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THE CRYSTAL STRUCTURES OF THE CUBIC FORMS OF ARSENIOUS AND ANTIMONOUS OXIDES

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Introduction

Octahedral crystals of arsenious oxide were prepared by slowly cooling a solution of the substance in hydrochloric acid with the addition of a small amount of sodium chloride. A crystal of the cubic form of antimonous oxide, senarmontite, from Mt. Hamimat, Algeria, was kindly supplied by Dr. G. P. Merrill of the National Museum. A careful qualitative examination of a part of this crystal carried out in accordance with the scheme of A. A. Noyes¹ showed about 3% of arsenic, about 10% of alkaline earths and a trace of bismuth.

The Spectral Photographs of Arsenious Oxide

Photographs were taken of line spectra reflected from (100), (110) and (111) faces. The results are given in Table I. Measurements are for the rhodium $K\alpha_1$ line whose wave length was found by Duane² to be 0.6121 Å.

TABLE I
REFLECTION DATA FOR ARSENIOUS OXIDE

Reflecting plane	Angle of reflection	Estimated intensity	Order of reflection	Length of unit cube	Calculated structure factors for $u = 0.895, v = 0.21$		
					S_{As}	S_{Ox}	S
(100)	6° 21'	strong	4	11.07	-112	40	-72
	12° 49'	medium	8	11.04	69	25	94
(110)	4° 29'	very weak	2	11.07	8	33	41
	9° 0'	medium	4	11.07	98	2	100
	13° 36'	weak	6	11.04	60	0	60
(111)	2° 46'	weak	1	11.0	24	8	32
	5° 30'	very strong	2	11.06	116	0	116
	8° 17'	medium weak	3	11.04	64	-23	41
	11° 2'	medium strong	4	11.08	-86	19	-67
	13° 51'	medium weak	5	11.07	-87	32	-55
		absent	6	...	-50	0	-50
	very weak	7	11.07	-89	-33	-122	

A consideration of these data shows that the smallest possible unit cube is 11.06 Å. on an edge. The orders of reflection given in Table I are on this basis. Combining these measurements with the density, which was found by Baxter and Hawkins³ to be 3.865, we find that this unit

¹ Noyes, "Qualitative Chemical Analysis," 8th ed., The Macmillan Co., New York, 1920.

² Duane, *Nat. Research Council Bull.*, 1, No. 6 (1920).

³ Baxter and Hawkins, *THIS JOURNAL*, 38, 269 (1916).

must contain 32 arsenic atoms and 48 oxygen atoms. A larger unit would contain 256 arsenic atoms and 384 oxygen atoms, and in this case neither the arsenic atoms nor the oxygen atoms could all be equivalent. Since no X-ray reflections were found which necessitated this larger unit, the smaller one was considered the true one.

The density calculated from the spectral measurements is 3.861, in good agreement with the observed value.

The Spectral Photographs of Antimonous Oxide

The results of the reflections of the molybdenum $K\alpha_1$ line, of wave length² 0.7078 Å., from a (111) face of the crystal, are given in Table II.

TABLE II
REFLECTION DATA FOR ANTIMONOUS OXIDE

Angle of reflection	Estimated intensity	Order of reflection	Length of unit-cube	Calculated structure factors for $u = 0.885, v = 0.23$		
				S_{Sb}	S_{Ox}	S
3° 9'	very weak	1	11.15	22	4	26
6° 19'	strong	2	11.14	203	0	203
9° 29'	very weak	3	11.15	57	-12	45
12° 43'	medium	4	11.14	-189	42	-147
15° 59'	weak	5	11.13	-90	20	-70
19° 17'	medium weak	6	11.14	-167	0	-167

The unit cube of antimonous oxide is thus found to be 11.14 Å. on an edge. With 32 antimony atoms and 48 oxygen atoms in the unit, the density calculated from these measurements is 5.11. Direct determinations of the density⁴ vary from 5.1 to 5.8.

The Arrangement of the Atoms

Laue photographs of the two substances showed holohedral cubic symmetry, so the arrangement must be that of one of the space groups isomorphous with the point groups T_d , O , and O_h . No spots were produced by first-order reflections from planes having one or two even indices, such as (521) and (421). Also, no spots were produced by first, second, or third order reflections from planes having one index zero and only one index odd, such as (320) and (100). Assuming all the arsenic or antimony atoms, and likewise all the oxygen atoms, to be equivalent, the only possible arrangement which will satisfy the above conditions and permit first-order reflections from planes having all odd indices is the following,⁵ derivable from the space-group O_h^7 :

⁴ Muir and Hutchinson, *J. Chem. Soc.*, 60, 143 (1889), and Doelter's "Handbuch der Mineralchemie," Steinkopff, Dresden and Leipzig, 1918, vol. 3, pt. 1, p. 757.

⁵ Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst. Washington, Pub., 318, 144 (1922).

As or Sb atoms at:

$$\begin{aligned}
 &uuu; \frac{1}{2}+u, \frac{1}{2}+u, u; \frac{1}{2}+u, u, \frac{1}{2}+u; u, \frac{1}{2}+u, \frac{1}{2}+u; \\
 &u\bar{u}\bar{u}; \frac{1}{2}+u, \frac{1}{2}-u, \bar{u}; \frac{1}{2}+u, \bar{u}, \frac{1}{2}-u; u, \frac{1}{2}-u, \frac{1}{2}-u; \\
 &\bar{u}u\bar{u}; \frac{1}{2}-u, \frac{1}{2}+u, \bar{u}; \frac{1}{2}-u, u, \frac{1}{2}-u; \bar{u}, \frac{1}{2}+u, \frac{1}{2}-u; \\
 &\bar{u}\bar{u}u; \frac{1}{2}-u, \frac{1}{2}-u, u; \frac{1}{2}-u, \bar{u}, \frac{1}{2}+u; \bar{u}, \frac{1}{2}-u, \frac{1}{2}+u; \\
 &\frac{1}{4}-u, \frac{1}{4}-u, \frac{1}{4}-u; \frac{3}{4}-u, \frac{3}{4}-u, \frac{3}{4}-u; \frac{3}{4}-u, \frac{1}{4}-u, \frac{3}{4}-u, \frac{3}{4}-u, \frac{3}{4}-u; \\
 &\frac{1}{4}-u, \frac{1}{4}+u, \frac{1}{4}+u; \frac{3}{4}-u, \frac{3}{4}+u, \frac{3}{4}+u; \frac{3}{4}-u, \frac{1}{4}+u, \frac{3}{4}+u; \frac{1}{4}-u, \frac{3}{4}+u, \frac{3}{4}+u; \\
 &\frac{1}{4}+u, \frac{1}{4}-u, \frac{1}{4}+u; \frac{3}{4}+u, \frac{3}{4}-u, \frac{1}{4}+u; \frac{3}{4}+u, \frac{1}{4}-u, \frac{3}{4}+u; \frac{1}{4}+u, \frac{3}{4}-u, \frac{3}{4}+u; \\
 &\frac{1}{4}+u, \frac{1}{4}+u, \frac{1}{4}-u; \frac{3}{4}+u, \frac{3}{4}+u, \frac{1}{4}-u; \frac{3}{4}+u, \frac{1}{4}+u, \frac{3}{4}-u; \frac{1}{4}+u, \frac{3}{4}+u, \frac{3}{4}-u.
 \end{aligned}$$

O atoms at:

$$\begin{aligned}
 &v00; \frac{1}{2}+v, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}+v, 0; v\frac{1}{2}\frac{1}{2}; \\
 &\bar{v}00; \frac{1}{2}-v, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}-v, 0; v\frac{1}{2}\frac{1}{2}; \\
 &0v0; \frac{1}{2}, 0, \frac{1}{2}+v; \frac{1}{2}+v, 0, \frac{1}{2}; \frac{1}{2}v\frac{1}{2}; \\
 &0\bar{v}0; \frac{1}{2}, 0, \frac{1}{2}-v; \frac{1}{2}-v, 0, \frac{1}{2}; \frac{1}{2}v\frac{1}{2}; \\
 &00v; 0, \frac{1}{2}+v, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}+v; \frac{1}{2}\frac{1}{2}v; \\
 &00\bar{v}; 0, \frac{1}{2}-v, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}-v; \frac{1}{2}\frac{1}{2}\bar{v}; \\
 &\frac{1}{4}+v, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}+v, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}+v, \frac{1}{4}; \frac{1}{4}+v, \frac{3}{4}, \frac{3}{4}; \\
 &\frac{1}{4}-v, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}-v, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}-v, \frac{1}{4}; \frac{1}{4}-v, \frac{3}{4}, \frac{3}{4}; \\
 &\frac{1}{4}\frac{1}{4}+v, \frac{1}{4}; \frac{3}{4}\frac{1}{4}, \frac{3}{4}+v; \frac{3}{4}+v, \frac{1}{4}, \frac{3}{4}; \frac{1}{4}\frac{1}{4}+v, \frac{3}{4}; \\
 &\frac{1}{4}\frac{1}{4}-v, \frac{1}{4}; \frac{3}{4}\frac{1}{4}, \frac{3}{4}-v; \frac{3}{4}-v, \frac{1}{4}, \frac{3}{4}; \frac{1}{4}\frac{1}{4}-v, \frac{3}{4}; \\
 &\frac{1}{4}, \frac{1}{4}, \frac{1}{4}+v; \frac{1}{4}, \frac{1}{4}, \frac{3}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}+v; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}+v; \\
 &\frac{1}{4}, \frac{1}{4}, \frac{1}{4}-v; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}-v; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}-v; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}-v;
 \end{aligned}$$

The Laue Photograph of Arsenious Oxide

The data from a Laue photograph of arsenious oxide, taken with the beam inclined about 2° to a trigonal axis, are given in the first 4 columns of Table III. The attempt has been made to make this table complete by including all forms below a certain complexity ($d/n = 0.78 \text{ \AA.}$) which could possibly have reflected X-rays onto the photographic plate as pure first-order or pure second-order reflections. First-order reflections from planes having an even index are not tabulated, for none was observed, and with the arrangement given above the structure factor S is identically zero for them. A few reflections involving wave lengths near and below 0.30 \AA. were also omitted, since the data are not useful. In the table, d denotes the interplanar distance expressed in Angstrom units and n the order of reflection. The wave lengths of the X-rays are expressed in Angstrom units.

Assuming that the reflecting powers of the atoms are proportional to their atomic numbers, the structure factor was calculated in the usual way for each of the planes listed in Table III for a considerable region near $u = 0.9$ and $v = 0.2$. The calculated structure factors agree best with the data when u is 0.895 and v is 0.21. The value of u cannot be changed more than 0.005 without destroying the agreement between calculated structure factors and observed intensities. Because of the comparatively small reflecting power of oxygen, however, the value of v may be changed as much as 0.02 without seriously affecting the agree-

ment. Values of u and v differing markedly from 0.9 and 0.2, respectively, were found by trial to be inconsistent with the data.

TABLE III
LAUE PHOTOGRAPHIC DATA FOR ARSENIOS OXIDE

$n(hkl)$	d/n	Wave length	Estimated intensity	Calculated structure factors for $u = 0.895, v = 0.21$		
				S_{As}	S_{Ox}	S
(531)	1.87	0.35	0.4	20	6	26
(353)	1.69	.37	.1	- 2	- 5	- 7
(155)	1.55	.34	2.0	69	24	93
2(032)	1.53	.41	0.0	0	0	0
2(232)	1.34	.42	.2	- 22	0	- 22
(715)	1.28	.45	.2	15	3	18
2(124)	1.21	.38	.6	- 50	0	- 50
(575)	1.11	.43	.0	- 10	10	0
2(304)	1.11	.32	.0	0	0	0
2(413)	1.08	.43	.03	- 12	-22	- 34
(737)	1.07	.40	.7	80	-30	50
(159)	1.07	.43	.5	- 69	22	- 47
2(521)	1.01	.41	.15	- 27	8	- 19
(577)	1.00	.46	.0	13	-11	2
2(305)	0.95	.42	.5	- 84	28	- 56
2(343)	.95	.41	.15	32	- 9	23
(3-11-3)	.94	.42	.2	71	-20	51
(937)	.94	.41	.1	- 25	-10	- 35
(5-11-1)	.91	.41	.1	- 47	- 9	- 56
2(434)	.86	.42	.2	- 67	0	- 67
2(162)	.86	.43	.15	60	0	60
2(145)	.85	.42	.0	16	- 8	8
(1-7-11)	.85	.43	.05	42	-12	30
(3-11-7)	.83	.45	.1	- 67	-23	- 90
(977)	.83	.38	.05	31	-13	18
2(245)	.82	.47	.0	- 16	0	- 16
(3-13-3)	.81	.45	.15	- 67	-17	- 84
(599)	.81	.38	.15	- 77	28	- 49
(13-1-5)	.79	.43	.1	53	12	65
2(354)	.78	.47	.05	- 45	5	- 40
2(146)	.76	.41	.25	-105	0	-105
2(712)	.75	.45	.0	27	-26	2
(5-9-11)	.73	.43	.02	- 43	15	- 28
(13-3-7)	.73	.47	.05	60	-20	40
2(454)	.73	.37	.01	28	0	28
2(370)	.73	.43	.1	86	30	116
2(364)	.71	.48	.05	79	0	79
(15-5-1)	.70	.45	.05	67	-20	47
(11-9-9)	.66	.33	.01	54	-13	40
2(257)	.63	.36	.03	105	36	141
2(418)	.61	.42	.03	95	0	95
(15-5-9)	.61	.40	.01	77	26	103

The structure factor can be separated into two parts, S_{As} due to the arsenic atoms alone, and S_{Ox} due to the oxygen atoms alone, so that $S = S_{As} +$

S_{Ox} . This separation is made in the tables, in order that it may be seen how the final value of S would change if the reflecting powers of the atoms were not considered to be proportional to their atomic numbers. The intensity of reflection of any plane is assumed to be some function of d/n , multiplied by S^2 .

The Laue Photograph of Antimonous Oxide

The Laue data for antimonous oxide are given in Table IV. It is seen that the intensity data are satisfied when $u = 0.885$ and $v = 0.23$. The same limitations apply to the values of the parameters that held in the case of arsenious oxide. With either substance the particular values $u = 7/8$ and $v = 1/4$ will not satisfy the data. Since antimony shows a critical absorption at 0.405 \AA ., reflections of wave lengths near or below this value have not in general been included, for they are extremely weak.

TABLE IV
LAUE PHOTOGRAPHIC DATA FOR ANTIMONOUS OXIDE

$n(hkl)$	d/n	Wave length	Estimated intensity	Calculated structure factors $u=0.885, v=0.23$		
				S_{Sb}	S_{Ox}	S
(353)	1.70	0.38	0.0	4	-2	2
(155)	1.56	.35	.15	68	15	83
2(320)	1.54	.49	.0	0	0	0
2(232)	1.35	.43	.1	-12	0	-12
(715)	1.29	.42	.1	8	-1	7
(575)	1.12	.44	.1	11	5	16
(377)	1.08	.43	1.0	98	-22	76
(159)	1.08	.44	1.0	-86	18	-68
(757)	1.00	.44	0.3	44	-11	33
2(305)	0.95	.45	.15	-45	-1	-46
2(343)	.95	.42	.1	25	-15	10
(1133)	.94	.43	.8	96	-19	77
2(621)	.87	.45	.1	35	0	35
(1711)	.85	.44	.5	88	-18	70
(1137)	.83	.44	.6	-111	-24	-135
2(452)	.83	.43	.01	-20	0	-20
(3133)	.81	.44	.15	-50	3	-47
(1351)	.80	.45	.3	100	19	119
2(354)	.79	.45	.05	-39	-8	-47
(1713)	.75	.46	.01	-40	4	-36
(1551)	.70	.44	.05	59	-3	56
2(455)	.69	.42	.05	63	-1	-62
(1715)	.67	.47	.1	-96	-18	-114
(1395)	.67	.43	.15	128	28	156
(1537)	.66	.46	.1	118	-24	94
2(456)	.63	.45	.01	-56	0	-56
(1751)	.63	.43	.05	-107	18	-89
2(148)	.62	.44	.05	84	0	84
2(457)	.59	.46	.05	-83	7	-76
(1795)	.56	.43	.01	-127	26	-101

Conclusions Concerning the Crystal Structure

The structure is represented diagrammatically by Fig. 1. It consists of As_4O_6 or Sb_4O_6 groups arranged in the same way as the carbon atoms in the diamond,⁶ each group corresponding to one carbon atom. It will be seen that the atoms in each As_4O_6 or Sb_4O_6 group are related among themselves in a way different from that in which they are related to the atoms of other groups, and that the groups themselves are separated by distances

THE DIAMOND ARRANGEMENT

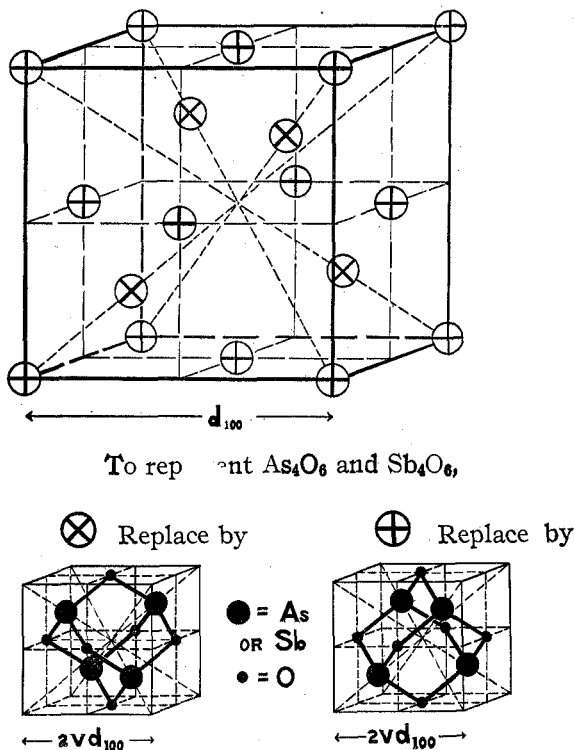


Fig. 1.—The arrangement of the atoms in As_4O_6 , and Sb_4O_6 . For As_4O_6 , $d_{100} = 11.06$, $u = 0.895$ and $v = 0.21$; for Sb_4O_6 , $d_{100} = 11.14$, $u = 0.885$ and $v = 0.23$

considerably greater than the distances between the atoms in any group. For example, the shortest distance between an arsenic and an oxygen atom within the same group is 2.01 Å., while the shortest distance between an arsenic atom and the nearest oxygen atom in a neighboring group is 2.78 Å. The corresponding distances in antimonous oxide are 2.22 Å. and 2.61 Å., respectively. Hence, in the solid as well as in the gaseous state, molecules of As_4O_6 and Sb_4O_6 may be considered to exist.

⁶ W. H. and W. L. Bragg, *Proc. Roy. Soc., London*, **89A**, 277 (1913).

This determination of the arsenic to oxygen distance is, so far as the writer is aware, the only basis for an experimental value of the arsenic radius. Taking the oxygen radius as 0.65 Å., the arsenic radius is 1.36 Å. The radius of antimony is found in the same way to be 1.57 Å.

The arrangement of the atoms within the molecule is the same as that of the carbon and nitrogen atoms in hexamethylenetetramine, $C_6N_4H_{12}$, as determined by Dickinson and Raymond.⁷ The considerations concerning the tetrahedral angles that hold for the latter compound apply also to arsenious and antimonous oxides.

Summary

The crystal structures of arsenious and antimonous oxides have been determined by means of Laue photographs and spectral photographs. These crystals may be regarded as composed of As_4O_6 and Sb_4O_6 molecules having a diamond arrangement, each molecule corresponding to 1 carbon atom. See Fig. 1. The arrangements are derived from the space group O_h^7 . The sizes of the unit cubes containing 8 molecules of As_4O_6 or Sb_4O_6 are 11.06 Å. for arsenious oxide and 11.14 Å. for antimonous oxide. The shortest distance between arsenic and oxygen atoms is 2.01 Å., and between antimony and oxygen atoms is 2.22 Å.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE MUSPRATT LABORATORY OF PHYSICAL AND
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THE EFFECT OF SUCROSE ON THE ACTIVITIES OF CERTAIN IONS

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Experiments with Potassium Chloride

With the object of investigating the mechanism of chemical change, a method has been adopted in this Laboratory in the case of reactions in aqueous solutions which consists in making use of an artifice, namely, the replacement of various amounts of the water by sucrose, such replacement being attended by measurable alterations in viscosity on the one hand, and in the activities of the participating individuals, (molecules and ions), on the other. On the basis of this simultaneous alteration, information can be obtained regarding the nature of the process taking place in presence of the sucrose. In the first instance, it is necessary to obtain, by direct experiment, a value for only the actual change in activity produced by the sucrose, in order to apply the method. At the same time, the question naturally arises as to the mechanism of the alteration in activity itself, as in the case of an ion, and in a previous communica-

⁷ Dickinson and Raymond, *THIS JOURNAL*, 45, 22 (1923).