The Crystal Structure of Stannite, Cu_2FeSnS_4.

By

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(With 2 figures.)

The crystal structure of stannite was investigated by R. Gross and N. Gross in 1923[1]) with the aid of powder photographs. They reported a tetragonal unit-cell $a_0 = 5.577$ Å; $c_0 = 5.180$ Å with: Sn at 000; Fe at $\frac{1}{2}\frac{1}{2}0$; $2Cu$ at $\frac{1}{2}0\frac{1}{2}$; and $4S$ at undetermined positions. It was pointed out in an abstract[2]) that these values for the dimensions of the unit-cell lead to an axial ratio of $a : c = 1 : 0.9287$ whereas a careful crystallographic examination of stannite by Spencer[3]) in 1901 gave $a : c = 1 : 0.9827$. This discrepancy cannot be ascribed to a typographical error since Spencer tabulates the measurements made on the angle between the developed faces (001) and (101) on several specimens (this angle being 44° 30′) while the other investigators report the actual dimensions of the cell.

The incompleteness of the foregoing study as well as the interest attached to obtaining accurate values of the interatomic distances in sulfide minerals made desirable a reinvestigation of the structure of stannite. The unexpected result of a previous study of chalcopyrite[4]) also indicated the need for a closer investigation of stannite. Crystals from Oruro, Bolivia, kindly provided by Professor Charles Palache, were used in the preparation of oscillation photographs and Laue photographs. These photographs looked very similar to those of chalcopyrite, but their analysis led to a structure based on a different space-group and having a quite different arrangement of metal atoms.

Unit of Structure and Space-Group Symmetry. The specimen, a tiny fragment of about one-tenth of a cubic millimeter in volume with only one developed face, was chosen because it was one of the few pieces in our sample which did not appear to be twinned. Photographs taken with the x-ray beam perpendicular to the developed face showed a pair of perpendicular symmetry planes with a twofold axis; the same symmetry elements appeared in photographs taken with the x-ray beam

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[1]) R. Gross and N. Gross, Neues Jb. Mineral., Geol., Paläont. **48** (1923) 113.

[2]) Z. Kristallogr. **60** (1924) 501.

[3]) L. J. Spencer, Z. Kristallogr. **35** (1901) 468.

[4]) L. Pauling and L. O. Brockway, Z. Kristallogr. **82** (1932) 188.

impinging on the face of the crystal at an angle of 45°. The presence of two pairs of perpendicular symmetry planes separated by 45° fixes the x-ray point-group symmetry as that of D_{4h}; the four-fold reflection axis indicated by the characteristic face development as described by Spencer hence determines the point-group symmetry of stannite to be that of D_{2d}. The *a*- and *b*-axes were chosen so that they lay 45° from the vertical symmetry planes in accordance with the convention of Hermann.

This choice of point-group symmetry was tested with the aid of photographs taken with the x-ray beam parallel to the four-fold axis. Since the structure deduced below based on D_{2d} is changed into one of lower symmetry based on S_4 by simply interchanging the iron with half of the copper atom positions and since copper and iron have nearly equal scattering powers for x-rays, it was recognized that photographs obtained from crystals having the structure of lower symmetry would very closely approximate the higher symmetry character with discrepancies appearing only in the intensities of the weaker reflections from planes for which the metal atom scattering is not all in phase. In the photographs taken along the *c*-axis the structure based on S_4 would require the four-fold axis while that based on D_{2d} requires the presence of four vertical symmetry planes as well. The irregular shape of the crystal caused unequal absorption in different directions, but the symmetry planes were as well defined as the four-fold axis. The evidence, which is not at all conclusive, could be improved by the examination of photographs from a thin section of a large single crystal; but such crystals are not available. In the absence of any positive discrepancy the point-group symmetry is chosen to be that of D_{2d}.

Oscillation photographs taken with 45° oscillation of the crystal about the *c*-axis from (110) using zirconia-filtered **Mo** radiation afforded measurements on the equatorial zone and layer line spacings which lead to the values $a_0 = 5.46$ Å and $c_0 = 5.36$ Å. However, at least six faint but apparently real reflections occurred which would require c_0 to be doubled. When gnomonic projections were prepared from Laue photographs No. 8 and 9 obtained with the x-ray beam parallel to (100) and (110), respectively, the following forms were found which gave reflections at $n\lambda$ values of 0.15 to 0.20 Å calculated on the basis of the small unit: {20.11}, {249}, {287}, {029}, {467}, {465}, {681} and {863}. In addition the following forms gave reflections at $n\lambda$ values of 0.21 to 0.22 Å: {42.13}, {4.10.9}, {285}, {0.6.13} and {247}. Since the short wave-length limit of the incident radiation was 0.24 Å these thirteen reflections eliminate the unit with $c_0 = 5.36$. If c_0 is doubled all of the data obtained on the

Laue and oscillation photographs is accounted for; the true unit may hence be assumed to have the dimensions

$$a_0 = 5.46\ \text{Å},\ c_0 = 10.725\ \text{Å}.$$

The value for c_0 is the average of those determined from the observed separation of nineteen pairs of reflections on the oscillation photograph; the value for a_0 is the average result of four measurements in the equatorial zone. These dimensions give an axial ratio for the pseudo-cubic unit (used by the previous investigators) of $a : c = 1 : 0.982$, in agreement with Spencer's value of 0.9827. Measurements on the dimensions of the gnomonic net of the projection of the (100) Laue photograph give 0.983. The ratio of the true unit-cell is $a : c = 1 : 1.964$.

The density calculated for $2\,Cu_2FeSnS_4$ in the unit is 4.44; Spencer's observed value for the density of stannite is 4.45.

The face-centered and end-centered lattices were eliminated by reflections in the first order from fourteen forms in which h is even and k is odd, such as $\{2.1.13\}$, $\{259\}$, $\{235\}$, $\{433\}$ etc. No reflections in the first order from forms with $h + k + l$ odd were observed; accordingly the body centered lattice was assumed to be the correct one. The only space-groups based on this lattice and isomorphous with the point-group D_{2d} are $D_{2d}^{11} - I\bar{4}2m$ and $D_{2d}^{12} - I\bar{4}2d$. The latter does not allow reflections from forms $\{hhl\}$ having $\frac{1}{2}(2h + 1)$ odd, while D_{2d}^{11} has no such restrictions. The two forms $\{22.14\}$ and $\{11.12\}$ gave fairly strong reflections at $n\lambda$ values of 0.35 and 0.39 Å, respectively; therefore D_{2d}^{12} is eliminated, and the correct space-group is shown to be

$$D_{2d}^{11} - I\bar{4}2m.$$

The Atomic Arrangement. The atoms to be placed in the unit-cell are $4Cu$, $2Fe$, $2Sn$ and $8S$. The sets of equivalent positions for D_{2d}^{11} given in Wyckoff's tabulation are twofold (a, b), fourfold (c, d, e), eightfold (f, g, h, i) or sixteenfold (j). The iron and tin atoms are placed in a and b, respectively. The copper atoms may be placed in c, d or e. If we put $4Cu$ in c the structure factor for all of the metal atoms is

$$F'_{hkl} = 2F_{Fe} + (-1)^l\, 2F_{Sn} + 2F_{Cu}\,\{(-1)^h + (-1)^k\}.$$

On the oscillation photograph mentioned above $\{336\}$ is observed to be stronger than $\{224\}$. If now we allow for the sulfur contribution in the most favorable way for fulfilling the observed comparison by adding $8F_S$ to the strong reflection and subtracting $8F_S$ from the weaker, we have

$$F'_{336} = 2F_{Fe} + 2F_{Sn} - 4F_{Cu} + 8F_S \quad (= 79.2)$$
$$F'_{224} = 2F_{Fe} + 2F_{Sn} + 4F_{Cu} - 8F_S \quad (= 101.1).$$

The indicated numerical values, calculated with the aid of the Pauling-Sherman F-values, show that there is no possible arrangement of the sulfur atoms which will compensate for the different contributions to the two reflections made by the copper atom scattering. Accordingly, c is eliminated.

The positions e may also be eliminated. The reflection from the form $\{448\}$ is observed to be from five to ten times as strong as that from $\{110\}$. The structure factor from the metal atoms alone is the same for both forms:

$$F'_{hkl} = 2F_{Fe} + (-1)^l\, 2F_{Sn} + 4F_{Cu} \cos lu\,.$$

If we again allow for the sulfur contribution by subtracting $8F_S$ from the observed weaker reflection we have

$$\sqrt{I_{110}} = \sqrt{\frac{1+\cos^2 2\theta}{2\sin 2\theta}}\,(2F_{Fe} + 2F_{Sn} + 4F_{Cu} - 8F_S) = 308\,.$$

For the $\{448\}$ reflection the most favorable value of the parameter u will lead to $\cos 8u = +1$; therefore, adding the $8F_S$ we have

$$\sqrt{I_{448}} = \sqrt{\frac{1+\cos^2 2\theta}{2\sin 2\theta}}\,(2F_{Fe} + 2F_{Sn} + 4F_{Cu} + 8F_S = 139\,.$$

It is evident that for this comparison the copper scattering must be just out of phase with that of iron and tin in the $\{110\}$ reflection to account for the observed relative intensities. This condition is met by the set of positions d; and the positions of the $4Cu$ have now been rigorously determined. The coordinates of the metal atoms are

$2Fe$ in $000,\ \frac{1}{2}\frac{1}{2}\frac{1}{2}$. (a)
$2Sn$ in $00\frac{1}{2},\ \frac{1}{2}\frac{1}{2}0$. (b)
$4Cu$ in $0\frac{1}{2}\frac{1}{4},\ 0\frac{1}{2}\frac{3}{4},\ \frac{1}{2}0\frac{1}{4},\ \frac{1}{2}0\frac{3}{4}$. (d)

This arrangement is that of cubic closest packing of the metal atoms which is observed in sphalerite.

Consideration of the positions of the eight sulfur atoms leads to six possible arrangements. They may be divided into two sets of four each occupying c and e or e and e' with the parameters u and u', or they may be equivalent and occupy one of the eightfold sets f, g, h and i. The respective structure factors for the first five arrangements are as follows:

c and e : $+\,2F_S\{(-1)^h + (-1)^k\} + 4F_S \cos lu$
e and e': $+\,4F_S \cos lu + 4F_S \cos lu'$
f: $+\,4F_S (\cos hu + \cos ku)$
g: $+\,(-1)^l\, 4F_S (\cos hu + \cos ku)$
h: $+\,4F_S\{(-1)^h + (-1)^k\} \cos lu$.

The structure factor for the metal atoms in the positions given above is

$$2F_{Fe} + (-1)^l\, 2F_{Sn} + (-1)^k\, (i)^l\, 2F_{Cu}\, \{1 + (-1)^l\}\,.$$

The form {440} is observed to reflect more strongly than {420}. The theoretical intensity expression which involves *c* and *e* or *e* and *e'* or *h* does not distinguish between these two forms (except for the factors which make the form with the smaller interplaner distance reflect less strongly); therefore these arrangements are eliminated. Similarly the intensity expression based upon $8S$ in *f* or *g* does not distinguish between the forms {325} and {321} whereas {325} is observed to reflect more strongly. The sulfur atoms accordingly can be placed only in the positions *i*:

$$uuv,\ u\bar{u}\bar{v},\ u+\tfrac{1}{2}\ u+\tfrac{1}{2}\ v+\tfrac{1}{2},\ u+\tfrac{1}{2}\ \tfrac{1}{2}-u\,\tfrac{1}{2}-v,$$
$$\bar{u}\bar{u}v,\ \bar{u}u\bar{v},\ \tfrac{1}{2}-u\ \tfrac{1}{2}-u\ v+\tfrac{1}{2},\ \tfrac{1}{2}-u\ u+\tfrac{1}{2}\ \tfrac{1}{2}-v.$$

Theoretical intensity curves have been calculated for a large number of forms by means of the formula

$$I_{hkl} = \frac{1+\cos^2 2\theta}{2\sin 2\theta}\, |F_{hkl}|^2$$

with

$$F_{hkl} = \sum_j F_j\, e^{2\pi i\,(hx_j + ky_j + lz_j)}\ .$$

The observed comparison $\{660\} > \{420\}$ fixes u between 0.23 and 0.27 since outside of that range for u the calculated intensity of reflection for {420} is not less than five times that for {660}. The parameter v is given an approximate value by the observed comparison $\{336\} > \{224\}$. The theoretical intensities for these two forms were calculated for the whole range of v for the following values of u: 0.23, 0.24, 0.25, 0.26, 0.27. Only between the values 0.100 and 0.140 for v is the calculated intensity of {224} as small as that for {336}.

Figure 1 shows the more accurate determination of the parameters. In each of the hatched areas the indicated observed intensity comparison is violated by the respective calculated comparisons. The comparison {848} greater than twice {648} is based on the observed relative intensities of the weaker component of the *Mo-Kα* doublet in the reflection {848} and the stronger component of the doublet in the {648} reflection. The small unhatched area indicates the limits of the possible variation of the parameters. The most probable values are chosen as

$$u = 0.245 \pm 0.002,\ v = 0.132 \pm 0.002.$$

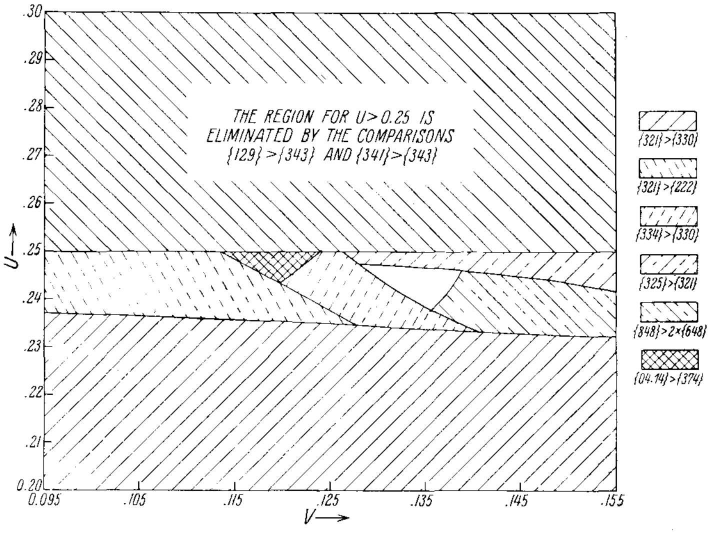

Fig. 1. Intensity comparisons limiting the parameters.

Description of the Structure. The structure found, in Figure 2, is closely similar to that of chalcopyrite and that of sphalerite. Each sulfur atom is surrounded by four metal atoms, two copper, one iron, and one tin, located at the corners of a not quite regular tetrahedron. Each metal atom is similarly surrounded by four sulfur atoms. In contra-distinction to the arrangement in chalcopyrite the copper atoms occupy planes by themselves. The copper-sulfur distance of 2.31 ± 0.03 Å is smaller than the sum of the tetrahedral radii[1]), 2.39 Å, but is in good agreement with the observed copper-sulfur distances in sulvanite[2]), 2.285 ± 0.014 Å; enargite[3]), 2.32 ± 0.03 Å; binnite[4]) 2.28 ± 0.03 Å;

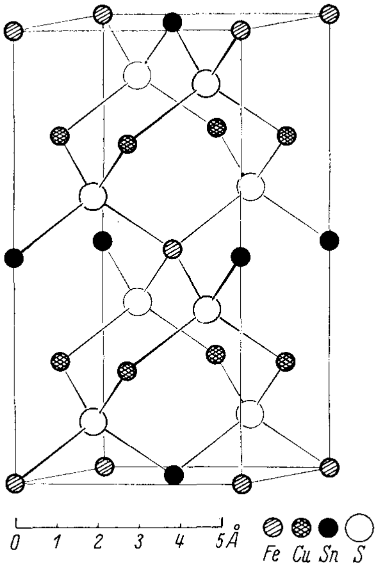

Fig. 2. The arrangement of atoms in the unit of structure of stannite.

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[1]) L. Pauling and M. L. Huggins, Z. Kristallogr. 87 (1934) 205.

[2]) L. Pauling and R. Hultgren, Z. Kristallogr. 84 (1933) 204.

[3]) L. Pauling and S. Weinbaum, Z. Kristallogr. 88 (1934) 48.

[4]) L. Pauling and E. W. Neuman, Z. Kristallogr. 88 (1934) 54.

wolfsbergite[1] 2.29 ± 0.04 Å; and chalcopyrite[2] 2.32 ± 0.03 Å. The tin-sulfur distance is 2.43 ± 0.03 Å for which the radius sum is 2.44 Å. The iron-sulfur distance of 2.36 ± 0.03 Å is much larger than that in chalcopyrite, 2.20 ± 0.03 Å, or in any other iron-sulfur compound which has been studied. No satisfactory explanation has been found for the stability of a structure with such an anomalous bond distance.

The other structure mentioned above, based on the space-group S_4^2, is as plausible in every respect as the one just described. The bond arrangement is again just that of sphalerite. The only difference lies in the interchange of the two iron with two of the copper atoms so that the copper atoms would no longer occupy planes by themselves; and probably there would be somewhat different values for the sulfur atom positions which would now involve three parameters. A set of values for the three parameters was chosen for which the tin-sulfur and copper-sulfur distances were only slightly altered while the iron-sulfur distance was reduced toward the observed value in chalcopyrite; but calculated intensities based on this structure gave rather poor agreement with the observed intensities of reflection. A complete test involving all possible sets of parameter values was not attempted. The difficulty of distinguishing between these structures by means of x-ray photographs has already been mentioned; and while the study of better crystal specimens might lead to the structure of lower symmetry the choice made here is compatible with the symmetry characteristics of the best Laue photograph obtainable.

It may be pointed out that the two previously described structures for chalcopyrite also differ in the positions of the copper atoms; but in that case the structure found to be correct, which does not have the copper atoms segregated in planes, requires a larger unit-cell and the appearance of reflections from some additional forms.

Summary. The tetragonal crystal stannite has been investigated with the use of oscillation and Laue photographs. The unit-cell $a_0 = 5.46$ Å, $c_0 = 10.725$ Å contains $2\,Cu_2FeSnS_4$. Space-group $D_{2d}^{11} - I\bar{4}2m$; atomic positions

$2Fe$ in $000,\ \frac{1}{2}\frac{1}{2}\frac{1}{2}$
$2Sn$ in $00\frac{1}{2},\ \frac{1}{2}\frac{1}{2}0$
$4Cu$ in $\frac{1}{2}0\frac{1}{4},\ \frac{1}{2}0\frac{3}{4},\ 0\frac{1}{2}\frac{1}{4},\ 0\frac{1}{2}\frac{3}{4}$
$8S$ in $uuv,\ u\bar{u}\bar{v},\ u+\frac{1}{2}\ u+\frac{1}{2}\ v+\frac{1}{2},\ u+\frac{1}{2}\ \frac{1}{2}-u\ \frac{1}{2}-v,$
$\bar{u}\bar{u}v,\ \bar{u}u\bar{v},\ \frac{1}{2}-u\ \frac{1}{2}-u\ v+\frac{1}{2},\ \frac{1}{2}-u\ u+\frac{1}{2}\ \frac{1}{2}-v$

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[1] W. Hofman, Z. Kristallogr. **84** (1933) 177.

[2] L. Pauling and L. O. Brockway, Z. Kristallogr. **82** (1932) 188.

with $u = 0.245 \pm 0.002$ and $v = 0.132 \pm 0.002$. The structure closely resembles that of chalcopyrite but can not be obtained from it by substituting half of the iron by tin atoms. Smallest interatomic distances are $Cu - S = 2.31 \pm 0.03$ Å, $Fe - S = 2.36 \pm 0.03$ Å and $Sn - S = 2.43 \pm 0.03$ Å.

I am glad to acknowledge my indebtedness to Professor Linus Pauling for suggesting the investigation and for invaluable aid in pursuing it.

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