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Indexing Powder Photographs of Orthorhombic Crystals

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A method for attempting to index the powder photograph of an orthorhombic substance is described and is illustrated by its successful application to the indexing of recently published data for KNO_3.

I was interested to read the paper by Hesse (1948) on the interpretation of powder photographs. Several years ago I devised rather similar methods, which, for the lack of suitable data on which to test them, were not published, although they are to be described in a book, now in the press, on the interpretation of X-ray diffraction photographs, written by Dr W. A. Wooster, Dr N. F. M. Henry and myself.

The publication of the data for KNO_3, however, led me to try out my method again and since it proved completely successful I propose to describe it in full in the present article. The method is essentially the same as that described by Hesse but is, I think, rather neater.

1. General principles

The method is based on that described by Bradley & Taylor (1937), who made use of the relation

$$q_{hkl} = \sin^2\theta_{hkl} = h^2A + k^2B + l^2C,$$

where $A = \lambda^2/4a^2$, $B = \lambda^2/4b^2$, $C = \lambda^2/4c^2$. The problem is to find values of A, B and C that account for all the observed values of q with integral values of h, k and l; the method is to examine systematically the differences between the observed values of q, in order to detect relationships such as

$$q_{0kl} - q_{1kl} = A,$$
$$q_{0kl} - q_{2kl} = 4A, \; \ldots, \text{ etc.}$$

In addition, it is useful to form some idea of the order of magnitude to be expected for the quantities A, B and C, so that one should know for what sort of difference to look.

2. Order of magnitude of A, B and C

The quantities A, B and C depend upon the cell dimensions and are larger for smaller unit cells. The larger the unit cell the larger the number of lines on the powder photograph, and hence, by examining the number of lines that appear within a given range of q, it should be possible to decide on the order of magnitude of A, B and C. So many simplifying assumptions have to be introduced that it is not possible to attain any high accuracy, but this is not necessary.

Suppose that the number of lines on the powder photograph with values of q less than q_m is M. The number of points in reciprocal space satisfying this condition is approximately

$$\frac{4\pi}{3}(2q_m^{\frac{1}{2}})^3\frac{1}{V^*},$$

where V^* is the volume of the unit cell of the reciprocal lattice.

This, however, is not equal to the number of lines on the powder photograph for several reasons: in the orthorhombic system, the reciprocal points hkl, $\bar{h}kl$, $h\bar{k}l$, etc., all represent reflexions with the same value of q, and so give only one powder line; moreover, many reflexions will be absent because their structure amplitudes are very small, or because they are forbidden by space-groups conditions. Both these effects are difficult to assess quantitatively, but as a rough approximation we may allow the factor 8—the multiplicity factor for the general reflexion in the orthorhombic system—for the former, and the factor 2 for the latter. Thus the number of lines to be expected is approximately

$$\frac{2\pi}{3}\frac{q_m^{\frac{3}{2}}}{V^*}\sim M.$$

Now,

$$V^* = \lambda^3/abc$$
$$= 8\sqrt{ABC}.$$

If we assume that A, B and C are of the same order of magnitude, then

$$M \sim \frac{2\pi}{3}\frac{q_m^{\frac{3}{2}}}{8A^{\frac{3}{2}}}$$
$$\sim q_m^{\frac{3}{2}}/4A^{\frac{3}{2}},$$

or

$$A \sim q_m/4^{\frac{2}{3}}M^{\frac{2}{3}}$$
$$\sim 0{\cdot}4\,q_m/M^{\frac{2}{3}}.$$

For example, for KNO_3, 40 lines are observed with $q_m = 0{\cdot}67$. Therefore $A \sim 0{\cdot}023$.

3. The difference diagram

The differences mentioned in § 1 can be calculated and arranged in tabular form. A much simpler method, however, is as follows.

Mark on a strip of paper all the values of q that are observed, as, for example, those for KNO_3 given by Hesse and reproduced in Table 1.

Table 1. *Values of* $\sin^2\theta$ *for the first* 40 *lines of the powder photograph of* KNO_3 (Hesse, 1948)

$q_1 = 0{\cdot}0923$	$q_{11} = 0{\cdot}2264$	$q_{21} = 0{\cdot}3462$	$q_{31} = 0{\cdot}4663$
$q_2 = 0{\cdot}0943$	$q_{12} = 0{\cdot}2339$	$q_{22} = 0{\cdot}3481$	$q_{32} = 0{\cdot}4963$
$q_3 = 0{\cdot}1271$	$q_{13} = 0{\cdot}2411$	$q_{23} = 0{\cdot}3513$	$q_{33} = 0{\cdot}5239$
$q_4 = 0{\cdot}1392$	$q_{14} = 0{\cdot}2496$	$q_{24} = 0{\cdot}3689$	$q_{34} = 0{\cdot}5427$
$q_5 = 0{\cdot}1427$	$q_{15} = 0{\cdot}2678$	$q_{25} = 0{\cdot}3766$	$q_{35} = 0{\cdot}5551$
$q_6 = 0{\cdot}1720$	$q_{16} = 0{\cdot}2731$	$q_{26} = 0{\cdot}4177$	$q_{36} = 0{\cdot}5624$
$q_7 = 0{\cdot}1789$	$q_{17} = 0{\cdot}2818$	$q_{27} = 0{\cdot}4223$	$q_{37} = 0{\cdot}5693$
$q_8 = 0{\cdot}1853$	$q_{18} = 0{\cdot}3060$	$q_{28} = 0{\cdot}4287$	$q_{38} = 0{\cdot}5748$
$q_9 = 0{\cdot}1877$	$q_{19} = 0{\cdot}3122$	$q_{29} = 0{\cdot}4500$	$q_{39} = 0{\cdot}6151$
$q_{10} = 0{\cdot}1898$	$q_{20} = 0{\cdot}3263$	$q_{30} = 0{\cdot}4600$	$q_{40} = 0{\cdot}6699$

They should be plotted on an open scale—not less than 1 cm. to 0·01 in q—and should be shown as short lines equal in length to the experimental error; Hesse suggests $\pm 0{\cdot}0005$. The first half of these values should be transferred to one line of a sheet of graph paper, as shown in Fig. 1. The strip of paper is then moved to the next parallel line of the graph paper and the operation repeated with the value of q_1 at the zero ordinate, the plotting being continued up to approximately the same range as for the lower line. This process is continued with each value of q successively at the zero ordinate. Part of the complete diagram is shown in Fig. 2.

The complete diagram, which is too complicated to be reproduced here, gives all the differences between the q's up to about half the maximum value. In order to find which values occur most frequently it is only necessary to run a vertical line across the diagram and to see at what positions it intersects a number of values, as shown in Fig. 2.

4. The use of the results

The complete diagram shows the following frequently occurring values:

$0{\cdot}0325 \pm 0{\cdot}0005$ (6 times)	$0{\cdot}0953 \pm 0{\cdot}0005$ (6 times)
$0{\cdot}0446 \pm 0{\cdot}0005$ (6 times)	$0{\cdot}1474 \pm 0{\cdot}0005$ (6 times)
$0{\cdot}0623 \pm 0{\cdot}0005$ (6 times)	$0{\cdot}1787 \pm 0{\cdot}0005$ (8 times)
$0{\cdot}0780 \pm 0{\cdot}0005$ (7 times)	

The last value is particularly important; it is almost exactly four times 0·0446, and the differences are often associated with the same line. For example,

$$q_4 - q_2 = 0{\cdot}0449 \quad \text{and} \quad q_{16} - q_2 = 0{\cdot}1788.$$

These facts suggest that line 2 is of the type $0kl$, line 4 of the type $1kl$, and line 16 of the type $2kl$, where k and l are the same throughout. This reasoning applies to four other sets of lines in the table, and since $q_7 = 0{\cdot}1789$, suggesting that line 7 is 200, it seems extremely likely that 0·0446 is one of the constants we are seeking. We may call it A.

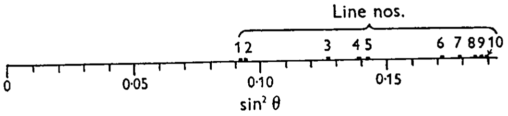

Fig. 1. Values of $\sin^2\theta$ from Table 1.

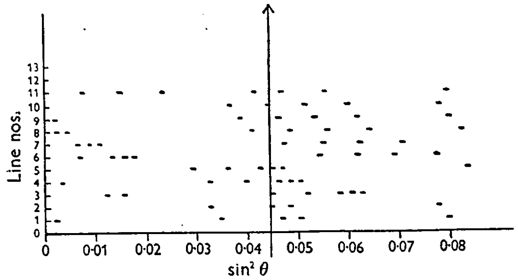

Fig. 2. Difference diagram. (The scale is twice that of Fig. 1.) The absence of points on the lowest line is due to the fact that the lowest value of $\sin^2\theta$ is outside the range of the figure.

Unfortunately, B and C do not emerge so clearly, and a process of trial and error has to be used to find them. Since the value of A is greater than 0·023, deduced in § 2, it is probable that the other values are smaller than this. We may therefore guess that some of the differences noted above are four times the required constants. The value 0·0325 is not likely to be so, and therefore we may try the following values:

$$0{\cdot}0446,\ 0{\cdot}0325,\ 0{\cdot}0156 \quad \text{and} \quad 0{\cdot}0195.$$

The value 0·0953 is about three times 0·0325, and so may represent the difference between say q_{h1l} and q_{h2l}. The value 0·1474 is rather large, but if no success is obtained with the values so far suggested, one-quarter or one-ninth of it may be tried. In general, however, it is better to try the simpler possibilities fully to begin with, rather than to make sure that all possibilities are considered.

It is necessary to see now if any three of these values can account for the lowest values of q. Consider, for example, the first eight lines. Make a table (Table 2) showing all values of the four constants multiplied by the squares of the natural numbers up to the highest value of q.

Table 2. *Possible values of h^2A, k^2B and l^2C*

Index	h^2A, k^2B or l^2C			
1	0·0446	0·0325	0·0156	0·0195
2	0·1784	0·1300	0·0624	0·0780
3	—	—	0·1404	0·1755

Then see if the values in Table 1 can be obtained by adding together not more than three values from this table. For example

$$q_1 = 0\cdot0923 \sim 0\cdot0446 + 0\cdot0325 + 0\cdot0156,$$

or $$q_1 = 0\cdot0923 \sim 0\cdot0156 + 0\cdot0780,$$

and $$q_2 = 0\cdot0943 \sim 0\cdot0325 + 0\cdot0624.$$

We find that, as 0·0446 is accepted as correct, if we choose the second solution for q_1, together with the solution for q_2, we have made use of all the four columns in Table 2. Therefore we choose the first solution and accept the first three columns as the correct ones for h^2A, k^2B and l^2C.

Attempts to fit these values to the first eight values of q are, however, not satisfactory, as shown in Table 3; the values shown by asterisks—the nearest approximations—are too high by about 0·0028. These values, however, all contain the quantity 0·1300, and if this were reduced to 0·1272 the agreement would be extremely good. Thus we try $A = 0\cdot0446$, $B = 0\cdot0317$, $C = 0\cdot0156$. On this basis we find it possible to index all the lines, the results for the first ten lines being given in Table 4.

Table 3. *Observed values of $\sin^2\theta$ compared with the nearest values obtainable from Table 2*

$q_1 = 0\cdot0923 \sim 0\cdot0446 + 0\cdot0325 + 0\cdot0156 = 0\cdot0927$
$q_2 = 0\cdot0943 \sim 0\cdot0325 + 0\cdot0624 = 0\cdot0949$
$q_3 = 0\cdot1271 \sim 0\cdot1300^*$
$q_4 = 0\cdot1392 \sim 0\cdot0446 + 0\cdot0325 + 0\cdot0624 = 0\cdot1395$
$q_5 = 0\cdot1427 \sim 0\cdot1300 + 0\cdot0156 = 0\cdot1456^*$
$q_6 = 0\cdot1720 \sim 0\cdot0446 + 0\cdot1300 = 0\cdot1746^*$
$q_7 = 0\cdot1789 \sim 0\cdot1784$
$q_8 = 0\cdot1853 \sim 0\cdot0446 + 0\cdot1404 = 0\cdot1850$

Table 4. *Final indexing of the first ten lines*

Line no.	q_1	hkl	$\sin^2\theta$ (calc.)
1	0·0923	111	0·0921
2	0·0943	012	0·0941
3	0·1271	020	0·1272
4	0·1392	112	0·1388
5	0·1427	021	0·1428
6	0·1720	120	0·1719
7	0·1789	200	0·1789
8	0·1853	103	0·1849
9	0·1877	121	0·1875
10	0·1898	022	0·1895

5. General remarks

It will be noted that there is still a great deal left to individual initiative in using the method, and the most that can be claimed for it, as for that described by Hesse, is that it takes the process of systematization rather further than those that have hitherto been described, for example, by Jacob & Warren (1937). There is still also a great deal of chance involved, as can now be seen in the derivation of the constant B; this was originally taken as 0·0325, a value suggested chiefly by the fact that $q_3 - q_2$ and $q_6 - q_4$ are both 0·0328. It is seen now that this is pure chance, as both these differences are really equal to $(3B - 4C)$. It is, therefore, interesting to see that chance can be a help as well as a hindrance. Nevertheless, one cannot rely on this, but the fact that at least one constant, A, was readily derived suggests that the problem would have been solved, although at the expense of a great deal more trial and error, if this chance had not occurred.

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