Acta Cryst. (1948). **1**, 290

A Third Graphical Method of Indexing Powder Photographs of Long-spacing Compounds

By Vladimir Vand

Research Department, Lever Brothers and Unilever Limited, Port Sunlight, Cheshire, England

(*Received* 24 *July* 1948)

A third graphical method of indexing X-ray powder photographs is described; it is suitable for compounds with identifiable long-spacing reflexions. If the long axis is the c axis, all the reflexions having the same h and k indices lie on the graph on a straight line. By this means all the possible solutions are displayed on the same graph, which can be prepared on a large scale, eliminating overcrowding and resulting in increased accuracy.

Introduction

Two graphical methods of indexing powder photographs of long-spacing compounds were described by Vand (1948) in a previous paper, to which readers are referred regarding symbols and mathematical theory.

A third graphical method has now been developed which seems to have sufficient advantages over the previous methods to merit description. The method was developed for indexing powder photographs of long-spacing compounds, such as fatty acids, fats and soaps, the so-called long spacings of which are unambiguously known. Otherwise the method is applicable to any crystal system, including triclinic.

In the previous paper it was shown that long-spacing compounds have their diffraction lines grouped in bands, each band containing all the lines with the same h and k indices and differing in l indices only. When dealing with the refinement of the constants of one such band by the method of least squares, the following equations were derived:

$$(D^*/c^*)^2-l^2=pl+q, \qquad (1)$$

where $D^*_{hkl}=n/d$ are the reciprocal spacings of lines belonging to the same band, characterized by two constants H^*, K^*, given by

$$H^{*2}_{hk}=c^{*2}(q-\tfrac{1}{4}p^2), \quad K^*_{hk}=\tfrac{1}{2}pc^*. \qquad (2)$$

Third graphical method

The third graphical method is based on the geometrical representation of all possible solutions of equation (1), the right-hand side of which represents a straight line.

The procedure used in applying this method is as follows:

The value of c^* is determined as accurately as possible. From measurements of diffraction lines a table of $(D^*/c^*)^2$ is prepared and, for better identification on the graph, all the lines are numbered consecutively. It is assumed (*a*) that any line might belong to any band, and (*b*) that any line might have any index l within any band. This amounts to the consideration of the expression $(D^*/c^*)^2-l^2$ for every observed line and for all values of l. A graph is prepared (see Fig. 1) with a horizontal X axis which represents all the values of l, and a vertical Y axis along which the expressions $(D^*/c^*)^2-l^2$ are plotted as a function of l.

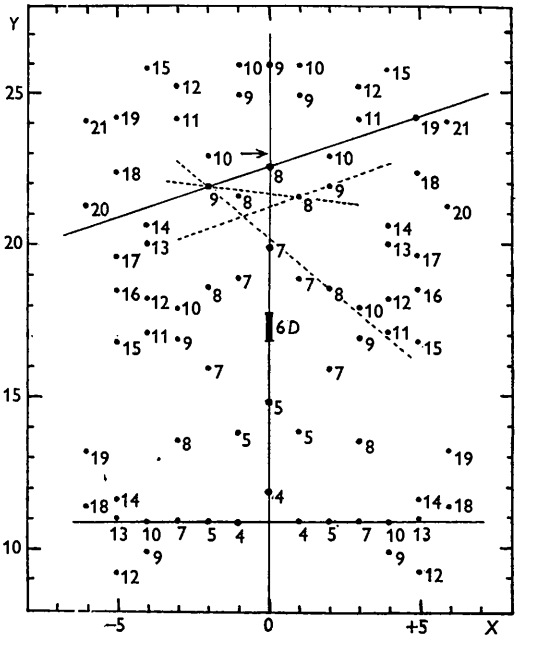

Fig. 1. Indexing of the powder pattern of potassium caproate by the third graphical method.

As values of l are whole numbers, the graph consists of many points; each diffraction line is represented by a series of points which all lie on a parabola. As l^2 are whole numbers, plotting is easy; one can subtract l^2 mentally from $(D^*/c^*)^2$ when plotting all the points as a function of l; another possibility is the use of a suitable stencil. The consecutive numbers of the lines are marked at the side of the corresponding points for ready identification.

When the graph is completed it is then inspected for any points lying on a straight line. When such a line is found, it means that equation (1) is fulfilled for this group of points and the reflexions can be indexed within the same band; the intercept of the Y axis gives then q, and the slope gives p; the indices are simply read along the X axis.

An inspection of the graph, however, usually reveals many chance straight lines; indeed, it represents in a permanent form all the solutions of the problem, real ones as well as chance ones. To eliminate the chance solutions as far as possible, the following technique is used: One begins at the bottom of the graph with the first line which is unaccounted for by long spacings. A low index l is preferably assumed for this point. It is known then that the first band probably goes through this point. If one solution is found, the band is marked and the same mark is affixed to all the points in the graph belonging to lines which can be accounted for by this band. This eliminates large numbers of points in the graph above the first band. The next step is to consider the lowest unaccounted line, and the procedure is repeated until all the lines are accounted for. A convenient marking system helps thus to reduce the number of points and therefore chance coincidences to a minimum; marking systems such as coloured pins or other mechanical marks might be used. Relations between crystalline inter-edge angles, density, intercepts and slopes of the bands, such as $p_{11}=p_{10}+p_{01}$, etc., can be used with great advantage for checking and locating the higher bands and for further elimination of chance solutions.

When a satisfactory solution is found, the values of p and q of each band are evaluated either from the graphs or by using the method of least squares; from them, by using equation (2), H^* and K^* are obtained, and from those the rest of the elements of the unit cell, as described in the previous paper.

Example

The method is demonstrated (see Fig. 1) on potassium caproate, which, in order to provide comparison of the three methods, is the same example as in the previous paper. Potassium caproate has $c^*=0{\cdot}05293$ kX.$^{-1}$. The graph immediately reveals a first band with $p=0$, $q=10{\cdot}85$, which indicates the monoclinic nature of the crystal and gives $B^*=0{\cdot}17435$, in good agreement with a value 0·1744 found previously. The first unaccounted-for line is 6, but this is very diffuse, being, indeed, a head of (11l) band. The next unaccounted-for lines are then 8 and 9. Four independent solutions are marked on the graph by full and dotted lines. Taking into account the density, one obtains $nA^*B^*=0{\cdot}0887$. For $n=4$, $2A^*=0{\cdot}2544$, and there should be a head of a band round $Y=23{\cdot}10$, as indicated by a small arrow on Fig. 1. This suggests that the solution indicated on Fig. 1 by a full line agrees with the density much better than the solutions indicated by dotted lines. This line gives $p=0{\cdot}35$, $q=22{\cdot}52$, giving $2A^*=0{\cdot}2510$. This agrees with 0·2508 found previously. From p is obtained $\cot\beta^*=0{\cdot}0369$, which gives $\beta=92°\,7'$, in agreement with $\beta=92°$ found previously.

This evidence is then further substantiated by measurement of higher bands, not shown on Fig. 1, and leads to the conclusion that potassium caproate is monoclinic with $a=7{\cdot}97$ kX., $b=5{\cdot}73$ kX., $c=18{\cdot}90$ kX., $\beta=92°$.

This method has several advantages over the first and second methods:

(1) It can be accurately plotted on a very large scale without using unwieldy compasses for drawing large circles.

(2) Like the second method, it permanently records all the possible solutions of the problem on the same graph.

(3) As squares of the reciprocal spacings are plotted, the graph is more spread out for large reciprocal spacings, which counteracts their increase in numbers. Unlike the second method, the graph is thus never overcrowded.

(4) An effective marking system can be used to indicate which line is accounted for by which bands. This is a decided advantage over the first two methods.

(5) Its accuracy surpasses the previous methods; it is, indeed, nearly equivalent to the least-squares method.

(6) The data are presented in a form which makes the application of the least-squares method easy.

Reference

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