Extension of the FIGATOM Program to the Automatic Plotting of Layers in Close-Packed Structures

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FIGATOM program, [Langlet (1972), J. Appl. Cryst. 5, 66-71], can already be used for drawing stereoscopic views of crystal structures or organic molecules. New facilities have now been added, so that projections of a structure as a slice parallel to any plane of the space can be plotted. The program is particularly designed to plot the close-packed plane, which is found by the program automatically (if it exists), so that condensed model-like representations can be obtained. The program can work either on real structures or on ideal stackings.

Introduction

The use of condensed models (Lima de Faria, 1965, 1966) has shown that many inorganic structures are built up by the stacking of equal layers, or in a few cases of different alternate layers (Lima de Faria & Figueiredo, 1969). It has also been noticed that many compounds belong to the same stacking type, although there seems to be little correlation between their unit cells and symmetry on one hand and the packing types on the other hand. Moreover, it is difficult in many cases to derive from the crystal structure projections the direction of the plane of the stacking layers. For instance, in the monoclinic structure of the mineral hodgkinsonite, if not already pointed out (Rentzeperis, 1963), it would be difficult to guess from the unit-cell projection that this structure is based upon a hexagonal close packing of oxygens, with closest-packed layers parallel to the (201) plane; still less apparent is the fact that the stacking layers are all alike (Figueiredo, 1974).

The purpose of the present extension of the FIGATOM program is to automate the search for the close-packed planes in any structure, as well as to enable the automatic plotting of such stacking layers to be carried out in a way very similar to that for the sheets of the condensed models of crystal structures.

1. Row method

If one considers, in order to simplify this explanation, that the compact layers will be formed by only one type of atom, for instance by the largest and the most frequent type, such as the oxygen atoms in many common minerals, one may take as central atom C any of these atoms and fill a table with its 12 closest neighbours - graded according to their distance from C.

The first atom (1) in the table is thus the closest neighbour. Let us take the point (1') symmetrical to atom (1), atom C being the centre of symmetry.

If the structure is ideal and has straight rows of atoms, (1') is superimposed on another atom (N) already listed in the table. If the structure is a real one, with distorted rows, let us look for the closest neighbour of point (1') among the atoms of our list; provided we find a satisfactory answer, i.e. an atom (N) located at a distance from point (1') less than the radius of the stacking atoms, the sequence 1-C-N may be the beginning of a row in the structure. Let us now try the same procedure again with atom (C) playing the role of atom (1) and atom (N) the role of atom (C) so that we extend the row to another atom (I).

If we repeat this successfully enough time to obtain a complete row 1-C-N-I-J...-L, i.e. up to the moment when the atom being found, let us say (L), is identical with atom 1 reproduced by a lattice translation within another cell, we may say that the structure is not a three-dimensional network but possesses at least one row.

When no row is found with atom (1) as a starting point, one will look for rows starting from atom (2), then (3) etc. ... Also when one row has been encountered, let us try to find a different one; if this can be done, the crystal structure can be considered as a layered structure. Moreover, the angle between these two rows will provide information about the layer type. Closest-packed layers have angles of 60° between rows. In compounds such as spinel, plane (111) is a closest-packed layer (triangular layer) of oxygen atoms, but plane (100) is a square layer (less dense) of oxygen atoms, so that, in the same compound, angles of 60° and 90° may be encountered. This means that, when two rows have been found by the row method, the closest-packing determination must not be considered as complete unless the angle between rows is about 60°. Then, one must look for other rows, either until a value of 60° has been found or until all atoms of the table have been tried; when no 60° angle is found, this means that the structure is not based on closest packing.
Fig. 1. Two compact layers of spinel MgAl₂O₄ parallel to plane (111). (a) Stereoscopic views of the real structure plotted by FIGATOM after data from Wyckoff (1965). Closest packing of oxygen atoms (large circles); Aluminum atoms (balls) in octahedral voids; Magnesium atoms (small dotted circles) in tetrahedral voids; Left-eye views are the real projections; Right-eye views present an artificial shift of atoms towards the left, proportional to their height above the best (111) plane through the oxygen atoms. (b) Partial representation of J. Lima de Faria's sheets of condensed models of the ideal structure (by permission of Estrutural, Lisbon, Portugal). All possible tetrahedral and octahedral voids are foreseen (dashed circles), but only dark sites contain Al and Mg atoms, as demonstrated by comparison with corresponding left-eye plottings. Layer II is located just below layer I; layers III and V would be the same as layer I, and layers IV and VI the same as layer II, with appropriate translations in order to realize the cubic close-packing sequence.
An unfavourable case arises when the layer contains at the same time squares and triangles of stacking atoms, for instance Al in CuAl₂. The distortion between two successive segments of the rows exceeds the value of the radius of the stacking atom. Because there may be wrong solutions, it is important to stop the row-method procedure as soon as an ambiguous situation is encountered. For such structures, the vector method, which will be described below, gives the right solution in a different way.

In favourable cases, when two rows have been found, the lowest value of the angle between the rows will define some type of stacking layer: triangular, square, etc. ... Then homologues of atom (C) on each row, (C') and (C''), will define, with atom (C) itself, the close-packed plane; solving the equations given by the coordinates of (C), (C') and (C'') gives the Miller indices of the layer.

2. Vector method

Let us keep in mind the closest-neighbour table which has been defined for the row method. Consider all the possible combinations of the vector (C)(N) in groups of three, i.e.

\[ \begin{align*}
(C)(1), & \quad (C)(2), \quad (C)(3) \\
(C)(1), & \quad (C)(2), \quad (C)(4) \\
& \quad \vdots \\
(C)(2), & \quad (C)(3), \quad (C)(4) \\
& \quad \vdots
\end{align*} \]

etc. ...

and calculate the corresponding determinant products, where (N) is any of the 12 atoms surrounding (C).

When three such vectors are located in the same plane, the determinant product value is equal to zero. (This is also true when two or more vectors are parallel to each other, which never occurs in this case). Let us build a new table, in which the groups of three atoms are graded according to the absolute value of the determinant product, and keep only the first combination for each group for which this product does not exceed a given value; this value has been chosen so that distorted lattices can also be taken into account.

The least-squares solutions of the equations built upon the coordinates of each remaining group of three atoms with atom (C), i.e. four atoms, will provide a list of Miller indices. These indices will have to be treated by an algorithm, with the symmetries within the cell taken into account, so that equivalent sets of indices are grouped together; then, the \((hkl)\) list is arranged in order of increasing frequency of occurrence for the planes. In such a way, the first set of indices gives the densest stacking plane, and the second one – if any – gives the second densest plane, e.g. \((111)\) and \((100)\) in spinel structures.

This procedure, with the help of the least-squares method, has always provided the best solution for all the compounds we have tried so far for both ideal structures and distorted ones. Of course, this method would be time consuming for manual calculations, since there are 220 combinations of 12 atoms in groups of three. In most cases of high symmetry, however, the solution may be found with 11 or 10 atoms, which reduces the number of combinations to 165 or 120 respectively.

Projects with FIGATOM

Since the first method gives good results in structures containing rows, it has been chosen for the extension of the FIGATOM program, also because Fortran programming was shorter in this case. As for previous features of FIGATOM, simple four-character keywords are used within the free-format data cards, in order to obtain the desired projections with the minimum of data input.

Thus, to get the illustration in Fig. 1(a) for the spinel structure, the only necessary instruction is keyword PRCM, which means PRojection as Condensed Model. Some default options are taken by FIGATOM:

(a) The stacking atom is supposed to be named O (oxygen) – if this were not true, the best way of getting the right result at once would be either to define the letter of the stacking atoms with the help of another keyword, or to name O the stacking-independent atoms in coordinate instructions, although they would not be oxygen atoms.

(b) The scale is 1 cm for 1 Å.

(c) The projection range is a circle around the central atom, with a radius of 10 Å, limited by the cells adjacent to the unit cell, i.e. within 27 cells.

(d) According to the definition of a layer represented by transparent sheets of condensed models (Lima de Faria, 1965), non-stacking interstitial atoms which are immediately above the stacking ones are assumed to belong to the same slice of space, so that atoms which are below will be plotted together with the stacking layer located underneath.

(e) The number of parallel slices thus defined, which will be plotted independently so as to realize the condensed model of the structure, is taken equal to three, because this number of planes seems sufficient in most cases to display the arrangement of layers within crystals.

Of course, other keywords allow the user to impose his own options on the program; for instance if one wants to get a complete set of sheets for hodgkinsonite corresponding to its complete condensed model, the number of slices to be plotted would be seven, in order for a sheet which repeats the first sheet to be included in this set.

A stereoscopic effect is ensured by a horizontal shift of atoms towards the left, proportional to their height above the mean height of the stacking plane, on right-eye views only, so that the left-eye view is the
Fig. 2. Structure of Hodgkinsonite $\text{MnZn}_2\text{Si}[\text{O}_4(\text{OH})_2]$. Stereoscopic views of real structure plotted by FIGATOM after data from Rentzeperis (1963) along plane (201) in a $P2_1/c$ monoclinic cell. Hexagonal stacking of oxygen atoms (large circles); Manganese atoms (medium-size circles) in octahedral voids; Zinc atoms (small dotted circles) in tetrahedral voids; Silicon atoms (small circles) in tetrahedral voids; Hydrogen atoms (dots). The same remark as in Fig. 1 applies concerning the stereoscopic effect. The height in Å × 100 above the best plane through the oxygen atoms has been plotted for Mn, Zn and Si atoms. Layer II is located just below layer I, and layer III just below layer II. Note that a layer differs from the preceding one essentially by the translation of the Mn–Zn–Si distribution pattern towards the right, so that layer VII will reproduce layer I. (b) Hodgkinsonite ($P2_1$ a cell) projected on (010) plane (after Wyckoff, 1968), (by permission of R.W.G. Wyckoff and Interscience Publishers, New York). The six planes with closest packing (parallel to (102) because of the inversion of $a_0$ and $c_0$) are suggested by slashes. No evidence of hexagonal close packing has appeared so far. Still less evident is the fact that the stacking layers are all alike.
real projection on the Miller plane, which has been
determined by the program according to the row
method. Then on Fig. 1, the kagome distribution of Mg
atoms appears clearly. Moreover, one obtains at the
same time these illustrations on the printed output of
the computer, with tables containing all atom coor-
dinates of the projections. The atom height above the
stacking plane, in Å x 100, can be plotted inside every
non-hidden atom on the stereoscopic views. One may
alternatively ask for plotting of the atom numbers,
which will correspond to the ones listed in the printed
tables.

How is FIGATOM used then, for layered structures
without straight rows? In this case, the normal answer
of the program is: No rows have been found, so that no
plotting can be completed. We could have included
the vector method, which would be used when no
answer is available with the row algorithm. However,
preference has been given to the writing of an auxiliary
program with the help of the APL conversational
language, which is a more suitable tool than
FORTRAN for the immediate solution of matrix
problems. Moreover we had already developed an
APL version of the WYCKO system for the computing of equivalent atoms in all space groups (Langlet,
1975). Getting an answer about the existence or non-
existence of closest packing in any compound now
demands only about ten seconds of real time on
average at the APL terminal. When the answer is
obtained, it is just necessary to replace keyword
PRCM in FIGATOM data cards by PRSH hkl – which
means PRojection on SHeets parallel to (hkl) values
given by the APL program – and one gets the correct
illustration set for structures without rows. Of course,
instruction PRSH may be also used to plot projections
on any other Miller plane, since FIGATOM accepts
up to ten different projection instructions for each
problem. Other forms of PRSH instruction exist, to
allow projections on any plane defined by three
points, with an alternative choice of the axis directions
and of the thickness of the space slice on both sides of
the plane for the plotted output.

The core requirement has not been increased by
these additional features, since with the help of overlay
facilities, FIGATOM now requires 320 K bytes i.e.
80 K words on the IBM 360-91 computer. Program
listings are available.

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