

INTERATOMIC DISTANCES FROM X-RAY POWDER PHOTOGRAPHS

THE CRYSTAL STRUCTURE OF MERCURIC TELLURATE

Thesis by  
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## Abstract

The Fourier series is discussed as a method for obtaining directly the arrangement of atoms within a crystal, and difficulties in this method are pointed out. A recently developed treatment of x-ray powder photographs giving interatomic distances is tested on various substances and found to be satisfactory when applied to compounds containing relatively few heavy atoms in reasonably simple arrangement. Crystalline diphenyliodonium iodide is shown to have an ionic bond between the iodine atoms. The sulfur bond angle in orpiment is measured, and great similarity is found to exist between the structures of orpiment and realgar. The arsenic-sulfur distance in sodium sulfantimonate is found to be smaller than that predicted by the table of radii of Pauling and Huggins. A short discussion is given of the difficulties encountered in applying this method.

On the basis of an incomplete investigation into the crystal structure of mercuric tellurate,  $\text{Hg}_3\text{TeO}_6$ , the  $\text{TeO}_6$  group is shown to exist as a unit here as in telluric acid, with a shape that is nearly regularly octahedral. The unit cell size is found, and a determination of the space group is made.

PART I. INTERATOMIC DISTANCES FROM X-RAY POWDER PHOTOGRAPHS.

INTRODUCTION

One of the most important problems that have confronted investigators who would determine the structures of crystals has been the discovery of a method by means of which a structure could be determined directly and explicitly from x-ray and other data. Many structures have been determined, and in most cases it has been possible to show that no other structure could account for the data, yet in all cases the method of determination has been one of trial and error: a configuration of atoms obeying known symmetry laws of the crystal is used in computing data, and these computed data are compared with that observed. The problem we have before us is to derive an expression for the distribution of scattering material within the crystals, using as independent variables such observable quantities as intensities of reflection and corresponding indices, angles of reflection and symmetry properties. This problem has not been solved, although it is not improbable that it will be solved at some future date. Several advances have been made in this direction; it is the purpose of Part I of this dissertation to present the results of an investigation into the merit of a quite recent advance made by Gingrich and Warren<sup>(1)</sup>.



## Fourier Series

The oldest and most widely used method for the direct determination of a structure is that of Fourier analysis, first suggested by W. H. Bragg in 1915<sup>(2)</sup>. In 1924 Epstein and Ehrenfest<sup>(3)</sup> showed that a Fourier series representing the density of the material scattering x-rays as a function of x, y, and z in the unit cell could be written in which the coefficients were proportional to the square roots of the intensities of the lines with corresponding indices. This idea was put into a usable form by Duane<sup>(4)</sup>, and a derivation of the series may be found in a paper of W.L. Bragg<sup>(5)</sup>. It is briefly repeated here for future reference. The structure factor of a crystal is defined by

$$F(hkl) = \frac{V}{abc} \int_{-\frac{a}{2}}^{+\frac{a}{2}} \int_{-\frac{b}{2}}^{+\frac{b}{2}} \int_{-\frac{c}{2}}^{+\frac{c}{2}} \rho(xyz) e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} dx dy dz, \quad (1)$$

where V is the volume of the unit cell, a, b, and c are the lengths of its edges, and  $\rho(xyz)$  is the electron density at a point in question. It is a complex quantity, and may, of course, be written in the form

$$F(hkl) = |F(hkl)| e^{i\theta(hkl)} \quad (2)$$

Since the intensity of reflection is proportional to  $|F(hkl)|^2$ , the phase angle  $\theta(hkl)$  is a quantity which is not observed experimentally. If we assume a general Fourier series expressing the density of the form

$$\rho(xyz) = \sum_{pqr} A(pqr) \cos \left[ 2\pi \left( \frac{px}{a} + \frac{qy}{b} + \frac{lz}{c} \right) + \alpha(pqr) \right], \quad (3)$$

substitute in (1), and integrate, we obtain

$$F(hkl) = |F(hkl)| e^{i\theta} = VA(hkl)e^{-i\alpha}$$

Thus  $VA(hkl) = |F(hkl)|$ ,  $\theta = -\alpha$ , so that

$$\rho(xyz) = \frac{1}{V} \sum_{hkl} |F(hkl)| \cos \left[ 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) - \theta(hkl) \right] \quad (4)$$

Thus we have an explicit expression for  $\rho$  involving the experimentally determinable quantity  $|F(hkl)|$  and an unknown phase angle  $\theta(hkl)$ . It is the lack of knowledge of this phase angle that robs the Fourier series method of most of its usefulness. If the crystal has a center of symmetry at the origin it may be shown that  $\theta(hkl)$  assumes the values 0 or  $\pi$ ; in this case there is no experimental method enabling one to decide which value to assign to it. However, if the approximate structure is known it is not difficult to decide the value of the phase angle for most of the lines; application of the series then furnishes a more exact and graphical picture of the structure. It is in this way that the method has been used by Duane<sup>(4)</sup>, Havighurst<sup>(5)</sup> on rock salt, calomel and other substances, W.L. Bragg on diopside<sup>(5)</sup>, Lonsdale on  $C_6Cl_6$ ,<sup>(7)</sup> and by others more recently. West<sup>(8)</sup> applied the series in a different and original way to potassium hydrogen phosphate, but his method is not generally applicable.

We see, then, that the Fourier series method is not a satisfactory answer to our problem. If a direct correspondence could be found between the unknown phase angle and the symmetry properties of the crystal the method could be made much more useful. That such a

correspondence may exist seems plausible in view of the effect of a center of symmetry on its value. It is to be doubted, however, that this fact has any general significance; we may expect a more subtle relationship if one exists. Calculations were made by the author of the phase angles to be assigned to the various terms in a series representing the projection upon the basal plane of scattering power of wurtzite. In wurtzite there is no center of symmetry or line of symmetry perpendicular to the basal plane, but there is a three-fold axis along  $c$  (using hexagonal axes). This calculation may be made in the following way: We have as a practical and nearly exact expression for  $F(hkl)$ , the structure factor,

$$F(hkl) = \sum_j f_j e^{2\pi i \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right)}, \quad (5)$$

where  $f_j$  is the factor for the  $j$  the atom, assumed real. This may be written in the form

$$F(hkl) = u + iV, \quad (6)$$

where

$$u = \sum_j f_j \cos 2\pi \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right); V = \sum_j f_j \sin 2\pi \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right). \quad (7)$$

$|F(hkl)|$  is the square root of the intensity observed, and it is

$$\begin{aligned} |F(hkl)| &= \sqrt{F(hkl)F^*(hkl)} \\ &= \sqrt{u^2 + V^2} \end{aligned} \quad (8)$$

We have from equation 2 that  $F(hkl) = |F(hkl)|e^{i\theta}$  where  $\theta$  is the phase angle, so

$$u + iV = \sqrt{u^2 + v^2} e^{i\theta} = \sqrt{u^2 + v^2} (\cos\theta + i \sin\theta) \quad (9)$$

and

$$\begin{aligned} \cos\theta = \frac{u}{\sqrt{u^2 + v^2}} &= \frac{\sum_j f_j \cos 2\pi \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right)}{|F(hkl)|} \\ \sin\theta = \frac{v}{\sqrt{u^2 + v^2}} &= \frac{\sum_j f_j \sin 2\pi \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right)}{|F(hkl)|} \end{aligned} \quad (10)$$

The results of calculations of  $\theta$  for wurtzite and for another structure in which Zn+S was added at the position  $(\frac{11}{22})$  are given in Table I, which is presented as an example of the behavior of the phase angle. No change of coordinates could be found that made the results seem related to the symmetry properties present. The effect of a center of symmetry is readily seen from equations 10; in this case  $V=0$  and  $\cos\theta = \pm 1$ ,  $\sin\theta = 0$ . Thus  $\theta = 0$  or  $\pi$ .

TABLE I. Calculations of Phase Angles from Known Positions

Positions of atoms	Nature of indices (n any integer)	
Wurtzite structure Zn+S at $x,y = 0,0; \overline{1/3}, 1/3$	$\frac{k-h}{3} = n$	0
	$\frac{k-h}{3} = n + 1/3$	+60°
	$\frac{k-h}{3} = n - 1/3$	-60°
Wurtzite structure as above, with Zn+S also at $x,y = 1/2, 1/2$	$\frac{k-h}{3} = n$	0
	$\frac{k-h}{3} = n \pm 1/3$ $\frac{k-h}{2} = n$	±30°
	$\frac{k-h}{3} = n \pm 1/3$ $\frac{k-h}{2} = n$	±120°

Patterson Method

Another method, recently developed by Patterson<sup>(9)</sup> employs a series resembling equation 4, using, as coefficient, the integrated intensity of scattering from the plane  $hkl$ , and involving no phase angle. This, as expected, results in less information; the function obtained is not  $\rho(xyz)$ , but one giving interatomic distances and their directions, weighed with the scattering power of the atoms involved. Thus if a peak in the

function occurs at the point  $(x_1, y_1, z_1)$ , we conclude that somewhere in the crystal two atoms are arranged with respect to each other as are the origin and the point  $(x_1, y_1, z_1)$ . This is without doubt a very useful method; it seems likely that with sufficient data this may become a useful part of routine crystal structure analysis.

### Powder Method for Obtaining Interatomic Distances

Interatomic distances in particular cases may also be found using a single powder photograph, without the use of indices of reflection. Here all interatomic distances are shown superimposed on the same curve; a maximum at  $r = r$ , shows that two atoms in the crystal are at a distance  $r$ , from each other, or that two or more distances near  $r$ , exist and are unresolved on the curve. The equation that is used was first derived by Debye and Menke<sup>(10)</sup>, who applied it to liquid substances. Gingrich and Warren applied this method to rhombic sulfur<sup>(1)</sup> and Warren applied it to amorphous carbon<sup>(11)</sup>.

We start with the expression for the intensity of scattering from a group of atoms due to Debye<sup>(12)</sup>.

$$I(s) = I_0 \frac{e^4}{m^2 c^4 R^2} \frac{1 + \cos^2 2\theta}{2} \sum_{pq} f_p f_q \frac{\sin sr_{pq}}{sr_{pq}} \quad (11)$$

where  $f_p$  is the atomic scattering factor for the  $p$ th

atom,  $r_{pq}$  is the distance between the  $p$ th and  $q$ th atom, and the summation is over all atoms in the scattering substance.  $S = \frac{4\pi \sin \theta}{\lambda}$ , and  $\theta$  is one-half the scattering angle. Let us assume for the present that there is only one kind of atom present, then  $f_p = f_q$ , and we have the single summation.

$$I(s) = N \psi(s) \sum_p \frac{\sin sr_p}{sr_p} \quad (12)$$

Here  $N$  is the number of atoms in the sample, and

$$\psi(s) = I_0 f^2 \frac{e^4}{m^2 c^4 R^2} \frac{1 + \cos^2 2\theta}{2}$$

If we represent the distribution of atoms about any central atom by means of a density function  $\rho(r)$  such that  $4\pi r^2 \rho(r) dr$  is the number of atoms between the distances  $r$  and  $r+dr$ , then equation 12 becomes

$$I(s) = N \psi(s) \left[ 1 + \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin sr}{sr} dr \right], \quad (13)$$

where unity represents scattering from atoms individually and the integral represents interatomic scattering. Define

$$i(s) = \frac{I(s)}{N \psi(s)} - 1, \quad (14)$$

Then, from (13),

$$s i(s) = 4\pi \int_0^\infty r \rho(r) \sin sr dr. \quad (15)$$

This we may invert as a Fourier integral to obtain  $\rho(r)$  in terms of  $i(s)$

$$r \rho(r) = \frac{1}{2\pi^2} \int_0^\infty s i(s) \sin sr \, ds. \quad (16)$$

Now while  $i(s)$  represents all except the independent unmodified scattering, it includes the interatomic scattering at zero angle. This (000) beam is unobservable, though it can be evaluated in terms of the density of the crystal in atoms per cc. If we designate this density as  $\rho_0$ , we have finally,

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty s i(s) \sin sr \, ds, \quad (17)$$

where now  $i(s)$  does not include the (000) beam. This is the form used by Debye and by Gingrich and Warren. Although equation 17 was derived on the assumption that only one kind of atom was present, it is applicable to a substance of any complexity. It may be shown that in the more complicated case  $\rho(r)$  represents a distribution of scattering power rather than of atoms, and that it is a superposition of several functions, each using a different atom as the origin and weighted with the scattering power of the central atom. In this case a quantitative expression corresponding to equation 17 may be derived(1).



Equation 17 may be applied to any type of matter, whether crystalline or not. If the substance is a powdered crystal, however, scattering which is not independent occurs at definite angles, forming the lines seen on the usual powder photograph.  $i(s)$  (equation 14) is just the intensity of this scattering, divided by the independent unmodified scattering which supplies most of the background. Thus we may replace the integral of equation 17 with a summation over the lines on a powder photograph and obtain

$$4 \pi r^2 \rho(r) = 4 \pi r^2 \rho_0 + \frac{2r}{\pi} \sum_j s_j i_j \sin s_j r, \quad (18)$$

where

$$i_j = \int_{j^{\text{th}} \text{ line}} i(s) ds.$$

In the work which follows equation 18 was used, in which visually estimated relative intensities were substituted for  $i_j$ . Since absolute intensities were not known, constant factors were omitted from the equation, as well as the term  $4 \pi r^2 \rho_0$ , which keeps the function positive and causes it to increase parabolically. Then in the resulting functions positions and relative heights of peaks were considered the significant results. It should be noticed in passing that the series is not convergent as it stands, since  $s_j$  increases with angle and  $i_j$  when

corrected for temperature effect does not decrease. The effect of temperature on  $\lambda_j$  is to cause it to decrease exponentially with a factor  $e^{-B's_j^2}$ , and this factor, when inserted, causes the series to converge. In any event, the high order terms are very important; in every case it was found necessary to include an additional arbitrary temperature factor to decrease the value of  $s$  at which the importance of the terms falls off, and to prevent the series from breaking off abruptly at  $\theta = 90^\circ$ .

The series was used in several instances; the results are described below under their several headings. In all cases where photographs were taken, the radiation used was  $\text{CuK}\alpha$  with  $\lambda = 1.5386 \text{ \AA}$ , filtered through nickel remove the  $\text{K}\beta$  line and most of the continuous radiation. The samples were mounted with collodion on the outside of fine tubes of low absorbing glass. The photographic films were placed on the inside of a camera of radius 5.065 cm., as calibrated from a powder photograph of sodium chloride taken under similar conditions.

#### a. Atoms at Simple Cubic Lattice Points

Theoretical intensities of reflection were calculated for a hypothetical crystal composed of point atoms located at the lattice points of the lattice  $\sqrt{c}$ . Fig. 1 shows the curve obtained with the use of 14 terms, while

in Fig. 2 we see the result of 22 terms. The vertical lines designate position at which peaks should appear. Resolution of peaks in Fig. 1 is not very satisfactory at distances greater than  $r = \sqrt{3}$ , while in Fig. 2 resolution seems to have improved out to  $r = 3$ . It must be pointed out, however, that for a photograph taken with  $\text{CuK}\alpha$  radiation to supply 14 lines the identity distance in the crystal must be greater than  $3.0\text{\AA}$ , and for the photograph to supply 22 lines the identity distance must be greater than  $3.8\text{\AA}$ . For resolution of peaks to be satisfactory at small or large values of  $r$  it is necessary to include terms having a large value of  $\frac{\sin \theta}{\lambda}$ .

b. Crystalline Iodine.

Equation 18 was applied to the powder data of Harris, Mack, and Blake<sup>(13)</sup> on iodine, for the purpose of finding out to what extent the relatively unimportant peak corresponding to the molecular I - I distance would appear. Around each atom in iodine there is another atom at a distance of  $2.70\text{\AA}$ , two at  $3.54\text{\AA}$ , and eleven at  $4.35\text{\AA}$ . It was found that the position of the first small peak depended greatly upon the number of terms used in the series and upon the value of the temperature factor employed. The curve is

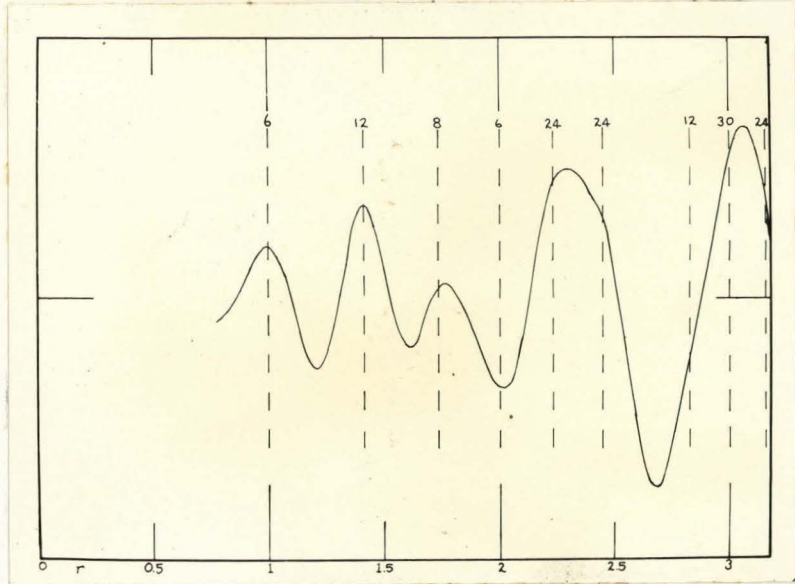


Fig. 1

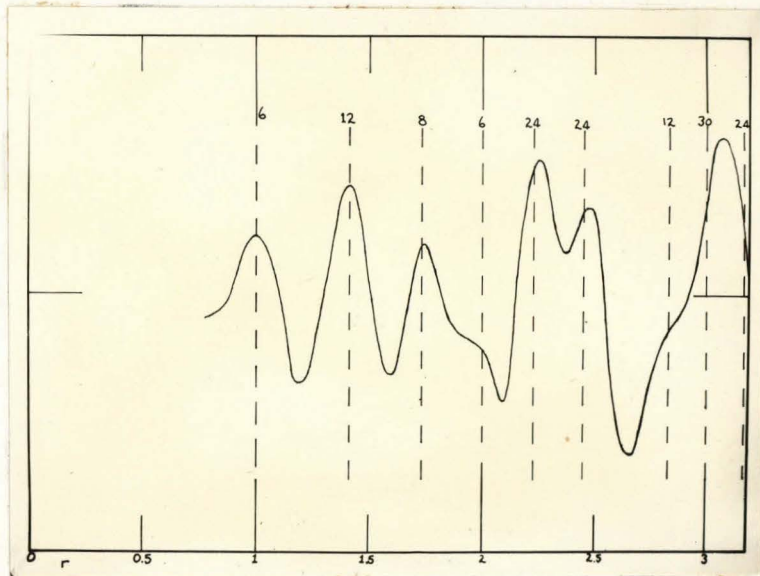


Fig. 2

Atoms at Simple Cubic Lattice Points

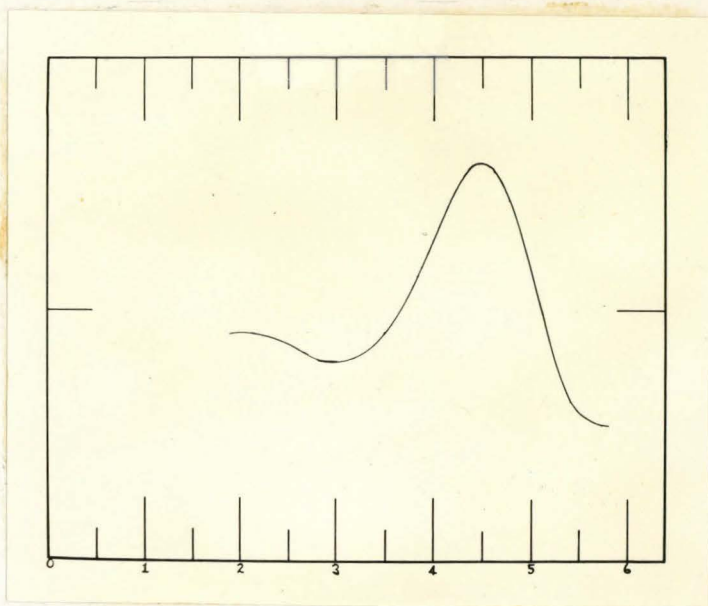


Fig. 3



reproduced in Fig. 3; there is a high peak in the correct position, although the second peak is not resolved. It was in connection with iodine that the remarkable stability of these curves was first noted. Multiplication of terms by such factors as  $\sin^2 \theta$  or the Lorentz factor produces no appreciable change in the more outstanding features of the curve.

c. Amorphous Carbon

Warren<sup>(11)</sup> applied equation 17 in its integral form to amorphous carbon, making quantitative measurements of  $I(s)$  and performing the integration on a harmonic analyzer. His photographs show four broad peaks of intensity. If these four broad peaks are considered to be lines with intensity equal to the height of the corresponding peak on the photometer curve and with the angle  $\theta$  equal to that of the center of the peaks, and equation 18 is applied, the curve shown in fig. 4 is obtained. The vertical lines show the position of the peaks found by Warren, using his precise method. The calculation was intended merely to demonstrate the stability of the method when a rough application is made of it.

d. Diphenyliodonium Iodide

The application of the method to a definite chemical problem is demonstrated in the case of

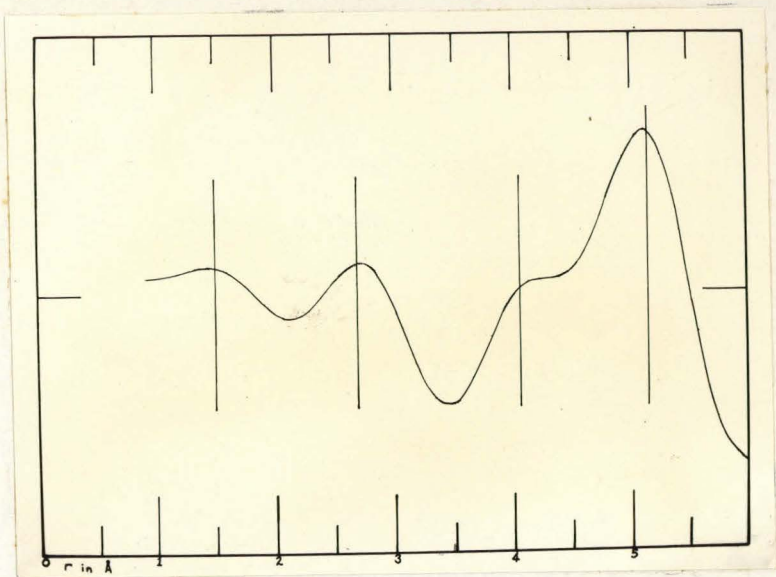


Fig. 4

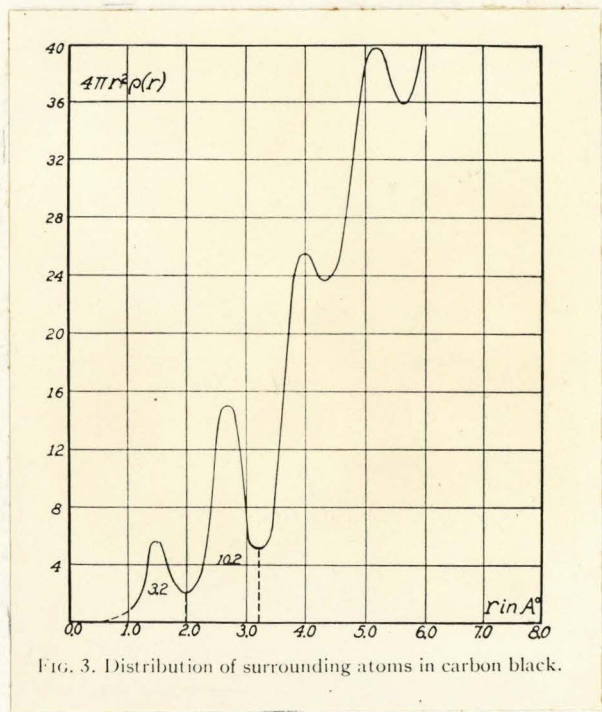


Fig. 3. Distribution of surrounding atoms in carbon black.

Fig. 4a. Warren's Curve

Amorphous Carbon

diphenyliodonium iodide,  $(C_6H_5)_2I_2$ . In this compound the two phenyl groups are attached to an iodine atom; either the second iodine atom is attached to the first by means of a covalent bond, or the substance is an ionic crystal containing the ions  $(C_6H_5)_2I^+I^-$ . If there is a covalent bond the distance between iodine atoms is expected to be that found in  $I_2$  or ammonium triiodide; this distance is shown to be  $2.70\text{\AA}$  in  $I_2$  and  $2.8\text{\AA}$  in  $NH_4I_3$  <sup>(14)</sup>, while the table of covalent radii of Pauling and Huggins <sup>(15)</sup> gives  $2.7\text{\AA}$ . If the bond is ionic the I-I distance would be much greater---probably not less than the  $3.54\text{\AA}$  found in  $I_2$  for unbonded iodine atoms. This question could be answered by applying equation 18 to a powder photograph of diphenyliodonium iodide, since the scattering due to the iodine atoms is large enough greatly to outweigh the contributions made by the other atoms of much less atomic number, and we should find a quite stable peak corresponding to the shortest I-I distance.

Fig. 5 shows the powder photograph obtained from diphenyliodonium iodide, and Fig. 6 is the curve obtained. We find a small peak occurring at  $2.24\text{\AA}$ , a large one at  $3.55\text{\AA}$ , a third at  $5.18\text{\AA}$ , and a fourth at  $6.9\text{\AA}$ . At the significant distance of  $2.7-2.8\text{\AA}$  there is a definite minimum. The first peak may be attributed to the unresolved C-C and C-I distances, hence the





Fig. 5

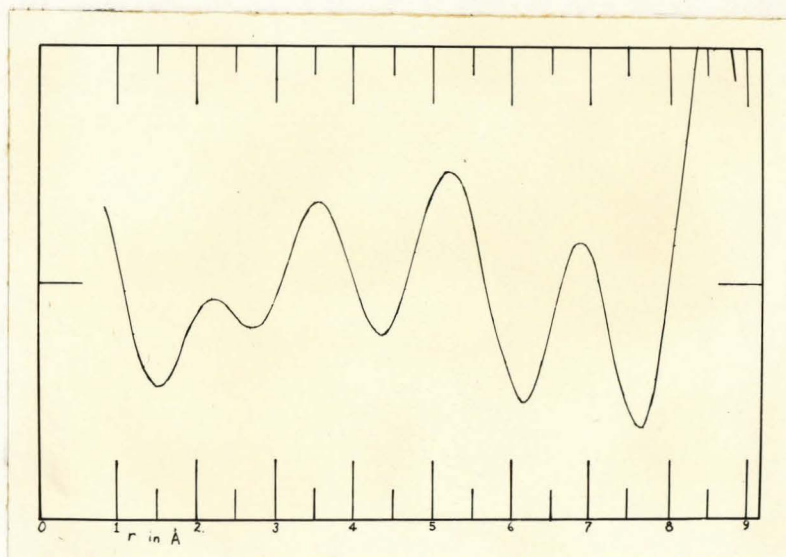


Fig. 6

Diphenyliodonium Iodide

shortest distance between iodine atoms is  $3.55\text{\AA}$ . This clearly shows that the compound is ionic. Other evidence likewise points to the ionic nature of the substance; recent work by Kennedy and Lucas<sup>(16)</sup> confirms this result in solution.

c. Orpiment and Realgar

The crystal structures of orpiment,  $\text{As}_2\text{S}_3$ , and realgar,  $\text{AsS}$ , are not known. Their simple formulas suggest that a distance-density function of the type we are concerned with would be useful in helping to determine the structures or in telling us something of the way in which the atoms are bonded together. Realgar is particularly interesting because of the apparent divalence of arsenic; if we assume that sulfur has a coordination number of two, then either there are arsenic-arsenic bonds or arsenic also has a coordination number of two.

Good photographs were obtained of both substances; they are reproduced in Figs. 7 and 8. Figs. 9 and 10 show respectively the curves obtained from these photographs. It is apparent that they are much alike, at those values of  $r$  for which the curves were calculated. In the case of orpiment the first small peak occurs at  $r = 2.24\text{\AA}$ , the second at  $3.46\text{\AA}$ , and a third

at 4.39 Å. In the curve for realgar the first is at 2.16 Å, the second at 3.54 Å, and the third at 4.52 Å. The covalent radius<sup>(15)</sup> of As is 1.21 Å and that of S is 1.04 Å, so that only the first peak may be attributed to two atoms which are bonded together; and the position of the peak is correct for the As-S separation. The atomic number of arsenic is approximately twice that of sulfur; if arsenic in realgar is to have a coordination number of three and sulfur a coordination number of two there must be four As-S bonds for each As-As bond. Hence with these coordination numbers the As-As interaction should be equal in importance to the As-S interaction. We must conclude then, that if the position of the first peak is to be taken in evidence there are no As-As bonds in realgar.

In the case of orpiment it is quite easy to understand the result obtained. We shall first assume that the structure is built upon bonds linking each arsenic atom to three sulfur atoms and each sulfur to two arsenics, with the chain running continuously in some manner throughout the crystal. The distance between arsenic atoms and bonded sulfur atoms is represented by the position of the first peak; the second peak then gives the unbonded As-As distance. We can calculate from the positions of these peaks the bond angle for sulfur; we find it to be  $97^{\circ} 14'$ . The third peak represents a distance more than twice that between sulfur and arsenic, hence it cannot represent the



Fig. 7  
Orpiment



Fig. 8  
Realgar



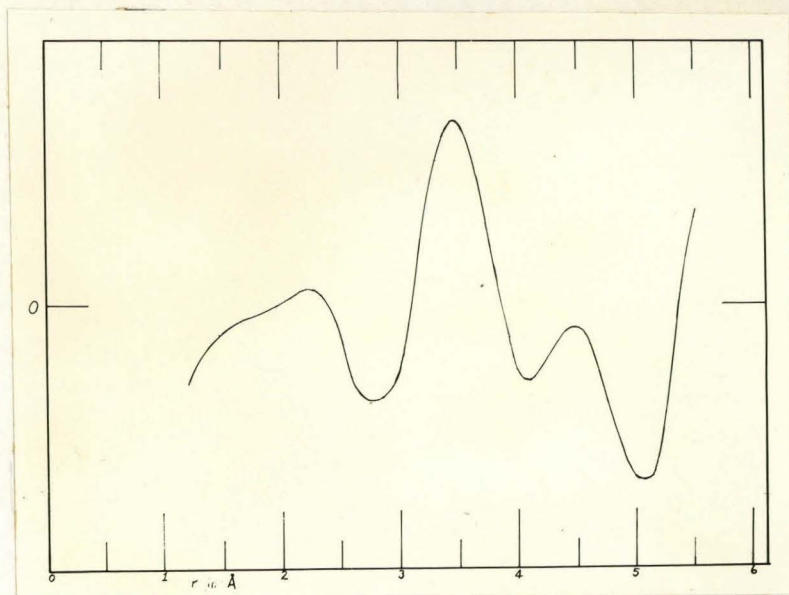


Fig. 9  
Orpiment

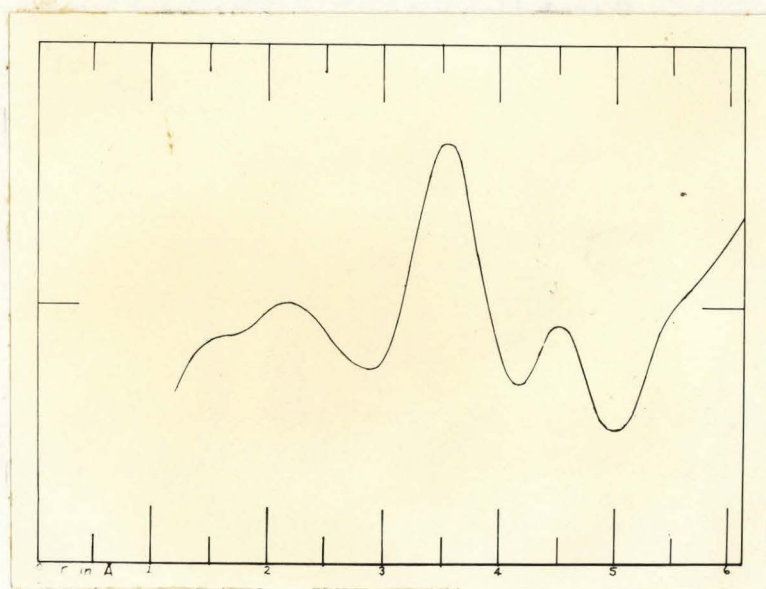


Fig. 10  
Realgar

nearest S-S distance. This S-S distance must then also be approximately  $3.4\overset{\circ}{\text{A}}$ , and the arsenic bond angle approximately that of sulfur. The three arsenic bonds, we see, are not coplanar. The As-As distance and the S-S distance are represented by the same peak, so that knowledge of both distances is made less accurate. The sharpness of the peak, however, indicates that these distances certainly do not differ from  $3.46\overset{\circ}{\text{A}}$  by more than three per cent.

The bond angles in realgar are approximately the same as those in orpiment, as evidenced by the similarity in the two curves.

f. Sodium Sulfantimonate Ennehydrate

The application of this method to sodium sulfantimonate ennehydrate,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$  (Schlippe's salt), was somewhat less successful than in previous cases. The photograph and resulting curve are shown in Figs. 11 and 12; we may be sure that the simplicity of the figure does not indicate a correspondingly simple structure. The first peak is found at  $2.26\overset{\circ}{\text{A}}$ , and there is no other with  $r$  less than  $4.31\overset{\circ}{\text{A}}$ . We should expect upon examining the photograph that the result would be quite simple because of a very important doublet occurring at  $\sin \theta = 0.415$  and  $0.420$ . This doublet largely determines the



Fig. 11

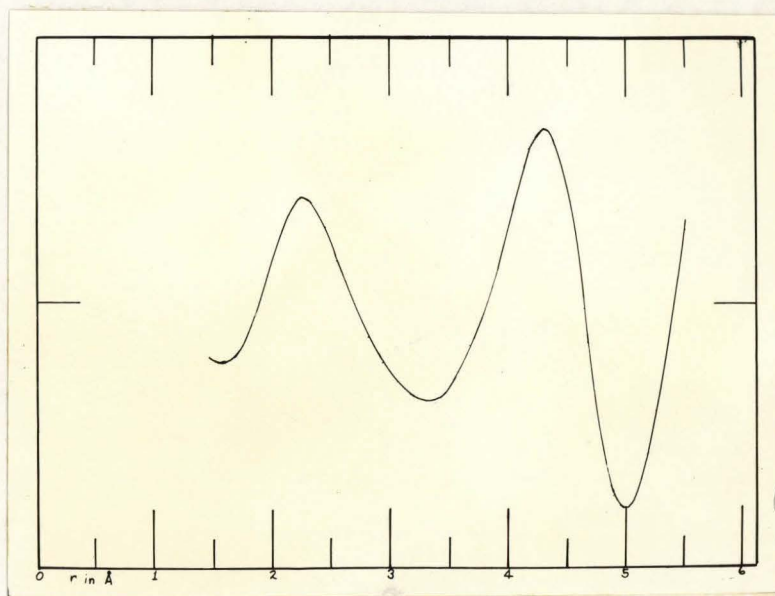


Fig. 12

Sodium Sulfantimonate Ennehydrate

positions of the peaks and the general shape of the curve. It is evident that terms at values of  $(\sin \theta)/\lambda$  much higher than those here available are necessary to furnish sufficiently great resolution.

The  $\text{SbS}_4$  group of sodium sulfantimonate is its outstanding feature, because of the comparatively great atomic numbers of the antimony and sulfur atoms; thus the Sb-S distance would be expected to appear strongly on the curve. The sum of the tetrahedral radii of these atoms is  $2.40\text{\AA}$ , and while this is not far from the value  $2.26\text{\AA}$  obtained from the position of the first peak, the difference is appreciable. The apparent discrepancy between the observed Sb-S distance and the sum of the radii is no doubt real; if so we have a case similar to that found in stannic chloride and similar compounds<sup>(17)</sup> explainable in terms of double bond formation. Electronic structures involving double bonds between antimony and one or more of the sulfur atoms can contribute to the normal state and act in shortening the bonds. The peak at  $4.31\text{\AA}$  again must involve antimony, and probably represents the shortest Sb-Sb distance.

#### g. Calcium Mercuric Bromide

Fig. 14 shows the density distribution curve obtained for calcium mercuric bromide,  $\text{CaHgBr}_4$ .



The first peak occurs at  $r = 2.24\overset{\circ}{\text{Å}}$ , probably too small a value to represent accurately the Hg-Br distance which must have caused it to appear. Experience with the compounds treated previously shows that the asymmetric shape of the peak may be used in establishing the presence of a distance larger than  $2.24\overset{\circ}{\text{Å}}$ . The sum of the tetrahedral radii for Hg and Br is  $2.59\overset{\circ}{\text{Å}}$ ; this value of  $r$  is shown in Fig. 14 by means of a vertical line.

The second peak is observed at  $4.01\overset{\circ}{\text{Å}}$ ; interpretation of this value depends upon an assumption as to the configuration of the atoms. If the bromine atoms are arranged tetrahedrally about the mercury atom, and this peak is assumed to represent the Br - Br distance, then calculation of the distance between mercury and bromine atoms gives  $2.47\overset{\circ}{\text{Å}}$ . This result is too low for the reason that this peak also represents the Br - Br distance in adjoining tetrahedra, and this distance we may expect to be approximately  $3.90\overset{\circ}{\text{Å}}$ , the diameter of bromide ion<sup>(18)</sup>. The position of the peak furnishes a value between the two Br - Br distances it represents; thus the size of the  $\text{HgBr}_4$  tetrahedron is slightly greater than the above calculation indicates. The third peak at  $5.35\overset{\circ}{\text{Å}}$  represents the closest approach of mercury atoms to each other, if this model is assumed to be correct.



Fig. 13

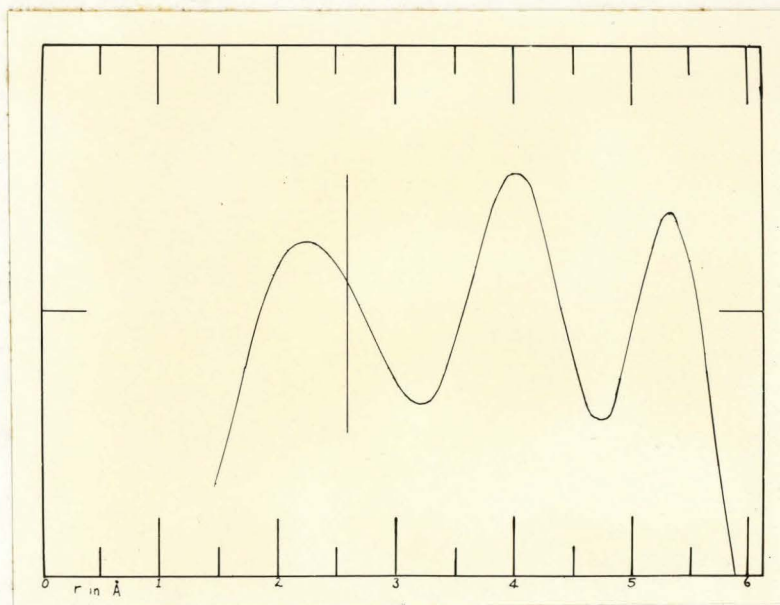


Fig. 14

Calcium Mercuric Bromide

Application of this method to calcium mercuric bromide, then, does not lead to a definite configuration of atoms, but it is consistent with the model consisting of tetrahedral  $\text{HgBr}_4^{--}$  ions which are in contact smaller  $\text{Ca}^{++}$  ions holding them together.

### Conclusion

The method which has been tested in these experiments shows promise of becoming quite useful in determining atomic configurations. If best results are to be obtained it is necessary to have accurate intensity data from powder photographs of high intensity. The series should be applied only to substances which contain a comparatively small number of highly scattering atoms, since the resulting curve readily smooths out the detail which characterizes a complex structure. An example of a type of compound to which this method might profitably be applied is the series of organic arsenical compounds consisting of carbon, hydrogen, and one or two arsenic atoms.

The need for accurate intensity data arises from the fact that the high order lines are necessary to give satisfactory resolution, and that these lines enter in the series importance increasing greatly with their order. The introduction of an arbitrary temperature factor is not a desirable step, and becomes

necessary to make the results trustworthy in view of the low accuracy with which the intensities of the weak lines of large scattering angle are known. The unsatisfactory result in the case of sodium sulfantionate is due largely to this difficulty.

There is also a question as to the correctness of the results at small and large values of  $r$ . For a given interval of distance from a central atom the number of peaks in a density distribution curve becomes greater at greater distances, hence greater resolution is required to separate the peaks at large  $r$ . In these experiments  $6\text{\AA}$  is an approximate upper limit of  $r$  beyond which the results become rather useless. At values of  $r$  much less than  $2.2\text{\AA}$  there seems to be a tendency for the peaks to fall too near the origin. This tendency is particularly noticeable in the last two examples, while the peculiar shape of the realgar and orpiment curves may be attributed to it. Gingrich and Warren also noticed this. Between  $2.5\text{\AA}$  and  $6\text{\AA}$ , however, the position of the peaks can be used with reasonably great confidence in their accuracy.

I wish to express my appreciation of the many helpful suggestions made in this work by Professor Linus Pauling.

References

- (1) Gingrich and Warren, Phys.Rev., 46, 368 (1934).
- (2) W. H. Bragg, Phil.Trans. of the Roy.Soc., A215, 253 (1915).
- (3) Epstein and Ehrenfest, Proc. Nat. Acad. Sci. 10, 133 (1924).
- (4) Duane, Proc.Nat. Acad.Wash., 11, 489 (1925).
- (5) W. L. Bragg, Proc.Roy.Soc., 123, 537 (1929).
- (6) Havighurst, Journ.Am.Chem.Soc., 48, 2113 (1926).
- (7) Lonsdale, Proc.Roy.Soc. A 133, 536 (1931).
- (8) West, Zeits. f. Krist. 74, 306 (1930).
- (9) Patterson, Phys. Rev. 46, 372 (1934).
- (10) Debye and Menke, Phys. Zeits. 31, 419 (1930).
- (11) Warren, Journ.Chem. Phys. 2, 551 (1934).
- (12) Debye, Ann. d. Physik 46, 809 (1915).
- (13) Harris, Mack, and Blake, Journ.Am.Chem.Soc. 50, 1583 (1928).
- (14) Mooney, Zeits, f. Krist. 90, 143 (1935).
- (15) Pauling and Huggins, Zeits. f. Krist. 87, 205 (1934).
- (16) Lucas and Kennedy, Journ.Am.Chem. Soc., To be published.
- (17) Brockway and Wall, Journ.Am.Chem.Soc. 56, 2373 (1934).
- (18) Pauling, Journ.Am.Chem. Soc. 49, 765 (1927).

PART II. THE CRYSTAL STRUCTURE OF MERCURIC TELLURATE.

## PART II. THE CRYSTAL STRUCTURE OF MERCURIC TELLURATE

### INTRODUCTION

The very great stability of hydrated telluric acid,  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ , was probably first noted by Berzelius, and it was later suggested that the two molecules of water be considered not as water of crystallization, but as a part of the molecule of telluric acid. This suggestion was made more plausible by Baker and Aldam<sup>(1)</sup>, who found that the dihydrate failed to lose water even after standing six months over phosphorus pentoxide in a vacuum; also that the substance failed to transmit water, as true hydrates do. Structurally the  $\text{TeO}_6$  group is satisfactory, as the greater atomic diameter of the tellurium atom allows a coordination number of six. Sulfuric and selenic acids do not form such extremely stable hydrates, nor would we expect them to do so in view of the smaller atomic diameter.

A determination of the crystal structure of telluric acid should settle the question of the coordination number of tellurium in this compound. Kirkpatrick and Pauling, in 1926<sup>(2)</sup>, studied Laue and rotation photographs of  $\text{H}_6\text{TeO}_6$  in its cubic



modification and found it to have a unit cell 15.48A. on an edge containing 32 molecules. The space group is  $O_h^8$ , and if the tellurium atoms are to be equivalent they are placed in special positions without variable parameters; the point group associated with each tellurium atom is then  $C_{3i}$  or  $D_3$ , indicating that symmetrical placing of six oxygen atoms is more likely than a  $TeO_4$  group. Thus in this incomplete analysis one is led to a coordination number of six.

The present work is an attempt to ascertain whether the  $TeO_6$  octahedron exists in a salt of telluric acid, namely mercuric orthotellurate,  $Hg_3TeO_6$ . Here we might consider the salt to be one of  $H_2TeO_4$ , with  $HgO$  molecules arranged in some manner, and that the tellurium atoms are tetrahedrally surrounded with oxygen. The results of this work seem to show that such is not the case, and that the tellurium atoms here, as in  $H_6TeO_6$ , have a coordination number of six. Again the conclusion is based on an incomplete structure determination.

#### Preparation and Laue Data

The substance was prepared in the manner described by Hutchins<sup>(3)</sup>. Telluric acid is first made by dissolving tellurium in concentrated nitric acid, oxidizing the resulting tellurium dioxide with



chromic acid, and separating out the telluric acid by crystallization. Then to a solution of telluric acid a slight excess of concentrated mercuric nitrate is added. White  $\text{HgTeO}_4$  is the immediate precipitate; it turns yellow almost at once. In a few days a group of small amber crystals form. In the present case the crystals were small, with only one or two as large as 0.3 mm. in diameter. They had no well-formed faces, and were roughly spherical in shape. They are cubic, according to Hutchins. Their density is unknown; the amount obtained was too small for measurements to be made. Formation of the crystals is rather sensitive to hydrogen ion concentration; they will not form if the pH is less than the highest that may be used to dissolve the mercuric nitrate.

Examination of the crystals under a microscope proved it impossible to indentify or even locate any faces, so a crystal which produced good Laue spots was photographed in varying positions, using radiation from a tungsten target with minimum wave length of 0.25A., until a pattern corresponding to that given by a beam perpendicular to the (110) face of a cubic crystal was observed. This pattern

showed a plane of symmetry, but no two-fold axis, corresponding to the point group  $T_h$ . Rotation of the crystal through  $35^\circ 15'$  in a plane perpendicular to the observed symmetry plane produced the typical trigonally symmetrical photograph of the cubic octahedral face. No symmetry planes could be found. Gnomonic projections were made of four Laue photographs: one in which the beam was nearly parallel to the trigonal axis, and those in which the beam made angles of  $3^\circ$ ,  $5^\circ$ , and  $7^\circ$  with the axis, respectively. Attempts to make oscillation or rotation photographs of this crystal failed; later an excellent powder photograph was obtained, using fresh material.

The size of the unit cell was determined from Laue data before the powder photograph was taken; this problem proved to be both interesting and profitable. In the first place, the large number of observed Laue spots suggested a large unit cell; each photograph contained approximately three hundred first order spots. The value of  $a_0$  was fixed roughly at  $14\text{\AA}$  by use of the short wave length limit of  $0.25\text{\AA}$  and the disappearance of certain reflections as the crystal was rotated. Then use was made of the known values of the K absorption edges of Ag and Te, as these were the only absorption edges involved in the experiment falling within the

range of wave-lengths producing first order spots in the Laue photographs. Using  $a_0 = 14\text{\AA}$ , forms were found in the nearly symmetrical photograph reflecting wave-lengths of approximately  $0.389\text{\AA}$  and  $0.485\text{\AA}$ , the K edge of Te and Ag respectively, and the intensities of the spots produced by various planes in these forms were compared. No effect of the Te edge could be found; in four forms reflecting near the Ag edge certain spots were found to be more intense than others of the same form reflecting at slightly greater angles. The summary in Table I gives the results obtained. The best value for  $a_0$  appears to be  $13.40\text{\AA}$ , with a probable error of about  $0.03\text{\AA}$ .

TABLE I

Form	hkl	Sin $\theta$	Observation	Conclusion
156	$\bar{1}\bar{5}\bar{6}$	.138	$\bar{5}\bar{6}\bar{1}$ is weaker than	$13.00 < a_0 < 13.66$
	$\bar{5}\bar{6}\bar{1}$	.147	$\bar{1}\bar{5}\bar{6}$ or $6\bar{1}\bar{5}$	
	$6\bar{1}\bar{5}$	.140		
165	$1\bar{6}\bar{5}$	.145	$1\bar{6}\bar{5}$ is much weaker than	$13.16 < a_0 < 13.40$ $a_0$ probably very nearly $13.40$
	$6\bar{5}\bar{1}$	.136	$6\bar{5}\bar{1}$ , and $\bar{5}\bar{1}\bar{6}$ only	
	$\bar{5}\bar{1}\bar{6}$	.143	slightly weaker	
1-10-5	$\bar{1}\bar{1}\bar{0}\bar{5}$	.204	$\bar{1}\bar{1}\bar{0}\bar{5}$ weaker than	$13.38 < a_0 < 13.68\text{\AA}$
	$1\bar{0}\bar{5}\bar{1}$	.194	the other two.	
	$\bar{5}\bar{1}\bar{1}\bar{0}$	.199		
273	$\bar{2}\bar{7}\bar{3}$	.148	$\bar{2}\bar{7}\bar{3}$ weaker than the	$12.91 < a_0 < 13.54$
	$7\bar{3}\bar{2}$	.137	other two	
	$\bar{3}\bar{2}\bar{7}$	.141		

The Laue photographs also made possible a definite choice of space group. Absence of first order reflections in which  $h+k+l$  is odd made it almost certain that the structure is based on a body centered lattice. Space groups based on this lattice isomorphous with the point groups  $T$  or  $T_h$  are  $T^3$ ,  $T^5$ ,  $T_h^5$ , and  $T_h^7$ . The space group  $T^3$  is obtained by passing all the tetrahedral symmetry axes through the lattice points of a  $\Gamma_c$  lattice; in the space group  $T^5$  only one three-fold axis passes through the lattice points and the other axes are arranged in such a way that none intersect.  $T_h^5$  and  $T_h^7$  are derived from  $T^3$  and  $T^5$  respectively by the addition of a center of symmetry at the lattice points. Of these space groups the only one with special criteria is  $T_h^7$ ; it requires that reflections  $(0kl)$  be missing if  $l$  is odd. In the Laue photographs of  $Hg_3TeO_6$  no first order reflections were observed of the type  $(0kl)$ , and these were the only striking absences aside from the absences due to lattice criteria. The following tables list planes  $(0kl)$  which were in position to reflect and did not reflect in an asymmetric photograph in which the x-ray beam made an angle of  $7^\circ$  with the trigonal axis:

$h k l$	$\sin \theta$	$n\lambda$
0. $\bar{1}\bar{1}$ .15	.218	.315
0. $\bar{9}$ .13	.239	.413
0. $\bar{7}$ .9	.195	.458
0. $\bar{1}\bar{3}$ .17	.200	.251
0.5. $\bar{3}$	.098	.437
0 9 $\bar{5}$	.125	.331
$\bar{5}$ 9 0	.168	.445
$\bar{7}$ . 11.0	.120	.247
7 $\bar{5}$ 0	.170	.531
9 $\bar{7}$ 0	.136	.332
$\bar{7}$ 0 9	.156	.367

It appears extremely probable, then, that the space group is  $T_h^7$ . If this is the case, the whole problem is greatly simplified, as we can then determine the number of molecules in the unit cell without knowing the density of the substance. As it is impossible to find less than eight equivalent points in the unit cell of space group  $T_h^7$ , we must conclude that the number of molecules in the unit cell is a multiple of eight. Later considerations substantiate this choice of space group.

### Powder Photographs

A reproduction of the powder photograph of mercuric tellurate is shown on the following page. It was made using Cu K $\alpha$  radiation filtered through nickel; the sample was cemented with collodion to the outside of a fine tube of low absorbing glass. The camera radius is 5.065 cm., as calibrated from a sodium chloride photograph taken under similar conditions. Table II lists the ninety-three lines observed; they are all attributable to a body centered cubic lattice, and, moreover, the three lines whose absences are required by the space group  $T_h^7$  are missing. The size of the unit cell was calculated, using lines reflected at large angle, correcting their position for absorption in a manner recently outlined by M.U.Cohen<sup>(4)</sup>, which was found to be satisfactory. The result of this calculation gave  $a_0 = 13.366\overset{\circ}{\text{A}}$  with a probable error of  $0.01\overset{\circ}{\text{A}}$ .

#### Determination of Parameters

If we now calculate the density of the crystal, using this value of  $a_0$ , we find it to be  $0.5705n$ , where  $n$  is the number of molecules in the unit cell. If  $n = 8$ ,  $\rho = 4.56$ ; if  $n = 16$ ,  $\rho = 9.13$ . We shall assume





Powder Photograph  
of  
Mercuric Tellurate



TABLE II. Powder Lines from Mercuric Tellurate.

$h^2 + k^2 + l^2$	$\sin \theta$	Est.Int.	$h^2 + k^2 + l^2$	$\sin \theta$	Est.Int.
14	.2173	.65	134	.6674	.50
16	.2318	.28	136	.6725	.20
18	.2466	1.5	138	.6725	.35
20	.2597	1.8	142	.6866	.14
22	.2718	.18	144	.6913	.12
24	.2837	1.3	146	.6962	.09
30	.3170	.35	150	.7055	.20
34	.3373	.36	152	.7102	.28
38	.3565	.41	154	.7150	.13
40	.3660	.38	158	.7241	.16
42	.3749	.20	164	.7373	.42
46	.3920	1.8	166	.7417	.34
48	.4002	.08	168	.7462	.30
50	.4082	.32	170	.7516	.08
54	.4245	.62	174	.7592	.18
56	.4322	.36	176	.7642	.12
62	.4551	1.2	182	.7768	.25
64	.4617	.15	184	.7814	.10
66	.4692	.48	186	.7854	.5
68	.4761	.44	192	.7972	.05
70	.4831	.36	198	.8099	.18
72	.4898	.24	200	.8143	.30
74	.4960	.28	206	.8259	.28
78	.5098	.40	210	.8337	.07
80	.5158	.60	212	.8384	.25
82	.5220	.24	214	.8424	.18
86	.5351	.75	216	.8460	.12
88	.5413	.18	222	.8574	.08 d
90	.5473	.15	226	.8657	.08 d
94	.5595	.38	230	.8728	.35
96	.5653	.38	232	.8763	.1
98	.5712	.28	234	.8805	.25
100	.5771	.03	238	.8874	.22
102	.5826	.19	246	.9027	.18
104	.5885	.46	248	.9062	.15
106	.5937	.29	250	.9096	.12
110	.6050	.80	254	.9172	.28
112	.6112	v.f.	258	.9245	.20
114	.6152	.14	260	.9283	.45
116	.6210	.24	262	.9317	.25
118	.6263	.42	264	.9347	.4
120	.6313	.05	266	.9384	.1
122	.6363	.25	270	.9455	.25
126	.6471	.30	272	.9489	.42
			278	.9591	.23
			280	.9623	.18
			282	.9662	.13
			286	.9726	.38
			288	.9760	.5

that 9.13 is the correct density, as it is by far the more reasonable value. This, then, requires that 48 Hg, 16 Te, and 96 O atoms be placed in the unit cell. The tellurium atoms must be placed on the three fold axes, so that their positions are those designated by the group 16e below and require the specification of one parameter, or they are placed on the fixed centers of symmetry (5) (8i and 8e).

$$\begin{aligned}
 (16e): & \quad uuu; u, u, \frac{1}{2}-u; \frac{1}{2}-u, u, \bar{u}; u, \frac{1}{2}-u, u; \\
 & \quad \bar{u}, \bar{u}, \bar{u}; \bar{u}, u, u+\frac{1}{2}; u+\frac{1}{2}, \bar{u}, u; u, u+\frac{1}{2}, \bar{u}; \\
 & \quad u+\frac{1}{2}, u+\frac{1}{2}, u+\frac{1}{2}; u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}; \bar{u}, u+\frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}-u, \bar{u}, u+\frac{1}{2}; \\
 & \quad \frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-u; \frac{1}{2}-u, u+\frac{1}{2}, u; u, \frac{1}{2}-u, u+\frac{1}{2}; u+\frac{1}{2}, u, \frac{1}{2}-u. \\
 (8e): & \quad \frac{111}{444}; \frac{1\bar{1}\bar{1}}{444}; \frac{31\bar{3}}{444}; \frac{3\bar{3}1}{444}; \\
 & \quad \frac{333}{444}; \frac{311}{444}; \frac{1\bar{3}1}{444}; \frac{11\bar{3}}{444}. \\
 (8i): & \quad 000; \frac{110}{220}; \frac{10\bar{1}}{220}; 0\frac{11}{22}; \\
 & \quad \frac{1\bar{1}\bar{1}}{222}; 00\frac{1}{2}; 0\frac{1}{2}0; \frac{1}{2}00.
 \end{aligned}$$

It is unlikely that the mercury atoms also lie on the trigonal axes, hence they must occur in the general position xyz and the 47 positions derived from it by symmetry. Similarly we place the oxygen atoms in general positions requiring six parameters, thus the problem becomes one of evaluating ten variable parameters to specify the structure. Straight forward evaluation of ten parameters is an almost endless task,

so it becomes necessary to look into the problem from another and somewhat more fruitful angle.

If the parameter describing the positions of the tellurium atoms is  $1/8$ , then the atoms are at maximum distances from each other along the cell diagonals. This maximum distance is  $5.79\text{\AA}$ , which approaches zero as  $u$  is made to approach 0 or  $\frac{1}{4}$ . The distance between Te atoms in different diagonals with  $u = 1/8$  is  $4.72\text{\AA}$ , which increases somewhat as  $u$  is changed, approaching  $6.68\text{\AA}$  as  $u$  approaches 0 or  $\frac{1}{4}$ . If  $u$  is greater than  $\frac{1}{4}$  the same configuration of Te atoms is repeated. Thus we see that  $u$  is not greatly different from  $1/8$ ; if the oxygen atoms surround Te in any configuration  $u$  must be close to  $1/8$ , or the atoms must occupy positions (8i) and (8e). If we assume that  $u = 1/8$  and calculate the contribution of Te to the structure factors for a few low order terms, we obtain the following results:

$$\frac{1}{4} \sum_{\text{Te atoms}} e^{2\pi i(hx + ky + lz)}$$

hkl	$u = 1/8$	Si, Se
002	0	0
112	-2	0
022	0	4
222	0	0
123	2	0
114	0	0
024	0	0
134	0	0
233	2	0
224	0	4
125	2	0
044	4	4
334	0	0
224	0	4

It is observed that in a large number of cases Te does not contribute to the scattering if  $u = 1/8$ , and it is to be expected that in these cases, if the indices are low, tellurium atoms are in general not contributing greatly to the scattering. Thus an approximate evaluation of the parameters describing the positions of the heavy mercury atoms can be made if we calculate for all values of the parameters the contribution of Hg to such

lines as 002, 022, 222, 114, 024, and 134. The limits which  $x$ ,  $y$ , and  $z$  take before the structure factor is repeated are:

$$0 < x < \frac{1}{2}$$

$$0 < y < \frac{1}{4}$$

$$0 < z < \frac{1}{4}.$$

It is unlikely that  $x < \frac{1}{4}$ , as this would crowd the mercury atoms too near to the tellurium atoms. Such calculations were made in the region  $\frac{1}{4} < x < \frac{1}{2}$ , for the lines mentioned above, with the exception of 222. Two-dimensional contour diagrams were prepared for various values of  $z$ , sufficiently accurate to enable one to follow the course of the values of the structure factors throughout the cube treated. All positions of the mercury atoms in this cube were eliminated definitely except for a small region near the center.

Attention should be drawn at this point to the large number of absences among the lines of low order. Table II lists no lines with  $q^2 < 14$ ; neither does it list the line with  $q^2 = 26$  (134). Lines 002 and 006 are missing or very weak, while 004 and 008 are quite strong. Thus in the above three dimensional diagrams we would expect the mercury atoms to lie near the points of intersection of the nodal surfaces of the

functions corresponding to the missing lines (002, 022, and 134). Actually the nodal surfaces of 002 and 022 do not intersect in the region studied; their distance of closest approach, however, is not large. Careful examination of the photograph revealed an extremely weak 002 reflection; moreover, the oxygen and tellurium atoms may influence these intensities to the extent we are concerned with here. In view of these considerations, the final values decided upon for the mercury parameters are:

$$x = 0.375$$

$$y = 0.138$$

$$z = 0.145$$

with probable errors amounting to about 0.005. All other regions were definitely eliminated. The statement seems reasonable that still further confidence can be placed in the determination of the space group since satisfactory values could be found for these parameters.

We see, then, that if the above analysis is correct, the values of the parameters are roughly  $y = z = 1/8$ ,  $x = 3/8$ , if  $u = 1/8$ . If we disregard the oxygen atoms we see that each tellurium atom is surrounded by six mercury atoms in a slightly distorted regular octahedron, with a Te-Hg distance of  $\frac{1}{4}a_0 = 3.34\text{\AA}$ , approximately. Each mercury atom, on the other hand, has



only two nearest Te neighbors, This suggests immediately an octahedral  $\text{TeO}_6$  group, each oxygen atom being bonded to tellurium and mercury. We can calculate the oxygen bond angle with the help of the atomic radii of Pauling and Huggins<sup>(6)</sup>. The Te-O distance should be  $1.98\text{\AA}$ , and the Hg-O distance  $2.14\text{\AA}$ . These give a bond angle of  $102^\circ$ , quite a reasonable value.

The exact shape of the  $\text{TeO}_6$  octahedron is not known and cannot be found from the calculations made thus far. The line Te-Hg-Te is not straight; indeed the angle at Hg approximates a right angle. It is difficult to decide from these results whether the coordination number of mercury is two or four; if it is four the  $\text{HgO}_4$  tetrahedra must share its edges with  $\text{TeO}_6$  octahedra. This seems more likely in view of the fact that otherwise mercury atoms are adjacent to one another without oxygen atoms to fill intervening spaces.

In the event that the tellurium atoms occupy positions 8e and 8i the above determination of the mercury parameters does not hold. This is due to the fact that the nodal surface of the structure factor for 022 figured largely in determining the parameters, and if the tellurium atoms occupy these positions they contribute greatly to this line. However, positions 8i and 8e are located at the centers of symmetry of the crystal, and the point group at these positions is  $C_{3i}$ . Hence the argument used by Kirkpatrick and Pauling to establish  $\text{TeO}_6$  applies here with equal certainty.

References

- (1) Baker and Aldam, Journ.Chem.Soc. 99, 507 (1911).
- (2) Kirkpatrick and Pauling, Zeits. f. Krist. 63, 502 (1926).
- (3) Hutchins, Journ.Am.Chem.Soc. 27, 1157 (1905).
- (4) Cohen, Rev.Sci.Inst. 6, 68 (1935).
- (5) Wyckoff, The Analytical Expression of the Results of the Theory of Space-Groups (1922).
- (6) Pauling and Huggins, Zeits. f. Krist. 87, 205 (1934).