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Interpretation of Line Profiles by the Fourier Method, with Special Reference to the Size Distribution of Carbon Black Crystallites†

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The Fourier transform of the (00, 2) line profile of amorphous carbon as defined by

$$\varphi_{(00,2)}(x) = \int_{-\infty}^{+\infty} A_0(s)\,\frac{\sin \pi a_{(00,2)}(s - s_{(00,2)})}{\pi(s - s_{(00,2)})}\exp\left[-2\pi i(s - s_{(00,2)})x\right]ds$$

with

$$|A_0(s)|^2 \propto I(s)$$

was made, where $a_{(00,2)}$ means the value of the (00, 2) spacing, say 3·51 Å, which is related to the profile centre $s_{(00,2)}$ by the Bragg relation.

The unfolded structure $\varrho_0(x)$ *of averaged convolution*, which is defined as

$$\varrho_0(x) * \varrho_0(x) = \frac{1}{N}\sum_{n=1}^{N}\{\varrho_n(x) * \varrho_n(x)\}$$

was obtained from $\varphi_{(00,2)}(x)$, where $\varrho_1(x), \varrho_2(x), \ldots, \varrho_N(x)$ represent the linear structures constituting all the crystallites of the material, and running parallel to their [00, 1] direction.

The number-fraction of the crystallites composed of M atomic layers parallel to (00, 1) plane was obtained from the Fourier transform of line profile (00, 2) which would be observed *when there were no irregularities in interlayer spacings at all*, and which can be readily derived from $\varrho_0(x)$. The number-fraction was found to be roughly proportional to 2^{-M}.

Remarks were given for the nature of information which is to be obtained by the above method.

1. Introduction

The diffraction diagrams of polycrystalline substances, which are essentially heterogeneous with respect to their atomic structures, are thus to be interpreted in terms of distribution functions describing the statistical characteristics in the atomic structures of crystallites which constitute the substance under examination. For instance, Bertaut (1950) has given a formula giving the size distribution of crystallites from the observed line profile, which, however, is not applicable unless the profile observations are extended infinitely in reciprocal space. In fact it demands the second derivatives of the Fourier transform of line profile to derive the distribution function of crystallite sizes. Further the formula ceases to be valid when there are other causes of line broadening which make the observed profile unsymmetrical, such as the irregularities in interlayer spacings in the direction perpendicular to the reflecting plane.

In this paper a method is described for deducing the size distribution of crystallites from the observed line profiles which are more or less confined to the neighbourhood of the profile centre, and is applied to the (00, 2) line profile of amorphous carbon.

2. Principle of analysis

Let us consider a polycrystalline substance which gives rise to a Debye–Scherrer line of index (*hkl*). The whole of the substance can be regarded as constituted of linear structures $\varrho_n(x)$'s which are arranged perpendicular to the (*hkl*) plane and in terms of which the (*hkl*) line profile is interpreted. The precise meaning of those linear structures are given in Appendix.

When we write the Fourier transforms of $\varrho_n(x)$'s as $A_n(s)$'s, the (*hkl*) line profile is expressed as (Guinier, 1956)

$$I(s) \propto \sum_{n=1}^{N}|A_n(s)|^2 \equiv N|A_0(s)|^2. \qquad (1)$$

Equation (1) means that the linear structures $\varrho_n(x)$'s diffract X-rays independently of each other, and consequently there is no way of defining the phase angles of diffracted X-rays at any point in the reciprocal space.

Let us introduce here *the unfolded structure* $\varrho_0(x)$ *of the averaged convolution* defined as

$$\varrho_0(x) * \varrho_0(x) = \frac{1}{N}\sum_{n=1}^{N}\{\varrho_n(x) * \varrho_n(x)\}\,. \qquad (2)‡$$

Then the Fourier transforms of both sides of (2) satisfy the relation (1) when $A_0(s)$ is the Fourier transform of $\varrho_0(x)$;

$$A_0(s) = \int_{-\infty}^{+\infty}\varrho_0(x)\exp 2\pi isx\,dx\,. \qquad (3)$$

It follows that, though the substantial phase as-

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† A part of this work was carried out at the Mineralogical Institute, Faculty of Science, University of Tokyo.

‡ $f(x) * g(x)$ means $\int f(u)g(u-x)du$.

signments are impossible and even insignificant for the polycrystalline substances as remarked above, we can yet assign *formally* the phase angles $\omega(s)$ for the square-root of $I(s)$;

$$A_0(s)=I(s)^{\frac{1}{2}}.\exp 2\pi i\omega(s) \tag{4}$$

to obtain the structure $\varrho_0(x)$ as defined by (2), with the inversion of (3);

$$\varrho_0(x)=\int_{-\infty}^{+\infty}A_0(s)\exp(-2\pi isx)ds\,. \tag{5}$$

The question now to be asked is, how to interpret the structure $\varrho_0(x)$ thus obtained in terms of the statistical parameters of $\varrho_n(x)$'s. We postpone this question to § 2·1, and confine ourselves at present to the problem of obtaining the structure $\varrho_0(x)$ from the observed line profile.

In order to obtain $\varrho_0(x)$ with the aid of (5), the profile measurement must be extended infinitely in reciprocal space, which is evidently not feasible in practice. In this connexion a procedure was described (Doi, 1957, 1960) which enables us to obtain as much information as possible in the limited region of reciprocal space, using the function:

$$\varphi_{(hkl)}(x)=\int_{-\infty}^{+\infty}A_0(s'+s_{(hkl)})K(s')\exp(-2\pi is'x)ds' \tag{6}$$

with

$$s'=s-s_{(hkl)},\ K(s')=\sin\pi a_{(hkl)}s'/\pi s' \quad \text{and}\quad a_{(hkl)}=1/s_{(hkl)}\,, \tag{7}$$

where $s_{(hkl)}$ means the position of the centre of the (hkl) profile. The function $\varphi_{(hkl)}(x)$ can be calculated practically with the knowledge of $A_0(s)$ only in the neighbourhood of $s=s_{(hkl)}$ where $K(s')$ has appreciable values, provided that there is no other Debye–Scherrer line there.

It was also shown that (Doi, 1957)

$$\varphi_{(hkl)}(x)=\int_{-\infty}^{+\infty}\varrho_0(x')\Delta(x-x')\exp 2\pi is_{(hkl)}x'dx', \tag{8}$$

with

$$\Delta(x)=\int_{-\infty}^{+\infty}K(s)\exp(-2\pi isx)ds=\begin{cases}1 & |x|<\frac{1}{2}a_{(hkl)}\\ 0 & |x|>\frac{1}{2}a_{(hkl)}\,,\end{cases} \tag{9}$$

which means that $\varphi_{(hkl)}(x)$ is equal to the structure factor (hkl) of $\varrho_0(x)$ for the part comprised between $x+(\frac{1}{2})a_{(hkl)}$ and $x-(\frac{1}{2})a_{(hkl)}$.

Suppose now that the structure $\varrho_0(x)$ is expressed by

$$\varrho_0(x)=\Sigma g_m(x-ma_{(hkl)}-\varepsilon_m)p(m)\,, \tag{10}$$

where $g_m(x)$ is a function having a maximum peak of normalized area at $x=0$ and more or less confined to the vicinity of the origin. That is, the structure $\varrho_0(x)$ is regarded as constituted of atoms of electronic contents p(m) which are situated at $ma_{(hkl)}+\varepsilon_m$. It is readily seen that, if the peaks in $\varrho_0(x)$ are all sufficiently narrow (Doi, 1960),

$$\varphi_{(hkl)}(ma_{(hkl)})=p(m)\exp(2\pi is_{(hkl)}\varepsilon_m) \quad (m=0,\ \pm1,\ \pm2,\ \ldots,\ \text{etc.})\,, \tag{11}$$

which means that the structure $\varrho_0(x)$ can be obtained with the profile measurement only in the neighbourhood of $s_{(hkl)}$, *so long as $\varrho_0(x)$ is described by finite sets of parameters, say $p(m)$'s and ε_m's.*

2·1. *The interpretation of $\varrho_0(x)$ in terms of statistical parameters of assembly $\varrho_n(x)$'s*

The structure $\varrho_0(x)$ thus obtained does not necessarily correspond to any real structure present in the assembly $\varrho_n(x)$'s which constitute the crystallites. But from (2) it is seen that the self-convolution of $\varrho_0(x)$:

$$V(x)\equiv\varrho_0(x)\ast\varrho_0(x)=\sum_m\sum_{m'}g_m(x-ma_{(hkl)}-\varepsilon_m)\ast g_{m'}(x-m'a_{(hkl)}-\varepsilon_{m'})p(m)p(m') \tag{12}$$

is significant in the sense that it represents the atomic-pair distribution in the substance examined.

Here, with a view to obtaining the size-distribution function of crystallites from $\varrho_0(x)$, we artificially let all the ε_m's be zero in $\varrho_0(x)$ and $V(x)$, i.e. we have

$$\varrho_0^*(x)=\sum_m g_m(x-ma_{(hkl)})p(m) \tag{13}$$

and

$$V^*(x)=\varrho_0^*(x)\ast\varrho_0^*(x)\,. \tag{14}$$

$V^*(x)$ is the Fourier transform of a virtual line profile $I^*(s)$ which would be obtained *if there were no lattice deformations at all* that make the line profile unsymmetrical, other structural parameters which broaden the profile symmetrically, such as the distribution of crystallite sizes, being left unchanged.

Now let

$$V^*(x)=\sum_M(g(M)/M)V_M(x)\,, \tag{15}$$

where $V_M(x)$ stands for the self-convolution of the linear lattice $\varrho_M(x)$ composed of M point-like atoms of unit electronic contents (Fig. 1). The meaning of this series expansion of $V^*(x)$ becomes obvious when we make the Fourier transforms of both sides of (15) (Guinier, 1956);

$$I^*(s')=\sum_M(g(M)/M)\sin^2(\pi Ma_{(hkl)}s')/\sin^2(\pi a_{(hkl)}s')\,, \tag{16}$$

that is, the coefficients of expansion $g(M)/M$, which we shall call hereafter the distribution function of crystallite sizes, represent the number-fraction of linear structures composed of M atoms in the substance examined. If it can be assumed, as in the case of amorphous carbons and graphites, that all the crystallites are of platy shapes with two faces both parallel to the reflecting plane and with the generatrices perpendicular to it, $g(M)$ represents directly the mass-fraction of crystallites having thickness $Ma_{(hkl)}$.

Now the problem to be solved is to determine the coefficients $g(M)/M$ in (16) (and consequently in (15))

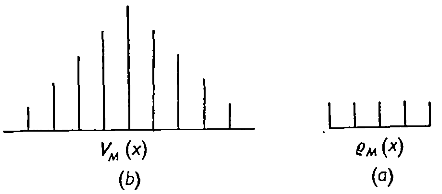

Fig. 1. (a) Linear lattice composed of M point-like atoms ($M=5$) of unit electronic content $\varrho_M(x)$. (b) Its self-convolution $V_M(x)=\varrho_M(x) * \varrho_M(x)$.

so as to get the best fit between the observed and calculated profiles.†

From the definition of $V_M(x)$ (Fig. 1) it is readily seen that,

$$g(M)/M = \Delta V^*(Ma_{(hkl)}) - \Delta V^*(M+1\,.\,a_{(hkl)}) \qquad (17)$$

with

$$\Delta V^*(M\,.\,a_{(hkl)}) = V^*(M-1\,.\,a_{(hkl)}) - V^*(M\,.\,a_{(hkl)})\,. \qquad (18)$$

The equation (17) corresponds to the equation (22) in Bertaut's paper (Bertaut, 1950) which states that the second derivatives of the Fourier transform of line profile $U(x)$ gives the size distribution function. As pointed out by Bertaut himself, however, the differentiation of Fourier transform demands precision in profile observations at the points extremely far away from the profile centre, as may be seen from the relation (Bertaut, 1950),

$$\frac{d^2U(x)}{dx^2} = -\int_{-\infty}^{+\infty} I(s')4\pi^2 s'^2 \exp 2\pi i s'x\, ds'. \qquad (19)$$

On the other hand the derivatives or the differences of $V^*(x)$ appearing in equations (17) and (18) can be obtained without much errors up to those of the second order, because $V^*(x)$ is derived from the amplitude distribution modulated by the kernel $K(s')$, i.e. from the observed intensity distribution modulated by a function which decreases with s' as s'^{-2}.

3. The determination of size-distribution function of amorphous carbon

As an example of the method of analysis above described, the (00, 2) line profile of amorphous carbon was analyzed to give the distribution function of crystallite sizes in the direction perpendicular to (00, 1) planes.

The sample‡ used in this work was one derived from natural gas by pyrolysis with CO, CO_2 and water vapour at about 1400 °C. The chemical analysis showed the content of fixed carbon to be 98·5%. Other physical and chemical properties were found almost identical with those of 'Thermal Black P-33' of Thermatomic Carbon Co., U.S.A. (H. Nagashima: private communication).

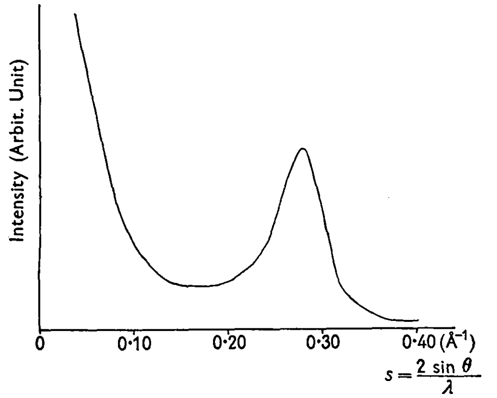

Fig. 2. Observed intensity distribution of amorphous carbon.

The (00, 2) line profile was obtained by X-ray diffractometer with a proportional counter. The diffractometer was so adjusted that only Cu $K\alpha$ radiation was permitted to be recorded on the diffractograms. Fig. 2 shows the intensity distribution thus obtained. For the purpose of correcting for the Compton scattering, the Debye–Scherrer diagrams of well-crystallized pure graphites were observed. The background intensities of the graphite diagrams, corrected for the different compactness of materials, were substracted from the observed line profile of amorphous carbon. Finally the intensity curve was corrected for the polarization and geometrical factors, and multiplied by s^2/f_c^2, where f_c means the atomic form factor of carbon (McWeeny, 1952). Thus we have the function $I(s)$ to be substituted in (4).

Now, with a view to applying the procedures described in the preceding sections, one has to assign the phase angle $\omega(s)$ to every point s in the Debye–Scherrer diagram. It is seen from equations (12)–(18), however, that the distribution function $g(M)/M$ to be obtained is not affected by the way with which the phase angle is allotted, because the distribution function is to be derived from $V(x)=\varrho_0(x) * \varrho_0(x)$, the unfolded structure $\varrho_0(x)$ being of use only for obtaining $V(x)$ from the intensity distribution in the vicinity of the profile centre.

Thus we can assume that

$$\omega(s)=0\,, \qquad (20)$$

which means that $\varrho_0(x)$ is centrosymmetric with respect to the origin where one of the atoms constituting $\varrho_0(x)$ is situated. In fact it was found that the distribution function was the same even when we assume in place of (20) that

$$\omega(s)=\tfrac{1}{2}\,. \qquad (21)$$

The profile centre $s_{(00,2)}$ was found to be 0·285 Å^{-1},

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† This kind of problem may be solved by the least-squares method, as developed by Diamond (1958). But this method of analysis may require so much computational work that it is hardly feasible to the case where there are causes of line broadening other than that of finite crystallite sizes, as is the case in the example treated here.

‡ Produced by Nippon Gas Kagaku Co., and furnished to the author through the courtesy of Toshiba Denko Co.

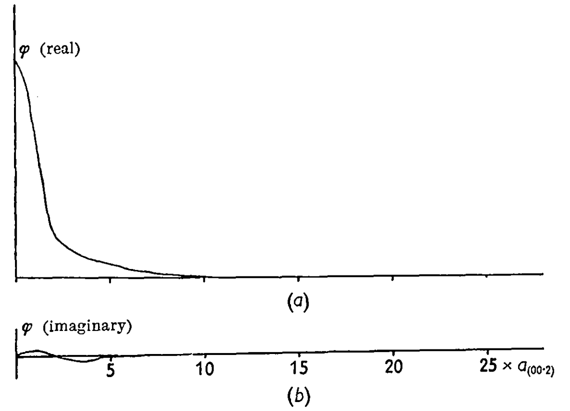


Fig. 3. The function $\varphi_{(00,2)}(x)$, in its real (*a*) and imaginary (*b*) components.

corresponding interplanar spacing being $a_{(00,2)} = 3{\cdot}51$ Å. These values were substituted in $K(s')$ of (7). The integrand of (6) was then calculated and extrapolated until $s=0$ and $s=s_{(00,4)}$, where the integrand vanishes. The function $\varphi_{(00,2)}(x)$ was calculated after (6) giving the results as shown in Figs. 3(*a*) and (*b*).

By sampling the values of φ-function at

$$x=0,\ \pm a_{(00,2)}\ \pm 2a_{(00,2)},\ \pm 3a_{(00,2)},\ \ldots,\ \text{etc.},$$

the parameters $p(m)$'s and ε_m's were obtained after (11), hence the unfolded structure $\varrho_0(x)$ was constructed using (10). We let then all the ε_m's be zero without modifying the $p(m)$'s, to obtain the function $V^*(x)$ by (13) and (14). Fig. 4 shows the results.

The equations (17) and (18) were applied to $V^*(x)$ thus obtained, and the distribution function $g(M)/M$ was calculated. The results, which were so normalized that

$$\sum_M (g(M)/M) = 100\%\,, \tag{22}$$

are shown in Fig. 5, where the numerals represent the percent values of the number-fraction of crystallites constituted of M layers. It is noted that the value for $M=1$ represents not only the fraction of the crystallites composed of one atomic layer but includes the fraction of the non-organized carbon atoms as termed by Franklin (1950). One can see easily here that $g(M)/M$ is roughly proportional to 2^{-M}.

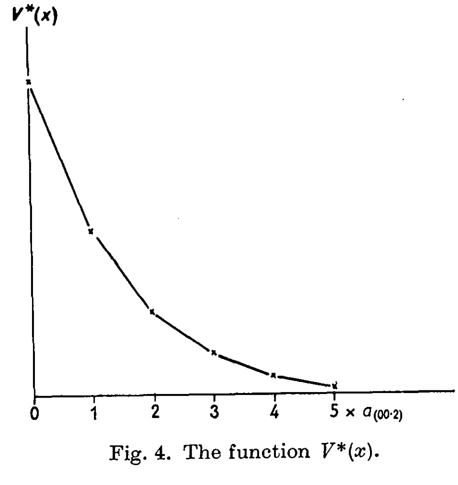


Fig. 4. The function $V^*(x)$.

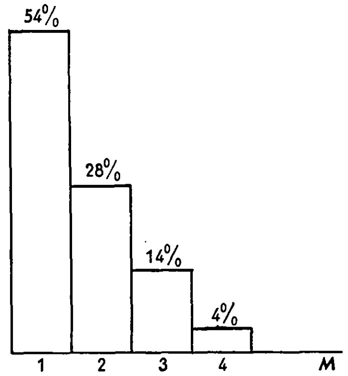


Fig. 5. The distribution function $g(M)/M$, the number-fraction of the crystallites constituted from M atomic layers parallel to (00, 1). It is seen that the values of $g(M)/M$ are roughly proportional to 2^{-M}.

The values of $g(M)/M$ were now substituted in (16) to calculate the theoretical line profile which would be expected for the assembly of crystallites having the size distribution of Fig. 5, when the layers were stacked without any irregularity in interlayer spacings. The comparison of observed and calculated line profiles is shown in Fig. 6, where one can see fairly good agreement between these two profiles except some tiny discrepancies due to the irregularities in interlayer spacings, which exist in reality in the material examined.

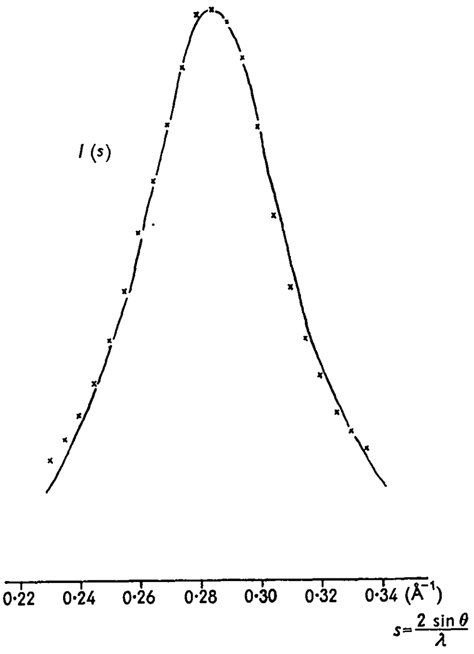


Fig. 6. The comparison of observed and calculated intensity distributions. × observed and — calculated.

4. Concluding remarks

We have seen in the preceding sections that when $\varrho_0(x)$ is expressed by a set of finite number of parameters, these are to be regarded as to represent in some way the statistical characteristics of the assembly $\varrho_1(x), \varrho_2(x), \ldots, \varrho_N(x)$.

On the other hand, it was shown (Doi, 1957) that a kind of averaging operation was indispensably introduced by finite samplings of the points in reciprocal space, even in the analysis of such a crystal that the structure can be represented uniquely by a function $\varrho(x)$, and consequently the phase angles are to be unequivocally defined for every point in reciprocal space. That is, if the points are sampled at a constant interval of $1/aL (L > 1)$, the structure to be obtained is not $\varrho(x)$ itself but the one averaged for $x, x \pm aL, x \pm 2aL, \ldots, x \pm naL, \ldots$, etc., which is denoted by $\overline{\varrho(x)}^L$.

Hence, strictly speaking, the procedure described in §§ 2–3 does not give the structure $\varrho_0(x)$ but the structure $\overline{\varrho_0(x)}^L$ defined as

$$\overline{\varrho_0(x)}^L * \overline{\varrho_0(x)}^L = \frac{1}{N}\sum_{n=1}^{N}\left\{\overline{\varrho_n(x)}^L * \overline{\varrho_n(x)}^L\right\} . \qquad (23)$$

The structure $\overline{\varrho_0(x)}^L$ means the value of $\varrho_0(x)$ averaged for $x, x \pm aL, x \pm 2aL, \ldots$, etc.[†]

In the analysis of carbon black described in § 3, observed intensities were sampled at an equal interval of $1/a_{(00,2)}L$ with $L = 28$, which means that the value of L was taken so large that there were in fact few crystallites for which $M \geq L$ (see Fig. 5), and hence we can assume that

$$\overline{\varrho_0(x)}^L \sim \varrho_0(x) . \qquad (24)$$

While in the structure analysis of disordered single crystals constituted of a number of coherent domains (mosaics) diffracting X-rays in an independent way, the diffuse scatterings should be interpreted in terms of $\overline{\varrho_0(x)}^L$ and not of $\overline{\varrho(x)}^L$. But when aL is not so large compared with the dimensions of coherent domains, each term in the right-hand side of (23) may be regarded as identical, hence we have

$$\overline{\varrho_0(x)}^L \sim \overline{\varrho(x)}^L . \qquad (25)$$

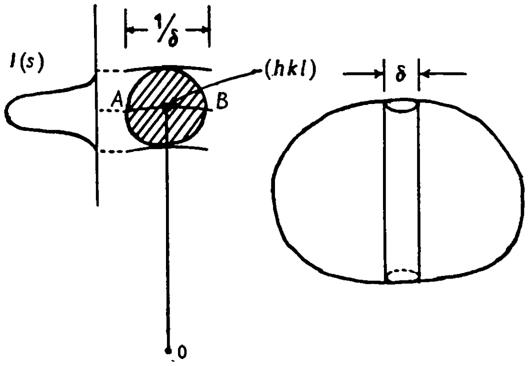
The condition (25) is expected to hold for the structure previously analyzed by the author (Doi, 1960).

APPENDIX

A remark on the meaning of $\varrho_n(x)$ appearing in equations (1) and (2)

Let the intensity distribution around the relpoint (hkl) given by a single crystallite be represented by a shaded area in Fig. 7(a), which give rise to the line profile $I(s)$ by projecting the distribution along the spherical shells centred at the origin of the reciprocal space O. The projection is carried out within the range AB in Fig. 7(a) of width $1/\delta$, in which the spherical shells can be approximated by planes.

In direct space (Fig. 7(b)) the volume of the crystallite is divided into a set of columns perpendicular to the (hkl) plane and their diameters are of the order of δ. Suppose now that all the crystallites present in the substance examined are divided in this way into a set of columns, and $\varrho_n(x)$ means the electronic distribution of the nth column projected upon a straight line perpendicular to the (hkl) plane, then it is readily seen that the Fourier transforms of $\varrho_n(x)$'s satisfy the relation (1) and the linear structures $\varrho_n(x)$'s the relation (2).



(a) (b)

Fig. 7. Intensity distribution.

For the case of the (00, 2) line profile of amorphous carbon treated in § 3, $1/\delta$ must be of the order of $a^*_{(10,0)}$ at the most, because the adjacent relpoint, (10, 2) or (01, 2), does not intervene in the (00, 2) profile. Accordingly the diameters of the columns, of which the crystallites are supposed to be constituted and in terms of which the line profile analysis is made, is of the order of $a_{(10,0)}$. Here $a^*_{(10,0)}$ and $a_{(10,0)}$ mean the unit cell translations in the plane parallel to the reflecting plane, of reciprocal and direct lattices respectively.

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[†] A similar result was obtained by Eastabrook & Wilson (1952) for the strain distribution function as derived from line-profile analyses.