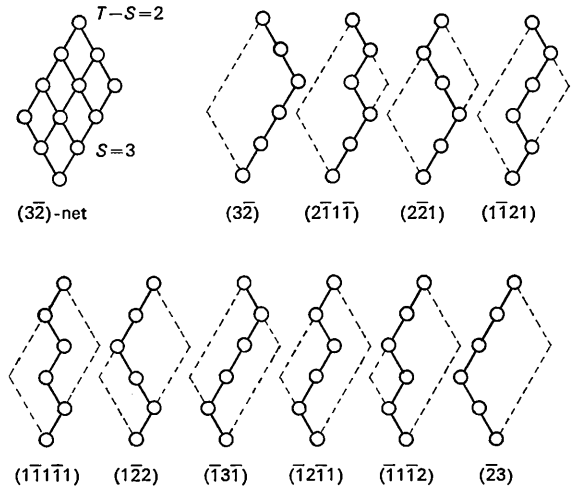

Fig. 1. Examples of Zhdanov sequences, (ZS), belonging to the (3,$\bar{2}$)-net.

$\boxed{m=3r+1}$

$$N_m^0=2rk-2r(n_1+n_{\bar{1}})+r(n_2+n_{\bar{2}})+2r(n_{1\bar{1}}+n_{\bar{1}1})$$
$$+\sum_{t=1}^{r-1}(r-t)\left(4\sum_{s=1}^{t}{}_{3t+1}M_{3s-1}-2\sum_{s=0}^{t}{}_{3t+1}M_{3s+1}\right.$$
$$-2\sum_{s=0}^{t}{}_{3t+1}M_{3s}-2\sum_{s=0}^{t}{}_{3t+2}M_{3s+1}+\sum_{s=0}^{t}{}_{3t+2}M_{3s}$$
$$+\sum_{s=1}^{t+1}{}_{3t+2}M_{3s-1}-2\sum_{s=0}^{t}{}_{3t}M_{3s}+\sum_{s=1}^{t}{}_{3t}M_{3s-1}$$
$$\left.+\sum_{s=0}^{t-1}{}_{3t}M_{3s+1}\right)$$
$$D_m^*=(a-b)/3+2r(n_1-n_{\bar{1}})+r(n_2-n_{\bar{2}})$$
$$+\sum_{t=1}^{r-1}(r-t)\left(2\sum_{s=0}^{t}{}_{3t+1}M_{3s+1}-2\sum_{s=0}^{t}{}_{3t+1}M_{3s}\right.$$
$$+\sum_{s=1}^{t+1}{}_{3t+2}M_{3s-1}-\sum_{s=0}^{t}{}_{3t+2}M_{3s}+\sum_{s=0}^{t-1}{}_{3t}M_{3s+1}$$
$$\left.-\sum_{s=1}^{t}{}_{3t}M_{3s-1}\right)$$

$\boxed{m=3r-1}$

$$N_m^0=2rk$$
$$+\sum_{t=1}^{r-1}(r-t)\left(4\sum_{s=0}^{t-1}{}_{3t-1}M_{3s+1}-2\sum_{s=0}^{t-1}{}_{3t-1}M_{3s}\right.$$
$$-2\sum_{s=1}^{t}{}_{3t-1}M_{3s-1}-2\sum_{s=0}^{t}{}_{3t}M_{3s}+\sum_{s=1}^{t}{}_{3t}M_{3s-1}$$
$$+\sum_{s=0}^{t-1}{}_{3t}M_{3s+1}-2\sum_{s=1}^{t-1}{}_{3t-2}M_{3s-1}+\sum_{s=0}^{t-1}{}_{3t-2}M_{3s+1}$$
$$\left.+\sum_{s=0}^{t-1}{}_{3t-2}M_{3s}\right)$$
$$D_m^*=-(a-b)/3+\sum_{t=1}^{r-1}(r-t)\left(2\sum_{s=2}^{t-1}{}_{3t-1}M_{3s}-2\sum_{s=1}^{t}{}_{3t-1}M_{3s-1}\right.$$
$$+\sum_{s=0}^{t-1}{}_{3t}M_{3s+1}-\sum_{s=1}^{t}{}_{3t}M_{3s-1}+\sum_{s=0}^{t-1}{}_{3t-2}M_{3s}$$
$$\left.-\sum_{s=0}^{t-1}{}_{3t-2}M_{3s+1}\right).$$

Even when the structure is rhombohedral, these general forms are also valid with some modifications in the definitions of quantities used.

The details will be reported in the near future.

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A statistical evaluation of absorption.

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This paper reports an empirical method for evaluating the three-dimensional transmission by the statistical treatment of the intensity differences among equivalent reflexions, and the accuracy of the method is discussed.

In the course of a crystal structure analysis, small crystals are usually used for collecting intensity data without any correction for absorption. However, it is essential to give proper treatment of absorption effects when great accuracy is required. Numerical or analytical methods for absorption correction are very accurate, as is well known, but they are not always practical because they require an exact knowledge of the crystal shape and much computer-time.

In the study of protein crystal structure, it is necessary to take account not only the crystal but also its mounting, which usually comprises a glass capillary in which it is enclosed in contact with some mother liquor. North,

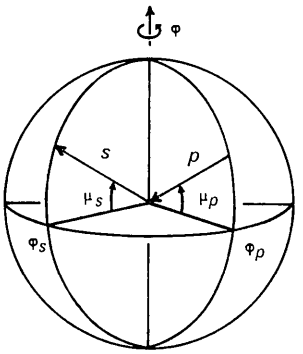

Fig. 1. Schematic representation of the angles φ_p, μ_p, φ_s and μ_s, which refer to the primary beam direction p and secondary beam direction s.

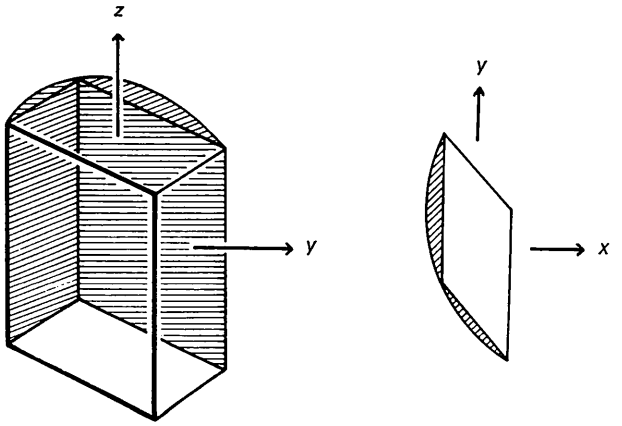

Fig. 2. The crystal viewed from the **x** and **z** directions. The additional absorber is illustrated by shadowing. The **z** direction is parallel to the goniometer φ axis.

Phillips & Mathews (1968) have improved a semi-empirical method based upon the method suggested by Furnas (1957). This method, however, cannot apply to the asymmetrical absorber, correction of which takes an important part in protein structure analysis when using the effects of anomalous scattering (Blow & Rossmann, 1961).

This paper reports an empirical method which can fit closely even to the asymmetrical absorber and requires no knowledge of crystal dimensions or of the linear absorption coefficient.

Method

Observed intensity differences among equivalent reflexions are largely due to the variation of transmission. By the statistical treatment of this information the three-dimensional transmission can be evaluated. This idea leads to a least-squares method in which the equation (1) is minimized.

$$R=\sum_{h}\sum_{i=1}^{N} w_{hi}[A(h,i)\,.\,I^{o}_{hi}-I^{t}_{h}]^2, \qquad (1)$$

where subscripts h and i represent an order of independent and equivalent reflexions respectively, $A(h,i)$ is the function of the absorption correction which should be obtained, I^o and I^t are the observed and true intensity, w is a weight and N is the total number of the equivalent reflexions in each Laue group. Anomalous scattering differences, being observed, will be considered as random errors in equation (1). As the true intensity is unknown, it is replaced by an average value as follows:

$$R=\sum_{h}\sum_{i=1}^{N} w_{hi}\left\{A(h,i)\,.\,I^{o}_{hi}-\left[\sum_{j=1}^{N} w_{hj}A(h,j)\,.\,I^{o}_{hj}\right]\Big/\sum_{j=1}^{N} w_{hj}\right\}^2 . \qquad (2)$$

It is very important what kind of function will be substituted for $A(h,i)$. This function must at least have periodicity, and therefore the following expansion is assumed:

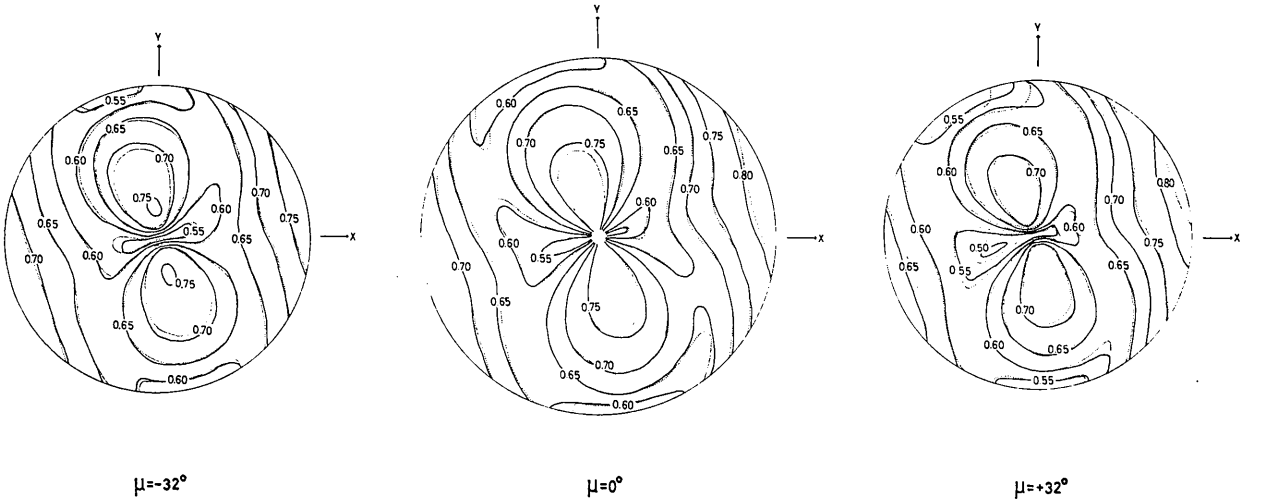

Fig. 3. The contour plots of transmission over the reciprocal planes corresponding to $\mu=0°$ and $\mu=\pm 32°$. Dotted lines are the plots of test data and continuous lines are those represented by our method.

$$A(h,i)=\sum_n\sum_{n'}\sum_m\sum_{m'}\{C_{nn'mm'}\cos(n\varphi_p+n'\varphi_s+m\mu_p+m'\mu_s)+S_{nn'mm'}\sin(n\varphi_p+n'\varphi_s+m\mu_p+m'\mu_s)\} \quad (3)$$

where $C_{nn'mm'}$ and $S_{nn'mm'}$ are coefficients to be determined, and φ_p, φ_s, μ_p and μ_s are the angles which refer to the primary beam direction p and secondary beam direction s of the reflexion hi as shown in Fig. 1. Since the transmission varies smoothly with the directions of the primary and secondary beams, this expansion will converge rapidly. The observational equation being linear, the coefficients $C_{nn'mm'}$ and $S_{nn'mm'}$ are obtained as the eigenfunctions corresponding to the minimum eigenvalue.

Tests of the method

The setting of equi-inclination is equivalent to the standard setting of the four-circle diffractometers. Our method being applied to this setting, the angles in equation (3) can be expressed as follows:

$$\mu_p=\mu_s=\mu$$
$$\varphi_p=\varphi+\Delta\varphi$$
$$\varphi_s=\varphi-\Delta\varphi$$
$$\sin\mu=\sin\chi\sin\theta$$
$$\tan\Delta\varphi=\cos\theta/(\cos\chi\sin\theta)\,,$$

where θ, χ and φ are angles of the standard setting and μ is the inclination angle. The sine terms of $\Delta\varphi$ can be eliminated, since the transmission does not change when the X-ray travels the reverse path. Furthermore, if cross terms of φ and $\Delta\varphi$ can be neglected, the following very simple equation is obtained:

$$A(h,i)\simeq\sum_n\sum_m\{C_{nm}\cos(n\varphi+m\mu)+S_{nm}\sin(n\varphi+m\mu)\}\cos(n\Delta\varphi)\,. \quad (4)$$

Test data were prepared by the computer program of Burnham (1963) based on the Gaussian integration method, and the shape of the crystal with asymmetrical absorber is illustrated in Fig. 2. The Laue group was assumed as $\bar{3}$, in which the symmetry axis is tilted about 77° from the φ axis; therefore $N=6$.

Fig. 3 shows the contour plots of transmission over the reciprocal planes corresponding to $\mu=0°$ and $\mu=\pm32°$. Dotted lines are the plots of test data and continuous lines are those represented by our method using 53 terms, namely $m=0\sim2$ and $n=0\sim8$, and there are close resemblances between both contour maps. The average error was 1·11 % in this case. From these results, it is clear that all reflexions are corrected with satisfactory and equal accuracy. This practicability may come from the fact that the value of transmission or absorption slowly varies depending upon the angle, and the summation over h as well as over i in equation (1) is effective in giving good statistical values.

While the test mentioned above was carried out with full data of 1934×6 reflexions, accuracy good enough for practical purposes can be obtained with fractional data. For example, the average error increased only 0·28 % even with 188 pairs of equivalent reflexions. In another test, anomalous dispersion differences were conserved after the correction.

For the application, it is necessary to omit very strong reflexions which may be influenced by the extinction effect, and such a mounting is also unfavourable, as some parameters have the same value over the equivalent reflexions. In addition, it is difficult to apply this method to the Laue groups $\bar{1}$ and $2/m$, so we are now investigating the extension of the present method to these groups.

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Röntgendiffraktometrische Parallelanregung von Kristall-Gitterebenen.

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X-rays with a very small angle of incidence to any reflecting plane, cause Bragg reflexions of the usual type. An explanation, based on the present theory of X-ray diffraction, cannot as yet be given.

Nach den üblichen interferenztheoretischen Vorstellungen sind die Netzebenen von Kristallgittern nur dann zu Reflexionen befähigt, wenn das einfallende Röntgenstrahlbündel (Wellenlänge λ) unter dem Braggschen Reflexionswinkel θ auf die betreffende Netzebenenschar (Ebenenabstand d) auftrifft und dabei die Braggsche Gleichung $2d\sin\theta=n\lambda$ (n ganzzahlig) erfüllt.

Überraschenderweise führten eigene Experimente mit Heidenhainschen Aufdampfgittern (Fig. 1) zu einem davon abweichenden Ergebnis: strahlt man unter sehr kleinen Glanzwinkeln (z.B. $\psi=0{,}25°\simeq0{,}01\,.\,\theta_{111}$) quer zu den metallisch auf Glas aufgedampften Teilungslinien ein, die voneinander isoliert und zueinander parallel ausgerichtet sind und in der Gitterfläche eine (111)-Vorzugsorientierung ihrer Au-Kristallite zeigen (Weyerer, 1971*a*, *b*), so entsteht dennoch in der gewohnten Reflexionsrichtung die (111)-Interferenz von Gold, vgl. Fig. 2. Die Intensität dieser Raumgitter-Interferenz ist zwar recht klein; doch hebt sich