Intensity Function for Crystallites with Non-Integral Number of Unit Cells

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The X-ray intensity function for a crystallite with a non-integral number of unit cells is derived. This new intensity function is taken account of two practical problems. One is to exclude a particle scattering from crystallites and the other is to calculate the intensity for crystallites having the non-integral number of unit cells. We have applied this intensity function to the meridional reflections of nylon 12 in order to 'examine the origin of an anomalous shape of the 0 2 0 meridional reflection. It reveals that the non-integral part of unit cell does not play an important role in the abnormal profile of the 0 2 0 reflection.

1. INTRODUCTION

Polymer materials consist of very small crystallites and the surrounding noncrystalline substance. When we investigate the structure of such materials, we often use an X-ray diffraction method. Regarding the X-ray diffraction of a small crystallite, the Laue lattice factor[1] or the shape factor[2,3] is considered. In this case, we must take account of the following two points: 1) In the Laue intensity function, it is assumed that the crystallite contains an integral number of unit cells. However, a real crystallite does not necessarily contain the integral number of unit cells. The effect of a non-integral part becomes important for the polymer crystallites since the crystallite size is so small that it is comparable to the monomer size. 2) It is also assumed that crystallites exist separately in vacuo; under this assumption the intensity function contains a strong particle scattering. However, the real crystalline materials consisting of small crystallites do not give such a strong particle scattering, because the crystallites are surrounded by similar crystallites or noncrystalline substance. Therefore, this effect should be also considered.

From these points of view, it is necessary to derive the more practical intensity function in which the effects of the non-integral number of unit cells and the electron density difference between crystallites and the surrounding noncrystalline substance are considered. Kaji and his coworkers[4,5] have derived intensity functions by taking account of the effects of the part of non-integral number

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of unit cells and the particle scattering, separately. In this study, we derive a new intensity function by considering these two effects, simultaneously. Further, the derived intensity function is applied to the wide-angle meridional reflections of polyamide 12 (Nylon 12).

2. THEORY

In general the intensity function $I(\mathbf{b})$ is given by the Fourier transform of the convolution square of scattering length density distribution,

$$I(\mathbf{b}) = \mathfrak{F}\rho(\mathbf{r}) \otimes \rho(-\mathbf{r}) \tag{1}$$

where $\rho(\mathbf{r})$ is the distribution function of scattering length density or the electron density of material, $\mathbf{b}$ the reciprocal vector, $\rho(\mathbf{r}) \otimes \rho(-\mathbf{r})$ the convolution square and $\mathfrak{F}$ the Fourier transform. Let us now consider a system consisting of two phases, small crystallites and noncrystalline regions. The electron density distribution $\rho(\mathbf{r})$ of this system is given by

$$\rho(\mathbf{r}) = [\rho_c(\mathbf{r}) - \rho_n] s(\mathbf{r}) + \rho_n \tag{2}$$

Here $\rho_c(\mathbf{r})$ designates the electron density distribution within crystallites and $s(\mathbf{r})$ is the shape function of all crystallites in the system defined by

$$s(\mathbf{r}) = \begin{cases} 1 & \text{within every crystallite} \\ 0 & \text{outside} \end{cases} \tag{3}$$

the density ρ_n in the noncrystalline region is assumed to be constant. Further, the density fluctuation is defined by

$$\eta(\mathbf{r}) = \rho_c(\mathbf{r}) - \rho_c \tag{4}$$

where ρ_c is the average crystalline density. From eqs. (2), (3), and (4) we obtain

$$\rho(\mathbf{r}) \otimes \rho(-\mathbf{r}) = [\eta(\mathbf{r}) s(\mathbf{r})] \otimes [\eta(-\mathbf{r}) s(-\mathbf{r})] + (\rho_c - \rho_n)^2 s(\mathbf{r}) \otimes s(-\mathbf{r}) +$$
$$(\rho_c - \rho_n) \{ [\eta(\mathbf{r}) s(\mathbf{r})] \otimes s(-\mathbf{r}) + [\eta(-\mathbf{r}) s(-\mathbf{r})] \otimes s(\mathbf{r}) \} +$$
$$[2\alpha\rho_n(\rho_c - \rho_n) + \rho_n^2] V \tag{5}$$

Here V is the total volume of the system, and α is the volume fraction of crystallites. The first term represents the interatomic correlation within the same crystallites. The second term corresponds to the pure particle scattering caused by the outer shapes of crystallites. The third one is the cross term of the first and the second term, which disappears only when $\rho_c = \rho_n$. The last term of eq. (5) is constant, so that it contributes only to the central or zero angle scattering. For simplicity we assume that $\rho_c \cong \rho_n$ and no interatomic correlations between different crystallites exist. Then, eq. (5) reduces to

$$\rho(\mathbf{r}) \otimes \rho(-\mathbf{r}) = [\eta(\mathbf{r}) s(\mathbf{r})] \otimes [\eta(-\mathbf{r}) s(-\mathbf{r})]$$
$$= \Sigma_j [\eta_j(\mathbf{r}) s_j(\mathbf{r})] \otimes [\eta_j(-\mathbf{r}) s_j(-\mathbf{r})] \tag{6}$$

where j designates the j-th crystallite in the system.

Let us consider a polycrystalline sample consisting of many identical crystallites having the non-intergral number of unit cells along only one direction. In this case the crystalline diffraction intensity of the sample is proportional to that of a single crystallite. The density fluctuation within the crystallite is given by

$$\eta_1(\mathbf{r}) s_1(\mathbf{r}) = [\rho_0(\mathbf{r}) - \rho_0) s_0(\mathbf{r})] \otimes z_N(\mathbf{r}) +$$
$$[(\rho_r(\mathbf{r}) - \rho_r) s_r(\mathbf{r})] \otimes (z_{N+1}(\mathbf{r}) - z_N(\mathbf{r})) \tag{7}$$

Here, $\rho_0(\mathbf{r})$ and $\rho_r(\mathbf{r})$ represent the electron density distribution within the com-

plete unit cell and the non-integral part of the unit cell, the average densities of which are given by ρ_0 and ρ_r, respectively, and $z_N(\mathbf{r})$ is the crystal lattice function expressed by

$$z_N(\mathbf{r}) = \Sigma_{k=1}^N \delta(\mathbf{r}-\mathbf{r}_k) \tag{8}$$

Here $\mathbf{r}_k$ is the position vector of the lattice point of the k-th unit cell, and $s_0(\mathbf{r})$ and $s_r(\mathbf{r})$ represent the shape functions of a unit cell and a non-integral part of unit cell near surfaces of the crystallite, respectively, defined by

$$s_0(\mathbf{r}) = \begin{cases} 1 & \text{within the unit cell} \\ 0 & \text{outside} \end{cases} \tag{9}$$

$$s_r(\mathbf{r}) = \begin{cases} 1 & \text{within the non-integral part} \\ 0 & \text{outside} \end{cases} \tag{10}$$

The symbol $\otimes$ designates convolution and δ the Dirac delta function. For the crystallite having the shape of parallelopiped with edges $N_1\mathbf{a}_1$, $N_2\mathbf{a}_2$, $N_3\mathbf{a}_3+\mathbf{a}_3'$ along the $\mathbf{a}_1$-, $\mathbf{a}_2$-, $\mathbf{a}_3$- axes of the unit cells, respectively, the intensity function of the crystallite is obtained as follows

$$I(\mathbf{b}) = \mathfrak{F}[\eta_1(\mathbf{r})s_1(\mathbf{r})]\mathfrak{F}^*[\eta_1(\mathbf{r})s_1(\mathbf{r})]$$
$$= [(I_1/v_0{}^2) \cdot G^2(\mathbf{b}) + (I_2/v_0 v_r) \cdot G(\mathbf{b}) + I_3/v_r{}^2 \tag{11}$$

$$I_1 = |F(\mathbf{b})|^2 - 2n_0 S_0(\mathbf{b})[\text{Re}(F(\mathbf{b}))\cos \pi\mathbf{b}\mathbf{a} + \text{Im}(F(\mathbf{b}))\sin \pi\mathbf{b}\mathbf{a}] + n_0{}^2 S_0{}^2(\mathbf{b}) \tag{11a}$$

$$I_2 = 2\{[\text{Re}(F(\mathbf{b}))\text{Re}(F_r(\mathbf{b})) + \text{Im}(F(\mathbf{b}))\text{Im}(F_r(\mathbf{b}))]\cos 2\pi\mathbf{a}_{N+1}\mathbf{b} + [\text{Re}(F(\mathbf{b}))\text{Im}(F_r(\mathbf{b})) + \text{Im}(F(\mathbf{b}))\text{Re}(F_r(\mathbf{b}))]\sin 2\pi\mathbf{a}_{N+1}\mathbf{b}\}$$
$$-2n_r S_r(\mathbf{b})\{\text{Re}(F(\mathbf{b}))\cos \pi\mathbf{b}(\mathbf{a}_r+2\mathbf{a}_{N+1}) + \text{Im}(F(\mathbf{b}))\sin \pi\mathbf{b}(\mathbf{a}_r+2\mathbf{a}_{N+1})\}$$
$$-2n_0 S_0(\mathbf{b})\{\text{Re}(F_r(\mathbf{b}))\cos\pi\mathbf{b}(\mathbf{a}_r-2\mathbf{a}_{N+1}) + \text{Im}(F_r(\mathbf{b}))\sin\pi\mathbf{b}(\mathbf{a}_r-2\mathbf{a}_{N+1})\}$$
$$+2n_0 n_r S_0(\mathbf{b})S_r(\mathbf{b})\cos(2\mathbf{a}_{N+1}-\mathbf{a}+\mathbf{a}_r) \tag{11b}$$

$$I_3 = |F_r(\mathbf{b})|^2 - 2n_r S_r(\mathbf{b})[\text{Re}(F_r(\mathbf{b}))\cos \pi\mathbf{b}\mathbf{a}_r + \text{Im}(F_r(\mathbf{b}))\sin \pi\mathbf{b}\mathbf{a}_r] + n_r{}^2 S_r{}^2(\mathbf{b}) \tag{11c}$$

where $\mathbf{a} = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, $\mathbf{a}_r = (0, 0, \mathbf{a}_3')$, $\mathbf{a}_{N+1} = (0, 0, (N_3+1)\mathbf{a}_3)$, $F(\mathbf{b})$ and $F_r(\mathbf{b})$ are the structure factor for the part containing an integral and non-integral number of unit cells, respectively, and $\text{Re}(F(\mathbf{b}))$ and $\text{Im}(F(\mathbf{b}))$ are the real and imaginary part of $F(\mathbf{b})$, respectively. $S_0(\mathbf{b})$ and $S_r(\mathbf{b})$ represent the shape amplitude for the integral and non-integral part when the origin is taken at the corner of the unit cell, which are, respectively, given by

$$S_0(\mathbf{b}) = \frac{\sin \pi\mathbf{b}\mathbf{a}_1}{\pi\mathbf{b}\mathbf{a}_1} \cdot \frac{\sin \pi\mathbf{b}\mathbf{a}_2}{\pi\mathbf{b}\mathbf{a}_2} \cdot \frac{\sin \pi\mathbf{b}\mathbf{a}_3}{\pi\mathbf{b}\mathbf{a}_3} \tag{12}$$

$$S_r(\mathbf{b}) = \frac{\sin \pi\mathbf{b}\mathbf{a}_3'}{\pi\mathbf{b}\mathbf{a}_3'} \tag{13}$$

$G(\mathbf{b})$ is the Laue lattice factor of the crystallite defined by

$$G(\mathbf{b}) = \frac{\sin \pi N_1\mathbf{b}\mathbf{a}_1}{\sin \pi\mathbf{b}\mathbf{a}_1} \cdot \frac{\sin \pi N_2\mathbf{b}\mathbf{a}_2}{\sin \pi\mathbf{b}\mathbf{a}_2} \cdot \frac{\sin \pi N_3\mathbf{b}\mathbf{a}_3}{\sin \pi\mathbf{b}\mathbf{a}_3} \tag{14}$$

and

$$n_0 = \rho_0 v_0 = \Sigma_j^l f_j \tag{15}$$

$$n_r = \rho_r v_r = \Sigma_j^q f_j \tag{16}$$

where v_0 is the volume of the unit cell and v_r is the volume of the non-integral

part.

As an example, we derive the intensity function of the meridional reflections. We can express the electron density distribution in the unit cell as

$$v_0\rho_0(\mathbf{r}) = \Sigma_j f_j \delta(\mathbf{r}-\mathbf{r}_j) \tag{17}$$

where f_j is the atomic scattering factor. Then

$$\mathfrak{F}[\eta_1(r)s_1(r)] = \{[\Sigma_m^l f_m \exp(2\pi i \zeta z_m) - n_0(\frac{\sin \pi \zeta a_3}{\pi \zeta}\cos \pi \zeta a_3 + i \frac{\sin^2 \pi \zeta a_3}{\pi \zeta})]/v_0\} G(\zeta)$$

$$+ \{[\Sigma_n^q f_n \exp(2\pi i \zeta z_n) - n_r(\frac{\sin \pi \zeta a_3'}{\pi \zeta}\cos \pi \zeta a_3' + i \frac{\sin^2 \pi \zeta a_3'}{\pi \zeta})]/v_r\} \times$$

$$\exp(2\pi i (N_3+1) a_3 \zeta) \tag{18}$$

Here a_3 is the fiber axis, ζ is the reciprocal coordinate in the meridional direction, l is the number of atoms in the unit cell, and q is the number of atoms in the non-integral part. $G(\zeta)$ is given by

$$G(\zeta) = \frac{\sin \pi N_3 \zeta a_3}{\sin \pi \zeta a_3} \tag{19}$$

Therefore, the intensity function for the meridional reflections is obtained as follows.

$$I(\zeta) = \mathfrak{F}[\eta_1(\mathbf{r})s_1(\mathbf{r})]\mathfrak{F}^*[\eta_1(\mathbf{r})s_1(\mathbf{r})]$$
$$= (I_1/v_0^2) G^2 + (I_2/v_0 v_r) G + I_3/v_r^2 \tag{20}$$

Here

$$I_1 = \Sigma_m^l f_m \cos^2(2\pi \zeta z_m) + \Sigma_m^l f_m \sin^2(2\pi \zeta z_m)$$

$$-2n_0(\sin(\pi \zeta a_3)/\pi \zeta)\{\Sigma_m^l f_m \cos(2\pi \zeta z_m)\cos(\pi \zeta a_3)$$

$$+\Sigma_m^l f_m \sin(2\pi \zeta z_m)\sin \pi \zeta a_3\} + n_0 \sin^2(\pi \zeta a_3)/(\pi \zeta)^2 \tag{20a}$$

$$I_2 = I_{21} + I_{22} + I_{23} + I_{24} \tag{20b}$$

$$I_{21} = 2\sqrt{A^2+B^2}\sqrt{C^2+D^2}\sin\{2\pi(N_3+1)a_3\zeta + \alpha\} \tag{20b-1}$$

$$I_{22} = 2n_r \frac{\sin \pi a_3' \zeta}{\pi \zeta}\sqrt{A^2+B^2}\sin\{2\pi(N_3+1)a_3\zeta + \beta\} \tag{20b-2}$$

$$I_{23} = 2n_0 \frac{\sin \pi a_3 \zeta}{\pi \zeta}\sqrt{C^2+D^2}\sin\{2\pi(N_3+1)a_3\zeta + \gamma\} \tag{20b-3}$$

$$I_{24} = 2n_0 n_r \frac{\sin \pi a_3' \zeta}{\pi \zeta}\frac{\sin \pi a_3 \zeta}{\pi \zeta}\sin\{2\pi(N_3+1)a_3\zeta + \delta\} \tag{20b-4}$$

$$\tan \alpha = \frac{AC+BD}{BC-DA} \qquad \tan \beta = \frac{AE+BF}{BE-AF}$$

$$\tan \gamma = \frac{CG+DH}{CH-DG} \qquad \tan \delta = \frac{GE-HF}{HE-GF}$$

$$A = \Sigma_m^l f_m \cos(2\pi \zeta z_m) \qquad B = \Sigma_m^l f_m \sin(2\pi \zeta z_m)$$

$$C = \Sigma_n^q f_n \cos(2\pi \zeta z_n) \qquad D = \Sigma_n^q f_n \sin(2\pi \zeta z_n)$$

$$E = \cos \pi \zeta a_3' \qquad F = \sin \pi \zeta a_3'$$

$$G = \cos \pi \zeta a_3 \qquad H = \sin \pi \zeta a_3$$

$$I_3 = \Sigma_n^q f_n \cos^2(2\pi \zeta z_n) + \Sigma_n^q f_n \sin^2(2\pi \zeta z_n)$$

$$-2n_1 \frac{\sin(\pi \zeta a_3')}{\pi \zeta}\{\Sigma_n^q f_n \cos(2\pi \zeta z_n)\cos(\pi \zeta a_3')$$

$$+\Sigma_n^q f_n \sin(2\pi \zeta z_n)\sin(\pi \zeta a_3')\} + n_1^2 \frac{\sin^2(\pi \zeta a_3')}{(\pi \zeta)^2} \tag{20c}$$

$(I_1/v_0^2)G^2$ is the intensity function for the crystallite containing the integral number of unit cells, I_3/v_r^2 is the structure factor for the non-integral part, and $(I_2/v_0v_r)G$ is a cross term between the integral part and the non-integral part.

3. APPLICATION TO POLYAMIDE 12 (NYLON 12)

The values of the fiber identity period of polyamides calculated from the observed peak positions of various orders of X-ray meridional reflections do not agree with one another. This phenomenon was first interpreted by Wallner[6] on the basis of X-ray diffactiron theory. The peak position of the meridional reflection shifts from its corresponding reciprocallattice point when the structure factor changes steeply near the reciprocal lattice point and the crystallite size is very small, because the intensity function is expressed by the product of Laue lattice factor and the structure factor[7].

In the case of nylon 12, this problem becomes very significant. Fig 1 shows the observed meridional reflections for the γ form of nylon 12. These meridional reflections show the following features: (a) As seen from Fig. 2, the 0 2 0 reflection is extraordinarily deformed and appears to consist of two components, the normal broad component the width and the peak position of which correspond to those of higher order reflections and the abnormally strong narrow component the peak position of which shifts to higher angle side. (b) The 0 4 0 reflection is slightly deformaed from the normal reflection.
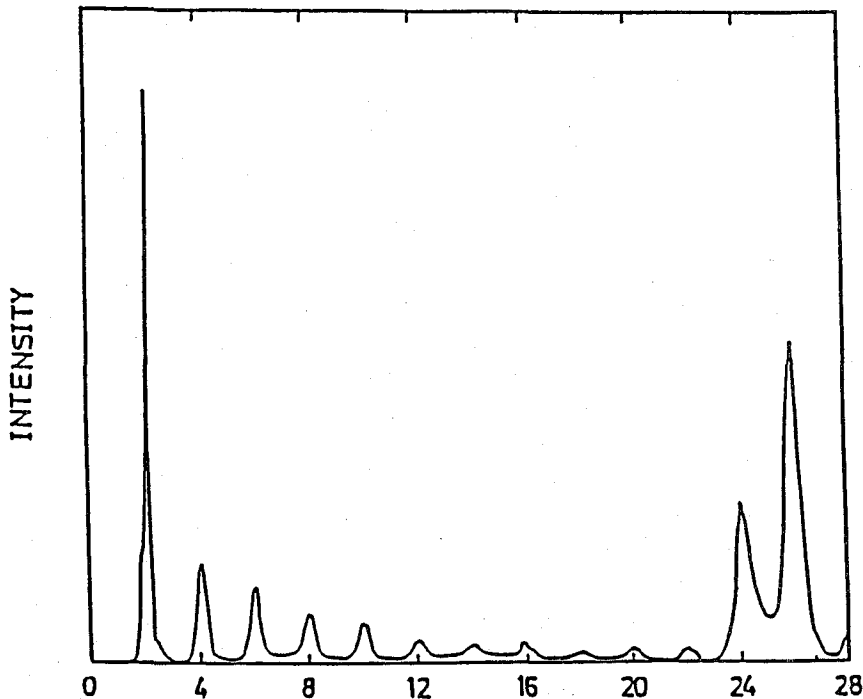

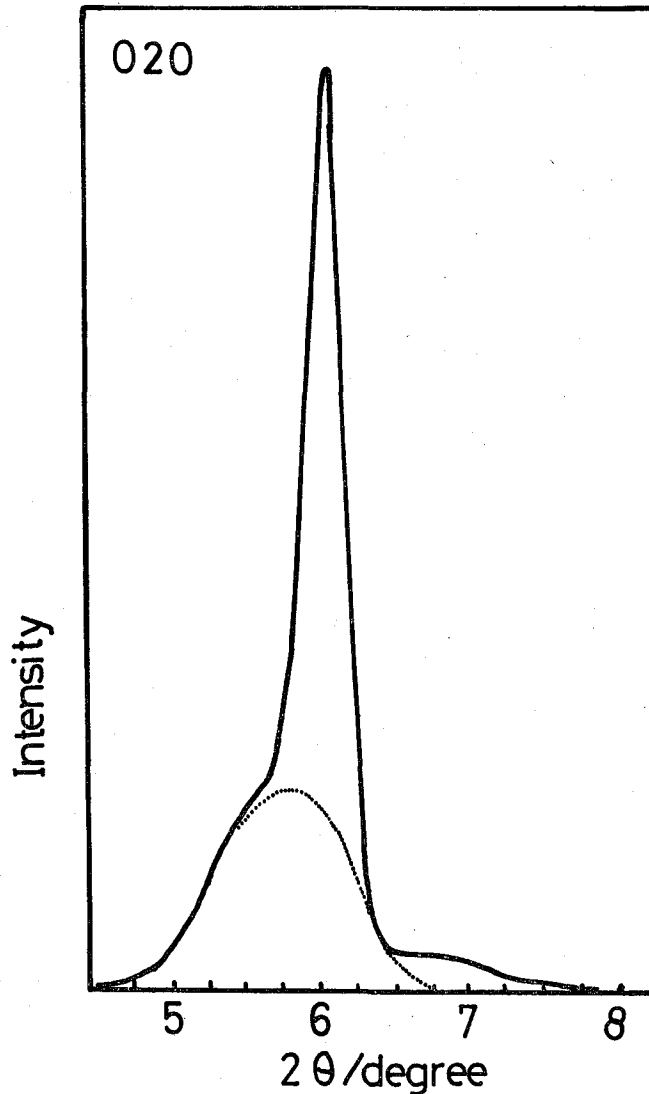Fig. 1. Observed profile of the meridional reflections for nylon 12.

Fig. 2. Observed profile of the 0 2 0 reflection for nylon 12.

The motivation of this paper was to explain the origin of the large deforma-
tion of the 0 2 0 reflection. Here, we consider from the two points of view. One
is the effect of the non-integral number of unit cells[4] and the other is the super-
position of reflections from another modification[8]. Concerning the former effect,
we have already calculated the intensity function for nylon 12 crystals with the
non-integral number of unit cells and found that the shoulder appears on the
lower angle side of the 0 2 0 reflection (Fig. 3)[4]. However, it has been presumed
that the tail of the strong particle scattering may deform the 0 2 0 reflection.
The possibility of another modification has been suggested from double melting
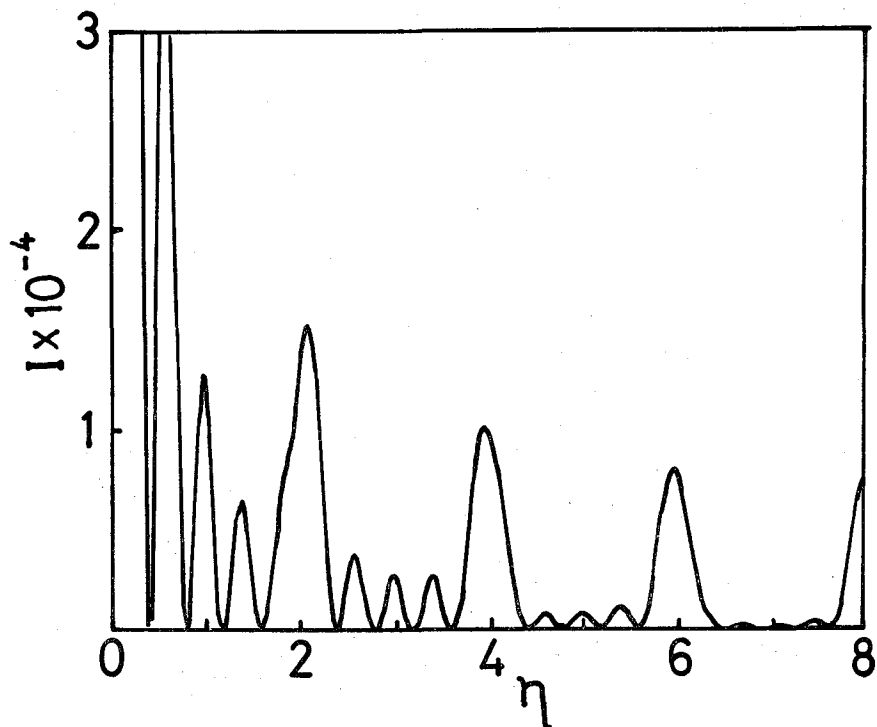peaks on the DSC curve of nylon 12[8]. In this paper we calculate the intensity

Fig. 3. Calculation of the effect of non-integral part on the intensity function along the meridian of nylon 12 (Ref. 4).

function without the particle scattering for the nylon 12 crystallite with non-integral number of unit cells in order to clarify the origin of the deformed 0 2 0 reflection.

In the practical calculation, the crystalline structure determined by Cojazzi et al[9] was used. The calculation method is the same as was previously described[4]; the number of monomer units in the crystallite is taken as 5.05 and the origin of the atomic coordinates used in the calculation is shifted by 0.15 along the fiber axis from the origin of Cojazzi et al[9].

Fig. 4 shows the intensity function on the meridian for the γ form of nylon 12 which was calculated using the newly derived eq. (20). The strong particle scattering peaks which are seen in the range of $\eta=0$ to 2.0 in Fig. 3, disappear in this calculation. Unfortunately the strong narrow component of the 0 2 0 reflection is however not reproduced. Thus, as far as $\rho_c=\rho_n$, the non-integral number of unit cells in the crystallite is not the origin of the deformation of the 0 2 0 reflection of the γ form of nylon 12. Therefore, at the moment, the origin of the deformed 0 2 0 reflection is probably the existence of another modification, though the effect when $\rho_c>\rho_n$ should be also investigated.
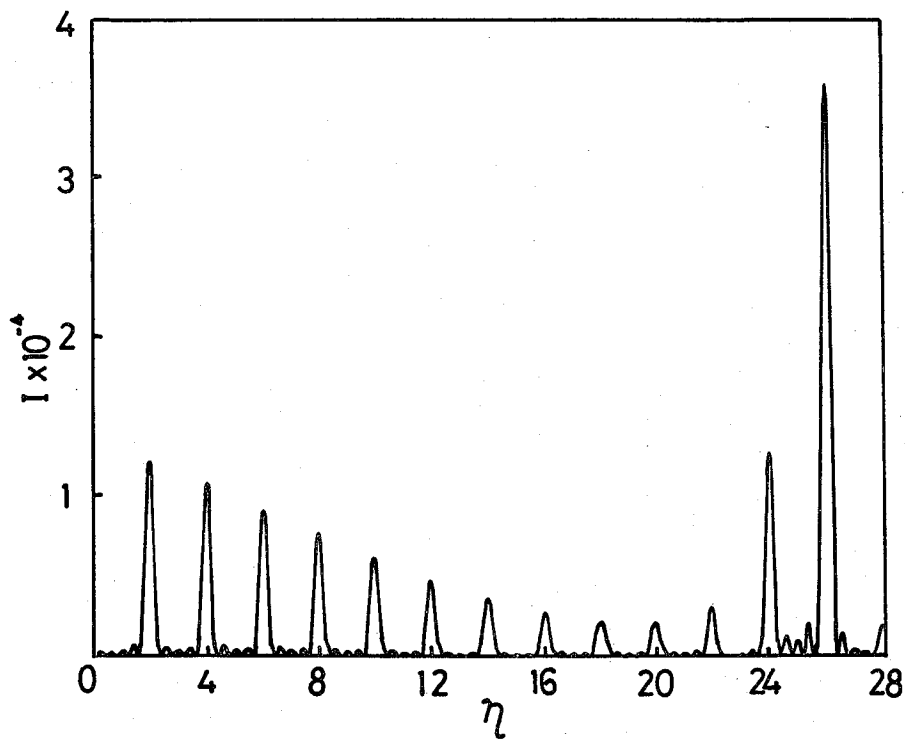
Fig. 4. Intensity function on the meridian calculated by eq. (20) for the γ form of nylon 12. The range is $\eta=0$ to 28.

REFERENCES

1) M. von Laue, Ann. *Phys. (Paris)* **26**, 55 (1936).
2) A.L. Patterson, *Phys. Rev.* **56**, 972 (1939).
3) P.P. Ewald, *Proc. Phys. Soc. London,* **52**, 167 (1940).
4) K. Kaji, H. Yamagishi, H. Horii and R. Kitamaru, *Makro Mainz* **3**, 1349 (1979).
5) K. Kaji and K. Katayama, *Bull. Inst. Chem. Res. Kyoto Univ.* **62**, 208 (1984).
6) L.G. Wallner, *Monatsh. Chem.* **79**, 279 (1948).
7) K. Kaji, H. Yamagishi, and R. Kitamaru, *J. Appl. Cryst.* **14**, 223 (1981)
8) M. Imai and K. Kaji, *Sen-i Gakkai Preprints,* F826 (1989).
9) G. Cojazzi, A. Fichera, C. Garbuglio, V. Malta and R. Zannetti, *Makromol. Chem.* **168**, 289 (1973).