

The Elimination of Multiple Reflection on the Four-Circle Diffractometer

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A procedure is described for the elimination of errors in observed intensities caused by multiple Bragg scattering. The necessary calculations can be done with an on-line computer, or after data have been collected. Experimental evidence supporting the proposed procedure is presented.

Introduction

The importance of multiple diffraction effects in X-ray and neutron diffraction has been emphasized in a number of articles (Moon & Shull, 1964; Zachariassen, 1965; Burbank, 1965; and others). Moon & Shull pointed out that the magnitude of the intensity perturbations is comparable to corrections resulting from secondary extinction. Hence, it is necessary to eliminate these effects when accurate intensity data are collected, as required, for example, for the examination of details of molecular electron density distributions.

The four-circle diffractometer is well suited for this purpose, as it allows rotation of the crystal around the reciprocal lattice vectors. Santoro & Zocchi (1964) have suggested recording each reflection under conditions at which no other reciprocal lattice points are on, or close to the sphere of reflection. They noticed, however, that in the case of a large unit cell the probability of this condition being fulfilled is very small, and therefore it might be necessary to increase the wavelength, or relax the condition that no reciprocal lattice point should be close to the sphere of reflection. The former solution is frequently unacceptable, while the latter might lead to an incomplete elimination of multiple reflections.

The alternative approach followed here uses the fact that the intensity of multiple reflection is dependent on the structure factors of the reflecting planes. Since for most crystals the majority of reflections are weak, only part of the crystal planes contribute significantly to intensity perturbations through multiple diffraction.

The proposed procedure is valid for an arbitrary orientation of the crystal on the goniometer head, and for all seven crystal systems.

The intensity of multiple reflections

Removal of power from the incident or the primary reflected beam can result in a diminution of the observed intensity of a reflection ('Aufhellung').

On the other hand, an appreciable fraction of the power diverted from the incident ray may be rescattered in the direction of the primary reflected beam when the conditions illustrated in Fig. 1 are satisfied ('Umweganregung').

These processes are summarized in an expression given by Moon & Shull, which is valid for a crystal large compared with the incident beam cross section:

$$\frac{\Delta I_1}{I_0} = \frac{1}{2} \sum_i -r_{01} l_0 r_{0i} l_0 - r_{01} l_0 r_{i1} l_1 + r_{0i} l_0 r_{i1} l_1. \quad (1)$$

Here ΔI_1 is the change in intensity of the primary diffracted beam; I_0 is the intensity of the incident beam, r_{ij} represents the linear reflection coefficient from beam i to beam j and l_i is the path length of beam i within the crystal. The reflection coefficients r are proportional to the Q_{ij} 's, where Q_{ij} is the usual crystallographic function equal to the integrated reflectivity per unit volume for reflection of beam i by plane j (Moon & Shull, 1964). We get for the case that only one additional plane removes power from the incident beam:

$$\Delta I_1 = -k Q_{01} Q_{02} - k' Q_{01} Q_{14} + k'' Q_{02} Q_{23}. \quad (2)$$

The subscripts in this expression refer to the planes defined in Fig. 1, or the beams diffracted by these planes. The proportionality factors k are dependent on the appropriate Lorentz and polarization factors, the mosaicity of the specimen and, as is evident in expression (1), on the path lengths of the beams within the crystal.

Thus, the sample geometry is of importance and it may in extreme cases lead to an inversion of the sign of the multiple diffraction effect (Moon & Shull, 1964). For a crystal smaller than the cross section of the incident beam the path lengths should be evaluated for all points on a grid within the crystal, as is done in the evaluation of the absorption correction (see for example Coppens, Leiserowitz & Rabinovich, 1965). However, it should be realized that in accurate structural work fairly isodimensional crystals are employed. For such crystals the l_i 's in expression (1) averaged over all grid points are similar for different i and the effect of sample geometry is greatly reduced. It should also be noted that our present purpose is not the quantitative evaluation of multiple diffraction but rather the avoidance of geometrical conditions under which the effect might be appreciable. It is therefore convenient and sufficient to predict the occurrence of intensity perturbations from the reflectivities only.

It follows from (2) that Aufhellung is the dominant effect when a strong reflection 1 is to be recorded. On the other hand, when 1 is a weak reflection, the last two terms will be small and an increase in intensity will be observed when the condition illustrated in Fig. 1 is fulfilled for two strong reflections 2 and 3. For reflections of intermediate strength both effects may occur. In other words, strong reflections are weakened and weak reflections are strengthened (Burbank, 1965), a conclusion supported by the experimental data presented below.

On the basis of these considerations the following criterion can be formulated: Significant intensity changes due to multiple diffraction will be avoided when no reciprocal lattice points representing *strong* reflections are located on either the sphere of reflection corresponding to the incident beam, or the sphere of reflection corresponding to the primary diffracted ray (this of course excludes the reciprocal lattice point of the reflection to be recorded.)

For weak reflections this criterion might be relaxed, as errors are introduced only when a reciprocal lattice point of a strong reflection 2 (Fig. 1) is on the incident

beam sphere and in addition a second strong reflection 3 exists for which $\mathbf{h}_3 = \mathbf{h}_1 - \mathbf{h}_2$.

This distinction should be made when experimentally observed multiple diffraction is to be interpreted. For routine collection of intensity data, however, it is convenient to apply the more stringent condition to all reflections to be measured. This assures elimination not only of double reflection, but also of triple, quadruple, etc. reflection effects, which occur when several reciprocal lattice points are located simultaneously on the sphere of reflection.

The elimination of multiple diffraction effects

On the four circle diffractometer one of the three setting angles φ , χ and ω can be chosen arbitrarily; the other angles are then uniquely determined for a given reflection and a known crystal orientation. The direction cosines of the incident and diffracted rays with respect to a crystal-fixed coordinate system can be calculated from the setting angles (Busing & Levy, 1967). The distances between the reciprocal lattice points representing strong reflections and the appropriate spheres

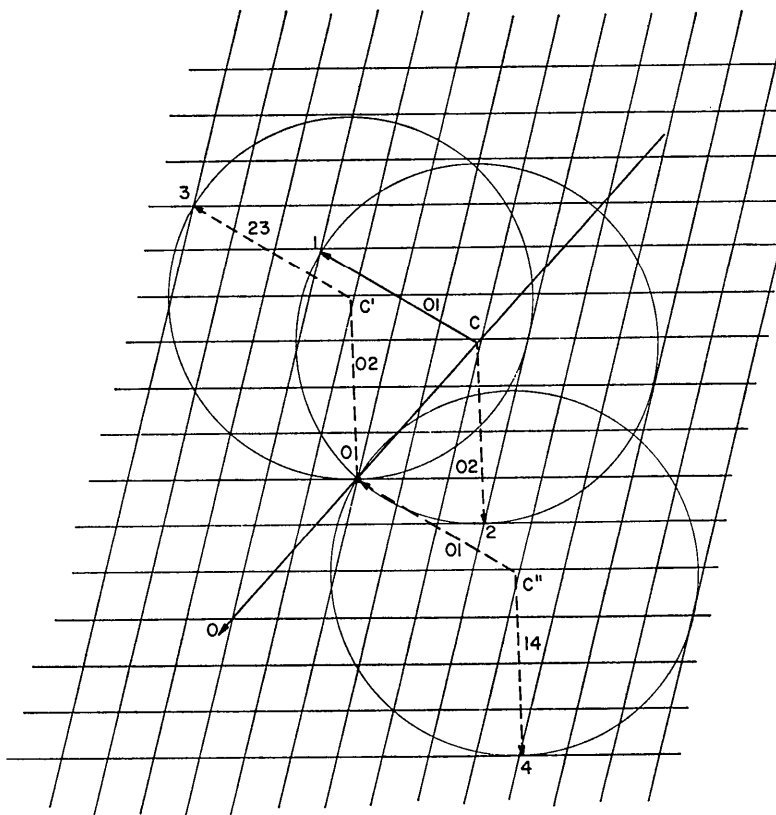


Fig. 1. The occurrence of multiple scattering. 0 is the origin of the reciprocal lattice. 1 and 2 are reciprocal lattice points on the sphere of reflection corresponding to the incident beam CO . 3 is on the sphere of reflection corresponding to the diffracted beam $O2$ while 4 is on the sphere corresponding to the primary diffracted beam $O1$. The relationships $\mathbf{h}_3 = \mathbf{h}_1 - \mathbf{h}_2$ and $\mathbf{h}_4 = \mathbf{h}_2 - \mathbf{h}_1$ exist between the reciprocal lattice vectors. Radiation diverted from the incident beam by 2 can be rescattered in the direction of the primary diffracted beam $O1$ by lattice point 3.

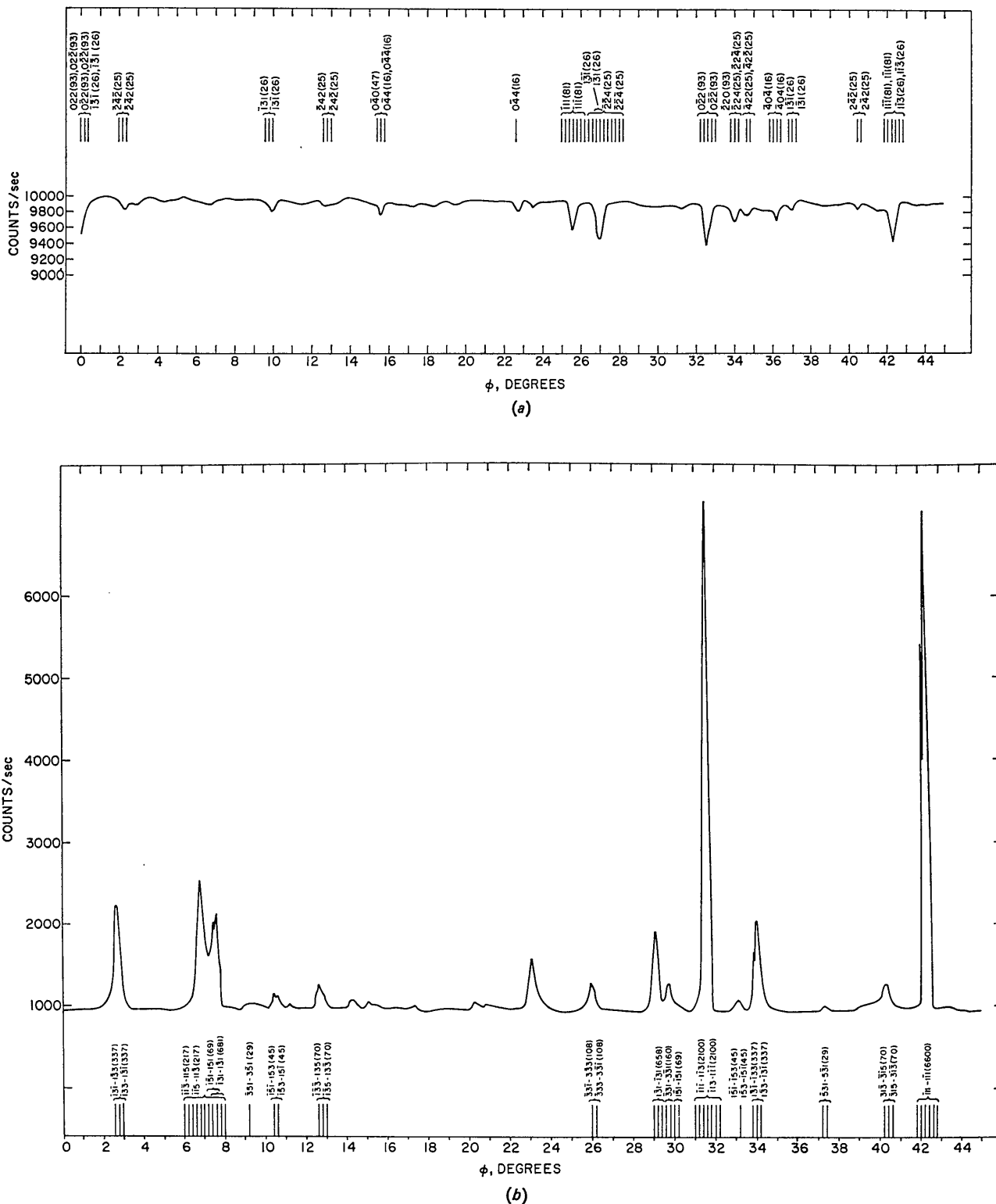


Fig. 2. CaF_2 scan at $\chi=90^\circ$ for two X-ray reflections. The results of the calculations are represented by the vertical lines. Indices of interfering reflections and calculated estimates of intensity perturbations are given. In the calculations the half-thickness λ of the sphere of reflection was assumed to be 0.002 \AA^{-1} . (a) 004 checked against strong reflections 400, 220, 440, 422, 111, 311 and symmetry equivalents. (b) 002 checked against 111, 311, 331, 511, 531 and symmetry equivalents. The peak at $\phi=23^\circ$ is caused by 022 and 024.

of reflection can then be evaluated as illustrated in Fig. 4. If any of these distances is smaller than a limiting value Δ , multiple scattering may be appreciable. (The parameter Δ is chosen to allow for crystal mosaicity and divergence of the incident beam; we have found values of 0.002–0.003 Å⁻¹ to give good fit with our experiments.)

The crystal should then be rotated around the scattering vector until a position is found at which multiple scattering effects are negligible.

A relation between α , the azimuthal angle of rotation around the scattering vector, and ω has been given by Hamilton (1965):

$$\tan \chi_0 \tan \omega = -\sin \alpha, \quad (3)$$

in which χ_0 is the angle at which the reflection can be recorded in the symmetrical setting ($\omega=0$).

From this expression a new value of ω can be derived. The other setting angles are then calculated in the usual manner. Equation (3) is not defined for $\chi_0=90^\circ$ and for $\chi_0=0^\circ$, but in the former case α is identical with φ , while for $\chi_0=0^\circ$ α becomes equivalent to χ , provided the diffractometer is set at $\omega=90^\circ$. Unfortunately, this position is not accessible on many commercially avail-

able diffractometers. On these instruments multiple scattering cannot be eliminated at $\chi=0^\circ$.

Comparison with experiment

For the purpose of testing the procedure against experimental data the distinction between strong and weak reflections described above was made. Calculations were performed on the CDC 6600 computer with a program written in FORTRAN, and applicable to all crystal systems.

CaF₂: The 002 and 004 reflections of a spherical crystal with a mosaic spread of about 10' were recorded at $\omega=0^\circ$, $\chi=90^\circ$ at intervals of 0.04° in φ (Fig. 2). The reflections of the cubic face-centered CaF₂ structure fall in three categories with $h+k+l=4n$, $4n+2$ or $2n+1$. The structure factors for these groups are, respectively, $4(f_{Ca}+2f_F)$, $4(f_{Ca}-2f_F)$ and $4f_{Ca}$. Thus 002 is very weak and 004 very strong. For the weak reflection the test consists of a search for pairs of reflections with $\mathbf{h}_2+\mathbf{h}_3=\mathbf{h}_1$ (see Fig. 1). For 002 \mathbf{h}_2 and \mathbf{h}_3 either both represent reflections of intermediate intensity (the third of the three groups), or one of the two reflections is strong and the other weak. Only one of the observed

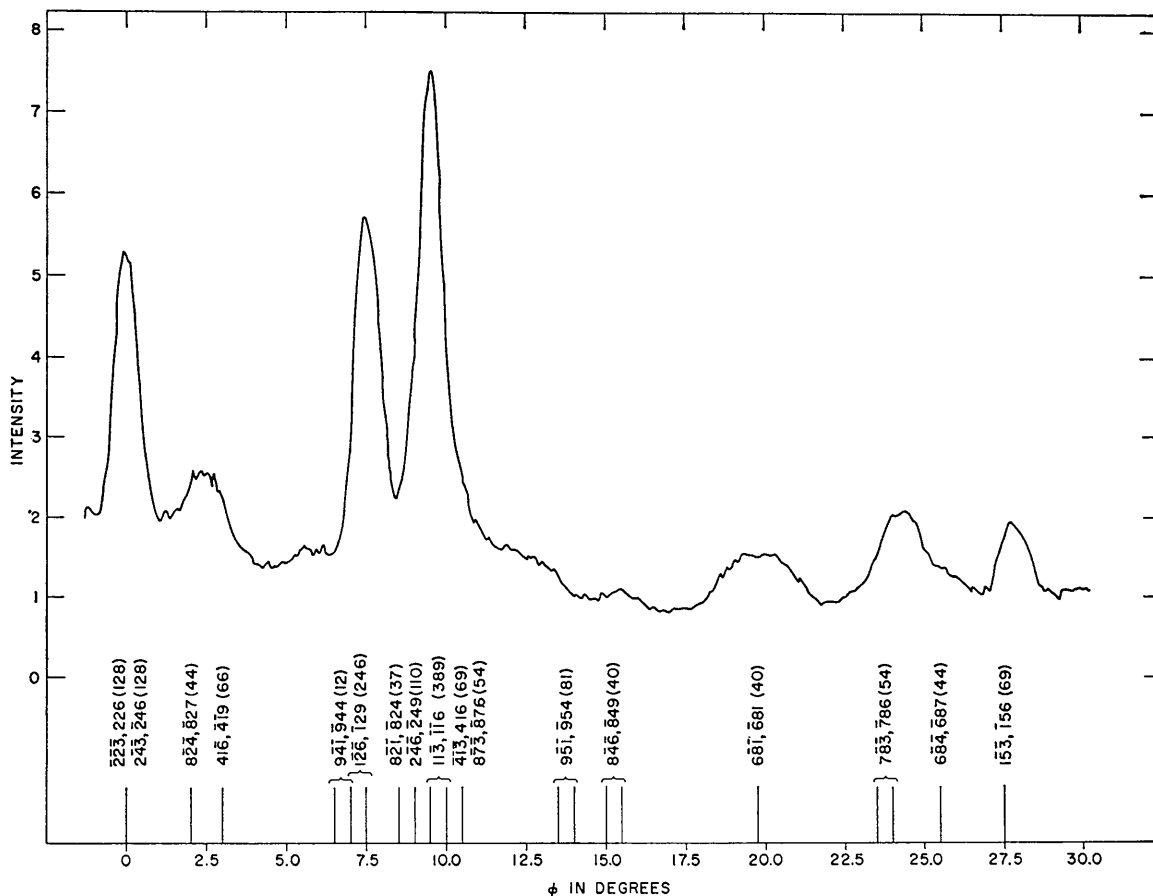


Fig. 3. Cr₂O₃ 003 neutron reflection, φ scan at $\chi=90^\circ$, $\Delta=0.003$ Å⁻¹. The intensity scale is in arbitrary units.

Table 1. *Multiple reflection in some miscellaneous crystals*

Compound	Space group	Reflection	Relative intensity	Radiation	Number of independent multiple reflections and their intensity as a fraction of the signal
LiClO ₄ ·3H ₂ O	<i>P</i> 6 ₃ <i>m</i> <i>c</i>	002	Strong	neutrons $\lambda = 1.06 \text{ \AA}$	0 (<5%)
		004	Weak		0 (<15%)
Heptafulvalene	<i>P</i> 2 ₁ / <i>c</i>	021	Medium	X-rays $\lambda = 1.54 \text{ \AA}$	0 (<4%)
Potassium hydrogen diaspirinate	<i>P</i> 2 ₁ / <i>c</i>	040	Weak	neutrons $\lambda = 1.07 \text{ \AA}$	2 (15%, 50%)

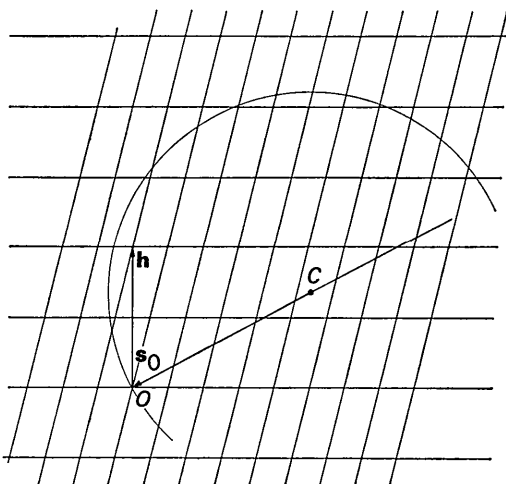


Fig. 4. The distance d from a reciprocal lattice point to the sphere of reflection. If s_0 is a unit vector in the direction of the incident beam and h is the reciprocal lattice vector, $d = |s_0/\lambda + h| - 1/\lambda$.

peaks in the scan [Fig. 2(b), $\varphi = 23^\circ$] falls in the latter category. The agreement between experiment and calculation is good. A calculation with a longer list of strong reflections also accounted for some of the smaller intensity variations in the curve, which are statistically significant.

Cr₂O₃: The 003 reflection of Cr₂O₃ is space-group forbidden (space group no. 167, *R* $\bar{3}$ *c*). The azimuthal sweep with neutrons at $\chi = 90^\circ$ (as recorded by Drs L. Corliss and J. Hastings) is reproduced in Fig. 3, together with the results of the calculations.

Other crystals: A number of reflections of three other crystals were investigated over the whole symmetry-independent range of α (Table 1). Multiple diffraction was only observed for potassium hydrogen diaspirinate. It was correctly predicted by the calculations.

Final remarks

Multiple reflection can cause significant intensity errors, especially for crystals with small mosaic spread. It is desirable to perform an azimuthal sweep of a few reflections before intensity data are collected, in order to assess the importance of the effect.

If multiple diffraction is observed, care should be taken that data are collected under conditions at which the effect is negligible. The testing procedure described above requires a list of strong reflections. The number of independent terms to be included in this list depends on the magnitude of the proportionality factors in expression (2), and it will therefore differ for different crystals. Generally, one should use the azimuthal sweeps to obtain an estimate of this number, which, in our calculations, varied between 5 and 30.

If such a list of strong reflections is available prior to data collection, the multiple diffraction test can be performed with an on-line computer. Alternatively, the data can be checked *a posteriori*. Intensities measured under multiple diffraction conditions may then be eliminated from the refinement, or better, redetermined at a different setting of the diffractometer.

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References

- BURBANK, R. D. (1965). *Acta Cryst.* **19**, 957.
- BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035.
- HAMILTON, W. C. (1965). Private communication.
- MOON, R. M. & SHULL, C. G. (1964). *Acta Cryst.* **17**, 805.
- SANTORO, A. & ZOCCHI, M. (1964). *Acta Cryst.* **17**, 597.
- ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 705.