extension of the arc shows the total range of misorientations in one grain. If the spots are arranged in a regular manner along the arc, as would be the case for a polygonized grain, the mean angle between neighbouring particles inside the grain can be determined. If β is the angle between normals to the reflecting planes giving rise to two spots along the arc, and γ the angle subtended by the pair of spots at the centre of the diffraction ring, it can be shown (Hirsch, 1950) that $\sin \frac{1}{2}\beta = \cos \theta \sin \frac{1}{2}\gamma$, where θ = Bragg angle.

Three examples of this technique may be quoted:

(1) In a recent study by R. J. Davis of α/β brass (in course of publication) a specimen annealed for 11 days was found to have metallurgical grain sizes $\sim 60\mu$ for α, and $\sim 500\mu$ for the β grains. Careful etching showed that what had previously been regarded as large crystals of the β-phase actually possessed a substructure of smaller grains, of size about 60μ. The X-ray method outlined above was used to determine the mean particle size of each phase. The presence of the two phases was taken into account in the calculation of the volume of each phase illuminated. The mean particle size of the β constituent was found to be $\sim 60\mu$, which is in agreement with the interpretation proposed from microscopic evidence. The spots were clustered along short arcs; the total range of misorientations in one 'metallurgical' grain was found to be of the order of 3°, while the smallest angle between adjacent mosaics was about 0·4°. Thus the X-ray method not only showed very clearly the existence of the mosaic structure, but also gave information on its nature which could not be obtained otherwise. By the same method, the mean particle size of the α constituent was found to be about 30μ, which is somewhat smaller than the metallographic size. The spots were randomly distributed around the ring and confirmed that the α grains did not show a mosaic structure. The low value of the grain size determined by the X-ray method is probably due to the presence of twins in the α grains.

(2) The method has also been applied to a fatigue specimen of a Ag–Al alloy (supplied by Mr P. J. Forsyth), in which slight markings, of separation about 20μ, were apparent in some of the original grains ($\sim 0{\cdot}1$ mm.) after etching. X-ray back-reflexion photographs consisted of 'spotty' arcs, each one corresponding to one original grain. From the method of counting spots the mean particle size was found to be $\sim 10\mu$, so that in this case, also, the etch-markings denoted boundaries between particles.* The total range of misorientations in one original grain was about 10°, while some of the neighbouring mosaics were inclined to each other by only a few minutes of arc.

(3) In a study of the brittle fracture (at $-180°$ C.) of tempered martensite, A. R. Entwisle found some microscopic evidence that the α-iron grains were preferentially orientated over areas of $\sim 50\mu$ diameter. X-ray back-reflexion photographs consisted mainly of a number of continuous arcs, but weaker blackening occurred at other parts of the rings. To obtain the mean volume of material contributing to one arc, the numbers of arcs on the rings were counted; whereas in the previous examples the angular range of reflexion (Δ) of each particle (see Kellar *et al.* 1950) could be neglected compared with the divergence of the beam, in this case Δ was large and was determined from the mean lengths of the arcs along the ring. The mean diameter of the volume of material contributing to one arc was found to be $\sim 60\mu$, in agreement with the value obtained from microscopic observations. The total range of misorientations in this volume was $\sim 3°$. It is of interest to note that, since the size of the original austenite grains was $\sim 100\mu$, on the average the martensite transformation took place in eight crystallographically distinct ways (out of a possible 24 ways) in each grain.

The authors believe that this method can be applied to many problems, particularly in the metallurgical field, in which standard metallurgical methods may fail to give conclusive results.

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* The experimental accuracy is such that, in this case, the difference between two estimates of particle size is probably not significant.

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A simplified method of steepest descents.

By VLADIMIR VAND,* *Chemistry Department, The University, Glasgow W. 2, Scotland*

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The method of steepest descents for refinement of coordinates of a crystal structure, as suggested by Booth (1947), minimizes a residual function R, which can be formed in several different ways. It is to be expected that the convergence of the method will be fastest if R is formed according to the principle of least squares, in which case R has the form

$$R = \sum_{hkl} W(|F_o| - |F_c|)^2, \qquad (1)$$

where $F_o(hkl)$ is the observed and $F_c(hkl)$ the calculated structure factor, $W(hkl)$ is a suitably chosen weighting factor and the sum is taken over the Miller indices (hkl).

For simplicity, only centrosymmetrical structures will be considered. If the same sign is assigned to F_o as to F_c, we have

$$R = \Sigma W(F_o - F_c)^2. \qquad (1a)$$

It has been shown by Booth (1948) that if the weighting function $W = 1/f$ is chosen, where $f(hkl)$ is the mean atomic scattering factor for the (hkl) plane, the application of the

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* Imperial Chemical Industries Fellow.

steepest-descents method to R is equivalent to a method based on a Fourier difference synthesis.

$$D=\sum_{hkl}(F_o-F_c)\cos 2\pi(hx+ky+lz). \tag{2}$$

In this series, x, y, z are the fractional co-ordinates, taken over one unit cell.

The method consists of drawing a map of the function D and marking the atomic positions x_i, y_i, z_i ($i=1, 2, \ldots, N$). The atomic shifts Δx_i, Δy_i, Δz_i, which would improve the structure according to the method of steepest descents, can be obtained by moving the atomic positions in the directions of the steepest ascent of D and by making the movements proportional to the gradient of D at the points x_i, y_i, z_i. Good use of this method in practical application has been made by Cochran (private communication).

As Booth (1949) has already pointed out, considerable simplifications in the steepest-descents calculations can be achieved if one takes

$$R=\sum_{hkl}|F_o-F_c|. \tag{3}$$

This function can be obtained from (1a) by taking for the weight

$$W=\frac{1}{|F_o-F_c|}.$$

This form of weighting is not quite correct, as it gives too little weight to large discrepancies between the observed and calculated values. However, the function (3) is often used as a basis for the calculation of the figure of merit.

As the use of the difference synthesis is very convenient, it is of interest to investigate whether an analogous simpler function exists, which would be based on (3). For this purpose we can write R in the following form:

$$R=\Sigma(\alpha\,|F_o|-\beta F_c)=\Sigma\alpha\,|F_o|-\Sigma\beta F_c, \tag{4}$$

where the coefficients $\alpha(hkl)$ and $\beta(hkl)$ have the values

$$\alpha=+1 \text{ for } |F_c|<|F_o|, \quad \alpha=-1 \text{ for } |F_c|>|F_o|,$$
$$\beta=+1 \text{ for } |F_o|>F_c>0 \quad\text{and}\quad F_c<-|F_o|,$$
$$\beta=-1 \text{ for } 0>F_c>-|F_o| \quad\text{and}\quad F_c>|F_o|,$$

i.e.

$$\beta=+1 \text{ for } (F_o-F_c)>0,$$
$$\beta=-1 \text{ for } (F_o-F_c)<0.$$

Limiting ourselves to a centrosymmetrical structure, we can substitute for F_c in (4):

$$F_c=2\sum_i^N f_i\cos 2\pi(hx_i+ky_i+lz_i), \tag{5}$$

where N is the number of atoms per half unit cell. We obtain

$$R=\sum_{hkl}\alpha\,|F_o|-2\sum_{hkl}\beta\sum_i f_i\cos 2\pi(hx_i+ky_i+lz_i).$$

On reversing the order of summation, we can write

$$R=R_0-\sum_i R_i, \tag{6}$$

where

$$\left.\begin{aligned} R_0&=\sum_{hkl}\alpha\,|F_o|,\\ R_i&=2\sum_{hkl}\beta f_i\cos 2\pi(hx_i+ky_i+lz_i).\end{aligned}\right\} \tag{7}$$

We have achieved separation of R into R_0, which depends on F_o only, and into N functions R_i, each of which depends on the co-ordinates of the ith atom only. In addition, R_i have the form of a Fourier synthesis analogous to the difference synthesis (2), i.e. if we replace in (7) the discrete co-ordinates x_i, y_i, z_i, by continuous x, y, z, a single function is obtained, defined over the whole unit cell, which has the values R_i at the atomic positions. The synthesis (7) differs from (2) in that its coefficients have absolute values independent of F_o and F_c; only their signs depend on the inequalities for β and are incidentally the same as in (2). It should be noted, however, that although R is a continuous function of the atomic co-ordinates x_i, y_i, z_i, the functions R_0 and R_i are discontinuous, the discontinuities occurring every time the coefficient β changes sign. One can visualize this by imagining R as a function of the co-ordinates x_i, y_i, z_i, in $3N$-dimensional space, which is subdivided into a number of small cells, the boundaries of which are given by the changes of sign of β. Within each of the cells, R_0 and R_i are continuous functions of the co-ordinates. The number of such cells depends on the number of F terms included in the summations.

As formula (7) is based on incorrect weighting, it is to be expected that the above method would converge more slowly than a method based on (2), and therefore more steps would be required to attain a given degree of accuracy. However, the use of the series (7) may in some cases have the advantage that its coefficients are fixed quantities, and only their signs change during calculation. The series (7) might lend itself therefore better to calculations on automatic machines, analogue or digital, as it is easier in a calculation to change the sign of a term than its value. The inequalities for α and β lend themselves also admirably for automatic evaluation on both digital and analogue machines. One can therefore conclude that the calculations based on formula (3) might be more suitable for a fully or partly automatic cycle, especially where the simplicity of setting or programming is of more importance than the speed of convergence per cycle.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. Copy should be sent direct to the British Co-editor (R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England).

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