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Phase-limiting relations following from a known maximum value of the electron density.*

By R. Pepinsky, *Department of Physics, The Pennsylvania State College, State College, Pa., U.S.A.* and Caroline H. MacGillavry, *Laboratory of Inorganic Chemistry, University of Amsterdam, Holland*

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The fact that the choice of phases of structure factors is limited by a number of conditions on the unknown density function ρ has been emphasized in a number of recent papers (MacGillavry, 1950 *a*, *b*; Karle & Hauptmann, 1950 *a*, *b*; Goedkoop, 1950). The analytical consequences of the positivity of a function upon the coefficients of a Fourier series representing it were actually derived by Toeplitz (1911) and by Herglotz (1911), and the determinant relations between Fourier coefficients, first presented to X-ray analysts by Karle & Hauptmann (1950 *a*, *b*), have been known to mathematicians as Herglotz's theorem.

The natural complement of the positivity condition is that ρ also cannot exceed a given maximum value R. This value can be taken equal to the maximum density of the heaviest atom present in the structure

$$\rho \leqslant R. \tag{1}$$

It is easily seen that the Herglotz theorem can be applied immediately to this condition, if written in the form

$$R-\rho \geqslant 0. \tag{2}$$

All inequalities that can be derived from the condition $\rho \geqslant 0$ hold also if we substitute the Fourier coefficients of $(R-\rho)$ for those of ρ. That is:

$$\left.\begin{array}{l}\text{for } F_{hkl}\text{, substitute } -F_{hkl}\text{, if } hkl \neq 000; \\ \text{for } F_{000}\text{, substitute } RV-F_{000},\end{array}\right\} \tag{3}$$

where V = volume of the unit cell.

Just as the Herglotz theorem shows that the conditions upon the Toeplitz forms are sufficient to ensure that ρ be non-negative, the inequalities to be derived from (2) ensure that ρ be smaller than R.

The usefulness of inequalities for phase determination depends strongly on the relative largeness of the zero term in the Fourier expansion compared with the other terms (Hughes, 1949). The smaller the latter are with respect to the zero term, the more ineffective in general are the inequalities. Now in almost any case the value of $(RV-F_{000})$ will be larger than F_{000}, whereas the absolute values of the other terms are the same in the ρ series and the $(R-\rho)$ series; therefore, it is to be expected that the effectiveness of inequalities derived from (2) will be smaller than those derived from (1).

Moreover, use of the 'sharpened-up' series, which increases the effectiveness of the Herglotz inequalities for (1), makes matters worse in the case of inequalities derived from (2). Whereas sharpening-up enhances the F_{hkl} with respect to F_{000}, the zero term in the $(R-\rho)$ series becomes very large; indeed, if we neglect temperature movement, R becomes infinite.

It seems, however, that inequalities derived from (2) might be useful in those projections where there is considerable overlap, such that the average projected electron density $F_{000} \cdot c/V$ lies closer to R' than zero (c = period of axis of projection). R', the maximum value of the projected electron density, can be estimated from the size and electron distribution of the individual atoms and the period of the axis of projection.

The fact that inequalities could be obtained from condition (2) was first pointed out by us at the Cornell University meeting of the American Society for X-ray and Electron Diffraction, 25 June 1949 (Pepinsky, 1949).

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An X-ray technique for the study of substructures in materials.

By P. Gay and P. B. Hirsch, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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Metallurgical etching techniques are often insufficiently sensitive to reveal the boundaries between particles inclined at small angles relative to each other. The use of the following X-ray technique permits the detection of particles misorientated by only a few minutes of arc.

A back-reflexion photograph is taken with an X-ray beam of diameter such that a spotty ring is obtained (for grains down to about 10μ, X-ray beams of 1 mm. diameter can be used). The mean particle size of the specimen can be determined from the known area of cross-section and divergence of the beam, by counting the number of spots on the same ring for two different exposures (Kellar, Hirsch & Thorp, 1950). If some of the particles are mosaics within larger 'metallurgical' grains, the spots lie along short arcs around the ring. Each arc corresponds to one 'metallurgical' grain; the angular

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

* Imperial Chemical Industries Fellow.