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MAGNETIC PROPERTIES AND CRYSTALLINE STRUCTURE OF AgO

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Abstract—From the diamagnetic and crystalline behaviour, AgO is found to be not a true bivalent silver oxide but an Ag(I)–Ag(III) covalent oxide, crystallizing in the space group $P2_1/c$. The positions of the atoms are given and the covalent character of the Ag(III)–O and Ag(I)–O bondings is discussed.

Silver oxide, AgO, has had the attention of many workers since the days it was believed to be a peroxide, prior to the clarifying work of Barbieri(1). Recently, interest has increased because AgO is the product of the oxidation of silver anodes in the so-called silver peroxide alkaline cells.(2,3) Its X-ray diffraction pattern has been used for its identification(4) (see Fig. 1). The first attempt to determine its crystalline structure was done by the author in 1954(5) finding a monoclinic lattice belonging to the space group $C2/c$–C_{2h}^{6} with the positions Ag(4*d*), O(4*e*).[6] More recently, Graff and Stadelmaier(7) and Scatturin *et al.*(8) have reached the same results, the latter independently of the author's former ones. Nevertheless, the choice of such a space group involves the assumption of four bivalent silver ions per unit cell. If it were so, the oxide should be paramagnetic since Ag(II) has one unpaired electron. According to Neiding and Kazarnovskii(9), however, the oxide is diamagnetic, its susceptibility being $\chi = -0{\cdot}155 \times 10^{-6}$ emu/g. These authors have also found that AgO is a semiconductor with a positive temperature coefficient between −40°C and 20°C and an electrical conductivity at 17°C of 0·07 mho/cm, determined on powdered samples pressed at 12000 kg/cm^2.

AgO not only appears during the electrolytic oxidation of silver anodes in alkaline media(7,10) but also during the chemical oxidation of monovalent silver solutions in analogous conditions.(11) It seems doubtful, however, whether the same oxide appears during the electrolytic oxidation of silver anodes in acid media.(4) Probably silver oxisalts of the type $(Ag_3O_4)_2Ag(I)An$ (where An stands for a monovalent anion like nitrate, fluoride, perchlorate or acid sulphate) are produced in this process.(12)

AgO is stable in water up to 100°C and slightly unstable in alkaline solutions(13) giving rise to Ag_2O and oxygen. It dissolves in strongly acidified media yielding Ag(II)

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in solution whose paramagnetism corresponds closely to the one expected from spin contribution only.(9) The same value for the paramagnetism has been found in many co-ordinated solid compounds of divalent silver(14,15) that are, therefore, magnetically dilute.

EXPERIMENTAL RESULTS AND DISCUSSION

As previously stated, a true bivalent silver oxide should exhibit paramagnetism, which is not the case for AgO. Neiding and Kazarnovskii(9) tried to explain the diamagnetism by assuming either a metallic bonding of silvers or a covalent bonding between two Ag(II) pairing the unpaired electrons and ionic bonding with oxygens. These hypotheses, however, are hard to accept since the metallic bonding should lead to much higher values of the conductivity and the Ag(II)–Ag(II) covalent bonding involves close linking between two small-radius dipositive kernels. It seems doubtful whether such a bonding could overcome the repulsive electrostatic potential, although this type of bonding has also been assumed in the case of the dark green diamagnetic Cu(II) derivative of diazoaminobenzene.(16) Otherwise, our results as well as those of Scatturin *et al.* indicate that silver ions are located in a face centred lattice which gives for the separation between neighbouring silver ions a value of 3·28 Å. This result, obtained assuming all silvers to be equivalent, is still valid if two Ag(III) are arranged in $(0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2})$ and two Ag(I) in $(\frac{1}{2}, \frac{1}{2}, 0;\ \frac{1}{2}, 0, \frac{1}{2})$ instead of arranging four Ag(II) in $(0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, 0)$. The relative differences between atomic scattering factors of the three kinds of silver ions are low. This change imposes a lower symmetry space group, namely $P2_1/c\text{–}C_{2h}{}^5$. The positions of the oxygens, however, remain undetermined. It should be noted in this respect that the former structure(5,8) leads to distances apart between oxygens of about 1·75 Å. The ionic radius of 0^{2-} being 1·32 Å, this distance should be at least 2·64 Å. Since the compound is diamagnetic, Ag(III) can only be present if there is co-ordinated filling of one *d*-orbital. This can be done by resorting to hybridization with two of four atoms, namely: *dp* (linear), *ds* (angular), dsp^2 (square planar) or dp^3 (irregular tetrahedral). From these, *dp* and dsp^2 are the only ones that are compatible with the structure due to the planar arrangement of oxygens in this space group. Hybridization dsp^2 (or better *dp* plus *sp*), in addition, accounts for the bonding in the (011) plane. Accepting the latter hybridization, the positions of oxygens are approximately settled. It should be noted that the high density of the compound restricts the election of the oxygen parameters. The general positions for the oxygens being $(x, y, z;\ \bar{x}, \bar{y}, \bar{z};\ \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z;\ x, \frac{1}{2} - y, \frac{1}{2} + z)$, this latter fact leads to $x \cong \frac{3}{4}$, $y \cong z \cong \frac{1}{4}$. Otherwise, from the standpoint of scattering, this arrangement is substantially equivalent to that chosen formerly.(5,8) The positions of the atoms are then:

AgO $\quad P2_1/c\text{–}C_{2h}{}^5 \quad Z = 4$

$a = 5{\cdot}85$ Å; $\quad b = 3{\cdot}48$ Å; $\quad c = 5{\cdot}50$ Å; $\quad \beta = 107°30'$

Ag(III)	$2a(\bar{1})$	$0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2}.$
Ag(I)	$2d(\bar{1})$	$\frac{1}{2}, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, 0.$
O	$4e(1)$	$\frac{3}{4}, \frac{1}{4}, \frac{1}{4};\ \frac{1}{4}, \frac{3}{4}, \frac{3}{4};\ \frac{1}{4}, \frac{3}{4}, \frac{1}{4};\ \frac{3}{4}, \frac{1}{4}, \frac{3}{4}.$

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Fig. 2 shows the lattice of AgO.

The following separations between neighbouring ions are obtained:

$\text{Ag(III)–O} \simeq \text{Ag(I)–O} \cong 2{\cdot}1$ Å, in agreement with the value found in the case of Ag_2O for the distance $\text{Ag(I)–O} = 2{\cdot}06$ Å,

$\text{O–O} \simeq 2{\cdot}8 \text{ Å} > 2{\cdot}64$ Å,

$\text{Ag(III)–Ag(III)} = \text{Ag(I)–Ag(I)} = 3{\cdot}28$ Å, and

$\text{Ag(III)–Ag(I)} = 3{\cdot}39$ Å.

Tripositive silver ions are then co-ordinated with four oxygens, two of them being closer (*dp*). From the four oxygens of the unit cell, two of them are the nearest neighbours of each Ag(I) ion. This suggests a linear *sp*-co-ordination as is usual in monovalent silver covalent compounds. The deep blackness of AgO, in addition, can be attributed to the Ag–O bondings since, according to Helmholtz and Levine(17), the greater the covalent character of the Ag–O bonding, the deeper the colour of the compound.

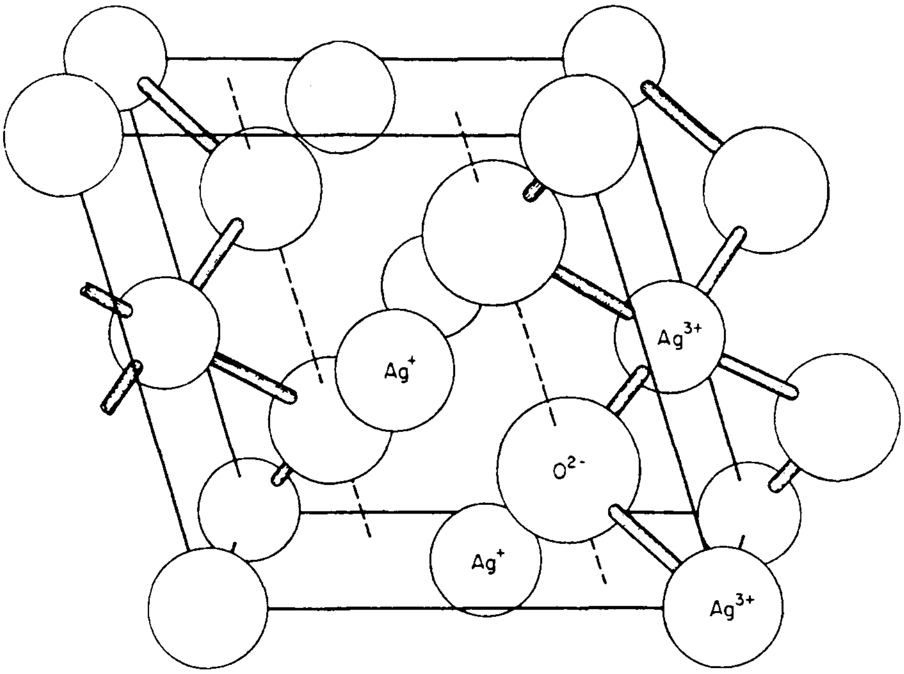

Fig. 2.—Arrangement of atoms in AgO. Only a few co-ordination bondings are shown to avoid complexity in the figure.

With respect to its property of semiconductivity, it should be emphasized that the value of the electrical conductivity is low and could be explained on the basis of an excess- or defect-oxygen lattice. There are, however, no experimental results to support this or any other assumption.

Further verification of the structure is very difficult since it has not been possible to obtain a single crystal of AgO but only finely divided powder samples.

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SUMMARY

The compound AgO crystallizes in the space group $P2_1/c\text{-}C_{2h}^5$. It is not a true bivalent silver oxide but an oxide of silver(I) and silver(III). Trivalent silver ions are coördinated with oxygens filling one *d*-orbital, being, therefore, diamagnetic. Monovalent silver ions are *sp*-co-ordinated with two oxygens. The property of semiconductivity of AgO can be attributed to an excess- or defect-oxygen lattice.