at every position of the plate displaced vertically, the collimator slits being 1 mm. wide and 3 mm. high. The result is given in Fig. 3. While the difference in intensity of reflexions from the etched and unetched areas is shown clearly, the boundary effect was not observed.

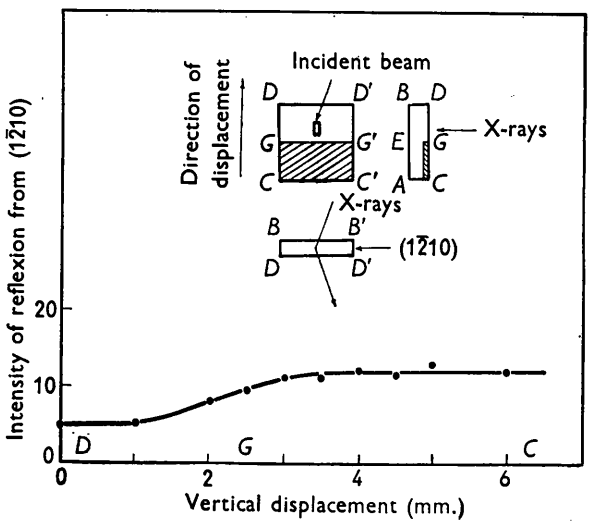

Fig. 3. The intensity of reflexion from net planes perpendicular to the boundary, showing no intensity anomaly at the boundary.

6. In the case of Bragg surface reflexion, using the various specimens mentioned at the beginning, no anomaly was found at the boundary.

The present author (Fukushima, 1935*a*, *b*, 1936) has measured the intensity of transmitted reflexion from different parts of a quartz plate to which a mechanical stress was applied. In seeking a relationship between the extent of the reduction in the extinction and the distribution of the strain generated in the plate, the author came to the conclusion that the reduction in the extinction effect is proportional to the gradient of the strain and not to the strain itself. In view of these investigations and the inadequacy of supposing, in the present case, a zone of especially strong mechanical stress (refer to (5)) or a step structure produced by etching at the boundary, the following seems to be a reasonable explanation of the present experiments. At the boundary between the etched and unetched areas there exists a zone of fairly large strain gradient in a direction parallel to the surface and perpendicular to the boundary. The existence of such a zone is the cause (through a reduction of the extinction effect) of the anomalous increase of the intensity of X-ray reflexion from the net planes at the boundary and perpendicular to the above-mentioned gradient. From this point of view the results of the apparent non-existence of the enhancement in the experiments (5) and (6) is explained by assuming that the strain gradient does not exist, or is small, in the directions perpendicular to the above-mentioned direction of large gradient.

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An analytic method for the determination of shape and location of Fourier peaks.

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In this note a rapid and efficient method of locating maxima of Patterson and electron-density maps is described. It is assumed (as is implicit in Booth's treatment (Booth, 1948)) that a peak resembles an elliptic paraboloid near the maximum. In addition to locating the maximum, the procedure outlined below gives information concerning the shape of the contours near the maximum and the directions of steepest and most shallow descents. The method avoids graphical procedures (e.g. Carpenter & Donohue, 1950) or extensive least-square methods (Shoemaker, Donohue, Schomaker & Corey, 1950).

It is assumed that the Fourier function (i.e. the Patterson or electron-density distribution) has been evaluated at the points of a net having grid lines parallel to crystallographic directions X' and Y'. The grid lines are separated by some convenient interval (usually 1/60 or 1/120 of the unit cell dimensions). Part of this net is shown in Fig. 1. The value of the Fourier function at each point (x', y') of the net is designated by $Z(x', y')$. Let the highest value of $Z(x', y')$ be called $Z(0, 0)$. The true maximum of the Fourier function will lie close to (0, 0). A good approximation of its true location can be determined from the value of $Z(0, 0)$ and the values of the eight surrounding points indicated in Fig. 1.

For convenience in studying the shape of the elliptic paraboloid that will be fitted to these nine points, the location of the maximum will be determined with respect to an orthogonal Cartesian coordinate system X, Y which is defined as follows: The X axis is collinear with the X_1

axis; the Y axis is perpendicular to the X axis. Distances measured along the X axis are equal to distances measured along the X' axis.

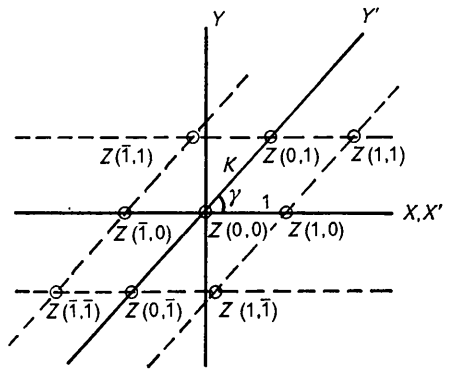

Fig. 1.

The values of the Fourier function are now used to obtain the coefficients of the equation of an elliptic paraboloid

$$Z(x, y) = Ax^2+By^2+Cxy+Dx+Ey+F \qquad (1)$$

in the X, Y coordinate system.

To transform information from the general (planar) coordinate system based on the net to the orthogonal Cartesian coordinate system that has been introduced, the following quantities are defined:

K is the ratio of the repeat distances of the net, i.e. (distance between adjacent points along Y') : (distance between adjacent points along X'). If the net was formed by taking two equal intervals along crystallographic directions, say a and b, then $K = b/a$.

γ is the angle between the positive directions of X' and Y'.

Let $\qquad s = K\cos\gamma \quad \text{and} \quad t = K\sin\gamma\,. \qquad (2)$

Using the above definitions, the coefficients of equation (1) are found to be:

$$\begin{aligned} F &= Z(0, 0)\,, \\ A &= \tfrac{1}{2}\{Z(1, 0)+Z(\bar{1}, 0)\}-F\,, \\ D &= \tfrac{1}{2}\{Z(1, 0)-Z(\bar{1}, 0)\}\,, \\ E &= \tfrac{1}{2}\{Z(0, 1)-Z(0, \bar{1})-2sD\}/t\,, \\ C &= \tfrac{1}{4}\{g-4sA\}/t\,, \\ B &= \tfrac{1}{2}\{Z(0, 1)+Z(0, 1)-2F-2s^2A-2stC\}/t^2\,, \end{aligned} \qquad (3)$$

where

$$g = Z(1, 1)+Z(\bar{1}, \bar{1})-Z(\bar{1}, 1)-Z(1, \bar{1})\,. \qquad (4)$$

In determining these coefficients, we have seemingly used more information than is necessary, i.e. we have used the values of the Fourier function at nine points to determine only six coefficients. In using the additional information we have effectively averaged together four paraboloids; at the same time a more symmetric array of data was used. The use of any one of the four diagonal terms $Z(\pm 1, \pm 1)$ leads to a set of six coefficients. By using all four (see equation (4)) the averaging is effected.

The coordinates of the maximum of the elliptic paraboloid in equation (1) are found by the usual method of equating the x and y partial derivatives of $Z(x, y)$ to zero, and solving these equations simultaneously for x and y. The coordinates of the maximum are:

$$x_{\max.} = \frac{2BD-CE}{C^2-4AB}\,; \quad y_{\max.} = \frac{2AE-CD}{C^2-4AB}\,.$$

Information about the shape of the peak is readily obtained. A plane (Z = constant) cutting the approximated peak, intersects the paraboloid in an ellipse with center at $x_{\max.}$, $y_{\max.}$. The 'a' axis of this ellipse,

$$(x-x_{\max.})^2/a^2+(y-y_{\max.})^2/b^2 = 1\,,$$

makes an angle θ with the X direction, where θ is given by:

$$\theta = \tfrac{1}{2}\tan^{-1}\{C/(A-B)\}\,.$$

The eccentricity of the ellipse ε, is given by

$$\begin{aligned} \varepsilon &= \sqrt{\{1-(b/a)^2\}} \quad \text{for} \quad b/a < 1; \\ \varepsilon &= \sqrt{\{1-(a/b)^2\}} \quad \text{for} \quad b/a > 1\,, \end{aligned}$$

where b/a is the ratio of the axes of the ellipse. This ratio in turn is given by

$$b/a = \sqrt{(A'/B')}\,,$$

where

$$\begin{aligned} A' &= \tfrac{1}{2}A\{1+(A-B)/\psi\}+\tfrac{1}{2}B\{1-(A-B)/\psi\}+\tfrac{1}{2}C^2/\psi\,, \\ B' &= \tfrac{1}{2}A\{1-(A-B)/\psi\}+\tfrac{1}{2}B\{1+(A-B)/\psi\}-\tfrac{1}{2}C^2/\psi, \end{aligned}$$

and

$$\psi = \sqrt{\{(A-B)^2+C^2\}}\,.$$

In refined electron-density maps, ε can be correlated with anisotropic vibrations of an atom.

For the special case of orthogonal nets, all the equations in (3) are much simplified, since, for this case, $s = 0$ and $t = K$. For a square net, $s = 0$, $t = K = 1$.

In practice, if only the position of the maximum is sought, the mesh of the net may be approximated to be square and the appropriate simplifications applied. If the angle θ is close to 90°, no serious error is introduced.

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