Acta Cryst. (1957). **10**, 590

On the Determination of Unit-Cell Dimensions from Powder Diffraction Patterns

By P. M. de Wolff

Technisch Physische Dienst T.N.O. en T.H., Delft, Netherlands

(*Received* 3 *December* 1956 *and in revised form* 4 *March* 1957)

The general approach proposed by Ito has been successfully used for the determination of the unit cells of many compounds. The analysis of three patterns is reconstructed to illustrate several conclusions:

Among the simplest algebraic relations between Q values, the one Ito mentions is the most powerful for finding clues leading to a zone. Some other relations are also useful, and a general relation yields information about the mutual orientation of three zones.

Determination of the Bravais type becomes automatic merely by arranging the Q's in a schematized reciprocal lattice. Any symmetry is immediately apparent because it causes the Q's to form sets of equal values for equivalent points. The analysis is simplified if this geometric point of view is taken consistently; indices need not be used explicitly until the lattice symmetry has been found.

The data, obtained by using standard equipment (114 mm. diameter focusing camera), were of sufficient quality to allow the determination of the unit cells even of steroids in a couple of hours, provided the line width did not appreciably exceed the instrumental width (0·05° θ at half height).

1. Introduction

The 'indexing problem' is essentially a puzzle: it cannot be stated in rigorous terms, or be solved in a general way by clear-cut methods, because of the unpredictable distribution of unobserved lines in a powder pattern. It would be quite an easy puzzle if errors of measurement did not exist. This added inconvenience, however, is enough to raise some doubt as to whether the determination of the unit cell of an arbitrary polycrystalline phase is possible in, say, an average of half a day's work or less.

From the literature on the subject one gets the impression that in the general opinion this question is subject to a very strong doubt indeed. With the exception of Ito (1949)*, all authors restrict themselves to special cases: unit cells without arbitrary angles (Hesse, 1948; Lipson, 1949; Stosick, 1949), or with unusual forms (Vand, 1948). On the other hand, Ito's general approach—which is from the triclinic rather than from the cubic side of the symmetry sequence—seems to be looked upon by many as a very elaborate one, to be used only when all other means have failed.

Experience gathered in the unit-cell determination of some 60 compounds of a wide range of symmetry and cell size has convinced the present author that there is no valid reason for such an opinion. The general approach is justified not only by the natural abundance of compounds with low symmetry, but equally by its usefulness in the determination of orthorhombic, and sometimes even of tetragonal and hexagonal unit cells (namely when they are not immediately recognized as such). It is not an unduly time-consuming procedure, especially if advantage is taken of simple reciprocal-lattice geometry.

Also it would perhaps have been better appreciated if Ito had laid less exclusive emphasis on the algebraic aspects.

A striking example is the final algebraic unit-cell reduction used by Ito to find the Bravais type. For that purpose the mere visual inspection of an array of numbers, which have to be calculated anyway, will be shown to be fully adequate (cf. § 3). Still, that does not make a large difference in the amount of work spent on analyzing a pattern. At any stage of the analysis, however, advantages can be gained by using geometry, as well as some algebraic relations not mentioned by Ito. Together with the one Ito did mention (our equation (4)), which is by far the most powerful key to the problem, all these features add up to the kind of technique which will now be described.

2. Algebraic relations

When the angles or distances measured in the powder diffraction pattern are expressed as a set of figures Q equal or proportional to $\sin^2\theta$, the problem is to fit to this set a theoretical quadratic form

$$Q(hkl) = a_{11}h^2+a_{22}k^2+a_{33}l^2+a_{12}hk+a_{23}kl+a_{13}hl \quad (1)$$

such that discrepancies and absences—not counting systematic extinctions—can be reconciled with the expected accuracy and sensitivity of the measuring device.

Obviously one has to find relations between the observed Q values, corresponding to theoretical relations derived by eliminating the a_{ij}'s from two or

---

* Cf. also Bunn (1955). The procedure described by Novăk (1954) is a graphical counterpart of Ito's general approach.

more of the equations (1). Such theoretical relations can be grouped as follows:

(*a*) Relations between reflexions of different orders from a common lattice plane:

$$n^2Q(m\mathbf{h}) = m^2Q(n\mathbf{h})\,, \qquad (2)$$

where $Q(\mathbf{h})$ refers to the reciprocal-lattice point with radius vector $\mathbf{h}$.

(*b*) Relations for a zone of lattice planes: The quadratic form (1) now can be transformed into

$$Q(h'k'0) = a'_{11}h'^2+a'_{12}h'k'+a'_{22}k'^2\,. \qquad (3)$$

In order to eliminate the three coefficients, four of these equations have to be used. The result will therefore be a linear equation in four Q's. There exists an infinite number of these; the most important one is Ito's equation:

$$Q(\mathbf{h}_1+\mathbf{h}_2)+Q(\mathbf{h}_1-\mathbf{h}_2) = 2\{Q(\mathbf{h}_1)+Q(\mathbf{h}_2)\}\,. \qquad (4)$$

Some others, however, are also valuable, especially

$$Q(\mathbf{h}_1+2\mathbf{h}_2)-Q(\mathbf{h}_1-2\mathbf{h}_2) = 2\{Q(\mathbf{h}_1+\mathbf{h}_2)-Q(\mathbf{h}_1-\mathbf{h}_2)\} \quad (5)$$

and

$$Q(\mathbf{h}_1+3\mathbf{h}_2)-Q(\mathbf{h}_1) = 3\{Q(\mathbf{h}_1+2\mathbf{h}_2)-Q(\mathbf{h}_1+\mathbf{h}_2)\}\,. \quad (6)$$

The relations (5) and (6) are special cases of the relation

$$Q(\mathbf{h}+x\mathbf{h}')-Q(\mathbf{h}-x\mathbf{h}') = x\{Q(\mathbf{h}+\mathbf{h}')-Q(\mathbf{h}-\mathbf{h}')\}$$

(for (5) $x = 2$; for (6) $x = 3$, $\mathbf{h} = \mathbf{h}_1+\frac{3}{2}\mathbf{h}_2$, $\mathbf{h}' = \frac{1}{2}\mathbf{h}_2$), which follows directly from the cosine rule, if one remembers that $Q(\mathbf{h})$ is proportional to $|\mathbf{h}|^2$.

The equations (5) and (6), apart from serving as a means to detect relations among the observed Q's, also make it possible to calculate by mental arithmetic any row for which Q's of three consecutive points are given, because the numbers involved are relatively small. This extrapolation permits a quick examination of each of the many zone trials which often have to be tested before a close fit is found.

(*c*) General relations: Seven equations of type (1) have to be used in order to eliminate the six coefficients. Of the resulting linear equations in 7 Q's, the following is the simplest:

$$\begin{aligned}Q(\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3)+Q(\mathbf{h}_3)-Q(\mathbf{h}_1+\mathbf{h}_3)-Q(\mathbf{h}_2+\mathbf{h}_3)\\ = Q(\mathbf{h}_1+\mathbf{h}_2)-Q(\mathbf{h}_1)-Q(\mathbf{h}_2)\,. \quad (7)\end{aligned}$$

This equation is easily proved by transforming $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{h}_3$ into (100), (010) and (001), and substituting equation (1). It is useful in the last stages of analysis as well as in the calculations needed for adjusting the constants of triclinic reciprocal lattices (cf. Example III of § 4).

3. Schematized lattices and their automatic reduction

Following Thewlis & Hutchinson (1955), we use the term 'reduction' in the sense of: 'bringing out the symmetry' and apply it to a lattice, so that confusion with unit-cell reduction can hardly occur.

In equations (2)–(7) we have expressly used a general notation, instead of putting $\mathbf{h}_1 = (100)$, $\mathbf{h}_2 = (010)$ etc., in order to stress the fact that there is no need to assign even provisional indices to these vectors. For instance, if we find observed values $Q_1, \ldots, Q_4$ satisfying (4):

$$Q_3+Q_4 = 2(Q_1+Q_2)\,,$$

we can place these Q's at lattice points corresponding to the vectorial relation expressed by (4) and proceed to calculate the Q values of neighbouring lattice points by using (2), (5) and (6), without even thinking of indices or of the constants a_{ij} in (1).

Now suppose a zone of the reciprocal lattice has been established, and suppose it contains two equal Q values $Q(\mathbf{h}_1) = Q(\mathbf{h}_2)$ (which means that $|\mathbf{h}_1| = |\mathbf{h}_2|$), no equalities occurring among lower Q values. Then the question arises whether lattice symmetry is the cause of this coincidence. If this is so, $\mathbf{h}_1\pm\mathbf{h}_2$ will be directions of symmetry in the reduced, orthogonal array. Referred to these axes, the points $\mathbf{h}_1$ and $\mathbf{h}_2$ can be shown to receive indices with a common absolute value, say, (h_r, h_r) and $(h_r, \bar{h}_r)$*.

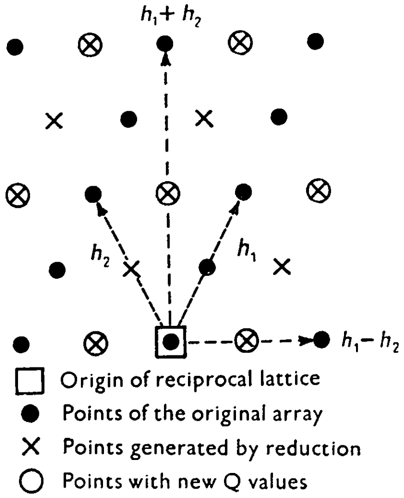

Fig. 1.

Consider the case shown in Fig. 1, where $h_r = 2$. It is seen that even assuming the reduced array to be centred, a number of new lattice points are generated by reduction. Some of these new points have Q values not necessarily equal to the original ones. If the supposed lattice symmetry is real, a reasonable number of these new Q values should occur among the observed data. Now it can be proved that in a given range on the average h_r-2+1/h_r new Q values are

---

* In terms of the original array, h_r is the number of primitive meshes contained in the parallelogram with edges $\mathbf{h}_1$ and $\mathbf{h}_2$ if $\frac{1}{2}(\mathbf{h}_1+\mathbf{h}_2)$ is not a lattice point, and half that number if it is.

generated for each original Q value. Thus, for a successful reduction h_r has to be small (mostly 1 or 2), or in other words: the smallest equal Q values should occur close to the origin.

When a few zones have been established, these must be combined to a three-dimensional lattice. In principle this can be done by using (7) (cf. Example III, § 4). However, reduction is often possible also in this stage of the analysis (cf. Examples I and II, § 4).

The final result will in any case be a reciprocal lattice schematized layer-wise, in which the lattice symmetry is clearly shown. By schematizing one of Ito's results in this way we shall prove that this is so even if one deliberately ignores symmetry up to the very last stage. The data are from Ito (1949), where the indices of a number of lines referred to a provisional triclinic unit cell are compared with the final indices. The scheme taken from the provisional indexing (expressed as $10^4/d^2$) is*:

$h=$	2	1	0	$\bar{1}$	$\bar{2}$	$\bar{3}$		
		5390	3332	2646	3332	5390	$k=2$	$l=0$
	4949	2205	833	833	2205	4949	1	
			0	686	2744		0	
			2447	1075	1075	2447	$k=1$	$l=1$
		2986	*928*	242	928	2986	0	
		2447	1075	1075	2447		$\bar{1}$	
			3712	1654	968	1654	$k=0$	$l=2$

The pairs of equal Q values for $l = 0$ show that the directions of symmetry in this zone are 0–2646 and 0–686. A similar symmetric configuration is observed in the layer $l = 1$, centered about 242. Therefore it is immediately apparent that the above scheme is a distortion of an orthorhombic lattice:

2646		3332		5390	$l=0$
	833		2205		
□		686		2744	
	1075		2447		$l=1$
242		928		2986	
968		1654		3712	$l=2$

Any further reduction is impossible because there are no longer any systematically equal sets of Q values in this octant.

This example, which is about the most intricate Ito could have produced, shows that even for final reduction Delaunay's method is rather far-fetched, however elegant and useful it may be for standardizing the unit cell of a triclinic lattice.

Only when the complete schematized lattice with its full symmetry has been obtained is there occasion to start the assignment of indices and to calculate the unit cell. Up to that point, what one is actually determining is not a unit cell, nor even a reciprocal unit cell, but a reciprocal lattice.

4. Examples

For three patterns a reconstruction of the analysis will now be given. The lists of $Q = 10^4 \sin^2\theta$ are given in Table 1.

I. *Desoxycholic acid*

The first two lines, taken as $\mathbf{h}_1$ and $\mathbf{h}_2$ in (4), satisfy approximately $2(Q_1+Q_2) = Q_2+Q_4$ (indices referring to line numbers from Table 1). The double appearance of Q_2 leads to the following reduced scheme (bold figures are corroborated by the data)

129·6	×	165·2	×	272·0
×	**41·3**	×	**112·5**	×
□	×	**35·6**	×	**142·4**

Some of the intermediate lattice points (crosses) are observed, but at this stage their number was not thought to be convincing.

Looking for clues among the remaining lines, combinations with either Q_1 or Q_2 in equation (4) were not immediately found. Instead, from $Q_{11}-Q_{10}=3(Q_8-Q_7)$ the following row was established, using (6):

239·6 151·3 145·6 222·5

the 'period' of which is calculated, using (4), as

$$\tfrac{1}{2}(151{\cdot}3+222{\cdot}5)-145{\cdot}6 = 41{\cdot}3 = Q_2\,.$$

Moreover, this row exceeds the first diagonal row from the above zone by 110·0. This points to an orthorhombic lattice in which, after completion, the remaining $Q_{\text{obs.}}$'s are found to fit neatly in the 'crosses position' of the above scheme; thus the lattice is not centered after all:

291·6	**300·5**	**327·2**	**371·7**	434·0				$l=0$
129·6	138·5	165·2	209·7	**272·0**	352·1	450·0		
32·4	**41·3**	**68·0**	**112·5**	**174·8**	**254·9**	352·8	468·5	
□	8·9	**35·6**	80·1	**142·4**	**222·5**	320·4	436·1	
401·6	**410·5**	**437·2**	**481·7**					$l=1$
239·6	**248·5**	**275·2**	309·7	**382·0**	**462·1**			
142·4	**151·3**	178·1	**222·5**	**284·8**	364·9	**462·8**		
110·0	118·9	**145·6**	190·1	252·4	**332·5**	430·4		
472·4	**481·3**							$l=2$
440·0	448·9	475·6						

In spite of the meagre coverage of the zone $l = 0$ by observed lines, this lattice is not a difficult one and could have been determined in many other ways. It is shown merely as an example of the use of equation (6).

II. *Progesterone*

Ito's equation (4) is successfully applied to the first two lines figuring as $\mathbf{h}_1$ and $\mathbf{h}_2$. The complete zone up to $Q = 600$, after some adjustment, is as follows:

---

* In this and the following schemes, the origin (sub-origin) of a zone (layer) of the reciprocal lattice is printed in italic type; the origin of a reduced zone as □.

Table 1*

Line No.	I		II		III	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1	35·6	35·7	68·6	69·3	166·3	165·9
2	41·3	41·4	86·6	87·3	175·5	176·1
3	68·0	68·6	93·0	93·5	261·1	261·2
4	112·5	112·5	124·1, 124·4	124·3	356·6, 356·3	356·0
5	118·9	119·5	150·0	150·1	462·7	463·9
6	142·4, 142·4	142·8	161·9	162·0	474·8	474·0
7	145·6	145·9	179·9	179·5	539·1	539·0
8	151·3	151·7	205·5	205·9	620·4	620·6
9	174·8	173·8	217·4	217·2	646·4	643·9
10	222·5, 222·5	222·3	222·0	221·7	664·4	665·5
11	239·6	240·0	236·6	237·4	702·0	701·9
12	248·5	248·8	253·0	252·2	772·7	773·7
13	254·9	254·2	274·4	274·5	824·1	823·4
14	272·0	271·7	290·6	290·4	838·1	835·4
15	275·2	274·5	329·9	329·8	869·9	869·5
16	284·8	285·3	346·4	346·2	898·1	899·2
17	300·5	300·8	372·9, 372·0	373·1	936·0	935·8
18	327·2	326·6	383·9	384·8	1005·1	1005·5
19	332·5	332·1	393·0	393·2	1044·4	1045·2
20	371·7	372·3	403·1	402·6	1091·0	1092·4
21	382·0	382·3	429·9	430·4	1104·7	1103·3
22	410·5	411·2	485·4	486·1	1143·5	1147·7
23	437·2	437·6	497·6, 496·4	496·5	1176·4	1178·2
24	462·1, 462·8	462·9	499·5, 501·9	500·3	1217·9	1217·9
25	481·7, 481·3	481·5	517·4	518·5	1276·0	1277·0
26	514·1	513·7	529·6	530·2	1313·2	1312·1
27	544·0	545·0	539·4	539·0	1368·8	1367·1
28	554·0, 552·5	552·9	553·1	552·9	1380·1	1380·6
29	—	—	568·1	567·0	1434·2, 1435·1	1436·8
30	—	—	590·6, 590·6	591·4	1479·2	1479·9
31	—	—	—	—	1494·6, 1494·9	1497·0

* I is desoxycholic acid; $a = 13{\cdot}53$, $b = 25{\cdot}8$, $c = 7{\cdot}34$ Å.
II is progesterone; $a = 12{\cdot}57$, $b = 13{\cdot}81$, $c = 10{\cdot}34$ Å.
III is $KBO_3.H_2O_2$; $a = 5{\cdot}86$, $b = 6{\cdot}39$, $c = 5{\cdot}43$ Å; $\alpha = 110{\cdot}55$, $\beta = 97{\cdot}11$, $\gamma = 89{\cdot}90°$.

$$\begin{array}{ccccccc}
 & \mathbf{538\tfrac{1}{2}} & \mathbf{346} & \mathbf{290\tfrac{1}{2}} & \mathbf{372} & \mathbf{590\tfrac{1}{2}} & (a_2) \\
\mathbf{484\tfrac{1}{2}} & \mathbf{217} & \mathbf{86\tfrac{1}{2}} & \mathbf{93} & \mathbf{236\tfrac{1}{2}} & \mathbf{517} & (a_1) \\
 & & \mathit{0} & \mathbf{68\tfrac{1}{2}} & \mathbf{274} & & (a_0)
\end{array}$$

Another zone is found upon combining the first remaining line (No. 4) with No. 1:

$$\begin{array}{cccccc}
 & \mathbf{590\tfrac{1}{2}} & \mathbf{496} & 536\tfrac{1}{2} & & (b_2) \\
424 & \mathbf{205\tfrac{1}{2}} & \mathbf{124} & \mathbf{179\tfrac{1}{2}} & \mathbf{372} & (b_1) \\
 & & \mathit{0} & \mathbf{68\tfrac{1}{2}} & \mathbf{274} & (b_0)
\end{array}$$

It is observed that there is a constant difference of $166\frac{1}{2}$ between the rows a_2 and b_1 (reading them in opposite directions: $166\frac{1}{2} = 290\frac{1}{2}-124 = 346-179\frac{1}{2}$, etc.). This means that the vector joining the reciprocal-lattice points $290\frac{1}{2}$ and 124, or any other of these pairs, is perpendicular to the rows of a and b. If this situation is not accidental, it might, for instance, be caused by the following symmetry in the array of rows parallel to a_0, projected end-on:

$$\begin{array}{ccc}
a_0+166\tfrac{1}{2} & & a_2 \\
 & a_1 & \\
\boxed{a_0} & & b_1
\end{array}$$

a centered monoclinic lattice. However, in this array the rows not belonging to a and b are not corroborated by the data. The following arrangement of the parallel rows a and b, projected end-on, is now envisaged:

$$\begin{array}{ccc}
a_0+222 & a_1+166\tfrac{1}{2} & a_2 \\
a_0+\ 55\tfrac{1}{2} & a_1 & b_1 \\
\boxed{a_0} & a_1-\ 55\tfrac{1}{2} & b_1-55\tfrac{1}{2}
\end{array}$$

based on $a_2-b_1 = 166\frac{1}{2} = (4-1)55\frac{1}{2}$.

The zone formed by the bottom row of this scheme is:

$$\begin{array}{cccccc}
316\tfrac{1}{2} & \mathbf{124} & \mathbf{68\tfrac{1}{2}} & 150 & 368\tfrac{1}{2} & (b_1-55\tfrac{1}{2}) \\
\mathbf{161\tfrac{1}{2}} & 31 & 37\tfrac{1}{2} & 181 & & (a_1-55\tfrac{1}{2}) \\
 & \mathit{0} & \mathbf{68\tfrac{1}{2}} & \mathbf{274} & & (a_0)
\end{array}$$

Though sparingly covered, it is seen to explain line No. 6 (162) which threatened to become an isolated stumbling-block. Furthermore, the number $68\frac{1}{2}$ is seen to occur twice, so that the zone can be reduced. The resulting orthorhombic lattice is easily calculated and is found to explain all data satisfactorily. After slight re-adjustment it becomes (starting with the last-mentioned zone which can now be called $l = 0$):

337·5	368·6	461·9			$l = 0$
150·0	181·1	**274·4**	**429·9**		
37·5	**68·6**	**161·9**	317·4	535·1	
□	31·1	**124·4**	279·9	**497·6**	
393·0	**424·1**	**517·4**			$l = 1$
205·5	**236·6**	**329·9**	**485·4**		
93·0	**124·1**	**217·4**	**372·9**	**590·6**	
55·5	**86·6**	**179·9**	336·4	**553·1**	
559·5	**590·6**				$l = 2$
372·0	**403·1**	496·4			
259·5	**290·6**	383·9	**539·4**		
222·0	**253·0**	346·4	**501·9**		
537·0	**568·1**				$l = 3$
499.5	**529·6**				

The remaining coincidences among these figures are far too few to meet the conditions for further reduction. It will be observed that the first-found zones a and b are both entirely oblique with respect to the final axes. This occurs frequently because of systematic extinctions and low multiplicity numbers for reflexions from a plane of symmetry.

III. $KBO_3.H_2O_2$

A somewhat diffuse pattern in which a number of lines stood out because of their perfect sharpness. These lines were easily brought together in the following zone:

	1044·4	**824·1**	**936·0**	**1380·1**			(k_2)
1313·2	**620·4**	**261·1**	234·0	**539·1**	1176·4		(k_1)
			0	**166·1**	**664·4**	**1494·9**	(k_0)

Combining each of the remaining broadened lines with Q_1 as $\mathbf{h}_1$ and $\mathbf{h}_2$ in equation (4), a close fit was obtained for Q_4. The resulting zone was extrapolated up to $R = 1500$:

1426·4	**898·1**	**702·0**	**838·1**	1306·4		(l_2)
869·9	**356·6**	**175·5**	326·6	809·9		(l_1)
		0	**166·1**	**664·4**	**1494·9**	(l_0)

No other zone containing Q_1 could be found. However, the following zone was established using the calculated $Q = 234·0$ from (k):

	1042·4	**702·0**	**829·6**	1425·2	(m_2)
1217·9	**462·7**	**175·5**	**356·3**	**1005·1**	(m_1)
		0	234·0	**936·0**	(m_0)

The problem is how to construct the layer parallel to zone (k) and containing l_1 and m_1. Usually their point of intersection is unambiguous, but in the present case we have two possibilities, $175\frac{1}{2}$ and $356\frac{1}{2}$. Each of these is examined in the following way: Suppose $175\frac{1}{2}$ is the intersection:

		(m_1)		
	Q_A	**356·3**		
(l_1)	**356·6**	**175·5**	**326·6**	(p)
		462·7		

Other points of the layer (p) such as Q_A are now determined by equation (7), taking 166·1 and 234·0 from zone (k) as $\mathbf{h}_1$ and $\mathbf{h}_2$. The right-hand side of this equation then amounts to 139·0. Taking for the Q's in the left-hand side the corners of the upper left mesh in (p), we find

$$Q_A = 356·3+(356·6-175·5)\pm 139·0\ ,$$

the sign depending on whether Q_A lies in the acute or in the obtuse angle between the rows (l_1) and (m_1). For each choice the complete layer can be calculated mesh by mesh, a procedure which is very quickly performed with the help of a simple adding machine. A satisfactory accordance with the observed data was obtained on the assumption that Q_A lies in the obtuse angle; the layer became:

	1143·5	908·2	**1005·1**	**1434·2**			(q_5)
1479·2	**772·7**	398·4	**356·3**	**646·4**	1268·7		(q_4)
	869·9	**356·6**	**175·5**	326·6	809·9		(q_3)
	1435·1	782·8	**462·7**	**474·8**	819·1	**1494·6**	(q_2)
			1217·9	**1091·0**	1296·3		(q_1)

when drawn in the correct orientation with respect to scheme (K), i.e. with translations 166·1 and 234·0 horizontal and vertical, respectively, and with the short diagonal 261·1 to the upper left.

The lattice is truly triclinic because equal Q values occur on a few rows only. The somewhat meagre coverage of layer (q) and of the next layer:

	1343·3	1425·2		
1276·0	886·7	829·6	**1104·7**	
1426·4	**898·1**	**702·0**	838·1	1306·4
	1377·5	1042·4	1039·5	**1368·8**

by observed lines is acceptable in view of the low multiplicity factor and the line broadening.

For triclinic and monoclinic lattices the first three zones to be found are sometimes collinear. In that case, too, equation (7) is used to fit them into a lattice. If, for instance, the third zone had been the one containing row (q_2) from the above layer, instead of (m), one would have sought for a difference between consecutive numbers of row (q_2) exceeding a given difference in row (l_1) $(= (q_3))$ by $\pm 139·0$—the value of the right-hand side of (7) with 166·1 and 234·0 from (k) for $\mathbf{h}_1$ and $\mathbf{h}_2$. Finding that, for example, $(326·6-175·5)-(474·8-462·7) = 139·0$, this would immediately permit us to draw the layer (q) in the correct orientation with respect to zone (k). Theoretically speaking, (l_1) and (q_2) might be two or more meshes apart, but this is not likely to happen if every subsequent zone is built up from the lowest remaining Q's.

5. General remarks

Whether the algebraic relations should be explored systematically or not is a matter of taste. For some patterns the author has made extensive tables of sums and differences, and has used these to apply equations (4), (5) and (6); however the result seldom seemed to justify the amount of work involved. In general it was found that application of these equations to the 5–10 lowest observed Q values only was more satisfactory since these are more accurate and less crowded than higher values. Ito's suggestion to substitute $\frac{1}{4}Q$, $\frac{1}{9}Q$, ... for Q if a relation does not hold, say, for a certain choice of $Q(\mathbf{h}_1)$ and $Q(\mathbf{h}_2)$ in equation (4), was rarely successful in the author's experience. The difficulty is that one does not know where to stop if every line must be suspected of being a harmonic.

If no satisfactory combination for $\mathbf{h}_1$ and $\mathbf{h}_2$ in (4) can be found among the first 5–10 lines, the chances are that the lattice is partly or wholly orthogonal since systematic extinctions are very often the cause of ill success with equation (4). Then a comparison of differences (e.g. by the graphical method of Lipson (1949)) will sometimes show that all the lines can be ordered in rows $Q = Q_i'+n^2Q''$ ($n = 0, 1, 2, \ldots$), after which the Q_i' values can be used to construct the basic zone perpendicular to $O-Q''$. The Q_i' themselves tend to be extinct or unobservable, so that differences within the rows will mostly be of the kind $(n_1^2-n_2^2)Q''$, $n_1 > n_2 > 1$. Though analogous to Lipson's statistical analysis of differences, this procedure is more powerful because it relates each individual difference relation to the corresponding geometrical relation, and because it is able to cope with monoclinic lattices too.

Many other characteristic situations not covered by the examples do happen more or less frequently—especially centred lattices. Enough has been said, however, to make clear how one can be prepared for and deal with such situations from a geometrical point of view.

No inordinate amount of experience, patience, and good luck is needed to make successful use of the present technique—provided the data are of sufficient quality. This brings us to the question raised before: Can 'indexing' be done in a reasonable time? In this connexion it may be of interest to state that the solution both of Examples I and II was found in 1–2 hr. The data came from visual measurement of a photograph made with Cu $K\alpha$ radiation in a 114 mm.-diameter focusing monochromator camera (de Wolff, 1948). The substances were well crystallized, since the line width did not appreciably exceed the instrumental value—about $0{\cdot}05°\ \theta$*. The measurements were accurate to within about $\pm 0{\cdot}01°\ \theta$. Of course the actual analysis was much less straightforward than its description in § 4, since no record was kept of many unsuccessful trials. Still, for such large unit cells, the time spent on these two compounds was somewhat less than usual. Example III, on the other hand, took actually something like 10 hr. to solve. As stated, this was a difficult case because of partial line broadening, even though the width of the broadened lines did not exceed $0{\cdot}15°\ \theta$.

It is difficult to say which of the consequences of line broadening is worse: the loss in accuracy, in resolving power or in peak-to-background ratio; anyhow, their combined effect is devastating for the 'indexability' of a pattern. Patterns with a line width of $0{\cdot}2°\ \theta$ or more for Cu $K\alpha$ can be regarded as almost hopeless, unless there is a reasonable chance that they may turn out to have higher symmetry than orthorhombic, or that the volume of the primitive unit cell is small, say not more than a few hundred cubic Ångström units.

Apart from this restriction, the author's experience proves that large unit cells up to 3000 Å^3 in volume —even with a triclinic lattice—do not offer special difficulties. Large size and low symmetry are infinitely less awkward than certain fortuitous circumstances, such as an unfortunate distribution of unobserved lines (culminating in sub-lattices!), or axial ratios approximating to the square root of simple fractions —truly harassing situations, but not insoluble and so rare that they should not discourage anyone. Our final answer to the question of feasibility is: With reasonably obvious exceptions, unit-cell determination from a powder pattern is feasible in a time short enough to justify its application—not only when single crystals are not available, but for some purposes even when they are.

---

* This refers to the width at half maximum intensity measured by a photometer. Doublets with much smaller separation—down to about $0{\cdot}02°\ \theta$—can be detected visually even if the components differ very much in strength.

References

BUNN, C. W. (1955). *X-ray Diffraction in Polycrystalline Materials*, chap. 14. London: Institute of Physics.

HESSE, R. (1948). *Acta Cryst.* **1**, 200.

ITO, T. (1949). *Nature, Lond.* **164**, 755.

ITO, T. (1950). *X-ray Studies on Polymorphism.* Tokyo: Maruzen.

LIPSON, H. (1949). *Acta Cryst.* **2**, 43.

NOVÁK, C. (1954). *Czech. J. Phys.* **4**, 496.

STOSICK, A. J. (1949). *Acta Cryst.* **2**, 271.

THEWLIS, J. W. & HUTCHINSON, T. S. (1953). *Acta Cryst.* **6**, 357.

VAND, V. (1948). *Acta Cryst.* **1**, 109, 290.

WOLFF, P. M. DE (1948). *Acta Cryst.* **1**, 207.