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On order–disorder structures.

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In a recent publication with the above title, Dornberger-Schiff (1956) has made reference to my investigation of the structure of disordered boric acid crystals by electron diffraction methods (Cowley, 1953). The suggestion that the method used to deduce the distribution-function projection, describing the distribution of origins of individual boric acid layers, is not justifiable indicates that some clarification of this point is desirable.

The electron diffraction patterns obtained from very small boric acid crystals, formed by evaporation of a solution of boric acid in water, had very nearly hexagonal symmetry, and intensities not very different from those to be expected from a single layer of the boric acid structure. It was concluded that the boric acid layer stacking was almost completely disordered. For purposes of structure analysis, a distribution function, $D(x, y, z)$, was introduced such that

$$V(x, y, z) = V^0(x, y, z)*D(x, y, z)\ , \qquad (1)$$

where $V(x, y, z)$ represents the potential distribution in the whole crystal, $V^0(x, y, z)$ is the potential distribution in one layer, and the symbol * denotes a convolution (or 'fold') operation.

Taking the Fourier transform of the projection of the functions in (1) gives

$$E_{hk0} = C_{hk0}.E^0_{hk0}\ , \qquad (2)$$

where E_{hk0} and E^0_{hk0} are the structure factors corresponding to the whole crystal and the individual layers, respectively, and C_{hk0} are the coefficients representing the values of the Fourier transform of the projection of $D(x, y, z)$ at the reciprocal-lattice points.

As Dornberger-Schiff (1956) points out, the C_{hk0} (her G_{hk0}) are, in general, complex, and will not necessarily be real for any choice of the origin of $D(x, y, z)$. It is therefore not practicable to use equation (2) in its general form in the process of refinement of the structure determination of the individual layers. For this purpose we consider, instead, the equivalent equations for the quantities derivable from the intensity data, namely

$$E_{hk0}.E^*_{hk0} = (C_{hk0}.C^*_{hk0}).(E^0_{hk0}.E^{0*}_{hk0}) \qquad (3)$$

and

$$P(X, Y) = Q(X, Y)*P^0(X, Y)\ , \qquad (4)$$

where $P(X, Y)$ and $P^0(X, Y)$ are the Patterson projections for the whole crystal and the single layer, and $Q(X, Y)$ is that for the distribution function. $Q(X, Y)$ or, more generally, $Q(X, Y, Z)$ contains all the information which is normally required about the stacking sequence. It gives the magnitude and direction of the displacement vectors between layer origin positions and the relative frequencies with which they occur.

We can then write

$$Q(X, Y, Z) = \sum_{n=1}^{N} D_n(X, Y, Z)\ ,$$

where $D_n(X, Y, Z)$ is the distribution function referred to the origin of the nth layer of atoms. Hence $Q(X, Y, Z)$ can be considered as the average distribution function giving the average arrangement of origins of neighbouring layers referred to the origin of any one layer.

The quantities $(C_{hk0}.C^*_{hk0})$ are real and positive. The Fourier coefficients, C'_{hk0}, given by

$$C'_{hk0} = |C_{hk0}| = |(C_{hk0}.C^*_{hk0})^{\frac{1}{2}}|$$

then define a function $D'(x, y)$, not very different from $Q(X, Y)$, having maxima in the same positions but of somewhat different relative magnitudes. The relation between the two functions is, in fact, similar to that of the modified Patterson function (Cowley, 1956*a*) obtained with quantities approximating to F_{hkl} as coefficients, and a normal Patterson function.

Since C_{hk0} can be replaced by C'_{hk0} in equation (3), equations (1) and (2) may be written with $D'(x, y, z)$ and C'_{hk0} replacing $D(x, y, z)$ and C_{hk0} respectively. In the structure analysis of disordered boric acid this is, in effect, what was done, although at that time the author wrongly supposed that it was necessary to *assume* that C'_{hk0} was always positive. The analysis therefore gave the true layer structure, $V^0(x, y)$, and the modified distribution function, $D'(x, y)$. In $D'(x, y)$ the directions and magnitudes of the stacking vectors are correctly represented, and, because in this case the amount of order was small, the peak heights are a good indication of the relative frequency of occurrence of the stacking vectors. The suggestion of Dornberger-Schiff that the stacking vectors deduced may be in error is therefore not justified.

It was demonstrated, in the course of the structure analysis of basic lead carbonate (Cowley, 1956*b*), that it is possible to deduce the layer structure, $V^0(x, y)$, and the distribution function Patterson, $Q(X, Y)$, without reference to the modified distribution function, $D'(x, y)$. This procedure will, in general, be preferable, since $Q(X, Y)$ is more readily interpreted than $D'(x, y)$. The use of $D'(x, y)$ may be convenient, however, where the layer structure is well known except for minor details, as was the case with boric acid.

In the above, the two-dimensional projected functions have been used for the sake of clarity in the discussion of the disordered boric acid structure. The extension to the more general three-dimensional case, with values of the index l not necessarily integral, is obvious. For X-ray diffraction work, of course, $V(x, y, z)$ and E_{hkl} are replaced by $\varrho(x, y, z)$ and F_{hkl}.

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