in reciprocal space, perpendicular to the planes (001) of the layers (see, for example, Zachariasen (1947)). This is the direction in which the streaks are actually observed. Similar streaks will, of course, be expected to occur in the diffraction pattern of the twin components II, IV, VI,.... The number of specimens which we have examined is comparatively small, but rather surprisingly the strongest streaks have been recorded with a specimen which does not appear to show twinning. Presumably, in this specimen, the twin components I, III, V, ... have grown much larger than the twin components II, IV, VI, ....

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# Vector Sets*

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This paper is concerned with the relations between a set of points, called the *fundamental set*, and the set of points at the ends of vectors between the points of the fundamental set, called the *vector set*. This is the same relation, in idealized form, that obtains between an electron-density map and the Patterson map of a crystal structure. A simple algebra is first set up to handle the characteristics of interest in these two sets of points. A most useful characteristic of the vector set is that in it are images of the polygons of points in the fundamental set. These polygon images can be systematically examined with the aid of a matrix concerned with the points of the vector set.

A vector set can be synthesized into images of several lines of the fundamental set. These line images can be combined in a very limited number of ways, one of which comprises the points of the fundamental set. Furthermore, any vector set of $n^2$ points can be synthesized into images of polygons in two different ways, either of which requires only $(n-1)$ steps. The last stage provides the fundamental set. Thus, any vector set can be solved for its fundamental set. This implies that, practical difficulties aside, a Patterson synthesis can be transformed into an electron-density synthesis.

The relations between the symmetries of the fundamental set and vector set are discussed with the aid of the vector-set matrix. It is shown that every symmetry element present in the fundamental set occurs as its parallel, translation-free residue at the lattice points of the vector set. Only twenty-three space groups occur in vector sets. A table provides a list of the space groups of vector sets corresponding with the space groups of fundamental sets.

Although the translation components of the symmetry elements of the fundamental set are not transferred to the symmetry elements of the vector set, nevertheless these translation components are not lost, and can be distinguished by concentrations of points in the vector set. With the aid of this feature, the space group of the fundamental set can be identified in the vector set, except that space groups of the fundamental set which differ only by a group of inversions, or which are related by an inversion, cannot be separately distinguished. An example of the practical use of this theory in determining the space group of a crystal is provided.


## Outline of topics



* The material of this paper was first presented as part of a series of lectures at the National Faculty of Philosophy, University of Brazil, Rio de Janeiro, in December 1948.

## Fundamental aspects of vector sets

*Introduction*

The developments in this paper constitute an extension of some basic ideas in a paper by Wrinch (1939) on 'Vector Maps'. The relations between a set of points and the vectors between the points are of considerable importance in the field of crystal-structure analysis because the locations of the atoms in a crystal correspond to a set of points, while the Patterson function (Patterson, 1934, 1935*a*, *b*) of the crystal corresponds to the vectors between the points. In this paper, it is shown, first, that any general 'vector set' can be solved for its fundamental point set or sets. In a broad way, this indicates that crystal structures can be solved from diffraction data. It is also demonstrated that a vector set contains a key to the symmetry of its fundamental set, and therefore space groups, with a few exceptions, can be determined from Patterson syntheses.

*Fundamental sets and vector points*

Consider a set of points, $a, b, c, \ldots$, in any number of dimensions. Let the sign $+$ be used to designate the adding of a term to a collection. Then the set of points $a$, $b$, $c$, ... is represented by the sum $a+b+c+\ldots$. Obviously addition is associative and commutative.

To emphasize the fact that the vector set is based on this set, it will sometimes be termed the *fundamental set* of points.

Let the vector from, say, point $p$ to point $q$ in the fundamental set be given the designation $\overrightarrow{pq}$. Let all such vectors constructed in the fundamental set be shifted so that they radiate from a common origin. The vectors are now said to exist in *vector space*. The point at the end of vector $\overrightarrow{pq}$ in vector space is designated $pq$, and is regarded as a kind of 'product' of $p$ and $q$, two points in the fundamental set. Since $\overrightarrow{pq} \neq \overrightarrow{qp}$, $pq \neq qp$, i.e. multiplication is not permutative. The distributive character of multiplication is examined in the next section.

*Images*

The point $ab$ is the point at the end of vector $\overrightarrow{ab}$. It can be described as the way point $b$ looks from point $a$. Similarly, $ab+ac$ consists of two points, one at the end of the vector $\overrightarrow{ab}$ and the other at the end of vector $\overrightarrow{ac}$. Since $ab$ is the way $b$ looks from $a$, and $ac$ is the way $c$ looks from $a$, $ab+ac$ is the way the two points $b$ and $c$, i.e. $b+c$, look from $a$. Since $b+c$ define and delimit the line $b$, $c$, $a(b+c)$ is the way the line $b+c$ looks from $a$. This is evidently equivalent to the way the points $b$ and $c$ look from $a$, so it follows that $ab+ac=a(b+c)$. In other words, multiplication is distributive.

According to Wrinch's nomenclature (Wrinch, 1939), $a(b+c)$ is called the *image* of the line $b+c$ in point $a$. Evidently this nomenclature can be extended to any collection of points. Thus $a(b+c+d)$ is the image in point $a$ of the triangle whose vertices lie at $b$, $c$ and $d$, and, more generally, $a(1+2+3+4+\ldots+n)$ will be spoken of as the image of a polygon of $n$ vertices (i.e. an $n$-gon) in $a$. This nomenclature should not be interpreted to mean that the polygon is necessarily planar.

*Vector sets*

Given a fundamental set, the vector set consists of the set of all points at the ends of vectors drawn between points in the fundamental set. Figs. 1 and 2 illustrate the relation between a set of points and its vector set. The fundamental set, shown in Fig. 1, consists of the locations of the five brightest stars in the constellation of the Southern Cross, the labels being their standard designations. If vectors are drawn between all pairs of points in Fig. 1 and then assembled at a common origin, the points at the ends of the vectors are those shown in Fig. 2.

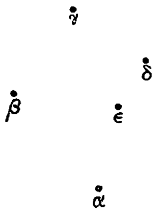



Fig. 1.

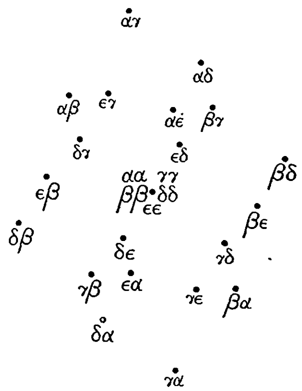



Fig. 2.

Evidently the vector set can be represented by the sum of all the products which can be formed by using two points at a time from the fundamental set. If the fundamental set is $a+b+c+d+\ldots$, the vector set is

$$\begin{aligned} V(a+b+c+d+\ldots) = {} & aa+ab+ac+ad+\ldots \\ & +ba+bb+bc+bd+\ldots \\ & +ca+cb+cc+cd+\ldots \\ & +da+db+dc+dd+\ldots \\ & +\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned} \qquad (1)$$

*The vector-set matrix*

A compact and orderly representation of a vector set is a square matrix composed of all the products which can be formed from points in the fundamental set:

$$V(a+b+c+d+\ldots) = \begin{pmatrix} aa & ab & ac & ad\ldots \\ ba & bb & bc & bd\ldots \\ ca & cb & cc & cd\ldots \\ da & db & dc & dd\ldots \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix}. \qquad (2)$$

The main diagonal of this matrix contains points at the end of vectors $aa$, $bb$, $cc$, $dd$, etc. These are null vectors, so the points lie at the origin of vector space. It is evident that if the primitive set contains $n$ points, the vector set contains $n^2$ points, of which $n$ are origin points and $n^2-n$ are non-origin points. Points symmetrical in the main diagonal are permuted products, such as $ab$ and $ba$. Since these points are at the ends of vectors $\overrightarrow{ab}$ and $\overrightarrow{ba}$, and since $\overrightarrow{ab}=-\overrightarrow{ba}$, it follows that $ab=-ba$. Thus the vector set matrix is skew symmetric. While the main diagonal of the matrix is a line of symmetry, it represents a center of symmetry in the vector set because $ab=-ba$. Thus, all vector sets are centrosymmetrical.

Because of the skew symmetry of the matrix, if any two columns (or rows) of the matrix are interchanged, the corresponding rows (or columns) become automatically interchanged also. Such an interchange merely corresponds to an interchange of labels on the corresponding points of the fundamental set.

## Synthesis of vector sets

*Image properties of the vector-set matrix*

Any column or part of a column of the vector-set matrix is a collection of images of the same point in the row points. For example, in (2), the part of the second column

$$\begin{array}{c} ab \\ bb \\ cb \end{array}$$

represents the images of point $b$ in points $a$, $b$ and $c$.

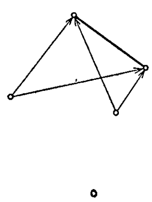


Fig. 3.

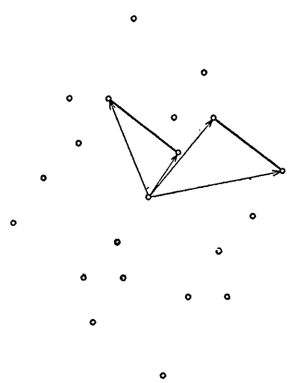


Fig. 4.

Corresponding parts of any two columns represent the images of a specific line in the row letters. For example, parts of the second and third columns,

$$\begin{array}{cc} ab & ac \\ bb & bc \\ cb & cc \end{array} = \left.\begin{array}{c} a(b+c) \\ b(b+c) \\ c(b+c) \end{array}\right\}, \tag{3}$$

is a collection of images of the line $b+c$ in the points $a$, $b$ and $c$. Figs. 3 and 4 show that the collection of images of a line are parallel displacements of the same line as it occurs in the fundamental set. Similarly, corresponding parts of $n$ columns represent a collection of images of a specific $n$-gon in the row points. The images are parallel displacements of the $n$-gon which occurs in the fundamental set.

Because of the symmetry of the matrix, the words 'columns' and 'rows', in the above discussion, can be inter-changed. Another aspect of this symmetry is as follows. Since

$$\begin{aligned} (a+b+c+\ldots)p &= ap+bp+cp+\ldots \\ &= -pa-pb-pc\ldots \\ &= -p(a+b+c+\ldots), \end{aligned} \tag{4}$$

it follows that the negative of an image is the centrosymmetrical image. Thus to each set of images represented by sets of columns, the vector set contains the corresponding centrosymmetrical images represented by sets of corresponding rows.

It is evident that a vector set derived from a fundamental set of $n$ points can be synthesized into $n$ images of an $n$-gon, or into $n$ images of an $(n-1)$-gon plus $n$ images of a point, or into $n$ images of an $(n-2)$-gon plus $n$ images of a line, or, in general, into any collection of images which can be represented by the columns.

The first synthesis, namely, $n$ images of an $n$-gon, is interesting. The $n$-gon is represented by the entire row and the image points by the column letters. This synthesis is

$$\begin{aligned} V(a+b+c+d+\ldots) &= a(a+b+c+d+\ldots) \\ &\quad +b(a+b+c+d+\ldots) \\ &\quad +c(a+b+c+d+\ldots) \\ &\quad +d(a+b+c+d+\ldots) \\ &\quad +\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned} \tag{5}$$

This signifies that the vector set can be synthesized into images of the primitive set in each of its points. An illustration of this for the vector set of Fig. 2 is shown in Fig. 16. The pentagon has vertices at the points of the fundamental set shown in Fig. 1.

*Synthesis into sets of lines*

The synthesis of a vector set into images of several lines is illustrated for the vector set of Fig. 2 in Figs. 5 and 6. Such a synthesis is guided by the matrix of the vector set. For the five-point fundamental set of Fig. 1 and its vector set of Fig. 2, this matrix representation, partitioned for purposes described below, is

$$V(a+b+c+d+e)=\left(\begin{array}{ccc|cc} aa & ab & ac & ad & ae \\ ba & bb & bc & bd & be \\ ca & cb & cc & cd & ce \\ \hline da & db & dc & dd & de \\ ea & eb & ec & ed & ee \end{array}\right). \tag{6}$$

Any pair of rows or columns may be chosen for images of the first line. By a labelling interchange accompanied by column (and row) interchanges, the chosen images may be made to occupy the last two columns. (This labelling transformation is unnecessary, but it simplifies the description of the illustration.) The last two columns are

$$\begin{matrix} ad & ae \\ bd & be \\ cd & ce \\ dd & de \\ ed & ee \end{matrix} \quad = \quad \left.\begin{matrix} a(d+e) \\ b(d+e) \\ c(d+e) \\ d(d+e) \\ e(d+e) \end{matrix}\right\}. \tag{7}$$

The bottom two terms represent the image of the line $(d+e)$ in its two ends. Since a labelling interchange of the fundamental set is permissible, a line from the origin to *any* point in the vector set may be identified with either of these two images. For the purposes of this illustration, the bottom image of (7) has arbitrarily been chosen as the line $\beta\beta+\beta\delta$ of Fig. 2. The remaining points in (7) can be identified by merely finding lines in Fig. 5 parallel and equal to the origin lines originally chosen. This procedure not only locates the five lines

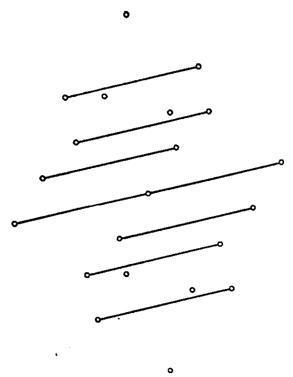


Fig. 5.

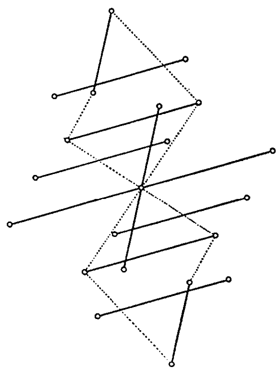


Fig. 6.

of (7), which accounts for the entire right partition of (6), but also the three more lines in the lower left partition of (6) which are symmetrical with (and, therefore, in the vector set of Fig. 5, centrosymmetrical with, and consequently parallel to) the lines in the upper right partition of (6).

The vector set of Fig. 5 now stands synthesized into eight lines, plus six non-origin points unconnected by lines. These unattached points are the six non-diagonal elements of the upper left partition of (6). This entire partition, subpartitioned for purposes described below, is

$$\begin{array}{c|cc} aa & ab & ac \\ \hline ba & bb & bc \\ ca & cb & cc \end{array} \tag{8}$$

Any two columns of (8) represent three images of either lines $a+b$, $a+c$ or $b+c$. For clearness, suppose that line $b+c$ is chosen. This is the right partition of (8), but in the case of lines, the images include centrosymmetrical lines, so that they include the lower left partition of (8). This means that if any of the remaining unattached points of Fig. 5 is connected with the origin, it establishes a total of four line images. Of these, (8) shows that two are origin images while two are non-origin images which are centrosymmetrical equivalents, namely, $a(b+c)$ and $(b+c)a$. These are drawn in Fig. 6 (as images of $\alpha\alpha+\alpha\epsilon$ of Fig. 2). Now, origin images can be recognized in the vector set (Fig. 6) as well as in the matrix. Omitting origin images, the matrix has been synthesized into the non-origin images of lines outlined in blocks, as follows:

$$\begin{pmatrix} aa & ab & ac & ad & ae \\ ba & bb & bc & bd & be \\ ca & cb & cc & cd & ce \\ da & db & dc & dd & de \\ ea & eb & ec & ed & ee \end{pmatrix}. \tag{9}$$

The non-origin images of lines can be combined in $2\times 6$ different ways, of which half are centrosymmetrical with the other. Two of these, taken together with an origin point, are the fundamental set and its centrosymmetrical equivalent. These are represented in the matrix (9) as the top row and left column. These two centrosymmetrical combinations are outlined as polygons in Fig. 6.

In general, the vector set of an $n$-point fundamental set contains $n^2-n$ non-origin points. The number of ways of selecting $n$ points from this set is ${}_{(n^2-n)}C_n$, while the number of ways of combining line images is

$$2(n-2)\,2(n-4)\,2(n-6)\ldots 2.1 \quad \text{for } n \text{ odd},$$

and $\quad 2(n-2)\,2(n-4)\,2(n-6)\ldots 2.2 \quad$ for $n$ even.

In both cases half are centrosymmetrical. For the five-point fundamental set one combination of points in 4845 is the fundamental set, whereas one line-image combination in six is the fundamental set (or its centrosymmetrical equivalent).

### *Synthesis into a spectrum of polygons*

A vector set based on a fundamental set of $n$ points can be easily and quickly solved for the fundamental set in $n-1$ stages. This is again illustrated with the aid of the vector set of Fig. 2, which is based on the five-point fundamental set of Fig. 1. The $n-1=4$ stages are illustrated in Figs. 7, 8, 9 and 10. By simply adding the appropriate number of additional stages, the same routine can be applied to any larger general vector set.

The first stage consists of establishing all the images of an origin line. For this purpose *any* point is selected and connected with the origin to form the image of that line containing the origin, and then all its images are located as discussed in the last section (Fig. 6).

At this stage all the points of the matrix have been connected with line images except those of the upper left partition of (6). Two of these line images contain the origin. Now to any of the remaining six non-origin line images there may be added a point in the same row, thus creating a triangle whose images can be found. A particular point can be easily identified, namely, the point on the main diagonal, for this corresponds to the origin point in Fig. 7. For convenience of discussion, let the diagonal point be added to the third row from the bottom, then form the images of this triangle from the

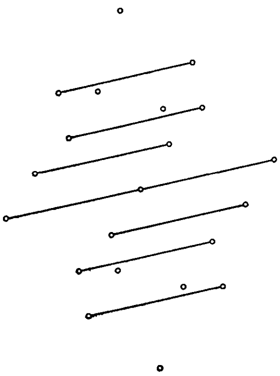


Fig. 7.

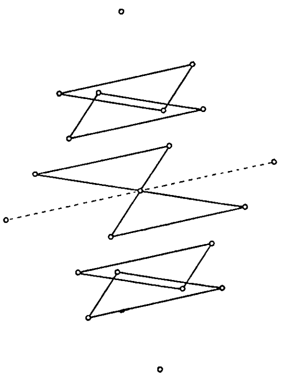


Fig. 8.

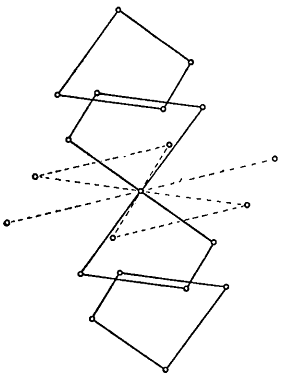


Fig. 9.

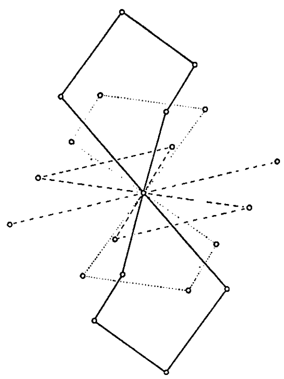


Fig. 10.

remaining non-origin line images plus unattached points. The synthesis of points in the matrix now stands

$$\begin{pmatrix} aa & ab & ac & ad & ae \\ ba & bb & bc & bd & be \\ ca & cb & cc & cd & ce \\ da & db & dc & dd & de \\ ea & eb & ec & ed & ee \end{pmatrix}. \tag{10}$$

In the vector set (Figs. 7 and 8) this stage consists of adding the origin point to *any* non-origin line image, then finding the appropriate unattached point in the region of each of the remaining non-origin line images which, together with it, comprise a triangle similar to the one established at the origin.

In a similar way, a point can be added to either of the non-origin triangle images, transforming it into a quadrilateral. A particular point can be readily identified, namely, the one on the main diagonal. For clearness, suppose the diagonal point is added to the fourth row from the bottom. This establishes a quadrilateral image in the last four columns. Form the image of this quadrilateral by adding the unattached point in the top row to the triangle in the top row. The polygons in the matrix can now be represented as

$$\begin{pmatrix} aa & ab & ac & ad & ae \\ ba & bb & bc & bd & be \\ ca & cb & cc & cd & ce \\ da & db & dc & dd & de \\ ea & eb & ec & ed & ee \end{pmatrix}. \tag{11}$$

The equivalent operations in the vector set (Figs. 8, 9) consist of attaching the point at the origin to *any* of the non-origin triangles, then finding the appropriate unattached point in the region of each of the remaining non-origin triangle images which, together with it, comprise a quadrilateral similar to the one established at the origin.

The final stage consists of adding the remaining origin point to the non-origin quadrilateral (Fig. 9). The vector set then appears as in Fig. 10, and the matrix appears decomposed into the following blocks:

$$\begin{pmatrix} aa & ab & ac & ad & ae \\ ba & bb & bc & bd & be \\ ca & cb & cc & cd & ce \\ da & db & dc & dd & de \\ ea & eb & ec & ed & ee \end{pmatrix}. \tag{12}$$

The vector set is now synthesized into (1) an image of a point in itself, (2) an image of a line in one of its points, (3) an image of a triangle in one of its vertices, (4) an image of a quadrilateral in one of its vertices, (5) an image of a pentagon in one of its vertices, all plus the centrosymmetrical polygons. That is, the vector set has been synthesized into a spectrum of images of polygons, each in a vertex, plus the centrosymmetrical spectrum. The polygon of greatest rank contains the points of the fundamental set. This is the first row, or first column of (12). One of the two pentagons of Fig. 10 contains the points of the fundamental set (Fig. 1), and the other contains its centrosymmetrical equivalent.

The choice of the particular 'polygon' to which the origin point is added at each stage is immaterial. Two alternate solutions to the same vector set are shown in Figs. 11 and 12.

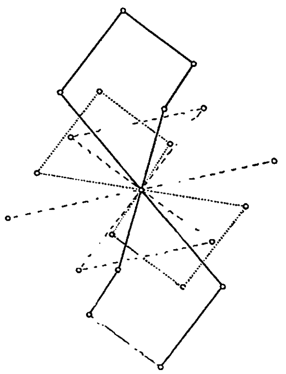


Fig. 11.

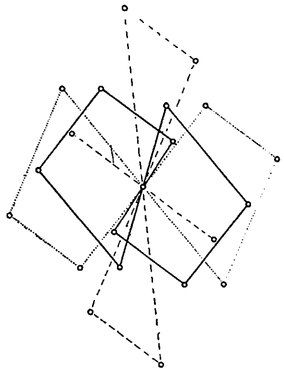


Fig. 12.

*Synthesis into identical polygons*

A vector set based on a fundamental set of $n$ points can be easily and quickly solved for the fundamental set in $n-1$ stages by an alternative procedure which results in the synthesis of the points into $n$ identical $n$-gons, namely, those indicated in (5). The stages of the solution are illustrated for the set of Fig. 2, which is based on the five-point fundamental set of Fig. 1, in Figs. 13, 14, 15 and 16.

The first stage consists of connecting *any* non-origin point with the origin, thus establishing a line, and then finding the images of the resulting line. This part of the procedure is identical with that described in the first stage of each of the two preceding methods of synthesis. The synthesis of the set then stands as shown in Fig. 13, and the matrix stands blocked into line images as follows:

$$\begin{pmatrix} aa & ab & ac & ad & ae \\ ba & bb & bc & bd & be \\ ca & cb & cc & cd & ce \\ da & db & dc & dd & de \\ ea & eb & ec & ed & ee' \end{pmatrix}. \quad (13)$$

The matrix shows that this results in eight separate line images, of which three non-origin lines can be regarded as 'right-handed' images, three more as the 'left-handed' equivalents of these, and two origin images which may be said to be 'right-handed' or 'left-handed' at pleasure. Since right-handed and left-handed parallel lines are indistinguishable as such, these eight cannot be classified and separated at this stage, but in the next stage one of the two sets of enantiomorphous lines will be discarded.

Any of the non-origin lines of (13) can be transformed into a triangle by adding a point. An origin point is added for this purpose, since it can be readily identified in both matrix and vector set. Suppose that the origin point is added to the line image in the middle of the last pair of columns of (13). The images of this triangle then occur in the matrix as blocked out as follows:

$$\begin{pmatrix} aa & ab & ac & ad & ae \\ ba & bb & bc & bd & be \\ ca & cb & cc & cd & ce \\ da & db & dc & dd & de \\ ea & eb & ec & ed & ee \end{pmatrix}. \quad (14)$$

To form all five images, it is necessary to utilize the two points of one of the enantiomorphous column line-images of (13). In the vector set (Figs. 13 and 14) the origin point is added to *any* line, thus establishing a triangle. In the example shown, the upper one of the two lines nearest the origin is arbitrarily chosen, thus establishing a triangle with an apex pointing *down*. (If the lower line had been chosen, thus establishing the centrosymmetrical triangle with an apex pointing *up*, the final solution achieved by the process discussed here would have been the centrosymmetrical solution.) The matrix, (14), shows that five parallel identical triangle images can be formed. This requires making use of the parts of one of the enantiomorphic line images, as pointed out above. When the five triangle images have

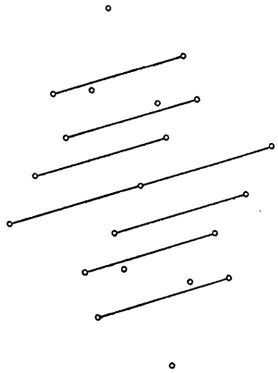


Fig. 13.

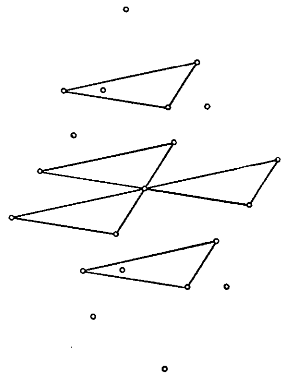


Fig. 14.

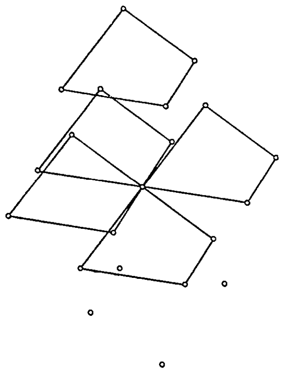


Fig. 15.

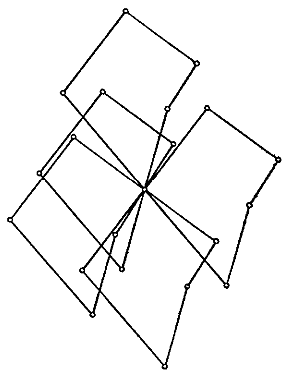


Fig. 16.

been located, this automatically identifies all five 'right-handed' line images of the previous stage, and disqualifies the three excess images from further use as being 'left-handed'. These are forthwith decomposed into their original points. Two of these released points are attached to two of the origin triangles, as described above, the other four being available for subsequent image-formation.

In the next stage, a point is added to either of the two non-origin triangles, creating a quadrilateral. A particular point, namely, the origin point, can be identified in the matrix and in the vector set (Fig. 14). The four additional images of this quadrilateral are now formed, and the matrix stands blocked into images as follows:

$$\begin{pmatrix} aa & \boxed{ab \quad ac \quad ad \quad ae} \\ ba & \boxed{bb \quad bc \quad bd \quad be} \\ ca & \boxed{cb \quad cc \quad cd \quad ce} \\ da & \boxed{db \quad dc \quad dd \quad de} \\ ea & \boxed{eb \quad ec \quad ed \quad ee} \end{pmatrix}. \tag{15}$$

The corresponding operations in the vector set (Fig. 14) consist of adding an origin point to either of the two non-origin triangles, thus creating an origin quadrilateral (Fig. 15). The four images of this quadrilateral are then formed in the usual way.

The final stage of the synthesis consists of adding an origin point to the one quadrilateral in (15) not containing a diagonal point, namely, the upper image. The images of this quadrilateral are the other four rows. The matrix now stands synthesized into pentagons as follows:

$$\begin{pmatrix} \boxed{aa \quad ab \quad ac \quad ad \quad ae} \\ \boxed{ba \quad bb \quad bc \quad bd \quad be} \\ \boxed{ca \quad cb \quad cc \quad cd \quad ce} \\ \boxed{da \quad db \quad dc \quad dd \quad de} \\ \boxed{ea \quad eb \quad ec \quad ed \quad ee} \end{pmatrix}. \tag{16}$$

In the vector set, the corresponding operations consist of adding an origin point to the only non-origin quadrilateral, thus transforming it into a pentagon, and finding the images of this pentagon. The result is shown in Fig. 16.

The collections of points at the vertices of each pentagon of Fig. 16 is identical with the original fundamental set (Fig. 1) (or with its centrosymmetrical equivalent, in case the original choice of lines and triangles was the centrosymmetrical set). This synthesis can be carried out for any larger set by adding a suitable number of additional stages.

## Periodic sets

The discussion has been tacitly confined to non-periodic sets and their vector sets. Attention is now directed briefly to periodic sets and their vector sets.

To illustrate the features involved in periodic sets, consider Fig. 17 (which shows a simple diperiodic fundamental set) and Fig. 18, its vector set. Select a unit cell in the fundamental set containing a representative motif set in the fundamental set, such as $a+b+c$. Consider the products between subset $a+b+c$ and any translation-equivalent subset $a'+b'+c'$. If $T$ is the translation which relates these two subsets, then the interperiod products are:

$$\left.\begin{array}{lll} aa' = aa+T, & ba' = ba+T, & ca' = ca+T, \\ ab' = ab+T, & bb' = bb+T, & cb' = cb+T, \\ ac' = ac+T, & bc' = bc+T, & cc' = cc+T. \end{array}\right\} \tag{17}$$

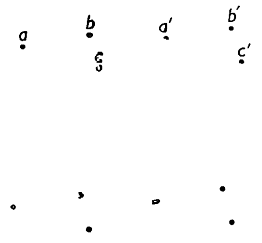



Fig. 17.

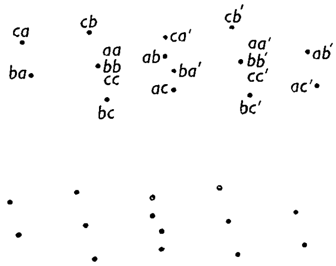



Fig. 18.

Some obvious conclusions can be drawn from this simple analysis of interperiod products:

(1) The vector set of a periodic fundamental set consists only of the vector set of the points of one fundamental cell, *modulo* **L** (where **L** is the translation group of the fundamental set).

(2) The vector set is therefore also periodic and has the same lattice as the fundamental set.

(3) No additional vector points arise which can be regarded as arising from interperiod vectors, which are not present due to the motif itself.

From the last conclusion, it follows that, in order to solve a periodic vector set for its periodic fundamental set, it is sufficient to consider a unit cell of the periodic vector set which centrosymmetrically surrounds the origin point. If the subset within this field is treated according to one of the solution methods outlined in the last section, the solution achieved consists of the points in the unit cell of the fundamental set, or its centrosymmetrical equivalent.

### Homometric sets

In the investigation of the crystal structure of bixbyite, Pauling & Shappell (1930) discovered that more than one fundamental set may have the same vector set. Patterson (1939) called such fundamental sets *homometric* sets. He has recently established the existence of a number of sets of homometric sets in certain comparatively simple kinds of fundamental sets.

If the vector set is solved for the fundamental set as suggested in a foregoing section, all homometric solutions are automatically encountered.

### Symmetry properties of vector sets

*Symmetry of vectors in the fundamental set*

The way in which the symmetry of the fundamental set appears in the vector set can be studied in a number of ways. It is interesting to make use of the vector-set matrix in this connection.

Consider a general symmetry element, say a screw, and let the points related to $a_0$ by the 0, 1st, 2nd, 3rd,... powers of the generating operation of the group of the symmetry element be designated by $a_0, a_1, a_2, a_3, \ldots$, and the points related to $b_0$ by these operations be designated $b_0, b_1, b_2, b_3, \ldots$, etc. The fundamental set is then

$$a_0+a_1+a_2+a_3+\ldots+b_0+b_1+b_2+b_3+\ldots. \qquad (18)$$

In this set, $a_1$ bears the same relation to $a_3$, say, as $a_2$ bears to $a_4$. Therefore, the vector $\overrightarrow{a_1a_3}$ in fundamental space is carried into vector $\overrightarrow{a_2a_4}$ by the first power of the generating symmetry operation. Similarly, $\overrightarrow{a_1b_2}$ is carried into $\overrightarrow{a_3b_4}$ by the second power of this operation. In general, the following sequences are related by the power of the operation indicated:

$$\left.\begin{array}{lll} \overrightarrow{a_pa_q}, & \overrightarrow{a_{p+1}a_{q+1}}, & \text{1st power,} \\ \overrightarrow{a_pb_q}, & \overrightarrow{a_{p+1}b_{q+1}}, & \text{1st power,} \\ \overrightarrow{a_pb_q}, & \overrightarrow{a_{p+n}b_{q+n}}, & n\text{th power.} \end{array}\right\} \qquad (19)$$

(Note that when $a=b$ and $p=q$, these sequences degenerate to $\overrightarrow{a_1a_1}$, $\overrightarrow{a_{1+n}a_{1+n}}$. This is a sequence of null vectors located at

$$a_1, \quad a_{1+n}, \qquad (20)$$

so that the vectors of (19) degenerate into those points of (18) which are related by the $n$th power of the same symmetry operation.)

*Symmetry of vectors and vector points in vector space*

The vectors of (19) in fundamental space conform to the symmetry element of fundamental space. But when the vectors are transferred to vector space, they are all shifted to a common point. This corresponds to a removal of the translations which separate the origins of the vectors. The transformation to vector space therefore results in a loss of the translation component of the symmetry element connecting them, although the angular relations between vectors remains intact. It follows that the vectors transferred to vector space retain only the translation-free aspects of the symmetry element. It also follows that the points at the ends of the vectors, namely, the vector points, are related by the translation-free residue of the symmetry element which related the points of fundamental space.

*Symmetry relations in the matrix of the vector set*

Let the points within a cell of the fundamental set be arranged in symmetry cycles with regard to a chosen symmetry element, as in (18). The matrix of the cell of the vector set, partitioned according to symmetry cycles, is

$$\left(\begin{array}{ccccc|ccccc} a_0a_0 & a_0a_1 & a_0a_2 & a_0a_3 & \cdots & a_0b_0 & a_0b_1 & a_0b_2 & a_0b_3 & \cdots \\ a_1a_0 & a_1a_1 & a_1a_2 & a_1a_3 & \cdots & a_1b_0 & a_1b_1 & a_1b_2 & a_1b_3 & \cdots \\ a_2a_0 & a_2a_1 & a_2a_2 & a_2a_3 & \cdots & a_2b_0 & a_2b_1 & a_2b_2 & a_2b_3 & \cdots \\ a_3a_0 & a_3a_1 & a_3a_2 & a_3a_3 & \cdots & a_3b_0 & a_3b_1 & a_3b_2 & a_3b_3 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \hline b_0a_0 & b_0a_1 & b_0a_2 & b_0a_3 & \cdots & b_0b_0 & b_0b_1 & b_0b_2 & b_0b_3 & \cdots \\ b_1a_0 & b_1a_1 & b_1a_2 & b_1a_3 & \cdots & b_1b_0 & b_1b_1 & b_1b_2 & b_1b_3 & \cdots \\ b_2a_0 & b_2a_1 & b_2a_2 & b_2a_3 & \cdots & b_2b_0 & b_2b_1 & b_2b_2 & b_2b_3 & \cdots \\ b_3a_0 & b_3a_1 & b_3a_2 & b_3a_3 & \cdots & b_3b_0 & b_3b_1 & b_3b_2 & b_3b_3 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{array}\right). \qquad (21)$$

According to the discussion given in the second last section above, the elements which conform to the sequence $a_pb_q, a_{p+1}b_{q+1}$ are related by the first power of the operation of the symmetry element. Such elements lie parallel to the main diagonal within any partition. Since the entire row (or column) is related to its neighboring rows (or columns) in this fashion, entire neighboring rows (or columns) conform to the symmetry element. But according to image theory, these rows (or columns) are images of the same polygon, and hence parallel. Each partition, therefore, consists of symmetrically placed parallel images of an $n$-gon, where $n$ is the number of operations in the group of the symmetry element.

In order to display the symmetry elements of the entire vector set of points, the matrix may be condensed in the following way: Since multiplication is distributive, products with common terms may be gathered together. The most general way in which this can be done is to add together corresponding terms from all partitions in (21). The condensed matrix is

$$\begin{pmatrix} (a_0+b_0+\ldots)(a_0+b_0+\ldots) & (a_0+b_0+\ldots)(a_1+b_1+\ldots) & (a_0+b_0+\ldots)(a_2+b_2+\ldots) & (a_0+b_0+\ldots)(a_3+b_3+\ldots)\ldots \\ (a_1+b_1+\ldots)(a_0+b_0+\ldots) & (a_1+b_1+\ldots)(a_1+b_1+\ldots) & (a_1+b_1+\ldots)(a_2+b_2+\ldots) & (a_1+b_1+\ldots)(a_3+b_3+\ldots)\ldots \\ (a_2+b_2+\ldots)(a_0+b_0+\ldots) & (a_2+b_2+\ldots)(a_1+b_1+\ldots) & (a_2+b_2+\ldots)(a_2+b_2+\ldots) & (a_2+b_2+\ldots)(a_3+b_3+\ldots)\ldots \\ (a_3+b_3+\ldots)(a_0+b_0+\ldots) & (a_3+b_3+\ldots)(a_1+b_1+\ldots) & (a_3+b_3+\ldots)(a_2+b_2+\ldots) & (a_3+b_3+\ldots)(a_3+b_3+\ldots)\ldots \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix}. \tag{22}$$

As an abbreviation, let

$$\left.\begin{aligned} (a_0+b_0+\ldots) &= A_0, \\ (a_1+b_1+\ldots) &= A_1, \\ (a_p+b_p+\ldots) &= A_p. \end{aligned}\right\} \tag{23}$$

Then (22) has the form

$$\begin{pmatrix} A_0A_0 & A_0A_1 & A_0A_2 & A_0A_3 & A_0A_4\ldots \\ A_1A_0 & A_1A_1 & A_1A_2 & A_1A_3 & A_1A_4\ldots \\ A_2A_0 & A_2A_1 & A_2A_2 & A_2A_3 & A_2A_4\ldots \\ A_3A_0 & A_3A_1 & A_3A_2 & A_3A_3 & A_3A_4\ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \end{pmatrix}. \tag{24}$$

All elements of (24) related by the direction of the main diagonal are related as (19), so they are related by the primitive operation of the translation-free residue of the symmetry element present in the fundamental set. It follows that both columns and rows of (24) are related by this symmetry element. This means that the vector set can be synthesized into subsets of complex parallel images related by the translation-free symmetry element of the fundamental set, as well as by an inversion center.

THEOREM. *If the fundamental set contains a given symmetry element, the vector set contains the parallel, translation-free residue of that symmetry element through the origin.*

*Note.* Since

$$A_pA_q = (a_p+b_p+\ldots)(a_q+b_q+\ldots), \tag{25}$$

the significance of each complex product in (23) and (24) is the image of a representative collection of all non-equivalent points in those of another such collection which is related to the first collection by the symmetry operation.

*The possible symmetries of vector sets*

It follows from the theorem given in the last section that the space group of a vector set can be derived from the space group of its fundamental set by substituting, at the lattice points of vector space, the translation-free residue of each generating symmetry element in the fundamental set, completing the group by forming the products of the operations of these elements with the lattice, and further requiring the vector space group to contain the operation of an inversion at the origin if not already present in the group. In Table 1 are listed the space groups of the vector sets corresponding with the space groups of the fundamental sets.

*Characteristics distinguishing the fundamental space groups in vector space*

Although the possible sets of points in vector space correspond to only the space groups listed in Table 1, this does not imply that the space group of the fundamental set from which the vector set is derived cannot be distinguished in the vector set. It is true that the characteristic translation component of any symmetry element in the fundamental set does not appear in the vector set as a part of the symmetry of the set, but it does appear in another way which permits it to be distinguished. When matrix (21) is arranged for a particular symmetry element, all products in the partitions along the main diagonal are products of symmetry-equivalent points in the fundamental set. Such products are concentrated in $n$ equally spaced levels per cell along the symmetry element in the vector set, where $n$ is the number of translation components of the symmetry operation equal to the lattice translation in that direction. All products of (21) which are not in the diagonal partitions are irregularly distributed throughout the unit cell of the vector set.

This implies that the translation components of all symmetry elements can be distinguished by recognizing the loci of concentration of points in vector space. Since the space lattice type and characteristic translation component of the generating symmetry elements can be thus recognized in vector space, it follows that *the space group of any fundamental set can be recognized in the vector set except that space groups differing only by a group of inversion centers cannot be separately recognized.* The space-group pair $P1$, $P\bar{1}$, also $C3$, $C\bar{3}$, for example, differ only by groups of inversion centers and cannot be separately distinguished in vector space.

These conclusions are identical with those reached by implication theory (Buerger, 1946) on a different basis, namely, that of the presence or absence of satellites.

*Example of space-group determination*

To illustrate the use of vector sets in space-group determination, the following example is cited with the permission of Dr Alfred E. Frueh (Frueh, 1947). In studying the structure of the monoclinic crystal claudetite, $As_2O_3$, the extinctions appeared to indicate the space group $P2_1/n$, but there appeared to be one questionable very weak reflection of $0k0$ with $k$ odd.

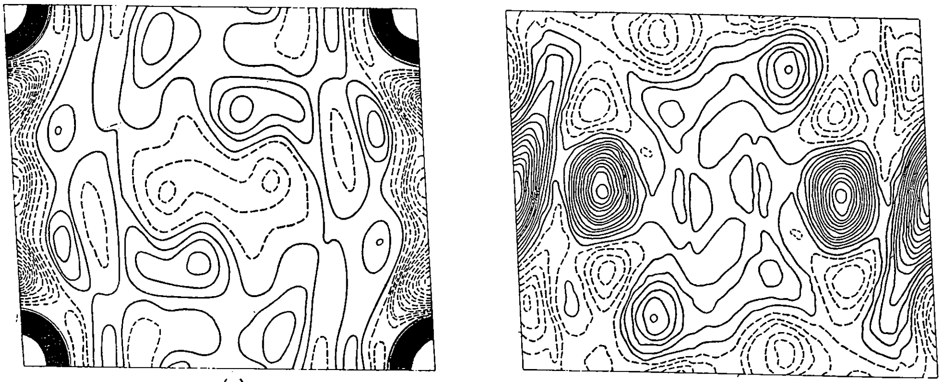
Table 1. *Space groups of the periodic fundamental points sets and the space groups of their corresponding periodic vector sets*

| Crystal system | Space group of fundamental point set | Space group of vector set |
|---|---|---|
| Triclinic | $P1$<br>$P\bar{1}$ | $P\bar{1}$ |
| Monoclinic | $Pm$, $Pc$<br>$P2$, $P2_1$<br>$P2/m$, $P2_1/m$, $P2/c$, $P2_1/c$ | $P2/m$ |
| | $Cm$, $Cc$<br>$C2$<br>$C2/m$, $C2/c$ | $C2/m$ |
| Orthorhombic | $Pmm2$, $Pmc2_1$, $Pcc2$, $Pma2$, $Pca2_1$, $Pcn2$, $Pmn2_1$, $Pba2$, $Pna2_1$, $Pnn2$<br>$P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$<br>$Pmmm$, $Pnnn$, $Pccm$, $Pban$, $Pmma$, $Pnna$, $Pmna$, $Pcca$, $Pbam$, $Pccn$, $Pbcm$, $Pnnm$, $Pmmn$, $Pbcn$, $Pbca$, $Pnma$ | $Pmmm$ |
| | $Cmm2$, $Cmc2_1$, $Ccc2$, $C2mm$, $C2ma$, $C2cm$, $C2ca$<br>$C222_1$, $C222$<br>$Cmcm$, $Cmca$, $Cmmm$, $Cccm$, $Cmma$, $Ccca$ | $Cmmm$ |
| | $Fmm2$, $Fdd2$<br>$F222$<br>$Fmmm$, $Fddd$ | $Fmmm$ |
| | $Imm2$, $Iba2$, $Ima2$<br>$I222$, $I2_12_12_1$<br>$Immm$, $Ibam$, $Ibca$, $Imma$ | $Immm$ |
| Tetragonal | $P\bar{4}$<br>$P4$, $P4_1$, $P4_2$, $P4_3$<br>$P4/m$, $P4_2/m$, $P4/n$, $P4_2/n$ | $P4/m$ |
| | $I\bar{4}$<br>$I4$, $I4_1$<br>$I4/m$, $I4_1/a$ | $I4/m$ |
| | $P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$<br>$P4mm$, $P4bm$, $P4cm$, $P4nm$, $P4cc$, $P4nc$, $P4mc$, $P4bc$<br>$P42$, $P42_1$, $P4_12$, $P4_12_1$, $P4_22$, $P4_22_1$, $P4_32$, $P4_32_1$<br>$P4/mmm$, $P4/mcc$, $P4/nbm$, $P4/nnc$, $P4/mbm$, $P4/mnc$, $P4/nmm$, $P4ncc$, $P4/mmc$, $P4/mcm$, $P4/nbc$, $P4/nnm$, $P4/mbc$, $P4/mnm$, $P4/nmc$, $P4/ncm$ | $P4/mmm$ |
| | $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$<br>$I4mm$, $I4cm$, $I4md$, $I4cd$<br>$I42$, $I4_12$<br>$I4/mmm$, $I4/mcm$, $I4/amd$, $I4/acd$ | $I4/mmm$ |
| Hexagonal | $C3$, $C3_1$, $C3_2$<br>$C\bar{3}$ | $C\bar{3}$ |
| | $R3$<br>$R\bar{3}$ | $R\bar{3}$ |
| | $C3m1$, $C31m$, $C3c1$, $C31c$<br>$C312$, $C321$, $C3_112$, $C3_121$, $C3_212$, $C3_221$<br>$C\bar{3}1m$, $C\bar{3}1c$, $C\bar{3}m1$, $C\bar{3}c1$ | $C\bar{3}1m$ |
| | $R3m$, $R3c$<br>$R32$<br>$R\bar{3}m$, $R\bar{3}c$ | $R\bar{3}m$ |
| | $C6$, $C6_1$, $C6_5$, $C6_2$, $C6_4$, $C6_3$<br>$C\bar{6}$<br>$C6/m$, $C6_3/m$ | $C6/m$ |
| | $C\bar{6}m2$, $C\bar{6}c2$, $C\bar{6}2m$, $C\bar{6}2c$<br>$C6mm$, $C6cc$, $C6cm$, $C6mc$<br>$C622$, $C6_122$, $C6_522$, $C6_222$, $C6_422$, $C6_322$<br>$C6/mmm$, $C6/mcc$, $C6/mcm$, $C6/mmc$ | $C\bar{6}/mmm$ |
| Isometric | $P23$, $P2_13$<br>$Pm3$, $Pn3$, $Pa3$ | $Pm3$ |
| | $F23$<br>$Fm3$, $Fd3$ | $Fm3$ |
| | $I23$, $I2_13$<br>$Im3$, $Ia3$ | $Im3$ |
| | $P\bar{4}3m$, $P\bar{4}3n$<br>$P43$, $P4_23$, $P4_33$, $P4_13$<br>$Pm3m$, $Pn3n$, $Pm3n$, $Pn3m$ | $Pm3m$ |
| | $F\bar{4}3m$, $F\bar{4}3c$<br>$F43$, $F4_13$<br>$Fm3m$, $Fm3c$, $Fd3m$, $Fd3c$ | $Fm3m$ |
| | $I\bar{4}3m$, $I\bar{4}3d$<br>$I43$, $I4_13$<br>$Im3m$, $Ia3d$ | $Im3m$ |

If this apparent reflection were real, the true space groups would be $P2/n$. Since crystals of claudetite are extremely plastic and can hardly be handled without bending, it appeared possible that this questionable reflection might arise from deformation of the structure. Whatever the cause, the symmetry was studied by sectioning the vector cell at $b=0$ and $b=\frac{1}{2}$ with the aid of the three-dimensional Patterson syntheses $P(x, 0, z)$ and $P(x, \frac{1}{2}, z)$, respectively. The resulting Harker sections are shown in Fig. 19. The concentration of interactions in $P(x, \frac{1}{2}, z)$ over $P(x, 0, z)$ is obvious. This indicates that the translation component of the twofold axis is $\frac{1}{2}$ and not 0. The space group is accordingly $P2_1/n$ and not $P2/n$.

Harker–Kasper inequalities (Harker & Kasper, 1947, 1948) and the relations pointed out by the writer (Buerger, 1948*a*) are partial Fourier solutions, but they cannot be complete solutions, since both are based on symmetry considerations, and these carry with them symmetry-born ambiguities (Buerger, 1948*b*). The Fourier representation of the relation between a fundamental point set and its vector set as presented in this paper remains to be found.

Secondly, the general nature of the above remarks requires, as a particular stage of the complete crystal-structure analysis, that the space group be determinable from the vector set. Specific proof is also offered of space-group determination from vector sets in this paper. This removes the limitation in the qualitative Fourier X-ray investigation of space groups by extinctions. By the qualitative method only 120 diffraction groups can be distinguished (Buerger, 1942, p. 511). But by the vector-set method, all space groups, not differentiated by a group of inversion centers alone, can be distinguished.



(*a*) (*b*)

Fig. 19. Harker sections of three-dimensional Patterson syntheses of claudetite. (*a*) $P(x, 0, z)-F^2_{000}$; (*b*) $P(x, \frac{1}{2}, z)-F^2_{000}$.

## Conclusions

In this discussion of vector sets no attention has been given to the weighting of points in the fundamental set and in the vector set. This matter has been discussed by Wrinch (1939). Furthermore, no attempt has been made to consider any of the practical difficulties which might attend the application of any of the devices which have been discussed to the solution of problems in crystal-structure analysis, and such practical difficulties are not to be construed as minimized. Nevertheless, there are some broad theoretical consequences of the theory of vector sets.

No proof has hitherto been presented that it is possible, in general, to solve a crystal structure from its diffraction data. The theory discussed in this paper supplies such proof. Since it is possible systematically to find the fundamental set or sets from the vector set, it is also theoretically possible to derive a set of atomic positions from a Patterson map. Since a Patterson map can always be prepared from diffraction data, the crystal structure can be solved from such data. It is not germane to argue that the actual process of solving a crystal structure does not necessarily proceed in this manner, but would preferably proceed by finding the phases of the $F_{hkl}$'s. This merely clothes the same problem in its Fourier representation. Since the vector representation of the problem can be solved, the Fourier representation can be solved. Doubtless the

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