimentation from suspension and by building up the required mat thickness by plying new layers onto those already prepared. These mats proved to be prerequisites not only for the present work but also for all further studies on the 002 line width

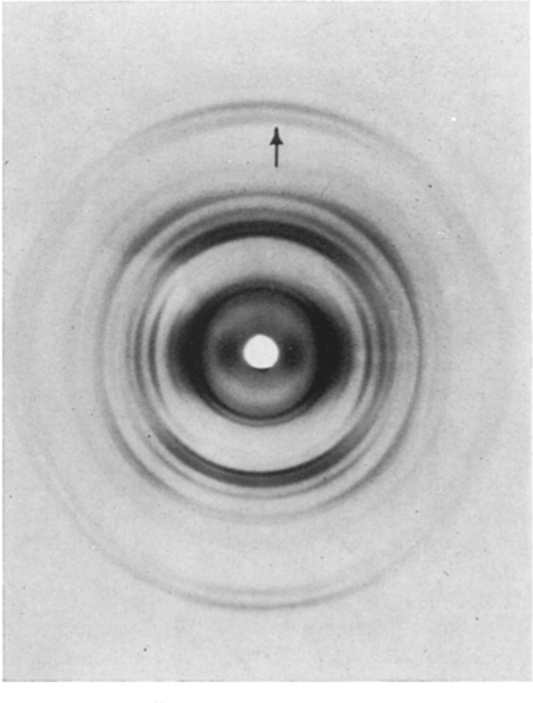

Figure 1 X-ray diffraction pattern of a typical sedimented mat of polyethylene single crystals such as used for the present study. The beam is parallel to the mat surface which itself is horizontal. The 002 reflection is marked by an arrow. (Photograph by A. H. Windle.)

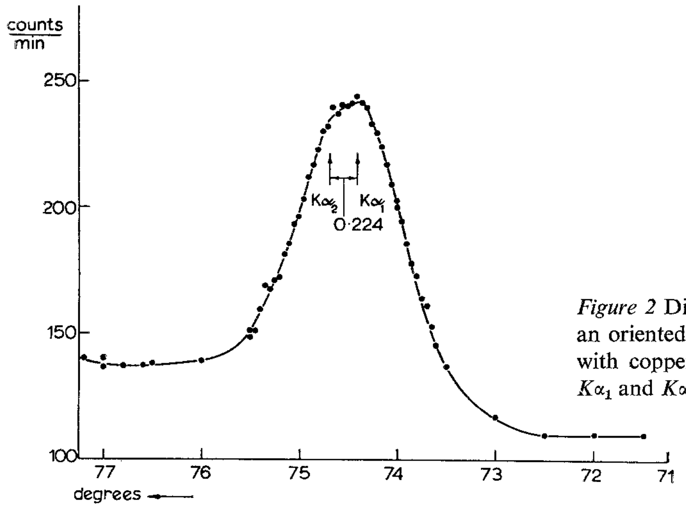

Figure 2 Diffractometer trace of the 002 reflection from an oriented mat of polyethylene single crystals obtained with copper $K\alpha$ radiation. The broadening due to the $K\alpha_1$ and $K\alpha_2$ doublet is indicated.

which followed [4]. The samples were subjected to heat-treatment in order to increase their fold period. This was achieved both by varying the annealing temperature and by varying annealing time at a given temperature. The mats thus prepared were then examined by X-rays.

The line profile of the 002 reflection was recorded by a counter goniometer in reflection setting. The 002 reflection is intrinsically weak but is the only one in polyethylene which can be used to assess the extension of the crystal along the chain direction directly. Thanks to the relatively high degree of the orientation, the reflection was appreciably intensified along the mat normal direction. This, together with collecting large numbers of counts at each angular position, enabled the 002 reflection to be recorded as a clearly resolved sizeable peak (Fig. 2). Further details will be given elsewhere [4]. Here it will only be stated that the breadth attributable to the polyethylene was assessed by comparison with a powdered elementary silicon standard (particle size ~ 10 μm), which conveniently gave a reflection, 311, at the same angular range (Fig. 3). The two peaks in Fig. 3 are due to $K\alpha_1$ and $K\alpha_2$ of the same reflection. The breadth of the individual silicon line is 0.063°. Accordingly, the main extraneous source of broadening for the polyethylene peak is due to the α_1 and α_2 doublet, the separation of which is 0.234°. Next to this the instrumental broadening is insignificant. The half widths measured from traces as in Fig. 1 were corrected for the $K\alpha$ doublet by the procedure of Jones [5]. (The different absorptions of polyethylene and of silicon were not taken into account at this stage. This has been done in subsequent work [4] and it was found that it does not affect the conclusions of the present study.)

The crystal thickness corresponding to the half width thus determined was calculated from first principles, namely from the broadening of the principal maximum of the one-dimensional interference function:

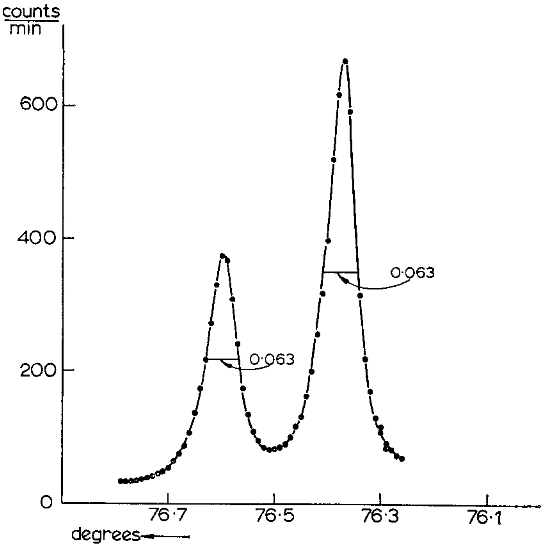

Figure 3 Diffractometer trace of the 311 reflection of powdered elementary silicon obtained under conditions identical to those in Fig. 2. Note the more extended scale along the abscissa. The two peaks correspond to $K\alpha_1$ and $K\alpha_2$.

$$I = \frac{\sin^2 \pi N \xi}{\sin^2 \pi \xi}$$

which describes the intensity distribution along a principal reciprocal lattice direction (ξ is the multiplier of the unit vector along this direction and N represents the number of repeating units, When expressing the corresponding crystal length (D^{W}) in terms of angular variation we get

$$D^{\mathrm{W}} = \frac{0.89}{b \cos \theta_{\mathrm{B}}}$$

where b is the peak half width in terms of the diffraction angle $2\theta_{\mathrm{B}}$ expressed in radians; $\lambda =$ wavelength; θ_{B} = the Bragg angle. This of course is the familiar Scherrer formula with the numerical constant 0.89. This is the constant obtained by Bragg [6] in the simplest derivation of the Scherrer formula where the crystal surfaces and the planes considered are parallel, and no further note is taken of complications arising from the actual shape of the crystal. In fact our derivation is identical to Bragg's. However, in view of the one-dimensional nature of the problem here this is not a simplification but the true representation of the actual situation. The exact assignment of the numerical constant is not a major practical (as opposed to theoretical) issue in line-broadening studies, where it is usually taken to equal unity. In our case, however, the fact that it is not 1.00 but 0.89 is of physical consequence as it is this number which defines the slope of the line in Fig. 4 (see below) which is a measure of the crystallinity deficiency, and even small differences in this slope may greatly affect the conclusions to be drawn.

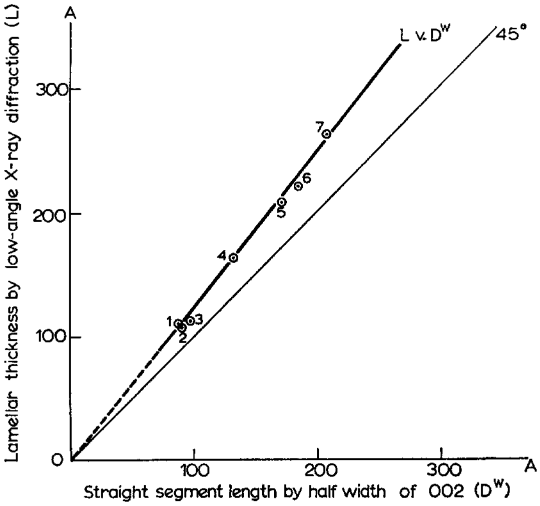

Figure 4 Crystal thickness as measured from the 002 X-ray line width (D^{W}) plotted against the layer thickness (L) as obtained from low-angle X-ray scattering for polyethylene crystals of different long periods. The particulars are given below.

Point no.	Annealing temp. (°C)	Annealing time (h)
1	unannealed	
2	80	2
3	100	2
4	120	2
5	120	24
6	125	½
7	125	24

The above evaluation of the broadening of the reflection relies on the effect of limited crystal size, the effect due to paracrystalline distortion being ignored. We consider this as a justified approximation in view of the fact that the lattice periodicity along c is defined by valence bonds which should be constant throughout. This *a priori* expectation has been fully brought out by explicit analysis of the broadening of hkl reflections (other than $00l$), such as present in several orders, in the work of Hosemann and co-workers [7] who conclude that lattice distortions along c are negligible.

Fig. 4 shows the results relevant for the present note. The following features are to be noted: the crystal thickness defined by line broadening (D^{W}) increases linearly with increasing long spacing (L). L is always larger than D^{W} (L versus D^{W} line is above the 45° line), thus L-D^{W} is positive and also increases linearly. Further, the L versus D^{W} line extrapolates to $D^{\mathrm{W}} = 0$ for $L = 0$. This means that the coherently diffracting crystal is thinner than the lamellar periodicity which, of course, might have been expected. What is new, however, is the finding that (L-D^{W}), which is usually referred to as a non-crystalline, or amorphous surface layer, is always a closely fixed fraction of the total layer thickness. As a sequel to this, crystallinity should be independent of the long period, or if there is a substantial variation, the amorphous material responsible for the variation must be located elsewhere than along the lamellar surface. Inspection of Fig. 4 will reveal that (L-D^{W}) thus determined depends only on L and not on the conditions under which this L value was achieved. In particular, (L-D^{W}) is not uniquely determined by the temperature of the annealing – a proposition featuring in the literature [8] – as comparison of points 4 and 5 and of points 6 and 7 will show. Both of the above inferences are clearly in conflict with existing views based on investigations along different lines. Without independent crystallinity measurements, not carried out at the time of the X-ray studies, the issue cannot be profitably discussed any further. Nevertheless, in the conviction that the results are real we thought it appropriate to place them on record.

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Comment on a paper by Ziniker, Rusin and Stoebe

In a recent study of thermoluminescent peaks in Al_2O_3, MgO and LiF (TLD-100) Ziniker *et al.* [6] discuss the variation in reported values of the activation energies obtained for each peak. They conclude that the energies obtained are related to the method of measurement, the most reliable for a first order peak being the isothermal decay method.

Whilst studying the thermoluminescent peaks in a quartz which had been used for archaeological dating (Aitken and Fleming, [1]), I found a similar discrepancy and was able to show that it could be attributed to the occurrence of thermal quenching [5]. Three methods of measuring the activation energy E for the 325° C peak were used:

(a) the isothermal decay method which gave $E = 1.7 \pm 0.1$ eV

(b) Hoogenstraaten's method [5], where the variation of peak temperature T_m with heating rate β is obtained and the slope of log T_m^2/β versus T_m^{-1} yielded $E = 1.69 \pm 0.02$ eV.

(c) the initial rise method which gave $E = 1.05 \pm 0.03$ eV.

Methods (a) and (b) can only be applied to a first order peak; the initial rise method is generally accepted to be the most widely applicable since the initial part of the glow curve is independent of the kinetics of trap emptying (Kelly and Bräunlich, [4]). This method assumes that the initial part of the glow curve obeys the relation

$$I = Cf(n)\exp(-E/kT)$$

where $f(n)$ represents the kinetics of trap emptying and C is related to the luminescence efficiency. Hence this method relies on the constancy of the luminescence efficiency, a point which is usually overlooked.

Now the luminescence efficiency of a phosphor may be expressed as the ratio

$$\eta(T) = \frac{P_r}{P_r + P_{nr}}$$

where P_r is the probability of radiative emission, assumed independent of temperature, and P_{nr} is the probability of a non-radiative transition, which rises with increasing temperature. The resulting decrease of η with temperature rise is known as thermal quenching (Curie).

If only one type of luminescence centre is present we have

$$\eta(T) = \frac{1}{1 + K\exp(-W/kT)}$$

where W is an energy depth characterizing the non-radiative process and K is a constant, and thus for $K\exp(-W/kT) \gg 1$, $\eta(T) \approx K^{-1}$