ART. XIV.—*The Crystal Structure of Silver Oxide (Ag_2O)*; by RALPH W. G. WYCKOFF.

Introduction.—Little is known of the crystallography of silver oxide (Ag_2O) other than that it crystallizes as a powder in microscopic isotropic crystals and can be grown as small octahedrons.[1] It is thus impossible to assign silver oxide crystals to any particular one of the classes of cubic symmetry.

Diffraction Data and the Number of Molecules within the Unit Cell.—Because of the difficulty of producing other than microscopic crystals the available diffraction data have been limited to those to be had from powder reflections. Powder photographs obtained in the customary manner showed lines of marked intensity. Measurements (upon two separate films) of the first four of them —all that are required to establish the structure of this crystal—are given in table 1.

The density of silver oxide[2] has been determined as 7.52. Because of the impossibility of immediately identifying the different lines as reflections from particular planes of atoms, the indices of the planes causing these reflections and the number of chemical molecules to be associated with the unit cell (or more precisely, the value of m/n^3) can be obtained only by assuming different values for m, calculating therefrom the spacings of simple planes in the corresponding unit and seeing whether the observed reflections can be identified in positions with some of these possible planes. Since as m is varied the resultant spacings change as the cube root, while the relative spacings of different planes stand in the ratio of the square roots, it should theoretically always be possible to make such an identification uniquely.[3] A determination of m for silver oxide by this procedure showed that if $m = 2$ the reflections observed in the photographs correspond with simple planes (see table 1). Since, furthermore this agreement would be equally well obtained from any unit having the

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[1] Vogel, Poggendorffs Ann. **118**, 145, 1863.

[2] Biedermann, Chem. Kalender, **1**, 53, 1914.

[3] The actual spectrum lines are so wide, however, that such a manner of determining the number of chemical molecules in the unit need be entirely satisfactory only in case the correct indices of the planes actually producing the reflections are simple.

same value of m/n^3, where n may be chosen as any integer, it is evident that m for Ag_2O can just as well be equal to 16.

TABLE 1. *Measurements upon two Silver Oxide Films.*

Distance of line from central image		d_{hkl}/n in A. U.		hkl	d_{100} in A. U.	
Film 1.	Film 2.	Film 1.	Film 2.		Film 1.	Film 2.
2.86 cm.	2.85 cm.	2.75^5	2.75^8	111(1)	4.775	4.779
3.30^5	3.30^5	2.38^5	2.38^5	100(2)	4.770	4.770
4.72^5	4.73^5	1.67^3	1.67^0	110(2)	4.758	4.752
5.55	5.54^5	1.42^6	1.42^7	113(1)	4.768	4.770
				Mean	4.768	4.768

The value d_{100} is of course the length of the side of the unit cube.

The Possible Structures for Silver Oxide.—If $m = 2$: There is but one way of arranging two molecules of Ag_2O within a unit cell so that the resulting structure will have any form of cubic symmetry.[4] It is as follows:

Arrangement (*a*): Oxygen atoms at

$000;\ \frac{1}{2}\frac{1}{2}\frac{1}{2}.$

Silver atoms at

$\frac{1}{4}\frac{1}{4}\frac{1}{4};\ \frac{1}{4}\frac{3}{4}\frac{3}{4};\ \frac{3}{4}\frac{1}{4}\frac{3}{4};\ \frac{3}{4}\frac{3}{4}\frac{1}{4}.$

This grouping can be deduced from the space groups T_h^2, O^2 or O_h^4.

If $m = 16$: If the two silver atoms in the molecule of Ag_2O are chemically (and hence crystallographically) alike, there are three ways of arranging sixteen molecules of Ag_2O in a unit cube so that the resulting structure has cubic symmetry.[5] They are:.

Arrangement (*b*): In this arrangement, which can be deduced from the space groups T_h^4, O^4 and O_h^7, the sixteen oxygen atoms lie in unique positions; the thirty-two silver atoms possess one variable parameter and are upon trigonal axes.

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[4] These results are taken from tables which form a portion of a book entitled "An Analytical Representation of the Theory of Space Groups" which is shortly to be published by the Carnegie Institution of Washington. Some of them are also given in P. Niggli, Geometrische Krystallographie des Discontinuums (Leipzig, 1919).

[5] If it were assumed that the two silver atoms could be different, then the several space groups having as special cases sixteen equivalent positions with one variable parameter would introduce additional possibilities. Such an assumption finds no justification from the chemistry of the compound and would run counter to the general trend of crystal structure determinations thus far made.

Arrangement (*c*): This grouping, deducible from the space group O^8, is simply a twice scale enlargement of arrangement (*a*).

Arrangement (*d*): In this arrangement, derived from O_h^{10}, the oxygen atoms lie in unique positions, the silver atoms upon trigonal axes.

The Choice of the Correct Structure.—An approximate calculation of the intensity of reflection from any plane for any of these possible structures can be made by the method already outlined.[6] For this purpose use was made of the expression

$$I \propto (A^2 + B^2) \cdot (d/n)^{2.35} \cdot p,$$

where I is the intensity of a line in the powder photograph, p is the number of planes of the reflecting form, d/n is the ratio of the spacing of the reflecting planes to the order of the reflection and $(A^2 + B^2)$ has the meaning previously given to it.

Arrangement (*a*): For this grouping

If n is odd:

When the indices of the reflecting plane are 2 odd and 1 even,

$A = 2\bar{O}, \ B = 0;$

Indices: 2 even, 1 odd,

$A = 0, \ B = 0;$

Indices: all odd,

$A = 0, \ B = \pm 4\ \overline{Ag}.$

If n is even:

Indices: 2 odd, 1 even,

$A = 2\bar{O} + 4\ \overline{Ag}, \ B = 0;$

Indices: 2 even, 1 odd or all odd,

$A = 2\bar{O} \mp 4\ \overline{Ag}$, $-$ when $n = 2$, $+$ when $n = 4$, $B = 0$.

In these computations $\bar{O}$ and $\overline{Ag}$, the scattering powers of oxygen and silver, respectively, are taken equal to the atomic numbers. A comparison between the estimated intensities of the four principal lines of the photograph and the intensities of these lines calculated for this arrangement is given in table 2; the other planes appear-

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[6] Ralph W. G. Wyckoff, this Journal, 2, 239, 1921; Jour. Wash. Acad. Sci. 11, 429, 1921.

ing in the photograph fit about equally well. The agreement is as good as could be expected in view of the uncertainties involved in these calculations.

TABLE 2.

Indices	Intensity (arbitrary units) Estimated	Calculated for arrangement (a)
111 (1)	10	77,800
100 (2)	7	34,900
110 (2)	7	43,200
113 (1)	6	50,500

Arrangements (*b*), (*c*) and (*d*).—Because of its identity with (*a*), *grouping* (*c*) requires no further treatment. Because of lack of knowledge of the laws of scattering, an entirely satisfying elimination of (*b*) and (*d*) can scarcely be made with these data. It can, however, be shown that they are both improbable.

These observations then have shown that there is but one simple structure, (*a*), the "cuprous oxide structure," which is in agreement with powder measurements obtained from silver oxide. Furthermore they have shown that neither of the two more complicated groupings which are possible structures from the determination of the value of the ratio m/n^3 are probable. In all likelihood, then, the atoms of silver oxide are arranged as defined by (*a*).

It is of interest that silver as oxide agrees with its analogue, monovalent copper, in departing from the perhaps more common cubic arrangement of two atoms of one kind and one of another, the "calcium fluoride structure." Since arrangement (*a*) can be deduced from space groups possessing either paramorphic or enantiomorphic hemihedry, or holohedry, this determination of the structure of silver oxide has not succeeded in defining uniquely its crystallographic symmetry. On the basis of recorded face development it has been customary to assign to cuprous oxide, with the same structure, an enantiomorphic hemihedry. It has been suggested[7] that this enantiomorphism could be explained if one or both of the kinds of atoms occupied positions slightly displaced from that of (*a*). Since in the arrangement of their atom positions,

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[7] W. H. and W. L. Bragg, X-rays and Crystal Structure, p. 157 (London, 1916).

not only the simple grouping (*a*) but likewise all of the more complicated groupings possess holohedral symmetry, it is evident that, assuming as we have that the two silver atoms of Ag_2O are equivalent, this explanation is untenable. If a real enantiomorphism exists in the case of cuprous oxide, it must be traced to some other cause than symmetry of the arrangement of the atoms.

Summary.—Employing the method of powders, it is shown that silver oxide has the same structure as that assigned to cuprous oxide. The length of the side of the unit cube is determined to 4.76^8 A. U.

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