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X-Ray Diffraction from Polycrystals Consisting of Very Small Crystallites

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The X-ray intensity function for polycrystals consisting of ideal crystallites has been derived ; this function is separated from the particle scattering of the crystallites considering the electron density fluctuation within the crystallite. This newly derived intensity function is useful especially when the crystallites are very small since the tail of particle scattering superposes on the wide-angle reflection. For examples, the new intensity function is applied to the profile calculation of the meridional reflections of the α- and γ-forms of polyamide 6. When the usual intensity function is used, strong ghost peaks appear in the low-angle regions, but the new function gives no such ghost peaks.

KEY WORDS: X-Ray Diffraction/ Modified Intensity Function/ Polycrystals Consisting of Very Small Crystallites/

1. INTRODUCTION

Regarding the X-ray diffraction of a small crystal, Laue[1] introduced the concept of the Laue lattice factor in which the external shape of crystal was assumed to be a parallelopiped. Patterson[2] and Ewald[3] derived a diffraction theory for a small crystal of arbitrary shape using the shape function. Hosemann separated the Laue lattice factor into the lattice factor and the shape factor to propose the so-called paracrystalline theory for a distorted crystal in which the degree of distortion is represented by the broadening of the lattice factor.[4] Recently, Ino & Minami[5] obtained the diffraction profile for a small crystallite by making the orientationl average of the diffraction intensity.

In the theories described above, however, it is assumed that crystals exist separately in vacuo, so that they are inapplicabe to real polycrystals consisting of small crystallites such as cold worked metals, bulk crystalline polymers, *etc.* Thus, the above theories give a strong particle scattering, whereas the real polycrystals produce no particle scattering or a much weaker one since a crystallite in the polycrystal is surrounded by similar crystallites or noncrystalline materials.

In the theoretical study of wide-angle X-ray diffraction it is desirable to separate or remove such a particle scattering because it often deforms the profile of the lower orders of reflection. This effect cannot be neglected when the crystallites are composed of several unit cells as in the case of synthetic polymers with large unit cell.

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In order to obtain the correct diffraction effect of a sufficiently large crystal consisting of small crystallites, the diffraction should be considered for the electron density fluctuation or the deviation of the density from its mean density. Weick & Hosemann[6] proposed such a treatment to evaluate the small-angle particle scattering of paracrystallites in the paracrystalline theory.

In this study we show that the crystalline diffraction of the polycrystal can be described by the density fluctuation in the crystallites, and derive the intensity function for polycrystals with parallelopiped crytstallites. Further, the derived intensity function is applied to the wide-angle meridional reflections of polyamides.

2. THEORY

In general the intensity function $I(\boldsymbol{b})$ is given by

$$\begin{aligned} I(\boldsymbol{b}) &= R(\boldsymbol{b})\, R^*(\boldsymbol{b}) = [\mathscr{F}\rho(\boldsymbol{r})][\mathscr{F}\rho(-\boldsymbol{r})] \\ &= \mathscr{F}[\rho(\boldsymbol{r}) * \rho(-\boldsymbol{r})] = \mathscr{F}\rho(\boldsymbol{r}) **2 \end{aligned} \tag{1}$$

where $\rho(\boldsymbol{r})$ is the electron density function of a material, $R(\boldsymbol{b})$ the structure amplitude, $\boldsymbol{b}$ the reciprocal vector, and the Fourier transform $\mathscr{F}$ and the convolution square $\rho(\boldsymbol{r}) **2$ are defined by

$$\mathscr{F} = \int \exp[-2\pi i(\boldsymbol{b}\cdot\boldsymbol{r})]\, dv_r \tag{2}$$

$$\rho(\boldsymbol{r}) **2 = \rho(\boldsymbol{r}) * \rho(-\boldsymbol{r}) = \int \rho(\boldsymbol{x})\, \rho(\boldsymbol{x}+\boldsymbol{r})\, dv_x \equiv Q(\boldsymbol{r}), \tag{3}$$

respectively.[4]

Let us now consider a system consisting of two phases, small ideal crystallites and noncrystalline regions. The electron density distribution $\rho(\boldsymbol{r})$ of this system is given by

$$\rho(\boldsymbol{r}) = \rho_c(\boldsymbol{r})\, s(\boldsymbol{r}) + \rho_n[1 - s(\boldsymbol{r})] = [\rho_c(\boldsymbol{r}) - \rho_n]\, s(\boldsymbol{r}) + \rho_n. \tag{4}$$

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

$$s(\boldsymbol{r}) = \begin{cases} 1 & \text{within every crystallite} \\ 0 & \text{outside.} \end{cases} \tag{5}$$

Further, the density ρ_n in the noncrystalline regions is assumed to be constant.

According to Debye & Bueche,[7] the density fluctuation of the system is next considered. However, the fluctuation introduced here is not in the particle (crystallite) scale, but in the atomic scale within crystallites. Thus, the density fluctuation is defined by

$$\rho_c(\boldsymbol{r}) = \bar{\rho}_c + \eta(\boldsymbol{r}) \tag{6}$$

where $\bar{\rho}_c$ is the average crystalline density. Substituting eq. (6) into eq. (4) and then into eq. (3), we obtain

$$\begin{aligned} Q(\boldsymbol{r}) = \rho(\boldsymbol{r}) **2 = [\eta(\boldsymbol{r})\, s(\boldsymbol{r})] **2 + (\bar{\rho}_c - \rho_n)^2 s(\boldsymbol{r}) **2 + \\ + [2\alpha\rho_n(\bar{\rho}_c - \rho_n) + \rho_n^2] V. \end{aligned} \tag{7}$$

Here V is the total volume of the system, $\alpha = V_c/V$ the fraction of crystallites, and V_c

the total volume of all crystallites in the system. The third term of eq. (7) is constant, so that it contributes only to the scattering angle of zero. The second term including interparticle correlation vanishes when $\rho_c=\rho_n$, which means that this term corresponds to the small-angle particle scattering. In other words, the first term representing the interatomic correlation in the crystallites does not contain the particle scattering. In order to remove the particle scattering, the scattering of the density fluctuation in the crystallites should be therefore considered.

Assuming that the interatomic correlation does not exist between any pair of crystallites, the first term of eq. (7) is simply given by summation of convolution squares of density fluctuation for individual crystallites. Thus,

$$[\eta(\boldsymbol{r})s(\boldsymbol{r})]**2=\sum_j[\eta_j(\boldsymbol{r})s_j(\boldsymbol{r})]**2 \tag{8}$$

where j designates the jth crystallite in the system.

For simplicity let us consider a polycrystalline sample consisting of many identical ideal crystallites with integral number of unit cells. In this case the crystalline diffraction of this sample is proportional to that of an arbitrary crystallite. The density fluctuation of the crystallite is given by

$$\eta_1(\boldsymbol{r})s_1(\boldsymbol{r})=[\rho_0(\boldsymbol{r})s_0(\boldsymbol{r})-\bar{\rho}_c s_0(\boldsymbol{r})]*[z_\infty(\boldsymbol{r})s(\boldsymbol{r})]. \tag{9}$$

Here $\rho_0(\boldsymbol{r})$ is the electron density distribution in the unit cell, and $z_\infty(\boldsymbol{r})$ is the crystal lattice function for the whole real space expressed by

$$z_\infty(\boldsymbol{r})=\sum_{m=1}^{\infty}\delta(\boldsymbol{r}-\boldsymbol{r}_m). \tag{10}$$

$s_0(\boldsymbol{r})$ and $s(\boldsymbol{r})$ are the shape functions of the unit cell and the crystallite, respectively, defined by

$$s_0(\boldsymbol{r})=\begin{cases}1 & \text{within the unit cell}\\ 0 & \text{outside}\end{cases}$$
$$s(\boldsymbol{r})=\begin{cases}1 & \text{within the crystallite}\\ 0 & \text{outside,}\end{cases} \tag{11}$$

and $\bar{\rho}_c$ is the mean electron density of the crystallite. The symbol $*$ designates convolution and δ the Dirac delta function. For the ideal crystallite having the shape of parallelopiped with edges $N_1\boldsymbol{a}_1$, $N_2\boldsymbol{a}_2$, and $N_3\boldsymbol{a}_3$ along the $\boldsymbol{a}_1$-, $\boldsymbol{a}_2$-, and $\boldsymbol{a}_3$-axes of the unit cell, respectively, the intensity function of the crystallite is obtained as follows

$$\begin{aligned}I(\boldsymbol{b})&=R(\boldsymbol{b})\,R^*(\boldsymbol{b})\\&=\{|F(\boldsymbol{b})|^2-2n_0S_0(\boldsymbol{b})[\mathrm{Re}(F(\boldsymbol{b}))\cos(\pi\boldsymbol{b}(\boldsymbol{a}_1+\boldsymbol{a}_2+\boldsymbol{a}_3))\\&\quad+\mathrm{Im}(F(\boldsymbol{b}))\sin(\pi\boldsymbol{b}(\boldsymbol{a}_1+\boldsymbol{a}_2+\boldsymbol{a}_3))]+n_0^2S_0^2(\boldsymbol{b})\}G^2(\boldsymbol{b})\end{aligned} \tag{12}$$

where $F(\boldsymbol{b})$ is the conventional structure factor of the unit cell, $\mathrm{Re}(F(\boldsymbol{b}))$ and $\mathrm{Im}(F(\boldsymbol{b}))$ are the real and imaginary part of $F(\boldsymbol{b})$, respectively, and v_0 is the unit cell volume. $S_0(\boldsymbol{b})$ and $G^2(\boldsymbol{b})$ represent the shape amplitude of the unit cell and the Laue lattice factor of the crystallite when the origin is taken at the center of the unit cell, which are, respectively, given by

$$S_0(\boldsymbol{b})=\frac{\sin(\pi\boldsymbol{b}\cdot\boldsymbol{a}_1)}{\pi\boldsymbol{b}\cdot\boldsymbol{a}_1}\,\frac{\sin(\pi\boldsymbol{b}\cdot\boldsymbol{a}_2)}{\pi\boldsymbol{b}\cdot\boldsymbol{a}_2}\,\frac{\sin(\pi\boldsymbol{b}\cdot\boldsymbol{a}_3)}{\pi\boldsymbol{b}\cdot\boldsymbol{a}_3} \tag{13}$$

$$G^2(\boldsymbol{b}) = \frac{\sin^2(\pi N_1 \boldsymbol{b}\cdot\boldsymbol{a}_1)}{\sin^2(\pi \boldsymbol{b}\cdot\boldsymbol{a}_1)} \frac{\sin^2(\pi N_2 \boldsymbol{b}\cdot\boldsymbol{a}_2)}{\sin^2(\pi \boldsymbol{b}\cdot\boldsymbol{a}_2)} \frac{\sin^2(\pi N_3 \boldsymbol{b}\cdot\boldsymbol{a}_3)}{\sin^2(\pi \boldsymbol{b}\cdot\boldsymbol{a}_3)}. \tag{14}$$

Here it should be noted that in eq. (12) the origin of the shape function of the unit cell is taken at a corner of the unit cell in spite of the definition of eq. (13) and (14); it must also coinside with the origin of the atomic coordinates in the unit cell. Further,

$$n_0 = \bar{\rho}_c v_0 = \sum_{j=1}^{n} Z_j, \tag{15}$$

Z_j being the number of electrons of the jth atom in the unit cell. In real crystals, electrons are not distributed in a random fashion, but localized in atoms. It is therefore more practical that Z_j is replaced by the atomic scattering factor f_j, *i. e.*,

$$n_0 = \sum_{j=1}^{n} f_j. \tag{16}$$

3. APPLICATION TO THE MERIDIONAL REFLECTION PROFILES OF POLYAMIDE

Kaji & Sakurada[8] calculated the meridional reflection profiles for the α- and γ-forms of polyamide 6 using the usual intensity function, $I_1 = |F|^2 G^2$ where $|F|^2$ is the structure factor and G^2 the Laue lattice factor. In this calculation very strong peaks appeared on the meridian between the origin in reciprocal space and the 020 reflection, although for the semicrystalline filaments of this polymer no strong peaks were practically observed in the corresponding region. The 020 reflection of the α-form was much deformed by such ghost peaks, so that the observed profile of this reflection could not be reproduced by calculation. In the profile analysis of anomalous meridional reflections of polyamide 12 this problem has become more significant[9] since there exist only a few unit cells in the chain-axial direction within a crystallite because of its large fiber identity period.[10] Therefore, it is interesting whether such ghost peaks will vanish using the above-derived intensity function of eq. (12).

The crystalline modification of the usual sample of polyamide 6 is the α-form, which is easily converted to the γ-form by iodine treatment.[11] The crystalline molecular chain of the α-form assumes an almost extended planar zigzag structure, whereas in the case of the γ-form it contracts slightly at the amide groups. For the present calculations, the crystal structure models of the α- and γ-forms proposed by Holmes, Bunn, and Smith[12] and Bradbury, Brown, Elliott, and Parry[13] were used, respectively. The crystal system for both α- and γ-forms is monoclinic, and the fiber identity periods or the b axes are 17.24 and 16.7 Å, respectively. The crystallite sizes along the fiber axis for the usual samples are 60 to 70 Å, in which about four unit cells are contained.[8]

For the meridional reflections in the fiber diagram, the intensity function reduces from eq. (12) to

$$\begin{aligned} I(\eta) = \{ |F(\eta)|^2 - 2n_0 S_0(\eta) [\mathrm{Re}(F(\eta)) \cos(\pi\eta) \\ + \mathrm{Im}(F(\eta)) \sin(\pi\eta)] + n_0^2 S_0^2(\eta) \} G^2(\eta) \end{aligned} \tag{17}$$

where η is the reciprocal coordinate in the meridional direction, and

$$F(\eta) = \sum_{j=1}^{n} f_j \cos(2\pi\eta y_j) + i \sum_{j=1}^{n} f_j \sin(2\pi\eta y_j) \tag{18}$$

$$S_0(\eta) = [\sin(\pi\eta)]/(\pi\eta) \tag{19}$$

$$G^2(\eta) = \sin^2(\pi N_2\eta)/\sin^2(\pi\eta)\,. \tag{20}$$

Here y_j is the b-coordinate of the jth atom and N_2 was taken to be 4 in the calculation. Figure 1 shows the usual intensity function $I_1 = |F|^2G^2$ on the meridian for the α-form. In the region of $\eta=0$ to 3.0, a series of strong ghost peaks are seen and some of them overlap with the 020 reflection. These ghost peaks disappear and the 020 reflection is separated in the newly derived intensity function of eq. (17) as shown in Fig. 2.

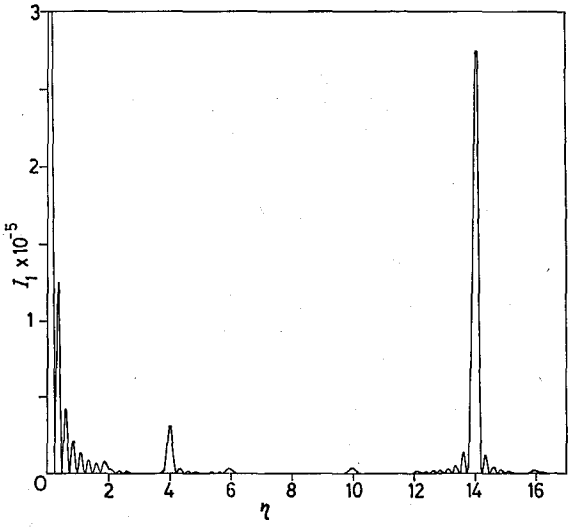

Fig. 1 Usual intensity function $I_1 = |F|^2G^2$ on the meridian for the α-form of polyamide 6. $|F|^2$ and G^2 are the structure factor and the Laue lattice factor, respectively. The crystallite size N_2 was taken to be 4.

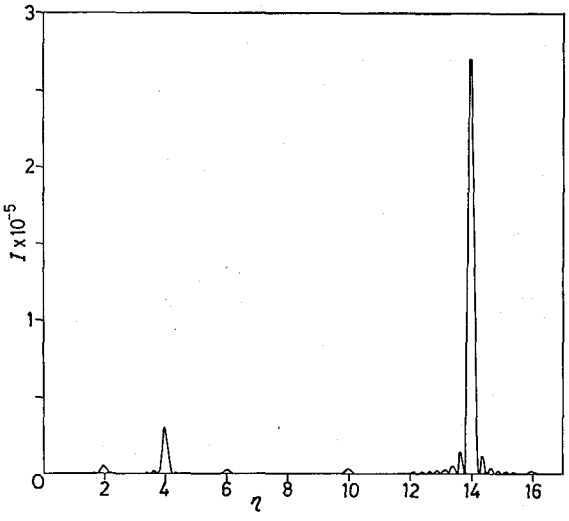

Fig. 2 Intensity function on the meridian calculated by eq. (17) for the α-form of polyamide 6. The crystallite size N_2 was taken to be 4.

For the γ-form, similar calculations have been also carried out. The results are shown in Figs. 3 and 4. In the calculation with the usual intensity function I_1, strong ghost peaks also appear between $\eta=0$ and 2.0 (Fig. 3), whereas in the intensity function from the density fluctuation no ghost peaks are seen (Fig. 4).

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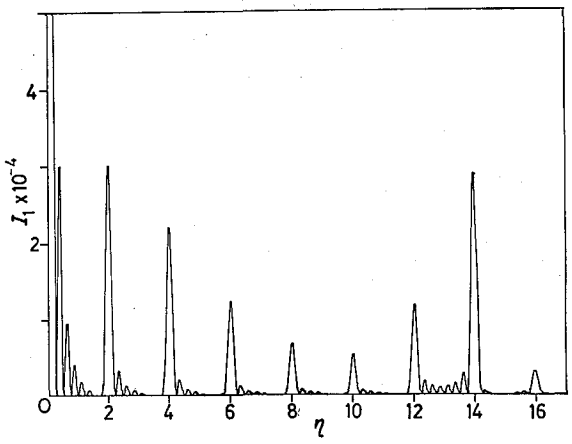

Fig. 3 Usual intensity function $I_1=|F|^2G^2$ on the meridian for the γ-form of polyamide 6. $|F|^2$ and G^2 are the structure factor and the Laue lattice factor, respectively. The crystallite size N_2 was taken to be 4.

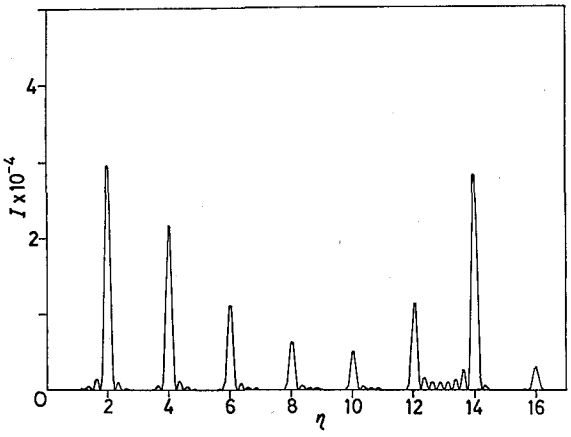

Fig. 4 Intensity function on the meridian calculated by eq. (17) for the γ-form of polyamide 6. The crystallite size N_2 was taken to be 4.

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) R. Hosemann and S. N. Bagchi, "*Direct Analysis of Diffraction by Matter*", North Holland, Amsterdam, 1962.
(5) T. Ino and N. Minami, *Acta Cryst.*, **A35**, 163 (1979).
(6) D. Weick and R. Hosemann, *Colloid Polym. Sci.*, **258**, 593 (1980).
(7) P. Debye and A. M. Bueche, *J. Appl. Phys.*, **20**, 518 (1949).
(8) K. Kaji and I. Sakurada, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 1491 (1974).
(9) K. Kaji, H. Yamagishi, F. Horii, and R. Kitamaru, *Preprints of Short Communicaions presented at IUPAC 26th International Symposium on Macromolecules*, Mainz, Vol. III, p. 223.
(10) K. Kaji, H. Yamagishi, and R. Kitamaru, *J. Appl. Cryst.*, **14**, 223 (1981).
(11) S. Ueda and T. Kimura, *Kobunshi Kagaku* (*Chem. High Polym.* [*Tokyo*]), **15**, 243 (1958).
(12) D. R. Holmes, C. W. Bunn. and D. J. Smith, *J. Polym. Sci.*, **17**, 159 (1955).
(13) E. M. Bradbury, L. Brown, A. Elliott, and D. A. D. Parry, *Polymer*, **6**, 465 (1965).