

The Application of the ThreeDimensional Patterson Method and the Crystal Structures of Proustite, Ag_3AsS_3 , and Pyrargyrite, Ag_3SbS_3

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Citation: [The Journal of Chemical Physics](#) **4**, 381 (1936); doi: 10.1063/1.1749863

View online: <http://dx.doi.org/10.1063/1.1749863>

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methyl carbon atoms are directly below the other carbon atoms a distance of 1.52Å, we get the values of μ marked *B* in the table. The difference is not very marked but it is sufficient to make it probable that the methyl carbon atoms are, as we have sketched them, above the plane of the oxygen atoms.

DISCUSSION OF RESULTS

While an apparatus has been developed by which one may make measurements of interatomic distances by means of the diffraction of electrons of only 6400 volts energy, the accuracy of the results is not as great as that of other workers using higher voltages. In the experiments reported here, the accelerating voltage was known with an accuracy of one percent. The ammeter and resistance used were thus accurate, the choke coil and condenser were sufficient to smooth out the pulsations of the rectified 60-cycle alternating current to this degree of accuracy, and the actual measurements showed that the variations in the input alternating current were no greater than this.

The distance from the jet to the photographic plates could be measured quite accurately, the error here being certainly less than one percent.

The greater error is in the actual measurement of the positions of the maxima on the plates. This is especially true since the maxima are not sharp lines but are rather broad. The fact that the measurements from the individual plates do not differ from the average by more than 3 percent indicates that the maxima can be determined fairly accurately. The final values of μ are probably accurate to within two percent. The relation between the positions of the maxima and the values of the interatomic distances is, in general, quite complicated, so that for a given error in the former it is difficult to estimate the error in the latter.

A real source of error in these experiments comes from the fact that only a few maxima and minima could be measured due to the limitations of the apparatus. When this is true, the fact that the observed and calculated values of μ agree very well is not a guarantee of like accuracy in the values of the interatomic distances. For small variations in the structure are best detected in the positions of the outer maxima, those beyond the third. It is difficult to say just how much effect this would have on the compounds studied here, but it is probable that the measurements recorded are accurate to $\pm 0.05\text{\AA}$.

JUNE, 1936

JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

The Application of the Three-Dimensional Patterson Method and the Crystal Structures of Proustite, Ag_3AsS_3 , and Pyrargyrite, Ag_3SbS_3 *

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(Received March 18, 1936)

It is shown that the three-dimensional Patterson method can be so simplified by the use of the symmetry properties of the crystal under consideration that its use in determining the positions of atoms in crystals is practicable. This method is then used to determine the positions of the heavy atoms in proustite, Ag_3AsS_3 . The positions of the sulfur atoms are found by the use of the covalent atomic radii and assumptions concerning bond directions. The structure so derived is found to be compatible with the observed data. Proustite is found to contain pyramidal AsS_3''' groups and silver atoms forming two bonds to sulfur in almost opposed directions. Pyrargyrite, Ag_3SbS_3 , is found to have almost the same structure as proustite. The analytical statement of the structures is as follows:—The space group, C_{3v}^6-R3c , is common to both proustite and pyrargyrite. The special positions of C_{3v}^6 are (in

hexagonal axes)

$$(2a) \quad 0, 0, Z; \quad 0, 0, \frac{1}{2} + Z;$$

$$(6b) \quad \begin{array}{lll} X, Y, Z; & \bar{Y}, X-Y, Z; & Y-X, \bar{X}, Z; \\ \bar{Y}, \bar{X}, \frac{1}{2} + Z; & X, X-Y, \frac{1}{2} + Z; & Y-X, Y, \frac{1}{2} + Z; \end{array}$$

and positions derived from these by the operations of the rhombohedral lattice. The parameter values are:

Proustite		Pyrargyrite	
$a_0 = 10.74\text{\AA}$,	$c_0 = 8.64\text{\AA}$	$a_0 = 11.04\text{\AA}$,	$c_0 = 8.71\text{\AA}$
2As in $2a$,	$Z_{\text{As}} = 0.000$	2Sb in $2a$,	$Z_{\text{Sb}} = 0.000$
6Ag in $6b$,	$X_{\text{Ag}} = 0.246$	6Ag in $6b$,	$X_{\text{Ag}} = 0.250$
	$Y_{\text{Ag}} = 0.298$		$Y_{\text{Ag}} = 0.305$
	$Z_{\text{Ag}} = 0.235$		$Z_{\text{Ag}} = 0.210$
6S in $6b$,	$X_{\text{S}} = 0.220$	6S in $6b$,	$X_{\text{S}} = 0.220$
	$Y_{\text{S}} = 0.095$		$Y_{\text{S}} = 0.105$
	$Z_{\text{S}} = 0.385$		$Z_{\text{S}} = 0.355$

INTRODUCTION

THE determination of the inner structure of a crystal by means of x-rays has been, in most cases, a process of trial and error. Once the space group of the crystal is known, the direct use of the x-ray data is abandoned. A structure which satisfies the symmetry requirements of the space group is then assumed and the intensities of the diffracted x-ray beams are calculated on this basis. If these do not agree with the experimentally determined intensities, another structure is assumed and the process is repeated. Systematic methods of carrying out this process have been devised which are remarkable for the rapidity and accuracy with which, in some cases, they lead to the elimination of every structure but the true one. In other cases, however, the systematic trial and error method breaks down and either fails completely or leads to the loss of much time.

If a convenient direct method for calculating the structure of a crystal from the experimental data were available, these inefficiencies and failures would, of course, be eliminated. Such a method has not as yet appeared. However, a very close approximation to such a treatment is provided by the Patterson method when used as described in the next section.

The determination of the structure of proustite by means of this method is described later in this paper and illustrates the advantages and limitations of the treatment.

USE OF THE THREE-DIMENSIONAL PATTERSON METHOD

Patterson¹ has shown that the three-dimensional Fourier series

$$P(x, y, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2 \times \cos 2\pi(hx + ky + lz)$$

—where x , y and z are the coordinates of points in the crystal lattice measured in units of the primitive translations and $F_{(hkl)}$ is the amplitude of the diffracted beam “reflected” from the crystal plane with indices (hkl) —represents a

function having maxima at vector distances from the origin equal to vector distances between pairs of maxima in the electron density in the crystal. Since there is a maximum in the electron density at the center of each atom, the coordinates of the maxima in $P(x, y, z)$ can be interpreted as the components of interatomic vectors. The evaluation of such a series at a sufficient number of points in the unit cell to show the true form of the function $P(x, y, z)$ has never been carried out, the calculation involving a prohibitive amount of labor. Instead, the projection of $P(x, y, z)$ on a plane perpendicular to one of the crystal axes has been used. If the projection is upon the plane perpendicular to the z axis, the projected function $p(x, y)$ is calculated thus

$$\begin{aligned} p(x, y) &= \int_0^1 P(x, y, z) dz \\ &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(hkl)}|^2 \times \int_0^1 \cos 2\pi(hx + ky + lz) dz \\ &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} |F_{(hk0)}|^2 \cos 2\pi(hx + ky). \end{aligned}$$

$p(x, y)$, which is represented by a two-dimensional Fourier series, has been evaluated completely by several authors in the course of various crystal structure investigations. Its use has proved very fruitful, in some cases making possible the determination of structures which would have been impracticably difficult otherwise.

The use of $p(x, y)$ has, however, two disadvantages. In the first place, there is a large probability that a given maximum is composed of the superposition of two or more maxima of $P(x, y, z)$ which have projected onto nearly the same spot. Secondly, the resolution of maxima which are near together is not as good as can be obtained by the use of $P(x, y, z)$, since only a small fraction of the terms in $P(x, y, z)$ are used in $p(x, y)$. The function $P(x, y, z)$ would consequently be preferred if the labor involved in its calculation could be reduced.

The use of the symmetry of the crystal under consideration often leads to the desired simplification. For example, let the crystal have a

* Contribution No. 535 from Gates Chemical Laboratory, California Institute of Technology.

¹ A. L. Patterson, *Zeits. f. Krist.* **90**, 517 (1935).

twofold axis (which will be taken coincident with the b axis). Then, if there is an atom at the point (x, y, z) , there will be another atom, crystallographically equivalent to the first, at (\bar{x}, y, \bar{z}) . The vector between these atoms has the components $(2x, 0, 2z)$ and consequently there will be a maximum in $P(x, y, z)$ at the point $(2x, 0, 2z)$. This maximum lies in the plane $y=0$. There will be a maximum in this plane for each (crystallographically) different kind of atom in the crystal. The x and y coordinates of all the atoms in the crystal can consequently be found by evaluating $P(x, y, z)$ for $y=0$ only. In this case the expression for $P(x, y, z)$ can be simplified as follows:

$$\begin{aligned} P(x, 0, z) &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}|^2 \\ &\quad \times \cos 2\pi(hx + lz) \\ &= \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \cos 2\pi(hx + lz) \\ &\quad \times \left\{ \sum_{k=-\infty}^{\infty} |F_{hkl}|^2 \right\}. \end{aligned}$$

Now let $\sum_{k=-\infty}^{\infty} |F_{hkl}|^2 = C_{hl}$

and we have

$$P(x, 0, z) = \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} C_{hl} \cos 2\pi(hx + lz).$$

$P(x, 0, z)$ is a two-dimensional Fourier series of the same general type as $p(x, y)$ and consequently its calculation is practicable. The same information about the x and z coordinates of the atoms is contained in $P(x, 0, z)$ as in $p(x, z)$, but in much clearer form; for (a) the maxima in $P(x, 0, z)$ will be sharper, in general, since there are usually more terms in its Fourier series than in that of $p(x, z)$ and (b) all the maxima corresponding to interatomic vectors not parallel to the plane $y=0$ appear in $p(x, z)$, but are eliminated in $P(x, 0, z)$. $P(x, 0, z)$ can be used to determine the x and z coordinates of atoms in case the b axis is parallel to a two-, three-, four-, or sixfold symmetry axis of the crystal, for in all these cases the vectors between equivalent atoms are parallel to the plane $y=0$.

In case the b axis is a twofold screw axis the treatment of $P(x, y, z)$ is slightly changed. The coordinates of equivalent atoms are now (x, y, z) and $(\bar{x}, y + \frac{1}{2}, \bar{z})$ and the vectors between equivalent atoms have components $(2x, -\frac{1}{2}, 2z)$. In this case $P(x, y, z)$ must be evaluated for $y = -\frac{1}{2}$ or, since $P(x, y, z)$ has a center of symmetry, for $y = \frac{1}{2}$. The calculation simplifies as follows:

$$\begin{aligned} P(x, \tfrac{1}{2}, z) &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}|^2 \\ &\quad \times \cos 2\pi(hx + k/2 + lz) \\ &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} (-1)^k |F_{hkl}|^2 \\ &\quad \times \cos 2\pi(hx + lz) \\ &= \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} C_{hl} \cos 2\pi(hx + lz), \end{aligned}$$

where $C_{hl} = \sum_{k=-\infty}^{\infty} (-1)^k |F_{hkl}|^2$.

It is easily seen what changes in the calculation must be made for threefold, fourfold and sixfold screw axes.

If the crystal contains a plane of symmetry, the form to which $P(x, y, z)$ reduces is even simpler than in the case of an axis of symmetry. Suppose the plane is perpendicular to the b axis. Then there are equivalent atoms at (x, y, z) and (x, \bar{y}, z) . The vector between these atoms has components $(0, 2y, 0)$ and the corresponding maximum in $P(x, y, z)$ lies on the b axis. To find this maximum it is only necessary to evaluate $P(0, y, 0)$. The calculation is as follows:

$$\begin{aligned} P(0, y, 0) &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}|^2 \cos 2\pi ky \\ &= \sum_{k=-\infty}^{\infty} B_k \cos 2\pi ky \end{aligned}$$

with $B_k = \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}|^2$.

This is a one-dimensional Fourier series and can be completely evaluated in a few hours. In the case of a glide plane the calculation is equally simple. In this case there are equivalent atoms at (x, y, z) and $(x, \bar{y}, z + \frac{1}{2})$ (the glide is taken to be

along the c axis) and there will be a maximum in $P(x, y, z)$ at $(0, 2y, \frac{1}{2})$. The simplification of $P(x, y, z)$ takes place thus,

$$P(0, y, \frac{1}{2}) = \sum_{k=-\infty}^{\infty} B_k \cos 2\pi ky$$

with
$$B_k = \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} (-1)^l |F_{(hkl)}|^2.$$

In Table I is given a summary of the forms of $P(x, y, z)$ best suited to the various symmetry elements. It is to be noted that at least one of these forms is available for the study of any crystal that is not triclinic.

TABLE I. *Forms of $P(x, y, z)$ best suited to the determination of atomic coordinates in crystals having various symmetry elements.*

	SYMMETRY ELEMENT	FORM OF $P(x, y, z)$
(a)	Axes parallel to b -axis	
	(i) 2, 4, 4 ₂ , 4, 6, 6* 3, 3, 6 ₃	$P(x, 0, z)$
	(ii) 2 ₁ , 4 ₁ , 4 ₃ , 6 ₁ , 6 ₅	$P(x, \frac{1}{2}, z)$
	(iii) 3 ₁ , 6 ₂ , 6 ₄	$P(x, \frac{1}{3}, z)$
(b)	Planes perpendicular to b -axis	
	(i) reflection planes	$P(0, y, 0)$
	(ii) glide plane, glide = $\frac{1}{2}a_0$	$P(\frac{1}{2}, y, 0)$
	(iii) " " " "	$P(0, \frac{1}{2}, 0)$
	(iv) " " " "	$P(\frac{1}{2}, y, \frac{1}{2})$
	(v) " " " "	$P(\frac{1}{2}, y, \frac{1}{3})$
	(vi) " " " "	$P(\frac{1}{3}, y, \frac{1}{2})$

It was then found that no planes reflected in the first order unless the indices satisfied the condition imposed by the rhombohedral lattice, $2H+K+L=0 \bmod 3$, although many planes not satisfying this condition were in position to give first-order reflections. The lattice is consequently rhombohedral and its unit cell has one-third the volume of the hexagonal cell for which dimensions are recorded above. It is impossible to account for much of the observed data on the basis of a unit cell smaller than this and no data requiring a larger one has been found, although several hundred reflections on various photographs have been indexed. This rhombohedral cell is therefore the true unit cell of proustite. For convenience, however, the hexagonal cell will be used throughout this paper, much of the analytic geometry of the structure appearing simpler when referred to these axes. The limits of density given above require the number of formulas of Ag_3AsS_3 in the hexagonal unit cell to lie between 5.89 and 5.96. There are thus $6\text{Ag}_3\text{AsS}_3$ in this cell.

DETERMINATION OF THE SPACE GROUP

No reflections of the type $(OK \cdot L)$, L odd, were observed in the first order on any photograph, although many planes of this type were in position to reflect on both the Laue and oscillation photographs. There are two space groups based on the rhombohedral lattice which require this absence: $C_{3v}^6 - R3c$ and $D_{3d}^6 - R\bar{3}c$. The hemihedral face development of proustite eliminates the latter. Consequently the space group of proustite is $C_{3v}^6 - R3c$.

DETERMINATION OF THE STRUCTURE

The space group $C_{3v}^6 - R3c$ furnishes the following sets of equivalent positions:

$$(2a) \ 0, 0, Z; \quad 0, 0, Z + \frac{1}{2};$$

and (6b) $X, Y, Z; \quad \bar{Y}, X - Y, Z; \quad -X + Y, \bar{X}, Z;$
 $X, X - Y, Z + \frac{1}{2}; \quad \bar{Y}, \bar{X}, Z + \frac{1}{2}; \quad -X + Y, Y, Z + \frac{1}{2};$
 and positions derived from these by the operations of the rhombohedral lattice.

There are 2 As, 6 Ag and 6 S atoms to distribute among these positions. The arsenic atoms must be placed in (2a) and the parameter Z_{As} may be

arbitrarily taken to be zero. The arsenic atoms are now fixed at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$ in the hexagonal cell and the positions derived from these by the operations of the rhombohedral lattice. The silver and sulfur atoms must be in the general positions (6a) and there are consequently six parameters to be determined: $X_{\text{Ag}}, Y_{\text{Ag}}, Z_{\text{Ag}},$ and $X_{\text{S}}, Y_{\text{S}}, Z_{\text{S}}.$

In order to determine these parameters, the Patterson method described in the previous section was applied. The crystal contains a glide plane and so it is necessary to evaluate the Patterson function, $P(X, Y, Z)$, for points along a line only, in order to determine the distances of the atoms from the plane. By subtracting the coordinates of points produced from each other by the action of the glide plane perpendicular to the Y axis, it was found that there would be maxima in $P(X, Y, Z)$ at $(0, \pm(X-2Y), \frac{1}{2}); (0, \pm(-2X+Y), \frac{1}{2}); (0, \pm(X+Y), \frac{1}{2});$ for each kind of atom in the crystal. It was, therefore, only necessary to evaluate $P(0, Y, \frac{1}{2})$ in order to determine X and Y for each atom. Now

$$P(0, Y, \frac{1}{2}) = \sum_{H=-\infty}^{\infty} \sum_{K=-\infty}^{\infty} \sum_{L=-\infty}^{\infty} |F_{HK \cdot L}|^2 \\ \times \cos 2\pi(KY + L/2) \\ = \sum_{K=-\infty}^{\infty} C_K \cos 2\pi KY$$

$$\text{with } C_K = \sum_{H=-\infty}^{\infty} \sum_{L=-\infty}^{\infty} (-1)^L |F_{HK \cdot L}|^2.$$

The coefficients C_K were calculated from the intensities of reflections on a series of oscillation photographs. A single small crystal was used throughout the series and all photographs were given the same exposure. The orientations of the crystal were so chosen that each possible reflection should have appeared near the equator on at least one of the series. The intensities of reflections were estimated by comparison with a series of spots of known exposure time on a strip of film, numbers proportional to the exposure times of the comparison spots being used to describe the intensities of the reflections. A complete search for reflections out to $(\sin \theta)/\lambda = 0.570$ was made, sixty-eight forms being observed to reflect within this limit. The intensities were divided by the

Lorentz and polarization factors in order to obtain the values of $|F_{HK\cdot L}|^2$. No corrections for extinction or absorption were made, as there was no way of estimating their effects.

The curve of $P(0, Y, \frac{1}{2})$ plotted against Y appears in Fig. 1. The large maximum at $Y=0$ is due, of course, to the vector between the arsenic atoms at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$. The maxima at $\frac{1}{6}, \frac{1}{3}$ and $\frac{1}{2}$ were considered to be due mainly to the vectors between silver atoms, for the maxima due to vectors between sulfur atoms would be expected to be only about one tenth the size of these.

The axes can be so chosen that the inequalities $X_{Ag} + Y_{Ag} > 2Y_{Ag} - X_{Ag} > 2X_{Ag} - Y_{Ag} > 0$ are satisfied. This choice and the positions of the maxima in $P(0, Y, \frac{1}{2})$ lead to the equations

$$X_{Ag} + Y_{Ag} = \frac{1}{2}; \quad 2Y_{Ag} - X_{Ag} = \frac{1}{3}; \quad 2X_{Ag} - Y_{Ag} = \frac{1}{6}.$$

These are solved by $X_{Ag} = 4/18 \cong 0.22$ and $Y_{Ag} = 5/18 \cong 0.28$. The silver atoms are now approximately located in the X, Y plane. The maxima in $P(0, Y, \frac{1}{2})$ are fairly broad and consequently the values of X_{Ag} and Y_{Ag} determined from these are not to be considered as accurate. However, a silver atom must lie near the line $X = 4/18, Y = 5/18$.

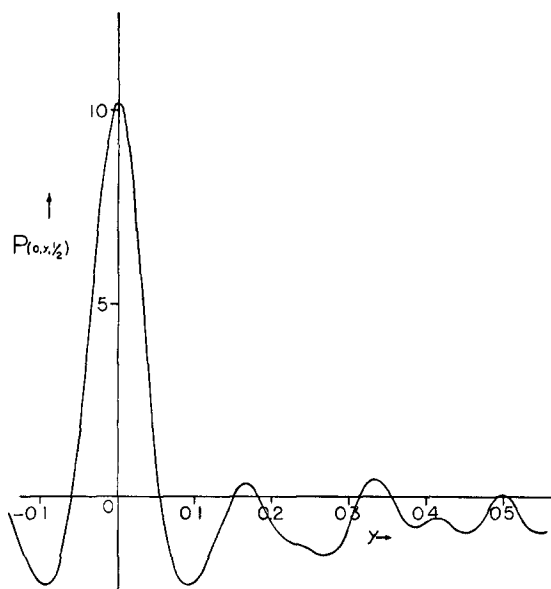


FIG. 1. $P(0, Y, \frac{1}{2})$ for proustite plotted against Y . The large maximum at $Y=0$ is due to As-As interaction, the maxima at 0.17, 0.33, and 0.50 are due to Ag-Ag interactions. There is a center of symmetry in $P(0, Y, \frac{1}{2})$ at $Y = \frac{1}{2}$, consequently only half the curve is plotted.

There is an arsenic atom at $(0, 0, 0)$ and there must therefore be a maximum in $P(X, Y, Z)$ at (X_{Ag}, Y_{Ag}, Z_{Ag}) . This maximum must lie near enough to the line $X = 4/18, Y = 5/18$ so that $P(4/18, 5/18, Z)$ should show a maximum at $Z = Z_{Ag}$. $P(4/18, 5/18, Z)$ was accordingly evaluated and the values plotted in Fig. 2 were obtained. The two sharp maxima at $Z = 0.227$ and $Z = 0.743$ can be due only to the vectors from the arsenic atoms at $(0, 0, 0)$ and $(0, 0, -\frac{1}{2})$ to the silver atom. The values of Z_{Ag} calculated from the positions of these two maxima are $Z_{Ag} = 0.227$ and $Z_{Ag} = 0.243$. The mean of these is $Z_{Ag} = 0.235$ with a probable error of about 0.008. The relation between the arsenic and silver atoms in the proustite structure is now approximately determined.

Hofmann³ has stated that the AsS_3''' and SbS_3''' groups are pyramidal with bond angles of about 95° and bond lengths about equal to the covalent radius sums calculated from the table of Pauling and Huggins.⁴ Corey and Wyckoff⁵ in the study of $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$ and West⁶ in the study of AgCN have shown that Ag' forms two covalent bonds in opposed directions with a covalent radius of 1.36Å. The assumption was accordingly made that the AsS_3''' groups in proustite were of approximately the form described by Hofmann and that silver atoms formed two covalent bonds to sulfur in opposed directions with a silver-sulfur distance of about 2.40Å, which is the sum of the covalent radii. It was also assumed that sulfur would form bonds in approximately tetrahedral directions. It was found that these conditions could all be satisfied approximately by placing the sulfur atoms in proustite in the general positions (6a) with $X_s \cong 0.22, Y_s \cong 0.11, Z_s \cong 0.40$. The complete structure of proustite was then roughly known.

The parameters X_{Ag} and Y_{Ag} were next fixed accurately by means of the intensities of the reflections $(HH\cdot 0)$, $H = 1, 2, 3, 4, 5, 6$; assuming the sulfur positions as above. These intensities are as follows:

H	1	2	3	4	5	6
Observed Intensity of $(HH\cdot 0)$	0.50	0.40	0.45	0.10	0.15	0.20

³ W. Hofmann, *Zeits. f. Krist.* **92**, 161 (1935).

⁴ L. Pauling and M. L. Huggins, *Zeits. f. Krist.* **87**, 205 (1934).

⁵ R. B. Corey and R. W. C. Wyckoff, *Zeits. f. Krist.* **87**, 264 (1934).

⁶ C. D. West, *Zeits. f. Krist.* **90**, 555 (1935).

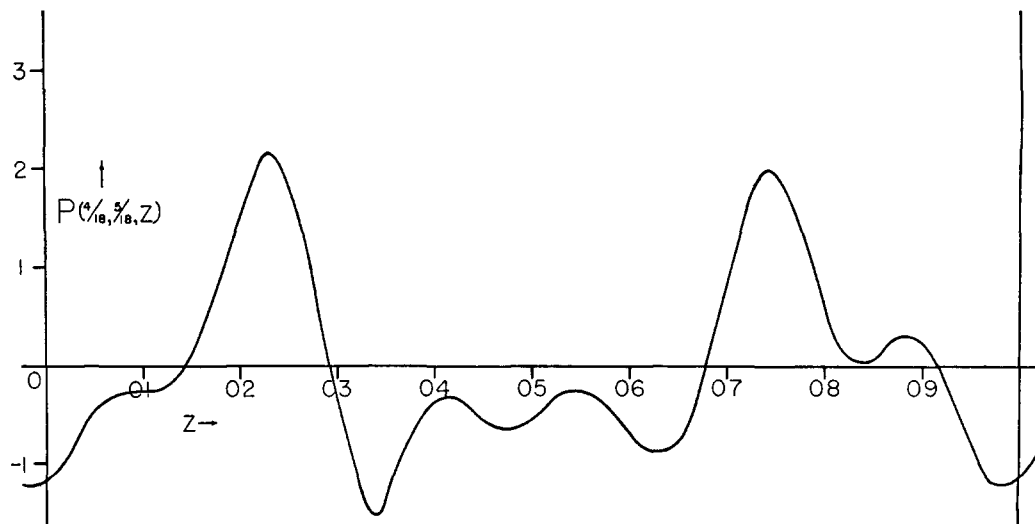


FIG. 2. $P(4/18, 5/18, Z)$ for proustite plotted against Z . The two large maxima are due to As-Ag interactions.

Fig. 3 shows the values of X_{Ag} and Y_{Ag} ruled out by the various comparisons. The center of the allowed region is at $X_{\text{Ag}}=0.246$, $Y_{\text{Ag}}=0.298$, and these values give calculated intensities in good agreement with the quantitative data with the sulfur parameters anywhere near $X_{\text{S}}=2/9$, $Y_{\text{S}}=1/9$. A change in X_{Ag} or Y_{Ag} of 0.005 in either direction places the point X_{Ag} , Y_{Ag} at, or beyond, the edge of the allowed region as shown in the figure. The limits of error in the determination of X_{Ag} and Y_{Ag} are consequently ± 0.005 . If the Patterson method determination of Z_{Ag} is accepted, the silver parameters are now completely determined. The silver positions were accordingly assumed to be accurately known and the sulfur atoms placed so as to be 2.25Å from arsenic atoms and 2.40Å from silver atoms, these being the distances calculated from the covalent radii of these elements. The structure of proustite

is now completely determined. The parameters are as follows:

$$\begin{aligned} X_{\text{Ag}} &= 0.246 \pm 0.005, & X_{\text{S}} &= 0.220 \pm 0.10, \\ Y_{\text{Ag}} &= 0.298 \pm 0.005, & Y_{\text{S}} &= 0.095 \pm 0.10, \\ Z_{\text{Ag}} &= 0.235 \pm 0.008, & Z_{\text{S}} &= 0.385 \pm 0.10, \\ & & Z_{\text{As}} &= 0.000. \end{aligned}$$

Intensities of all reflections for which $(\sin \theta)/\lambda \leq 0.375$ were calculated and compared with the observed data. The results of this calculation appear in Table II. The agreement between the observed and calculated values proves the structure of proustite described above to be correct.

The structure of proustite being known, it is possible to discuss the positions at which maxima should fall in $P(0, Y, \frac{1}{2})$ and $P(4/18, 5/18, Z)$. Sulfur to sulfur distances should give maxima in $P(0, Y, \frac{1}{2})$ at $Y=0.030, 0.315$ and 0.345 corresponding to $X_{\text{S}}-2Y_{\text{S}}$, $X_{\text{S}}+Y_{\text{S}}$ and $2X_{\text{S}}-Y_{\text{S}}$,

TABLE II. Observed and calculated intensities for proustite. In each square the top row gives the indices, and in the second row the first figure is the observed, the second figure is the calculated intensity.

(12·5) 0.9-0.87		(31·5) 0.45-1.02		(23·5) 0.15-0.45					
(10·4) 0.7-1.93	(02·4) 1.3-1.00	(21·4) 1.3-0.71	(13·4) 1.2-1.55	(40·4) 0.9-1.48	(32·4) 0.10-0.22	(05·4) 0.10-0.42	(24·4) 0.15-0.49		
	(11·3) 4.0-4.39		(22·3) 0.25-0.17		(14·3) 0.30-0.13	(41·3) 0.25-0.15	(33·3) 0.25-0.05	(25·3) 0.15-0.37	(52·3) 0.15-0.29
(01·2) 0.40-0.16	(20·2) 4.5-2.86	(12·2) 2.5-1.97	(31·2) 1.0-0.60	(04·2) 0.30-0.20	(23·2) 1.3-1.40	(50·2) 1.2-1.22	(42·2) 0.45-0.62	(15·2) 0.40-0.33	(34·2) 0.10-0.14
		(21·1) 1.5-1.51	(13·1) 2.0-1.79		(32·1) 0.8-0.77		(24·1) 0.40-0.53	(51·1) 0.00-0.07	(43·1) 0.30-0.37
	(11·0) 0.50-0.35	(03·0) 1.8-1.71	(22·0) 0.40-0.10		(41·0) 0.40-0.22		(33·0) 0.45-0.24	(06·0) 0.60-1.20	(52·0) 0.40-0.54
								(44·0) 0.10-0.04	

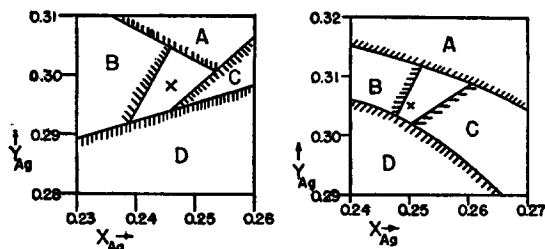


FIG. 3. (left) Determination of X_{Ag} and Y_{Ag} for proustite using comparisons of intensities of reflections ($HH \cdot 0$).

Region A	is ruled out by	$I(55 \cdot 0)$	calc.	$> I(66 \cdot 0)$
" B	"	"	"	$> I(33 \cdot 0)$
" C	"	"	"	$> I(44 \cdot 0)$
" D	"	"	"	$> I(55 \cdot 0)$

X marks the point giving the best quantitative agreement.

FIG. 4. (right) Determination of X_{Ag} and Y_{Ag} for pyrargyrite by comparisons of intensities of reflections ($HH \cdot 0$).

Region A	is ruled out by	$I(66 \cdot 0)$	calc.	$< \frac{1}{2} I(55 \cdot 0)$
" B	"	"	"	$> I(33 \cdot 0)$
" C	"	"	"	$> \frac{1}{2} I(22 \cdot 0)$
" D	"	"	"	$> I(55 \cdot 0)$

X marks the point giving the best quantitative agreement.

respectively, silver to silver distances should give maxima at $Y=0.194, 0.350, 0.456$ and 0.544 corresponding to $2X_{Ag} - Y_{Ag}, 2Y_{Ag} - X_{Ag}, 1 - X_{Ag} - Y_{Ag}$ and $X_{Ag} + Y_{Ag}$ respectively, and arsenic-arsenic distances account for a maximum at $Y=0$. No other interatomic vectors should give maxima in $P(0, Y, \frac{1}{2})$. Comparing these figures with the curve for $P(0, Y, \frac{1}{2})$ in Fig. 1, it is seen that the maximum at $Y=0$ must be due to an As-As and a S-S distance, that at $Y=0.17$ must be due to a Ag-Ag distance, that at $Y=0.33$ must be due to two S-S and one Ag-Ag distance, and that at $Y=0.50$ to two Ag-Ag distances. The small maxima at $Y=0.25$ and $Y=0.41$ are not accounted for by any interatomic vectors and must consequently be due to the background fluctuation which occurs in any Fourier series treatment using only a finite number of terms. The small maxima in $P(4/18, 5/18, Z)$ (see Fig. 2) must be due to this same background effect as only the Ag-As vectors should produce maxima in this function.

THE CRYSTAL STRUCTURE OF PYRARGYRITE Ag_3SbS_3

The pyrargyrite used in this study was from Freiberg in Saxony and occurred in the form of metallic appearing, hexagonal prisms measuring about 0.5 mm by 2.0 mm.

Groth² assigned pyrargyrite to the ditrigonal pyramidal class (C_{3v}) with the axial ratio $c/a=0.7892$. The density ranges from 5.75 to 5.85. In this case, as in the case of proustite, the assignment to the polar class C_{3v} is well grounded on observations of unsymmetrical face development.

Measurements of reflections on oscillation photographs led to the axial lengths $a_0=11.04\text{\AA}$, $c_0=8.71\text{\AA}$ for the hexagonal unit cell. The axial ratio is $c_0/a_0=0.789$, in good agreement with the ratio $c/a=0.7892$ calculated from crystallographic measurements. The number of formulas of Ag_3SbS_3 in this unit cell was calculated from the density range given above to lie between 5.92 and 6.03. There are thus 6 formulas of Ag_3SbS_3 in the unit cell.

Both the Laue and oscillation photographs of pyrargyrite show great similarity to the corresponding photographs of proustite. In particular, the conditions required by the rhombohedral lattice and the space group $C_{3v}^6 - R\bar{3}c$ were never violated. These observations, together with the

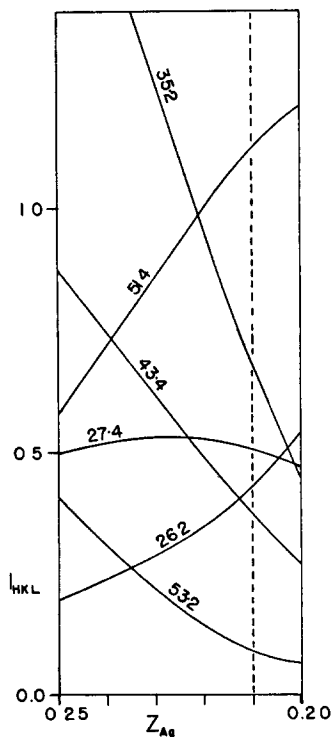


FIG. 5. Determination of Z_{Ag} for pyrargyrite by comparisons of intensities. $I_{HK \cdot L}$ plotted on an arbitrary scale against Z_{Ag} . The dotted line shows the chosen value. The observed intensities satisfy the inequalities: $I(51 \cdot 4) > I(35 \cdot 4) > I(27 \cdot 4) > I(26 \cdot 2) > I(43 \cdot 4)$.

similarity between the chemical compositions, crystallographic data, and unit cell dimensions of pyrrargyrite and proustite, led to the assumption that these two substances have nearly the same structure, the chief difference being the substitution of the arsenic atoms in proustite by antimony atoms in pyrrargyrite. That this assumption was justified is amply proved by the agreement between the calculated and observed intensities of reflection which resulted from its adoption.

Gossner and Mussnug⁷ made layer line measurements on oscillation photographs of pyrrargyrite from which they determined the lengths of the hexagonal axes to be $a_0 = 11.06\text{\AA}$ and $c_0 = 8.84\text{\AA}$ in good agreement with the results obtained in this research. They also proved the lattice to be rhombohedral and determined the space group to be $C_{3v}^6 - R3c$. They did not determine the structure, however.

The assumption that proustite and pyrrargyrite have almost the same structure leads at once to the approximate structure for pyrrargyrite:

$$\begin{aligned} C_{3v}^6; 2\text{Sb in } 2a, Z_{\text{Sb}} = 0.000; 6\text{ S in } 6b \quad X_{\text{S}} \leq 0.22, \\ 6\text{ Ag in } 6b, X_{\text{Ag}} \leq 0.25, \quad Y_{\text{S}} \leq 0.10, \\ Y_{\text{Ag}} \leq 0.30, \quad Z_{\text{S}} \leq 0.40, \\ Z_{\text{Ag}} \leq 0.23; \end{aligned}$$

The silver parameters X_{Ag} and Y_{Ag} were determined, as in the case of proustite, by use of the intensities of the reflections $(HH \cdot 0)$, $H = 1$ to 6. These intensities were as follows:

H	1	2	3	4	5	6
Observed Intensity of $(HH \cdot 0)$	0.0	5.0	6.0	0.40	1.5	0.80

The regions of variation of X_{Ag} and Y_{Ag} ruled

⁷ B. Gossner and F. Mussnug, Centralbl. f. Min. (A), 65 (1928).

out by the various comparison are shown in Fig. 4. Values of the parameters differing from $X_{\text{Ag}} = 0.250$, $Y_{\text{Ag}} = 0.305$ by as much as 0.005 gave poor agreement with the observed data, and these values were therefore accepted as being correct to ± 0.005 . The parameter Z_{Ag} was determined by comparisons, some of which are shown in Fig. 5, to be within 0.005 of $Z_{\text{Ag}} = 0.210$. The sulfur atoms were then placed so as to make the SbS_3''' groups pyramidal with the Sb-S distance 2.45Å and the Ag-S distance 2.40Å, in agreement with the covalent radii of these elements. The determination of the structure of pyrrargyrite was then complete. The parameters are

$$\begin{aligned} X_{\text{Ag}} &= 0.250 \pm 0.005, & X_{\text{S}} &= 0.220 \pm 0.010, \\ Y_{\text{Ag}} &= 0.305 \pm 0.005, & Y_{\text{S}} &= 0.105 \pm 0.010, \\ Z_{\text{Ag}} &= 0.210 \pm 0.005, & Z_{\text{S}} &= 0.355 \pm 0.010, \\ & & Z_{\text{Sb}} &= 0.000. \end{aligned}$$

Intensities were calculated on the basis of this structure for all the reflections for which calculations had been made for proustite.

The results of these calculations appear in Table III. The agreement between the observed and calculated intensities of reflection proves the above structure to be correct.

DISCUSSION OF THE STRUCTURES OF PROUSTITE AND PYRRARGYRITE

The structure of proustite is shown in Fig. 6, and the structure of pyrrargyrite is so similar that this figure may be used for the discussion of both. Both structures contain $(\text{AgS})_\infty$ groups of almost the same shape. In these, the sulfur atoms form the corners of a triangular spiral, while the silver atoms lie almost in the centers of the legs of the spiral. The sulfur to silver distance is 2.40Å, the

TABLE III. Observed and calculated intensities for pyrrargyrite. In each square the top row gives the indices, and in the second row the first figure is the observed, the second figure is the calculated intensity.

	(12·5) 2.0-2.94	(31·5) 1.2-3.59	(23·5) 0.45-1.00							
(10·4) 10.0-12.50	(02·4) 3.0-1.09	(21·4) 6.0-5.56	(13·4) 7.0-6.04	(40·4) 4.5-5.65	(32·4) 0.00-0.40	(05·4) 0.00-0.42	(24·4) 2.0-2.82			
	(11·3) 12.0-15.37	(22·3) 0.9-1.08			(14·3) 0.45-0.40	(41·3) 0.45-0.43	(33·3) 0.50-0.44	(25·3) 0.60-0.68	(52·3) 0.45-0.69	
(01·2) 6.0-3.60	(20·2) 12.0-12.28	(12·2) 10.0-10.50	(31·2) 4.0-3.19	(04·2) 1.5-1.09	(23·2) 5.0-4.73	(50·2) 5.5-5.23	(42·2) 3.0-2.49	(15·2) 2.5-2.00	(34·2) 0.50-0.27	(61·2) 1.0-0.91
		(21·1) 5.0-5.79	(13·1) 5.5-6.66		(32·1) 2.0-1.61		(24·1) 1.5-1.82	(51·1) 0.00-0.19	(43·1) 1.3-1.29	(16·1) 0.7-0.80
	(11·0) 0.00-0.13	(03·0) 8.0-10.0	(22·0) 3.0-1.39		(41·0) 1.5-0.92		(33·0) 3.5-1.75	(06·0) 3.0-3.62	(52·0) 2.5-3.12	(44·0) 0.40-0.16

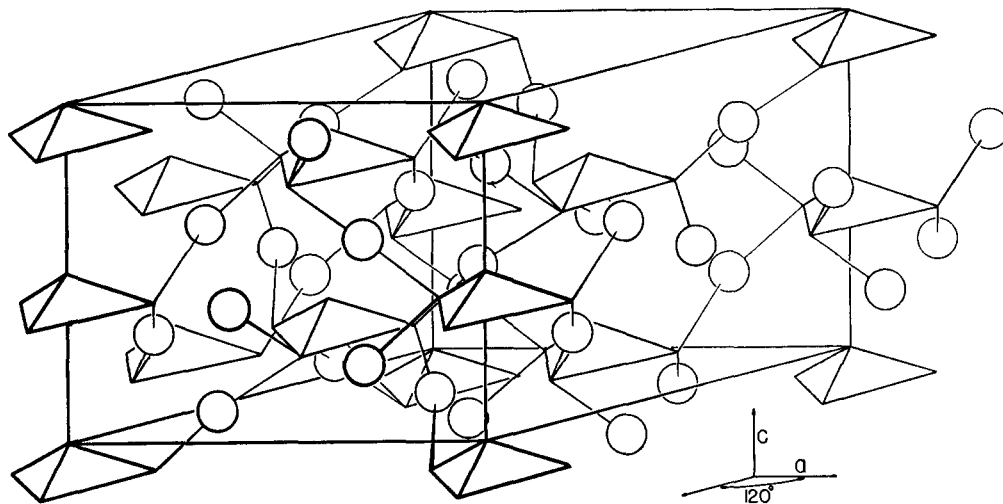


FIG. 6. The structure of proustite. Pyramids represent AsS_3''' groups, balls represent silver atoms, and lines represent covalent bonds. The structure of pyrargyrite is almost the same.

S—Ag—S bond angle is about 165° , and the Ag—S—Ag bond angle is about $83\frac{1}{2}^\circ$. One complete turn of the spiral is equivalent to a translation of c_0 in the crystal. These spirals are fastened together by the As or Sb atoms to make up the structural frameworks of proustite or pyrargyrite, respectively. The sulfur to arsenic bond distance in proustite is 2.25Å and the S—As—S bond angle is 103° . The sulfur atom in proustite forms three bonds, two to silver and one to arsenic with these angles: As—S—Ag = 101° and $105\frac{1}{2}^\circ$, Ag—S—Ag = $83\frac{1}{2}^\circ$. In pyrargyrite the antimony atoms form three bonds to sulfur 2.45Å long at mutual angles of $95\frac{1}{2}^\circ$. The sulfur atoms in pyrargyrite form three bonds with the angles: Sb—S—Ag = 97° and 111° , Ag—S—Ag = $83\frac{1}{2}^\circ$.

An interesting feature of these structures is the fact that they are composed of two interpenetrating frameworks of the type described in the last paragraph which are apparently not

connected by any bonds at all. The relation of the two frameworks can best be understood by a study of Fig. 6. The As or Sb atoms at $(0, 0, 0)$ belong to one framework and the crystallographically equivalent As or Sb atoms at $(0, 0, \frac{1}{2})$ belong to the other. The two frameworks are in the relation to each other required by the operation of the glide planes. One framework contains only right-handed $(\text{AgS})_\infty$ spirals, the other only left-handed ones. Another example of two interpenetrating frameworks apparently not interconnected by chemical bonds is furnished by the structure of cuprite, Cu_2O .

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor Linus Pauling, who suggested the study of proustite and pyrargyrite, for sparing neither criticism nor encouragement throughout the course of this research.