AIDED, a Program for the Automatic Indexing of Epitaxic Derivatives; Application to the Graphite Lamellar Compounds

BY A. SETTON AND R. SETTON

Laboratoire d'Etudes Physicochimiques, UER de Sciences Fondamentales et Appliquées, 45045 Orleans, France

(Received 21 June 1978; accepted 26 September 1978)

Abstract

An algorithm, suitable for small computers with low memory capacity, is presented and applied to the diffractograms of graphite lamellar compounds crystallizing in the hexagonal, orthorhombic or monoclinic systems. The basic input data consist of the Bragg angle \( \theta \) and its uncertainty \( \Delta \theta \), and \( n \), the ratio of graphite atoms to intercalated molecules. All possible lattices corresponding to a given value of \( n \) are investigated and means are also provided to explore lattices with \( 2n \), \( 3n \), etc. (centered lattices) or with a value for the parameter \( c \) equal to \( 2I_c \), \( 3I_c \), etc. (where \( I_c \) is the so-called identity period) should there exist a screw axis parallel to the \( c \) axis.

Introduction

There already exist a number of programs for the computerized indexing of powder X-ray patterns (Jamard, Taupin & Guinier, 1966; Kohlbeck & Hörnl, 1976, etc.) but these programs are usually too complex to be used with a 'small' computer with a small memory capacity (such as a PDP-8E with 16 kbytes). In some particular cases however, supplementary data can be used to lighten the program: thus, in the case of most of the lamellar derivatives of graphite, their epitaxy simplifies to a large extent the indexing of their diffractograms (Setton, 1967) as it implies that if the unit cell is positioned so that \( a \) and \( b \) are imbedded in a graphite plane, the length of these parameters must be a simple function of \( G \), the distance between two adjacent carbon atoms in the graphite plane.

The successive steps in the indexing of the powder pattern of one of these compounds are then:

1. a search for and the identification of the \( h00 \), \( 0k0 \) and \( hnk \) lines, for which the value of \( \theta \) is only linked to \( G \) and to the type of lattice;
2. the computation of \( a \) and \( b \) as well as of the angle \( \gamma \);
3. among the remaining lines, a search for and the identification of the \( 00l \) lines whose characteristics only depend on \( c \);
4. the calculation of \( c \);
5. a trial at the indexing of the remaining \( hkl \) lines;
6. if all the lines have not been successfully indexed, a search for a new lattice.*

Unfortunately, the overall composition of the graphite lamellar compound does not lead unambiguously to a single parallelogram for the basis of the cell prism: thus, for a first stage \( MC_n \) compound with \( n \equiv 8 \), there are at least an orthorhombic and a hexagonal cell, either of which could turn out to be the right one. It is therefore necessary to design a program capable of exploring all the possibilities arising from a given value of \( n \) and even those connected with the values \( 2n \), \( 3n \), ... etc., since the formula of the layer compound could just as well have been \( M_2C_{2n} \), \( M_3C_{3n} \), etc.

Description

The program which has been evolved examines all the epitaxic lattices characterized by:

- \( a \neq b \neq c \), \( \gamma \neq \pi/2 \) or \( 2\pi/3 \) (monoclinic cell),
- \( a = b \neq c \), \( \gamma \neq \pi/2 \) or \( 2\pi/3 \) (monoclinic cell),
- \( a \neq b \neq c \), \( \gamma = \pi/2 \) (orthorhombic cell),
- \( a = b \neq c \), \( \gamma = 2\pi/3 \) (hexagonal cell),

which cover a very large proportion of the graphite compounds encountered, but not the triclinic case:

\[
ar \neq b \neq c, \quad \alpha \neq \beta \neq \gamma \neq \pi/2 \text{ or } 2\pi/3 .
\]

The lattices which have been retained correspond to the two-dimensional (2D) lattices which are, respectively:

- oblique, \( p \), symmetry group 2,
- rectangular, \( p \), symmetry group 2mm,
- hexagonal, \( p \), symmetry group 6mm,

while doubling the value of \( n \) will lead to centered lattices with different symmetry groups and/or parameters.

Each of the 2D parallelograms to be examined can be referred to a specific setting with respect to the underlying 2D hexagonal graphite network and set, for instance, with its four vertices at the center of four hexagons (Fig. 1). From symmetry considerations, we * Implicit in this scheme is, of course, the assumption that both angles \( \alpha \) and \( \beta \) of the lattice are \( 90^\circ \).

© 1979 International Union of Crystallography
can restrict vertex 1 to lie within the first 60° sector, while vertex 2 must be within the right angle MON since, in accordance with standard practice, we restrict y to be right-angled or obtuse.

It is easy to show that if we let \((P_i, Q_i)\) be the coordinates of the \(i\)th vertex, the surface of the parallelogram is such that

\[
n = P_2Q_1 - P_1Q_2.
\]

There are, of course, an infinite number of parallelograms which fulfill this condition; they can all be derived from the 'fundamental' parallelogram \(OABC\) in Fig. 1 by simple translations of the sides \(AB\) and/or \(BC\) (leading, for instance, to the parallelogram \(OAB'C'\) with equal area), but all these extraneous lattices can be eliminated by fairly simple tests. Along with the standard requirement that \(a \leq b\), all these conditions enable bounds to be found for the possible positions of vertices 1 and 2.

The general strategy is to place vertex 1 at the center of one of its possible sites and then find the position of vertex 2 which gives the correct value for the surface of the parallelogram; with \(a\) and \(b\) thus determined (as well as \(y\)), all possible values of the Miller indices \(h\) and \(k\) can be tried and each calculated value of \(d\) compared with the experimental values, each within its own range of uncertainty. As a general rule, this process turns up a number of alternative possibilities so that some 001 lines could mistakenly be indexed as 000 lines. The value of the Miller index \(l\) can then be computed from \(l_i = |l(D_i/D)\|/2\) by arbitrarily assigning the indexing 001 to that line which has the smallest \(D\) (largest \(d\)) value among all those recognized as being 000 lines. It is obvious that if the line which has been retained is not 001 but, for instance, 002, the value of \(c\) which is derived from the known values of \(D\) and \(l\) would be halved with respect to the true value and it would be impossible to index any line with \(l\) odd. This would again become possible if the value of \(c\) is doubled, indicating the probable presence of an identity period \(I_c = c/2\). Since it is impossible to know \(a\) \(priori\) whether the need to double \(c\) is due to a failure in computing the real value of \(c\) or whether it is rendered necessary by the presence of an asymmetry along the \(c\) axis, provision must be made for the possibility of trying \(c, 2c, 3c\) etc. Extraneous considerations can however be sometimes used to exclude erroneous values of the parameter and it is even possible to impose a value of \(c\) as part of the input data.

### Choice of \(\Delta \theta\)

The maximum (constant) reading error \(\Delta \theta\) connected with the experimental values of \(\theta\) is known. Using this value of \(\Delta \theta\) does not necessarily lead to the best result: too large a value makes for too many indexing possibilities so that some 00l lines could mistakenly be indexed as \(hhk\) lines, for instance, and thus be removed from the lines among which the subsequent search for 001 lines is to be made, while too small a value could prevent the indexing of some \(hhk\) lines whose presence in the list could mar the calculation of the correct value of \(c\). It is therefore advisable, in all cases, to explore the effect of slight modifications of \(\Delta \theta\) on the overall indexing.

### Choice of the lattice

It may so happen that the indexing process suggests more than one lattice as possible solutions. The final choice can, of course, only be based on structure factor calculations but, even then, it is convenient to have a 'first choice' on which to start subsequent calculations. We have used a classification criterion based on the number of \(hhk\) lines found since these are the only ones that truly reflect the epitaxic nature of the lattice and since their indexing does not depend on the determination of \(c\). [The index of reliability \(M\) (de Wolff, 1968) is unfortunately not applicable since the number of lines in the diffractogram is very often much less than 20.]

---

\[\text{Fig. 1. Orientation of the oblique 2D lattice (at the basis of a 3D monoclinic cell) with respect to the plane of graphitic atoms. The coordinates of vertices 1 and 2 are respectively (3.5) and (1, -3).}\]
Refinement of the values of the parameters

The epitaxy of the intercalated layers results in the fact that the parameters $a$ and $b$ are simple functions of $G$ so that only the values of $G$ and $c$ need to be refined. This is achieved (in a separate program) through a least-squares analysis of the residues after weighting the individual values of $D$ by $\cot \theta$.

Tests of the program

It should be emphasized, at this point, that there are extremely few - if any - epitaxic lamellar derivatives of graphite whose structure can be considered as being fully known. Indeed, one of the purposes of this work was to obtain means of studying these structures systematically.

The program has been tested on X-ray diffraction data given by various authors. In most cases, the published indexing was fully confirmed. As expected, the program showed that other indexings were also possible, so that a final choice could only be based on structure-factor calculations. *

C$_4$F. The first indexing given for this compound (Rüdorff & Rüdorff, 1947) corresponds to C$_4$F$_2$ and was based on an orthorhombic cell with $a=2.469$, $b=4.273$ and $c=5.411$ Å, although a sketch of the carbon and fluorine layers clearly suggests a hexagonal cell with $a=4.934$ and $c=5.411$ Å.

The cell corresponding to C$_4$F and the three possible cells corresponding to C$_8$F$_2$ are shown in Fig. 2. The coordinates of the vertices are

- For C$_4$F:
  - Cell A: $(0,0)$, $(1,3)$, $(1,-1)$, $(2,2)$ orthorhombic
  - Cell B: $(0,0)$, $(2,2)$, $(0,-4)$, $(2,-2)$ hexagonal
  - Cell C: $(0,0)$, $(2,2)$, $(1,-3)$, $(3,-1)$ orthorhombic
  - Cell D: $(0,0)$, $(2,6)$, $(1,-1)$, $(3,5)$ orthorhombic.

Cell C is apparently the one used as a basis for the indexing by Rüdorff while cell B corresponds to the one suggested.

All but one of the given lines could be indexed with $\Delta \theta = 0.1^\circ$, while a value of $\Delta \theta = 0.17^\circ$ was needed to permit immediate indexing of all the lines.

Later, (Lagow, Badachpape, Ficalora, Wood & Margrave, 1972) other values were given which also correspond to C$_8$F$_2$ and which were indexed on the basis of an hexagonal cell with $a=4.934$ and $c=5.411$. (The diffractogram is not quite identical to the previous one.)

In this diffractogram, a line at $d=1.870$ Å could only be indexed on the basis of cell D whereas all the other lines could be indexed on the basis of any one of the three other cells (the index 111 given by the author for this line is obviously in error and does not tally with the value of $d$).

LiC$_6$. An 11-line spectrum has been given (Guérard & Hérold, 1975) corresponding to a hexagonal cell with $a=4.26$ and $c=3.706$ Å.

The two possible cells corresponding to a formula MC$_6$ are shown in Fig. 2:

- Cell E: $(0,0)$, $(1,3)$, $(1,-3)$, $(2,0)$ hexagonal
- Cell F: $(0,0)$, $(3,1)$, $(0,-2)$, $(3,-1)$ monoclinic.

Computer indexing of the 11 lines was possible with $\Delta \theta = 0.1^\circ$ but three of the original double indexings were not duplicated for this range of uncertainty, giving a total of 13 indexings instead of the 16 given in the paper. Again, indexing was found to be possible on the basis of either cell so that only structure-factor calculations could enable a choice to be made in favor of one or the other cell.

APPENDIX

The values of $n$, $\lambda$, and $\theta_1$ constitute the input, as well as $\Delta \theta$ (the uncertainty on the readings) and the values of any multiplication factors for $c$ and $n$.

If the intercalated species forms an epitaxic layer over the graphite planes, two lines must exist in the diffractogram at approximately $d_{G(110)}=2.12$ and $d_{G(110)}=1.23$ Å since these distances (which correspond respectively to the 100 and the 110 reflexions in graphite) are directly connected with the in-plane $a$ and $b$ parameters of the new lattice; in that case, the latter

---

* In a very large number of cases, there were serious discrepancies between some calculated intensities and the experimental values while, at times, discrepancies were also found with published calculated values of the intensities. In view of these facts, the proper choice of the lattice in each specific case will be discussed elsewhere.
line is picked out and the value of $G$ calculated from

$$G = (2/\sqrt{3})d_{6(110)}.$$

The moduli of the unit vectors $i$ and $j$ shown in Fig. 1 are respectively $3G/2$, for the abscissae, and $\sqrt{3}G/2$, for the ordinates. With these units, and if the origin is at the center of a hexagon, the center of any other hexagon can be associated with the coordinates $(P_i, Q_i)$ where $P_i$ and $Q_i$ must be of identical parity. The parameters $a$ and $b$ are now given by

$$a^2 = (3P_1^2 + Q_1^2)3G^2/4 \quad (2)$$
$$b^2 = (3P_2^2 + Q_2^2)3G^2/4 \quad (3)$$

and it can be shown that, with the value of $n$ given by (1), one can write

$$\sin \gamma = (n\sqrt{3}/ab)(3G^2/4),$$
$$\cos \gamma = \frac{3P_1P_2 + Q_1Q_2}{ab} (3G^2/4). \quad (4)$$

The relation

$$1/d^2 = D = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} - \frac{2hk \cos \gamma}{ab}\right) \sin^2 \gamma + l^2/c^2 \quad (5)$$

characteristic of a monoclinic lattice, can be reduced to

$$D = U[h^2(3P_1^2 + Q_1^2) + k^2(3P_2^2 + Q_2^2) - 2hl(3P_1P_2 + Q_1Q_2)] + l^2/c^2 \quad (6)$$

with $U = 4/9n^2G^2$ by substituting (1), (2), (3) and (4) into (5); finally, (6) can itself be reduced to the 2D case by letting $l = 0$.

The conditions that $(P_i, Q_i)$ be in the first sector, that $a \leq b$ and that, in the case of monoclinic cells, all but the fundamental lattice be excluded, are expressed in the conditions

$$Q_1 \leq 3P_1,$$
$$3P_2^2 + Q_2^2 \leq 3P_1^2 + Q_1^2,$$
$$-(3P_2^2 + Q_2^2) \leq 2(3P_1P_2 + Q_1Q_2) < 0.$$

By taking into account the fact that the smallest value of $a$ is obtained when the vertex 2 lies at $(1, -1)$ or $(0, -2)$ or $(-1, -1)$, the following relations can be worked out:

$$\sqrt{n^2/4} \leq P_1 \leq n/4 \quad \text{if } n \text{ is a multiple of 4} \quad (7)$$
$$\sqrt{n^2/3} \leq P_1 \leq n/2 \quad \text{if } n \text{ is a multiple of 2} \quad (8)$$

with $\sqrt{n^2/3 - 3P_1^2} \leq Q_1 \leq 3P_1 \quad (9)$
$$-P_1 \leq P_2 \leq (n - P_1)/Q_1 \quad (10)$$
$$Q_2 = (P_2Q_1 - n)/P_1. \quad (11)$$

For each integral positive value of $P_1$ between the bounds given by (7) or (8), one can successively set the values of $Q_1$ within the range (9) and, in each case, try successive integral values of $P_2$ within the range (10). With $P_1$, $Q_1$ and $P_2$ thus fixed, $Q_2$ is computed from (11), thus completing the coordinates of the parallelogram to be tried.

We thank F. Béguin for numerous fruitful discussions.

References