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Orientation of Single-Crystal Fragments by Means of X-ray Rotation Photographs

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The general problem of orientation of a single-crystal fragment for rotation about a unit-cell edge is considered. The method consists of utilizing three rotation photographs to determine the position of two reciprocal-lattice points relative to the plane of the lower arc of the goniometer and the corrections necessary to move the arcs to bring the crystal into orientation.

1. Introduction

The following situation is postulated: A crystal with poorly developed faces, or even with few or no faces, is mounted in a random orientation in the X-ray goniometer and a rotation photograph is taken. There will result a chaotic arrangement of spots on the film. If the orientation of the crystal is changed so that two spots move to the zero level, *an* orientation will have been achieved, for two reciprocal lattice vectors are sufficient to define a zone.

The essential point in orientation by the technique outlined is the use of spots on the film that lie closest to the center of the film and to the zero level. If a major zone of the crystal is originally oriented so that the corrections to be applied to each arc of the goniometer are not more than 20° respectively, then there is a high probability that these spots closest to the center of the film and to the equator will have one index zero. A situation where this might not be the case occurs when the dimension of the final rotation axis is relatively long, i.e. of the order of magnitude of 20 Å or more. In the example used in this paper, the original orientation was found to be 3° off on the lower arc, and 17° off on the upper arc, with a rotation axis dimension of 10·7 Å.

If the two spots chosen happen to be of the *hkl* type, an orientation about a minor axis will have been achieved. This might give a clue as to further adjustment, or it might be practically worthless. But it is a simple matter to try other pairs of spots since the required photographs can so easily be obtained.

2. Geometry of correction

In the following description the upper arc of the X-ray goniometer is designated as arc *UU* and the lower arc as arc *LL*. The first rotation photograph, of the series of three, is taken with both arcs of the goniometer set at zero. If the first rotation photograph is taken when the arcs are not at zero the formulas derived below are only approximate and not exact. This is because the upper-arc correction is dependent on its position on the lower arc. In general, there are three unknown and two variable quantities involved in the geometry of correction. These are α and β, the corrections to be applied to the lower and upper arcs respectively, γ, the angle the lattice vector, in corrected position, makes with the plane of the lower arc, and the original settings of the arcs. If the arcs are set at zero before the first photograph is taken we have effectively reduced the number of quantities to be considered from five to three.

Fig. 1 illustrates the general disorientation of a major reciprocal-lattice line, *OP*, which is not parallel to the plane of either arc of the goniometer head. Planes are drawn in the octant parallel to the reference planes of *LL* and *UU*, and the motion of the reciprocal lattice point *P* by the movement of arcs *LL* and *UU*

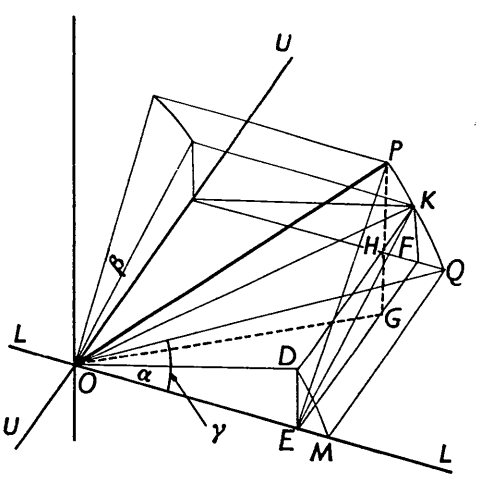


Fig. 1. General disorientation of a reciprocal-lattice line, *OP*,

is confined to these planes. Since we are interested only in the angular relationships the particular value of the distance from the origin to point *P* is arbitrary.

For simplicity this value of *OP* in Fig. 1 is set equal to unity. *OK* is also equal to unity, *OK* being the line *OP* rotated toward orientation by movement of arc *UU* through angle β. *OQ* is also equal to unity, *OQ* being the line *OK* rotated toward orientation by movement of arc *LL* through angle α. The problem is to find the relationship of the ζ and ξ measurements

of this point P, which are measured on the rotation film, and which yield the tangent of angle N, angle POG, by the ratio of ζ, PG, to ξ, OG, and the angles of disorientation α and β, and the angle γ. From Fig. 1 the following formula can be derived relating these quantities:

$$\tan N = \frac{\zeta}{\xi} = \frac{\sin\left[\tan^{-1}\left[\frac{\tan\gamma}{\sin\alpha}\right]-\frac{1}{2}\beta\right].2\sin\frac{1}{2}\beta[(\sin\gamma)^2+(\cos\gamma\sin\alpha)^2]^{\frac{1}{2}}+\cos\gamma\sin\alpha}{\left[(\cos\gamma\cos\alpha)^2+\left\{\sin\gamma-\cos\left[\tan^{-1}\left[\frac{\tan\gamma}{\sin\alpha}\right]-\frac{1}{2}\beta\right].2\sin\frac{1}{2}\beta[(\sin\gamma)^2+(\cos\gamma\sin\alpha)^2]^{\frac{1}{2}}\right\}^2\right]^{\frac{1}{2}}}. \quad (1)$$

There is always the possibility that arc UU should move in the opposite direction to move point P toward orientation. This yields a second formula similar to the first. Formula (2) can be derived from (1) by the substitution of $-\beta$ for $+\beta$.

3. Orientation procedure

The procedure for orientation is as follows: Set both arcs at zero on the goniometer. The first rotation photograph is taken. Arc LL is moved a given amount in a known direction and the second photograph is taken. The ratio of ζ to ξ of two spots, one controlled more by arc LL, called the LL spot, and one controlled more by arc UU, called the UU spot, yield the tangents of certain angles. Determine the angles on both the first and second photographs. The LL spot is the spot having the largest difference in angular measurement on the film, between the first and second photograph. No spot can have an angular difference greater than the movement of arc LL. In general, the differences detected on the film are less than the movement of arc LL. This means that the lattice vectors are inclined to the plane of arc LL. The angle γ is determined, for each spot, LL and UU, approximately by

$$\cos\gamma = \frac{\text{angular difference between } N \text{ on 1st and 2nd photos}}{\text{angular difference on arc } LL}$$

There is a fairly easy method of determining which formula, (1) or (2), should be used and of determining the α and β corrections. This involves the consideration of the direction in which the spots LL and UU move on rotation photographs.

Table 1 shows all the possible combinations that can be observed on the second and third photographs of the movements of the LL and UU spots. It also shows whether these movements are toward or away from orientation. It gives the algebraic sign of the α and β corrections (to be used in the formulas only). From this table the correct formula to use and the directions for correct orientation are determined. The α and β corrections are applied to the goniometer arcs in their initial setting, i.e. both arcs at zero.

For example, suppose that on photograph No. 2, spot LL moves up and spot UU moves down. With this limited information the column in Table 1 for photograph No. 2 shows that either formula (1) or formula (2) may apply. The table also shows that such a movement is away from orientation. For the third photograph, arc UU is moved a given amount in a known direction and the photograph is taken. Suppose

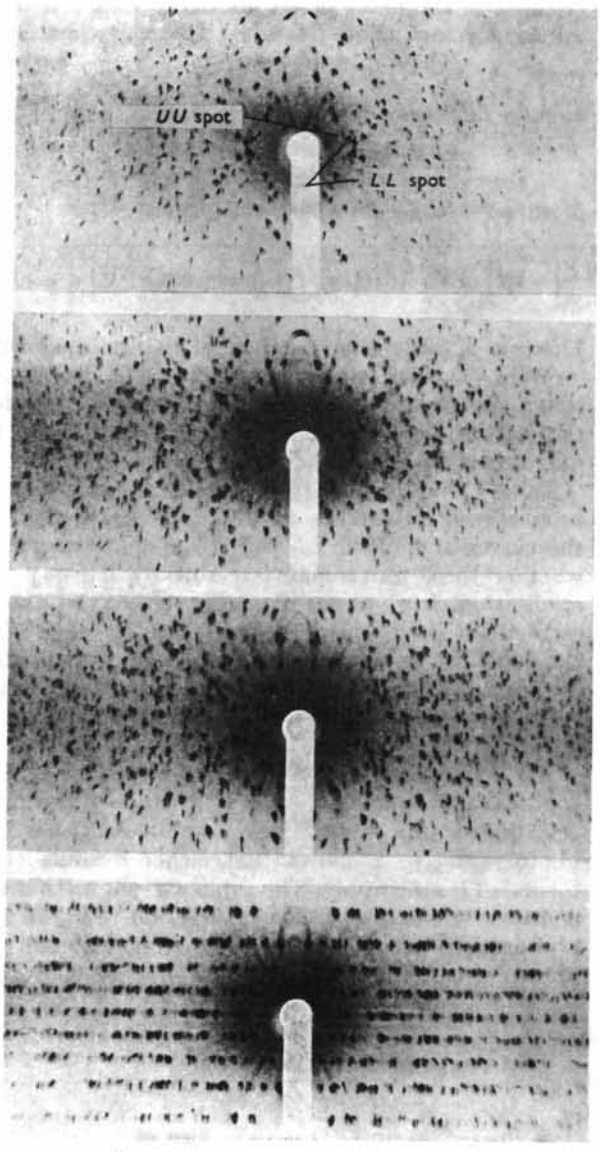
Table 1

Formula (1)

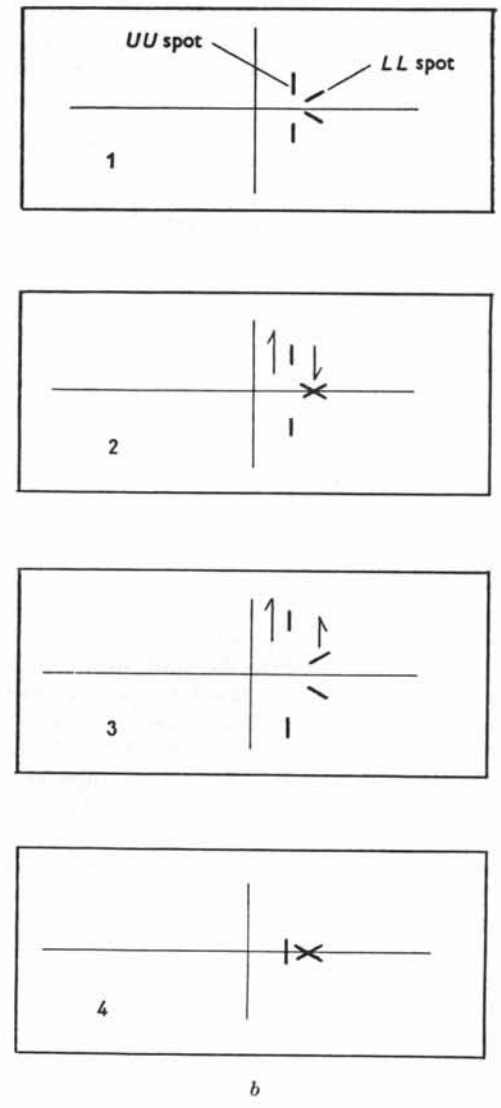
Directions are from the positions on photograph No. 1	Directions are from the positions on photograph No. 2	Orientation	Sign of corrections
Photograph No. 2	Photograph No. 3		
LL down, UU down	LL down, UU down	Toward	LL, α, β
LL up, UU up	LL up, UU up	Away from	UU, α, β
LL down, UU up	LL down, UU down	Toward	LL, α, β
LL up, UU down	LL up, UU up	Away from	UU, $-\alpha, \beta$

Formula (2)

Directions are from the positions on photograph No. 1	Directions are from the positions on photograph No. 2	Orientation	Sign of corrections
Photograph No. 2	Photograph No. 3		
LL down, UU up	LL up, UU down	Toward	LL, α, β
LL up, UU down	LL down, UU up	Away from	UU, $-\alpha, -\beta$
LL down, UU down	LL up, UU down	Toward	LL, α, β
LL up, UU up	LL down, UU up	Away from	UU, $\alpha, -\beta$



a



b

Fig. 2. (*a*) Sequence of photographs taken to orient a $CuSO_4 \cdot 5H_2O$ crystal. (Cu $K\alpha$ radiation.)
(*b*) Enlarged diagram of movement of spots for orientation.

that photograph No. 3 reveals that spot *LL* moves up and *UU* moves down. Table 1 shows that only formula (2) applies and that this movement on arc *UU* is toward orientation. Thus we now know the correct formula that must be used, the directions necessary to move the arcs for orientation, and the algebraic signs of the corrections.

A word of caution is necessary at this point. In Table 1 the combinations presented represent the most general cases. A special case may occur when movement of the lower arc *LL* produces no differentiation between the proposed *LL* and *UU* spot. In this case the consideration of a third point is sufficient to enable the investigator to select a *LL* and *UU* spot.

From the formulas two charts have been prepared which greatly facilitate the solution of the formulas for the values of α and β. The use of the charts is as follows: From the first and second photographs the angle γ is determined and from the third photograph the proper chart is selected, either for formula (1) or formula (2). A line is drawn from $\tan N_{LL}$, photograph No. 1, through some arbitrary value of α for the γ of spot *LL*. Then a line is drawn from $\tan N_{UU}$, photograph No. 1, through the same arbitrary value of α for the γ of spot *UU*. *Care must be taken to observe the algebraic sign of the corrections as given in Table* 1. In general, the two *numerical* values of β so determined will not be equal. Adjustments are made until

the two values agree. After adjustments the values of α and β are read from the chart.

The speed of the method is determined by the time necessary to take three rotation photographs. The films do not have to be washed and dried, as measurements on the wet films with a pair of dividers is as accurate as measurement of dry films.

4. Orientation of a triclinic crystal

For the illustration of this method of orientation a small crystal of $CuSO_4.5H_2O$ was selected and mounted in the goniometer so that when orientation had been achieved rotation would be about the conventional b axis. Fig. 2 shows the sequence of photographs taken to orient the crystal. The first photograph is at the top of Fig. 2, the oriented crystal at the bottom. The center sections of the rotation photographs are shown and are slightly reduced in reproduction.

The first photograph of Fig. 2 was taken with both arcs set at zero. The second photograph was taken when arc LL was moved 10° to the right and arc UU remained set at zero. The third photograph was taken when arc LL remained 10° to the right and arc UU was moved 10° to the left. The fourth photograph shows the oriented crystal after the corrections have been made; arc LL 3° to the right, arc UU 17° to the right. These corrections were calculated as follows:

First photograph:

$$UU \text{ spot: } \tan N_1 = \frac{\zeta_1}{\xi_1} = \frac{0{\cdot}075}{0{\cdot}255} = 0{\cdot}294;$$

$$N_1 = 16° 23'.$$

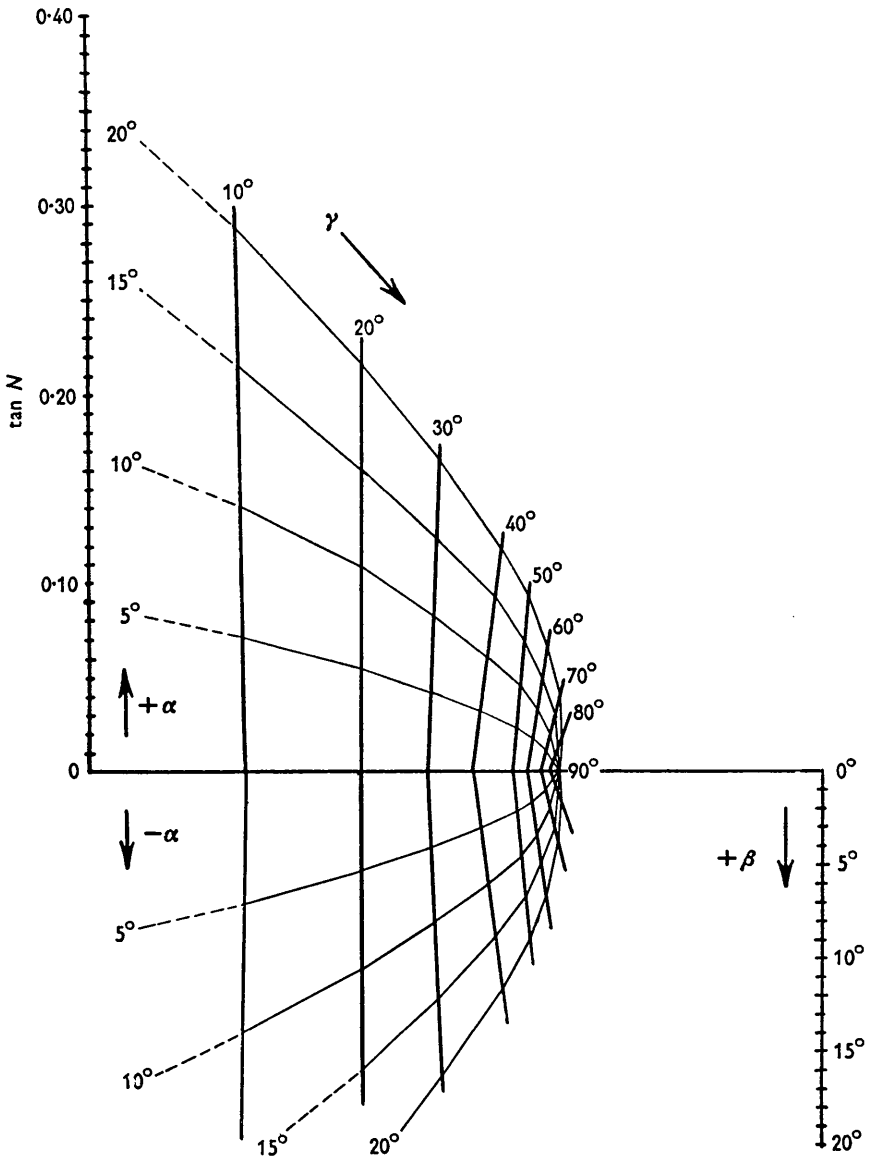


Fig. 3. Nomograph for formula (1).

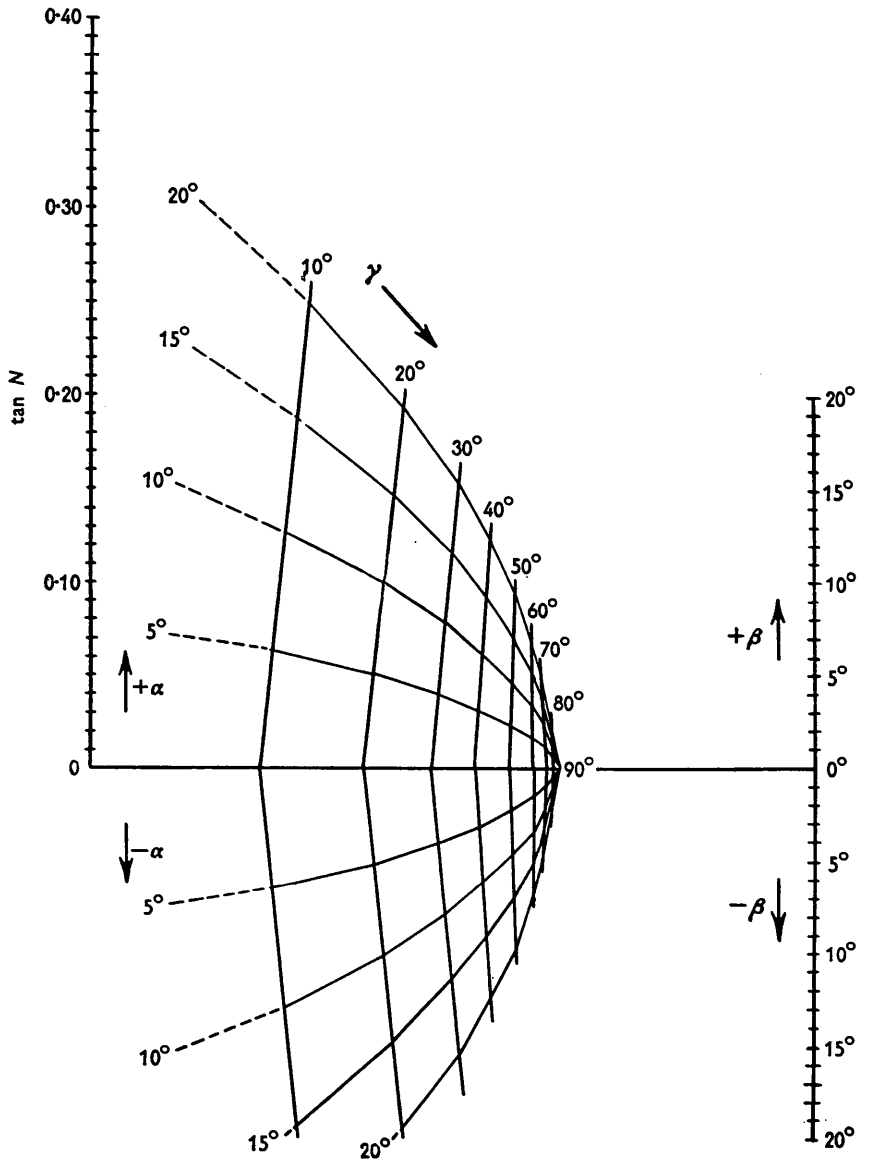


Fig. 4. Nomograph for formula (2).

LL spot: $\tan N_1 = \dfrac{0{\cdot}048}{0{\cdot}295} = 0{\cdot}163$;

$N_1 = 9° 15'$.

Second photograph:

UU spot: $\tan N_2 = \dfrac{\zeta_2}{\xi_2} = \dfrac{0{\cdot}077}{0{\cdot}255} = 0{\cdot}302$;

$N_2 = 16° 48'$.

LL spot: $\tan N_2 = \dfrac{0{\cdot}000}{0{\cdot}290} = 0{\cdot}000$;

$N_2 = 0°$.

Whence we have:

LL spot: $N_2 - N_1 = 9° 15'$;

$\cos\gamma = 9° 15'/10° = 0{\cdot}925$ and

$\gamma = 22° 20'$.

UU spot: $N_2 - N_1 = 0° 25'$;

$\cos\gamma = 0° 25'/10° = 0{\cdot}041$ and

$\gamma = 87°$.

On the second photograph the LL spot moves down and the UU spot moves up from their respective first-photograph positions. On the third photograph the LL and UU spots move up from their respective second-photograph positions (see Fig. 2(*b*); the shapes of the spots are a great help in identifying the spots and following their movement on the film). Table 1 shows that formula (1) applies. The solution for the values of α and β was outlined in § 3.

5. Nomographs

Fig. 3 shows the chart for formula (1) and Fig. 4 for formula (2), for the determination of α and β. No excessive claims are made for the accuracy of the charts. Their chief advantage is convenience and the

condensation of a large amount of data into a compact arrangement. The usual goniometer arcs cannot be moved more than 20° from zero and therefore the extension of the chart beyond $\gamma = 20°$ is not justified.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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An unusual double reflection in α-phenazine.

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During the investigation of the crystal structure of α-phenazine (Herbstein & Schmidt, 1955*a*, *b*), an extra spot was observed, corresponding in position to the forbidden 500 reflection, on all *h*0*l*, but not *hk*0, Weissenberg photographs, with both Cu and Mo $K\alpha$ radiation, and both at room temperature and in boiling nitrogen. This spot, whose shape and intensity varied for different crystals and even on different photographs of the same crystal, remained unexplained until it was realized that in normal-beam photography about [010] the reciprocal-lattice points 210 and 310, as well as $2\bar{1}0$ and $3\bar{1}0$, cut the sphere of reflection almost simultaneously with 500, this coincidence resulting from the axial ratio $b^*/a^* = 6\frac{1}{2}$ and being virtually independent of wavelength. Since 210 and 310 are, respectively, the fourth and second strongest reflections recorded, with observed structure factors of 40·1 and 46·0 at room temperature, the conditions are highly favorable for the appearance of a sizable double reflection in the 500 position. What is particularly unusual in this situation is the fivefold coincidence that permits four distinct kinds of double reflection to arise at the same time, these being $(210+3\bar{1}0)$, $(2\bar{1}0+310)$, $(310+2\bar{1}0)$, and $(3\bar{1}0+210)$.

It might be expected that since, in space group $P2_1/a$, the 210 and $2\bar{1}0$ structure factors have opposite signs while 310 and $3\bar{1}0$ have the same sign, rays reflected from 210 and $3\bar{1}0$, in whichever sequence these reflections occur, should be opposite in phase to those reflected from $2\bar{1}0$ and 310, with consequent destructive interference between the two pairs of twice-reflected beams. That such destructive interference, if it occurs at all, is far from complete seems to confirm the conclusion of Lipscomb (1949) that interference effects of this sort would ordinarily be unobservable because of the convergence of the X-ray beam and the mosaic character of the crystal. Indeed, the occurrence of the 500 spot in α-phenazine is even more conclusive in this regard than is the failure of such experiments as those of Fankuchen and of Lipscomb to use the interference between single and double reflections for determining phase relationships among the structure factors. For in such experiments, even if the crystal were perfect, the conditions for single reflection would be satisfied, for a given crystal orientation, by a wide range of directions of the incident radiation, whereas only a minute fraction of the incident beam would arrive in precisely the proper direction for double reflection. Under these conditions the effects of interference would probably be imperceptible. In the phenomenon described here, on the other hand, if the crystal were perfect then the same portion of the incident beam would produce simultaneously two coherent double reflections opposite in phase, and interference between them would be complete. For if, at a particular instant, the points 500 and 210 lie on the sphere of reflection corresponding to a particular ray of incident radiation, then the point 310 must simultaneously lie on the same sphere of reflection, this being a necessary consequence of the orthogonality of the a^* and b^* axes. Thus whenever the crystal is so oriented as to produce the double reflection $(210+3\bar{1}0)$, it must simultaneously produce $(310+2\bar{1}0)$ with equal amplitude and opposite phase. The appearance of 500 must, therefore, be due to the mosaic spread of the crystal, which permits, for example, the 210 reflection from one crystal block to be subsequently reflected by the $3\bar{1}0$ planes of a second crystal block even though no double reflection is possible in either of these individual blocks. If a similar experiment could be set up with a nearly perfect crystal some degree of destructive interference might be detectable. Such an experiment could be of value in testing the feasibility of interference methods in general for the determination of the relative phases of structure factors.

The author is grateful for a very helpful discussion of this subject with Prof. I. Fankuchen.

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