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A SYSTEMATIC APPROACH TO INDEXING POWDER PATTERNS OF LOWER SYMMETRY USING DE WOLFF'S PRINCIPLES

K. VISWANATHAN, *Institut für Mineralogie, Universität Münster, Münster, West Germany.*

ABSTRACT

Using De Wolff's (1957) equations two centrosymmetrical reciprocal lattice planes are found which intersect along a common axis. Assuming the Q-value of a particular lattice point to be R, planes parallel to the centrosymmetrical planes are constructed. The value of R is found by considering the differences in the Q-values of a particular row of the parallel planes. The nature of distribution of equal Q-values on the parallel planes exhibit the symmetry of the crystal.

INTRODUCTION

Runge (1917) and Ito (1949, 1950) presented methods for indexing powder photographs regardless of symmetry, which were based on the relationship between the reciprocal lattice vectors and $\sin^2\theta$ values. Based on this approach De Wolff (1957) suggested a more elegant method to construct directly the reciprocal lattice of a crystal from Q-values ($Q=\sin^2\theta\times 10^4$). De Wolff has given the following four important equations, which give the relationship between different reciprocal lattice vectors.

$$Q(h_1+h_2)+Q(h_1-h_2) = 2Q(h_1)+2Q(h_2) \tag{1}$$

$$n^2Q(mh) = m^2Q(nh) \tag{2}$$

$$Q(h+xh')-Q(h-xh') = x\cdot[Q(h+h')-Q(h-h')] \tag{3}$$

$$Q(h_1+h_2+h_3)+Q(h_3)-Q(h_1+h_3)-Q(h_2+h_3) = Q(h_1+h_2)-Q(h_1)-Q(h_2) \tag{4}$$

De Wolff has also given three examples to show how these equations can be used for different purposes. But his approach gives the impression that it is necessary to find three reciprocal lattice planes with Eq. (1), if a powder pattern of a monoclinic or triclinic crystal is to be indexed. It is found that in some cases it is almost impossible to get more than two planes. Therefore this method has been suggested which requires only two intersecting centrosymmetrical planes to start with. Further an attempt has been made to evolve a systematic procedure to index powder patterns of unknown symmetry.

First the Q-values are tested for cubic, tetragonal and hexagonal symmetries according to the methods described by Azaroff and Buerger (1958). After eliminating these three possibilities, the procedure of De

Wolff is followed to find two intersecting planes using Eq. (1). In a systematic procedure it is not advisable to use Eq. (3) to find a parallel plane as done by De Wolff for his example 1 because of the following reasons: (1) If the first plane found by Eq. (1) is an orthogonal array, there will be success only if the crystal is orthorhombic and only when the orthogonal plane contains two of the three principal axes a^*, b^* and c^*. (2) If the first plane is not an orthogonal array, it is possible to find a parallel plane with Eq. (3) only if the crystal is monoclinic and only when the first plane contains the axes a^* and c^*.

It may be noted that if four Q-values satisfy Eq. (3) and if they give a periodicity equal to one of the Q-values, say Q_A, of the first plane found by Eq. (1), the same data can be used to construct a second plane intersecting the first one along the vector giving the value Q_A.

After finding four Q-values with Eq. (1) and forming a plane, the other Q-values of it can be found with Eqs. (2) and (3) as suggested by De Wolff. Then the two planes must be tested for the following: (1) Whether any one of them show pairs of equal Q-values and if so, whether it can be reduced to an orthogonal array. (2) Assuming that the two planes intersect along the h_2-axis and one has h_1 and h_2 as translation directions and the other h_3 and h_2, it must be checked whether $Q(h_1)$, $Q(h_2)$ and $Q(h_3)$ are really the "unit"[1] Q-values in the respective directions and do not correspond to higher orders (probably second order). De Wolff formed the first plane of his example III by considering the Q-values 936.0 and 166.1. Later it was found that 234.0 and not 936.0 is the fundamental Q-value in that direction. Such cases may occur especially if the Q-values selected for Eq. (1) occur among the higher values.

Method

The method of constructing the reciprocal lattice after finding two intersecting planes is described by considering the powder data (Table 1) given by De Wolff for triclinic $KBO_3 \cdot H_2O_2$ and orthorhombic progesterone.

Example I. $KBO_3 \cdot H_2O_2$. De Wolff first found the following two planes.

Plane *A*

	1044.4	824.1	936.0	1380.1		(a_2)
1313.2	620.4	261.1	234.0	539.1	1176.4	(a_1)
			0.0	166.1	664.4	(a_0)

[1] "Unit" Q-value has been used in the sense that it will be the first Q-value in that particular direction considered from the origin and all other Q-values in that direction will be higher orders of this value.

Plane *B*

		702.0	838.1	1306.4		(b_2)
869.9	356.6	175.5	326.6	809.9		(b_1)
		h_1 ↑				
		0.0 ——→	166.1	664.4	1494.9	(b_0)
			h_2			

An examination of the planes A and B reveals that they intersect along the row 0–166.1–664.4. Now the three axes 234.0, 166.1 and 175.5 are assumed to be the axes h_3, h_2, and h_1 and the plane A is imagined to stand on plane B along the common axis h_2 (*i.e.* the rows a_0 and b_0 coincide) at some angle. Then a plane A_1 is constructed along the first row (b_1) of plane B parallel to the plane A using Eq. (4)

$$Q(h_1 + h_2 + h_3) + Q(h_3) - Q(h_1 + h_3) - Q(h_2 + h_3) = Q(h_1 + h_2) - Q(h_1) - Q(h_2)$$

The positive direction of h_3 is above the plane of paper. The positive directions of h_1 and h_2 are indicated in the table. The value $Q(h_1+h_3)$ in this equation is assumed to be some value R and is the Q-value of the point lying above 175.5. $Q(h_1+h_2+h_3)$ lies above the point 326.6. Therefore using Eq. (4) a relationship between R and $Q(h_1+h_2+h_3)$ can be established.

$$Q(h_1 + h_2 + h_3) + 234.0 - R - 539.1 = 326.6 - 175.5 - 166.1$$

$$Q(h_1 + h_2 + h_3) = R + 290.1$$

The point $Q(h_1-h_3)$ which lies below 175.5 (*i.e.* below the plane of the paper) is equal to $819.0-R$ according to the equation

$$Q(h_1 - h_3) + R = 2(175.5 + 234.0)$$

Similarly the point $Q(h_1+h_2-h_3)$ below 326.6 gets the value $831.1-R$. The Q-values above and below the point 809.9 can be determined by a similar procedure. Thus the following values of the plane A_1 have been determined.

R	$R+290.1$	$R+912.4$
175.5	326.6	809.9
$819.0-R$	$831.1-R$	$1175.4-R$

Now with the help of the Eq. (3) the other values in the plane A_1 are calculated. To find the value of R it is enough if Q-values are calculated for two or three rows parallel to the row $R-175.5-(819.0-R)$ and for two rows parallel to the row (b_1). Thus the plane A_1 is constructed.

Plane A_1

430.9+2R (1147.7)	195.6+2R	292.5+2R (1005.5)	721.6+2R (1436.8)	1482.9+2R	(c_2)
R +416.4 (773.7)	R +42.1	R (356.0)	R +290.1 (643.9)	R +912.4	(c_1)
869.9	356.6	175.5	326.6	809.9	(b_1)
1791.4−R (1435.1)	1139.1−R	819.0−R (463.9)	831.1−R (474.0)	1175.4−R	($c_{\bar{1}}$)
	2389.6−2R	1930.5−2R (1217.9)	1803.6−2R (1092.4)	2008.9−2R	($c_{\bar{2}}$)

(Values in parentheses are the corresponding observed Q-values).

If the value of R is found, the other values can be calculated. The best method of obtaining the value of R is to proceed systematically as follows:

The lowest Q-values on the plane A_1 must be lying in the neighborhood of the central point 175.5. It can therefore be expected that many of the low unidentified Q-values in Table 1 can be from the first rows which run parallel to the middle row (b_1). Hence two tables of differences are prepared, one between the Q-values of the first upper row (c_1) and the other between those of the lower row ($c_{\bar{1}}$):

Differences in Q-values (c_1)

R+42.1	870.3	374.3	248.0
R+290.1	622.3	126.3	
R+416.4	496.0		
R+912.4			

Differences in Q-values ($c_{\bar{1}}$)

819.0−R	972.4	356.4	320.1	12.1
831.1−R	960.3	344.3	308.0	
1139.1−R	652.3	36.3		
1175.4−R	616.0			
1791.4−R				

The lowest five unidentified Q-values are tabulated and the differences listed.

Differences in lowest five unidentified Q-values

463.9	541.6	309.8	180.0	10.1
474.0	531.5	299.7	169.9	
643.9	361.6	129.8		
773.7	231.8			
1005.5				

On comparison of these three tabulations it is found that there are three possible combinations.

1. 129.8 (near to 126.3) relates $643.9(R+290.1)$ and $773.7(R+416.4)$ giving an average R-value 355.6.
2. 309.8 (near to 308.0) relates $463.9(831.1-R)$ and $773.7(1139.1-R)$ giving an average R-value 366.3.
3. 10.1 (near to 12.1) relates $463.9(819.0-R)$ and $474.0(831.1-R)$ giving an average R-value 355.7.

It is clear that observations (1) and (3) agree with each other and (2) is not compatible with either (1) or (3). If the other Q-values are calculated with $R=355.7$, many of them are found to agree with the observed values which are given in parentheses on plane A_1. Therefore the advantage of this method as compared with that of De Wolff is that there is no necessity of finding the third plane and later orienting it.

If a plane A_1 has been drawn through the first row of the plane B parallel to plane A, it is comparatively easy to draw a plane B_1 through the first row (a_1) of A parallel to B. There is no necessity to construct the plane B_1 if the value of R could be obtained from the first rows (c_1) or $(c_{\bar{1}})$ of plane A_1 and if the symmetry of the crystal could be unequivocally ascertained from the same. For the example under consideration plane B_1 is constructed to check whether it shows any symmetry because the plane A_1 does not give any useful information regarding the symmetry.

It must be expected that, as the two parallel planes A_1 and B_1 are drawn through the first rows of B and A respectively, they will intersect along the first row above the respective central lines (rows b_1 and a_1) and their first rows below the respective central lines will be centrosymmetrical. This will become clear if the planes A_1 and B_1 are compared.

Plane B_1

$2R+563.4$ (1277.0)	$2R+174.1$	$2R+117.0$	$2R+392.1$ (1103.3)	$2R+999.4$	(d_2)
$R+416.4$	$R+42.1$	R	$R+290.1$	$R+912.4$	(d_1)
620.4	261.1	234.0	539.1	1176.4	(a_1)
$1175.4-R$	$831.1-R$	$819.0-R$	$1139.1-R$	$1791.4-R$	$(d_{\bar{1}})$
$2081.4-2R$ (1367.1)	$1752.1-2R$	$1755.0-2R$	$2090.1-2R$		$(d_{\bar{2}})$

(Values in parentheses are corresponding observed Q-values).

It is seen that row (d_1) is identical to (c_1) because it is the row along which the two parallel planes intersect each other and the row ($d_{\bar{1}}$) is centrosymmetrical to the row ($c_{\bar{1}}$). Q-values of (d_2) and ($d_{\bar{2}}$) of plane B_1 can be calculated within minutes with Eq. (3) and we get three more Q-values which agree with those given in Table 1.

It may also be noted that the plane B_1 also gives a row (d_2) of lattice points with Q-values in terms of $2R+\ldots$ Therefore if the value of R could not be found from the first rows (c_1 or $c_{\bar{1}}$), then the second rows (c_2) and (d_2) can be considered, which give ten Q-values ranging between $2R+117$ and $2R+1482.9$. Omitting the two high Q-values, the remaining eight have accounted for five of the observed Q-values. Conversely, if the differences between these eight Q-values had been compared, the five observed Q-values could have been identified, thereby obtaining the value of R.

TABLE 1. OBSERVED Q-VALUES (DE WOLFF, 1957)

Line No.	I. $KBO_3.H_2O_2$	II. Progesterone	Line No.	I. $KBO_3.H_2O_2$	II. Progesterone
1	165.9	69.3	17	935.8	373.1
2	176.1	87.3	18	1005.5	384.8
3	261.2	93.5	19	1045.2	393.2
4	356.0	124.3	20	1092.4	402.6
5	463.9	150.1	21	1103.3	430.4
6	474.0	162.0	22	1147.7	486.1
7	539.0	179.5	23	1178.2	496.5
8	620.6	205.9	24	1217.9	500.3
9	643.9	217.2	25	1277.0	518.5
10	665.5	221.7	26	1312.1	530.2
11	701.9	237.4	27	1367.1	539.0
12	773.7	252.2	28	1380.6	552.9
13	823.4	274.5	29	1436.8	567.0
14	835.4	290.4	30	1479.9	591.4
15	869.5	329.8	31	1497.0	—
16	899.2	346.2			

A consideration of all Q-values of plane B_1 does not indicate the presence of a binary axis or a symmetry plane. (A discussion of symmetries that can be expected in such reciprocal lattice planes is given later.) Therefore the crystal is triclinic. A consideration of the Q-values of planes A_1 and B_1 indicates that the three assumed translations 234.0, 166.1 and 175.5 are the shortest and hence the conventional axes. After finding the true symmetry of the reciprocal lattice and ascertaining whether the assumed axes are the true axes, indexing can be attempted.

If we assume the translations 234.0, 166.1 and 175.5 to be the c^*, b^* and a^* axes, the planes A, B, A_1 and B_1 give all the reflections with indices $(0kl)$, $(hk0)$, $(1kl)$ and $(hk1)$ respectively. For $KBO_3 \cdot H_2O_2$, all the observed Q-values given in Table 1 could be indexed only with these four planes. But if there are still higher Q-values, they can be indexed by constructing planes parallel either to A_1 or B_1. While constructing the second plane A_2 parallel to A_1, the Q-values of the rows (d_2) and $(d_{\bar{2}})$ of B_1 can be used.

Example II. Progesterone.

Plane A

		538.5	346.0	290.5	372.0		(a_2)
889.0	484.5	217.0	86.5	93.0	236.5	517.0	(a_1)
			0.0	68.5	274.0	616.5	(a_0)
			86.5	217.0	484.5	889.0	

Plane B

		536.5	496.0	590.5			(b_2)
	372.0	179.5	124.0	205.5	424.0	779.5	(b_1)
			0	68.5	274.0	616.5	(b_0)

De Wolff noted systematic differences in the Q-values of the two rows (a_2) and (b_1) and suggested an elegant method to determine the reciprocal lattice. The same powder pattern is considered here to show that if such differences had not been observed for some reason or other this method could be used as an alternative. Furthermore this example shows how the derived parallel planes (A_1, B_1) exhibit the symmetry of the crystal.

The first parallel plane A_1 was constructed through the first row (b_1) of the plane B and is parallel to plane A. Four of the first seven unidentified Q-values were found to be from the first rows, three being from the lower row $(c_{\bar{1}})$ and one from the upper one (c_1). The R-value was found to be 161.5.

Plane A_1

868.0	(551.5)	(372.0)	(329.5)	(424.0)		(c_2)
533.5	279.0	(161.5)	181.0	337.5		(c_1)
372.0	179.5	124.0	205.5	424.0		(b_1)
(383.5)	(253.0)	259.5	(403.0)			$(c_{\bar{1}})$
(568.0)	(499.5)	(568.0)	773.5			$(c_{\bar{2}})$

Plane B_1

	589.0	(484.5)	(517.0)			(d_2)
533.5	279.0	(161.5)	181.0	337.5		(d_1)
484.5	217.0	86.5	93.0	236.5	517.0	(a_1)
	(403.0)	259.5	(253.0)	(383.5)		$(d_{\bar{1}})$

(Q-values in parentheses are observed values.)

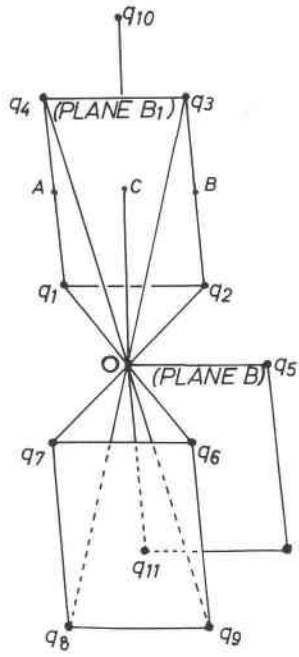

FIG. 1. Portion of the reconstructed reciprocal lattice of progesterone.

q_1, q_2, q_3, q_4, q_5 and q_{11} represent the lattice points with Q-values 86.5, 93.0, 253.0, 259.5, 68.5 and 124.0 respectively.

$q_6q_7q_8q_9$ represents a plane centrosymmetrical to plane B_1. A and B are the midpoints of the sides q_1q_4 and q_2q_3 and C is the midpoint of AB.

q_{10} represents a lattice point along the lattice row OC above the plane B_1.

A consideration of the plane A_1 shows the emergence of three binary axes, namely the lattice points having the Q-values 279.0, 337.5 and 499.5. All three points show pairs of equal Q-values on their sides, one (337.5) along the vertical row, the second (279.0) along the diagonal row and the third (499.5) along the horizontal row (c_2).

The plane B_1 seems to show apparently only two axes with values 279.0 and 337.5. But a consideration of the differences between the corresponding Q-values of the rows (a_1) and ($d_{\bar{1}}$) indicates the presence of the third axis as illustrated in Figure 1. In accordance with the observation

$$(86.5 - 93.0) = (253.0 - 259.5)$$

the lengths of the lines Oq_1, Oq_2, Oq_3 and Oq_4 in this figure must be so assumed that

$$(Oq_2)^2 - (Oq_1)^2 = (Oq_4)^2 - (Oq_3)^2$$

Rearranging,

$$(Oq_2)^2 + (Oq_3)^2 = (Oq_4)^2 + (Oq_1)^2$$

Considering the triangle Oq_1q_4, we get

$$(Oq_1)^2 + (Oq_4)^2 = 2[(OA)^2 + (Aq_1)^2]$$

Similarly

$$(Oq_2)^2 + (Oq_3)^2 = 2[(OB)^2 + (Bq_2)^2]$$

Therefore

$$(OA)^2 + (Aq_1)^2 = (OB)^2 + (Bq_2)^2$$

But $Aq_1 = Bq_2$; and hence

$$OA = OB$$

Therefore OAB is an isosceles triangle and OC is perpendicular to AB. Hence OC is perpendicular to Oq_5 of plane B (by construction). Therefore OC represents the direction of the third axis. As the lines q_8q_1, q_9q_2, q_6q_3 and q_7q_4 are parallel to OC, there should be a lattice point q_{10} along the axis OC at a distance Oq_{10} (equal to q_8q_1). But $q_8q_1 = 2OC$.

This means that the plane B_1 cuts the third axis OC exactly between some two lattice points. Now

$$\begin{aligned}(Oq_{10})^2 &= 4(OC)^2 = 4[(OB)^2 - (BC)^2] \\ &= 4\left[(OB)^2 - \frac{(AB)^2}{4}\right] \\ &= 4(OB)^2 - (AB)^2\end{aligned}$$

But

$$(OB)^2 = 1/2[(Oq_2)^2 + (Oq_3)^2] - (Bq_2)^2$$

Therefore

$$(Oq_{10})^2 = 2[(Oq_2)^2 + (Oq_3)^2] - (q_3q_2)^2 - (AB)^2$$

But by construction

$$AB = Oq_5 \quad \text{and} \quad q_3q_2 = Oq_{11}$$

Therefore

$$(Oq_{10})^2 = 2[(Oq_2)^2 + (Oq_3)^2] - (Oq_{11})^2 - (Oq_5)^2$$

Substituting the values

$$(Oq_2)^2 = 93,\ (Oq_3)^2 = 253.0,\ (Oq_5)^2 = 68.5$$

and

$$(Oq_{11})^2 = 124.0$$

We get

$$(Oq_{10})^2 = 2(93.0 + 253.0) - 68.5 - 124.0$$
$$= 499.5$$

Thus 499.5 is either the unit Q-value along the third axis or a higher (odd) order of it. In this case it happens to be the third Q-value ($9 \times 55.5 = 499.5$). This example shows that such systematic differences indicate the presence of an axis and that it is possible to calculate the length of the axis after finding the value of R.

Discussion

For triclinic $KBO_3 \cdot H_2O_2$ the assumed axes h_1, h_2 and h_3 happen to be the shortest axes and hence the reciprocal lattice is directly obtained. For the second example, both planes A_1 and B_1 indicate the presence of three binary axes and hence the reciprocal lattice can be easily constructed (Fig. 2). By drawing the planes parallel to the principal planes,

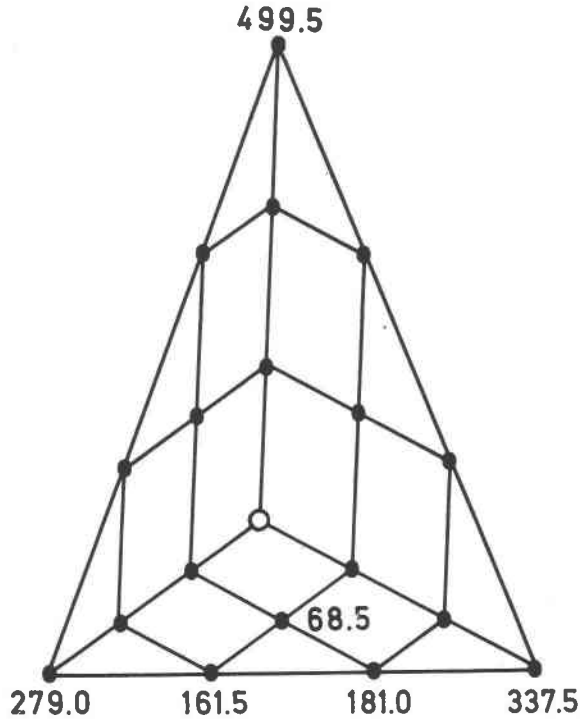

Fig. 2. Reconstruction of the reciprocal lattice if three binary axes are exhibited by the parallel planes (Example II. progesterone).

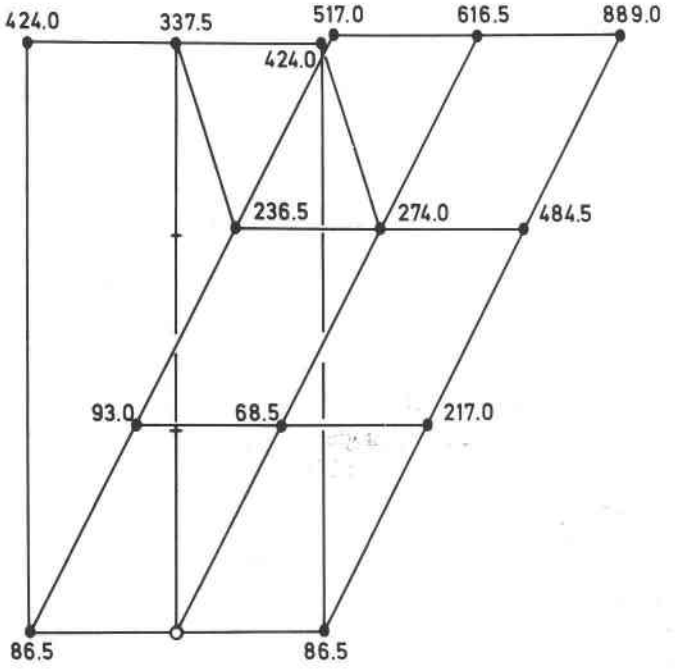

FIG. 3. Reconstruction of the reciprocal lattice, assuming only one binary axis has been observed on plane A_1 of progesterone.

it is found that the unit Q-values along the three axial directions are 55.5, 37.5 and 31.0. The following method is suggested to reconstruct the reciprocal lattice, when only one binary axis is observed (*e.g.* in the case of a monoclinic crystal).

Taking example II, it is assumed that only the binary axis (with Q-value 337.5) is found on plane A_1. The axis is at right angles to the vector with Q-value 86.5 (424.0−337.5)—a vector common to plane A and passing through the origin. Figure 3 shows an orthogonal array with 337.5 and 86.5 as axes and also a portion of the centrosymmetrical plane A intersecting the former along the common axis O-86.5. The lattice points of A_1 are connected to the corresponding points of A by vectors parallel to one with Q-value 124.0. Hence the pairs of points 337.5, 236.5 and 424.0, 274.0 are connected in Figure 3. Plane A is inclined to the binary axis. The rows 93.0–68.5 and 236.5–274.0 are lower than the row 337.5–424.0. As there should be a symmetry plane at the foot of the binary axis, planes drawn parallel to it along the rows 93.0–68.5 and 236.5–274.0 should cut the binary axis at two points below 337.5. Therefore the third Q-value 337.5 should be nine times the unit

Q-value 37.5. With these data the basal plane can be constructed. But the situations may not always be identical. It must be borne in mind that if a binary axis is located on one of the parallel planes, the following conditions exist to reconstruct the reciprocal lattice.

1. There is a vector lying at right angles to the axis and passing through the origin and the value of this vector can be obtained by subtracting the Q-value of the axis from one of the two adjacent equal Q-values.

2. This vector is also common to the centrosymmetrical plane parallel to which the plane, on which the binary axis is located, has been drawn.

A consideration of the three reciprocal lattices, orthorhombic, monoclinic and triclinic, reveals that the distribution of Q-values in the parallel planes (A_1 and B_1) will exhibit one of the following symmetries: (1) two mirror planes at right angles to each other, (2) a single mirror plane, (3) three binary axes or one binary axis, or (4) absence of all the above-mentioned symmetries.

Sometimes, the derived planes may show rows with pairs of equal Q-values (plane A_1, Example I) which are not symmetrically situated with reference to a central lattice point. Such rows show equal values only accidentally and are not due to a symmetry axis. Only when the point of intersection of the axis is observed as a lattice point, does it give rise to pairs of equal values on its sides. Plane B_1 (Example II) shows this phenomenon. It does not show the presence of the third axis because the point of intersection is not a lattice point. But it can be seen that the mid-points between the pairs of Q-values (86.5, 259.5) and (93.0, 253.0) are equidistant from the origin. (Fig. 1).

It may be noted that the cases (1) and (2) will be met with only if the centrosymmetrical plane, parallel to which the first plane is constructed, is an orthogonal array. In such cases the plane parallel to the orthogonal array can be drawn very easily on the basis of the following equations. Applying the Eq. (4) to the lattice points $Q(h_1+h_2+h_3)$ and $Q(h_1+h_2-h_3)$, the following Eq. (5) valid for all types of lattices can be derived.

$$\begin{aligned} &Q(h_1 + h_2 + h_3) - Q(h_1 + h_3) - Q(h_2 + h_3) \\ &\quad = Q(h_1 + h_2 - h_3) - Q(h_1 - h_3) - Q(h_2 - h_3) \end{aligned} \tag{5}$$

If it is assumed that the orthogonal plane A has the axes h_3 and h_2 and the second centrosymmetrical plane B the axes h_1 and h_2 (h_2 being the axis of intersection) and if a plane A_1 is drawn through the first row of B parallel to the orthogonal array A, the Eq. (5) becomes

$$\begin{aligned} &Q(h_1 + h_2 + h_3) - Q(h_1 + h_3) \\ &\quad = Q(h_1 + h_2) - Q(h_1) = Q(h_1 + h_2 - h_3) - Q(h_1 - h_3) \end{aligned} \tag{6}$$

If the Eq. (6) is generalized to all other lattice points of plane A_1, it would be found that the differences in Q-values of the horizontal rows are equal to those between the corresponding Q-values of the first row of plane B to which they are parallel. Hence it suffices to calculate the Q-values along the central vertical row in terms of R, assuming $Q(h_1+h_3)$ to be R. Also, the first row containing R is interchangeable with the lower first row containing $Q(h_1-h_3)$. The value R can therefore be assumed to lie on the obtuse-angle side. This assumption means that R is less than $Q(h_1-h_3)$. But caution must be exercised while finding the value of R. By assuming R to lie on the obtuse-angle side the range of R is set between O and $[Q(h_1)+Q(h_3)]$. But if R happens to be much smaller than $Q(h_1)$, then the lattice point $Q(h_1+2h_3)$ from the second upper row may also have a value between the above mentioned range. As both these rows show the same differences, the group of two or three Q-values found with the help of their differences may belong to the first row containing R or the second upper row. Sometimes the difference between R and $Q(h_1+2h_3)$ will solve the problem. Otherwise it is advisable to find a second group of Q-values having the expected differences. These two groups belong to two different rows in the first plane A_1, thus determining the value of R unequivocally. Similarly if none of the Q-values from the first upper row occurs in the list of observed Q-values because of systematic extinctions or other causes, it may be difficult to distinguish whether the identified row of Q-values belongs to the second upper row or the first lower row. Theoretically it may belong to still higher rows; but as the selected Q-values are low such a possibility is considerably less.

The problem may appear to become more difficult if the axis of intersection (h_2) of the two centrosymmetrical planes happens to be a binary axis, *i.e.* if both planes are orthogonal arrays. On the contrary, in such cases, there is no necessity to construct the parallel planes at all. Only the plane (h_1Oh_3) has to be constructed using h_1 and h_3 as axes and assuming $R[i.e.\ Q(h_1+h_3)]$ to lie on the obtuse-angle side. All other Q-values in this reflection plane will be in terms of R. As in the previous cases a table containing the mutual differences between the first three Q-values along the axis h_2 is prepared. From the list of unidentified (low) Q-values at least two groups of Q-values can be found with the expected differences. These two groups will give two Q-values which lie near the origin on the plane (h_1Oh_3). Using these two values the value of R can be determined unequivocally.

Before concluding it may be said that what De Wolff stated regarding the "accuracy of measurements" is also applicable to this method, because the success depends upon the correctness of the Q-values of the first two centrosymmetrical planes.

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