Slit-Height Correction in Small-Angle Scattering without Spherical Symmetry

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It is shown that the unsmeared diffuse small-angle diffraction pattern of an arbitrary shape can be exactly derived from the integrated intensities measured along lines parallel to the trace of the direct beam of linear cross-section. These intensities should be measured for different orientations realized by turning the sample about the beam direction. The knowledge of the intensity distribution along the direct-beam height is not required in this treatment. The total direct-beam intensity as well as the slit height of the detector enter the conversion formula as constant factors and therefore need not be known for relative intensity measurements.

Introduction

The true small-angle diffraction pattern corresponds to the use of direct beam of point-like cross-section; the finite dimensions in the ordinary small-angle cameras implies a smearing of the diffraction pattern. The current methods of correcting for the imperfect collimation of the direct beam are limited only to the special intensity distribution of the beam and to the special shapes of the true scattered intensity distribution (Guinier & Fournet, 1955, pp. 111–120). The general case was treated by Kranjc (1955) using the convolution theorem for multiple Fourier transforms. The knowledge of the intensity distribution in the direct-beam cross-section is essential in the use of this method. The measurement of the latter quantity is not required in the present treatment.

Derivation of correction formula

The smearing of the diffuse small-angle pattern of an arbitrary shape due to the slit height is schematically represented in Fig. 1. In this figure the trace of the beam cross-section lies along the *y*-axis, where the density of points denotes the variation of the direct-beam intensity. The contour lines indicate the intensity distribution of two partial diffuse patterns. Let the scattered intensity be integrated along the *t*-axis parallel to and distant by R from the *y*-axis. This is indicated in the left hand part of Fig. 1 for the position 1 of the sample. The intensity resulting by integration of the pattern along the *t*-axis is equal to the sum of the integrated intensities of all partial diffraction patterns along that line. The resulting integrated intensity is thus independent of the distribution of these partial patterns along the beam trace, i.e. of the
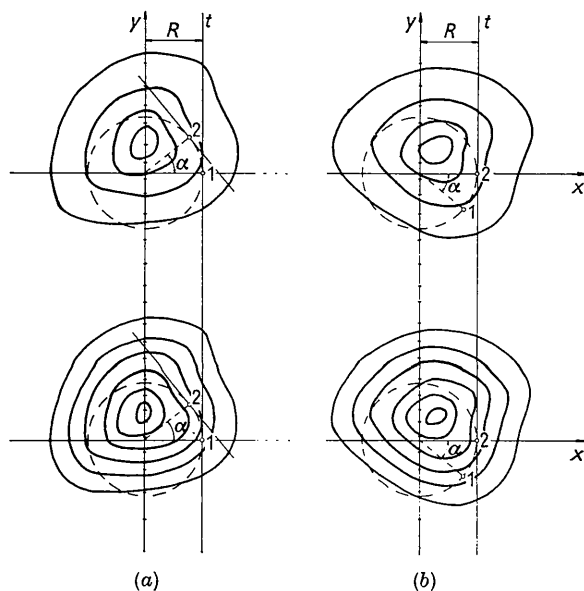

Fig. 1. Two of partial patterns (contour lines) composing the diffraction pattern before (*a*) and after (*b*) rotating the sample through the angle α.
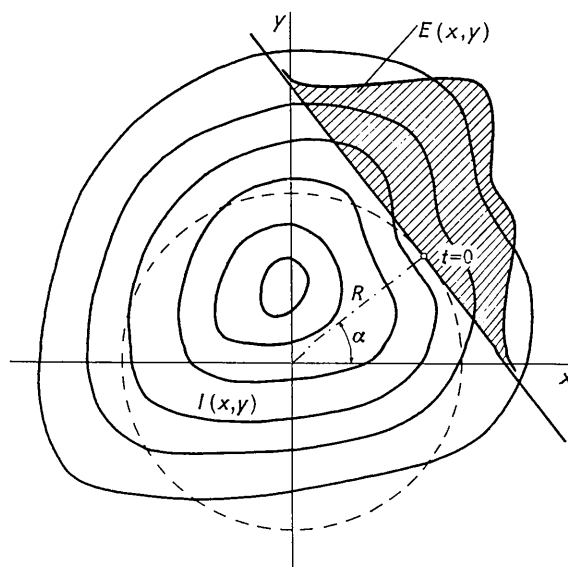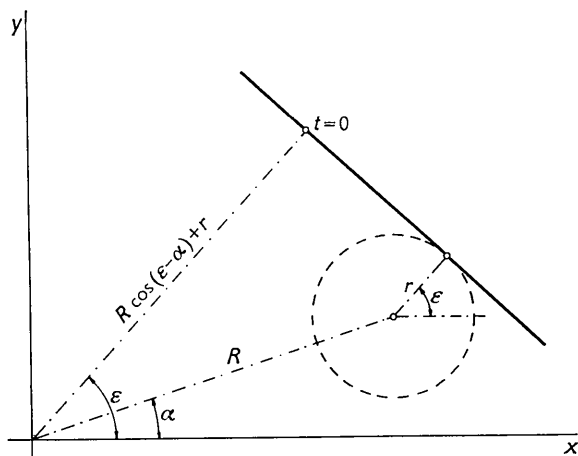

Fig. 2. Schematic representation of the true intensity distribution (contour lines) and of intensity scattered into a line (shadowed area).

Fig. 3. Geometry of relation (4) defining $\Psi(r)$.

direct-beam intensity distribution. The same value would be obtained with the beam of point-like cross-section the intensity of which would be equal to the total intensity of the real beam. The right-hand side of Fig. 1 shows the rotation of the partial patterns through the angle α resulting from turning the sample through this angle about the axis parallel to the beam direction. The integrated intensity is then measured along the same t-axis. This procedure can be carried out for sufficiently close values of α ranging from 0 to 2π. The values obtained in this way are proportional to the integrated intensities of the unsmeared pattern along the tangent lines to the circle of radius R circumscribed round the origin. One such value is indicated by the shadowed area on Fig. 2. By ascribing these values of integrated intensities to the corresponding tangent points $[x, y]$ with polar coordinates R and α, the two-dimensional function $E(x, y) \equiv E(R \cos \alpha, R \sin \alpha)$ is defined. The whole plot of E-function is obtained by repeating the above procedure in a sufficient range of R.

The direct reasoning given above leads immediately to the following relation between the true intensity function $I(x, y)$, the measured function $E(x, y)$ of integrated intensities and the distribution function $i(y)$ of the direct-beam intensity:

$$E(R \cos \alpha, R \sin \alpha)$$
$$= c \int_{-\infty}^{+\infty} I(R \cos \alpha - t \sin \alpha, R \sin \alpha + t \cos \alpha) dt , \quad (1)$$

where

$$c = \int_{-\infty}^{+\infty} i(y) dy .$$

This relation enables us to calculate the desired I-function from the measured E-function. To determine the value of the I-function in some chosen point $[x, y]$ let us first of all define the auxiliary function

$$\Phi(r) = (1/2\pi) \int_0^{2\pi} I(R \cos \alpha + r \cos \varepsilon, R \sin \alpha + r \sin \varepsilon) d\varepsilon . \quad (2)$$

This function has the property of being radially symmetrical round the point $[R \cos \alpha, R \sin \alpha]$ in which it follows from the definition (2)

$$\Phi(0) = I(R \cos \alpha, R \sin \alpha) . \quad (3)$$

Although the function $\Phi(r)$ cannot be directly measured it can be derived from the other function $\Psi(r)$ which can be expressed in terms of the measured E-function. The value of $\Psi(r)$ in a point r is equal to the integral of $\Phi(r)$ along the straight line distant by r from $[R \cos \alpha, R \sin \alpha]$. The following expression of $\Psi(r)$ can be at first found using the definition (2) of $\Phi(r)$ after some geometrical consideration (see Fig. 3):

$$\Psi(r) = (1/2\pi) \int_0^{2\pi} \left[\int_{-\infty}^{+\infty} I([R \cos (\varepsilon - \alpha) + r] \cos \varepsilon - t \sin \varepsilon, \right.$$
$$\left. [R \cos (\varepsilon - \alpha) + r] \sin \varepsilon + t \cos \varepsilon) dt \right] d\varepsilon . \quad (4)$$

This relation can be immediately rewritten by means of E-function using its definition (1) with the result

$$\Psi(r) = (1/2\pi c) \int_0^{2\pi} E([R \cos (\varepsilon - \alpha) + r] \cos \varepsilon,$$
$$[R \cos (\varepsilon - \alpha) + r] \sin \varepsilon) d\varepsilon . \quad (5)$$

The function $\Phi(r)$ can be derived from $\Psi(r)$ in the same way as for radially symmetrical small-angle scattering when deriving the unsmeared I-function from the distribution of intensities integrated along the straight lines parallel to the trace of the direct beam (Syneček, 1960). Using this analogy we find for $\Phi(0)$ which according to (3) is the only desired value of $\Phi(r)$:

$$\Phi(0) = - (1/\pi) \int_0^{\infty} (1/r) \frac{d}{dr} \Psi(r) dr . \quad (6)$$

From (3), (5) and (6) we obtain finally the formula expressing the desired I-function by means of the measured E-function in the form

$$I(R \cos \alpha, R \sin \alpha)$$
$$= - (1/\pi c) \int_{r=0}^{\infty} (1/r) \frac{\partial}{\partial r} \left[\frac{1}{2\pi} \int_{\varepsilon=0}^{2\pi} E([R \cos (\varepsilon - \alpha) + r] \right.$$
$$\left. \times \cos \varepsilon, [R \cos (\varepsilon - \alpha) + r] \sin \varepsilon) d\varepsilon \right] dr . \quad (7)$$

The total direct beam intensity given by c need not be known for relative intensity measurements. A simple consideration shows that the slit height of the detector represents similarly a constant factor which can be introduced into (7).

Remarks on practical application

The practical use of determining the unsmeared small-angle intensity distribution of a general shape according to (7) can be recommended only when counter technique is used; all necessary measured

data cannot be obtained from a single diffraction photograph. The sample-holder of the small-angle camera must allow the sample a possibility of turning about the axis parallel to the beam direction. The measurement of integrated intensities is simplified by adopting the geometrical arrangement in such a way that the vertical extension of the measured diffuse pattern does not exceed the height of the counter entrance-slit, corresponding to the constant radial sensitivity of the counter. The integration of the intensity along the various t-axes is then performed automatically. The total amount of the measured data necessary for carrying out the mathematical operations

involved in (7) with sufficient accuracy is in this case practically the same as with the frequent point-by-point intensity measurements.

References

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The Crystal Structure of the Zeolite, Phillipsite

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The crystal structure of phillipsite has been determined from the $0kl$, $h0l$, and $hk0$ electron density projections and has been refined by means of a three dimensional least-square procedure. The unit cell is orthorhombic, $B2mb$, $a = 9.96_5$, $b = 14.25_2$, $c = 14.25_2$ Å and there are two formula weights of probable composition $(K_xNa_{1-x})_5Si_{11}Al_5O_{32}.10H_2O$ in the unit cell. The silicate framework can be described as consisting of a fundamental unit of two tetrahedra linked head to head through an apical oxygen atom. Ten of these double units are then linked together by sharing corners into an S shaped configuration which is approximately 14 Å long and 7 Å wide. The open ends of this S configuration link to other S units through the oxygen atoms of the upper and lower bases of the double unit into a three dimensional network. Adjacent S units are $\frac{1}{2}a$ apart so that large channels exist both parallel to a and to b. The channel parallel to a is octagonally shaped and has an open passage with a 12 Å² cross section. The channel parallel to b has a rectangular cross section which is approximately 9 Å². The locations of the exchangeable ions and of the water molecules are discussed.

Introduction

The crystal chemical investigations of the zeolite minerals have received a sharp stimulus because of the almost simultaneous recognition that these compounds can participate in many industrially useful physico-chemical reactions and that they also frequently constitute an important fraction of sedimentary rocks in which they occur both as a diagenetic product and also as accessory authigenic crystals. The general features of zeolite structures were established by many of the early workers in X-ray crystallography (Bragg, 1937) and recently many zeolite structures have been redetermined by modern methods (Nowacki & Bergerhoff, 1957; Meier, 1960). Little attention had been devoted to the naturally occurring

lamellar type zeolites. Strunz (1957) investigated the lattice constants of phillipsite and reports

$$a = 10.02, \quad b = 14.28, \quad c = 8.64 \text{ Å}; \quad \beta = 125° 40'$$

and Wyart (1938) reports similar values for the mineral christianite. The minerals phillipsite and offretite also have similar unit cells and compositions. All these minerals probably have an almost identical silicate framework and may differ only in the type of exchangeable ion which is present.

The mineral phillipsite was chosen for this investigation because of its widespread occurrence in sediments; it is considered to have a structural relationship to some of the synthetically produced molecular sieves and it is a member of a group of zeolites whose structure until recently (Sadanaga et al., 1960) had not been studied in detail. The material which was used in this investigation was supplied by Dr. G. Arrhenius of the Scripps Institution of Ocean-

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