

Short Communications

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Detection of simultaneous zone relations among powder diffraction lines. By P. M. DE WOLFF,
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Let two given lines of a powder pattern (with $Q \equiv 10^4 \sin^2 \theta = Q', Q''$) correspond to reciprocal-lattice vectors \mathbf{h}' and \mathbf{h}'' . These vectors define a zone consisting of all vectors of the form $m\mathbf{h}' \pm n\mathbf{h}''$, where m and n are positive integers.

Suppose that the vector corresponding to the i_0 th observed line of the pattern belongs to this zone, with $m = m_0$ and $n = n_0$. Then if γ is the angle between \mathbf{h}' and \mathbf{h}'' , the cosine rule yields the equation

$$Q_{i_0} = m_0^2 Q' + n_0^2 Q'' \pm 2m_0 n_0 (Q' Q'')^{\frac{1}{2}} \cos \gamma \quad (1)$$

because Q is proportional to $|h|^2$. Hence

$$(Q_{i_0} - m_0^2 Q' - n_0^2 Q'') / m_0 n_0 = \pm 2(Q' Q'')^{\frac{1}{2}} \cos \gamma. \quad (2)$$

Therefore, if one calculates

$$|Q_i - m^2 Q' - n^2 Q''| / mn = R_{imn}$$

for all observed lines ($i = 1, 2, 3, \dots$) and for various integral values of m and n , the same number will always result when a line belonging to the zone of Q' and Q'' is combined with its own zonal coordinates m and n .

If now the values of R_{imn} are listed in progressive order, this concentration of equal numbers may be expected to stand out from the otherwise random distribution of numbers in the list.

As a test, the pattern of $\text{Na}_4\text{P}_2\text{O}_7$ and three indexed patterns of phosphates with low crystal symmetry have been subjected to the above procedure. The computation and computer programming was performed entirely by the 'Afdeling Bewerking Waarnemingsuitkomsten T.N.O.', The Hague, with a Bull 'Gamma' computer and punched-card machines.

The index field was limited to $m, n = 1, 2, 3, 4$ (16 pairs). For each pattern, each of the first two lines was taken as Q' and each of the first five as Q'' —yielding seven pairs in total because only pairs of different lines were taken.

For Q_i , the observed Q -values of the first 35 lines of each pattern were taken. The standard deviation from calculated angular values for the indexed patterns amounted to $0.007^\circ \theta$ (Cu $K\alpha$; focusing camera of the Guinier type (de Wolff, 1948); corundum admixed for calibration). The accuracy of the small Q' and Q'' -values was, whenever possible, improved by taking obvious higher orders into account. All patterns were rather dense, having between 20 and 40 lines with $d > 2.5 \text{ \AA}$.

The resulting lists of R_{imn} , ranging up to $2(Q' Q'')^{\frac{1}{2}}$ (cf. (2)) were then scrutinized for concentrations. Afterwards, a comparison with the 'true' R -values defined by (2) was made for the indexed patterns. In most of the

Table 1. Part of the list of R_{imn} for the first two lines of $\text{Na}_4\text{P}_2\text{O}_7$ ($Q' = 100.5$, $Q'' = 130.5$) with a 'true' concentration of fourteen R -values at 188*

$Q_i (10^4 \sin^2 \theta)$	$1.44 R_{imn}$	m	n
1290.1	179.09	4	3
1132.2	179.60	4	2
944.7	181.49	3	3
1119.8	181.84	4	2
816.2	182.47	2	3
1107.4	184.07	4	2
1420.0	184.80	3	1
1242.2	184.84	4	3
1446.0	185.58	3	4
916.8	185.95	3	3
1217.9	187.42	4	1
884.3	187.54	1	3
794.8	187.61	2	3
1087.0	187.74	4	2
1217.9	187.75	4	3
271.7	187.78	2	1
100.5	187.92	1	1
1446.0	187.92	2	2
1446.0	187.92	2	4
642.9	188.06	3	2
642.9	188.21	3	1
884.3	188.50	1	2
1420.0	188.70	3	4
794.8	188.86	2	1
1406.3	190.34	3	4
884.3	191.15	3	3
1420.0	192.60	2	4
1380.6	193.43	3	4
769.0	193.80	2	3
1406.3	195.07	2	4
605.9	196.94	3	2
846.3	197.23	3	3
1446.0	197.28	3	1
1132.2	198.04	4	3
1335.8	198.80	3	4
1119.8	199.52	4	3
1380.6	199.69	2	4
1020.0	199.80	4	2
1016.0	200.52	4	2

* The small concentration at 199 has rather improbable m, n values and is indeed a spurious one.

lists, only a single true concentration occurs because of the low multiplicity of the lines taken as Q' and Q'' .

The majority of the smaller observed concentrations turned out to be false, whereas many true concentrations of a few R 's had escaped detection. However, for each pattern one or two large true concentrations exist and these were invariably detected. It is perhaps significant that for each of the patterns one of these large concentrations occurred in the list for the first two lines figuring as Q' and Q'' . For the unindexed pattern, this concentration (see Table 1) proved to correspond to the $(h0l)$ zone of a hexagonal lattice, with $Q' = 100.5 = (101)$ and $Q'' = 130.5 = (002)$.

It was concluded that the most successful strategy of indexing with the present method is probably as follows:

- For Q' and Q'' take combinations of the first two or three lines. Combination of a line with itself is allowed and perhaps even advisable, since the corresponding orthogonal zone occurs rather frequently, while the R -list is shorter because the pairs (m, n) and (n, m) now give identical values. The range for m and n might be restricted to 1, 2, 3.
- From these lists the most obvious concentrations are selected either by visual inspection or by automatic sorting methods.
- If the zones thus found do not easily lead to the complete interpretation of the pattern, a judicious second choice of Q' , Q'' -pairs can be made for the detection of further zones.
- When two zones have been established, there remains only one unknown lattice parameter, namely the angle between them. This parameter can be found in the same way as the angle γ , by a simultaneous

detection method differing from the present one only in the number of dimensions involved.

The methods of Runge* (1917) and of Ito (1949) can be considered as special cases of the present one. Indeed the first is obtained by reducing the index field to a single point $m = n = 1$, the second by examining an extended index field point by point. These techniques, as well as the application of other relations (de Wolff (1957)), are less powerful than the present method for the following reason.

The density of R -values in the list of R_{imn} is, to a first approximation, proportional to the number N of points (m, n) in the index field. So is the size of a true concentration; but the size of large spurious concentrations increases merely with $N^{\frac{1}{2}}$ for a given interval in R and a given chance of occurrence. Hence the true concentrations become more conspicuous as N increases, the more so because the value of R_{imn} is in general more accurate for the higher values of m and n . The useful size of the index field is limited by the range of Q_i .

Further tests along the lines indicated above are in progress.

References

- ITO, T. (1949). *Nature, Lond.* **164**, 755.
 RUNGE, C. (1917). *Phys. Z.* **18**, 509.
 WOLFF, P. M. DE (1948). *Acta Cryst.* **1**, 207.
 WOLFF, P. M. DE (1957). *Acta Cryst.* **10**, 590.

* The author regrets having overlooked Runge's work when writing his 1957 paper. Several statements in the latter turn out to be 40 years old.

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The identification of sorbitol by X-ray diffraction. By T. R. LOMER,* *Physics Department, St. Mary's Hospital Medical School, London, W. 2*

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In a recent investigation conducted in the Physiology Department of this Medical School, Britton (1958) succeeded in isolating from the ram seminal vesicle a substance which, from chromatographic and enzymatic evidence, appeared to be sorbitol and thus confirmed a previous finding of Hers (1957). Britton also detected the same substance in foetal whale blood. It was decided to try to confirm the identification by X-ray analysis and accordingly the substance was converted to the hexa-acetate and recrystallized from a mixture of ethylene-dichloride and amyl acetate. A commercial sample of *d*-sorbitol (L. Light and Co.) was also converted to the hexa-acetate and similarly recrystallized. The resulting crystals, both from the biological and commercial sources were transparent platelets, elongated in one direction. The X-ray rotation photographs of all three samples were identical with each other and so confirmed the presence of sorbitol in ram seminal vesicle and foetal whale blood.

The crystal from the commercial source was rotated about its long axis and equi-inclination Weissenberg

photographs were taken of the first four layers of the reciprocal lattice. These showed the long axis to be the symmetry axis of a monoclinic unit cell of dimensions

$$a = 12.51 \pm 0.1, \quad b = 8.39 \pm 0.1, \quad c = 10.21 \pm 0.1 \text{ \AA}, \\ \beta = 95.7 \pm 0.2^\circ.$$

The density of the crystal was determined by flotation in an aqueous solution of zinc chloride and was found to be $1.30 \pm 0.05 \text{ g.cm.}^{-3}$. The density calculated by assuming two molecules per unit cell was $1.34 \pm 0.03 \text{ g.cm.}^{-3}$. The only systematic absences in the diffraction pattern were $(0k0)$ with k odd, so that from the diffraction data the possible space groups were $P2_1$ and $P2_1/m$. The latter space group, however, must be excluded since it requires four asymmetric units per unit cell, whereas in fact there are only two molecules per unit cell; these are known to lack centres and planes of symmetry since a solution of the hexa-acetate in chloroform is optically active.

References

- BRITTON, H. G. (1958). *Biochem. J.* In the Press.
 HERS, H. G. (1957). *Biochem. J.* **66**, 30P.

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