THE PROCEDURE IN SOLVING THE STRUCTURE
OF SOME TWINNED CRYSTALS

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Difficulties in solving the crystal structure of substances which crystallize as twins are discussed. The procedure used in certain special cases of twinning is demonstrated on two examples.

1. INTRODUCTION

With a number of substances the solution of the crystal structure is hampered by the twinning of the crystals. Some classes of substances, due to their arrangement, have a strong tendency to crystallize as simple or multiple twins. We met with such a case when solving the structure of iodide crystals of organic radicals which are studied in our institute on account of their pronounced semi-conducting properties. In this paper we shall describe the procedure used and demonstrate it on several special cases.

2. DISCUSSION OF INTENSITY OF X-RAYS DIFFRACTED BY A TWIN

By a crystal twin we shall understand the growing together of two differently oriented individual crystals in the sense of the laws described, for example, in volume II of the international crystallographic tables [1]. Let us assume for simplicity that the lattices of the two parts of the twin are rotated with respect to one another so that all the points of the reciprocal lattice coincide. We further assume that both parts of the twin are macroscopic individuals so that they reflect independently. Then the experimentally measurable intensities ($I_m$) are the superposition of the intensities of the reflections of different indices from both parts of the twin ($I_1, I_2$):

$$I_m = I_1 + I_2.$$

In such a case a Patterson function can be constructed as the superposition of Patterson functions from the two differently oriented parts of the twin. However, a similar superposition is no longer generally valid for the Fourier function of electron density because

$$\sqrt{I_m} = \sqrt{(F_1^2 + F_2^2)} = F_1 + F_2.$$

Therefore we tried to find how to divide the experimentally determined intensity $I_m$ into its components $I_1$ and $I_2$. We shall show that this is possible if certain assumptions are fulfilled.

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We shall confine ourselves below to the case of twinning by rotation through an angle $\tau = 180^\circ$. If we choose the auxiliary system of reciprocal axes so that one axis is identical with the axis of rotation of twinning T (Fig. 1), then we can write

$$I_H^m = (1 - v)I_H + vI_H$$
$$I_H^n = vI_H + (1 - v)I_H,$$

where $I_H^m$ and $I_H^n$ are the conjugate, experimentally found intensities of the reflection of the twin; $I_H$ and $I_H$ are the conjugate reflections of the single crystal; $v$ is the volume of one part of the twin on the assumption that the total volume of the twin is regarded as unit volume. In solving system (1), several special cases can arise:

(1) $I_H^m \neq I_H^n$.

In this case system (1) has a solution on the assumption that $v \neq 1/2$, which is certainly fulfilled since for $v = 1/2$ we obtain $I_H^m = I_H^n$ which, according to our assumption, does not hold in this case. Then $I_H$ and $I_H$ can be expressed in a simple way:

$$I_H = \frac{1 - v}{1 - 2v} I_H^m - \frac{v}{1 - 2v} I_H^n$$
$$I_H = -\frac{v}{1 - 2v} I_H^m + \frac{1 - v}{1 - 2v} I_H^n,$$

where we do not know the volume $v$ expressing the ratio of the two parts of the twin. The volume $v$ must be found by further measurement, e.g. by observing the different optical properties of the two parts of the twin under the microscope or by estimation from the asymmetry of conjugate reflections. For this we make use of the fact that $I_H, I_H \geq 0$. Then the following two inequalities are obtained from system of equations (2)

$$0 \leq v \leq \frac{I_H^m}{I_H^m + I_H^n}$$
$$0 \leq v \leq \frac{I_H^m}{I_H^m + I_H^n}.$$