A TECHNIQUE FOR THE CONSTRUCTION OF MODELS ILLUSTRATING THE ARRANGEMENT AND PACKING OF ATOMS IN CRYSTALS

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INTRODUCTION

Recent developments have demonstrated that the vast accumulations of empirical knowledge in theoretical mineralogy and crystallography have rational explanations in the manner of arrangement of the constituent atoms in the crystals. This is not only the case regarding data bearing on what are generally considered the physical and chemical properties of crystals, but it is now also clearly indicated with regard to the external morphology or crystal habit as well.

In order to make intelligent use of the data developed by crystal structure investigations, it is necessary to obtain correct visual pictures of the structures themselves. Data in the form of cell dimensions, space group, and atomic coordinates are of very little use in this connection. Projections or drawings of the structures are more useful, but usually serve to display only certain features. Three dimensional models alone give true insight into the intricacies and interrelationships of even relatively simple structures. Their value in research in theoretical mineralogy cannot be too greatly stressed, and by the same token truly modern mineralogy can hardly be taught without their aid.

Methods for the construction of models illustrating the arrangement of atoms in crystals have been described by Wyckoff and Ksanda[1] and by Gruner.[2] Neither of these methods gives any idea of the packing of the atoms in the structures.

Several years ago a general method for illustrating both arrangement and packing of atoms in crystals was developed in this laboratory. After considerable experimentation and improvement, especially in some of the minor details of the routine, a very workable technique for the construction of such models has been evolved. It is believed that a neat, strong, packing model of any crystal structure can be made by this method no matter how complicated the structure, provided only that, in the case of the complicated arrangements, the time and labor spent on calculation and construction are worth the effort.

[1] Wyckoff, Ralph W. G., and Ksanda, C. J., A simple model for illustrating the atomic arrangements in crystals: *Am. Jour. Sci.*, 5th series, vol. 11, pp. 377–380, 1926.

[2] Gruner, John W., A new method of building crystal structure models: *Am. Mineral.*, vol. 17, pp. 35–37, 1932.

It is now pretty clearly established that atoms in crystals behave as if they were rigid or semi-rigid spheres in contact. The radius of such a sphere is constant, or very approximately so, in all cases in which the atom has the same electronic state and coordination, but differs with a change of these internal and external conditions. These radii are listed in standard references.[3,4,5] Models of crystal structures may therefore be constructed of spheres of appropriate sizes bonded together in positions to correspond with those indicated by the coordinates of the atoms established by *x*-ray investigations. The technique developed in this laboratory consists of pinning balls together by means of metal pins. Because of easy workability, wooden balls, painted to represent various atomic species, have been employed.

GENERAL TECHNIQUE

OUTLINE OF PROCEDURE

Given the data furnished by the crystal structure investigator, it is necessary, in general, to proceed by a series of distinct steps, taken in correct sequence, in order to construct a packing model of the structure. These steps are as follows:

1. Calculation of the atomic environments in the actual crystal.
2. Adjustment of atomic environments to available material.
3. Calculation of drilling coordinates.
4. Painting the balls.
5. Drilling the balls.
6. Assembling the model.

In the following section each of these steps will receive detailed consideration and in a subsequent section illustrations of the principles involved will be given by means of representative examples.

CALCULATION OF THE ATOMIC ENVIRONMENTS IN THE ACTUAL CRYSTAL

Before it is possible to proceed, the general plan of the structure must be grasped. This is sometimes illustrated in original papers; frequently it is not. Fortunately, the excellent illustrations in *Strukturbericht*[6] and

[3] Goldsmidt, V. M.; Geochemische Verteilungsgesetze der Elemente, vol. 7: *Skrifter utgitt av Det Norske Videnskaps-Akademi i Oslo I. Matem.-Naturvid. Klasse*, No. 2, **1926**.

[4] Wyckoff, Ralph W. G., *The Structure of Crystals*, 2nd ed.: pp. 192–193, New York, **1931**.

[5] *International Tables for the Determination of Crystal Structures*, 2nd vol.: pp. 610–616, Berlin, **1935**.

[6] Ewald, P. P. and Hermann, C., *Strukturbericht:* **1913–1928**; Supplement to *Zeit. Krist.*, 1931.

Wyckoff's book[7] usually provide sufficient information to reveal the plan of the structure for crystals whose structures have been known long enough to be included in these two standard references.

The plan having been grasped, the first step is to calculate the interatomic distances of the nearest neighbors of each kind of atom present. For structural types which have appeared early enough to be included in *Strukturbericht*, the coordinates of the atoms are listed in tables entitled, *Raumgruppentabelle*. The components of interatomic distances in terms of cell dimensions may be found in tables entitled, *Nachbarschaft*, to be used in conjunction with the stereographic projection, *Nachbarschaftsbild*, of the environment of the atom in question. In the latter projection the largest circles indicate nearest neighbors, the sizes decreasing with increasing distance. These circles are lettered to correspond with the components of interatomic distances given in the tables. Strukturbericht provides another table, entitled, *Substanztabelle*, in which the cell dimensions and atomic parameters together with numerical values of certain of the important interatomic distances are given for important representatives of the structural type.

When the information regarding interatomic distances cannot be obtained from *Strukturbericht* or the original article, it is necessary to calculate them from knowledge of the space group symmetry operations, cell dimensions, and parameters of the atoms as determined by the structure analysis, and available usually only in the paper describing the original investigation. Often it is possible to make the entire computation of interatomic distances graphically on a large scale with sufficient accuracy for subsequent requirements. Under any circumstances, a graphical solution is recommended as a check on the analytic geometric computations.

The calculation of interatomic distances by analytic methods is based upon the familiar relation that if the coordinates of two points, 1 and 2, referred to an orthogonal, isometric coordinate system, are x_1, y_1, z_1 and x_2, y_2, z_2, their distance apart is,

$$d = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}.$$

The coordinates x, y, z of an atom may be expressed in terms of the unit cell dimensions and angles, the parameters of the atom, and the space group operations.

It cannot be too strongly emphasized that in any but the simplest structures, it is essential to understand the space group before computations for a structure can be undertaken, and even with the computations

[7] Reference 4, part II; also, Wyckoff, R. W. G., *The Structure of Crystals:* Supplement for 1930–1934 to the 2nd ed., New York **1935**.

carried out as they are in many cases in *Strukturbericht*, a knowledge of
the space group is essential to enable one to assemble the structure.
An important point in this connection concerns the matter of right- and
left-handed units. Atoms or other units related to one another in the
space group by operations of the first sort (translations, rotations,
screws) are both right-handed or both left-handed, while if the space
group operations of the second sort (inversions, reflections, glide-reflec-
tions) relate them, they have opposite senses. This implies also that
their environments are related in this manner, and therefore the ball
drillings and ball assemblies must take into account both right-handed
and left-handed analogues in the latter instance, except under special
conditions. Failure to recognize this results in considerable confusion.

ADJUSTMENT OF ATOMIC ENVIRONMENTS

After the interatomic distances of neighboring atoms have been
calculated as above, it is possible to select balls of appropriate size to
represent the atoms to scale. Because of convenience and considerations
of availability and cost of material, the writers have chosen to build
models to the scale of 1 inch $= 2$ Å. This brings the required ball di-
ameters to between about $\frac{1}{4}$ inch and 2 inches, with the great majority
of atoms centering around a value in the region of $1\frac{1}{4}$ inches, a very
convenient dimension from several standpoints.

The sizes of the atoms in a given crystal structure are not often men-
tioned by the author of a paper describing the structure, partly because
an individual structure may in itself give no clue to absolute sizes.
The sizes can be determined, however, by a number of methods. In
the first place, there are certain definite sizes to be expected for a
given atomic species in a given electronic and coordination condition,
from which sizes the atoms deviate but little from structure to structure.
Such sizes are listed in tables.[3,4,5] Ordinarily, however, they are not
sufficiently accurate for use in a model of any given structure, and in-
ternal evidence may be usually found in each structure for refining the
values somewhat. The values for the sizes of the atoms in a crystal
can be had if the crystal has an atom, A, one of whose closest neighbors
is another atom of the same species, A. The radius of A is then half
the interatomic distance of this $A:A$ pair. The radius of A being estab-
lished, the radius of any other atom, B, which also is a closest neighbor
to A, can be had by subtracting the radius of A from the interatomic
distance $A:B$.

If the structure provides no atoms in pairs, it is then necessary to
utilize expected radius values as they stand. When this is done, it will
be found, in general, that the sum of these radii does not correspond

exactly with values required for the interatomic distances as calculated in the foregoing sections. In such instances, it is necessary to make adjustments of the standard radii either arbitrarily or based on past experience so that the interatomic distances come out approximately correct. Ordinarily, one tries to keep the ratio of the standard radii unaltered in making them fit the actual interatomic distance. This is the first kind of adjustment.

A second kind of adjustment is necessary in instances of an atom A surrounded by several atoms B at very nearly, but not quite, the same distance. In order to utilize spherical balls, it is necessary to adjust the actual position of the A atom so that all the B atoms are at the same distance, at the same time keeping all other features of the structure as nearly true as possible.

A third kind of adjustment is often necessary if the structure contains more than two species of atoms. In such cases if the interatomic distances from species A to B are satisfied by a pair of radii selected for A and B, and then the radius of C is chosen to give the correct interatomic distance AC, it frequently happens that the radius of B plus the radius of C turns out to be incompatible with the distance BC in the structure. This is because the atoms were assumed to be exactly spherical and in contact, which is an approximation. By slight adjustments of the positions of A, B, and C, the distances AB, AC, and BC may be made consistent.

A fourth kind of adjustment is necessary if the actual radii, as calculated and adjusted above, are found to require balls of sizes not available commercially. Wooden balls are available in diameters ranging from $\frac{1}{4}$ inch to $2\frac{1}{4}$ inches by steps of $\frac{1}{8}$ inch, i.e., in radius intervals of $\frac{1}{16}$ inch.[8] Interatomic distances can therefore only be approximated to

[8] Obtainable from Newton & Thompson Mfg. Co., Brandon, Vermont. Prices quoted May 24, 1935, to the writers are as follows:

Ball diameter	Price/M in lots of 5M
$\frac{3}{4}''$	$ 1.50
$\frac{7}{8}''$	1.80
$1''$	2.50
$1\frac{1}{8}''$	3.25
$1\frac{1}{4}''$	3.75
$1\frac{3}{8}''$	4.50
$1\frac{1}{2}''$	6.00
$1\frac{5}{8}''$	7.50
$1\frac{3}{4}''$	8.50
$1\frac{7}{8}''$	10.50
$2''$	11.25
$2\frac{1}{8}''$	12.75
$2\frac{1}{4}''$	14.00

An additional machine change-over charge of $2.50–$3.00 is made for each ball size.

the nearest $\frac{1}{16}$ inch in the model, corresponding with 0.125 Å in the actual crystal for the scale here adopted, 1 inch = 2 Ångstroms. All atomic positions must consequently be adjusted so as to make interatomic distances come out in integral eighth Ångstroms.

In actual practice, all of the four above adjustments are carried out simultaneously. The technique of adjustment is something of an art. The attempt is made to distort the actual structure as little as possible in carrying it out. It is important to avoid serious changes in angles of interatomic bonds in this procedure, especially in structures of non-polar nature; secondarily, it is desirable to avoid important changes in radius ratios of the atomic species involved, especially in structures of ionic nature; finally, it is desirable to avoid changes in the axial ratio and cell dimensions generally.

CALCULATION OF DRILLING COORDINATES

Before reading this section, the subject matter of which is discussed here in its correct sequence, a reader previously unfamiliar with the technique should first read the following sections on painting, drilling, and assembling in order to understand the physical requirements for the calculation of drilling coordinates.

After the adjusted structure has been completely determined, the data have to be transformed to convenient drilling coordinates. This must be borne in mind as the calculation of the structure progresses.

An atom having several packing neighbors in the structure will be represented in the model by a ball having the same number of holes. Any one of these holes may be taken as the initial hole but it is convenient to choose this origin in a position of high symmetry. This is equivalent to choosing "normal coordinates" in any analytic problem: it simplifies the entire calculating, drilling, and assembling procedure.

Ordinarily one aims to choose the origin so that in drilling there will result the smallest number of settings, in particular the smallest number of ρ settings, even at the expense of a greater number of total settings. For example, the construction of a body-centered cubic packing model requires the drilling of eight holes in each ball to represent the cubic (eight-fold) coordination of each ball. Any one of these holes could be chosen as the origin, and the subsequent drilling would require two ρ settings with three holes each, and one other ρ setting with one hole, making a total of eight holes. It is much simpler, however, to drill *nine* holes in this case: an origin hole, taken pointing along the [001] axis, and eight holes pointing along [111] axis, made with two ρ settings having four holes each. The initial hole is not used for bonding in this case;

it simply affords a convenient hold for the ball to utilize the most convenient drilling coordinates. This feature is illustrated in the sulvanite calculation given beyond.

<div align="center">PAINTING</div>

The writers have found that the best and quickest painting procedure is as follows:

Drilling first hole. In order to paint a ball it is necessary to provide some means by which the ball may be grasped and handled. This is accomplished by drilling an initial hole in the ball and inserting a matchstick, the head of which has been removed. All holes are made with a $\frac{1}{8}$ inch drill, and drilled exactly $\frac{3}{8}$ inch deep, except in balls $\frac{3}{4}$ inch in diameter or smaller.

The wooden balls as received from the manufacturer are slightly elliptical. Inconvenience and distortion of models may result unless the effects of this ellipticity are minimized by drilling the first hole in the direction of the axis of the rotation ellipsoid. This hole is taken as the origin to which subsequently drilled holes are referred. The axis of a ball is readily ascertained by the flattening at the poles and the concentric striations which were formed during the manufacture.

Priming coat. As indicated above, the balls are handled by means of matchstick inserts. The balls are mounted in racks by sticking their matchsticks into rows of holes drilled in wooden'boards. The priming coat is applied to many balls at once by inverting these racks and dipping the appended balls into a bath of the priming material or agent. Raw shellac, mixed with an equal volume of methyl alcohol, constitutes a cheap and efficient agent. A narrow sheet copper trough makes a suitable container for the bath.

Non-metallic finish. After the priming coat on the balls has dried, they are dipped individually[9] in Duco of the desired color. After dipping, the matchstick handle of a ball is replaced in the rack and the ball allowed to dry. This technique gives a durable, smooth, glossy finish to each ball. An advantage is the presence of a slight puckering in the paint which occurs around the matchstick while the ball is drying. This serves to distinguish the initial origin-of-coordinates hole from other holes, a great convenience when assembling the model.

Metallic finish. Metallic elements have been successfully represented by gilding balls with metallic powders suspended in lacquer. After the priming coat, the balls are individually dipped into a suspension of Sapolin metallic gilding powder (Sapolin Co., Inc., New York) in Rogers clear brushing lacquer (Detroit White Lead Works, Detroit, Mich.).

[9] Spraying by means of a paint gun has been tried but found to be unsatisfactory; the finish is uneven and much paint is wasted.

The proportions of the proper mixture seem to vary slightly from time to time. About 0.5 oz. of copper powder or 15 c.c. of aluminum powder to 100 c.c. of lacquer provide a mixture which does not have to be greatly diluted or thickened to attain the desired consistency. Mechanical agitation is required to mix the materials evenly. The writers have used the following metallic powders: copper, aluminum, and brass. Bronze and gold powders are also available.

DRILLING

Drilling of the appropriate holes in the balls is accomplished on the machine illustrated in figure 1. It has been described in detail elsewhere.[10]
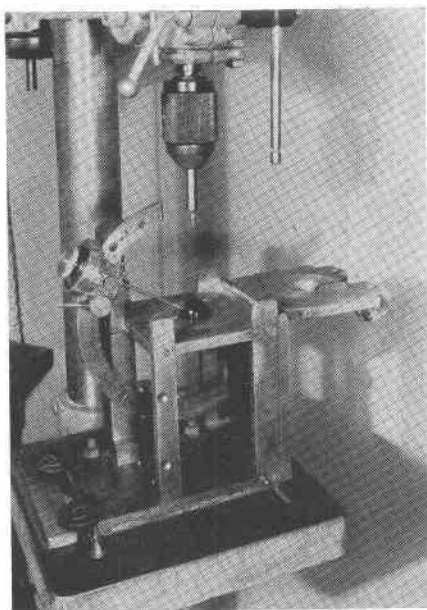
FIG. 1. Ball orienting device attached to drill press.

The device has been designed so as to drill any possible holes which are necessary to bond the individual ball to its neighbors in the completed model. The coordinates for the holes are expressed in ρ and ϕ angles, where ρ is the co-latitude and ϕ the longitude. Thus, the first hole, which has already been drilled and into which the matchstick handle was inserted in the painting procedure, has for coordinates $\rho=0$, $\phi=0$. Any hole on the equator of a ball has the co-latitude co-

[10] Buerger, M. J., A device for drilling oriented holes in spheres required in the construction of crystal structure models: *Rev. Sci. Inst.*, Vol. 6, pp. 412–416, 1935.

ordinate, $\rho = 90°$. A steel orienting rod is inserted in the initial hole of the ball about to be drilled, and this is then attached to the instrument through a hollow shaft to which it is clamped.

The dial attached to the hollow shaft indicates the meridian angle, ϕ. The entire ϕ assembly slides in a grooved track in the ρ arc to which it may be clamped at any desired ρ setting. In figure 1, the ρ angle setting is about 60°.

The procedure for drilling a hole consists of setting the ρ angle on the vertical arc, turning to the correct ϕ angle on the dial, clamping the ball tightly, and then drilling the hole. The clamp is always completely opened when settings are changed.

In any machine of this type clamping may introduce a slight rotation of a ball in its seat about the orienting rod axis. This presents a serious error. The rotation can be easily detected by the change in reading of the ϕ dial which is free to rotate with any movement of the ball. When this error occurs, the clamp should be opened, the ϕ dial reset, and the clamp again tightened.

After all required holes are drilled in a ball, the rod is unclamped from the hollow shaft and the ball removed. An experienced operator can drill between 15 and 40 balls per hour, depending, of course, on the number of individual settings involved.

Assembling

Pinning. The models are assembled by bonding the drilled balls to one another by means of short brass pins. Eighth-inch brass rod stock is clipped into pins $\frac{5}{8}$ inch long. Clipping burrs, present on the ends of the pins, are easily removed by rotating the pin held in a special clamp, against a small emery wheel.

Layer types of structures, of which molybdenite is an example, consist of discreet sheets of atoms. Atoms within the same sheet pack normally, but the nearest atoms of neighboring sheets are separated by greater than packing distances. To bond these separated sheets in the representation of the actual structure, pins are used which have been cut to the length required to separate the atoms by the appropriate spacing as shown in figure 2. Models of such layer structures are packing models in every sense, the packed sheets being held apart at their actual scale non-packing distance by the brass rods.

Omission of outside holes in the outer balls of a model, because no further bonding is necessary in this direction, involves greater difficulty in the end in the way of calculation, orientation, and assembly than is required to drill *all* holes, whether used or not. Furthermore, the presence of outside holes on the finished model allows it to be extended,

should the need arise. These outside holes also indicate the positions of neighboring atoms in the extended structure.

Orientation. The orientation of the ball with respect to its normal coordinates can be recognized by picking out the ellipsoid axis by means of the puckered ring of paint around the first hole, together with the arrangement of holes about this axis. In cases of close correspondence of the actual, distorted coordination environment with an ideal one (octahedral, for example), the orientation may be recognized by plugging all holes with long brass pins.
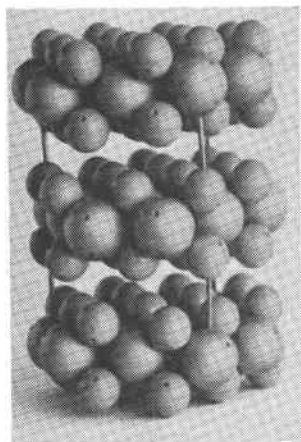
Fig. 2. Model of a layer structure: molybdenite. Large balls represent molybdenum atoms, small balls, sulfur atoms. The structure displays normal packing within sheets, but there is no packing between the atoms of adjacent sheets. In the model, the sheet spacing is maintained by occasional spacing rods of appropriate length.

In general, it is necessary to orient a ball in the structure so that the axes and drilling array of equivalent balls are related by space group symmetry operations.[11] This requires the axes of equivalent balls to be related by these symmetry operations. In some cases, however, simpler drilling and assembling may be attained by purposely disregarding space group symmetry with respect to the ball axes, and arranging to have all ball axes point the same way. For example, in the diamond structure, the balls ought to have tetrahedral symmetry; actually they have an approximately cylindrical symmetry. The diamond structure and certain derived structures are accordingly best built by taking

[11] In this connection the reader should reread the last part of the section entitled, CALCULATION OF THE ATOMIC ENVIRONMENT IN THE ACTUAL CRYSTAL, with particular regard to the possibility of atoms being related by having right- and left-handed environments.

the ball axis as either the crystallographic [001] axis or the crystallographic [111] axis, and orienting *all* balls along either one or the other of these two axes. This gives the resulting structure a slight dimensional distortion of tetragonal or hexagonal symmetry, respectively, because of the slightly elliptical nature of the balls, but gives a well-fitted model.

Methods. Models are assembled by pegging the holes in the balls with the brass pins and uniting balls to their proper neighbors. Various difficulties are likely to be encountered in the very close-packed structures. These are minimized by omitting brass pins in certain holes. This omission, if appropriately practiced, does not weaken the model.

Most favorable assembly conditions are realized in models assembled in sheets which can be pegged together. The construction of the sheets is easiest if they can be made up of strings which can be pegged together. Worst construction conditions occur if the structure does not permit sheet-like assemblage, but requires balls or units to be placed into the structure as individuals.

Each separate structure presents a distinct problem in calculation, adjustment, drilling, orientation, and assembling which, when correctly carried out, may be made to yield an excellent model.

EXAMPLES OF CALCULATIONS
INTRODUCTION

In the foregoing section, the calculations required for the construction of crystal models have been discussed in very general terms. In order to illustrate the application of some of the more important principles discussed, examples of calculations for two structures, marcasite and sulvanite, are included in the present section. Marcasite provides an illustration in which very little adjustment is necessary for the construction of an appropriate model, while sulvanite illustrates the adjustments necessary when three different atomic species of dimensions incompatible with available ball sizes, must be fitted into a structure.

MARCASITE STRUCTURE

Introduction. The data necessary for the construction of a model of the marcasite structure are found in the original article[12] which should be consulted in connection with the following calculations. These include the following information:

Unit cell: $a = 3.37$ Å
             $b = 4.44$ Å
             $c = 5.39$ Å

[12] Buerger, M. J., The crystal structure of marcasite: *Am. Mineral.*, vol. **16**, pp. 361–395, 1931.

Space group: V_h^{12}

Iron atoms (on symmetry centers) at: $[[000]]$ and $[[\frac{1}{2}\frac{1}{2}\frac{1}{2}]]$

Sulfur atoms (on reflection planes) at: $[[0u_b v_c]]$, $[[0\bar{u}_b \bar{v}_c]]$,

$$[[\tfrac{1}{2},\tfrac{1}{2}-u_b, \tfrac{1}{2}+v_c]], \text{ and } [[\tfrac{1}{2},\tfrac{1}{2}+u_b, \tfrac{1}{2}-v_c]]$$

where
$$u_b = .203 + .01$$
$$v_c = .375 + .01$$

(Conventional marcasite orientation, origin at a symmetry center.)

Paired sulfur distances   2.25 Å
Sulfur-iron distances   2.21 Å and 2.24 Å

It will be observed that the sulfur-iron distances actually found for marcasite are of two kinds which are almost, but not quite identical, namely 2.21 Å and 2.24 Å. Since it is physically impossible to pack spheres in contact so that there will be two non-identical central distances between spheres of two kinds, after this fashion, it is necessary to adjust the structure so that all iron-sulfur packing distances are equal.

Choice of ball sizes. The appropriate ball sizes are selected as follows: The paired sulfur distance is 2.25 Å. From this it follows that the sulfur radius is half this, or 1.125 Å. The sulfur atom can therefore be represented exactly by a ball $1\frac{1}{8}$ inches in diameter on the scale adopted (1 inch = 2 Ångstroms). By subtracting the actual sulfur radius, 1.125 Å, from the sum of the iron and sulfur radii, one arrives at two apparent iron radii, depending on which sulfur-iron distance is used:

$$Fe + S = 2.21 \text{ Å and } 2.24 \text{ Å}$$
$$S = 1.125 \quad \text{and } 1.125$$
$$\overline{Fe \quad = 1.085 \text{ Å and } 1.115 \text{ Å}}$$

The available ball diameters in this region represent radii of 1.000 Å and 1.125 Å, respectively. Obviously, the iron atom is best represented by a ball of $1\frac{1}{8}$ inches diameter.

Adjustment to packing requirements. The actual marcasite structure must now be slightly distorted so that it appears to be composed of sulfur atoms 1.125 Å in radius and iron atoms 1.125 Å in radius, with a paired sulfur distance of 2.25 Å and a closest iron-sulfur distance of 2.25 Å. This can be accomplished in many different ways. The situation can be grasped from figures 3a and 3b, the notation of which is the same as in the illustration in the original article. The distances AO and AD must be reduced to equality with BA, which is already correctly 1.125 inches. Two simple ways are open to accomplish this:

(1) Alter the sulfur parameters until AO is 1.125 inches, keeping the sulfur-sulfur spacing constant; then respace the (100) sheets until the iron-sulfur spacing AD equals 1.125 inches.

(2) Leave the sulfur atoms untouched, increasing the cell height slightly until the iron-sulfur spacing, AO, equals 1.125 inches; then respace the (100) sheets until the iron-sulfur spacing AD equals 1.125 inches.
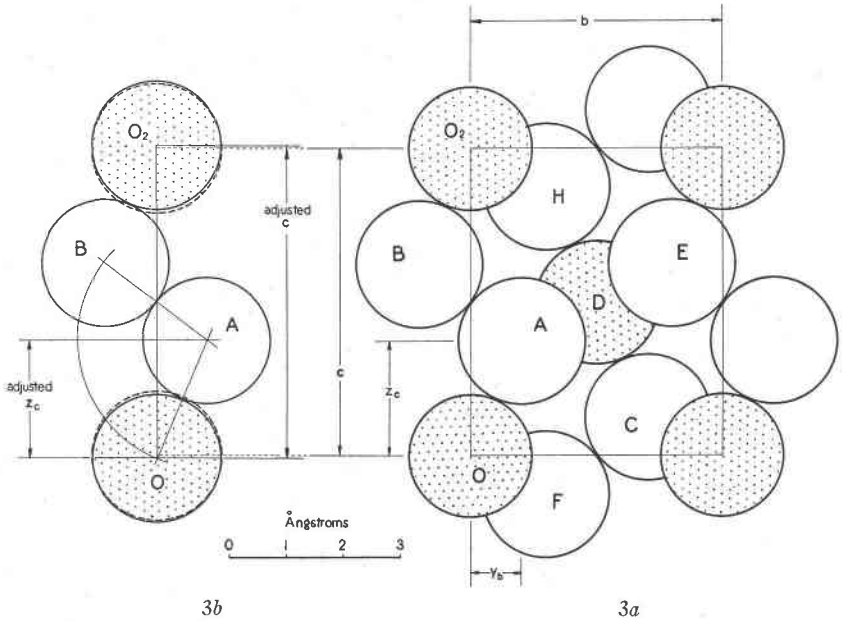

3b   3a

FIG. 3. Projection of the marcasite structure on (100). 3a. Projection of the actual structure. 3b. Graphical adjustment of the structure to the requirements of commercially available balls.

The second alternative is arbitrarily adopted here, and illustrated in figure 3b.

The adjustment is readily accomplished graphically as shown in the illustration. $AB \wedge (001)$, 36.9° (determined from the cosine relation of y_b and $AB/2$) has been laid off at $[[00\frac{1}{2}]]$ on the scale projection of part of the (100) plane. The dotted horizontal lines on the projection represent the traces of (001) planes which limit the c-axis length of the actual cell.

If spheres 1.125 Å in radius are used to represent Fe atoms (dotted circles), the overlap represents the obvious misfit in this actual cell. The correct packing condition is given by the full circles which determines the adjusted cell height indicated by the full lines.

On the scale projection the equality, $AB = AO$, is realized graphically by describing an arc using A as a center and AB as radius. The adjusted position of O is indicated by the full-lined circle. The distance separating the nearly coincident dotted and full circles is one-half the c-axis adjustment. The net results of this adjustment are a slight change in the length of the c-axis of the unit cell, and consequent changes in the z_c parameter and dependent angles.

Revised data to this point are as follows:

New c-axis length $= 5.52$ Å (graphically)

New $z_c =$ original $z_c + \dfrac{\text{new } c - \text{original } c}{2} = 2.08$ A

New $v_c = \dfrac{2.08}{5.52} = .377.$

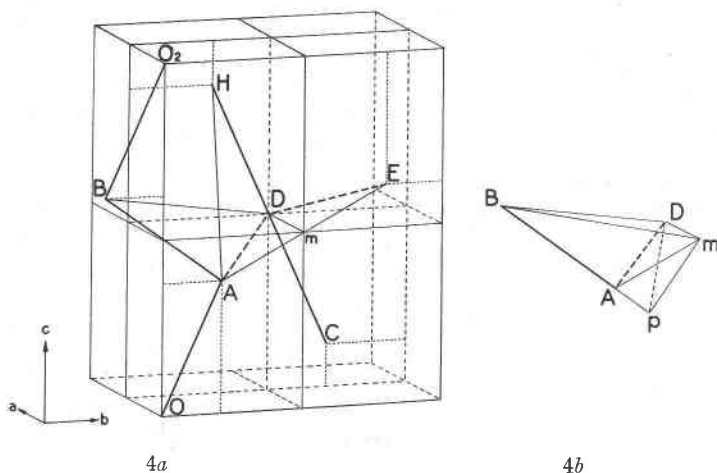4a   4b

Fig. 4. Some geometrical aspects of the marcasite crystal structure useful in the derivation of adjusted structure data and in the calculation of drilling coordinates.

The clinographic projection, figure 4a, has been constructed to show the essential coordination of an Fe atom, D, and a sulfur atom, A. The entire unit cell is outlined, but only the positions of certain atoms in two adjacent (100) planes are indicated.

Heavy full lines in the projection represent bondings within (100) planes; heavy dashed lines, the bondings between adjacent (100) planes; and the lighter lines indicate the unit cell, certain triangles useful in the computation, and parameters which fix atomic positions. Capitalized block letters denote atoms, and small letters, points useful in the computations.

For subsequent computations, the length of the *a*-axis of the structure when using the requisite ball diameters is necessary. This adjustment fits together the adjacent (100) planes. The interatomic distance, *DA*, of the actual structure is 2.24 Å, and the distance in the model must correspond to 2.25 Å, thus requiring a change in the distance *Dm*. The length of the *b*-axis and the positions of the two sulfur atoms, *A* and *E*, are not altered in this type of adjustment. Right triangle, *ADm*, is readily solved by the relation,

$$Dm = \sqrt{(AD)^2 - \left(\frac{AE}{2}\right)^2} = 1.694 \text{ Å}.$$

The increase in $a/2$ is 0.009 Å.

These calculations provide a slightly idealized marcasite structure composed of spheres in packing contact. This revision of cell constants constitutes a necessary preliminary to the calculation of drilling coordinates.

Calculation of Drilling Coordinates. As stated before, the most convenient origin of coordinates (initial hole of ball) is chosen with due regard to the space group symmetry and such that the easiest drilling coordinates will be realized. In the marcasite structure, the origin of coordinates for both Fe and S has been chosen in the (100) plane. Fe atom, *D*, has six S atoms grouped about it. The most convenient origin of coordinates about *D* is in the direction $D \rightarrow H$. Similarly, $A \rightarrow B$ is selected as the direction of origin of coordinates about S atom, *A*.

The $\angle$ BAO can be determined graphically from figure 3*b* as 103.5°. This is one of the necessary ρ angles for the drilling of S atom, *A*. In order to obtain the value of the other ρ angle for the S atom, $\angle$ *BAD*, triangle *BAD* must be solved. Triangle *BAD* is isosceles as a result of previous adjustment to ball sizes.

$$BA = AD = 2.25 \text{ Å}$$
$$B = [[0, -y_b, 1-z_c]]$$
$$D = [[\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}]].$$

According to the relation given on page 152,

$$BD = \sqrt{\left(\frac{a}{2} - 0\right)^2 + \left(\frac{b}{2} - [-y_b]\right)^2 + \left(\frac{c}{2} - [c - z_c]\right)^2} = 3.61 \text{ Å}.$$

$$\sin \angle \frac{BAD}{2} = \frac{\tfrac{1}{2}(BD)}{AD}, \text{ whence } \angle \frac{BAD}{2} = 53.3°$$

$$\angle BAD = 106.6°.$$

Solution of triangle HDA for HDA, a necessary angle of Fe, is similar to the solution of triangle BAD.

$$AD = DH = 2.25 \text{ Å}$$
$$A = [[0, \, y_b, \, z_c]]$$
$$H = \left[\left[\tfrac{1}{2}, \tfrac{1}{2} - y_b, \tfrac{1}{2} + z_c\right]\right]$$
$$AH = \sqrt{\left(\frac{a}{2} - 0\right)^2 + \left(\left[\frac{b}{2} y_b\right] - y_b\right)^2 + \left(\left[\tfrac{1}{2} + z_c\right] - z_c\right)^2} = 3.16 \text{ Å}.$$
$$\sin \angle \frac{HDA}{2} = \frac{\tfrac{1}{2}(AH)}{HD}, \text{ whence } \angle \frac{HDA}{2} = 44.6°$$
$$\angle HDA = 89.2°.$$

Figure 4b illustrates the relation between bond angles and ϕ angles. Half the bond angle, DAm, projects on a plane normal to the origin direction, AB, to give a ϕ-angle, Dpm, of the ball A.

$$\angle DAp = 180° - \angle BAD = 73.4°$$
$$\sin 73.4° = pD/DA, \text{ whence } pD = 2.16 \text{ Å}$$
$$\sin \angle Dpm = Dm/Dp = \frac{a/2}{Dp}, \text{ whence } \angle Dpm = 51.3°.$$

Ordinarily, the calculation of the ϕ angle for the drilling of the iron atom, D, would be carried out in a manner analogous to the calculation of the ϕ angle for drilling of the sulfur atom, A, just discussed. The fortuitous position of the plane containing the atoms A, D, and E, however, at a deviation of only 0.8° from normality with the origin direction, DH, renders the ϕ angle substantially equivalent to the bond angle $\angle ADE$, and simplifies calculations. In this case, therefore, solution of triangle ADE will give the ϕ angle of Fe atom, D. $\angle ADE/2 = \angle ADm$ is desired.

$$AD = DE = 2.25 \text{ Å}$$
$$AE = 2.96 \text{ Å (original paper)}$$
$$\sin \angle ADm = \frac{AE/2}{AD}, \text{ whence } \angle ADm = 41.1°.$$

Derivation of Drilling Coordinates. In the previous section, angles necessary for the derivation of the drilling coordinates, ρ, the co-latitude, and ϕ, the longitude, have been calculated. Appropriate choice of ball orientation with regard to the symmetry of the positions of the atoms leads to a minimum amount of further calculation.

Consideration of figures 4 and 5 illustrates the application of symmetry to derivation of drilling coordinates. Figure 5 shows the elevation and plan of the drilling environments of S atom, A, and Fe atom,

D. Projection points, p and m, are diagrammatically indicated. The Fe atom, D, has a center of symmetry; the S atom, A, does not possess one. In each case, the position of the symmetry plane, (001), is indicated on the plan view.
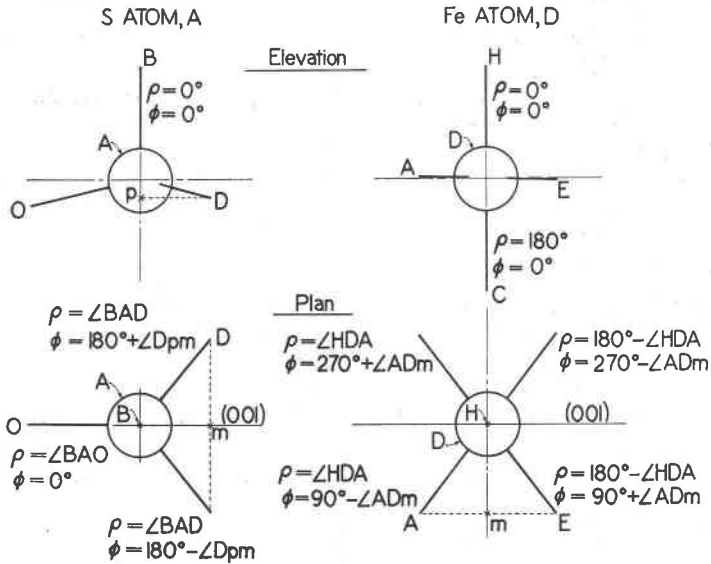

FIG. 5. Plans and elevations of balls representing sulfur and iron atoms in the model of the marcasite structure, showing drilling coordinates.

Since the origin of coordinates of S atom, A, has been chosen in the direction, $A \rightarrow B$, and atom O is located on the symmetry plane which is chosen in the direction $\phi = 0°$ and $\phi = 180°$, the determination of $\angle BAO$ locates the hole to be drilled in A which will bond it to atom O. The machine in use (figure 1) requires drilling coordinates to increase in longitude angles in a counterclockwise direction. Drilling of the hole for the bond, $A \rightarrow D$, has been located by ρ angle BAD, and ϕ angle Dpm which is referred to the $A \rightarrow O$ direction in the (001) plane. Coordinates of the remaining hole to be drilled in the S atom are immediately apparent from the symmetry.

The centro-symmetrical aspect of the environment of the Fe atom, D, plus the presence of the symmetry plane permit the coordinates of one bond to be established with reference to an origin, from which the drilling coordinates of the others may be immediately derived from symmetry. Thus, ρ angle HDA, and the complement of ϕ angle ADm locate the drilling coordinates of the hole, $D \rightarrow A$ of atom D, with reference to $D \rightarrow H$ as the initial hole, and to the symmetry plane (001) as the direction, $\phi = 0°$ and $\phi = 180°$. The coordinates for the reflection equivalent of

atom A are easily derived by symmetry, from which the coordinates for bonds to the atoms of the centro-symmetrical pair may be determined. The coordinates to atom C are obviously $\rho = 180°$, $\phi = 0°$ as $D \rightarrow H$ is the initial hole.

Drilling coordinates for the marcasite model are given in Table 1.

TABLE 1

DRILLING COORDINATES FOR BALLS USED IN MARCASITE
CRYSTAL STRUCTURE MODEL

Atom	Bond to	Drilling Coordinates	
		ρ	ϕ
S	Fe	0	0
	Fe	$\angle BAO = 103.5°$	0
	Fe	$\angle BAD = 106.6°$	$180° - \angle Dpm = 128.7°$
	Fe	$\angle BAD = 106.6°$	$180° + \angle Dpm = 231.3°$
Fe	S	0	0
	S	$\angle HDA = 89.2°$	$90° - \angle ADm = 49°$
	S	$\angle HDA = 89.2°$	$270° + \angle ADm = 311°$
	S	$180° - \angle HDA = 90.8°$	$90° + \angle ADm = 131°$
	S	$180° - \angle HDA = 90.8°$	$270° - \angle ADm = 129°$
	S	$180°$	0

A photograph of the completed model of marcasite is shown in figure 6.
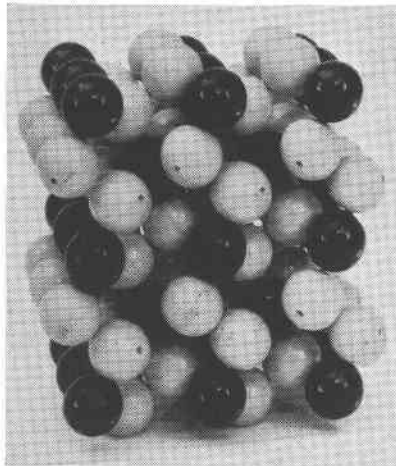

FIG. 6. Model of the crystal structure of marcasite constructed in accordance with the procedure outlined in the accompanying text. The model contains eight unit cells plus some bordering sulfur atoms necessary to complete the sulfur pairs.

SULVANITE STRUCTURE

Introduction. The data needed to calculate the coordinates for a model of the sulvanite structure are found in the original article.[13] These include the following:

Unit cell: $a_0 = 5.37$ Å

Contains 1 Cu_3VS_4

Space group: $T_d{}^1 - P\bar{4}3m$

Atomic arrangement:

V at [[000]]

3 Cu at [[$\frac{1}{2}$00]], [[0$\frac{1}{2}$0]], [[00$\frac{1}{2}$]]

4 S at [[uuu]], [[$u\bar{u}\bar{u}$]], [[$\bar{u}u\bar{u}$]], [[$\bar{u}\bar{u}u$]].

where $u = 0.235$

Coordination distances:

Cu: S = 2.285 Å

S: S = 2.186 Å

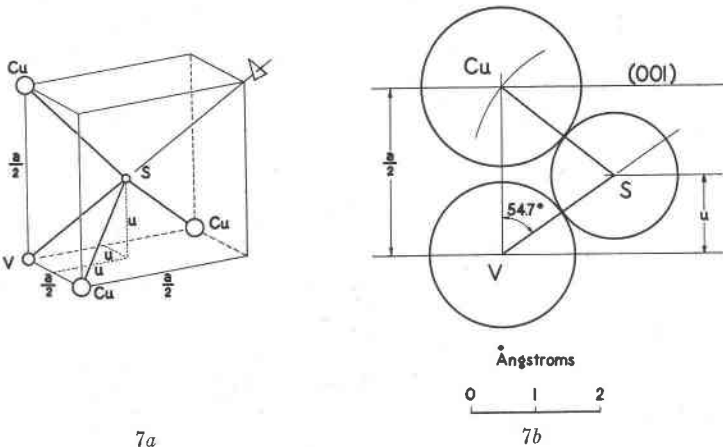7a   7b

FIG. 7. Some geometrical features of the sulvanite structure.

7a. Positive octant of the structure containing the origin (at V).

7b. (1$\bar{1}$0) plane through the origin of 7a, illustrating the adjustment of the structure to the packing requirements of commercially available balls.

The diagram in the original article gives an excellent idea of the structure. Some of its essential characteristics necessary for the present purposes are illustrated in figure 7a which shows one octant of a unit cell. The metals occupy special positions at certain corners while the S is located along the trigonal axis, its position being defined by the parameter u.

[13] Pauling, Linus and Hultgren, Ralph, The crystal structure of sulvanite, Cu_3VS_4: *Zeit. Krist.*, vol. **84**, pp. 204–212, 1933.

Choice of ball sizes. The packing conditions can be best studied in the (1$\bar{1}$0) plane through the origin; this contains all three atoms. Figure 7*b* illustrates this. It will be observed that with the V, Cu, and S positions as shown it is possible to have various coordination effects depending on the relative atomic sizes. Thus, if the S is small it would be possible for the V and Cu atoms to be in contact. In order to get some notion of the packing, the normal radii of Cu, S, and V in tetrahedral and other non-polar structures[14,15] may be tested. These radii are as follows:

$$Cu = 1.35 \text{ Å}$$
$$S = 1.04 \text{ Å}$$
$$V = 1.32 \text{ Å}$$

These radii prove to be definitely inconsistent with the sulvanite structure as given. The sum of the expected V and S radii, 2.36 Å, is considerably in excess of the V:S distance, 2.186 Å, given by Pauling and Hultgren. If the S parameter were approximately .25 instead of .235 as given, the V and S would not only pack perfectly with the expected radii, but the Cu atoms would also be surrounded by an ideally tetrahedral S environment which is not the case in Pauling and Hultgren's structure. The object of the present discussion, however, is to lead to a model of the sulvanite structure substantially identical with the one described in the original article. In selecting atomic dimensions for the structure, the following actual radius relations are important:

$$Cu + S = 2.285 \text{ Å}$$
$$\frac{V + S = 2.186 \text{ Å}}{Cu - V = 0.099 \text{ Å}}$$

This indicates that whatever ball sizes are chosen to represent the Cu and V atoms, the radius of the Cu atom should exceed the radius of the V atom by 0.099 Å. The best approximation possible with the ball sizes available is to have the Cu and V balls differ in diameter by 0.125 inch.

This condition gives no clue to the absolute atomic radii necessary to represent the structure. If, however, the radius of any one atom is decided upon, the radii of the other two follow from the geometry of the positions of the three atoms, figure 7*b*, together with the condition noted above. Taking the radius of the S atom as the standard non-polar sulfur radius 1.04 Å the atomic radii become:

[14] Pauling, Linus and Huggins, M. L., Covalent radii of atoms and interatomic distances in crystals containing electron-pair bonds: *Zeit. Krist.*, vol. **87**, p. 218, 1934.

[15] *Ref.* 4, pp. 192–193.

$$S = \qquad 1.04 \text{ Å}$$
$$Cu = 2.285 - 1.04 = 1.245 \text{ Å}$$
$$V = 2.186 - 1.04 = 1.146 \text{ Å}.$$

Adopting the standard scale of 1 in. = 2 Å, the available ball diameters best approximating these atomic sizes are as follows:

S   1.00 inch   diameter = 1.00 Å radius

Cu 1.25 inches diameter = 1.25 Å radius

V   1.125 inches diameter = 1.125 Å radius

Adjustment to packing requirements. The necessary adjustment of these ball sizes to the structure may be conveniently and simply carried out by graphical means as illustrated in figure 7*b*. Half the tetrahedral angle, angle Cu−V−S = 54.7°, is laid off in a (1$\overline{1}$0) plane. The S position is located in this direction at the adjusted V:S interatomic distance, 2.125 Å. The intersection of the *a*-axis with an arc of radius equal to the adjusted Cu+S interatomic distance, 2.25 Å, centered at the adjusted S position, fixes the adjusted Cu position satisfying packing requirements. Revised cell data are:

$$a = 5.35 \text{Å}$$
$$u = .234$$

Calculation of drilling coordinates. The origin of coordinates of V may be chosen either in the direction V→S or V→Cu. By choosing V→Cu as the origin direction, the ρ angle for V is the angle Cu−V−S = 54.7° of figure 7*b*, and may be read from the figure. This choice eliminates the effects of irregularities in the balls. The ϕ angles are fixed by the space group symmetry at 90° intervals.

Choosing the direction Cu→V as the origin direction of Cu, the requisite ρ angle, V−Cu−S, may be read from figure 7*b* as 49.8°. This origin direction eliminates effects of ball irregularities as well as calculation of ϕ angles, which are fixed by space group symmetry at 90° intervals.

The most convenient drilling coordinates for the S atom are referred to the trigonal symmetry axis, S→V, as origin direction with ϕ angles at 120° intervals. The ρ angle for S, angle V−S−Cu, is graphically determined from figure 7*b* as 75.5°.

Derivation of drilling coordinates. It has been indicated in the foregoing section that the directions of origin of coordinates for both V and Cu are in directions in which there is no neighboring atom in packing contact; the initial holes, therefore, are not bonded in the completed

model. These holes are useful only for manipulation. The origin hole of S, however, is bonded to V in the model.

With reference to figures 7*a* and 7*b*, the direction of origin of ρ angles has been noted, and the most convenient reference direction of ϕ angles for all atoms is in a $(1\bar{1}0)$ plane. The completed derivation of all angles is given in Table 2, showing the bond for which each hole is intended.

TABLE 2

DRILLING COORDINATES FOR BALLS USED IN THE SULVANITE CRYSTAL STRUCTURE

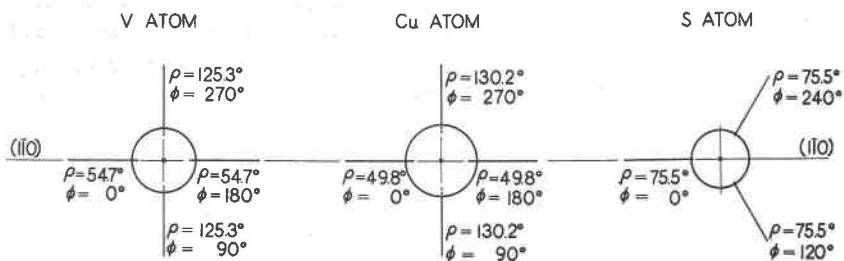| Atom	Bond to	Drilling coordinates	
		ρ	ϕ
V	S	54.7°	0°
	S	54.7°	180°
	S	180°−54.7°=125.3°	90°
	S	180°−54.7°=125.3°	270°
Cu	S	49.8°	0°
	S	49.8°	180°
	S	180°−49.8°=130.2°	90°
	S	180°−49.8°=130.2°	270°
S	V	0°	0°
	Cu	75.5°	0°
	Cu	75.5°	120°
	Cu	75.5°	240°

FIG. 8. Plans of balls representing copper, vanadium, and sulfur atoms in the model of the sulvanite structure, showing drilling coordinates.

Diagrammatic representation is shown in figure 8, where the drilling coordinates are projected onto a plane perpendicular to the origin direction of each atom.

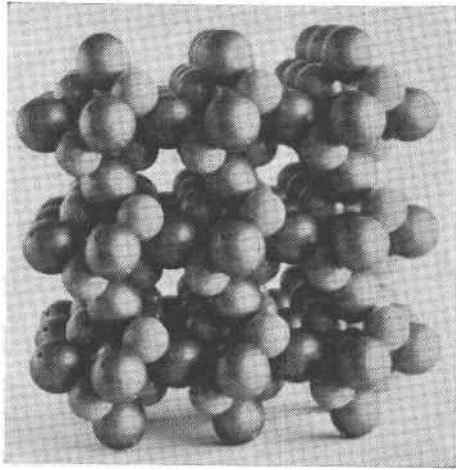Figure 9 illustrates the complete sulvanite model.

FIG. 9. Model of the crystal structure of sulvanite constructed in accordance with the procedure outlined in the accompanying text. The octahedron-like clusters contain copper atoms at the octahedron corners, sulphur atoms near the centers of alternate octahedron faces, and vanadium atoms at the octahedron centers. The model contains eight unit cells plus additional atoms necessary to complete the environments of the vanadium atoms.

COLLECTED DRILLING COORDINATES

During the past few years the writers have had occasion to construct packing models of some forty odd crystal structures. A considerable amount of labor has been expended in the adjustment of the structures and in the calculation of drilling coordinates. These drilling coordinates will be published in a subsequent paper for the benefit of those wishing to duplicate these structural models.