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A General Method of Indexing Photographs of Low-Symmetry Crystals

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Starting from Vand's 'third graphical method', a general method has been developed for indexing powder photographs of low-symmetry crystals. If the crystal has at least monoclinic symmetry, after the identification of one edge of the conventional unit cell the indexing may be accomplished without trial, and there is no need for further reduction. Therefore the method is most advantageous in the monoclinic system, but it can also be used in other systems, where a later reduction may be required. As an application of this method, the indexing of the powder photograph of $Na_2S_2O_3$ is given.

Introduction

A general method for indexing powder photographs of low-symmetry substances has been described by T. Ito (1949). This method is not altogether satisfactory, the greatest difficulty being caused by missing reflexions on the powder photographs, and it may happen that a great proportion of the lowest-index reflexions are just among these unobserved. (Systematic absences for centred lattices are not considered missing.) This leads to the fact that there are some points in the reciprocal lattice to which no observable reflexions belong. Due to this lack of reflexions some lattice points seem to be missing, and the lattice criterion is not strictly fulfilled. In particular, if some points are missing from the immediate vicinity of the origin then the unit cell based on the first three reflexions is not necessarily primitive and does not correctly describe the reciprocal lattice (Fig. 1). This,

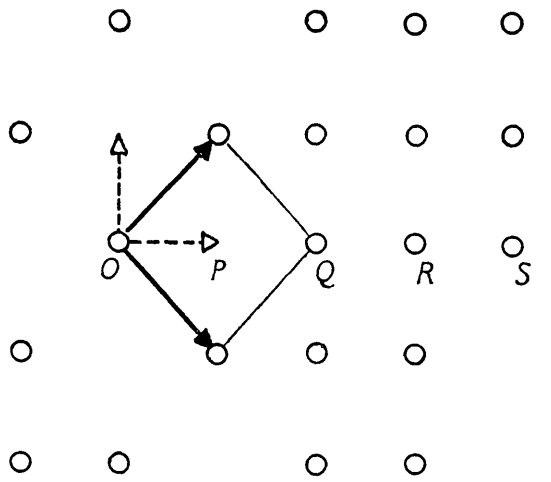

Fig. 1. A two-dimensional example in order to show that, due to the missing reflexions, the unit cell based on the first two lines is not necessarily primitive.

of course, does not mean that in such cases the indexing by the Ito method is impossible.

Another disadvantage of Ito's method is its essentially tentative character, and again missing reflexions often make it difficult to find symmetrical line pairs.

The difficulties mentioned above are brought about by the necessity of fixing two edges of the unit cell initially. Vand (1948*a*) published several methods for indexing powder photographs of long-spacing compounds; in these methods the 'long-spacing' has been used for the reliable determination of only one edge of the unit cell, to be denoted by *c*. Edge *c* having been determined, we may then begin the problem of finding the other two edges. In the present paper, it is shown that the same method can be used also for substances which have no long spacing. Based on the spacing data at our disposal, at least one point of type 001 can always be selected from the lattice points near the origin even if it is eventually found to be missing. (For a non-primitive lattice this of course refers to a primitive unit cell with the shortest edges.)

Suppose for instance that no observable line belongs to point P (Fig. 1), but those lines which belong to the points Q and R or R and S occur among the reflexions observed. Then

$$\tfrac{3}{2}d_Q^* = d_R^*, \quad \tfrac{4}{3}d_R^* = d_S^* .$$

Thus, if we multiply the measured values successively by $\frac{3}{2}, \frac{4}{2}, \frac{4}{3}, \ldots$ and compare with the original values, we can find coincident values in both sets, from which the lines of type 002, 003, 004 can readily be selected and $d_p^* = d_{001}^*$ may be computed.

This reconstruction of the missing points is not absolutely necessary, for it leads only to a unit cell which is nearer to the conventional one; although this undoubtedly makes the indexing easy, nevertheless the problem can still be solved by assigning the indices 001 to the first line appearing.

Thus Vand's 'third graphical method' may be used as a basis of a general method. But first it is essential to see clearly the geometrical interpretation of the mathematical formulae.

Description of the method

We know that

$$d^{*2}_{hkl} = h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2hka^*b^*\cos\gamma^* +2klb^*c^*\cos\alpha^*+2hla^*c^*\cos\beta^*, \quad (1)$$

where the symbols have the usual meaning. Introducing the expressions

$$p = \frac{1}{c^*}(2ha^*\cos\beta^*+2kb^*\cos\alpha^*), \quad (2)$$

$$q = \frac{1}{c^{*2}}(h^2a^{*2}+k^2b^{*2}+2hka^*b^*\cos\gamma^*) \quad (3)$$

(1) can be reduced to the following form:

$$(d^*_{hkl}/c^*)^2-l^2 = pl+q\,. \quad (4)$$

If now, after assigning $d^*_{001} = c^*$, we draw the values $(d^*/c^*)^2-l^2$ as a function of l; that is we assign a set of points to each reflexion so that the abscissae of the different points should be equal to $l = 0, \pm1, \pm2, \ldots$ and the ordinates of the same $(d^*/c^*)^2-l^2$. Then according to equation (4) all the points belonging to identical h and k but to different l lie on the same straight line. The slope of this line is p and it crosses the vertical axis at height q (p and q are independent of l.)

This mathematical transformation means geometrically that by fixing the value of c^* we choose a direction and thence a point-row in the three-dimensional reciprocal lattice (Fig. 2(a)). We consider the whole space-lattice constructed from such parallel point-rows. Along each point row h and k are constant; consequently in the above drawing different straight lines belong to each such point-row (Fig. 2(a) and (b)). The distance between the origin of the lattice and the point of the index $l = 0$ is equal $c^*\sqrt{q}$, and if we denote by φ the angle between the vectors [001] and [hk0], then $\cos\varphi = p/2\sqrt{q}$. If $\varphi = 90°$, the line is horizontal.

For the application of this method it is important to note that, apart from the symmetrically identical lines (one of such a pair is marked by the dotted line in Fig. 2(b)), many different straight lines belong to each point-row. For example, if we assign the index $l = 0$ to the different points of a point-row (for example the A, B, C, D row in Fig. 2(a) and (b)) we obtain different straight lines. Among these lines we should select the line with the smallest p and q.

Based on the above facts the indexing process is as follows. From the measured d_i^{*2} values (i represents a consecutive index) we try to choose d^{*2}_{001}. If d_1^{*2} is not too large we may suppose that

$$d_1^* = d^*_{001} = c^*, \quad (5)$$

and, if this eventually does not correspond to the conventional unit cell, the indexing can be accomplished with a necessary subsequent reduction (Delaunay, 1933). But if d_1^* is too large and therefore

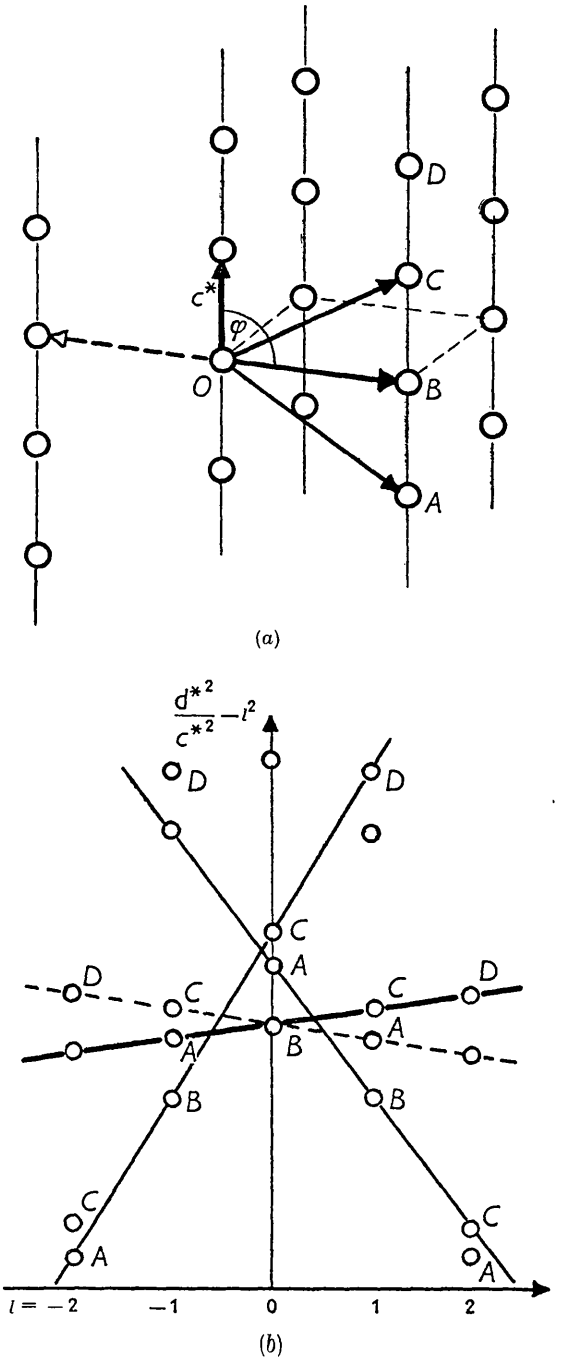

Fig. 2. The geometrical interpretation of equation (4). (a) The representation of the space lattice by sets of point-rows. $\overline{OB} = c^*\sqrt{q_B}$, $\cos\varphi = p_B/2\sqrt{q_B}$. ($b$) The different lines which can be assigned to the point-row A, B, C, D of (a).

equation (5) is probably not valid, we search—by means of the method mentioned in the introduction—for a missing line to which the index 001 will be assigned.

After this we draw the $(d_i^*/c^*)^2-l^2$ values as a function of l and try to connect some points with

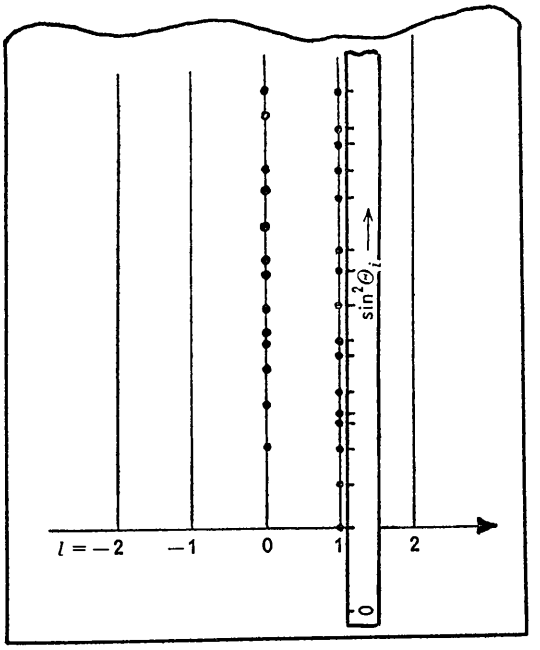

Fig. 3. The construction of the graph.

straight lines on this graph. At this stage we may restrict ourselves to the lines containing a point on the column $l = 0$. This simplification is justified for, if we know only one straight line of each point row, we can construct the others from it (Fig. 2(*b*)). If a line does not contain a point on the column $l = 0$ it means that the index $l = 0$ belongs to a missing reflexion. Having thus obtained several lines the indices h and k can be determined from p and q.

The construction of the graph may be simplified if we plot $\sin^2\theta_i - l^2 \sin^2\theta_{001}$ instead of $(d_i^*/c^*)^2 - l$. We plot the values of $\sin^2\theta_i$ on a strip of paper (on a scale such that 0,0005 should be greater than 1 mm.) and transfer these to the lines $l = 0, \pm 1, \pm 2, \ldots$, with the strip zero displaced in accordance with $l^2 \sin^2\theta_{001}$ (Fig. 3).

Example

A powder photograph has been taken of $Na_2S_2O_3$, dehydrated over P_2O_5, in a camera of diameter

Table 1. *The powder data of* $Na_2S_2O_3$

No.	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	*hkl*
1	0·00830	0·00830	001
2	0·01716	0·01728	011
3	0·02354	0·02356	110
4	0·02910	0·02903	$11\bar{1}$
5	0·03316	0·03320	002
6	0·03476	0·03473	111
7	0·03595	0·03592	020
8	0·04394	0·04422	021
9	0·05060	0·05052	120
10	0·05602	0·05597	$12\bar{1}$
11	0·05840	0·05840	200
12	0·06244	0·06280	112
13	0·06910	0·06912	022

Table 1 (*cont.*)

No.	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	*hkl*
14	0·07805	0·07802	$12\bar{2}$
15	0·08126	0·08138	211
16	0·08962	0·08942	122
		0·08973	$11\bar{3}$
17	0·09406	0·09432	220
18	0·09729	0·09692	$22\bar{1}$
19	0·10058	0·10087	$13\bar{1}$
20	0·1029	0·1030	202
21	0·1065	0·1066	131
22	0·1128	0·1120	212
23	0·1171	0·1167	$12\bar{3}$
		0·1179	$22\bar{2}$
24	0·1226	0·1229	$13\bar{2}$
25	0·1260	0·1250	$21\bar{3}$
26	0·1336	0·1338	123
27	0·1390	0·1389	222
		0·1392	230
28	0·1417	0·1418	014
		0·1418	$23\bar{1}$
29	0·1460	0·1450	$11\bar{4}$
30	0·1516	0·1520	041
31	0·1555	0·1555	033
32	0·1612	0·1616	$13\bar{3}$
33	0·1674	0·1673	320
		0·1671	$32\bar{1}$
		0·1678	114
34	0·1724	0·1719	$12\bar{4}$
35	0·1842	0·1838	232
		0·1842	321
		0·1845	303
36	0·1902	0·1907	312
37	0·1961	0·1968	$23\bar{3}$
38	0·2120	0·2122	330
		0·2120	$33\bar{1}$
39	0·2173	0·2176	322
		0·2168	$13\bar{4}$
		0·2168	$11\bar{5}$
40	0·2232	0·2230	214
41	0·2304	0·2310	233
42	0·2398	0·2391	150
		0·2396	134
43	0·2448	0·2445	$15\bar{1}$
		0·2453	$11\bar{5}$
44	0·2490	0·2492	$23\bar{4}$
45	0·2539	0·2533	$40\bar{1}$
46	0·2593	0·2597	$24\bar{3}$
47	0·2659	0·2659	$32\bar{4}$
48	0·2738	0·2741	$40\bar{3}$
		0·2733	$22\bar{5}$
49	0·2789	0·2780	152
50	0·2883	0·2883	035
51	0·2932	0·2939	243
52	0·3022	0·3025	144
53	0·3053	0·3052	$15\bar{3}$
		0·3053	$11\bar{6}$
		0·3057	$31\bar{5}$
54	0·3106	0·3100	$42\bar{3}$
		0·3108	$33\bar{4}$
55	0·3243	0·3248	$43\bar{2}$
56	0·3337	0·3341	431
		0·3343	324
57	0·3403	0·3405	$25\bar{3}$
58	0·3540	0·3549	$34\bar{4}$
59	0·3589	0·3589	$22\bar{6}$
		0·3590	$50\bar{1}$
60	0·3725	0·3720	351
61	0·3788	0·3784	423
		0·3787	$50\bar{2}$
		0·3787	$44\bar{1}$
		0·3792	334

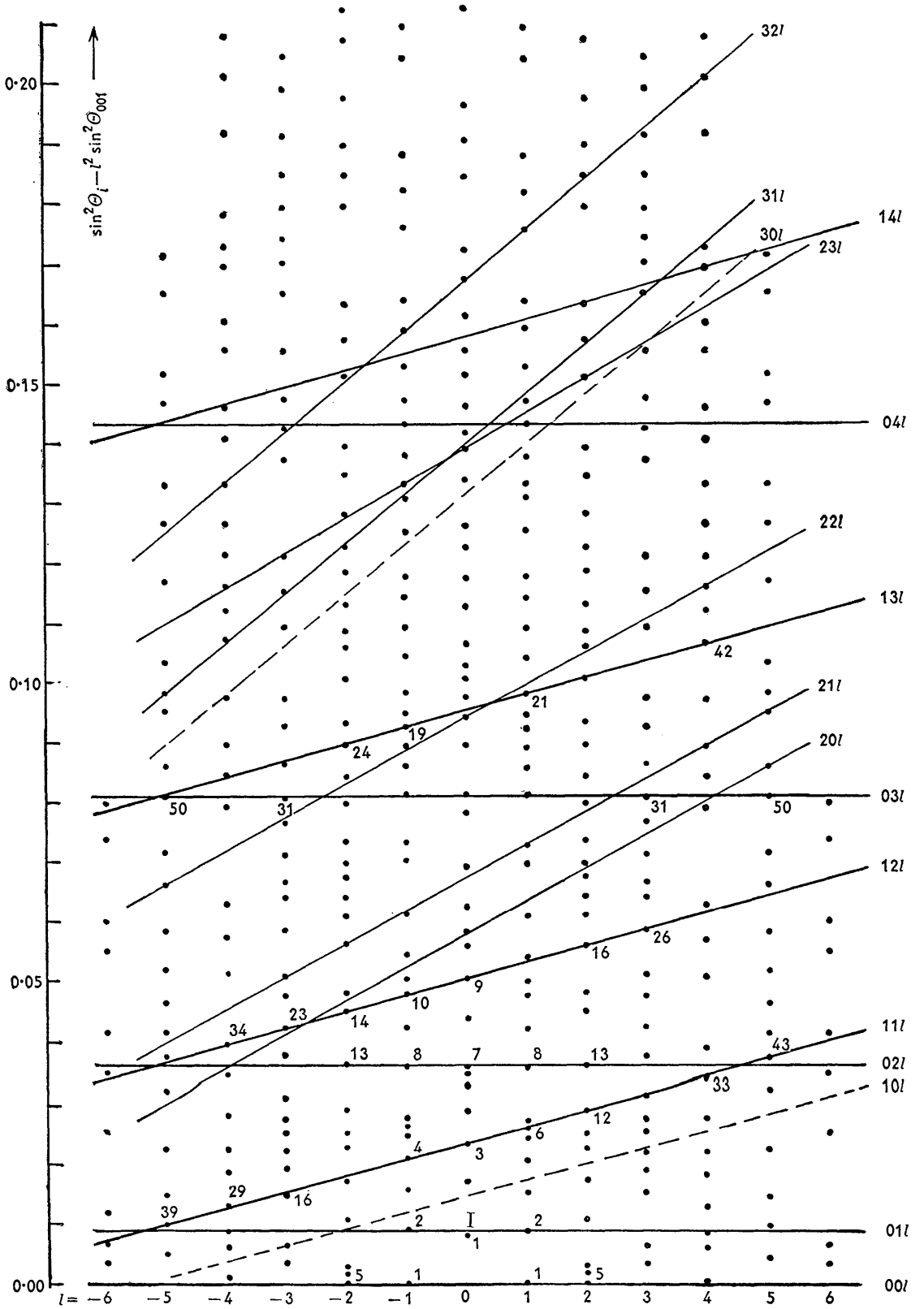

Fig. 4. The graph of the powder pattern of $Na_2S_2O_3$.

114,6 mm. with Cu $K\alpha$ radiation. The diameter of the specimen was 0,3 mm. The values of $\sin^2\theta_i$ are given in the second column of Table 1. The line $d = 4{\cdot}13$Å was very broad in the powder photograph, probably because it was composed of several unresolved lines; a special photograph was therefore taken by the Bragg–Brentano focusing method in this region and the line was found to have three components (lines 5, 6 and 7).

The first line corresponds to a spacing $d_1 = 8{\cdot}56$ Å. We have looked for a line with a greater spacing but none was found and therefore we have supposed that

$$\sin^2\theta_{001} = \sin^2\theta_1 = 0{\cdot}00830\,.$$

In Fig. 4 the values of $\sin^2\theta_i - l^2\sin^2\theta_{001}$ are shown plotted against l. For the sake of easier inspection consecutive indices are allotted only to those points which lie along the important straight lines containing a great number of points. In the figure three such straight lines are found.

A horizontal line may be drawn across the points 13, 8, 7, 8, 13. It means that $p_7 = 0$ (for the sake of simplicity the different lines are denoted by the index belonging to its point on $l = 0$). This condition can be fulfilled in virtue of equation (2) only if $h = 0$ and $\alpha^* = 90°$ or $k = 0$ and $\beta^* = 90°$. Let us suppose therefore that the line going through point 7 corresponds to $h = 0$ and $\alpha^* = 90°$; that is the unit cell is at least monoclinic. As $d_7 = 4{\cdot}06$ Å, it is not probable that $k = 1$ ($d_7 \neq d_{010}$). Let us suppose that $k = 2$ and we may see at once that our supposition was right, for the distance from the origin of the horizontal line crossing the points 2 is a quarter of q_7; consequently the indices $h = 0$, $k = 1$ belong to this straight line. The crossing point of this line and the $l = 0$ axis is denoted by I. This point should belong to the missing 010 reflexion. In the same way, the line with indices $h = 0$, $k = 3$ may be recognized.

Besides the above line the lines crossing the points 39, 29, 16, 4, 3, 6, 12, 33, 43 and 23, 14, 10, 9, 26 are also clearly recognizable. It is striking that

$$p_9 = p_3 \neq 0 \qquad (6)$$

and

$$q_9 - q_3 = q_7 - q_I\,. \qquad (7)$$

Equation (6) means that

$$h_9a^*\cos\beta^* + k_9b^*\cos\alpha^* = h_3a^*\cos\beta^* + k_3b^*\cos\alpha^*.$$

It is evident that this relation can be obeyed only if the corresponding terms of both sides are equal; otherwise it would mean a restriction of the values of the lattice parameters. Now because $\cos\alpha^* = 0$, this does not give any condition for k but postulates that $h_9 = h_3$. As there is no line lying less steeply it is evident that $h_9 = h_3 = 1$.

Next we turn to the determination of index k. From equation (7) and by the use of (3)

$$(h_9^2 - h_3^2)a^{*2} + (k_9^2 - k_3^2)b^{*2} + 2(h_9k_9 - h_3k_3)a^*b^*\cos\gamma^* = (h_7^2 - h_I^2)a^{*2} + (k_7^2 - k_I^2)b^{*2} + 2(h_7k_7 - h_Ik_I)a^*b^*\cos\gamma^*.$$

The corresponding terms of both sides must be equal in this case too; consequently

$$h_9^2 - h_3^2 = h_7^2 - h_I^2 = 0\,,$$

and

$$k_9^2 - k_3^2 = k_7^2 - k_I^2 = 4 - 1 = 3\,,$$

and this may be realized only if $k_9 = 2$, $k_3 = 1$. Finally

$$(h_9k_9 - h_3k_3)\cos\gamma^* = (h_7k_7 - h_Ik_1)\cos\gamma^*,$$

from which $\cos\gamma^* = 0$.

Thus the indices of the two oblique parallel lines are $(11l)$ and $(12l)$. We can construct the straight line with the index $(10l)$ also, but no observable reflexions belong to it; if there is a glide plane a, for the $(h0l)$ reflexions h must be even.

Of course we may detect several other lines in the figure. To compute the lattice parameters these are not needed, for the unit cell has $\alpha = \gamma = 90°$ which simplifies the matter considerably. Nevertheless it is worth while drawing these lines in order to test our deductions. Besides, it can be clearly seen that, for example in the case of a monoclinic unit cell, the whole set of lines consists of smaller groups of parallel lines. The distance between the lines in each group varies according to the same rule; that is, it is proportional to k^2, and within each group h is constant. The indices of the several lines are shown on the right side of Fig. 4.

Having obtained the indices, the lattice parameters may be readily computed. The results are

$$a = 6{\cdot}43\pm0{\cdot}02,\quad b = 8{\cdot}13\pm0{\cdot}01,\quad c = 8{\cdot}54\pm0{\cdot}02\text{ Å},\quad \beta = 97{\cdot}4\pm0{\cdot}4°.$$

Besides the indices Table 1 contains the measured and calculated values of $\sin^2\theta$.

The relatively large error in the lattice parameters is due to the considerable half-width of the lines—about 0·5–0·6°. More precise values of the lattice parameters can be derived only from back-reflexion lines.

It should be noted that the indexing may be performed even from less accurate data. In the above example $\Delta\theta \approx 0{\cdot}05°$, which corresponds to an error of 0·0003–0·0009 in $\sin^2\theta$ for the Bragg-angle range of 10° to 45°.

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