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

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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.

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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