

familie geschlossen werden. Zu jedem Stab gibt es 4 Stäbe, die als nächste Nachbarn zu bezeichnen sind. Das Auftreten ausgeprägter Maxima liess weiterhin vermuten, dass in der Struktur geordnete Bereiche von maximalem Ordnungsgrad vorliegen, eine Vermutung, die durch die Symmetrie der Intensitätsverteilung in den diffusen Scheibchen eine weitere Stütze findet.

Es wird gezeigt, in welcher Weise die experimentell zugänglichen Intensitäten der Maxima auf den diffusen Scheibchen zur Berechnung von verallgemeinerten Patterson- und Elektronen-Dichteprojektionen herangezogen werden können, wie mit ihrer Hilfe zwischen ketten- und ringförmigen Anionen und zwischen 'b-Fall' und 'n-Fall' unterschieden werden kann.

Meinen Mitarbeitern, Frau H. Grell-Niemann, Frau Ch. Krause und Herrn Dr. P. Sedlacek möchte ich für viele fruchtbare Diskussionen danken.

Acta Cryst. (1964). **17**, 491

A Method for the Determination of Complex Cubic Metal Structures and its Application to the Solution of the Structure of NaCd_2 *

BY STEN SAMSON

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

(Received 21 March 1963 and in revised form 17 July 1963)

Structures of intermetallic compounds of certain cubic space groups can be completely surveyed or determined with the use of a single map, the packing map, apparently irrespective of the size of the unit cell and the number of parameters involved. For certain cubic space groups two or perhaps three packing maps will have to be used. Sections through coordination polyhedra represented with transparent templates can be fitted together on the packing map which then guides the search for a reasonable structural motif. This technique is of particular value if the atomic arrangement is such as to render the interpretation of Patterson maps extremely difficult. The structure of NaCd_2 (cube edge $a_0 = 30.56 \text{ \AA}$, space group $Fd\bar{3}m (O_h^7)$) was derived with the use of a single packing map, avoiding the time-consuming construction of three-dimensional models.

Introduction

The method described here utilizes the idea of Bragg & West (1926) to determine all the possible positions of the atoms in the unit cell relative to their symmetry elements through evaluation of the domains of neighbors that must not overlap. It is well known that if a structure is sufficiently simple it can be determined this way by straightforward, completely logical argu-

ments. If a structure is of considerable complexity, however, the purely geometrical reasoning can only serve as a guide in the search for a reasonable structural motif and guesses have to be made as to the structural elements (coordination polyhedra *etc.*) as well as to other features that may be exhibited in the structure. This method of treating structure problems was termed the stochastic method by Pauling (1933, 1955). So far, it has apparently been carried out only with the use of three-dimensional models.

The present method represents a refinement of the stochastic method of treating crystals of complex cubic intermetallic compounds. It differs from the methods described by Bragg & West (1926) and

References

- DORNBERGER-SCHIFF, K. (1956). *Acta Cryst.* **9**, 593.
 DORNBERGER-SCHIFF, K. (1959). *Acta Cryst.* **12**, 246.
 DORNBERGER-SCHIFF, K. (1960). *Acta Cryst.* **13**, 999.
 DORNBERGER-SCHIFF, K. (1961). *Acta Cryst.* **14**, 1003.
 DORNBERGER-SCHIFF, K. (1964). *Grundzüge einer Theorie der OD-Strukturen aus Schichten. Abh. Dtsch. Akad. Wiss.*
 DORNBERGER-SCHIFF, K. & GRELL-NIEMANN, H. (1961). *Acta Cryst.* **14**, 167.
 DORNBERGER-SCHIFF, K. & GRELL-NIEMANN, H. In Vorbereitung.
 GRIFFITH, J. E. (1956). *Phys. inorg. Chem.* **78**, 3867.
 GRZYDER, J. W., DONNAY, G. & ONDIK, H. M. (1958). *Acta Cryst.* **11**, 38.
 JAGODZINSKI, H. (1959). *Phy. Bl.* **15**, 500.
 JARCHOW, O. H. (1964). *Acta Cryst.* Im Druck.
 JARCHOW, O. H. & DORNBERGER-SCHIFF, K. (1960). *Acta Cryst.* **13**, 1020.
 RAEUCHLE, R. F. & RUNDLE, R. E. (1952). *Acta Cryst.* **5**, 85.
 SEDLACEK, P. & DORNBERGER-SCHIFF, K. In Vorbereitung.
 WOLFF, P. M. DE (1952). *Acta Cryst.* **5**, 286.

* Contribution No. 2951 from the Gates and Crellin Laboratories of Chemistry. The work reported in this paper was carried out under Contract No. Nonr-220(33) between the California Institute of Technology and the Office of Naval Research.

Pauling (1933, 1955) inasmuch as it eliminates the time-consuming construction of three-dimensional models. This is done through the use of two-dimensional graphs, the 'packing maps', which at a glance provide the necessary information regarding the geometrical requirements for packing of coordination polyhedra to fill space. Sections through such polyhedra or through smaller or larger, more-or-less symmetrical, atom complexes may be represented with transparent templates; these can be fitted together on the packing map, and the map then guides the search for a reasonable structural motif much more efficiently than would a three-dimensional model.

It was found that structures of certain cubic space groups can be completely determined and described with the use of a single packing map, apparently irrespective of the size of the unit cell and the number of the atomic positional parameters involved.

So far, trial structures with up to 48 positional parameters and 32 crystallographically different positions with space-group symmetry $F\bar{4}3m (T_d^2)$ have been completely surveyed, each one requiring only a single packing map. The atomic arrangement in the crystal of NaCd_2 (cube edge $a_0 = 30.56 \text{ \AA}$, space group $Fd\bar{3}m (O_h^7)$) was derived, again, with the use of a single map.

The determination of such structures with the use of three-dimensional models would require a formidable effort, the total number of atoms per smallest unit cube being between 1100 and 1200. The application of Patterson maps to such structures or other more or less direct methods did not seem to offer much promise for success.

The most useful planes

Cubic crystals of metals and intermetallic compounds have always been observed to incorporate atoms in special positions. This feature probably arises from the difficulty or perhaps impossibility of achieving a cubic space-filling structure by utilizing general positions alone. One may profitably begin with the hypothesis that a special position is always needed to define the center of a coordination shell described solely or partially by a general position. Hence, if in a cubic crystal the configuration of atoms is known around each point that can be defined by a special position, the atomic arrangement of the crystal is completely determined.

In each one of the space groups $F23$, $P2_13$, $Fd\bar{3}$, $Pa\bar{3}$, $F432$, $F\bar{4}3m$, and $F\bar{4}3c$ every special position places at least one point on the (110) plane*. To determine a structure having one of these space groups

* Throughout this discussion it is understood that the origin of coordinates of the cube is placed in accordance with the Space Group Tables given in *International Tables for X-ray Crystallography* (1952). The (100) plane and the (110) plane referred to below are always those passing through the origin of the cube.

it is necessary only to determine the coordination shell around each atom or available site that is located on the (110) plane.

A similar rule applies to structures of the space groups $F4_132$, $P4_332$, $P4_132$, $Fd\bar{3}m$, $Fd\bar{3}c$ except that the special positions of the kind $\frac{1}{2}, x, \frac{1}{2} \pm x$, etc. eventually may have to receive special treatment. These positions are of such a nature, however, that they most likely will represent vertices of coordination shells around single atoms or available sites on the (110) plane, as will be seen in the following section. In the twelve space groups just referred to, the (110) plane shall be called 'the most useful plane'.

Most of the remaining cubic space groups have two most useful planes, i.e. the (100) plane and (110) plane which will have to be investigated simultaneously. In some rare cases it may be necessary to investigate one especially selected additional plane.

The packing map

A means of recognizing the possible configurations of atoms around single atoms on the most useful plane is the packing map, an example of which is shown in Fig. 1. This map has been drawn for the (110) plane of a crystal of space group $Fd\bar{3}m$ and cube edge $a_0 = 30.6 \text{ \AA}$, scale $1 \text{ \AA} = 1 \text{ cm}$ on the original map.

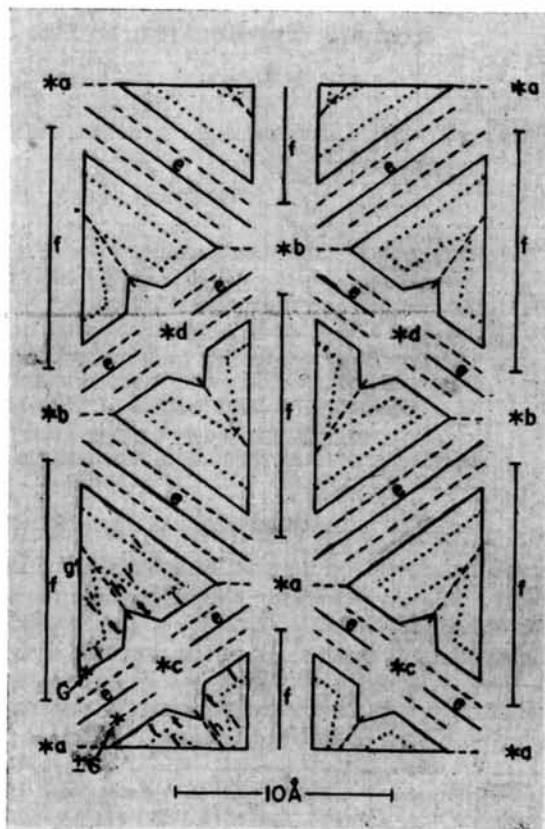


Fig. 1. Packing map for the (110) plane for a cube of edge $a_0 = 30.6 \text{ \AA}$, space group $Fd\bar{3}m$.

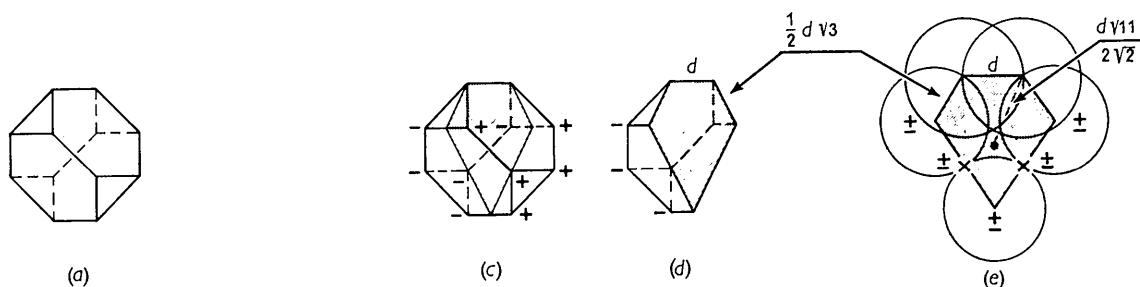


Fig. 2

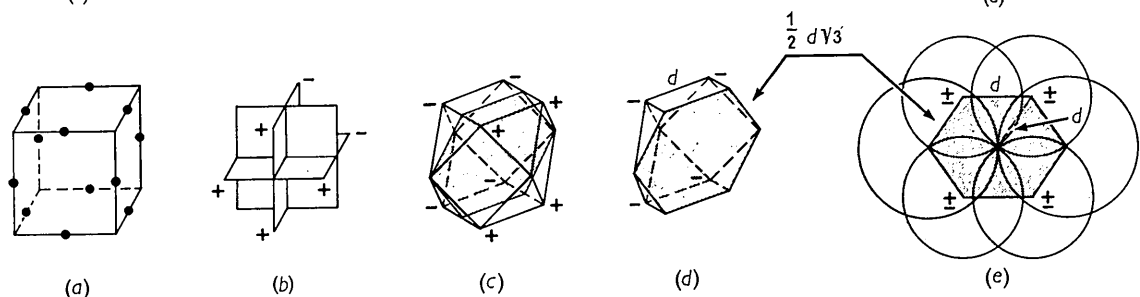


Fig. 3

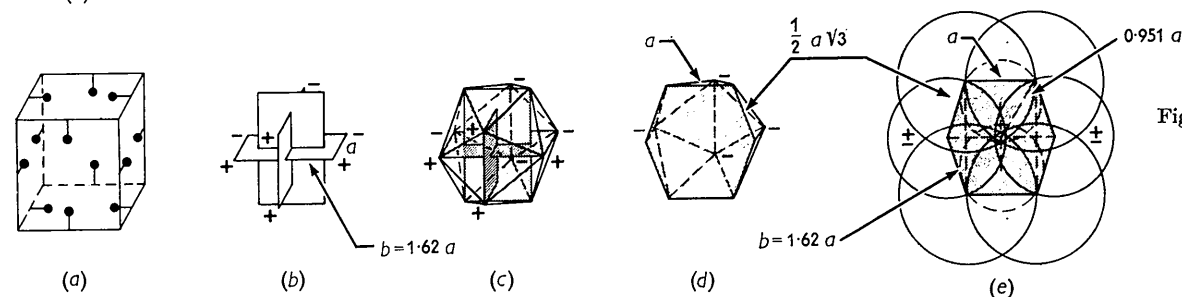


Fig. 4

Fig. 2. The truncated tetrahedron.

Fig. 3. The cubo-octahedron.

Fig. 4. The icosahedron. In Figs. 2, 3, and 4 the most practical representation of the polyhedra with respect to packing maps is shown at (e) in each case.

The points a and b are defined by the two eightfold positions, 000 etc. and $00\frac{1}{2}$ etc. respectively; c and d are points of the two 16-fold positions $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ etc. and $\frac{1}{8}\frac{1}{8}\frac{5}{8}$ etc. respectively, which are centers of symmetry. The letters correspond to the notations used for this space group in the *International Tables for X-ray Crystallography* (1952), p. 340. The same notations are referred to below.

The lines e and f are the loci of points of one degree of freedom, xxx , etc. and $00x$, etc., described by the space group positions e and f respectively. If rigid spheres of radius 1.40 \AA , equal to one-half the average interatomic distance assumed in the crystal, are placed in these positions the centers of such spheres on the (110) plane are confined as indicated in Fig. 1.

The points with two degrees of freedom, xxz , etc., positions g , are confined within the ten areas bounded by solid lines. The indentation t can be seen to be necessary to avoid interference of the spheres as they approach the center of symmetry. If G is the point xxz , its surrounding sphere of radius 1.40 cm is in contact with two equivalent contiguous spheres. The centers of these two spheres, which we call $+G$ and

$-G$, project normally onto the point $\pm G$. Since e is a threefold axis of symmetry, i.e. G , $+G$, and $-G$ are at the corners of an equilateral triangle, the point $\pm G$ is at a distance $r/\sqrt{3}$ from the line e , when G is at a distance $2r/\sqrt{3}$ from e , where r is the radius of the spheres. The broken lines are referred to as 'plus-minus' lines. A 'plus-minus' point can never lie between the solid line e and a broken line.

Positions $96h(\frac{1}{8}, x, \frac{1}{4}-x, \text{etc.})$ describe plus-minus points located on the broken lines h . These points are at the vertices of a hexagon around c , the size of which is determined by x .

The areas limited by the dotted lines i and i' and the solid line g' are 'plus-minus' fields for the general set $192i$. The isosceles triangle of the sides i' can, again, be seen to be necessary to avoid interference of the spheres as they approach the center of symmetry.

The representation of coordination polyhedra

A few examples of how coordination polyhedra may be represented for their immediate recognition on the packing map are given below.

A very frequently observed coordination polyhedron is the symmetrically truncated tetrahedron bounded by four hexagons and four triangles (Fig. 2(a)). A mirror plane of the polyhedron traces the polygonal section shown in Figs. 2(c) and (d). The packing of atoms around such a polyhedron is explored by describing around each vertex a sphere of a radius equal to the distance d between the vertex and the center of its assumed nearest neighbor outside the polyhedron. The section plane through such an arrangement of spheres is shown in Fig. 2(e). For the sake of simplicity all the distances are taken to be equal in this figure. The center of any circle of radius d is allowed to lie upon the circumference of any other circle but not inside it, while the center of any 'plus-minus' circle representing two contiguous spheres, one above and one below the section plane, is allowed to be as close as $\frac{1}{2}d/\sqrt{3}$ to the center of a circle of radius d .

Fig. 3 shows a cubo-octahedron which is represented according to the same principles. Fig. 4 demonstrates how the icosahedron can be derived through deformation of a cubo-octahedron. The three mutually perpendicular squares in Fig. 3(b) have been substituted by rectangles in Fig. 4(b); the sides of the rectangles are a and $b=1.62a$, where the side b is also the diagonal of the pentagon of side a as shown in Fig. 4(c). The representation of the icosahedron according to Fig. 4(e) was found to be the most perspicuous one with regard to packing maps so far explored. An example of the usefulness of this representation can also be found in an earlier paper (Samson, 1949), which, however, does not show the packing map.

It is seen that the circles around the vertices of the polyhedron shown in Fig. 2(e) leave a free area around the center, while in Fig. 3(e) the circles intersect at the center and in Fig. 4(e) overlap at the center. This feature demonstrates the metrical nature of these polyhedra. With twelve contiguous spheres of equal size at the vertices of the truncated tetrahedron, it is possible to accommodate a sphere 34.5% larger in radius at the center, since $(r_{\text{cent}}/r_{\text{vert}}) = (\sqrt{11}/\sqrt{2}) - 1 = 1.345$ (Fig. 2(e)) while for the icosahedron the central sphere is nearly 10% smaller than the sphere of the vertex (Pauling, 1947). The cubo-octahedron corresponds to a radius ratio equal to unity, as is well known.

Packing of coordination polyhedra

Fig. 5 represents a packing map of the (110) plane of a cube of edge $a_0=25.8$ Å, space group $F43m$, $r=1.25$ Å (smallest assumed radius). Transparent templates of polyhedra, such as are shown in Figs. 2 and 3, are held in position with pins.

The discs around e_1 and $\pm e_1$ (Fig. 5) represent a positive tetrahedron, which is surrounded by a negative tetrahedron (e_2 and $\pm e_2$). The discs at f_1 are at the vertices of an octahedron. If more discs are added at the points h_1 , h_2 , and h_3 and the corresponding \pm points, as is indicated with arrows, the arrangement

of points around f_1 is similar to that shown in Fig. 4(e); *i.e.* f_1 is at the center of an icosahedron.

It is obvious that transparent templates of sections through large atom complexes commonly observed in complex metal structures may appreciably facilitate the search for a reasonable structural motif. Such a template, which represents an atom complex observed in the γ -brass type structures is placed at point d , Fig. 5.

The derivation of structures of extreme complexity

General considerations

There exist a number of cubic intermetallic compounds for each of which the number of possible atomic arrangements provided by the theory of space groups appears to be so great that a successful attack on the problem of solving the structure may seem hopeless. A more penetrating study of such problems will, however, in general reveal that there are only a very limited number of atomic arrangements that are in accord with known fundamental structural principles and accordingly need to be considered as possible trial structures, at least in the initial stage.

A profitable approach to the problem of finding a reasonable structural motif is, of course, to consider structural elements that occur over and over again in crystals of complex intermetallic compounds. One of the most frequently observed coordination shells, the icosahedron, appears to be present in almost every complex cubic metal crystal. It is accordingly advisable to explore the packing map with templates of the kind shown in Fig. 4(e) and to mark off the points and regions at which such a coordination shell may be accommodated. In cases where there is reason to assume the simultaneous occurrence of certain types of smaller and larger coordination shells, it will be most profitable to use the largest possible shells as a starting point, as will be shown below.

The derivation of the structure of NaCd₂

The assumption was made that in the crystal of NaCd₂ (space group $Fd3m$, cube edge $a_0=30.56$ Å) many of the large atoms, the sodium atoms, have sixteen ligates, twelve cadmium atoms that are at the vertices of a truncated tetrahedron such as is shown in Fig. 2 and four sodium atoms that are located out from the centers of the hexagons of the truncated tetrahedron. The resulting polyhedron, in previous papers (Samson, 1958, 1961, 1962) referred to as the Friauf polyhedron, is very frequently observed in crystals containing atoms with metallic radii differing by about 15 per cent or more from one another. It was first observed in the Friauf phases MgCu₂ and MgZn₂ (Friauf, 1927a, b).

The packing map drawn for this crystal as shown in Fig. 1 was accordingly explored with the use of transparent templates of truncated tetrahedra of approxi-

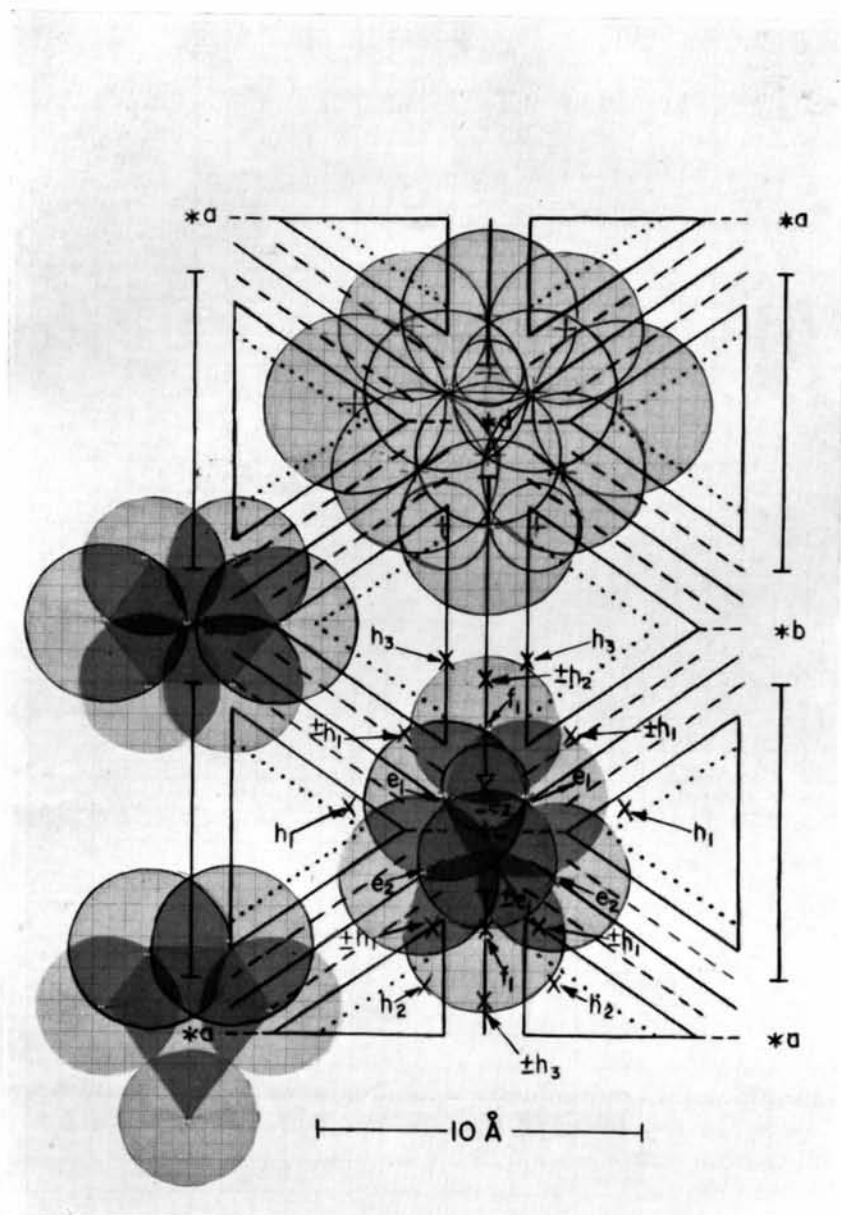


Fig. 5. Exploration of the packing spheres with the use of a packing map of the (110) plane of a cube of edge 25.8 \AA , space group $F43m$.

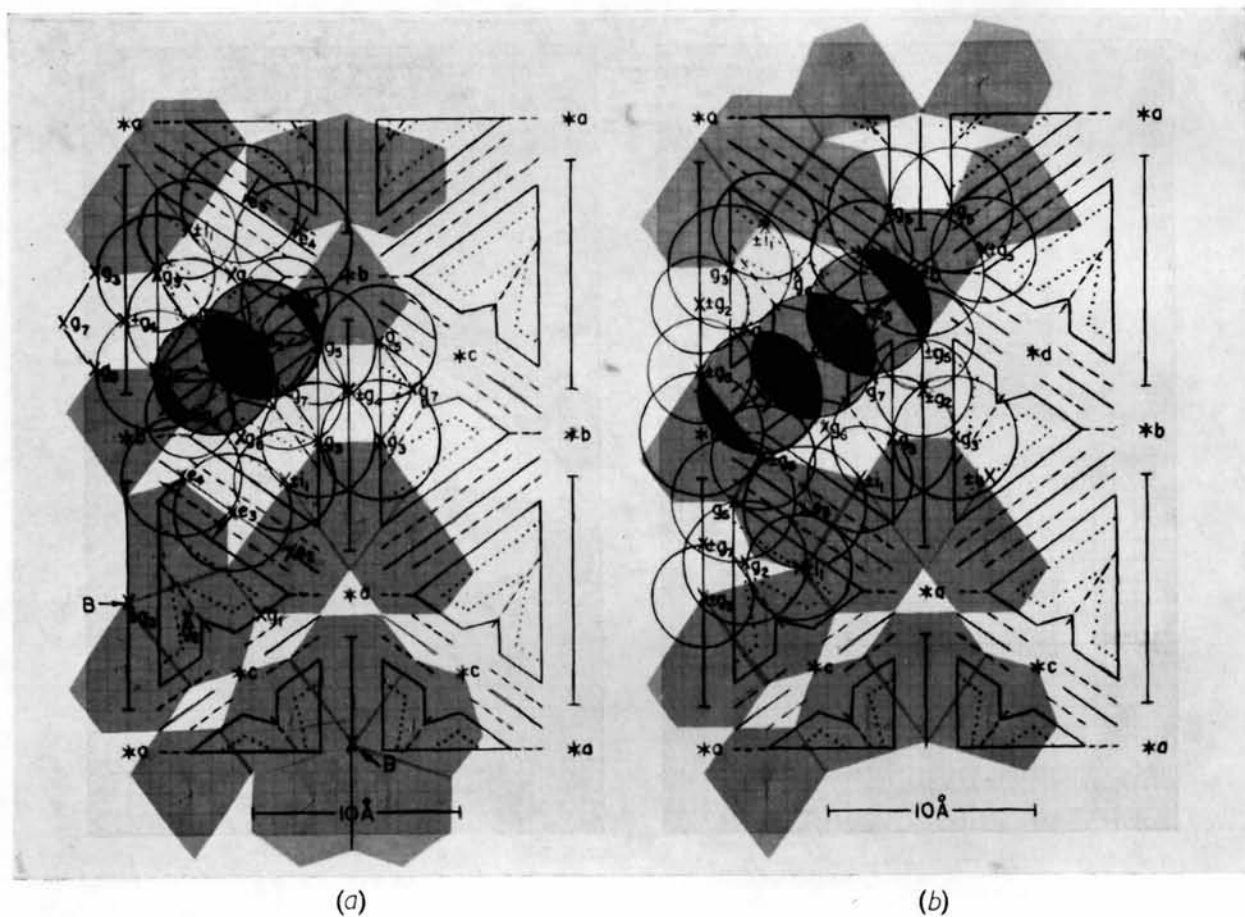


Fig. 6. The two trial structures derived for NaCd_2 . (a) The correct structure. (b) The incorrect structure. The latter motif may apply to Mg_2Al_3 .

mately the correct size as determined by the chart itself (see template at point *b*, Fig. 6*a*).

It was quickly recognized that the unit cube is most efficiently packed if the truncated tetrahedra are arranged according to Fig. 6*a*). It is seen that five such tetrahedra are located about an approximate fivefold axis of symmetry through the two points *B*, which represent vertices of an octahedron of T_d symmetry such as is described in the previous paper (Samson, 1962). Such sets of five Friauf polyhedra, referred to as the F_5 polyhedra, (Samson, 1962) share in their turn two additional Friauf polyhedra, one around *b* and the other around e_2 , Fig. 6*a*), in accordance with the $\bar{4}$ axis and the *d*-glide. This arrangement accounts for 1160 atoms distributed over 16 crystallographically different positions.

The remaining space was next explored with transparent discs, which for simplicity have been partially substituted by circles in Fig. 6*a*). Thirty-two more atoms ($32e_5$) were thus located; these are indicated with the transparent discs placed at the points e_5 . The unit cube hence contains 1192 atoms.

Fig. 6*a*) describes completely the asymmetric unit of the crystal and provides the approximate positional parameters for each crystallographically different atom. For a more detailed description of the structure refer to the earlier paper (Samson, 1962).

Fig. 6*b*) represents an alternative trial structure for NaCd_2 which is as reasonable as the one just described. It was obtained by rotating the Friauf polyhedron centered at point *b* 90° around the [001] direction and rearranging some of the other atoms. This motif of structure places 1176 atoms per unit cube, but was found by comparison of observed and calculated X-ray data not to be the motif of NaCd_2 . It remains, however, a possible trial structure for $\beta\text{Mg}_2\text{Al}_3$ (Samson, 1962).

It probably would have been possible to deduce the trial structure by using icosahedra as a starting point. Only a few icosahedra need be placed around their appropriate points, say the points *c* and g_1 , in order to suggest the existence of Friauf polyhedra, say around e_2 and g_2 (Fig. 6*a*)), and from here on there is not too much reasonable latitude for positions of the remaining atoms if due judgment is applied. It is most convenient, however, to use as a starting point the largest atom complexes anticipated in the struc-

ture, here the Friauf polyhedra. This becomes evident if one considers that there are only 280 Friauf polyhedra in the unit of structure, but that these in their turn produce 912 other polyhedra of which 528 are icosahedra. The icosahedron represents a 13-atom complex whereas a Friauf polyhedron accommodates 17 atoms, *i.e.* 31% more.

Miscellaneous considerations

The technique suggested will in general require considerable judgment and knowledge of fundamental structural principles. A few cases have been experienced, however, where the trial structure for a fairly complex crystal, for instance the crystal of $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$ (Samson, 1958), was almost rigorously derived with the technique described here. The derivation of this structure from Patterson maps would certainly have required considerable effort and time, if it would have been possible at all.

No test has as yet been made of the applicability of this method to structures other than those of complex intermetallic compounds. It seems nevertheless very likely that it will be useful for the study of any cubic crystal that is to be treated by the stochastic method, in particular if the structure is reasonably well packed, such as for example, structures of certain silicate minerals.

I thank Prof. Linus Pauling for his interest in this work. I also thank Prof. J. H. Sturdivant for valuable suggestions and discussions.

References

- BRAGG, W. L. & WEST, J. (1926). *Proc. Roy. Soc. A*, **111**, 691.
 FRIAUF, J. B. (1927*a*). *J. Amer. Chem. Soc.* **49**, 3107.
 FRIAUF, J. B. (1927*b*). *Phys. Rev.* **29**, 34.
International Tables for X-ray Crystallography (1952).
 Vol. I. Birmingham: Kynoch Press.
 PAULING, L. (1933). *Z. Kristallogr.* **84**, 442.
 PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
 PAULING, L. (1955). *Amer. Scient.* **43**, 285.
 SAMSON, S. (1949). *Acta Chem. Scand.* **3**, 809.
 SAMSON, S. (1958). *Acta Cryst.* **11**, 851.
 SAMSON, S. (1961). *Acta Cryst.* **14**, 1229.
 SAMSON, S. (1962). *Nature, Lond.* **195**, 259.