THE APPLICATION OF THE THREE DIMENSIONAL PATTERSON METHOD AND THE CRYSTAL

STRUCTURES OF PROUSTITE, Ag_3AsS_3, AND PYRARGYRITE, Ag_3SbS_3.

Thesis

by

David Harker

In Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

1936

Abstract

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 - $\underline{R3c}$, is common to both proustite and pyrargyrite. The special positions of $\underline{C}_{3v}^6$ are (in hexagonal axes)

2a) $0,0,z;$ $0,0,\frac{1}{2}+z$

6b) $x,y,z;$ $\bar{y},x-y,z;$ $y-x,\bar{x},z;$

      $\bar{y},\bar{x},\frac{1}{2}+z;$ $x,x-y,\frac{1}{2}+z;$ $y-x,y,\frac{1}{2}+z;$

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

	Proustite	Pyrargyrite
	$a_0 = 10.74$ Å, $c_0 = 8.64$ Å	$a_0 = 11.04$ Å, $c_0 = 8.71$ Å
2As in 2a)	$Z_{As} = 0.000$	2Sb in 2a) $Z_{Sb} = 0.000$
6Ag in 6B)	$x_{Ag} = 0.246$	6Ag in 6b) $x_{Ag} = 0.250$
	$y_{Ag} = 0.298$	$y_{Ag} = 0.305$
	$z_{Ag} = 0.235$	$z_{Ag} = 0.210$
6S in 6b)	$x_S = 0.220$	$x_S = 0.220$
	$y_S = 0.095$	$y_S = 0.105$
	$z_S = 0.385$	$z_S = 0.355$

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.

The Use of the Three Dimensional Patterson Method

Patterson[1] has shown that the three dimensional Fourier Series

$$P(x,y,z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \left| F_{(hk\ell)} \right|^2 \cos 2\pi (hx + ky + \ell z)$$

--where $\underline{x}$, $\underline{y}$, and $\underline{z}$ are the coordinates of points in the crystal lattice measured in units of the primitive translations and $\underline{F}_{(hk\ell)}$ is the amplitude of the diffracted beam "reflected" from the crystal plane with indices $(hk\ell)$ -- represents a function having maxima at vector distances from the origin equal to the vector distances between pairs of atoms in the crystal. The evaluation of such a series at a sufficient number of points in the unit cell to show the true form of the function $\underline{P}(x,y,z)$ has never been carried out, the calculation involving a prohibitive amount of labor. Instead, the projection of $\underline{P}(x,y,z)$ on a plane perpendicular to one of the crystal axes has been used. If the projection is upon the plane perpendicular to the $\underline{z}$-axis, the projected function $\underline{p}(x,y)$ is calculated thus

$$\begin{aligned} p(x,y) &= \int_o^1 P(x,y,z)\, dz \\ &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \left| F_{(hk\ell)} \right|^2 \int_o^1 \cos 2\pi (hx + ky + \ell z)\, dz \\ &= \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \left| F_{(hk0)} \right|^2 \cos 2\pi (hx + ky) \ . \end{aligned}$$

$\underline{p}(x,y)$, 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 determinations of structures which would have been impracticably difficult otherwise.

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

$$P(x,0,z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \left| F_{(hk\ell)} \right|^2 \cos 2\pi(hx + \ell z)$$

$$= \sum_{h=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \cos 2\pi(hx + \ell z) \left\{ \sum_{k=-\infty}^{\infty} \left| F_{(hk\ell)} \right|^2 \right\}$$

Now let $\displaystyle\sum_{k=-\infty}^{\infty} \left| F_{(hk\ell)} \right|^2 = C_{h\ell}$

and we have $P(x,0,z) = \displaystyle\sum_{h=-\infty, \ell=-\infty}^{\infty} C_{h\ell} \cos 2\pi(hx + \ell z)$.

$\underline{P}(\underline{x},0,\underline{z})$ is a two dimensional Fourier series of the same general type as $\underline{p}(\underline{x},\underline{y})$ and consequently its calculation is practicable. The same information about $\underline{x}$ and $\underline{z}$ coördinates of the atoms is contained in $\underline{P}(\underline{x},0,\underline{z})$ as in

$p(\underline{x},\underline{z})$, but in much clearer form; for (a) the maxima in $P(\underline{x},0,\underline{z})$ will be sharper, in general, since there are usually more terms in its Fourier series than in that of $p(\underline{x},\underline{z})$ and (b) all the maxima corresponding to interatomic vectors not parallel to the plane $\underline{y} = 0$ appear in $p(\underline{x},\underline{z})$, but are eliminated in $P(\underline{x},0,\underline{z})$. $P(\underline{x},0,\underline{z})$ can be used to determine the $\underline{x}$ and $\underline{z}$ coördinates of atoms in case the $\underline{b}$-axis is parallel to a two-, three-, four-, or six-fold symmetry axis of the crystal, for in all these cases the vectors between equivalent atoms are parallel to the plane $\underline{y} = 0$.

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

$$P(x,\tfrac{1}{2},z) = \sum_{\substack{h,k,\ell \\ =-\infty}}^{\infty} \left| F_{(hk\ell)} \right|^2 \cos 2\pi (hx + \tfrac{k}{2} + \ell z)$$

$$= \sum_{\substack{h,k,\ell \\ =-\infty}}^{\infty} (-)^k \left| F_{(hk\ell)} \right|^2 \cos 2\pi (hx + \ell z)$$

$$= \sum_{h,\ell=-\infty}^{\infty} C_{h\ell} \cos 2\pi (hx + \ell z)$$

where $C_{h\ell} = \sum_{k=-\infty}^{\infty} (-)^k \left| F_{(hk\ell)} \right|^2$.

It is easily seen what changes in the calculation must be made for three-fold, four-fold, and six-fold screw axes.

If the crystal contains a plane of symmetry, the form to which $P(\underline{x},\underline{y},\underline{z})$ 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:

$$P(0,y,0) = \sum_{h,k,\ell = -\infty}^{\infty} \left| F_{(hk\ell)} \right|^2 \cos 2\pi ky$$

$$= \sum_{k=-\infty}^{\infty} B_k \cos 2\pi ky$$

$$\text{with } B_k = \sum_{h=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \left| F_{(hk\ell)} \right|^2 .$$

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,

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

$$\text{with } B_k = \sum_{h=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} (-)^\ell \left| F_{(hk\ell)} \right|^2 .$$

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.

There are other cases in which the values of some of the atomic coördinates in a crystal can be determined by the evaluation of $P(x,y,z)$ throughout a plane or along a line only. For instance, it might be known from symmetry considerations that the position $(0,0,0)$ is occupied by an atom and that there are

TABLE I

Forms of $\underline{P}(\underline{x},\underline{y},\underline{z})$ best suited to the determination of atomic coördinates in crystals having various symmetry elements.

Symmetry element	Form of $\underline{P}(\underline{x},\underline{y},\underline{z})$
a) Axes parallel to $\underline{b}$-axis	
i) 2, 4, 4_2, $\bar{4}$, 6, 6_2 *	$P(x,o,z)$
3, $\bar{3}$, 6_3	
ii) 2_1, 4_1, 4_3, 6_1, 6_3	$P(x,1/2,z)$
iii) 3_1, 6_2, 6_4	$P(x,1/3,z)$
b) Planes perpendicular to $\underline{b}$-axis	
i) reflection planes	$P(o,y,0)$
ii) glide plane, glide $= \frac{1}{2}a_o$	$P(1/2,y,0)$
iii) " " " $= \frac{1}{2}c_o$	$P(0,y,1/2)$
iv) " " " $= \frac{1}{2}(a_o + c_o)$	$P(1/2,y,1/2)$
v) " " " $= \frac{1}{4}(a_o + c_o)$	$P(1/4,y,1/4)$
vi) " " " $= \frac{1}{4}(3a_o + c_o)$	$P(3/4,y,1/4)$

In cases (a) $\underline{x}$ and $\underline{z}$ are determined for each atom.

In cases (b) $\underline{y}$ is determined for each atom.

*The nomenclautre of symmetry axes is taken from the "Internationale Tabellen zur Bestimmung von Kristallstrukturen".

other atoms in the plane $y = \frac{1}{2}$ with coordinates (say) $(x_1, \frac{1}{2}, z_1)$, $(x_2, \frac{1}{2}, z_2)$, etc. Then there will be maxima in $P(x,y,z)$ at just these points, for vectors from the origin to these atoms are also interatomic vectors. The evaluation of $P(x, \frac{1}{2}, z)$ would determine the x and z coördinates of all these atoms. Or, for another example, suppose again that $(0,0,0)$ is occupied by an atom and that other atoms must lie on the line $x = \frac{1}{2}$, $z = \frac{1}{2}$. The y coördinates of all these atoms could be found by calculating $P(\frac{1}{2}, y, \frac{1}{2})$, for there will be a maximum in this function at each value of y occupied by one of these atoms. Such examples could be multiplied almost indefinitely.

It is plain from the above that the function $P(x,y,z)$ furnishes a powerful and simple method of attack on the structures of all crystals not belonging to the triclinic class. All that is required is a complete set of X-ray diffraction data, for from these not only can the symmetry of the crystal be determined, but also the values of $\left| F_{(hk\ell)} \right|^2$ calculated.

An illustration of the use of $P(x,y,z)$ is furnished by the determination of the structure of the mineral proustite, Ag_3AsS_3, which will be described below.

Determination of the Structure of Proustite, Ag_3AsS_3.

The proustite used in this determination came from Schneeberg in Saxony. It occurred in the form of tiny, brilliant red, hexagonal prisms measuring about 0.2 mm. by 1.0 mm. which were bounded by beautiful faces.

Groth[2] describes proustite as ditrigonal pyramidal (C_{3v}) with the axial ratio c/a = 0.8038. The density varies among different specimens from 5.55 to 5.62. This assignment to a polar class is made on the basis of many observations of unsymmetrical face development and seems exceptionally well grounded.

A Laue photograph taken perpendicular to a prism face showed a two-fold axis of symmetry, another Laue photograph taken along a line bisecting the angle between two prism faces and perpendicular to the prism axis showed a plane of symmetry parallel to the prism axis, and a third Laue photograph taken along the prism axis showed a three-fold axis and three planes of symmetry. The Laue symmetry is therefore D_{3d} and the crystal must belong to one of the point groups C_{3v}, D_3, or D_{3d} on the basis of X-ray data alone.

Measurements on oscillation photographs led to the dimensions $a_0 = 10.74$ Å, $c_0 = 8.64$ Å for the hexagonal unit cell. The ratio $c_0/a_0 = 0.804$ is in excellent agreement with the ratio c/a = 0.8038 obtained from crystallographic measurements. The two Laue photographs taken perpendicular to the prism axis were indexed by the aid of gnomonic projections and the wave length of the radiation producing each reflection calculated. It was then found that no planes reflected in the first order unless the indices satisfied the condition imposed by the rhombohedral lattice, $2H + K + L = 0$ mod 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 number of formulas of Ag_3AsS_3 in this unit was calculated from the density range given above to lie between 5.89 and 5.96, or 6 within the experimental error.

Determination of the Space Group

No reflections of the type $(\underline{OK \cdot L})$, $\underline{L}$ 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: $\underline{C}_{3v}^6 - \underline{R3c}$ and $\underline{D}_{3d}^6 - \underline{R\bar{3}c}$. The hemihedral face development of proustite eliminates the latter. Consequently the space group of proustite is $\underline{C}_{3v}^6 - \underline{R3c}$.

Determination of the Structure

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

2a) $0,0,u;$ $\qquad$ $0,0,u+\tfrac{1}{2}$

and 6b) $X,Y,Z;$ $\qquad$ $\overline{Y},X-Y,Z;$ $\qquad$ $-X+Y,\overline{X},Z;$

$\qquad\qquad$ $X,X-Y,Z+\tfrac{1}{2};$ $\qquad$ $\overline{Y},\overline{X},Z+\tfrac{1}{2};$ $\qquad$ $-X+Y,Y,Z+\tfrac{1}{2};$

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 $\underline{u}$ may be arbitrarily taken to be zero. The arsenic atoms are now fixed at $(0,0,0)$ and $(0,0,\tfrac{1}{2})$ 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 6b) and there are consequently six parameters to be determined:

$\underline{X}_{Ag}$, $\underline{Y}_{Ag}$, $\underline{Z}_{Ag}$, and $\underline{X}_S$, $\underline{Y}_S$, $\underline{Z}_S$.

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, $\underline{P}(\underline{x},\underline{y},\underline{z})$ only for points along a line, in order to determine the distances of the atoms from the plane. By subtracting the coördinates of points produced from each other by the action of the glide plane perpendicular to the $\underline{Y}$ axis, it was found that there would be maxima in $\underline{P}(\underline{x},\underline{y},\underline{z})$ at $(0,\pm(\underline{X}-2\underline{Y}),\frac{1}{2})$; $(0,\pm(\underline{X}+\underline{Y}),\frac{1}{2})$; $(0,\pm(-2\underline{X}+\underline{Y}),\frac{1}{2})$; for each kind of atom in the crystal. It was, therefore, only necessary to evaluate $\underline{P}(0,\underline{y},\frac{1}{2})$ in order to determine $\underline{X}$ and $\underline{Y}$ for each atom. Now

$$P(0,y,\tfrac{1}{2}) = \sum_{H,K,L=-\infty}^{\infty} \left| F_{HK\cdot L} \right|^2 \cos 2\pi (Ky + \tfrac{L}{2})$$

$$= \sum_{K=-\infty}^{\infty} C_K \cos 2\pi Ky$$

with

$$C_K = \sum_{H,L=-\infty}^{\infty} (-)^L \left| F_{HK\cdot L} \right|^2.$$

The coefficients $\underline{C}_K$ were calculated from the intensities of reflections on a series of oscillation photographs so taken that each possible reflection appeared near the equator on at least one of the series. The intensities were divided by the Lorentz and polarization factors in order to obtain the values of $\left| F_{HK\cdot L} \right|^2$. No corrections for extinction or absorption were made, as there was no way of estimating their effects.

The curve of $\underline{P}(0,\underline{y},\frac{1}{2})$ plotted against $\underline{y}$ appears in Figure 1. The large maximum at $\underline{y} = 0$ is due, of course, to the vector between the arsenic atoms at $(0,0,0)$ and $(0,0,\frac{1}{2})$. The maxima at 1/6, 1/3, and 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.
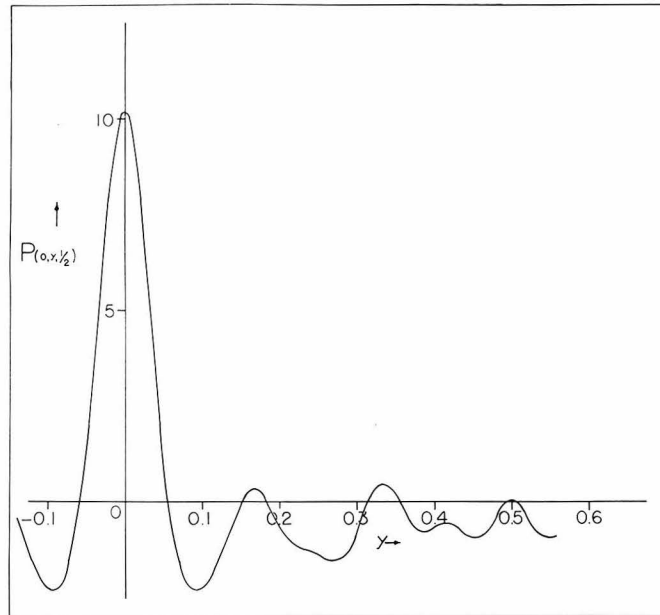
Figure 1. P(0,y,½) for proustite plotted against y. The large maximum at y = 0 is due to As-As interaction, the maxima at 0.17, 0.33, and 0.50 are due to Ag-Ag interactions. There is a center of symmetry in P(0,½,y) at y = ½, consequently only half the curve is plotted.

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

$$X_{Ag} + Y_{Ag} = 1/2$$
$$2Y_{Ag} - X_{Ag} = 1/3$$
$$2X_{Ag} - Y_{Ag} = 1/6$$

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

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

Hofmann[3] 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 Wyckoff[5] in the study of $\left[Ag(NH_3)_2\right]_2SO_4$ and West[6] in the study of AgCN have shown that Ag' forms two covalent bonds in apposed directions with a covalent radius of 1.36 Å. The assumption was accordingly made that the AsS_3 groups in proustite were of approximately the form described by Hofmann and that

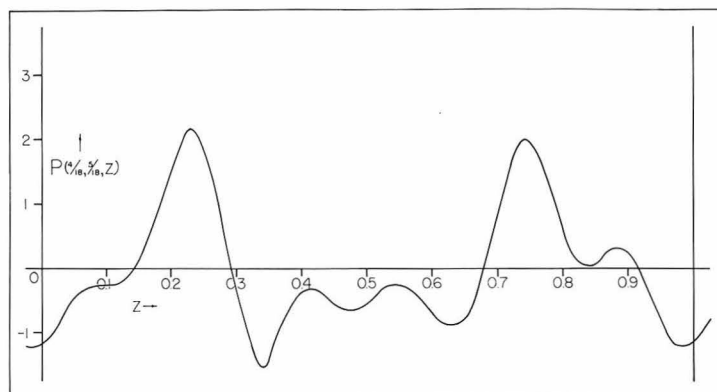Figure 2. $\underline{P}(3/18,5/18,\underline{Z})$ for proustite plotted against $\underline{Z}$. The two large maxima are due to As–Ag interactions.

silver atoms formed two covalent bonds to sulfur in opposed directions with a silver-sulfur distance of about 2.40 Å, 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 now roughly known.

The parameters X_{Ag} and Y_{Ag} were next fixed accurately by means of the intensities of the reflections (HH·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·0)	0.50	0.40	0.45	0.10	0.15	0.20

Figure 3 shows the values of X_{Ag} and Y_{Ag} ruled out by the various comparisons. The center of the allowed region is at $X_{Ag} = 0.246$, $Y_{Ag} = 0.298$, and these values give calculated intensities in good agreement with the quantitative data with the sulfur parameters anywhere near $X_S = 2/9$, $Y_S = 1/9$. 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 $\pm$ 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 2.25 Å from arsenic atoms and 2.40 Å 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:

$$X_{Ag} = 0.246 \pm 0.005 \qquad X_S = 0.220 \pm 0.10$$

$$Y_{Ag} = 0.298 \pm 0.005 \qquad Y_S = 0.095 \pm 0.10$$

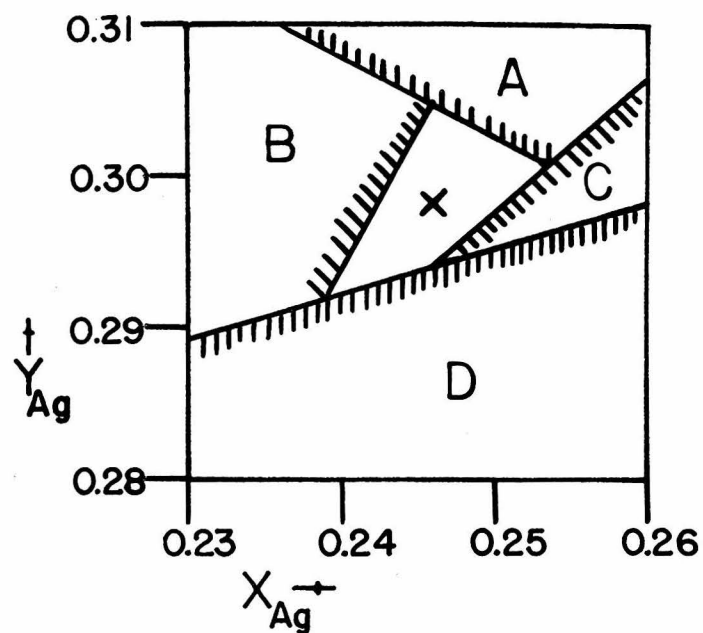$$Z_{Ag} = 0.235 \pm 0.008 \qquad Z_S = 0.385 \pm 0.10$$

$$Z_{As} = 0.000$$

Figure 3. 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. $> I(66 \cdot 0)$

Region B is ruled out by $I(22 \cdot 0)$ calc. $> I(33 \cdot 0)$

Region C is ruled out by $I(44 \cdot 0)$ calc. $> I(22 \cdot 0)$

Region D is ruled out by $I(44 \cdot 0)$ calc. $> I(55 \cdot 0)$

X marks the point giving the best quantitative agreement.

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 2. The agreement between the observed and calculated values proves the structure of proustite described above to be correct.

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.

Groth[2] 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 $a_o = 11.04$ Å, $c_o = 8.71$ Å for the hexagonal unit cell. The axial ratio is $c_o/a_o = 0.789$, 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 - R3c were never violated. These observations, together with the similarity between the chemical compositions, crystallographic data, and unit cell dimensions of pyrargyrite and proustite, led to the assumption that these

Table 2

Observed and Calculated Frequencies 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.

Indices	obs–calc
(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)	4.5—2.86
(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
(20·2)	4.0—4.39
(01·2)	0.40—0.16
(12·2)	2.5—1.97
(31·2)	1.3—1.40 / 1.0—0.60
(04·2)	0.30—0.20
(23·2)	1.2—1.22
(42·2)	0.45—0.62
(15·2)	0.40—0.33
(34·2)	0.10—0.14
(61·2)	0.15—0.14
(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)	0.40—0.53
(52·0)	0.00—0.07
(44·0)	0.30—0.37
(06·0)	0.15—0.12
(21·1)	1.5—1.51
(13·1)	2.0—1.79
(32·1)	0.8—0.77
(24·1)	0.45—0.24
(51·1)	0.60—1.20
(43·1)	0.40—0.54
(16·1)	0.10—0.04

two substances have nearly the same structure, the chief difference being the substitution of the arsenic atoms in proustite by antimony atoms in pyrargyrite. 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 Mussgnug[7] made layer line measurements on oscillation photographs of pyrargyrite from which they determined the lengths of the hexagonal axes to be a_o = 11.06 Å and c_o = 8.84 Å 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 pyrargyrite have almost the same structure leads at once to the approximate structure for pyrargyrite:--

C_{3v}^6 :　　　2 Sb in 2a), Z_{Sb} = 0.000;

　　　　　　6 Ag in 6b), $X_{Ag} \cong 0.25$,

　　　　　　　　　$Y_{Ag} \cong 0.30$,

　　　　　　　　　$Z_{Ag} \cong 0.23$;

　　　　　　6 S　in 6b), $X_S \cong 0.22$,

　　　　　　　　　$Y_S \cong 0.10$,

　　　　　　　　　$Z_S \cong 0.40$.

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·0), H = 1 to 6. These intensities were as follows:

H	1	2	3	4	5	6
Observed Intensity of (HH·0)	0.00	5.0	6.0	0.40	1.5	0.80

The regions of variation of X_{Ag} and Y_{Ag} ruled out by the various comparisons are shown in Figure 4. Values of the parameters differing from X_{Ag} = 0.250
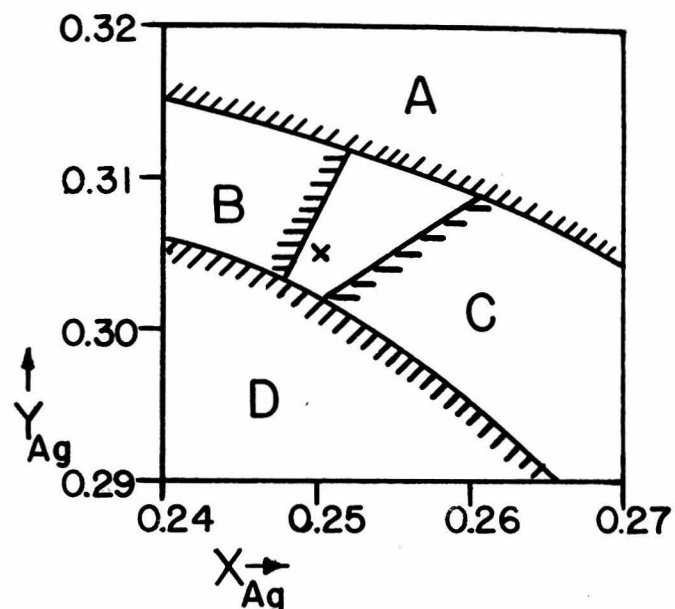
Figure 4. Determinations of $\underline{X}_{Ag}$ and $\underline{Y}_{Ag}$ for pyrargyrite by

comparisons of intensities of reflections (HH·0).

Region A is ruled out by I(66·0) calc. $< \frac{1}{4}$I(55·0)

Region B is ruled out by I(22·0) calc. $>$ I(33·0)

Region C is ruled out by I(44·0) calc. $> \frac{1}{4}$I(22·0)

Region D is ruled out by I(66·0) calc. $>$ I(55·0)

X marks the point giving the best quantitative agreement.

Y_{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 $\pm$ 0.005. The parameter Z_{Ag} was determined by comparisons, some of which are shown in Figure 5, to be within 0.005 of Z_{Ag} = 0.210. The sulfur atoms were then placed so as to make the SbS_3 groups pyramidal with the Sb-S distance 2.45 Å and the Ag-S distance 2.40 Å, in agreement with the covalent radii of these elements. The determination of the structure of pyrargyrite was then complete. The parameters are

$$X_{Ag} = 0.250 \pm 0.005 \qquad X_{S} = 0.220 \pm 0.010$$

$$Y_{Ag} = 0.305 \pm 0.005 \qquad Y_{S} = 0.105 \pm 0.010$$

$$Z_{Ag} = 0.210 \pm 0.005 \qquad Z_{S} = 0.355 \pm 0.010$$

$$Z_{Sb} = 0.000$$

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 3. The agreement between the observed and calculated intensities of reflection proves the above structure to be correct.

Discussion of the Structures of Proustite and Pyrargyrite

The structure of proustite is shown in Figure 6, the structure of pyrargyrite being so similar that this figure may be used for the discussion of both. Both structures contain $(AgS)_\infty$ 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 2.40 Å, the S-Ag-S bond angle is about 165°, and the Ag-S-Ag bond angle is about $83\frac{1}{2}°$. One complete turn of the spiral is
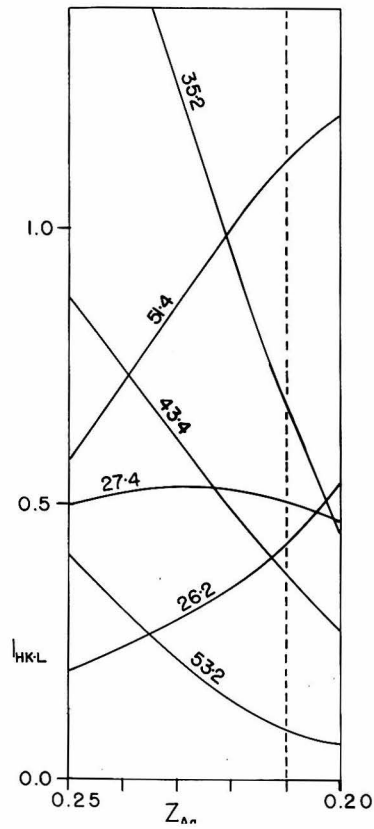
Figure 5. Determination of Z_{Ag} for pyrargyrite by comparisons of intensities. $I_{HK \cdot L}$ plotted on an arbitrary scale against Z_{Ag}. The dotted line shows the chosen value. The observed intensities satisfy the inequalities:

$I(51 \cdot 4) > I(35 \cdot 4) > I(27 \cdot 4) > I(26 \cdot 2) > I(43 \cdot 4)$

Table 3

Observed and Calculated Intensities for Pyrargyrite

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.

Indices	Observed--Calculated
(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
(05·4)	0.00--0.40
(32·4)	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
(23·2)	1.5--1.09
(04·2)	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--10.00
(22·0)	3.0--1.39
(41·0)	1.5--0.92
(33·0)	3.4--1.75
(06·0)	3.0--3.62
(52·0)	2.5--3.12
(44·0)	0.40--0.16

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 2.25 Å 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$\frac{1}{2}$°, Ag-S-Ag = 83$\frac{1}{2}$°. In pyrargyrite the antimony atoms form three bonds to sulfur, 2.45 Å long at mutual angles of 95$\frac{1}{2}$°. The sulfur atom in pyrargyrite forms three bonds with the angles : Sb-S-Ag = 97° and 111°, Ag-S-Ag = 83$\frac{1}{2}$°.

An interesting feature of these structures is the fact that they are composed of two interpenetrating frameworks or 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 Figure 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 AgS 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.

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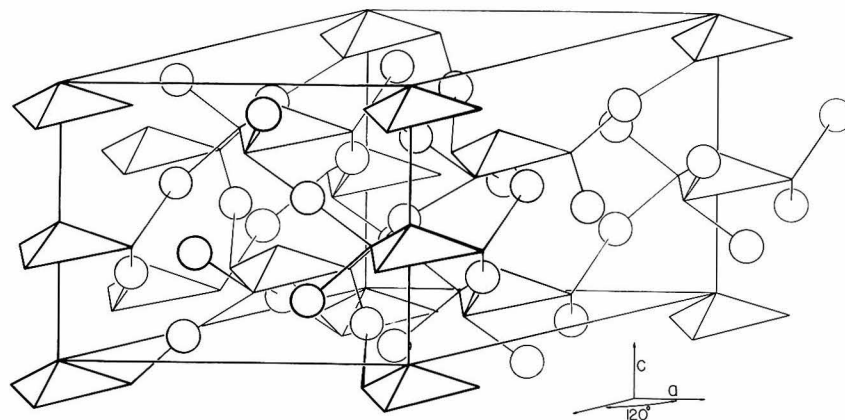
Figure 6. The structure of proustite.
Pyramids represent AsS_3 groups, balls represent silver
atoms, and lines represent covalent bonds. The structure
of pyrargyrite is almost the same.

References

(1) A. L. Patterson, Zeit. Krist., 90, 517 (1935)

(2) P. Groth, Chemische Kristallographie

(3) W. Hofmann, Zeit. Krist., 92, 161 (1935)

(4) L. Pauling and M. L. Huggins, Zeit. Krist., 87, 205 (1934)

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

(6) C. D. West, Zeit. Krist., 90, 555 (1935)

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