CRYSTAL STRUCTURE OF SILVER PHOSPHATE AND SILVER ARSENATE (Ag_3XO_4).

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Introduction. Until very recently[1] there have been no X-ray diffraction data to indicate the manner of arrangement of the atoms in crystals of the type R_3X, where R and X are either single atoms or groups of several atoms which function together as simple chemical units. The following measurements upon Ag_3PO_4 and Ag_3AsO_4 were made partly to throw light upon the crystal structure of such compounds.

These crystals were obtained as precipitates by mixing equivalent quantities of aqueous solutions of $AgNO_3$ and either $NaNH_4HPO_4$ or $(NH_4)_3AsO_4$. The precipitated phosphate is colorless or light yellow, the arsenate is dark reddish brown. Silver phosphate is soluble in dilute acetic acid and in ammonia. By slowly removing ammonia from such a solution, a crystal with its greatest diameter about one-half a millimeter was obtained.

The few faces developed upon these crystals are ones to be expected from cubic crystals. This cubic character is further assured by the fact that they are optically isotropic.

The X-ray data employed in the following determinations of structure were Laue and powder photographs prepared and analyzed in the usual fashion.[2] From the small single crystal of Ag_3PO_4 mentioned above, a series of six Laue photographs were made with the incident X-ray beam (1) normal to the (100) face, (2) normal to a (110) face and (3) occupying various intermediate positions in the plane of these two normals. Powder photographs were obtained from precipitates of Ag_3PO_4 and Ag_3AsO_4. Accurate spacing measurements were carried out upon the two salts through the analysis of comparison photographs of mixed samples with MgO. Because the existing spacing data upon MgO agree poorly amongst themselves, it was necessary to analyze another series of NaCl-MgO comparison powder photographs. This indirect procedure was followed because NaCl and Ag_3PO_4 (or Ag_3AsO_4) react together during the making of their mixed collodion film.

[1] O. Hassel and H. Mark, Zeit. f. Physik **27**, 89 (1924); L. Pauling, J. Am. Chem. Soc. **46**, 2738 (1924).

[2] R. W. G. Wyckoff, The Structure of Crystals (New York, 1924) Chap. IV and VI.

The Correct Unit Cell. Data for the most conspicuous lines in a powder photograph of Ag_3PO_4 are shown in Table I. The sine-squares of the reflection angles of these lines are given in column 2 of this table. They are in the ratio of the

TABLE I.   Some Powder Photographic Data from Ag_3PO_4.

Spacing	$sin^2\theta_n$	Ratio of $sin^2\theta_n$ Observed	Correct	Indices hkl(n)	a_0
4.272A°	0.00693	1.97	2	110(1)	6.041A°
3.016	.01392	3.96	4	100(2)	6.033
2.681	.01760	5.01	5	120(1)	5.995
2.447	.02100	5.98	6	112(1)	5.994
1.893	.03511	10.00	10	130(1)	6.000
1.730	.04213	12.00	12	111(2)	5.992
1.660	.04576	13.03	13	230(1)	5.982
1.597	.04924	14.02	14	123(1)	5.975
1.304	.07405	21.09	21	124(1)	5.975
1.111	.10215	29.09	29	234(1) ;025(1)	5.977

Average $= 5.99_6 A°$

numbers of column 3 which are themselves equal, within the limit of experimental error, to the whole numbers of column 4. Since in a cubic crystal these integers are in the ratio of the appropriate values for $n^2(h^2 + k^2 + l^2)$, where (hkl) are the indices and n is the order of a reflection, it follows that

TABLE II.   Some Powder Photographic Data from Ag_3AsO_4.

Spacing	$sin^2\theta_n$	Ratio of $sin^2\theta_n$ Observed	Correct	Indices	a_0
3.062A°	0.01344	4.00	4	100(2)	6.123A°
2.735	.01685	5.01	5	120(1)	6.116
2.506	.02006	5.96	6	112(1)	6.140
1.769	.04026	11.98	12	111(2)	6.128
1.700	.04358	12.97	13	230(1)	6.130
1.641	.04678	13.92	14	123(1)	6.140
1.532	.05371	15.98	16	100(4)	6.127
1.369	.06721	20.00	20	120(2)	6.124
1.340	.07022	20.90	21	124(1)	6.139
1.306	.07391	21.99	22	233(1)	6.125
1.137	.09755	29.02	29	234(1) ;025(1)	6.089
1.115	.10129	30.14	30	125(1)	6.112
1.080	.10797	32.13	32	110(4)	6.114

Average $= 6.12_4 A°$

the indices of the observed reflections must be those of column 5 of this table. The value of a_0, the length of the edge of the unit cube, must approximate the numbers of the last column. Corresponding data from a photograph of Ag_3AsO_4 are contained in Table II.

TABLE III. Average Spacings for MgO from Comparison
Films with NaCl.

Film No.	a_0 for MgO
1	4.200A$^\circ$
2	4.204
3	4.204
4	4.204
	Average = 4.20$_3$ A$^\circ$

A similar treatment of four MgO comparison photographs of Ag_3PO_4 and of Ag_3AsO_4 has led to accurate determinations of the cube edges a_0. The length of the edge of a unit cube of the MgO used as a standard was determined from comparisons with NaCl ($a_0 = 5.628A^\circ$). The averages of the values calculated for the observed lines in each of four such comparison films are collected in Table III. Similar averages

TABLE IV. Average Spacing Measurements from Comparison
Photographs with MgO.

Film No.	a_0 for Ag_3PO_4	a_0 for Ag_3AsO_4
1	5.996A$^\circ$	.....
2	5.993	.....
3	5.989	.....
4	5.995	.....
5	.....	6.122A$^\circ$
6	.....	6.122
7	.....	6.113
8	.....	6.118
	Average = 5.99$_3$ A$^\circ$	Average = 6.11$_9$ A$^\circ$

from Ag_3PO_4-MgO and Ag_3AsO_4-MgO comparison films are contained in Table IV.

The smallest cube for Ag_3PO_4 compatible with the data of Table I will have for a_0 the value 5.99A$^\circ$. None of the attainable powder data conflicts with a unit of this size. The

Laue photographs were taken with an X-ray beam containing wave lengths down to, but not lower than, 0.25A°. In the analyzed data from these Laue photographs no reflections were found with values of $n\lambda$ below this wave length limit. All the attainable X-ray data thus agree in pointing to the cube with $a_0 = 5.99$A° as the correct unit cell. The numerous
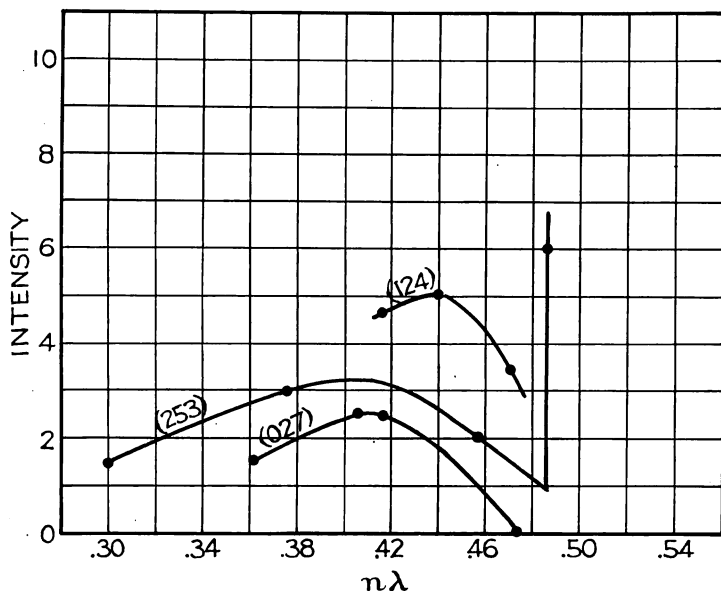

Fig. 1.—A plot showing the variation of intensity of first order Laue reflection with wave length for several forms. No importance is to be attached to the relative intensities of the reflections from these different forms.

powder data from Ag_3AsO_4 likewise fit a corresponding small unit (with $a_0 = 6.12$A°).

A further check upon the analysis up to this point is furnished by the peculiarities in the Laue data that are introduced by the fact that silver has a characteristic absorption limit in the range of useful wave lengths. Under the customary conditions for taking Laue photographs, the maximum photographic effect is obtained from rays with wave lengths from about 0.44A° up to the characteristic absorption limit of silver at $\lambda = 0.485$A°. With silver in the diffracting crystal, how-

ever, a blotting out of this maximum is to be expected. The Laue data fully meet these demands; typical intensity curves for the observed reflections are reproduced in Figure 1.

Calculation from the density of Ag_3PO_4 and the known length of the edge of the unit cube—$a_0 = 5.99A°$—shows that two molecules of Ag_3PO_4 are contained within the unit. This density, $\rho = 6.37_0$,[3] has been determined with great accuracy. An inverse computation of the length of the cube edge from this density thus will furnish a check upon the accuracy of the X-ray spacing measurement. The values a_0 for Ag_3PO_4 found in these two ways are

$a_0 = 6.00_8A°$ from $\rho = 6.37$

$a_0 = 5.99_3$ from the X-ray measurements. The agreement is good.

As a result of the foregoing data and their treatment, it can be concluded that the unit cube of Ag_3PO_4 contains two molecules and has a length of edge $a_0 = 6.00A°$. The similar unit cube for Ag_3AsO_4 has the edge length $a_0 = 6.12A°$. The density of Ag_3AsO_4 calculated from this spacing is $\rho = 6.66$.

The Crystal Structure. The class of symmetry to which these silver salts should be assigned is not known. The symmetry of their Laue photographs is, however, the maximum

TABLE V. Some Typical Laue Photographic Data from a Crystal of Ag_3PO_4.

Indices	Estimated Intensity	$n\lambda$
702	2	$0.405A°$
501	0.5	.400
273	4	.486
253	6	.486
141	7	.493
151	0	.328
601	1	.269
251	1	.292
331	0	.480
341	0.5	.333
221	0	.457

possible for a cubic crystal. The point groups T and Ti may therefore be excluded from further consideration. Inspection

[3] G. P. Baxter and G. Jones, Zeit. f. anorg. Chem. **66**, 97 (1910).

of the data of Tables I and V shows that planes with two odd and one even, two even and one odd and all odd indices are all reflecting in odd orders. The fundamental space lattice must therefore be the simple cubic Γ_c. The presence[4] of 100(2) and odd orders of (0kl) where k is even and l is odd eliminates the space groups O-6, O-7, Oi-2 and Oi-4. Of the remaining possibilities Te-4 and Oi-3 are distinguished from the rest by the absence in odd orders of (hkl) where $h = \pm k$ and either h is even and l is odd or both h and l are odd. From the powder and Laue data of Tables I, II and V, it is clear that though several had the opportunity to do so, no planes of this sort have yielded odd order reflections for either Ag_3PO_4 or Ag_3AsO_4. It may consequently be concluded that the corresponding space group of Ag_3PO_4 (and of Ag_3AsO_4) is either Te-4 or Oi-3. Since there are two molecules of Ag_3PO_4 in the unit, it must contain two phosphorus, six silver and eight oxygen atoms. The phosphorus atoms must have the arrangement[5] (2a) and the oxygen atoms either (8a) or (8e) depending upon whether the crystal symmetry is tetrahedral or holohedral. There are three groupings for the silver atoms—at (6e), (6f) or (6g). The first of these, (6e), like (2a) and (8a), or (8e), is body-centered; the distinctly simple cubic character of the structure thus makes it impossible that the silver atoms be located at (6e). Atomic arrangements developed from (6f) do not differ fundamentally from those employing (6g). The oxygen positions (8e) are simply the special case of (8a) obtained by making u in the latter equal to $\frac{1}{4}$. It is necessary, therefore, to conclude that the arrangement of the atoms in crystals of Ag_3PO_4 and Ag_3AsO_4 must be the following (Figure 2):

Phosphorus, or arsenic, atoms, (2a);
$$000; \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$$
Silver atoms (6f):
$$0\tfrac{1}{2}\tfrac{1}{4}; \ \tfrac{1}{4}0\tfrac{1}{2}; \ \tfrac{1}{2}\tfrac{1}{4}0; \ 0\tfrac{1}{2}\tfrac{3}{4}; \ \tfrac{3}{4}0\tfrac{1}{2}; \ \tfrac{1}{2}\tfrac{3}{4}0.$$
Oxygen atoms (8a):
$$uuu; \ \bar{u}u\bar{u}; \ u+\tfrac{1}{2}, \ u+\tfrac{1}{2}; \ u+\tfrac{1}{2}; \ \tfrac{1}{2}-u, \ u+\tfrac{1}{2}, \ \tfrac{1}{2}-u;$$
$$u\bar{u}\bar{u}; \ \bar{u}\bar{u}u; \ u+\tfrac{1}{2}, \ \tfrac{1}{2}-u, \ \tfrac{1}{2}-u; \ \tfrac{1}{2}-u, \ \tfrac{1}{2}-u, \ u+\tfrac{1}{2}.$$

where the value of u_0 is thus far undetermined.

The correctness of this assignment of structure can be checked by inspecting all the possible ways of placing two molecules of Ag_3XO_4 in a unit cube. Such a study will show that

[4] R. W. G. Wyckoff, this Jour. 4, 175 (1922).
[5] R. W. G. Wyckoff, An Analytical Expression of the Results of the Theory of Space Groups (Washington, 1922), p. 130. See also P. Niggli, Geometrische Kristallographie des Discontinuums (Leipzig, 1919), p. 373.

the chosen grouping is the only one that will' be simple cubic rather than body-centered.

It remains therefore to see how well the deduced atomic arrangement accounts for the detailed features of the X-ray spectra and to ascertain whether the exact oxygen positions can
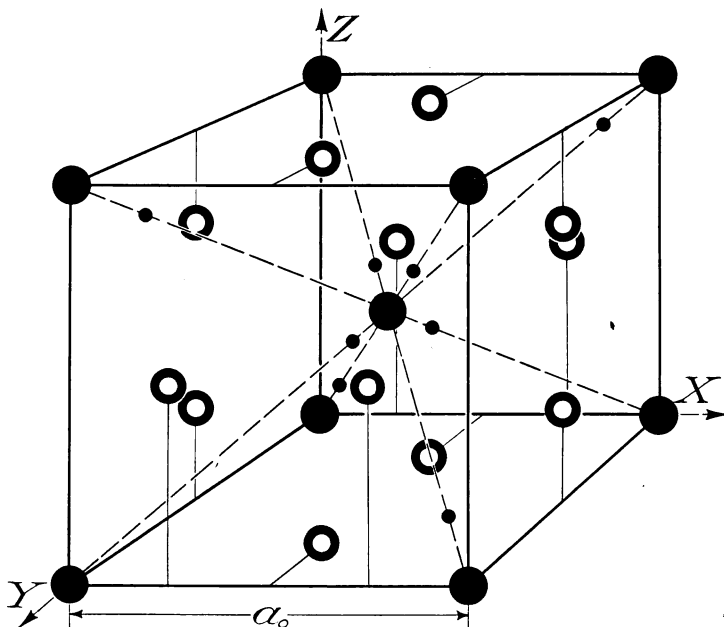

Fig. 2.—The unit cube of Ag_3PO_4 and Ag_3AsO_4. In this figure silver atoms are shown as annuli, phosphorus, or arsenic, atoms by the large and oxygen atoms by the small black circles. The exact positions of the oxygen atoms on the three-fold axes are not significant.

be discovered. For the present structure the usual intensity proportionality[6] will have the following form:

$$I \propto A^2 + B^2 \text{ where}$$

$A = \overline{Ag} \left[\cos \pi n \left(k + \frac{1}{2} l \right) + \cos \pi n \left(\frac{1}{2} h + l \right) + \cos \pi n \left(h + \frac{1}{2} k \right) + \cos \pi n \left(k + \frac{3}{2} l \right) + \cos \pi n \left(\frac{3}{2} h + l \right) + \cos \pi n \left(h + \frac{3}{2} k \right) \right] + \overline{P} [1 + \cos \pi n s_0] + \overline{O} [\cos 2\pi n u s_0 + \cos 2\pi n u s_1 + \cos 2\pi n u s_2 + \cos 2\pi n u s_3 + \cos 2\pi n \left(u s_0 + \frac{1}{2} s_0 \right) + \cos 2\pi n \left(u s_1 + \frac{1}{2} s_0 \right) + \cos 2\pi n \left(u s_2 + \frac{1}{2} s_0 \right) + \cos 2\pi n \left(u s_3 + \frac{1}{2} s_0 \right)]$, where $s_0 = h + k + l$, $s_1 = -h + k - l$, $s_2 = h - k - l$; $s_3 = -h - k + l$.

[6] R. W. G. Wyckoff, The Structure of Crystals (New York, 1924), pp. 107 and 201.

$B = \overline{Ag}[o] \dot{+} P\overline{[o]} + O[\sin 2\pi n u s_0 + \sin 2\pi n u s_1 + \sin 2\pi n u s_2, + \sin 2\pi n u s_3 + \sin 2\pi n(u s_0 + \tfrac{1}{2}s_0) + \sin 2\pi n(u s_1 + \tfrac{1}{2}s_0) + \sin 2\pi n(u s_2 + \tfrac{1}{2}s_0) + \sin 2\pi n(u s_3 + \tfrac{1}{2}s_0)].$

The silver and phosphorus terms of the preceding expression simplify as follows:

I.   If the indices are two odd and one even
$A = 2\,\overline{Ag}\,[\cos\pi n\,\{(2m + 1) + \tfrac{1}{2}(2p)\}] + 2\,\overline{P} + \overline{O}$ term,
When n is odd
$A = 2\,\overline{P} + 2\,\overline{Ag}$ if p is odd
$A = 2\,\overline{P} - 2\,\overline{Ag}$ if p is even.
When $n = 2, 6$, etc.
$A = 2\,\overline{P} - 2\,\overline{Ag} + \overline{O}$ term
When $n = 4, 8$, etc.
$A = 2\,\overline{P} + 6\,\overline{Ag} + \overline{O}$ term

II.   If the indices are two even and one odd,
$A = \overline{P}\,[1 + \cos 2\pi n s_0] + 2\,\overline{Ag}[\cos\pi n\,\tfrac{1}{2}(2p) + \cos\pi n\,\{(2m + 1) + \tfrac{1}{2}(2n)\}] + \overline{O}$ term.
When n is odd,
$A = o$ if n and p are both either even or odd.
$A = \pm\,4\,\overline{Ag}$ if n and p are one even, the other odd.
When $n = 2, 6$, etc.
$A = 2\,\overline{P} + 2\,\overline{Ag} + \overline{O}$ term
When $n = 4, 8$, etc.
$A = 2\,\overline{P} + 6\,\overline{Ag} + \overline{O}$ term

III.   If indices are all odd,
When n is odd
$A = o$
When $n = 2, 6$, etc.
$A = 2\,\overline{P} - 6\,\overline{Ag} + \overline{O}$ term
When $n = 4, 8$, etc.
$A = 2\,\overline{P} + 6\,\overline{Ag} + \overline{O}$ term

Bearing in mind the predominantly great scattering powers of the silver atoms, it is evident from the preceding intensity expressions that in general odd order reflections $[(2m + 1), (2n + 1), 2p]$ are more intense if $2p$ is divisible by 2 (p is

odd) than if $2p$ is divisible by 4; furthermore, this difference will be greater for Ag_3AsO_4 than for Ag_3PO_4. No reflections will be found in odd orders from $[(2m + 1), 2n, 2p]$ unless $2n \pm 2p$ and one but not the other is divisible by 4. In the 2, 6, etc. orders $[(2m + 1), 2n, 2p]$ reflections will be more intense than others and this difference will be more marked
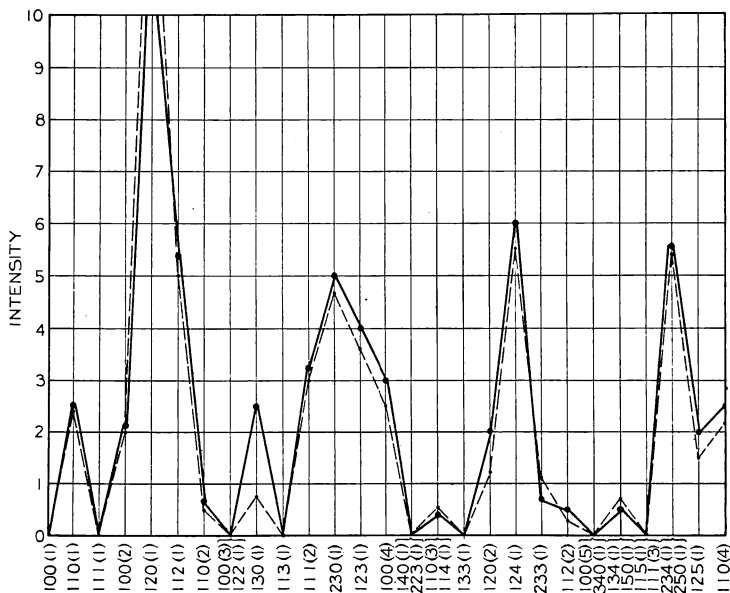

Fig. 3.—A plot comparing the observed intensities of powder reflections from Ag_3PO_4 with the intensities calculated for all planes up to $n^2(h^2 + k^2 + l^2) = 32$. In these calculations the scattering due to the oxygen atoms was disregarded.

for the arsenate than for the phosphate. All reflections in the 4, 8, etc. orders will be relatively stronger than in the 2, 6, etc. orders. The powder and Laue data of Tables I, II and V meet all these requirements. In none of the observed first order Laue reflections from $[(2m + 1), (2n + 1), 2p]$ was the relative effect of the oxygen atoms sufficient to make a reflection with greater spacing more intense than one with a smaller spacing. The Laue data, cannot, therefore, be safely used in an attempt to place the oxygen atoms accurately. In Figure 3 the intensities of all the powder reflections from Ag_3PO_4 up to $n^2(h^2 + k^2 + l^2) = 32$,

TABLE VI. Intensity Data upon Powder Reflections from Ag$_3$PO$_4$ and Ag$_3$AsO$_4$.

Indices	Ag$_3$PO$_4$ Intensity Calc.	Observed	Ag$_3$AsO$_4$ Intensity Observed	Calc.
100(1)	0	ab	ab	0
110(1)	2.4	2.5	ab	0.5
111(1)	0	ab	ab	0
100(2)	2.0	2	3.5	3.3
120(1)	14.1	>10	>10	14.1
112(1)	5.0	5.5	8	8.4
110(2)	0.5	0.7	ab	0.1
100(3);122(1)	0	ab	ab	0
130(1)	0.7	2.5	1	0.1+
113(1)	0	ab	ab	0
111(2)	3.0	3	3	2.2
230(1)	4.6	5	5	4.7
123(1)	3.6	4	6	6.1
100(4)	2.5	3	3	1.2
223(1);140(1)	0	ab	ab	0
110(3);114(1)	0.5	0.5	ab	0.1
133(1)	0	ab	ab	0
120(2)	1.2	2	2.5	2.0
124(1)	5.5	6	4	5.4
233(1)	1.1	0.7	1	1.8
112(2)	0.3	0.5	ab	<0.1
100(5);340(1)	0	ab	ab	0
134(1);150(1)	0.7	0.5	ab	0.15
111(3);115(1)	0	ab	ab	0
234(1);250(1)	5.4	5.5	5	5.4
125(1)	1.5	2	2	2.5
110(4)	2.2	2.5	3	2.7
225(1);144(1)	0	ab	ab	0
334(1);350(1)	0.3	<0.5	ab	<0.1
135(1)	0	ab	ab	0
100(6);122(2)	0.7 ⎱		1	1.3
160(1)	1.3 ⎰ ±2	±3	⎰ 1.3	
161(1);235(1)	1.7 ⎰		⎱ 2.8	
130(2)	0.1	<0.5	ab	0.1
126(1);450(1)	0	ab	ab	0
145(1)	0.3	<0.5	ab	<0.1
335(1)	0	ab	ab	0
113(2)	2.0 ⎱ ±2.5	±1.5	⎰ 1.5	
120(3)	1.1 ⎰		⎱ 1.1	
136(1)	0.9 ⎱ ±0.5	±0.75	⎰ 1.5	
111(4)	0.9 ⎰		⎱ 1.1	
100(7);236(1)	0	ab	ab	0
170(1);110(5);345(1)	0.4	<0.5	ab	<0.1
117(1);155(1)	0	ab	ab	0
230(2)	0.4 ⎱			⎧ 0.7
146(1);270(1)	2.7 ⎰ ±2	±2	⎨ 2.6	
112(3);127(1);255(1)	1.5 ⎰		⎩ 2.4	

calculated for only the phosphorus and silver atoms, are plotted against their observed intensities. In these calculations the ratio of the scattering powers of phosphorus and silver is taken to be that of their atomic numbers. Except for an apparently too great 130 (1), the agreement is astonishingly good. These same data are compared with similar calculations for Ag_3AsO_4 in Table VI. Such agreement is only to be expected if either (1) the scattering power of the oxygen atoms is negligible or (2) they occupy positions at or near $u = \frac{1}{4}$. The existing knowledge of scattering is insufficient to decide between these two possibilities.

Discussion of the Structure. The structure that has thus been deduced for Ag_3PO_4 and Ag_3AsO_4 does not contain these molecules as such but is of what may be called the "ion type." If u for oxygen actually were equal to $\frac{1}{4}$, the structure would be holohedral, (Oi-3) rather than tetrahedral (Te-4). In such a case PO_4 groups or ions would not exist but the structure (Figure 2) would be most simply considered as a composite of individual atoms or ions of silver, oxygen and phosphorus (or arsenic). For all other values of u it appears as an aggregate of silver atoms and PO_4 (or AsO_4) groups; each phosphorus atom, as the center of such groups, is equally distant from twelve silver atoms and each silver atom is surrounded by four phosphorus atoms.

Since the positions of the oxygen atoms cannot be determined with certainty, only speculations are possible upon the significant interatomic distances in Ag_3PO_4 and Ag_3AsO_4. In Ag_2O the Ag-O distance[7] is 2.04A°, in Ag_2MoO_4 it[8] is close to 2.31A°. In the former crystal each silver atom has four oxygen atoms near to it and each oxygen atom two silver atoms; in the latter, six oxygen atoms surround each silver atom and four atoms (3 Ag, 1 Mo) are nearest each oxygen atom. From these data alone it is clear that the Ag-O interatomic distance is not a constant. It might be assumed, however, that interatomic distances are nearly constant for similar atomic environments of an atomic pair; furthermore, it might be assumed that the greater the number of atoms equally near to a central atom, the less would be the attraction between the central atom and a neighboring one and the larger would be the observed interatomic distance. Under such conditions it could be predicted that the Ag-O distance for Ag_3PO_4 and Ag_3AsO_4 would lie between the correspond-

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[7] R. W. G. Wyckoff, this Jour. **3**, 184 (1922); P. Niggli, Zeit. f. Krist. **57**, 253 (1922); W. P. Davey, Phys. Rev. **19**, 248 (1922).
[8] R. W. G. Wyckoff. J. Am. Chem. Soc. **44**, 1994 (1922).

ing distances for Ag_2O and Ag_2MoO_4 with a value nearer to that for Ag_2MoO_4. No phosphorus to oxygen distance has ever been determined but the separation[9] of arsenic and oxygen atoms in As_4O_6 is close to $2.01A°$. If a similar value holds true in Ag_3AsO_4, the parameter u_0 would be about 0.19 and the Ag-O distance is $2.25A°$—a distance near to but less than the corresponding one in Ag_2MoO_4. If, as may well be the case, the As-O distance is somewhat greater in Ag_3AsO_4 than in As_4O_6, the parameter u_0 will be greater than 0.19 and the Ag-O distance will be slightly less than $2.25A°$. The P-O distance, calculated upon the assumption that Ag-O is the same as in Ag_3AsO_4 and equal to $2.25A°$, would be $1.87A°$.

Optical and crystallographic examinations of the single crystals of the Ag_3PO_4 were carried out by H. E. Merwin. Many of the calculations of spacings involved in this determination of structure were made by Elizabeth B. Derby.

SUMMARY.

Laue and powder photographs have been used to establish the structure for Ag_3PO_4 and for Ag_3AsO_4. Two molecules are contained in the unit cube. The atomic arrangement, (2a, 6f, 8a), is a new one; its corresponding space group probably is Te-4. The position of the oxygen atoms could not be established in either crystal. The length of the edge of the unit cube is $a_0 = 6.00A°$ for Ag_3PO_4 and $6.12A°$ for Ag_3AsO_4. Several spacing measurements gave $a_0 = 4.20_3A°$ as the length of the edge of the unit cube of a sample of MgO.

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[9] R. M. Bozorth, J. Am. Chem. Soc. **45**, 1621 (1923).