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THE CRYSTAL STRUCTURE OF COVELLITE.

H. S. ROBERTS AND C. J. KSANDA.

This paper is the first of a series to be published on the crystal structure of the compounds and solid solutions occurring in the system copper-iron-sulphur. The stability relations in this system have been investigated in detail at the Geophysical Laboratory by Allen, Crenshaw, Johnston and Larsen;[1] by Posnjak, Allen and Merwin[2] and by Lombard and Merwin.[3] In the course of these investigations problems were encountered that resisted solution by the physico-chemical and optical methods available. It was in the hope of clearing up some of these problems that the present study of the internal structure of crystalline phases within the system was undertaken.

At least three attempts have been made to find the crystal structure of covellite by X-ray diffraction methods. Alsen[4] found that Laue photographs showed full hexagonal symmetry, and he gives the value $a_0 = 6.66\text{Å}$, $c_0 = 9.0\text{Å}$. Ramsdell[5] found that covellite is not isomorphous with cinnabar (rhombohedral). Gossner and Mussgnug[6] assign covellite to one of the groups of higher symmetry in the hexagonal system, with the probability in favor of D_{6h}^4. They give $a_0 = 3.81\text{Å}$ and $c_0 = 16.46\text{Å}$ and suggest an arrangement of twelve atoms in the unit cell based on Goldschmidt's data for the atomic radii[7] of copper and sulphur. Our own work, which was completed before their paper came to hand, shows that their arrangement could not give rise to the diffraction effects observed by us.

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[1] The Mineral Sulphides of Iron; this Journal, 33, 169, 1912.
[2] The Sulphides of Copper; Econ. Geol. 10, 491, 1915.
[3] In manuscript.
[4] Geologiska Förenigen Stockholm, 47, 54, 1925.
[5] Am. Min., 10, 281, 1925.
[6] Centralblatt fur Mineralogie, Geologie and Paläontologie, A, 1927, 412.
[7] Skrifter Norsk. Vidensk. Akad. Oslo, I Matem. Naturv. Kl., 1926, 22.

J. W. H. Adam[8] has made an exhaustive study of the crystallography of covellite from Alghero, Sardinia, for which, however, he does not give an analysis. He finds that it is hexagonal with the axial ratio a:c = 1:2.150.

Covellite cleaves very readily into thin sheets parallel to 0001. Cleavage is apt to cause the thinner sheets to curl but they may be flattened out again readily and without apparent injury. These two observations seem to indicate not only that the interatomic forces are weakest in a direction parallel to the c axis but that atomic planes perpendicular to this axis are capable of gliding over one another without serious obstruction and without twinning. This condition of gliding is encountered in certain pure metals where it is associated with planes whose atoms do not interlock.

MATERIAL.

Material was obtained from two sources:

1. Synthetic cupric sulphide prepared by heating pure copper in an evacuated pyrex tube with an excess of distilled sulphur.[9] After ten days at about 500° the tube was opened. the contents ground and placed in another tube. This was evacuated and the heating continued for ten days more. A few grams of the material obtained from the second heating was powdered and heated in sulphur vapor for several days at about 300°. It did not sinter together, showing that the reaction was probably complete. The material used was from this third heating. Covellite made by this method is too finely crystalline for Laue or spectrometer methods, but is satisfactory for powder photographs.
2. Natural covellite from Summitville, Colorado. This was specimen number 87293 of the United States National Museum collection and was obtained through the kindness of Dr. Wm. F. Foshag. The sample was made up of groups of thin hexagonal plates. The plates in each group are nearly but not quite parallel. The specimen contains several percent of chalcopyrite intergrown between the groups and as a film on some of their surfaces.

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[8] Beitr. Kryst. Mineral., 3, 50, 1926.

[9] Posnjak, Allen and Merwin, op. cit., p. 527.

METHOD OF MEASUREMENT.

We are primarily interested in the investigation of covellite as one of the solid phases of the system Cu-Fe-S rather than as a natural mineral whose structure may be distorted by the presence of impurities. Therefore since we found no synthetic material having individual crystals large enough for the spectrometer, we made a preliminary comparison of the powder spectra obtained with the Summitville material and with two synthetic preparations. The data are given in Table I. It will be seen that there are no significant differences in spacing or in intensity. Consequently the arrangement of the atoms is presumably the same for the synthetic as for the Summitville material and the dimensions of their unit cells do not differ by more than one part in about 300.

TABLE I.

Comparison of powder photographs of synthetic and natural covellite.

Direct Synthesis		Precipitated		Summitville	
mm	I	mm	I	mm	I
48.0	m	47.6	f	47.6	f
50.8	s	50.7	m	50.8	m
55.2	ss	54.9	ss	55.2	ss
57.1	m	57.1	m	57.3	m
67.2	f	....		67.1	f
....		....		73.6	ff
76.2	ff	....		76.1	ff
82.2	ss	82.1	ss	82.1	ss
90.2	s	90.0	m	89.9	s
100.1	ss	100.4	ss	100.0	ss
106.8	ff	....		106.6	ff
112.8	f	....		112.9	ff
116.1	f	116.7	ff	116.5	f
122.7	f	122.7	ff	122.7	f
130.1	ff	....		129.8	f
135.4	ff	....		135.4	ff
143.9	m	143.9	f	144.0	m
149.0	ff	149.0	ff	149.2	ff
156.2	ff	....		155.9	ff
159.7	ff	....		159.9	ff
167.2	f	....		167.5	f
177.8	ff	....		177.8	ff
188.0	ff	....		187.9	ff

The letters have the following significance: f, faint; m, medium; s, strong. The radius of the cylindrical camera is 109.0 mm.

Laue photographs made with the natural material were found to be very unsatisfactory. The spots were so distorted that the location of their centers was very uncertain. Therefore the data used in assigning the structure were obtained entirely with the spectrometer, using the oscillation method. After the structure had been worked out it was tested by calculating the intensities of all of the forms having spacings greater than that of ($30\bar{3}0$) and comparing the results with the corresponding lines on a powder photograph.

From the Summitville covellite three pieces were selected for the spectrometer:

A. One in which the basal plane was nearly flat and about 5 mm. across. It was mounted in the spectrometer in such a way that it could be rotated through a small angle around any axis lying in the basal plane, i. e. its orientation with respect to the axis of rotation was adjustable by rotation around the c axis. Spectrograms were obtained by reflection of the X-rays from the basal plane.

B. A sheet about 0.2 mm. thick split from another fragment. In this also the breadth of the sheet was parallel to 0001. It was mounted in the spectrometer in the same manner as piece A except that the adjustment by rotation around the c axis was limited to about 50°. Spectrograms were made by passing the X-rays through the sheet.

C. A lamella about 0.5 mm. thick in the middle of a plinth about 4 mm. square. This was one of several squares cut with a saw from larger fragments and digested over night in dilute hydrochloric acid at about 100°. It was found that this treatment selectively removed material from between the lamellae or perhaps from their 0001 faces. At any rate, it was possible to break off the thinner sheets at the corners of the plinth leaving only one sheet to project into the X-ray beam. Piece C was mounted in the spectrometer for rotation about the c axis.

The method used in dealing with the spectrograms has been described in detail by J. D. Bernal[10] and by E. Schiebold.[11] Their methods differ only in details, but since Bernal's paper includes tables and charts that greatly simplify calculation his was the method and notation followed.

Both methods make use of an artifice due to P. P. Ewald[12]

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[10] "On the interpretation of X-ray single crystal photographs." Proc. Roy. Soc., London A 113, 117 to 160, 1926.

[11] "Die Drehkristallmethode," Fortschr. der Mineral, 11, 113 to 280, 1927.

[12] "Das reciproke Gitter in der Strukturtheorie," Zeitschr. f. Krist., 56, 129, 1921.

by means of which the crystallographic planes and their spacings are represented by a three dimensional collection of points called the Reciprocal Lattice.

Any point P_{hkl} of the reciprocal lattice lies on a perpendicular from the origin to the crystallographic plane (hkl) at a distance ρ_{hkl} from the origin inversely proportional to the spacing d_{hkl}. Then, for the n-th order of reflection, if we write (nh, nk, nl) as indices (I) $d_{nh,nk,nl} = \frac{1}{n} d_{hkl}$; $\rho_{nh,nk,nl} = n\rho_{hkl}$; (II) each point in the reciprocal lattice represents a reflection and (III) any reflection of whatever order has a corresponding point in the reciprocal lattice.

The axes $\overset{*}{a}\overset{*}{b}\overset{*}{c}$ of the reciprocal lattice are related to the axes abc and the angles $\alpha\beta\gamma$ of the original lattice as follows:

$$\overset{*}{a} = \frac{k^2bc}{\Delta} \sin\alpha \text{ and is perpendicular to the plane bc}$$

$$\overset{*}{b} = \frac{k^2ac}{\Delta} \sin\beta \text{ and is perpendicular to the plane ac}$$

$$\overset{*}{c} = \frac{k^2ab}{\Delta} \sin\gamma \text{ and is perpendicular to the plane ab}$$

Where Δ is the volume of the parallelopiped abc and k^2 is a constant which Bernal for convenience takes equal to λ, the wave length of the X-rays.[13] We have then by definition: $\rho = \lambda/d$ and $d = \lambda/\rho$.

By Bragg's law ($\lambda = 2d \sin\theta$), $\rho = 2 \sin\theta$ .... (1) which provides the connecting link between the spectrogram and the reciprocal lattice.

The Rotation Diagram used by Bernal to assign indices to the spots on the spectrogram is obtained from the latter by graphical or by analytical methods. It may be obtained from the reciprocal lattice as follows: the reciprocal lattice is rotated around an axis through its origin parallel to the crystallographic direction of the axis of rotation of the crystal in the spectrometer. A fixed plane is imagined containing this axis and the rotation diagram formed on the plane as the points of the reciprocal lattice pass through it.

Bernal locates the points of the reciprocal lattice by the cylindrical coördinates $\zeta\xi\omega$ where ζ is the length of the per-

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[13] Schiebold chooses the value $R\lambda$ for k^2 and suggests that 500 mm. for R is convenient for graphical analysis.

pendicular from the axis of rotation to the point P; ξ the distance from the origin to the foot of the perpendicular; and ω the angle between the perpendicular and some fixed direction perpendicular to the axis. ζ and ξ are then the rectangular Cartesian coördinates of the points in the rotation diagram and, as in the lattice, ρ is the distance from the origin to a given point.

In the hexagonal system

$$\overset{*}{a} = \frac{\lambda}{\sqrt{\tfrac{3}{4}}a_0} \text{ and } \overset{*}{c} = \frac{\lambda}{c_0};\ \overset{*}{\alpha} = \overset{*}{\beta} = 90^\circ,\ \overset{*}{\gamma} = 60^\circ$$

The reciprocal lattice is then an hexagonal lattice whose axes lie symmetrically between the axes of the real lattice.

DIMENSIONS OF THE UNIT CELL.

Fig. 1 shows the relation between the reciprocal lattice of an hexagonal crystal and the layer lines in the rotation diagram for the two simplest cases when the crystal is oriented with the basal plane parallel to the axis of rotation. The projection of the reciprocal lattice on the basal plane is shown on the left and the layer lines and axis of rotation of the rotation diagram on the right. For these two cases all of the points in the lattice are contained in two sets of planes perpendicular to the axis of rotation. The intersections of these planes with the plane of the rotation diagram are the layer lines.[14] Further, the points in the lattice form rows parallel to the axis of rotation and give rise to row lines[15] perpendicular to the layer lines in the rotation diagram. The points on any row line lie on alternate layer lines thus making it possible to detect cases where the odd layer lines are missing. In Fig. 1A the axis of rotation is parallel to an a axis of the crystal; in Fig. 1B it makes an angle of 30° with an a axis.

In Fig. 2 are rotation diagrams obtained from four of the spectrograms. A and B were obtained from piece B and are for the two positions of the axis of rotation giving the largest separation of the layer lines. These positions were 30° apart, the spacings in the two diagrams are in the ratio $1 : \sqrt{3}$ and there are two sets of row lines, one for the even and one for the odd numbered layer lines in each figure. It can be shown

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[14] Schiebold's "Schichtlinien I Art."

[15] Schiebold's "Schichtlinien II Art."

that these conditions are not at all likely to be satisfied by any pair of orientations of the reciprocal lattice, 30° apart, other than those of Fig. 1. Consequently we may write $\overset{*}{a} = .216$, twice the spacing of the layer lines in B.

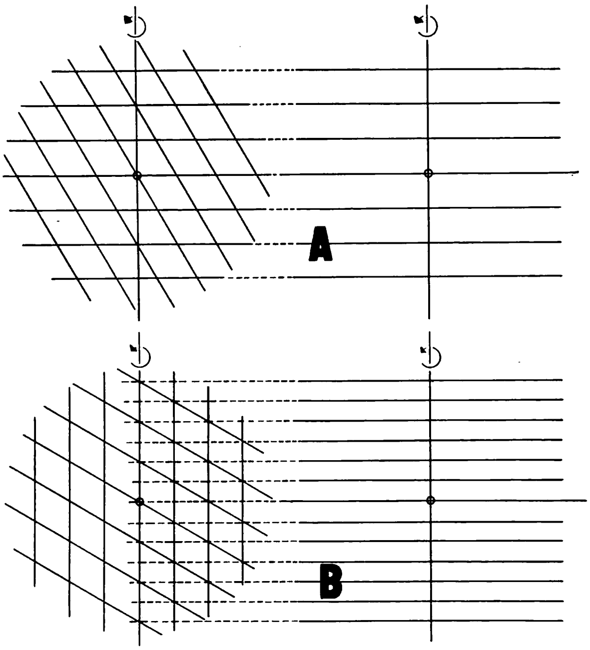

Fig. 1. Relation between rotation diagram and reciprocal lattice for hexagonal crystals.

In Fig. 2C the crystal was rotated around the c axis. Consequently $\overset{*}{c}$ is equal to the spacing of the layer lines. The spots on the center line of Fig. 2D are reflections from the basal plane. Odd orders of reflection are absent.

More accurate values of the dimensions of the unit cell were obtained by direct measurement of the angle 2θ for $11\bar{2}0$, $30\bar{3}0$, 0006 and 0008, using Seemann's edge method.[16] These are tabulated in Table 2.

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[16] Vollständige Spektraldiagramme von Kristallen. Phys. Zeitschr. 20, 169, 1919.

TABLE II.

Dimensions of the unit cell.

hkil	$11\bar{2}0$				$30\bar{3}0$	
λ	.71187	.70759	.63075	.61927	.71187	.63075
2θ	21°34′	21°28′	19°06′	18°43′	37°53′	33°24′
d	1.9024	1.8996	1.9010	1.9043	1.0965	1.0975
a_0	3.8048	3.7992	3.8020	3.8086	3.7984	3.8019

Mean $a_0 = 3.802$

hkil	0008				0006			
λ	.71187	.70759	.63075	.61927	.71187	.70759	.63075	.61927
2θ	20°00′	19°51′	17°40′	17°22′	14°56′	14°50′	13°12′	12°57′
d	2.0597	2.0528	2.0529	2.0512	2.7390	2.7405	2.7436	2.7462
c_0	16.398	16.422	16.431	16.411	16.434	16.443	16.461	16.477

Mean $c_0 = 16.43$

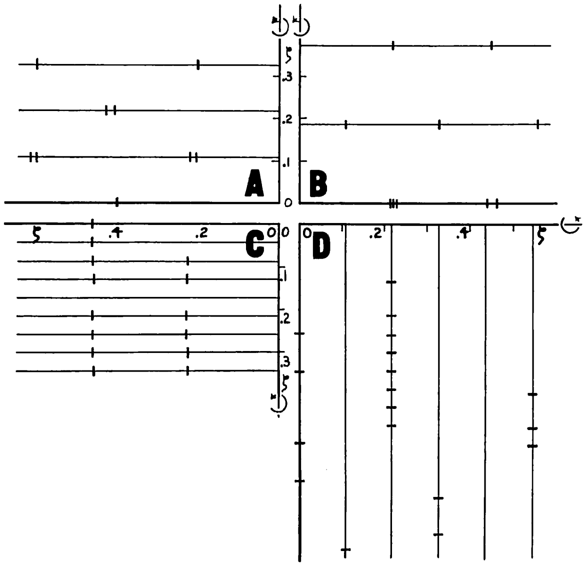

Fig. 2. Rotation diagrams derived from four spectrograms of covellite.

Taking these dimensions and a density of 4.681[17] we obtain 6.053 for the number of molecules in the unit cell. For the axial ratio, c_0/a_0, we obtain 4.321 which is close to twice the value, 2.150, given by Adam.

SPACE GROUP.

Spectrograms made with piece A oscillating through an angle of 12° about an axis in 0001 showed identical patterns

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[17] Posnjak, Allen, and Merwin, op. cit., p. 529.

for positions of this axis 60° apart. This indicates that the c axis is an axis of 6-fold symmetry.

A spectrogram made with piece C oscillating around the c axis showed a pattern symmetrical as to both the position and intensity of spots above and below the center line. In the absence of rather intimate twinning this fact indicates a plane of symmetry perpendicular to the c axis.

We have then 6 copper and 6 sulphur atoms to locate in the unit cell and shall first consider the z coördinate alone. Since there is a plane of symmetry parallel to 0001 the coördinate z must be accompanied by $\bar{z}$; since we find reflections from 0001 only in even orders z must be accompanied by $\frac{1}{2} + z$ and $\bar{z}$ by $\frac{1}{2} — z$. The 12 z coördinates must then consist of one or more of the following four groups:

$$\text{A. } 0, \tfrac{1}{2}. \quad \text{B. } \tfrac{1}{4}, \tfrac{3}{4}. \quad \text{C. } u, \bar{u}, \tfrac{1}{2}+u, \tfrac{1}{2}-u. \quad \text{D. } u', \bar{u}', \tfrac{1}{2}+u', \tfrac{1}{2}-u'$$

Turning to Wyckoff's tabulation[19] of the space groups we find that these arrangements of z coördinates are possible only in space groups D_6^6 and D_{6h}^4. The same sets of two and sets of four appear in both groups. They are listed in Table 3, where the capital letters after each set refer to the groups of z coördinates given above.

TABLE III.

Set of two and sets of four in space group $D_{6h}^{'}$.

(a)	000; $00\frac{1}{2}$.	A
(b)	$00\frac{1}{4}$, $00\frac{3}{4}$.	B
(c)	1/3, 2/3, $\frac{1}{4}$; 2/3, 1/3, $\frac{3}{4}$.	B
(d)	2/3, 1/3, $\frac{1}{4}$; 1/3, 2/3, $\frac{3}{4}$.	B
(e)	$00u$; $00\bar{u}$; $0,0,\frac{1}{2}+u$; $0,0,\frac{1}{2}-u$.	C,D
(f)	$1/3,2/3,u$; $2/3,1/3,\bar{u}$; $2/3,1/3,\frac{1}{2}+u$; $1/3,2/3,\frac{1}{2}-u$.	CD

From R. W. G. Wyckoff, The analytical expression of the results of the theory of space-groups. Carnegie Institution of Washington, Publication No. 318.

The photographic intensities of different orders of reflection from 0001 are, in descending sequence, 6, 8, 4, 12, 2, 14, 16, 10. It is evident that if the z coördinates include only groups A and B the second or fourth order or both will have a higher intensity than higher orders. It is also evident from Table 3 that there are not enough positions with z coördinates corresponding to A and B to take care of more than 8 of the 12 atoms in the unit cell.

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[18] The analytical expression of the results of the theory of space-groups. Carnegie Institution of Washington, Publication No. 318.

The combination of groups A, B and C were tested by comparing the intensities observed for the various orders of 0001 with the intensities calculated by the relation:

$$I \propto \left(\frac{d_{hkl}}{n}\right)^{2.35} \left\{ \left[\sum_{s} \sigma_s \cos 2\pi n(hx_s + ky_s + lz_s)\right]^2 + \left[\sum_{s} \sigma_s \sin 2\pi n(hx_s + ky_s + lz_s)\right]^2 \right\} \quad (3)$$

It was assumed that the atoms in covellite are double ionized, that is, that each copper atom has given up two electrons and each sulphur atom gained two. If this is the case their scattering powers may be assumed to satisfy the proportion:

$$\sigma_{Cu} : \sigma_S = (29 - 2) : (16 + 2) = 27 : 18 = 1.5 : 1$$

We therefore chose the values: $\sigma_{Cu} = 1.5$; $\sigma_S = 1$ for intensity calculations. It is not to be expected that the proportionality will be satisfactory over such a long range of the angle of deviation as these reflections cover, but it should be true that groups of three consecutive orders should show the same sequence of intensity for calculated as for observed values. No value of u was found to satisfy this condition for the combination A, B, C.

There remain those combinations including both C and D. Three sets of z coördinates are possible:

I Cu at $\frac{1}{4}$, $\frac{3}{4}$, u, $\bar{u}$, $\frac{1}{2}+u$, $\frac{1}{2}-u$; S at $\frac{1}{4}$, $\frac{3}{4}$, u', $\bar{u}'$, $\frac{1}{2}+u'$, $\frac{1}{2}-u'$.
II Cu at 0, $\frac{1}{2}$, u, $\bar{u}$, $\frac{1}{2}+u$, $\frac{1}{2}-u$; S at $\frac{1}{4}$, $\frac{3}{4}$, u', $\bar{u}'$, $\frac{1}{2}+u'$, $\frac{1}{2}-u'$.
III Cu at $\frac{1}{4}$, $\frac{3}{4}$, u, $\bar{u}$, $\frac{1}{2}+u$, $\frac{1}{2}-u$; S at 0, $\frac{1}{2}$, u', $\bar{u}'$, $\frac{1}{2}+u'$, $\frac{1}{2}-u'$.

II and III are identical except for the position of the origin. The variables u and u′ were evaluated for I, II and III by assigning arbitrary values to them and comparing the calculated intensities of 000n with those observed. On the spectrograms 0002 is very weak, 000,10 is absent, and 0006 and 0008 nearly equal in intensity. Accordingly a graph was prepared for I and another graph for II and III including (A) a curve connecting the values of u and u′ for which 0002 is zero, (B) similar curves for 000,10 and (C) a curve for which 0006 and 0008 are equal. In this way the choice was limited to values of u and u′ lying close to curve C in the vicinity of its intersection with curve B.

The results are as follows: for I, $u_{Cu} = .099$, $u_S = .017$; for II, $u_{Cu} = .157$, $u_S = .124$; for III, $u_{Cu} = .093$, $u_S = 1.26$. If the assumptions implied in equation (3) are valid these values are correct within about ± .002. The intensities calculated for the three sets are given in Table IV. In the first

TABLE IV.

Calculated intensities for different orders of 0001.

Order	Intensity	
	I	II and III
6	1073	974
8	994	946
4	885	605
12	324	136
2	214	276
14	296	90
16	1	5
10	51	70

column the names of the reflections are arranged in the order of their observed intensities, the highest being first. We have, then, for the coördinates of atomic positions for the three groups:

I Cu at $xy\tfrac{1}{4}$, $xy\tfrac{3}{4}$, $xy.099$, $xy.901$, $xy.599$, $xy.401$;
S at $xy\tfrac{1}{4}$, $xy\tfrac{3}{4}$, $xy.017$, $xy.983$, $xy.517$, $xy.483$.
II Cu at $xy0$, $xy\tfrac{1}{2}$, $xy.157$, $xy.843$, $xy.657$, $xy.343$;
S at $xy\tfrac{1}{4}$, $xy\tfrac{3}{4}$, $xy.124$, $xy.876$, $xy.624$, $xy.376$.
III Cu at $xy\tfrac{1}{4}$, $xy\tfrac{3}{4}$, $xy.093$, $xy.907$, $xy.593$, $xy.407$;
S at $xy0$, $xy\tfrac{1}{2}$, $xy.126$, $xy.874$, $xy.626$, $xy.374$.

If the sulphur atoms in I occupy position (e) in Table 3, that is lie along the Z axis, the distance between the centers of the atoms at .483 and .517, etc. will be only .56Å which is considerably less than the diameter assigned to sulphur atoms in other crystals. We shall therefore consider that this arrangement is impossible. All of the positions in Table 3 lie on the three lines 00z, 1/3, 2/3, z and 2/3, 1/3, z, parallel to the Z axis. If the arrangement of atoms is such that the scattering power is the same for all of these lines reflections from $10\bar{1}0$, $20\bar{2}0$, etc. will be absent. These reflections are present on the spectrograms but are weak in comparison with $10\bar{1}3$, $10\bar{1}2$, and $20\bar{2}3$, $20\bar{2}2$ respectively. It therefore seems likely that the correct arrangement is one for which the scattering powers along these three lines are unequal but not very different. The following combinations of the sets in Table III satisfy these conditions:

For I: (1) Cu at (c) and (e), S at (d) and (f);
(2) Cu at (d) and (e), S at (c) and (f).
For II: (3) Cu at (a) and (f), S at (c) and (e);
(4) Cu at (a) and (f), S at (d) and (e).
For III: (5) Cu at (c) and (f), S at (a) and (e);
(6) Cu at (d) and (f), S at (a) and (e).

The intensities of the reflections $10\bar{1}0$, $10\bar{1}1$, $10\bar{1}2$ and $10\bar{1}3$ calculated for these arrangements are given in Table 5. The second line gives the distribution of scattering power $\Sigma\sigma$ between the three lines parallel to Z; the second column gives a rough estimate of the intensities observed on the spectrogram. Agreement between calculated and observed intensities is satisfactory only in the case of arrangement (6). The numerical coördinates of this arrangement are: Cu at 2/3 1/3 $\frac{1}{4}$; 1/3 2/3 $\frac{3}{4}$; 1/3 2/3 .093; 2/3 1/3 .907; 2/3 1/3 .593; 1/3 2/3 .407. S at 000; 00$\frac{1}{2}$; 0,0,.126; 0,0,.874; 0,0,.626; 0,0,.674.

TABLE V.

Intensities for six probable arrangements.

Plane	I Obs.	(1)	(2)	(3)	(4)	(5)	(6)
$10\bar{1}0$	ff	82	82	328	328	82	82
$10\bar{1}1$	ff	52	8	1652	1652	1022	80
$10\bar{1}2$	f	187	187	2682	2682	159	159
$10\bar{1}3$	s	1	96	328	328	126	1550
$\Sigma\sigma$ for 00z		6	6	7	7	6	6
$\Sigma\sigma$ for $\frac{1}{3}\frac{2}{3}$z		4$\frac{1}{2}$	4$\frac{1}{2}$	4	4	4$\frac{1}{2}$	4$\frac{1}{2}$
$\Sigma\sigma$ for $\frac{2}{3}\frac{1}{3}$z		4$\frac{1}{2}$	4$\frac{1}{2}$	4	4	4$\frac{1}{2}$	4$\frac{1}{2}$

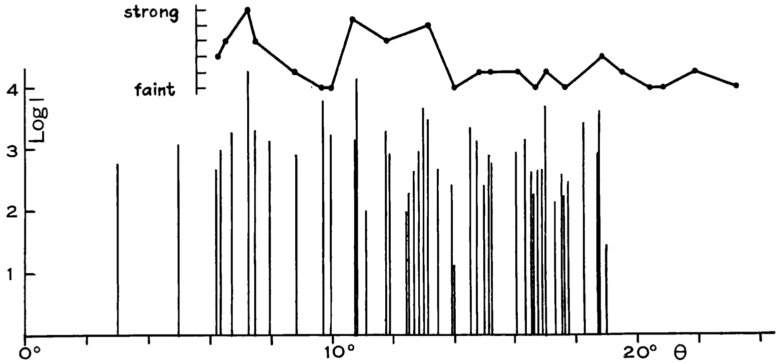

Fig. 3. Comparison of calculated intensities with those observed on a powder photograph of Summitville covellite.

Using these coördinates, intensities were calculated for all planes having intensities less than that of $30\bar{3}0$. These, multiplied in each case by j, the number of planes in the form, are plotted as vertical lines in Fig. 3. In the upper part of the figure the data from a powder photograph of Summitville covellite are plotted to an arbitrary intensity scale. The numerical data for the first 18 lines appearing on the powder film and for three additional planes whose calculated intensities were great enough for their lines to be expected on the film are given in Table VI. For most of the lines agreement between observed and calculated values is satisfactory.

TABLE VI.

Powder Spectra of Summitville Covellite. Calculated and Observed Intensities.

	Calculated		Observed	
Form	θ	log I	θ	I
$10\bar{1}0$	6°11′	3.16	6°16′	m
$10\bar{1}1$	6 19			
$10\bar{1}2$	6 40	3.38	6 40	s
$10\bar{1}3$	7 14	4.27	7 04	sss
0006	7 23	3.29	7 28	m
$10\bar{1}5$	8 48	2.92	8 46	f
$10\bar{1}6$	9 42	3.80	9 40	ff
0008	9 59	3.28	10 01	ff
$11\bar{2}0$	10 47	4.13	10 47	ss
$10\bar{1}8$	11 44	3.31	11 50	s
$20\bar{3}3$	13 00	3.90	13 09	ss
$11\bar{2}6$	13 09			
$20\bar{2}4$	13 27	2.68	Absent	
$20\bar{2}5$	13 57	2.42	14 02	ff
$20\bar{2}6$	14 34	3.36	14 39	f
$10\bar{1}, 11$	15 08	3.15	15 13	f
$20\bar{2}7$	15 17			
$20\bar{2}8$	16 05	2.96	16 07	f
$10\bar{1}, 12$	16 19	3.17	Absent	
$12\bar{3}2$	16 46	2.65	16 44	ff
$12\bar{3}3$	17 00	3.69	17 06	f
$12\bar{3}5$	17 47	2.50	17 51	ff
$12\bar{3}6$	18 16	3.46	Absent	
$30\bar{3}0$	18 53	3.62	18 51	m

The shortest distance between the centers of two sulphur atoms is 2.07Å and between the centers of sulphur and copper atoms 2.23Å. In order to form a picture of the structure we may think of it as built up of spherical atoms whose radii are 1.035 for sulphur and 1.195 for copper. Two views of this arrangement of spherical atoms are drawn to scale in Fig. 4. It will be seen that all six of the sulphur atoms and four of the six copper atoms in the unit cell are in contact with their nearest neighbors. These atoms form compact strata running through the crystal in a direction parallel to 0001 with the remaining copper atoms in comparative isolation between them. This feature of the structure seems to offer a satisfactory explanation of the basal cleavage and of the possibility of gliding parallel to the base.

It is conceivable that the "isolated" copper atoms, of which there are two in the unit cell, and the same number of sulphur atoms, probably the middle ones of the two groups of sulphur atoms, are not ionized. If this were the case we should presumably have atoms of four different sizes and it would be a simple matter to picture a structure of spherical atoms all of which were in contact with their neighbors. This hypothesis was tested by calculating the intensities of some of the reflections but the results were inconclusive.

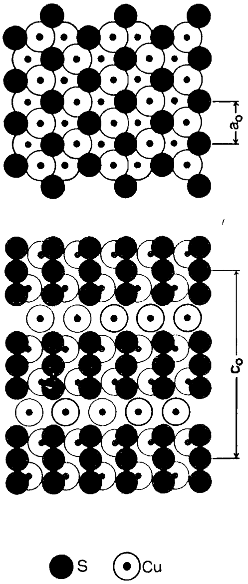

Fig. 4. Two views of the covellite structure, assuming that the atoms are spheres.

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CONCLUSION.

The structure of covellite was worked out by X-ray spectrographic methods. The unit cell was found to be hexagonal with the dimensions $a_0 = 3.802$Å, $c_0 = 16.43$Å and $c_0/a_0 = 4.321$. It contains six copper atoms and six sulphur atoms in Wyckoff's special position (d) and (f), and (a) and (e) respectively of space group D^4_{6h}, where $u_{Cu} = .093$ and $u_S = .126$. All of the other combinations of special cases in D^4_{6h} that seemed to offer any hope of satisfying the data were tested by comparing calculated with observed intensities and none was found to be satisfactory. The assigned structure offers a satisfactory explanation for the perfect basal cleavage and for the possibility of gliding parallel to the base.

Geophysical Laboratory,
Carnegie Institution of Washington.