

## The Crystal Structure of Livingstonite, $\text{HgSb}_4\text{S}_8$

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With 14 figures

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### Zusammenfassung

Die Raumgruppe des Livingstonits ist  $A2/a$ ; die Elementarzelle mit den Gitterkonstanten  $a = 30,25 \text{ \AA}$ ,  $b = 4,00 \text{ \AA}$ ,  $c = 21,48 \text{ \AA}$ ,  $\beta = 104^\circ 12'$  enthält 8  $\text{HgSb}_4\text{S}_8$ . Diese Formel wurde an Stelle der bisher angegebenen ( $\text{HgSb}_4\text{S}_7$ ) durch eine neue chemische Analyse gewonnen und durch die in mehreren Verfeinerungsschritten ausgeführte PATTERSON- und FOURIER-Analyse bestätigt.

Das Kristallgitter weist eine  $\text{S}_2$ -Gruppe mit einem S—S-Abstand von  $2,07 \text{ \AA}$  auf, was in Einklang mit der neuen chemischen Formel steht.

Das Gitter setzt sich aus zwei Arten von Schichten zusammen, die beide parallel (001) verlaufen. In den Schichten der einen Art werden je zwei Doppelketten von  $\text{Sb}_2\text{S}_4$  durch S—S-Bindungen in Gestalt von  $\text{S}_2$ -Gruppen, in den Schichten der zweiten Art durch Hg-Atome miteinander verknüpft. Jedes Sb-Atom hat drei S-Atome als nächste Nachbarn und weitere vier in größeren Abständen. In den Ecken eines deformierten Oktaeders um ein Hg-Atom befinden sich sechs S-Atome, von denen zwei stärker gebunden und, wie beim Zinnober  $\text{HgS}$ , linear angeordnet sind. Die vollkommene Spaltbarkeit parallel (001) kann durch das Aufbrechen der schwachen Bindungen zwischen den Schichten der beiden Arten erklärt werden.

### Abstract

The crystal structure of livingstonite has been determined. A new chemical analysis of the mineral gives the formula  $\text{HgSb}_4\text{S}_8$  instead of the previously assigned  $\text{HgSb}_4\text{S}_7$ . The space group is  $A2/a$ , and the unit-cell dimensions are  $a = 30.25 \text{ \AA}$ ,  $b = 4.00 \text{ \AA}$ ,  $c = 21.48 \text{ \AA}$ , and  $\beta = 104^\circ 12'$ . This unit cell contains 8  $\text{HgSb}_4\text{S}_8$ . Intensities were measured by the single-crystal GEIGER-counter method with  $\text{CuK}\alpha$  and  $\text{MoK}\alpha$  radiations. The structure was analyzed by direct interpretations of the PATTERSON map  $P(xz)$ , and the three-dimensional PATTERSON sections,  $P(x, n/60, z)$ . The refinement of the structure was performed by successive FOURIER and difference-FOURIER trials, and finally by the three-dimensional least-squares method. The structure obtained confirms the new chemical formula. In the structure an  $\text{S}_2$  group is found with an S—S distance of

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2.07 Å. The existence of this  $S_2$  group was suspected from the new chemical formula. In the structure, there are two kinds of layers, both running parallel to (001). In one kind of layer, two  $Sb_2S_4$  double chains are joined together by an S—S bond to form an  $S_2$  group between them. In the other, two  $Sb_2S_4$  double chains are cemented together by Hg atoms. Each Sb atom has three closest neighboring S atoms, and four additional ones at greater distances. The coordination of the Hg atom is a distorted octahedron of six S atoms, of which two are strongly bonded ones arranged in a linear way as found in cinnabar, HgS. The perfect (001) cleavage can be explained as the breaking of the weaker bonds between the two kinds of layers.

### Introduction

There have been two crystallographic investigations of the mineral livingstonite. RICHMOND<sup>2</sup> described it as monoclinic, and GORMAN's presentation<sup>3</sup> was triclinic. BUERGER and NIIZEKI<sup>4</sup> carried out a preliminary structure determination of the mineral assuming GORMAN's triclinic cell was correct. They succeeded in obtaining the structure projected along the shortest axis (4 Å). Our result suggested doubt concerning the number of sulfur atoms in the chemical formula.

Livingstonite crystallizes in an elongated needle form with one perfect prismatic cleavage. The mineral belongs to the group of acicular sulfosalts. Structure determinations for several minerals of this group have recently been published<sup>5-9</sup>. Livingstonite is the only known sulfosalt mineral containing mercury.

### Preliminary structure investigation

For the preliminary phase of the structure investigation we are greatly indebted to Dr. GORMAN of the University of Toronto, Canada.

<sup>2</sup> W. E. RICHMOND, Crystallography of livingstonite. *Amer. Mineralogist* **21** (1936) 719.

<sup>3</sup> D. H. GORMAN, An x-ray study of the mineral livingstonite. *Amer. Mineralogist* **36** (1954) 480-483.

<sup>4</sup> M. J. BUERGER and N. NIIZEKI, The crystal structure of livingstonite,  $HgSb_4S_8$ . *Amer. Mineralogist* **39** (1954) 319-320.

<sup>5</sup> M. J. BUERGER and T. HAHN, The crystal structure of berthierite,  $FeSb_2S_4$ . *Amer. Mineralogist* **40** (1955) 226-238.

<sup>6</sup> F. E. WICKMAN, The crystal structure of galenobismutite,  $PbBi_2S_4$ . *Arkiv Min. Geol.* **1** (1951) 219-225.

<sup>7</sup> F. E. WICKMAN, The crystal structure of aikinite,  $CuPbBiS_3$ . *Arkiv Min. Geol.* **1** (1953) 501-507.

<sup>8</sup> N. NIIZEKI and M. J. BUERGER, The crystal structure of jamesonite,  $FePb_4Sb_6S_{14}$ . *Z. Kristallogr.* **109** (1957) 161-183.

<sup>9</sup> N. NIIZEKI, The crystal chemistry of the mineral sulfosalts. To appear in *Geochemica Acta*.

We were kindly offered not only a massive aggregate of cleavage flakes of livingstonite from Guerrido, Mexico, but also his original single crystal used for the above-mentioned description of his triclinic unit cell.

The first intensity data were collected from the equator WEISSENBERG photograph taken with  $\text{CuK}\alpha$  radiation<sup>10</sup>. The intensities were then

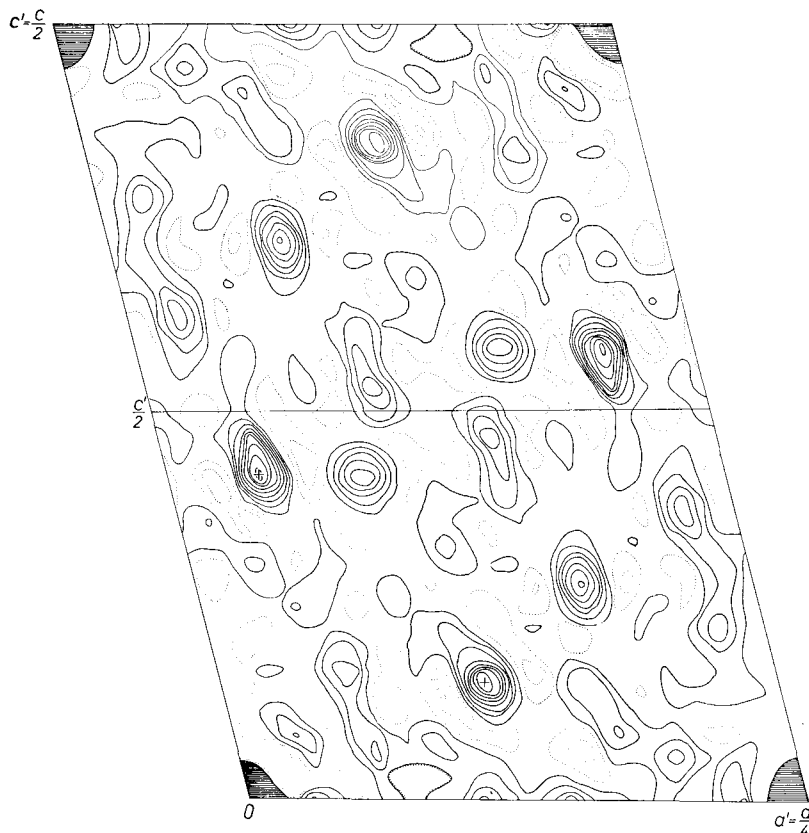


Fig. 1. PATTERSON diagram  $P(xz)$ . The dotted contours represent depressions. The details of the heavy peak at the origin are omitted.

corrected for LORENTZ and polarization factors, but no allowance was made for absorption. The resulting  $F^2(h0l)$ 's were used to prepare the PATTERSON map,  $P(xz)$ , Fig. 1.

Since GORMAN's unit cell contained  $\text{HgSb}_4\text{S}_7$ , there is only one Hg atom in the cell. Its position is fixed at a center of symmetry if the

<sup>10</sup> RALPH H. V. M. DAWTON, The integration of large numbers of x-ray reflections. Proc. Phys. Soc. [London] 50 (1938) 919–925.

space group is  $P\bar{1}$ . A statistical check of the centrosymmetry<sup>11</sup> was applied to the observed intensity data, and the resulting curve is shown in Fig. 2. Although the chemical composition of the mineral is not ideal for the statistical treatment, the result was considered as indicating a center of symmetry in the projection.

Once the position of the mercury atom was fixed, the interpretation of the PATTERSON map, Fig. 1, was straightforward. The two heavy

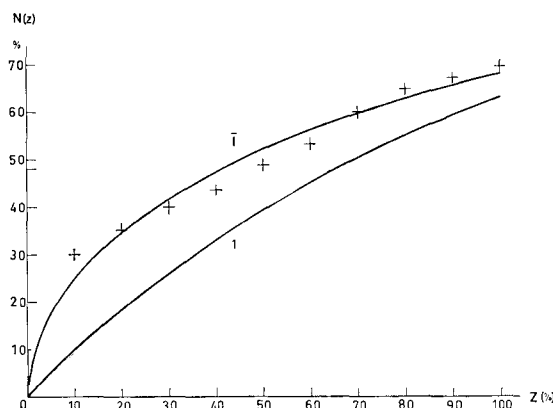


Fig. 2. Statistical test of the centrosymmetry. The theoretical curve for the centrosymmetric crystal is designated by  $\bar{I}$ , and for the noncentrosymmetric crystal by 1. The crosses represent the result with  $F^2(h0l)$ 's of livingstonite.

peaks, indicated by crosses in Fig. 1, must be due to Hg—Sb interactions. Since Hg is at the origin, these peaks could be assumed as the atomic sites for the two Sb atoms in the asymmetric unit. The first FOURIER map of the projection, Fig. 3, was computed using signs determined by heavy atoms only, provided the contributions to the amplitudes by them exceeded one third of the observed values. From this map information concerning the locations of the S atoms could be obtained. The structure was refined by four successive FOURIER trials. With an assumed chemical formula of  $\text{HgSb}_4\text{S}_7$ , one of the S atoms must be placed on one set of centers of symmetry. From these FOURIER trials, however, the following facts became evident: First, there are two peaks surrounding the center of symmetry at  $(\frac{1}{2} 0 \frac{1}{2})$  each with peak heights as high as the other three kinds of S atoms. Second, there is no indication of an atom on the center of symmetry, and the sign changes caused

<sup>11</sup> E. R. HOWELLS, D. C. PHILLIPS and D. ROGERS, Experimental investigation and the x-ray detection of centers of symmetry. *Acta Crystallogr.* **3** (1950) 210—214.

by placing one S atom on this inversion center did not bring back the assumed atom onto the center in the resulting FOURIER map. The atomic coordinates of the fourth trial are tabulated in Column I of Table 1.

If the peak at  $x = 0.598$ ,  $z = 0.444$  did actually represent the fourth S atom in the asymmetric unit, the chemical formula of livingstonite should be  $\text{HgSb}_4\text{S}_8$  instead of  $\text{HgSb}_4\text{S}_7$ .

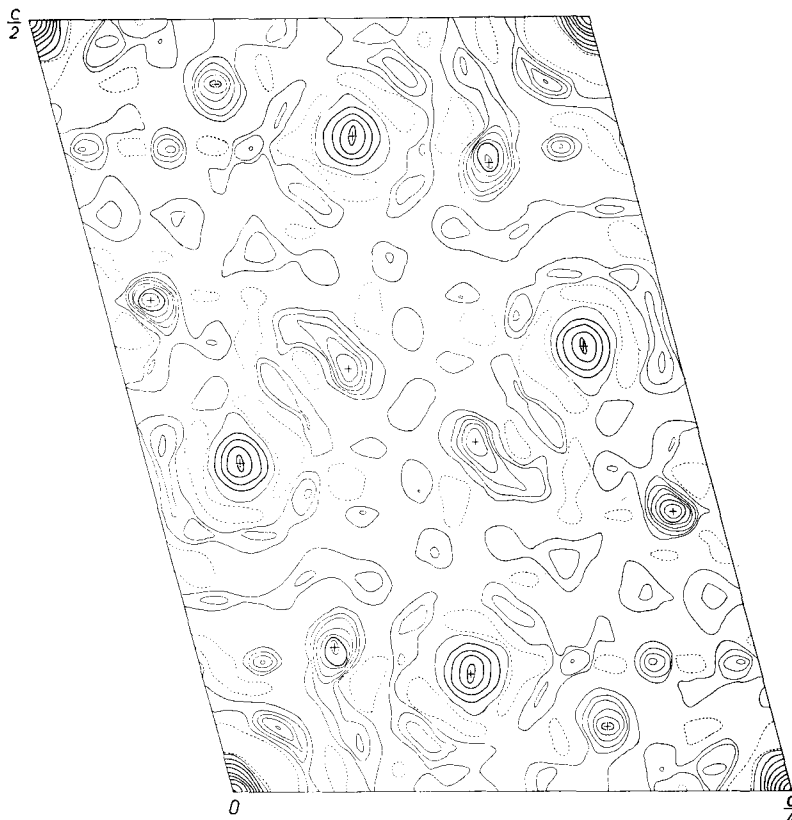


Fig. 3. The first electron-density map  $\rho(xz)$ . The broken lines represent depressions. One interval between heavy contours corresponds to five intervals of light contours. The details between successive heavy contours are omitted. The crosses indicate the atomic sites listed in Column I of Table 1.

#### Chemical composition of livingstonite

In the face of this anomaly of composition, it was felt that new data for the chemical composition of the mineral, as well as more exact X-ray diffraction data, were essential. A specimen from Huitzco, Mexico, was kindly offered for this purpose by Dr. FOSHAG of the

National Museum, Washington, D.C. This specimen (U.S. National Museum No. 105 163) was a beautiful crystal of selenite with numerous inclusions of fine needles of livingstonite.

First the selenite crystal was carefully cleaved to separate the livingstonite needles. After repeated washings in a warm dilute solution of hydrochloric acid, the remaining grains of selenite were separated by the heavy liquid method. Finally the sample was placed under the binocular for manual separation of the mineral. The material collected

Table 1. *Coordinates of atoms referred to projected cell with  $a' = \frac{a}{4}$  and  $c' = \frac{c}{4}$*

Atom		I DAWTON data	II GEIGER- counter data
Hg	$x'$	.000	.000
	$z'$	.000	.000
Sb <sub>I</sub>	$x'$	.479	.482
	$z'$	.150	.153
Sb <sub>II</sub>	$x'$	.170	.170
	$z'$	.429	.423
S <sub>I</sub>	$x'$	.243	.237
	$z'$	.160	.185
S <sub>II</sub>	$x'$	.915	.910
	$z'$	.364	.363
S <sub>III</sub>	$x'$	.693	.685
	$z'$	.085	.081
S <sub>IV</sub>	$x'$	.598	.597
	$z'$	.444	.443

Table 2. *Analysis of livingstonite*

Element	Weight percent	
Hg	19.49 %	
Sb	50.46	
S	27.61	
As	0.29	
Fe	0.22	
Pb	0.24	
Si	0.1–1.0 %	} estimated by spectro- graph
Al	0.1–1.0 %	
Ca	500–3000 ppm.	
Cu	200–1000 „	
Mg	100–500 „	
Bi	100–500 „	
Mn	50–300 „	
Ag	5–25 „	
Na	5–25 „	
Tl	2–10 „	

was then chemically and spectrographically analyzed. The result of this analysis is tabulated in Table 2.

The interpretation of the chemical data was carried out under the following two assumptions. First, Si and Al detected by the spectrograph were presumed due to minor impurities of some kind of unidentified silicate mineral which escaped separation. Later it was observed that some livingstonite needles were aggregated around impurity grains as cores. Second, As was assumed to substitute for Sb, and it was assumed that Pb and Fe could occupy Hg sites.

The weight percentages of Al and Si were subtracted from the total amount. The amount subtracted was half of the value of the maximum estimation by the spectrographical method. The values determined in

this way (1.1 % for Si, and 0.6 % for Al) summed to 1.7 %, which was very close to the deficiency of the total weight percentage of the major elements from 100 %. The elements Hg, Pb, and Fe were grouped together in one group, and Sb and As into another group, as shown in Column I of Table 3. All the other minor elements were neglected. Then these three values for (Hg, Pb, Fe), (Sb, As) and S were converted into the values listed in Column II of Table 3 to make up the total to 100 %.

Table 3. *Interpretation of chemical data*

Element	I Original Analysis	II Normalized to 100 %	III $\text{HgSb}_4\text{S}_7$	IV $\text{HgSb}_4\text{S}_8$
	%	%	%	%
Hg	19.49	20.29	21.99	21.25
Pb	0.24			
Fe	0.22			
Sb	50.46	51.63	53.40	51.48
As	0.29			
S	27.61	28.08	24.61	27.17
Total	98.31	100.00	100.00	100.00
Density measured	5.00 (FRONDEL)			
Density computed			4.88	5.06

In Columns III and IV of Table 3, the ideal weight percentages of the composition  $\text{HgSb}_4\text{S}_7$  and  $\text{HgSb}_4\text{S}_8$  are tabulated. Comparison of the result in the Column II with these two kinds of ideal composition indicated definitely the composition  $\text{HgSb}_4\text{S}_8$  as that of livingstonite. The value of the density, 5.00, measured by FRONDEL<sup>12</sup>, was found to agree well with 5.06, the calculated density of  $\text{HgSb}_4\text{S}_8$ .

#### Unit cell dimensions and space group

Several good single crystals were selected for the X-ray investigation from the livingstonite needles used for the chemical analysis. WEISSENBERG, precession, and DE JONG photographs were taken for the equator and up to the 4th layer, with the crystal set so that the needle axis was parallel to the goniometer axis. The crystals used for the preliminary stage were re-examined by the same methods, and were identified as the same material as the needles.

<sup>12</sup> C. PALACHE, H. BERMAN and C. FRONDEL, *The System of Mineralogy* (John Wiley and Sons, New York: 1952) 485–486.

The crystal was monoclinic, and the unit-cell dimensions obtained were as follows:

$$\begin{aligned} a &= 30.25 \text{ \AA} \\ b &= 4.00 \text{ \AA} \quad \beta = 104^\circ 12'. \\ c &= 21.48 \text{ \AA} \end{aligned}$$

This unit cell contains  $8\text{HgSb}_4\text{S}_8$ .

The following systematic absences were observed for the recorded spectra:

$$\begin{aligned} hkl &\text{ with } k + l = \text{even only} \\ h0l &\text{ with } l = \text{even, and } h = 4n \text{ (} n = 0, 1, 2, 3, \dots \text{) only.} \\ 0k0 &\text{ with } k = \text{even only} \end{aligned}$$

From these rules the space group is  $A2/a$  if it is centrosymmetric, and  $Aa$  if non-centrosymmetric. The observed systematic absences for reflections  $h0l$  are rather unusual. For the two possible space groups the required systematic absences for this type of reflection are  $h = \text{odd}$  and  $l = \text{odd}$ . Therefore, the extra systematic absences with  $h = 4n + 2$ , and  $l = \text{odd}$  are to be interpreted as due to the structural arrangement. Satisfactory twinning rules to explain the above-mentioned facts could not be obtained. The centrosymmetrical space group  $A2/a$  was assumed for the starting point.

#### Relations between unit cell data

Because of the extinction already described, a sub-multiple cell with  $a' = a/4$ , and  $c' = c/2$  could be taken for the projection on (010). These dimensions are as follows:

$$\begin{aligned} a' &= 7.56 \text{ \AA} \\ c' &= 10.74 \text{ \AA} \quad \beta = 104^\circ 12'. \end{aligned}$$

These values were identical with those obtained at this stage by checking GORMAN's result from the equator WEISSENBERG photograph. There must be some relation between the present unit cell and the ones previously described by RICHMOND and GORMAN. The relations between these unit cells are tabulated in Table 4.

Our cell and RICHMOND's are almost identical except that our  $a$  unit is double RICHMOND's. GORMAN's triclinic cell can be explained as a primitive triclinic setting of our  $A$ -centered monoclinic cell if taken with the sub-multiple units,  $a' = a/4$ , and  $c' = c/2$ . The three shortest vectors of this setting of our cell are represented by vectors  $A$ ,  $B$ ,

and  $C$  in Table 4. The vectorial expression of these three new axes is also found in Table 4. The good agreement between this cell and GORMAN's cell supports the relation discussed above.

Space group  $A2/a$  is illustrated in Fig. 4 by projections along the  $b$  and  $c$  axes. The sub-multiple unit cell in the projections on  $(010)$  is indicated by a heavy outline in the drawing. The statistical test with

Table 4. Comparison of cell data for livingstonite

	RICHMOND	GORMAN (original kX units converted to Å units)	NIIZEKI and BUERGER	NIIZEKI and BUERGER's cell referred to $A = \frac{1}{4}a - \frac{1}{2}b$ $B = \frac{1}{2}b - \frac{1}{2}c$ $C = b$
$a$	$15.14 \text{ \AA} = 7.57 \cdot 2$	$7.67 \text{ \AA}$	$30.25 \text{ \AA} = 7.64 \cdot 4$	$7.62 \text{ \AA}$
$b$	3.98	4.00	4.00	4.00
$c$	$21.60 = 10.80 \cdot 2$	10.84	$21.49 = 10.75 \cdot 2$	10.93
$\alpha$	—	$99^\circ 12'$	—	$100^\circ 31'$
$\beta$	$104^\circ 00'$	$102^\circ 01'$	$104^\circ 12'$	$104^\circ 49'$
$\gamma$	—	$73^\circ 48'$	—	$73^\circ 46'$
cell contents	$4 \text{ HgSb}_4\text{S}_7$	$\text{HgSb}_4\text{S}_7$	$8 \text{ HgSb}_4\text{S}_8$	$\text{HgSb}_4\text{S}_8$

$F^2(h0l)$ 's, which was considered to indicate the existence of the center of symmetry in the projection, must now be interpreted as the proof of a pseudo center of symmetry at  $(\frac{1}{8}, 0, \frac{1}{4})$ , which is indicated by a cross in Fig. 4.

### Three-dimensional intensity determination

Three-dimensional intensities were collected by the single-crystal GEIGER-counter-goniometer method developed in the Crystallographic Laboratory of M.I.T. The  $h0l$  intensities were first measured with  $\text{MoK}\alpha$  radiation. But the large size of the true unit-cell dimensions made the successive reciprocal-lattice points in the upper levels too close to be resolved by this radiation. Thus  $\text{CuK}\alpha$  radiation was necessary for collecting the  $hkl$  intensities, although this longer wavelength resulted in an increase in the linear absorption coefficient of the crystal. These intensities were corrected for LORENTZ and polarization factors, but no allowance was made for absorption factor until the last stage of analysis.

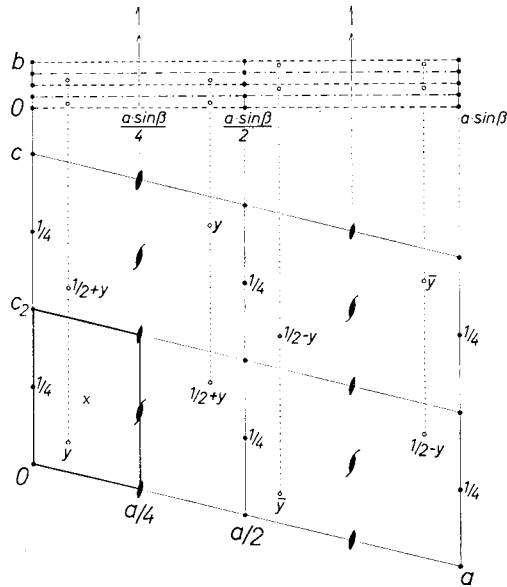


Fig. 4. Representations of space group  $A2/a$ . The lower drawing shows the symmetry elements and the general equipoint  $8(f)$  in the projection on  $(010)$ . The heavy outline in this diagram indicates the sub-multiple unit cell of the projection. A cross inside this unit shows the location of the pseudo center of symmetry. The upper drawing represents the projection on the plane normal to the  $c$  axis.

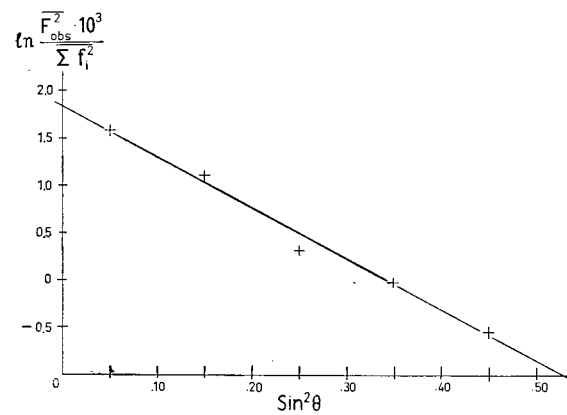


Fig. 5. Determination of scale factor and temperature coefficient of livingstonite by WILSON's statistical method. The observed  $I^{h0l}$ 's collected with  $\text{MoK}\alpha$  radiation were used to obtain the result.

### Refinement of the projected structure

With the new set of  $F^2(h0l)$ 's collected with  $\text{MoK}\alpha$  radiation, the refinement of the electron-density map  $\rho(xz)$  was carried out. The statistical treatment of WILSON<sup>13</sup> applied to the  $F^2$  values, shown in Fig. 5, determined the scaling factor and temperature coefficient. With

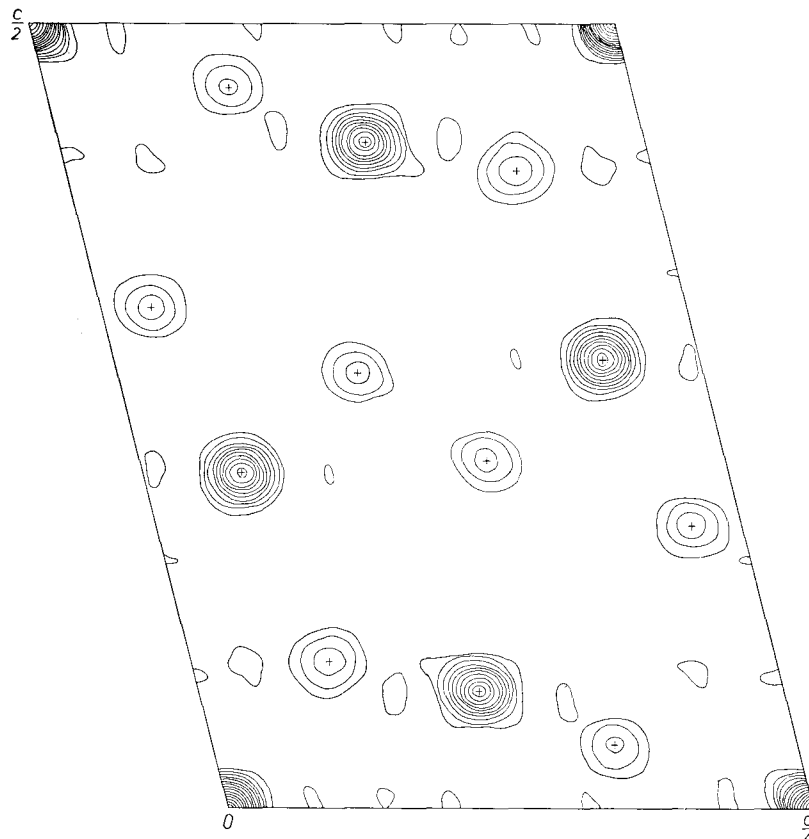


Fig. 6. Final electron-density map of the projection on (010). This  $\rho(xz)$  map represents the crystal structure in the sub-multiple unit cell outlined by heavy lines in Fig. 4. Negative contours are omitted.

the final atomic coordinates determined in the preliminary stage, and these new  $F^2$  values, the refinement of the projection was done by successive FOURIER and difference-FOURIER trials. The final atomic coordinates are tabulated in Column II of Table 1. The temperature

<sup>13</sup> A. J. C. WILSON, Determination of absolute from relative x-ray intensity data. *Nature* **150** (1942) 151–152.

