Fourier-transform analysis of models for the orthorhombic crystal phase of the alternating ethylene–tetrafluoroethylene copolymer

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Disorder in the relative positions of neighbouring chains in the orthorhombic form of ethylene–tetrafluoroethylene (ETFE), which has a polyethylene-like packing in the projection along the *c* axis, has been studied through a comparison of the observed diffraction profiles on the layer lines with the calculated Fourier transforms of models. The analysis suggests that, along the *c* axis, integral translational displacements of *c*/2 are present in the crystals owing to the inclusion of defects in the alternation of the comonomers. On the basis of the analysis, an approximate evaluation of the amount of constitutional defects included in this crystal structure has been attempted. In the crystalline phase, associated with this kind of constitutional disorder, large nearly random translational displacements are present; correlations in relative positions do not go much beyond the first neighbours.

(Keywords: modelling; crystal structure; copolymer; ethylene; tetrafluoroethylene; X-ray diffraction)

INTRODUCTION

Several X-ray diffraction studies on the alternating ethylene–tetrafluoroethylene (ETFE) copolymer have been reported in the literature[1–4]. The ETFE copolymer shows at low temperatures ($T<0°C$) an orthorhombic crystal structure[1,2], which gradually and reversibly, in a large temperature range (0–100°C), is transformed into a hexagonal mesophase[3,5].

Detailed structural studies of the orthorhombic crystal form have already been reported[1,2]. As suggested by Tanigami *et al.*[2], the unit cell has $a=8.57$ Å, $b=5.60$ Å, $c=5.04$ Å, the conformation of the chain is *trans*-planar and the packing of the chains in the projection along the *c* axis is similar to that of polyethylene. (In order to account for the position of the very broad intensity maximum on the first layer line, Tanigami *et al.* formally suggest a unit cell with a double value for the *b* axis, although they assert that the unit cell should be considered just as a convenience derived for indexing the reflections and it would also be reasonable for the subcell to be regarded as a unit cell and the first layer line reflection to be treated as special due to the irregularity[2].)

The presence of irregularities in the comonomer alternation of the chains prevented those authors[2] undertaking a detailed analysis of the three-dimensional crystal structure. The three-dimensional model proposed for consideration arises mainly from the energy analysis of Farmer and Lando[6], and no experimental support is added.

In this paper, by a comparison of the observed diffraction profiles on the layer lines with the calculated Fourier transforms of models, the possible correlations between the chains in the orthorhombic form of ETFE (besides the polyethylene-like packing in the projection along the *c* axis) have been studied.

On the basis of this comparison, an approximate evaluation of the amount of constitutional defects included in the crystal structure has also been attempted.

EXPERIMENTAL PART AND CALCULATION METHOD

The ETFE fibres were supplied by Montefluos S.p.A. The X-ray diffraction patterns for stretched fibres were obtained by using a Nonius automatic X-ray diffractometer with Ni-filtered Cu K_α radiation. The Lorentz polarization (*LP*) correction was applied ($LP=(1+\cos^2 2\theta)/\sin 2\theta$) for all the layer lines according to the diffraction geometry.

The corrected diffraction intensities (I) are reported in *Figure 1a* for the equator and for the three layer lines, as a function of the reciprocal lattice coordinate ξ. The reported results are in good agreement with the data by Wilson and Starkweather[1]. For the same layer lines, the diffraction intensities (I') integrated over the reciprocal cylindrical coordinate φ, obtained by multiplying the measured intensity I by ξ, are reported in *Figure 1b*. The procedure for the calculations of the Fourier transforms is that already used for the mesomorphic form of isotactic polypropylene[7] and the disordered phases of polytetrafluoroethylene (PTFE)[8,9].

The square of the modulus ($|F(\xi,\varphi,\zeta)|^2$) of the Fourier transform was calculated for each model as a function of the cylindrical reciprocal lattice coordinates ξ and ζ for a fixed value of the third coordinate φ. The mean value of $|F(\xi,\varphi,\zeta)|^2$ with respect to φ, henceforth indicated $\langle|F(\xi,\zeta)|^2\rangle$, was obtained by averaging the results for 90

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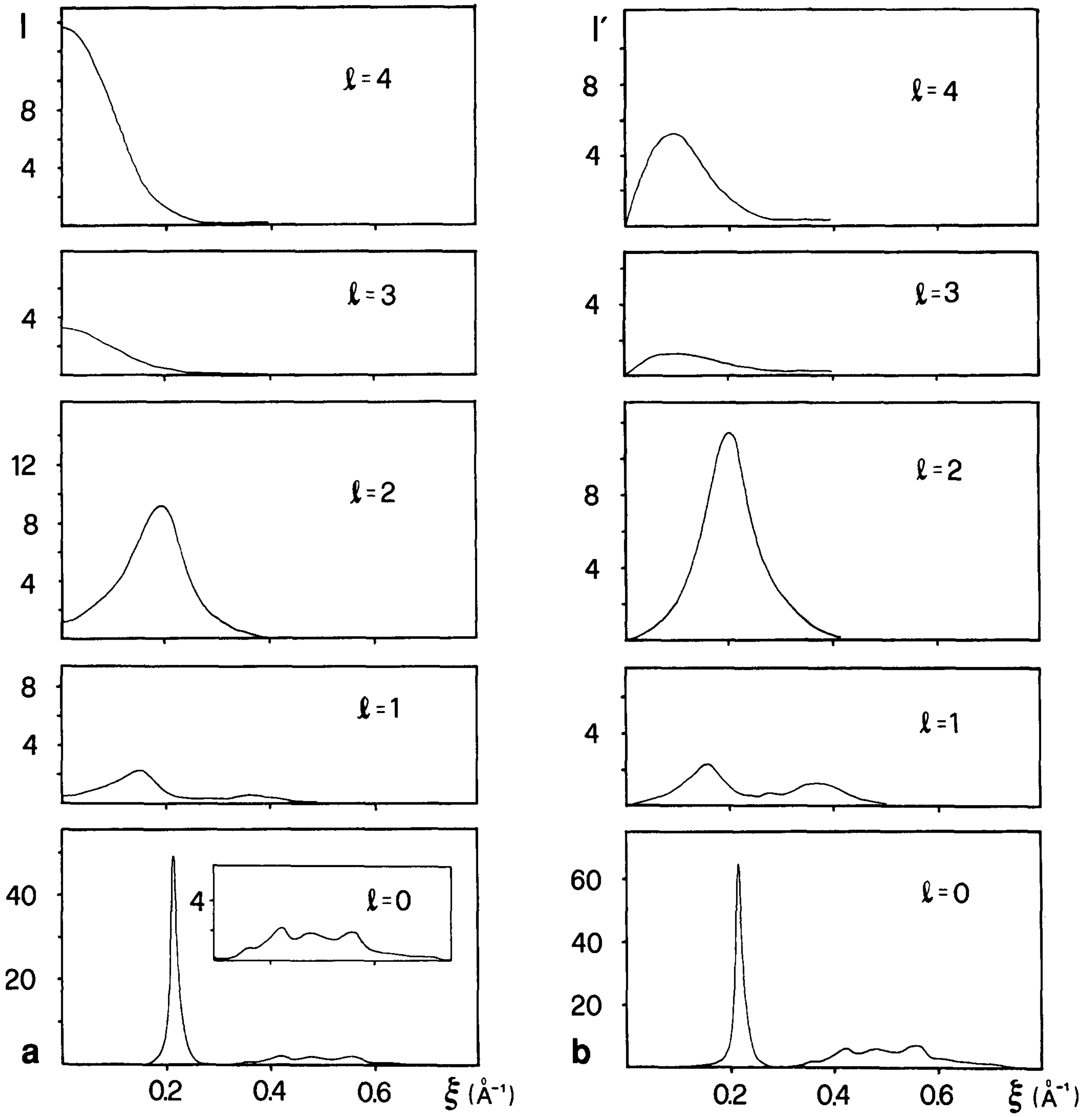

Figure 1 Experimental X-ray diffraction patterns of an ETFE fibre, for the equatorial and the four layer lines: (a) measured intensities I as a function of the reciprocal lattice coordinate ξ; (b) diffraction intensities I' integrated over the reciprocal cylindrical coordinate φ, obtained by multiplying the measured intensity I by ξ, as a function of the reciprocal lattice coordinate ξ (Å^{-1})

different fixed rotations of the models around an axis parallel to the chain axes. The integral:

$$I(\xi,\zeta)=\int_0^{2\pi}|F(\xi,\varphi,\zeta)|^2\,\mathrm{d}\varphi$$

which is the quantity to be compared with experimental data such as those of *Figure 1b*, is then obtained through multiplication of $\langle|F(\xi,\zeta)|^2\rangle$ by $2\pi\xi$.

The calculated intensities $I(\xi,\zeta)$ were multiplied by a thermal factor of the kind:

$$\exp(-\tfrac{1}{2}B_\xi\xi^2)\exp(-\tfrac{1}{2}B_\zeta\zeta^2)$$

The B_ζ parameter has been fixed equal to zero by an approximate optimization of the intensities on the layer lines, for the case of an isolated chain. In particular, since in the chains constitutional defects (errors in the alternation of the comonomers) are present, which also in small quantities produce a strong reduction of the diffracted intensities on the odd layer lines, the optimization of B_ζ was based on the ratio of the maximum intensities on the second and on the fourth layer lines, which instead is substantially independent of this kind of defect (see next section). The B_ξ parameter (12 Å^2) has been chosen by optimization of the intensity of the reflections at low and high 2θ values on the first layer line, again for the case of an isolated chain.

The diffracted intensity along ζ, at $\xi=0$, is similar to those reported in refs. 1 and 2. The broadness along ζ of the meridional diffraction of the fourth layer line indicates average coherent length along the chain axis of the order of 50 Å.

On this basis, our calculations of Fourier transform were then performed on chains or bundles of parallel chains, with axes of nearly 50 Å (20 monomer units in a *trans*-planar conformation). The diameter of the bundles was assumed to be nearly 35 Å on the basis of the broadening of the most intense reflection on the equator. This does not exclude the possibility that the bundles may be larger, and even much larger, but according to the wide-angle X-ray diffraction data, any correlation for the relative positions of the atoms is lost at a distance not far from 35 Å.

FOURIER-TRANSFORM CALCULATIONS AND DISCUSSION

Owing to the broadness of the diffracted intensities on the layer lines (*Figure 1b*), it is particularly convenient to start the analysis with the calculation of the Fourier transforms of models of isolated chains.

The Fourier transform on the non-equatorial layer lines for a perfectly alternating ETFE chain is shown in *Figure 2*. It is apparent that the positions of the intensity maxima on the layer lines are in fair agreement with the experimental data (cf. *Figure 2* full curve and *Figure 1b*) while the intensities are not. An appropriate value of B_ζ (taken as 0 in the calculations shown) adjusts the ratio between the values of the intensity maxima on the second and fourth layer lines as well as the ratio between the values of the intensity maxima on the first and third layer lines to the experimental results. However, the calculated values of the intensities are too high for the odd layer lines (in particular, the ratio between the calculated intensity maxima of the second and first layer lines is 1.6, while the experimental value is close to 4.3).

The intensities on the odd layer lines in the calculated patterns can be easily reduced (leaving unaltered the intensities on the even layer lines) by introducing in the isolated chain some irregularities in comonomer alternation. Such irregularities disrupt the periodicity of 5.04 Å, corresponding to the regular alternation of ethylene and tetrafluoroethylene units, while the periodic repetition of the carbon atoms of the backbone, which is one half of the previous one (2.52 Å), remains unchanged.

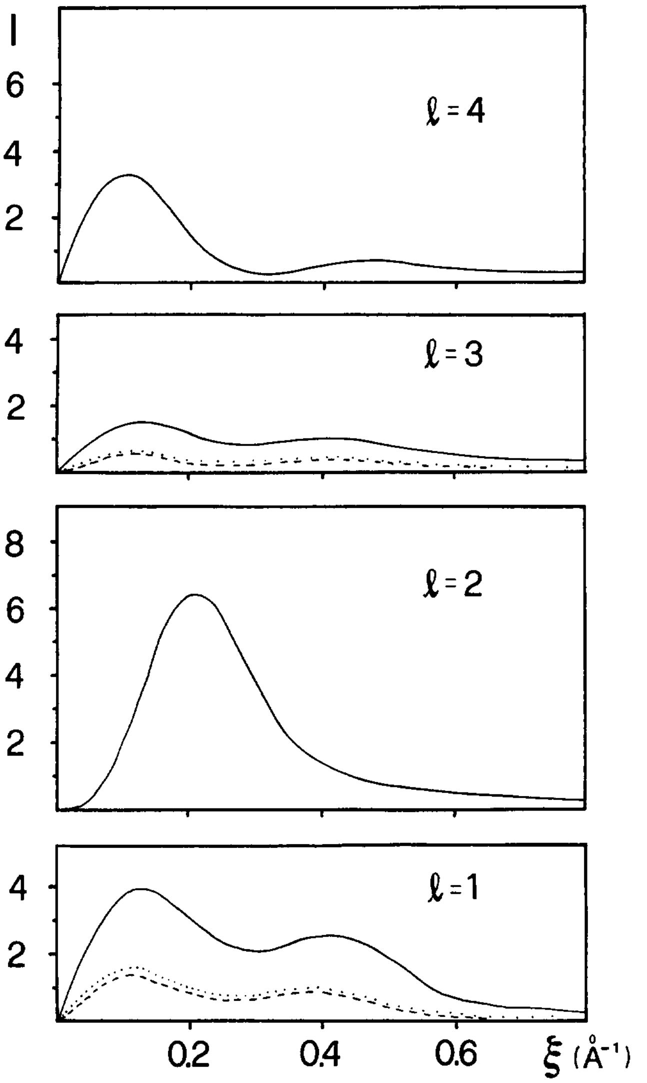

Figure 2 Results of the calculations of Fourier transforms on the layer lines for zig-zag planar isolated chains of ETFE. For the odd layer lines: (——) regular alternation of comonomer; (– – –) one constitutional defect per 15 monomer units; (· · · · ·) one constitutional defect per 20 monomer units

(The nearly complete independence of the errors in the comonomer sequence of the transform on the even layer lines can also be derived by simple general considerations. Consider a row of molecular units of two kinds, such units being displaced by amounts jc along z, with j integer (e.g. in our case $c=5.04$ Å). Suppose that the generic nth atom of the molecular unit of kind A (e.g. a sequence ethylene–tetrafluoroethylene) has fractional coordinates $[x_n, y_n, z_n]$, while the corresponding atom of the molecular unit of kind B (e.g. a sequence tetrafluoroethylene–ethylene) has fractional coordinates $[x_n, y_n, z_n+\frac{1}{2}]$ or $[x_n, y_n, z_n-\frac{1}{2}]$. The contribution to the Fourier transform of the atom n of the unit of kind A can be written as:

$$G_A^n(h,k,l) = f_n \exp[2\pi i(hx_n + ky_n + lz_n)]$$

while the contribution of the corresponding atom n of the unit of kind B is:

$$G_B^n(h,k,l) = f_n \exp[2\pi i(hx_n + ky_n + lz_n)] \exp(2\pi i l/2)$$

or

$$G_B^n(h,k,l) = f_n \exp[2\pi i(hx_n + ky_n + lz_n)] \exp(-2\pi i l/2)$$

Then:

$$G_B^n = G_A^n \quad \text{for } l \text{ even}$$

$$G_B^n = -G_A^n \quad \text{for } l \text{ odd}$$

In conclusion, units of kind A and B give the same contributions on the even layer lines but opposite contributions on the odd layer lines.)

The Fourier transform on the first and third layer lines for isolated chains with one defect (a pair of consecutive C_2F_4 units) per 20 and per 15 monomer units (averaged over 50 different calculations) are also reported in *Figure 2*. It is apparent by a comparison with the experimental pattern of *Figure 1b* that, according to the considered model (length of the chain of 50 Å), good agreement of the intensity ratios is reached for the case of one defect per 15–20 monomer units.

The comparison of these values of amounts of defects with the experimental values obtained for the whole polymer, on the basis of the elementary analysis (e.g. one defect per 10 monomer units[1]), is very difficult. In fact, the concentration of defects may be different in the crystalline and amorphous phases.

A closer comparison of the experimental patterns of *Figure 1b* with the calculated pattern of *Figure 2* shows that the distribution of intensity on the layer lines, along ξ, is sharper. In particular, the difference in sharpness is very small for the fourth layer line but increases on decreasing the number of the layer line.

This comparison suggests that translational displacements of the chains, in the direction of the chain axis, are not completely random. In fact, for these not completely random translational displacements, the intensity of the reflections remains unchanged on the equator while it should be reduced on all other layer lines by a factor that is proportional to the number of the layer line[10,11].

By calculations of Fourier transforms of bundles of chains, it is easy to show that any possible partial correlation along *c* between parallel chains has to be very local.

Let us consider, for instance, a bundle of perfectly alternating copolymer chains, packed in the projection along *c* as assumed by Tanigami *et al.*[2,3] on the basis of the energy calculation of Farmer and Lando[6], which is shown in *Figure 3*. The corresponding Fourier transform is shown in *Figure 4*. By a comparison with the experimental pattern of *Figure 1b*, a fair agreement is apparent only for the equatorial reflections. Particularly difficult to adjust is the strong disagreement on the first layer line. In fact, for the determined unit cell[2], no reflection corresponds to the observed maximum of intensity ($\xi = 0.154$ Å^{-1}).

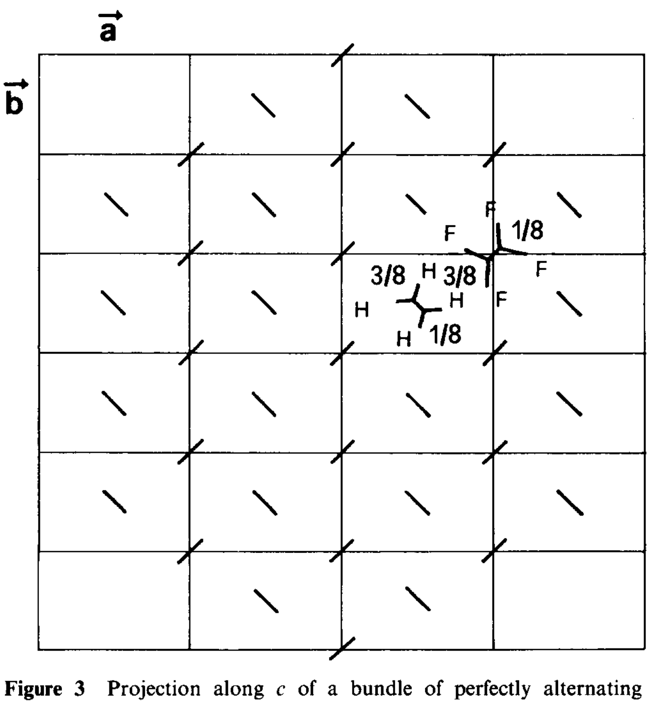

Figure 3 Projection along *c* of a bundle of perfectly alternating copolymer chains packed as assumed by Tanigami *et al.*[2,3]. Only for two chains are the projections of the hydrogen and fluorine atoms shown and the relative positions of the carbon atoms are indicated. For the remaining chains only the lines corresponding to the projections of the backbones are sketched

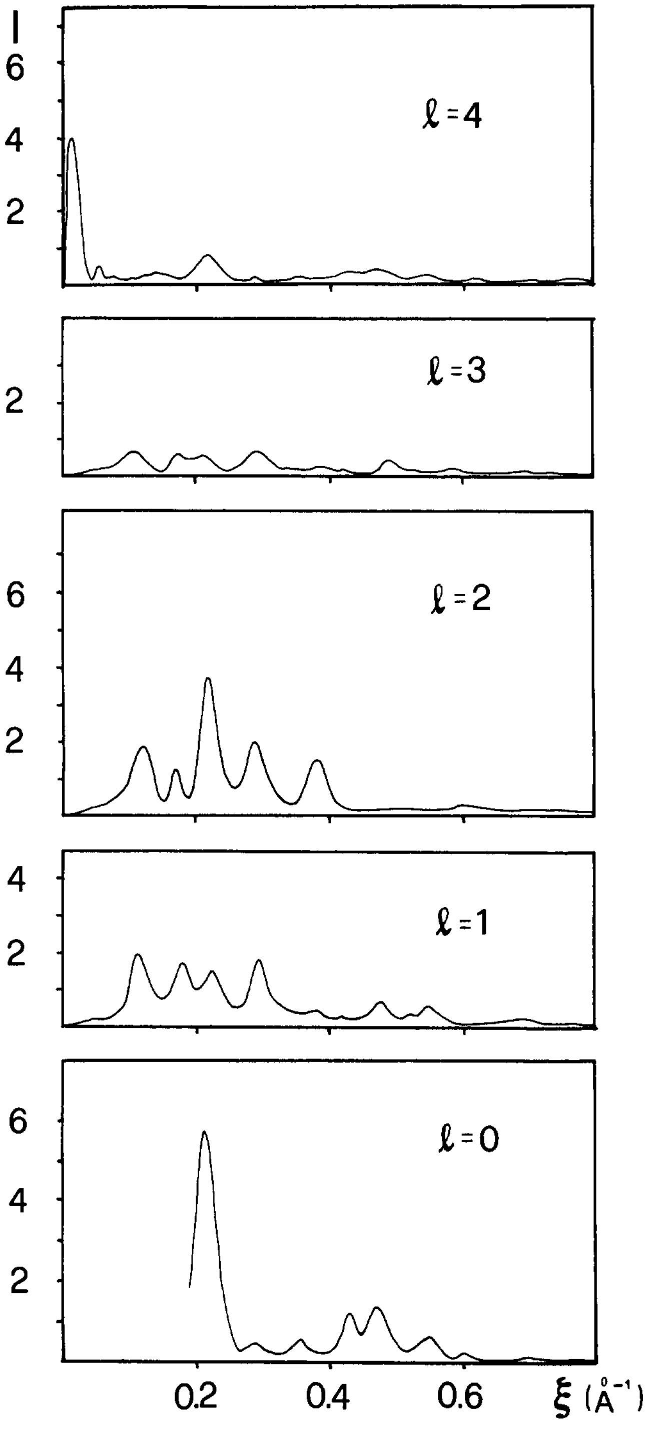

Figure 4 Results of the Fourier-transform calculations of the bundle shown in *Figure 3*

This aspect cannot be changed by introduction of a small rotational or translational displacement along the *c* axis as well as by considering the errors in the comonomer alternation. On the other hand, large rotational displacements are not suitable, since they are not compatible with the observation of reflections on the equator at high 2θ values.

The calculated pattern of the first layer line can be adjusted only by large translational displacements, which imply the presence of only very local correlations, at distances much smaller than the size of the considered bundles. The energetic feasibility of a nearly random translational disorder is consistent with the loose packing of the adjacent ETFE chains in the crystal structure[2]. In fact, also in the absence of any angular displacements of the chains with respect to the polyethylene-like arrangement, translational displacements along the *c* axis can be considered nearly completely free. In particular, for adjacent chains aligned along the $\boldsymbol{a}+\boldsymbol{b}$ direction, the F–F distances are never lower than 2.8 Å while the corresponding Van der Waals distance is 2.7 Å. For chains aligned along the $\boldsymbol{b}$ direction, the translational displacements along the *c* axis are slightly more restrained: with reference to the three-dimensional packing of *Figure 3*, the F–F distance becomes lower than 2.7 Å for displacements of nearly $\pm\frac{1}{4}c$ and as low as 2.3 Å for the maximum displacements of $\pm\frac{1}{2}c$.

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REFERENCES

1 Wilson, F. C. and Starkweather Jr., H. W. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 919
2 Tanigami, T., Yamaura, K., Matsuzawa, S., Ishikawa, M., Mizoguchi, K. and Miyasaka, K. *Polymer* 1986, **27**, 999
3 Tanigami, T., Yamaura, K., Matsuzawa, S., Ishikawa, M., Misoguchi, K. and Miyasaka, K. *Polymer* 1986, **27**, 1521
4 Scheerer, K. and Wilke, W. *Colloid Polym. Sci.* 1987, **265**, 206
5 Iuliano, M., De Rosa, C., Guerra, G., Petraccone, V. and Corradini, P. *Makromol. Chem.* 1989, **190**, 827
6 Farmer, B. L. and Lando, J. B. *J. Macromol. Sci.-Phys.* (*B*) 1975, **11**(1), 89
7 Corradini, P., De Rosa, C., Guerra, G. and Petraccone, V. *Macromolecules* 1986, **19**, 2699
8 Corradini, P., De Rosa, C., Guerra, G. and Petraccone, V. *Macromolecules* 1987, **20**, 3043
9 De Rosa, C., Guerra, G., Petraccone, V., Centore, R. and Corradini, P. *Macromolecules* 1988, **21**, 1174
10 Cochran, W., Crick, F. H. C. and Vand, V. *Acta Crystallogr.* 1952, **5**, 581
11 Clark, E. S. and Muus, L. T. *Z. Kristallogr.* 1962, **117**, 108