

The Crystal Structure of Jamesonite, $\text{FePb}_4\text{Sb}_6\text{S}_{14}$

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With 19 figures

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Zusammenfassung

Die Kristallstruktur des Jamesonits gehört der Raumgruppe $P2_1/a$ an; die Elementarzelle mit den Gitterkonstanten $a = 15,07 \text{ \AA}$, $b = 18,98 \text{ \AA}$, $c = 4,03 \text{ \AA}$, $\beta = 91^\circ 48'$ enthält 2 $\text{FePb}_4\text{Sb}_6\text{S}_{14}$.

Drei Sb_3S_3 -Gruppen sind parallel $[120]$ angeordnet und können zusammen als Sb_3S_7 -Gruppen aufgefaßt werden, die durch lose Bindung größere Gruppen Sb_6S_{14} ergeben. Fe- und zwei Lagen von Pb-Atomen nehmen die Räume zwischen S-Atomen der Sb_6S_{14} -Gruppen ein und verknüpfen die Sb-S-Gruppen miteinander. Jedes Fe-Atom wird von sechs S-Atomen in den Ecken eines verzerrten Oktaeders umgeben. Die Pb-Atome haben entweder 7 oder 8 S-Atome als nächste Nachbarn. Starke Bindung längs Ketten oder Schichten parallel der Längsrichtung der nadeligen Kristalle tritt beim Jamesonit nicht klar in Erscheinung. Die Spaltbarkeit des Minerals wird auf Grund der beobachteten interatomaren Abstände gedeutet.

Abstract

The crystal structure of the mineral jamesonite has been determined. The space group is $P2_1/a$, and the unit cell dimensions are: $a = 15.07 \text{ \AA}$, $b = 18.98 \text{ \AA}$, $c = 4.03 \text{ \AA}$, and $\beta = 91^\circ 48'$. This unit cell contains 2 $\text{FePb}_4\text{Sb}_6\text{S}_{14}$. The intensities were measured by the single-crystal GEIGER-counter method with $\text{CuK}\alpha$ radiation. The structure projected along c axis was solved by the minimum function method. The z parameters of the atoms were determined by the implication method. The structure was refined by the successive FOURIER, and difference-FOURIER trials, and finally by the three-dimensional least-squares method.

In the structure three Sb_3S_3 groups are arranged parallel to $[120]$, and can be described as forming Sb_3S_7 groups. Two Sb_3S_7 groups are loosely bonded together into a larger Sb_6S_{14} group. Fe and two kinds of Pb atoms are located in the interstices provided by the S atoms of the Sb_6S_{14} groups, and play the role of cementing these Sb-S groups. Fe has a distorted octahedral coordination of six S atoms. The Pb atoms have either 7 or 8 atoms of sulfur as closest neighbors.

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The strongly bonded chains or layers running parallel to the acicular axis of the mineral is not well defined in jamesonite. The cleavage of the mineral has been accounted for in terms of the observed interatomic distances.

Introduction

The crystallographic description of the mineral jamesonite, $\text{FePb}_4\text{Sb}_6\text{S}_{14}$, has been presented by BERRY². Jamesonite is a member of the group of acicular sulfosalts, concerning which there has been a considerable increase in structural knowledge in recent years³⁻⁷. As in the case of livingstonite⁶, HgSb_4S_8 , the crystal system of jamesonite is monoclinic. The needle axis of jamesonite is parallel to the c axis, while in livingstonite it is parallel to the unique 2-fold (or b) axis.

The cleavages of the members of the group of acicular sulfosalts are known to occur in two ways. In one type, cleavage parallel to the acicular axis, or prismatic cleavage only, is observed. All the sulfosalts crystals of the acicular group with previously determined structures are of this type. In these crystal structures there are layers or chains composed of submetal atoms and sulfur atoms running parallel to the needle axis of the mineral. The prismatic cleavage of the mineral has been explained as due to the breaking of the weaker chemical bonds between the layers or chains in the structure, and, as a result, parallel to the acicular axis. A second type of cleavage occurs perpendicularly to the acicular axis. This basal cleavage is observed with or without accompanying prismatic cleavage. Among the minerals with this type of cleavage are jamesonite, owyheeite⁸, and falkmanite⁹. Accordingly, a somewhat different structural scheme than found in the previously determined structures can be expected for jamesonite.

² L. G. BERRY, Studies of mineral sulpho-salts: II. Jamesonite from Cornwall and Bolivia. *Miner. Mag.* **25** (1940) 597-608.

³ F. E. WICKMAN, The crystal structure of galenobismutite. *Arkiv Chem. Geol.* **1** (1951) 219-225.

⁴ F. E. WICKMAN, The crystal structure of aikinite, CuPbBiS_3 . *Arkiv Chem. Geol.* **1** (1953) 501-507.

⁵ M. J. BUERGER and THEODOR HAHN, The crystal structure of berthierite, FeSb_2S_4 . *Am. Mineralogist* **40** (1955) 226-238.

⁶ N. NIIZEKI and M. J. BUERGER, The crystal structure of livingstonite, HgSb_4S_8 . *Z. Kristallogr.* **109** (1957) 129-157.

⁷ N. NIIZEKI, The crystal chemistry of the mineral sulfosalts. To be published in *Geochemica Acta*.

⁸ S. C. ROBINSON, Owyheeite. *Am. Mineralogist* **34** (1949) 398-402.

⁹ J. E. HILLER, Über den Falkmanit und seine Unterscheidung von Boulangerit. *Neues Jb. Mineralog. Mh.* **1955**, 1-10.

Unit cell and space group

The unit cell and space group of the mineral were determined from precession and DE JONG photographs using crystals from Cornwall, England, kindly furnished for our investigation by Professor CLIFFORD FRONDEL from the Harvard mineralogical collection. The results obtained for the unit cell dimensions are:

$$\begin{aligned} a &= 15.57 \text{ \AA} \\ b &= 18.98 \text{ \AA} \quad \beta = 91^\circ 48' \\ c &= 4.03 \text{ \AA} \end{aligned}$$

These values are in good agreement with those of BERRY. The space group $P2_1/a$ assigned by BERRY² was confirmed. The unit cell contains $2\text{FePb}_4\text{Sb}_6\text{S}_{14}$.

Intensity determination

A single crystal of needle form having dimensions 0.03 mm. \times 0.04 mm. \times 1.5 mm. was selected for the intensity determination. The three-dimensional intensities were measured by the single-crystal

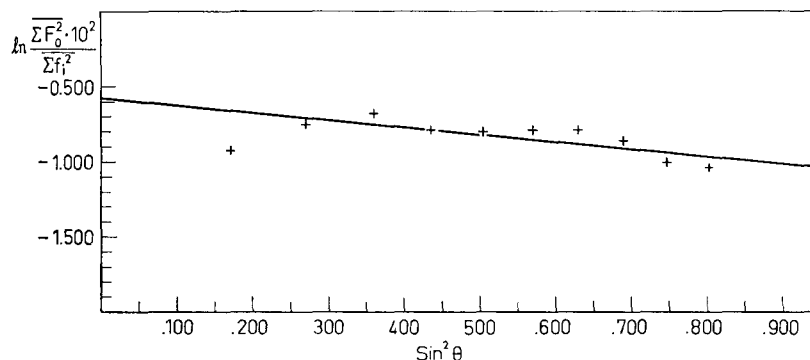


Fig. 1. Determination of scale factor and temperature coefficient by WILSON's statistical method applied to three-dimensional intensity data

GEIGER-counter goniometer method developed in the Crystallographic Laboratory, M.I.T., using $\text{CuK}\alpha$ radiation. Intensities were corrected for LORENTZ and polarization factors, but no allowance was made for the absorption factor. The $F^2(hkl)$ values were placed on an absolute basis using WILSON's method¹⁰ applied three-dimensionally, Fig. 1. The temperature coefficient obtained by this method was $B = 0.59$.

¹⁰ A. J. C. WILSON, Determination of absolute from relative intensity data. Nature 150 (1942) 151-152.

General outline of the structure determination

Space-group equipoint considerations fix the position of the Fe atoms on one set of centers of symmetry. All the rest of the atoms presumably must occupy the general position $4(e)$. The existence of one short axis of length 4 \AA suggests the possibility of solving the crystal structure as projected along this axis by means of minimum function method¹¹.

As pointed out by BUERGER and HAHN elsewhere⁵, errors in solutions by the minimum-function method can arise if the PATTERSON peak chosen as the image point is not a single peak, but rather a coalescence of several peaks. During the present case of the structure determination of jamesonite, a false structure was obtained from an image point incorrectly selected. This false structure appeared very similar to the expected structure, at least in numbers of heavy peaks representing Pb and Sb atoms. The falseness of the structure could not be detected until a final electron-density map indicated certain abnormalities of the structure. Since this kind of confusion is apt to occur when the image-seeking method is applied to solve structures with large unit cells having many heavy atoms, such as those of many of the sulfosalt minerals, the discussion of the procedure will be given in some detail.

Interpretation of PATTERSON peaks

The PATTERSON map $P(xy)$, Fig. 2, was obtained from the $F^2(hk0)$'s. The plane group of the projection along the c axis of space group $P2_1/a$ is $p2gg$, and the corresponding PATTERSON plane group is $p2mm$. The relation between a rotation peak and its reflection satellites in this plane group is illustrated in Fig. 3. Since there are 2 Pb atoms and 3 Sb atoms in the asymmetric unit, then if no overlapping occurs, there must be 5 rotation peaks of single weight, and 10 reflection satellites of double weight in a quarter of PATTERSON space. Actually, as shown in Fig. 2, there are 6 peaks along the line $x = 1/2$, and 8 peaks along the line $y = 1/2$. These peaks have various heights, and the broadened shapes of some peaks at once suggest a considerable amount of overlapping at these locations. The excess number of peaks appearing along these lines is considered due either to interatomic vectors with accidental x or y component of $1/2$, or coalescence of reflection satellites of S atoms.

¹¹ M. J. BUERGER, A new approach to crystal-structure analysis. *Acta Crystallogr.* **4** (1951) 531–544.

Since it was impossible to choose definite satellite peaks, all the satellite-like peaks were used to find possible rotation peaks. Among the 48 possible positions for rotation peaks, Fig. 4, only three of them are associated with peaks which can be assumed reasonably as single-weight rotation peaks. The peak-height analysis was made assuming

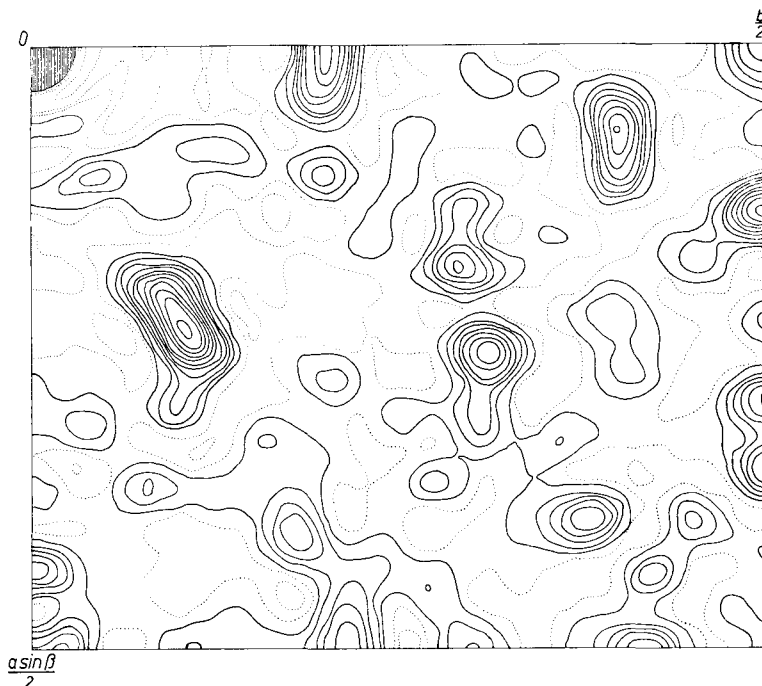


Fig. 2. PATTERSON diagram $P(xy)$. Contours are drawn at intervals of 50 units on an arbitrary scale. The dotted contours represent depressions. The details of the heavy peak at the origin are omitted.

a probably true zero contour, and it was found that all three of the peaks could be Pb—Pb rotation peaks. These peaks are numbered I, II, and III in Fig. 4.

Solutions by the image-seeking method

Assuming each of these three peaks as an image point in turn, three sets of M_2 functions were obtained, and each of them was folded into an M_4 function using a glide operation. These three M_4 maps are shown in Figs. 5, 6 and 7. Among them the $^{\text{III}}M_4$ map (an M_4 map based upon the assumption that peak III is a Pb—Pb rotation peak)

gave a result completely unrelated to the expected number of heavy atoms in the structure, Fig. 7, and was accordingly discarded. Since both the $^I M_4$ map and the $^{II} M_4$ map gave 6 heavy peaks, no choice between them was considered at this stage. The structures based on peaks I and II will be identified as structures I and II, respectively. To resolve an extra peak in each map, another M_4 map was tried for each structure. The peak with the heaviest contour in each M_4 map was

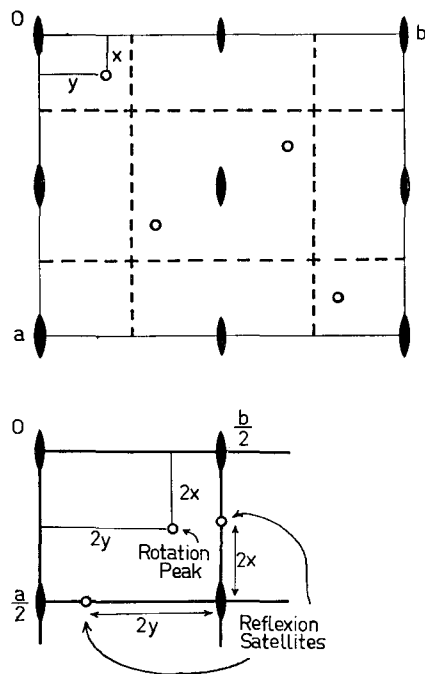


Fig. 3. Geometrical relation between a rotation peak and its reflection satellites in PATTERSON diagrams having plane symmetry $p2mm$

assumed as the second probable atomic site for the *Pb* atom. In structure I, Fig. 5, it is designated as peak *a*, and in structure II, Fig. 6, as peak *A*. The $^a M_4$ map and the $^A M_4$ map were then prepared. Under the assumption that the atoms at I and *a* in one structure, and II and *A* in the other, are all of the same atomic specie (i. e., *Pb*) the $^{I+a} M_8$ and $^{II+A} M_8$ maps can be obtained by superposing the proper M_4 maps. The $^{I+a} M_8$ map, which was later found to represent the correct structure, is shown in Fig. 8. Also in Fig. 9, two M_8 maps were compared, one map $^{I+a} M_8$ in full lines, and the other $^{II+A} M_8$ in dotted lines. From this comparison, however, nothing indicates which is the correct one.

False structure

First the structure II was assumed to be correct, and since the

identification of heavy peaks in the M_8 map with *Pb* and *Sb* was impossible, structure factors were computed using an average *f* curve: $\frac{1}{2}(f_{Pb} + f_{Sb})$. An electron-density map was prepared using signs determined in this way, and then refined by the usual procedures. The final electron-density map of structure II and its structural scheme, are shown respectively in Figs. 10 and 11. An examination of $\rho(xy)$, Fig. 10, however, reveals several peculiarities which are enough to

raise a question as to the validity of this structure. First, the relative weights of the five heavy peaks do not correspond to the chemical formula of jamesonite in a clear-cut way. Above all, there is one peak (peak *D* in Fig. 10) significantly too low to be assigned to an Sb atom. Furthermore, the shape of this particular peak is not well defined. The

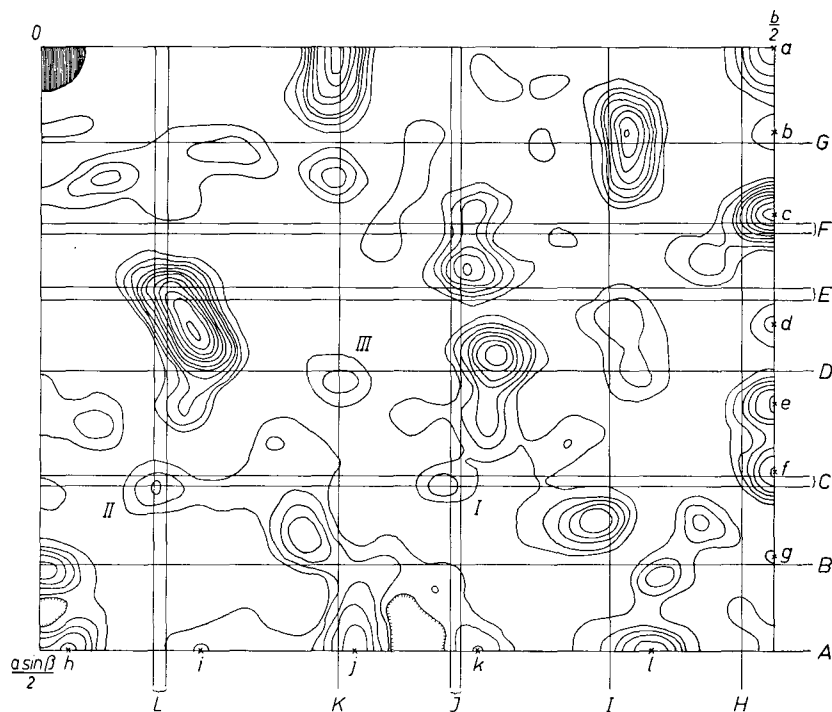


Fig. 4. Solution of rotation peaks from satellite-like peaks. Solutions are obtained at the intersections of horizontal and vertical lines drawn according to the relation illustrated in Fig. 3. Satellite-like peaks are designated by letters *a* to *l*, and the corresponding lines are designated by letters *A* to *L*. Three probable rotation peaks obtained by this method are indicated by I, II, and III.

above-mentioned aspects of the structure could not be improved by exchanging Pb with Sb in some of the atomic sites. Second, the peak shapes of the lighter atoms, especially of the Fe atom at the origin, are obscure. For these reasons structure II was considered incorrect. The significance of those features in the FOURIER diagrams which suggest an incorrect structure was recently pointed out by PINNOCK et al.¹²

¹² P. R. PINNOCK, C. A. TAYLOR and H. LIPSON, A re-determination of the structure of triphenylene. *Acta Crystallogr.* 9 (1956) 173–179.

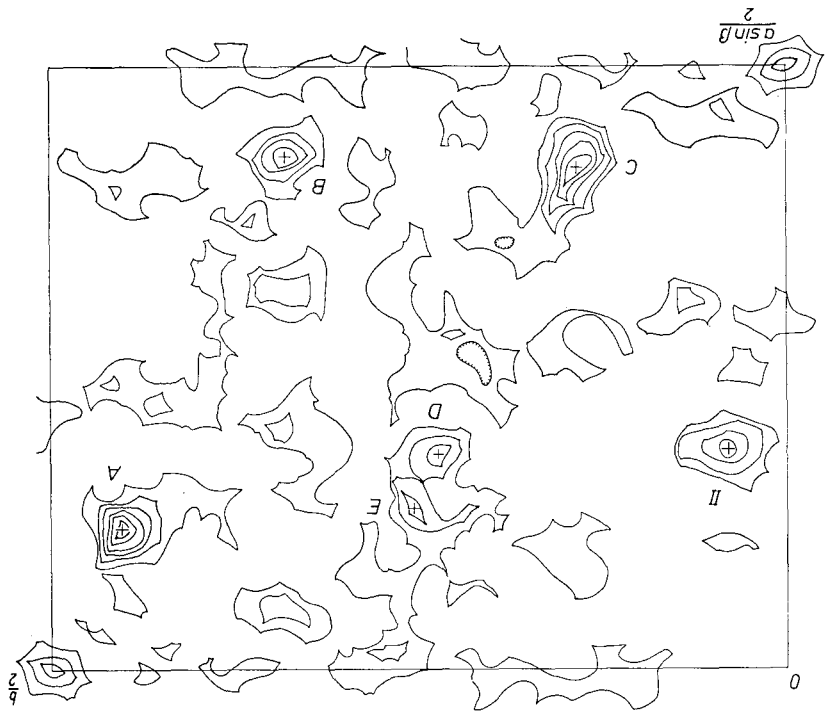


Fig. 6. M_4 map

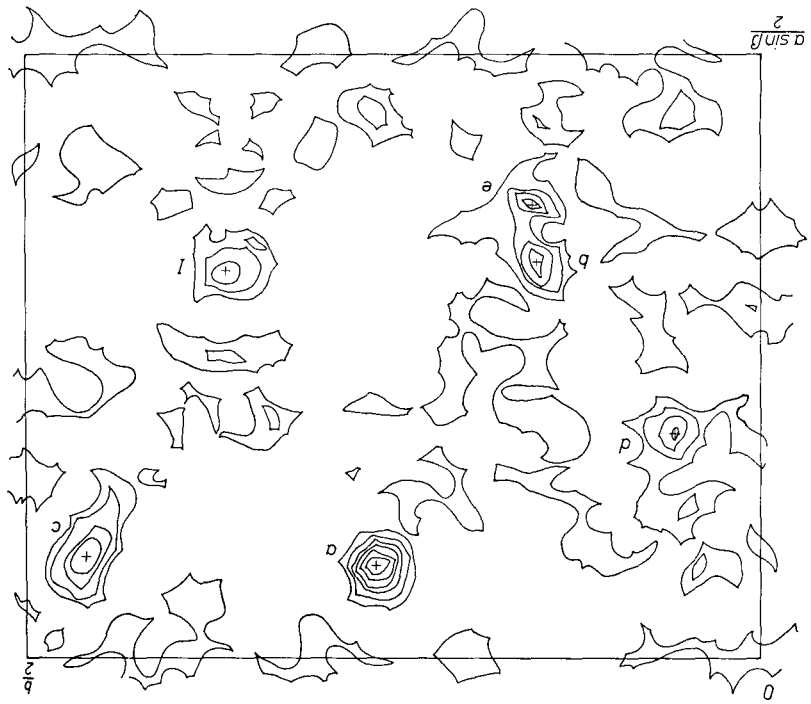


Fig. 5. M_4 map

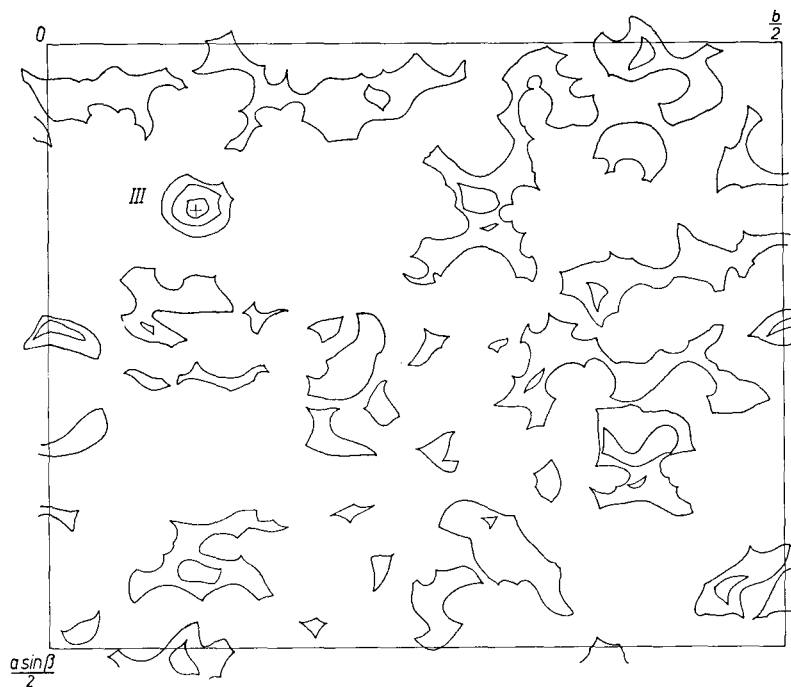


Fig. 7. III M_4 map

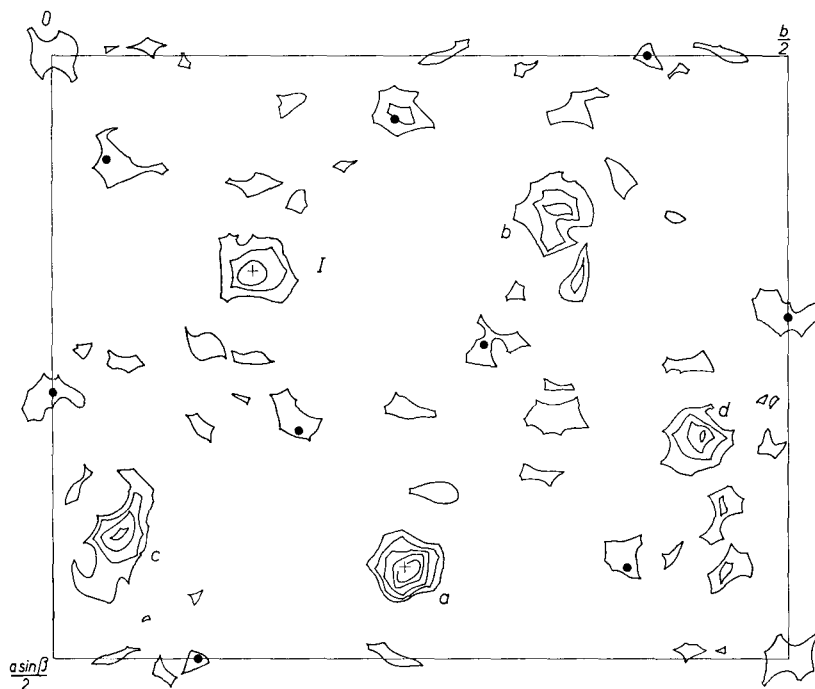


Fig. 8. I + aM_8 map. Black dots indicate the final atomic sites for S atoms determined by FOURIER methods

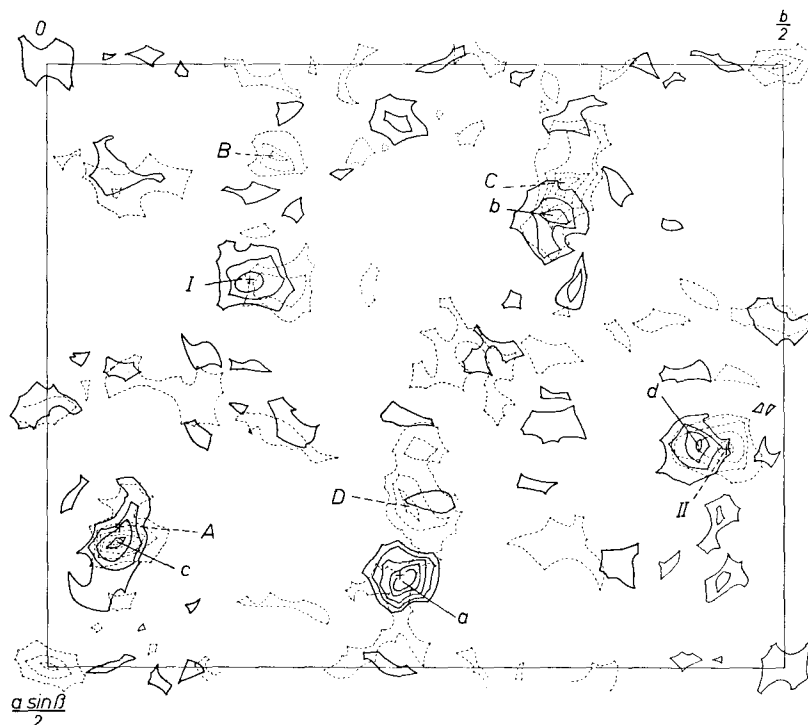


Fig. 9. Comparison of two M_8 maps. The $I+^a M_8$ map is drawn in full lines, and the $II+^d M_8$ map in broken lines

Correct structure

The alternative structure I based on the $I+^a M_4$ map was then tried. Structure factors were computed as before with the averaged f curve. The electron-density map is shown in Fig. 12. In this map the shapes and the weight relations among the five heavy peaks are well defined. Peaks I and a are assigned to Pb atoms, and peaks b , c , and d to the three Sb atoms.

Because of the identity of peaks I and a , the superposition of the $I M_4$ map and the $^a M_4$ map was justified, and this $I+^a M_8$ map, Fig. 8, should contain enough information concerning the locations of S atoms. Although the refinement of the electron-density map, Fig. 12, should naturally indicate the sulfur peaks, it was considered useful to see how the image-seeking method would narrow the allowed region for the S atoms. This process was carried out by further constructing a $b+c M_8$ map based on the rotation peaks b and c , both Sb—Sb rotation peaks. This map is shown in broken lines in Fig. 13 superposed on the

previously obtained $I+^aM_8$ map, which is drawn in full lines. Since these two M_8 maps are based on rotation peaks of different weights (different atomic species), the simple superposition to obtain an M_{16} map could not be made without proper weighting of contours. The final sulfur positions found by the FOURIER method are indicated in

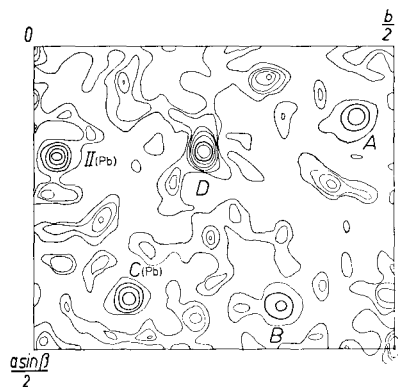


Fig. 10

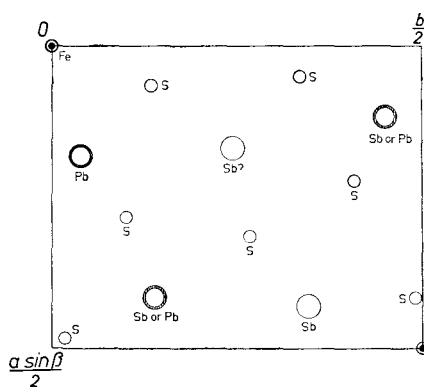


Fig. 11

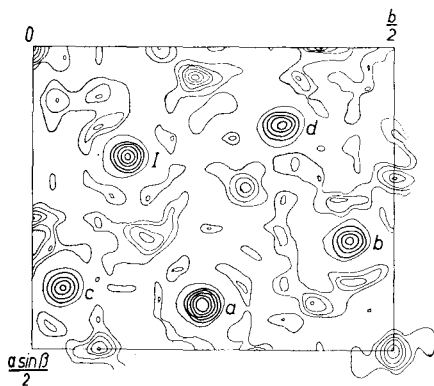


Fig. 12

Fig. 10. Electron density map $\rho(xy)$ of false structure based on $II+^aM_8$ map

Fig. 11. Structural scheme of false structure, Fig. 10

Fig. 12. Electron density map $\rho(xy)$ of correct structure based on $I+^aM_8$ map

Fig. 13 by black dots. They are all found at locations permitted by the minimum-function maps. Including these sulfur atoms in the structure-factor computation, the refinement of structure I was done by successive difference-FOURIER maps. The final atomic coordinates determined by this process are presented in Column III of Table 1. The reliability factor for this projection was computed as $R = 0.19$.

The final electron density map prepared with signs after the three-dimensional refinement is shown in Fig. 14 for the full unit cell.

