Acta Cryst. (1953). **6**, 522

Structure Analysis of Single Crystals by Electron Diffraction. II. Disordered Boric Acid Structure

By J. M. Cowley

Chemical Physics Section, Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

(*Received* 11 *December* 1952)

The techniques of structure analysis using single-crystal electron-diffraction patterns have been applied to the study of very small boric acid crystals in which there is almost complete disorder in the stacking of the two-dimensional layers of atoms. The structure of the layers and the nature of the order present are derived by a method involving a 'distribution function' which defines the distribution in space of equivalent points in the layers. The hydrogen ions in the hydrogen bonds are shown to have their most probable positions approximately 1 Å from an oxygen atom. An apparent interaction between parallel hydrogen bonds is observed. Suggestions are made for the further application of the distribution-function method.

1. Introduction

The techniques of structure analysis using single-crystal electron-diffraction patterns, described elsewhere (Cowley, 1953, hereafter referred to as Part I), have been applied to the study of the structure of boric acid in a disordered state.

The structure of normal boric acid was determined by Zachariasen (1934) using conventional X-ray methods. The unit cell is triclinic, space group C_i^1–$P\bar{1}$, with dimensions

$$a = b = 7{\cdot}04 \pm 0{\cdot}04,\ c = 6{\cdot}56 \pm 0{\cdot}04 \text{ Å and}$$
$$\alpha = 92^\circ\,30',\ \beta = 101^\circ\,10',\ \gamma = 120^\circ\,.$$

The structure is built up of plane parallel sheets of atoms bound together by van der Waals forces only. In the sheets, BO_3^{3-} groups are arranged at the apices of hexagons and joined together by pairs of parallel hydrogen bonds (Fig. 1). Zachariasen assumed that the hydrogen ions in the hydrogen bonds are situated half-way between the oxygen atoms. The individual layers have hexagonal symmetry. In going from one layer to its neighbour, the displacement parallel to the plane of the layers is such that a boron atom in the second layer comes almost vertically over an oxygen atom in the first. If the boron atom came directly over an oxygen atom, it is evident from the symmetry of the layers that there would be six equivalent displacements of this sort possible. Since the boron atom in one layer actually comes a little to one side of the oxygen atom in the adjacent layer, there are twelve equivalent displacements between layers. The normal three-dimensional structure is built up by an alternation of two of these twelve possible displacements so that the unit cell contains portions of two layers and is triclinic.

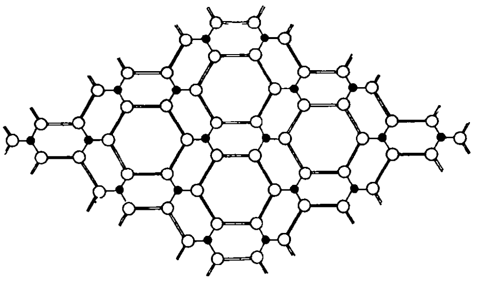

Fig. 1. The structure of a boric acid layer, according to Zachariasen. The double lines indicate hydrogen bonds.

The X-ray intensity measurements were not sufficiently accurate to allow the positions of the hydrogens to be determined. It is doubtful whether careful work using the most advanced X-ray diffraction techniques of the present time would give even a rough indication of the hydrogen-ion positions since the scattering power of hydrogen ions for X-rays is very small. It has been shown in Part I that the scattering power of hydrogen ions for electrons is much greater relative to that of other atoms, so that it is to be expected that structure analysis by electron-diffraction methods may be more effective in revealing the hydrogen-ion positions.

2. Electron-diffraction observations

Specimens were prepared by the evaporation of a solution of boric acid in water on a 200 nickel grid without a supporting film. Small thin crystals grew with the plane of their atom layers usually nearly parallel to the plane of the grid. The specimens were examined in the electron-diffraction camera (Cowley & Rees, 1953) using a finely collimated electron beam focused on the specimen so that the diameter of the beam at the specimen level was only a few microns.

When the beam was nearly perpendicular to the layers in a crystal, the diffraction pattern was an extensive array of spots having hexagonal symmetry in their positions and intensities. When the crystal was tilted, the angle of tilt could be calculated from the deviations of the dimensions of the pattern from those of a hexagonal array. The spot intensities varied with the angle of tilt, but for no angle of tilt were any of the spots completely extinguished. These observations suggest that the reciprocal-lattice representation of such a crystal consists of a set of parallel lines, all perpendicular to the layers of the crystal, with a limited variation in scattering power along them. Hence the crystals are disordered in one dimension, having a disordered stacking of the well-defined boric acid layers. The amount of disorder present, as judged qualitatively from the relative intensities of spots from tilted crystals, varies widely from crystal to crystal, but in no case is disorder absent and in many cases almost complete disorder is indicated.

Two forms of randomness may contribute to the disorder. In the first, the possible displacements, in the *a*–*b* plane, between neighbouring layers are limited to the twelve displacements which are equivalent to those occurring in the normal bulk structure. The sequence of displacements is more or less random. Such a disorder may be described in terms of repeated twinning on the basal plane with a varying number of layers between twin planes. For a large number of layers the projection of all the displacements on the basal plane has approximately hexagonal symmetry. The continuous lines in the reciprocal lattice show a regular variation of scattering power with a period equal to the reciprocal of the inter-layer spacing. In the second form of randomness the displacements between layers are arbitrary although the orientation of all layers is the same. The layers then scatter individually and the reciprocal-lattice representation is the same as for a single layer, i.e. the continuous lines have uniform intensity. In practice the two forms of randomness are probably present in relative amounts which vary from crystal to crystal.

There is evidence that such disorder in layer stacking is very common in small crystals of layer-lattice materials. A number of authors have published 'bent-crystal' patterns showing continuous hyperbolae and 'tilted fibre patterns' showing continuous ellipses, indicating that such stacking disorder occurs in crystals of CdI_2, $CdCl_2$ and molybdenite. Also, many extensive spot patterns which have been attributed, rather vaguely, to 'two-dimensional' diffraction, probably originate in this way.

The intensities of the spots in a number of patterns from boric acid crystals were measured by the new method outlined in Part I. Fig. 2 shows such a pattern in which each spot has been spread out over a small rectangular area by means of linear 'saw-tooth' deflecting voltages applied to two perpendicular sets of deflecting plates placed below the specimen. The deflection on the microphotometer trace was calibrated in terms of intensity by using a non-linear deflecting voltage applied to one pair of plates.

The intensities of the spots in the pattern shown in Fig. 2 have very nearly hexagonal symmetry, and are close to those to be expected from a single boric acid layer. The disorder in the layer stacking is almost complete. In the Patterson projection calculated from the measured intensities, the vectors corresponding to the inter-layer displacements to be expected from the bulk structure are not prominent.

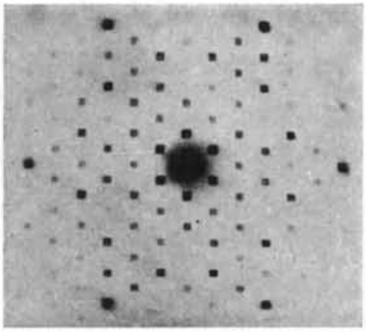

Fig. 2. Spot pattern from a disordered single crystal of boric acid. Each spot has been spread over a small rectangular area by the application of deflecting voltages.

A Fourier projection (Fig. 3) was calculated from the observed intensities, using phases determined from the structure of the boric acid layer given by Zachariasen (Fig. 1). The observed intensities were not exactly centrosymmetric because the beam was not quite perpendicular to the crystal layers. The values of I_{hk} and $I_{\bar{h}\bar{k}}$ were averaged and a centre of symmetry was assumed. The intensities did not have exact hexagonal symmetry, and no assumption of hexagonal symmetry was made. Hence the resulting potential map does not have hexagonal symmetry but only a centre of symmetry.

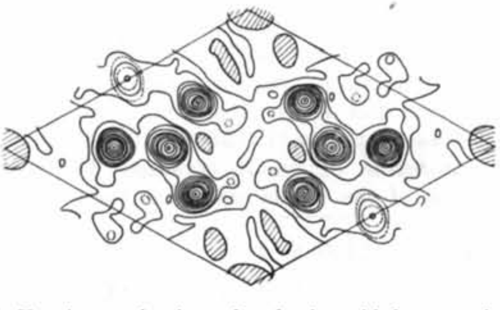

Fig. 3. Fourier projection of a boric acid layer, calculated from observed intensities. The contours are drawn at equal intervals of potential, on an arbitrary scale. The broken contours indicate half intervals. The shaded areas are depressions.

The principal features of the Fourier projection are in exact agreement with the X-ray results. The oxygen peaks, all of equal height to within the accuracy of measurement, and the boron peaks are well resolved and their positions are those given by Zachariasen. The minor features of the projection are less definite. Several small spurious peaks occur, such as those at $(\frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2})$, apparently as a result of the tilt of the crystal and the amount of order present. At the hydrogen positions assumed by Zachariasen there are depressions rather than peaks. The distribution of slight maxima suggests that the hydrogen positions may be closer to the oxygen atoms and displaced slightly towards the $(\frac{1}{2}, 0)$, $(0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2})$ positions.

No refinement of the Fourier projection can be made by assuming other positions for the hydrogen ions, since no reasonable shift of the hydrogen ions changes any of the signs of the structure factors. The only possible way to improve the projection to give a better indication of the location of the hydrogen ions is to correct the intensities for the effects of the amount of ordering which is present. It is possible to do this by a method involving the use of a 'distribution function'.

3. Use of the distribution function

A crystal which is made up by the translational repetition of a single structural unit, such as a group of atoms, a molecule, a chain or sheet of atoms or molecules, may be represented in terms of the individual unit and a distribution function. Let $V^0(x, y, z)$ represent the potential distribution in the structural unit. $D(x, y, z)$ is a distribution function which consists of a set of δ-functions, with integrated value unity, defining the points in space at which a given point of the structural unit occurs. It is analogous to the 'peak function' used by Ewald (1940) in discussions of the shape-transforms of small crystals. The potential distribution of the whole crystal is then

$$V(x, y, z) = \iiint D(X, Y, Z) \times V^0(x-X, y-Y, z-Z)\,dX, dY, dZ\,. \tag{1}$$

Following Ewald, the integral is called the 'fold' of D and V^0 and is written $\widehat{D.V^0}$ ('D fold V^0').

The Fourier transform of $V(x, y, z)$ is $E(\xi, \eta, \zeta)$, where ξ, η and ζ are co-ordinates in reciprocal-lattice space. If the Fourier transforms of $V^0(x, y, z)$ and $D(x, y, z)$ are $E^0(\xi, \eta, \zeta)$ and $C(\xi, \eta, \zeta)$ respectively, it follows from a well known theorem of Fourier integrals that

$$E(\xi, \eta, \zeta) = C(\xi, \eta, \zeta).E^0(\xi, \eta, \zeta)\,. \tag{2}$$

If $V(x, y, z)$ is periodic, then either $D(x, y, z)$ or $V^0(x, y, z)$ is periodic, and the values of the transforms E, C and E^0 are important only for integral values, h, k, l of the co-ordinates ξ, η, ζ. Then

$$E_{hkl} = C_{hkl}.E^0_{hkl}\,. \tag{3}$$

Similar relations apply, of course, for the electron density $\varrho(x, y, z)$ and the X-ray structure factor $F(\xi, \eta, \zeta)$ or F_{hkl}. Equivalent relations hold when the projection of the potential distribution (or electron density) on a plane or on a line is considered.

As an example to illustrate the nature and the method of derivation of a distribution function, the basal projection of the distribution function for the layers in an ordered boric acid structure has been calculated. The values of the coefficients $C_{hk} = E_{hk}/E^0_{hk}$ were determined, using the values of E_{hk} and E^0_{hk} calculated from the bulk and layer structures given by Zachariasen. Since C_{hk} is defined only for integral h and k, the distribution function $D(x, y)$ obtained by Fourier summation must be periodic. It may be interpreted either as a superposition of an array of distribution functions spaced at the unit-cell corners, or else as the distribution function not of a unit consisting of a whole layer but of a unit consisting of the portion of a layer contained within a unit cell. The E_{hk} and E^0_{hk} were each calculated with respect to the centre of symmetry of the appropriate potential distribution. The magnitudes of the coefficients C_{hk} did not, in general, decrease with increasing h and k. In order to avoid large errors due to the termination of the series, therefore, the values of C_{hk} were multiplied by an 'artificial temperature factor' of the form $a \exp(-b^2(\sin^2\theta)/\lambda^2)$. The sharp peaks of the peak-function $D(x, y)$ were thus replaced by maxima with error-function profiles. The resulting distribution function projection is shown in Fig. 4. The pair of peaks near the origin indicates that, if one looks down the c axis of the triclinic unit cell, the centres of symmetry of the layers are seen to be displaced alternately in one direction and the opposite direction, the projected displacement being 0·76 Å each way.

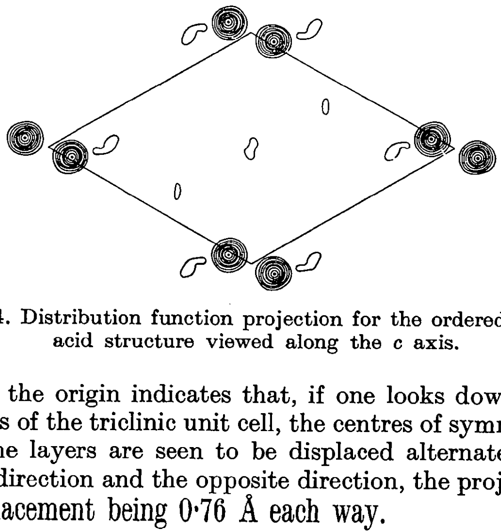

Fig. 4. Distribution function projection for the ordered boric acid structure viewed along the c axis.

The Fourier projection (Fig. 3) was refined by the alternate calculation of distribution functions and trial Fourier projections. As a first step, an approximate layer structure, $V^0(x, y)$. was deduced from Fig. 3 and used to calculate E^0_{hk} values. C_{hk} values were found from equation (3), multiplied by an artificial temperature factor and used in a Fourier summation to give the approximate distribution-function projection shown in Fig. 5. It was assumed that the disorder was so nearly complete that the signs of E_{hk} and E^0_{hk}

were identical, and C_{hk} was always positive. To calculate the E^0_{hk} it was assumed that half a hydrogen atom was at $\pm(\frac{1}{3}, \frac{2}{5})$, $\pm(\frac{2}{5}, \frac{1}{3})$ and the eight other equivalent positions.

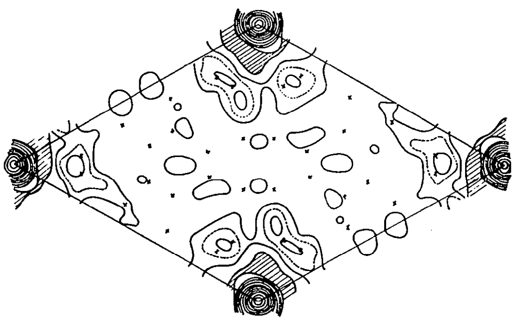

Fig. 5. Distribution function projection for disordered boric acid calculated on the basis of the Fourier projection, Fig. 3.

The distribution-function projection (Fig. 5) shows a number of small maxima around the peak at the origin. The crosses mark the positions where peaks would occur if only inter-layer displacements equivalent to those of the ordered structure were present. There is a rough correspondence between these positions and the minor maxima, especially for the positions nearest the origin. Hence, as a first approximation, it was assumed that the distribution function consisted of peaks at the positions of the crosses. A new set of C_{hk} was calculated by giving these peaks relative weights estimated from the relative heights of the maxima. This set was then used to calculate a new set of E^0_{hk} from the observed E_{hk}, and so a second approximation to the layer structure was obtained.

This process was repeated until no further improvement in the projections of the potential distribution and the distribution function seemed possible. The final projection of the layer structure is shown in Fig. 6. The final distribution-function projection is given in Fig. 7. The refining process improved the agreement between the observed and calculated structure factors, as is shown in Table 1. The discrepancy factor, $\Sigma||F_o|-|F_c||\div\Sigma|F_o|$, was reduced from 28% to 20%.

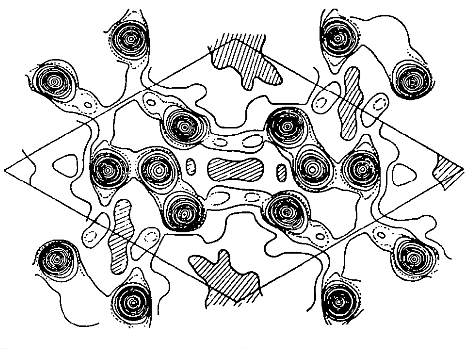

Fig. 6. Fourier projection of a boric acid layer, corrected for the effects of ordering by the distribution-function method.

Compared with the original Fourier map (Fig. 3), the corrected map (Fig. 6) shows a marked improvement. The spurious maxima, including the relatively large one at $(\frac{1}{2}, 0)$, have almost disappeared. The hydrogen positions are indicated much more clearly. Effects due to the lack of hexagonal symmetry in the diffraction pattern are, however, still noticeable. The back-ground is uneven, and the heights of the hydrogen maxima vary.

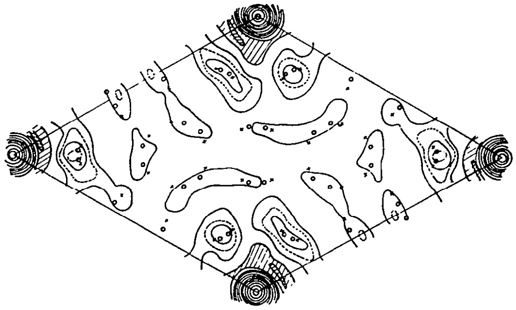

Fig. 7. Distribution-function projection corresponding to the Fourier projection, Fig. 6.

The boric acid layer presumably has exact hexagonal symmetry, at least on an average. The scattering power at the reciprocal-lattice points $hk0$ should then have hexagonal symmetry. Since it is not possible to determine the exact tilt of the crystal giving the pattern (Fig. 2), the correction of the intensities for the effects of the tilt is not feasible. The best representation of the boric acid layer structure is probably given by assuming hexagonal symmetry and averaging the values of the structure factors of equivalent reflexions, after refining them as much as possible by the above method. When this is done, the discrepancy factor is further reduced to 15%, and the Fourier map is as shown in Fig. 8.

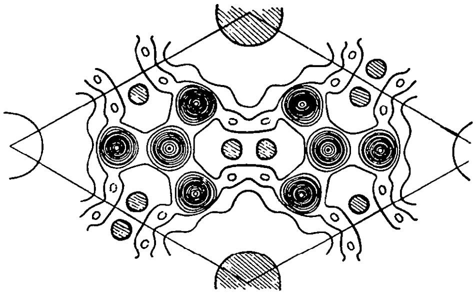

Fig. 8. Fourier projection of a boric acid layer obtained by using the corrected structure factors and assuming hexagonal symmetry.

4. The structure of boric acid layers

The co-ordinates of the atoms, referred to the two-dimensional hexagonal unit cell, are given from Fig. 8 as follows:

Table 1. *Comparison of the observed structure factors, and the structure factors corrected for the effects of ordering, with those calculated from the finally determined boric acid layer structure*

hk	$\lvert E_{hk}\rvert$ (obs.)	E_{hk} (corr.)	E_{hk} (calc.)
01	15	−16	−18
02	7	−11	−14
03	2	− 3	− 3
04	5	5	4
05	3	4	6
06	2	− 3	− 3
07	2	− 1	− 2
08	1	− 1	− 1
09	3	3	4
10	20	−21	−18
11	7	7	10
12	7	9	10
13	11	−12	− 9
14	3	4	4
15	4	− 4	− 4
16	3	3	3
17	1	2	1
18	1	− 1	− 1
$\bar{1}1$	19	−19	−18
$\bar{1}2$	6	6	10
$\bar{1}3$	7	9	10
$\bar{1}4$	9	− 9	− 9
$\bar{1}5$	3	4	4
$\bar{1}6$	4	− 5	− 4
$\bar{1}7$	2	3	3
$\bar{1}8$	1	1	1
20	9	−13	−14
21	10	13	10
22	5	4	4
23	4	− 2	− 2
24	2	3	3
25	2	3	1
26	2	2	2
27	2	− 3	− 2
$\bar{2}1$	7	7	10
$\bar{2}2$	8	−12	−14
$\bar{2}3$	7	9	10
$\bar{2}4$	5	3	4
$\bar{2}5$	6	− 3	− 2
$\bar{2}6$	4	− 4	− 3
$\bar{2}7$	2	3	1
$\bar{2}8$	2	2	2
$\bar{2}9$	2	− 3	− 2
30	3	− 3	− 3
31	12	−13	− 9
32	5	− 2	− 2
33	11	11	12
34	3	− 3	− 2
35	2	− 3	− 3
36	1	− 1	− 2
$\bar{3}1$	6	8	10
$\bar{3}2$	6	8	10
$\bar{3}3$	2	− 3	− 3
$\bar{3}4$	10	−11	− 9
$\bar{3}5$	5	− 2	− 2
$\bar{3}6$	11	11	12
$\bar{3}7$	3	− 4	− 2
$\bar{3}8$	2	− 3	− 3
40	5	5	4
41	4	6	4
42	4	− 4	− 4
43	3	− 3	− 2
44	1	2	2
45	2	2	2
46	2	− 1	− 1
$\bar{4}1$	13	−14	− 9
$\bar{4}2$	6	4	4
$\bar{4}3$	9	− 9	− 9
$\bar{4}4$	5	5	4
$\bar{4}5$	5	6	4
$\bar{4}6$	2	− 3	− 4
$\bar{4}7$	2	− 3	− 2
$\bar{4}8$	1	2	2
50	4	5	6
51	5	− 5	− 5
52	2	3	2
53	2	− 3	− 3
54	2	1	2
55	1	1	1
$\bar{5}1$	4	5	4
$\bar{5}2$	9	− 4	− 2
$\bar{5}3$	8	− 4	− 2
$\bar{5}4$	4	6	4
$\bar{5}5$	5	6	6
$\bar{5}6$	5	− 6	− 5
$\bar{5}7$	1	2	2
$\bar{5}8$	2	− 3	− 3
$\bar{5}9$	2	1	2
60	2	− 3	− 3
61	2	2	3
62	2	2	2
63	1	− 1	− 2
64	1	− 1	− 1
$\bar{6}1$	4	− 4	− 4
$\bar{6}2$	3	− 4	− 3
$\bar{6}3$	14	14	12
$\bar{6}4$	4	− 5	− 4
$\bar{6}5$	3	− 4	− 5
$\bar{6}6$	2	− 3	− 3
$\bar{6}7$	3	3	3
$\bar{6}8$	2	2	2
$\bar{6}9$	1	− 1	− 2
70	3	− 2	− 3
71	1	1	1
72	1	− 2	− 2
$\bar{7}1$	4	4	3
$\bar{7}2$	2	3	1
$\bar{7}3$	3	− 3	− 2
$\bar{7}4$	4	− 5	− 2
$\bar{7}5$	2	3	1
$\bar{7}6$	2	2	3
$\bar{7}7$	2	− 1	− 3
$\bar{7}8$	1	1	1
$\bar{7}9$	1	− 2	− 2
80	1	− 1	− 1
$\bar{8}1$	2	1	1
$\bar{8}2$	2	2	2
$\bar{8}3$	2	− 3	− 3
$\bar{8}4$	1	2	2
$\bar{8}5$	2	− 3	− 3
$\bar{8}6$	2	2	2
$\bar{8}7$	1	1	1
$\bar{8}8$	1	− 1	− 1
90	2	3	4
$\bar{9}1$	1	− 2	− 1
$\bar{9}2$	1	− 2	− 2
$\bar{9}3$	1	− 1	− 2
$\bar{9}4$	3	2	2
$\bar{9}5$	2	2	2
$\bar{9}6$	1	− 1	− 2
$\bar{9}7$	2	− 3	− 2
$\bar{9}8$	1	− 2	− 1
$\bar{9}9$	2	3	4

B at $\pm(\frac{2}{3}, \frac{1}{3})$;
O at $\pm(0{\cdot}444, 0{\cdot}222)$ and equivalent positions;
$\frac{1}{2}$H (most favoured sites) at $\pm(0{\cdot}427, 0{\cdot}357)$,
$\pm(0{\cdot}357, 0{\cdot}427)$ and equivalent positions.

The interatomic distances are thus

B–O : 1·36 Å;
O–O : 2·36 Å within a BO_3^{3-} group,
2·72 Å between groups;
O–H : 1·00–1·05 Å.

This value for the O–H distance is in agreement with the values derived from spectrographic data for other O–H · · · O bonds. (Pauling, 1945).

The most favoured positions for the hydrogen ions in the hydrogen bonds do not lie on the straight lines joining pairs of neighbouring oxygen atoms in adjacent groups, but are displaced towards the points $(\frac{1}{2}, 0)$, $(0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2})$. Thus the hydrogen bonds occur in pairs in which each appears to be bent towards the other in an arc, as if by mutual attraction.

A possible interpretation of this observation is that hydrogen bonds may tend to form not only between oxygen atoms which are nearest neighbours in adjacent

BO_3^{3-} groups, but also between those which are second nearest neighbours. The probability distribution of hydrogen positions is then given by the combination of the eight canonical arrangements in Fig. 9, which are the eight possible arrangements of two hydrogen bonds between the four oxygen atoms in a rectangular array. It may be assumed that for each arrangement of hydrogen bonds, the hydrogen ions are of the order of 1 Å from the nearest oxygen atoms. The eight arrangements then combine, as shown in Fig. 9, so that the most probable position for a hydrogen ion is approximately 1 Å from an oxygen atom and between the two lines indicating possible hydrogen bond directions.

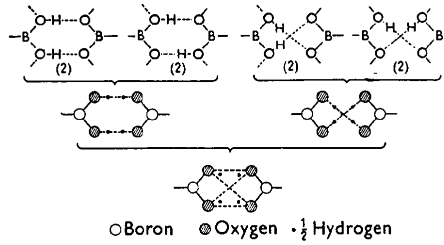

Fig. 9. The combination of eight canonical arrangements of hydrogen ions in hydrogen bonds between four oxygen atoms to give the observed distribution.

This interaction between neighbouring hydrogen bonds may be expected to take place in many structures where hydrogen bonds occur in parallel or near-parallel pairs. Favourable configurations occur in the structures of many organic compounds, such as the carboxylic acids and, possibly, proteins. The interaction of the hydrogen bonds may play an important part in determining the structures of these substances.

Another point of interest in the Fourier projections is that the boron and oxygen peaks are very nearly equal in height, in spite of the large relative difference in the atomic numbers. This effect may be ascribed to the state of ionization of the atoms. It has been shown in Part I that, relative to the atomic scattering for a neutral atom, a positive ion scatters more strongly and a negative ion scatters less, especially for low values of $(\sin\theta)/\lambda$. The peaks in Fourier maps will be correspondingly increased or decreased in height.

Information on the states of ionization of the atoms in a structure could be deduced from the peak heights or diffraction intensities in a number of ways. Three possible procedures are as follows:

(1) If the variation of the X-ray atomic scattering factor, f, with the degree of ionization of an atom is known, the variation of the scattering factor for electrons, $\varepsilon = (Z-f)\lambda^2/\sin^2\theta$, can be found. The observed peak height can then be compared with peak heights calculated for various degrees of ionization. For this calculation it may be assumed that, for an A atom at (x_1, y_1), only that part of the structure factor due to A atoms contributes to the peak height, so that

$$V(x_1, y_1) = \sum_h \sum_k E_{A,hk} \exp\left[-2\pi i(hx_1+ky_1)\right] .$$

(2) With the same assumptions as for (1), if n kinds of atom are present, the degree of ionization of each of the n may be found by so choosing the scattering curve for each that the intensities of n reflexions with low values of $(\sin\theta)/\lambda$ are correctly given.

(3) The atomic scattering curve for each atom present may be deduced, by a method of successive approximations, from the observed values of the structure factors. Thus, for a structure containing only A and B atoms, a reasonable atomic scattering curve is assumed for the A atoms. The atomic scattering factor for B is then calculated from the observed structure factor for each reflexion. The resulting values will then be scattered about the true atomic scattering curve for B, the scatter being due to the errors in the curve assumed for A. The best smooth curve is then drawn through the scattered points for B and this curve is assumed as correct for B in the calculation from the observed structure factors of the values of the atomic scattering factor for A for the various reflexions. This process is repeated until atom scattering curves are obtained for A and B which are consistent with the observed intensities within the limits of experimental error. These curves may then be compared with theoretical curves for various degrees of ionization of the atoms. The scale of the experimental curves may be adjusted by fitting them to the theoretical curves for $(\sin\theta)/\lambda > 0{\cdot}4$, since the effect of ionization on the curves is negligible in this region.

The method (3) seems to be the most fundamental approach and also the most practicable. The information on the variation of f or ε with the degree of ionization required for (1) and (2) is mostly not available at present. When available, this information refers to isolated atoms and ions with spherical symmetry. Considerable errors may result from the assumption that it is valid for ions in a crystal lattice.

An attempt has been made to apply method (3) to determine the atomic scattering curves for boron and oxygen in boric acid, assuming reasonable values for the hydrogen scattering factor. However, the number of reflexions with $(\sin\theta)/\lambda < 0{\cdot}2$ was too small to allow the curves to be determined in this region, which is the only region for which the effects of ionization are marked.

5. Stacking disorder in boric acid

The nature of the stacking disorder of the boric acid layers in the particular crystal studied may be deduced from the Fourier projection of the distribution function (Fig. 7). As in Fig. 5, the crosses indicate displacements from the origin equivalent to those occurring in the ordered structure, as determined by X-ray diffraction. The small circles mark a similar set of points which fit the observed maxima more closely. The differences in the positions of the circles and crosses indicate that, in the disordered lattice, a boron atom in one layer is more nearly over an oxygen atom in the layer below than in the ordered lattice.

The distribution function projection may be interpreted in terms of the two forms of randomness described above: (*a*) that in which the displacements between layers are limited to those occurring in the ordered structure, and equivalent displacements; and (*b*) that in which the displacements between layers are arbitrary except that the inter-layer spacing is not greatly affected.

The crystal can be considered as built up of a large number of small regions with randomness of type (*a*) separated by regions with randomness of type (*b*). The type (*a*) regions scatter independently and the distribution-function projection may be considered as the projection of the average distribution function for such a region. The small thickness of these regions may be inferred from the rapid decrease in the height and resolution of the small maxima in Fig. 7 as the distance from the origin increases. It appears that, on the average, the region consists of only three or four layers on either side of the layer chosen as origin.

In order to calculate the correction to apply to the observed structure factors to get the coefficients for the Fourier projection (Fig. 6), this distribution-function projection was idealized. The relative strengths of the peaks were taken as

100	at	(0, 0);
8	at	(0·27, 0·115), (0·115, 0·27) and equivalent points;
4	at	(0·385, −0·04), (−0·04, 0·385) and equivalent points;
5	at	(0·54, 0·23), (0·23, 0·54) and equivalent points.

6. The distribution function: further discussion

The resolution of the structure of a crystal into a structural unit and a distribution function may be a useful step in dealing with a number of problems of structure analysis. It may be applied to both ordered and disordered structures. In the form used above, the application is limited to cases where the phases of the Fourier coefficients are known, at least approximately, for two of the three functions V, V^0 and D (or ϱ, ϱ^0 and D).

For an ordered structure in which the unit cell contains several translational repetitions of one group of atoms, if the structure is known approximately it may be refined by resolving it into one structural unit at the origin of the unit cell and a distribution function consisting of a set of peak functions. By calculating Fourier maps of the structural unit and the distribution function alternately, and idealizing each by the elimination of obviously spurious detail at each stage, the maximum of accuracy in the structure determination could be achieved. When only two-dimensional projections are possible, the method could be used to give a clear picture of the projection of a molecule where, in the normal projection, several molecules overlap.

For disordered structures, the equation (2) or (3) may be used directly if the amount of ordering is so small that E and E^0 have the same sign, or when special circumstances allow the differences in phase to be determined.

When the relative phases are not known, it is possible to use relations between the Patterson functions, equivalent to the equations (1), (2) and (3). Thus

$$P(X, Y, Z) = \overbrace{Q(X, Y, Z) . P^0(X, Y, Z)}\,, \tag{4}$$

where $Q(X, Y, Z)$ is the Patterson function corresponding to the distribution function $D(x, y, z)$,

and $$E . E^* = (C . C^*) . (E^0 . E^{0*})\,. \tag{5}$$

For ordered structures with a translational repetition of a structural unit, the problem of the interpretation of $P(X, Y, Z)$ can be reduced to the simpler problem of the interpretation of $P^0(X, Y, Z)$, if $Q(X, Y, Z)$ can be deduced from the strong peaks occurring in $P(X, Y, Z)$. In this way an approximate structure can be found, and the relative phases determined, so that the method of refining the structure by using $D(x, y, z)$, as described above, can be applied.

For disordered structures, the function $Q(X, Y, Z)$ is usually sufficient to give all the required information on the nature of the disorder in a structure composed of known structural units. It gives the average distribution of structural units about a given one. The relation (5) is, in fact, equivalent to the expressions for the intensity of scattering from disordered structures which have been used widely in the study of disordered layer stacking, disorder in alloys, and so on. To date, however, the emphasis has usually been on the calculation of the $C . C^*$ on the basis of postulated forms of disorder and comparison with experiment, rather than on the experimental determination of the $C . C^*$ and the investigation of the nature of the disorder by an examination of the distribution Patterson, $Q(X, Y, Z)$.

In cases where the structural unit is not completely known, the relation (5) could be used, in the same way as (2) has been used to determine $P^0(X, Y, Z)$ more exactly, and so allow the exact structure of the unit to be deduced.

The distribution function, or its Patterson, is very sensitive to errors in the potential distribution V^0 (or the electron density ϱ^0) of the structural unit which affect those E^0 values which are very small. In the process of refining a structure, any very large values of C (or $C . C^*$) which correspond to very small E^0 values may well be ignored in the preliminary stages of refinement.

In conclusion I wish to thank Dr A. L. G. Rees for valuable discussion on the hydrogen-bond configuration and for his continued interest throughout the course of the work.

References

Cowley, J. M. (1953). *Acta Cryst.* **6**, 516.
Cowley, J. M. & Rees, A. L. G. (1953). *J. Sci. Instrum.* **30**, 33.
Ewald, P. P. (1940). *Proc. Phys. Soc.* **52**, 167.
Pauling, L. (1945). *The Nature of the Chemical Bond*, 2nd ed., chap. 9. Ithaca: Cornell University Press.
Zachariasen, W. H. (1934). *Z. Krystallogr.* **88**, 150.

Acta Cryst. (1953). **6**, 529

The Crystallography of the Titanium Transformation

By Carl J. McHargue

University of Kentucky, Lexington 29, *Kentucky, U.S.A.*

(*Received* 6 *October* 1952)

The orientation relationships between hexagonal close packed and body-centered cubic titanium have been found to be $(0001)_{\text{h.c.p.}}$ parallel to $(110)_{\text{b.-c.c.}}$ and $[11\bar{2}0]_{\text{h.c.p.}}$ parallel to $[111]_{\text{b.-c.c.}}$. These were determined by noting the relationships between several large α grains which had been formed from a single β grain. These relationships agree with those reported for zirconium and lithium.

The habit plane of titanium has been shown to be $(331)_{\text{b.-c.c.}}$ within an experimental error of 2°. This was determined from the relief effects present in large α grains and the orientation relationships developed above.

Introduction

Titanium, like zirconium and lithium, undergoes a transformation from a body-centered cubic structure to a hexagonal close-packed structure. In each case, the cubic form is the higher-temperature structure. Burgers (1934) found that the orientation relationships for the zirconium transformation were $(0001)_\alpha$ parallel to $(110)_\beta$ and $[11\bar{2}0]_\alpha$ parallel to $[111]_\beta$. Barrett (1951) has reported the same orientation relationships for the transformation in lithium. Barrett's measurements indicated an angle of 3° between the close-packed directions, while Burgers's measurements indicated an angle of 0–2° for zirconium.

As a result of his study of the orientation relationship, Burgers (1934) proposed that the transformation, body-centered cubic to hexagonal close-packed, occurred by heterogeneous shear on (112) $[11\bar{1}]$. Inasmuch as the habit plane is a plane of zero distortion, it was thought that the habit plane of zirconium would be $(112)_{\text{b.-c.c.}}$. Bowles (1951) has reported that the habit plane of lithium is $\{441\}_{\text{b.-c.c.}}$. As a result of the investigation of Bowles (1951), Burgers & Ginneken (1952) have conducted a limited investigation which indicated the habit plane of zirconium to be possibly {569} or {145}. These more recent results are similar to the habit planes reported for other shear transformations in body-centered cubic metals. In most instances, the habit plane is one of high indices or is irrational.

Experimental procedure

Materials

Iodide titanium which had been arc melted on a water-cooled copper block in an argon atmosphere was used throughout this investigation. In an attempt to grow very large grains of α titanium, it was noted that it was frequently possible to observe two, three, or four large α grains forming from a single β grain. For the present study, specimens were heated in evacuated quartz tubes at 850° C. for 24 hr., then held at 1100° C. for 4 hr. and furnace cooled.

Orientation relationship

Back-reflection Laue patterns were made with a precision camera in order that the orientations of the α grains could be determined. The α grains studied were 2–3 mm. in size. Specimens were chosen in which three or four α grains had formed from each β grain. In all, α grains transformed from eight β grains were studied. The orientations for all hexagonal grains resulting from the same cubic grain were plotted on a single stereographic projection and the angles between various planes and directions were measured.

In Fig. 1, the results for four α grains which formed from the same β grain are plotted. The poles of the four basal planes are shown in Fig. 1(*a*) at their positions with respect to the surface of the specimen. The plane of projection lies parallel to the specimen surface. In Fig. 1(*b*) the basal poles have been placed