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# Structure and Magnetic Properties of Tetragonal Silver(I,III) Oxide, AgO

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Tetragonal silver(I,III) oxide, AgO, was prepared as a black powder by ozonation of Ag or $Ag_2O$ in aqueous suspension, and investigated by neutron diffraction and magnetic susceptibility measurements. It crystallizes with a body-centered tetragonal structure ($a$ = 6.833(3), $c$ = 9.122(4) Å, space group $I4_1/a$, $Z$ = 16) and contains two nonequivalent Ag atom sites of which one shows a linear O atom coordination ([Ag(I)–O] = 2.18 Å) and the other a slightly deformed square-planar O atom coordination ([Ag(III)–O] = 2.02 and 2.04 Å). The magnetic susceptibility data suggest diamagnetic behavior and the presence of an oxygen-rich impurity phase which orders antiferromagnetically at $T_N \simeq 50$ K.

## 1. Introduction

Silver oxide, AgO, is used in galvanic cells of high-energy density (*1*). It usually crystallizes with a monoclinic structure ($a$ = 5.85, $b$ = 3.47, $c$ = 5.49 Å, $\beta$ = 107.5°, space group $P2_1/c$, $Z$ = 4) which consists of a deformed face-centered cubic metal atom arrangement with equal proportions of linear coordinated Ag(I) and approximately square-planar coordinated Ag(III) atoms (*2, 3*). As expected the compound was found to be diamagnetic (*4*).

Until recently the existence of a second AgO modification was a matter of controversy. Early X-ray powder diffraction data on samples which were synthesized by oxidation of Ag by ozone (*5*) were interpreted in terms of a tetragonal structure ($a$ = 4.816, $c$ = 4.548 Å, $Z$ = 4) built up by an unusual combination of Ag(I), Ag(II), $O_2^{2-}$, and $O^{2-}$ atoms (*6*). Magnetic measurements suggested that this modification was paramagnetic (*7*). Later its existence was ques-

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tioned by some workers (*8*) but confirmed by others on samples obtained by electrochemical oxidation of silver with asymmetrical current (*9, 10*). Its structure and properties, however, were never investigated in detail, presumably because of difficulties to obtain samples of sufficient size and quality.

Recently, tetragonal silver oxide, AgO, was synthesized by a method (*11*) which yielded samples of sufficient size and purity to perform both neutron diffraction and magnetic measurements. In this communication we report on the results of these measurements.

## 2. Experimental and Results

*2.1. Synthesis.* The tetragonal AgO modification was obtained by ozonation of a suspension of $Ag_2O$ or Ag in stirred water. With an $O_3$ flow of 2.6 g/hr at room temperature, 100 g of silver were totally oxidized in 20 hr. Three samples with O contents of $AgO_{0.99}$, $AgO_{1.06}$, and $AgO_{1.11}$ were prepared, corresponding to reaction times of 20, 29, and 40 hr, respectively. For comparison a fourth sample ($AgO_{0.96}$) containing the monoclinic modification was prepared by a method described previously (*12*). The oxygen contents were determined by chemical analysis and thermogravimetry. In contrast to previous work (*6, 9, 10*) no metallic Ag or $Ag_2O$ was found in any sample.

*2.2. Diffraction experiments.* All samples were investigated by X-ray Guinier photographs ($CuK\alpha$ radiation) and those containing the tetragonal modification also by neutron powder diffraction. For the latter ($AgO_{0.99}$, $AgO_{1.06}$, $AgO_{1.11}$) the strongest lines of the X-ray patterns could be indexed on a tetragonal cell with $a' = 4.82$ Å and $c' = 4.55$ Å similar to that reported (*6, 9, 10*) previously. The diffraction intensities were consistent with a face-centered metal atom arrangement. However, overexposed Guinier photographs revealed the presence of additional diffraction lines of which the majority was attributed to the monoclinic modification of AgO. Their intensities were strongest in $AgO_{1.06}$, indicating that this sample contained the highest concentration (about 5%) of monoclinic AgO. The remaining lines (in particular those at $d = 5.46$, 2.89, and 2.15 Å) could be indexed on a body-centered tetragonal cell with $a = \sqrt{2}.\ a'$ and $c = 2 \cdot c'$, suggesting that the cell volume of the tetragonal modification had to be increased by a factor of four. No significant variation of the lattice parameters as a function of overall oxygen content of the samples was observed, indicating that the tetragonal phase had only a small homogeneity range. Apart from monoclinic AgO no evidence for the presence of other impurity phases was found in the samples. In particular none was found in the most oxygen-rich sample $AgO_{1.11}$.

The neutron diffraction patterns of samples $AgO_{0.99}$, $AgO_{1.06}$, and $AgO_{1.11}$ were recorded at room temperature (Fig. 1), and that of sample $AgO_{1.11}$ also at 8 K (not shown here), by using the multidetector powder spectrometer DMC at the reactor SAPHIR (Würenlingen). The patterns were corrected for absorption (cylindrical sample geometry) by using $\mu R$ values of 0.261, 0.222, and 0.201 for $AgO_{0.99}$, $AgO_{1.06}$, and $AgO_{1.11}$ respectively, as determined by transmission measurements. Except for minor intensity differences between the room temperature patterns, and a general intensity increase in the low-temperature pattern, they were all identical. They could be indexed on the same lattice as that used to index the X-ray patterns, thus confirming the body-centered tetragonal cell. The reflections which were weak (or absent) in the X-ray patterns were generally strong in the neutron diffraction patterns, suggesting that their intensities were mainly due to oxygen atoms. The reflection conditions ($hkl$: $h + k + l = 2n$, $hk0$: $h(k) = 2n$, $00l$: $l = 4n$) indicated space group $I4_1/a$ (*13*). A structure model was constructed and refined by the Rietveld method (*14*) with the room

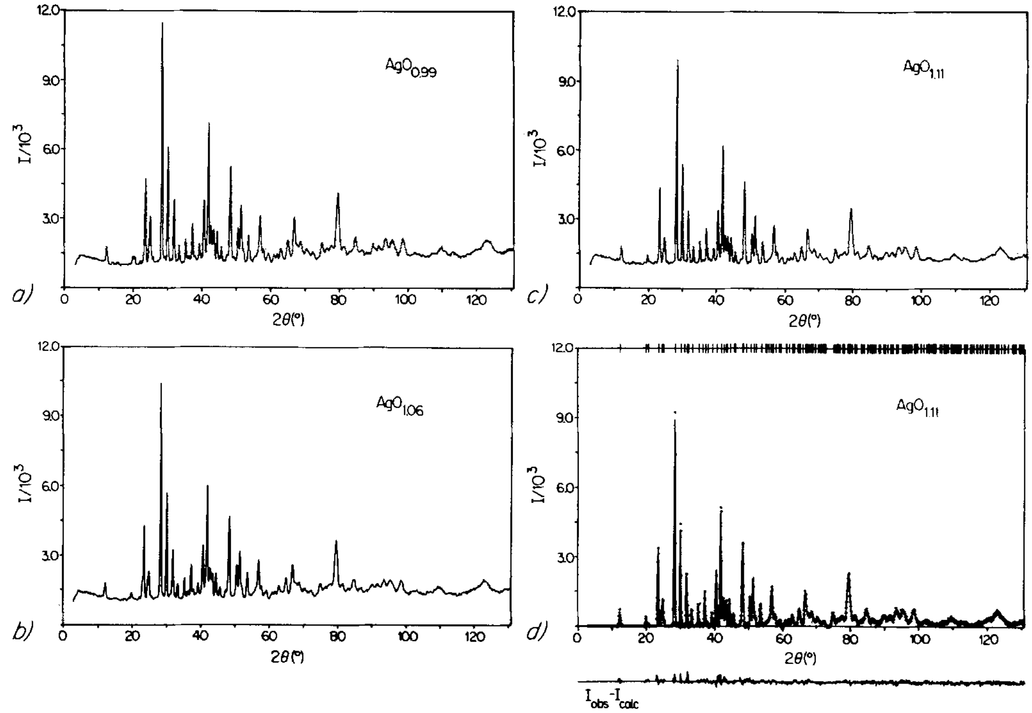

FIG. 1. Observed, absorption-corrected neutron diffraction patterns for three samples of tetragonal silver oxide. (a) $AgO_{0.99}$; (b) $AgO_{1.06}$; (c) $AgO_{0.11}$; (d) observed, background-corrected (dots), versus calculated (solid line) neutron diffraction patterns (top), and difference pattern (bottom) of $AgO_{0.11}$ (wavelength $\lambda$ = 1.189 Å, angular step 0.1°, diameter of cylindrical vanadium container 8 mm).

temperature data of $AgO_{1.11}$ (Figs. 1c,d) to a consistency factor of $R_I = 0.066$ (7 atomic and 2 cell parameters, a scattering angle zero point, and 3 profile parameters; 401 nonequivalent reflections, neutron scattering amplitudes used: 5.92 fm (Ag), 5.81 fm (O)). The most oxygen-rich sample, $AgO_{1.11}$, was chosen for the refinement to test for the possible occurrence of defects on the Ag sites. The results are summarized in Table I. Refinements based on variable occupancy factors for the metal atom sites (pp(Ag(I)) = 1.02(1), pp(Ag(III)) = 1.04(1)) gave no indication for the presence of defects in the structure.

*2.3. Magnetic measurements.* The magnetic susceptibilities of samples $AgO_{0.99}$, $AgO_{1.06}$, $AgO_{1.11}$ (tetragonal modification), and $AgO_{0.96}$ (monoclinic modification) were measured by using a SQUID magnetometer (*15*). The temperature was varied between 5 and 250 K, and the applied magnetic field between 0.5 and 2 *T*. Results for the sam-

TABLE I

STRUCTURE DATA OF TETRAGONAL AgO

| | | |
|---|---|---|
| Space group $I4_1/a$ (No. 88, origin at center) (*13*) | | |
| Cell parameters[a] | $a = 6.833(3)$ Å | |
| | $c = 9.122(4)$ Å | |
| Atom positions[a] | Ag(I) | in 8*c*, 0, 0, 0, etc. |
| | Ag(III) | in 8*d*, 0, 0, ½, etc. |
| | O | in 16*f*, *x*, *y*, *z*, etc., $x = 0.0798(3)$ |
| | | $y = 0.0130(5)$ |
| | | $z = 0.2128(3)$ |
| Thermal parameters (×100)[a] | $\langle u^2\rangle$Ag(III) | = 0.58(6) $Å^2$ |
| | $\langle u^2\rangle$Ag(I) | = 1.68(8) $Å^2$ |
| | $\langle u^2\rangle$O | = 0.66(4) $Å^2$ |
| Agreement factors[b] | $R_{wp} = 0.127$, $R_I = 0.066$, $R_e = 0.077$ | |

[a] Estimated standard deviations (*14*) of least significant digits given in parentheses.

[b] For definition see Ref. (*14*).

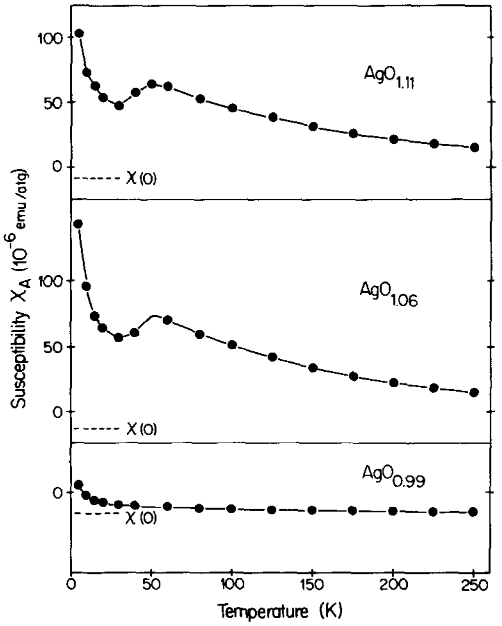

FIG. 2. Temperature dependence of magnetic susceptibility for three samples of tetragonal AgO.

ples containing the tetragonal modification are shown in Fig. 2. As is usual in most cases, magnetic measurements are very sensitive to the presence of a very small amount of ferromagnetic and paramagnetic impurities and need to be corrected. The full curves in Fig. 2 represent the magnetic susceptibilities per atom-gram, $\chi_A$, corrected for ferromagnetic impurities ($AgO_{0.99}$: 1 ppm Fe, $AgO_{1.06}$: 2 ppm Fe, $AgO_{1.11}$: 18 ppm Fe). The systematic increase of $\chi_A$ below 30 K was attributed to paramagnetic impurities (less than 150 ppm $Fe^{2+}$ for all samples) and corrected by assuming that their contributions follow a Curie law, i.e., by plotting $\chi^{meas} \cdot T$ as a function of $T$.

For the two oxygen-rich samples, $AgO_{1.11}$ and $AgO_{1.06}$, the maximum of $\chi_A$ at $T \simeq 50$ K was attributed to the presence of a paramagnetic impurity phase which orders antiferromagnetically. The contribution of this phase to $\chi_A$ was estimated by assuming that it contained a *localized* paramagnetic moment of 1.7 $\mu_B$ (i.e., one unpaired electron) and by applying the Curie law. The amount of paramagnetic atoms calculated under these assumptions was less than 2 at.% for both samples. Increasing the assumed value of the magnetic moment decreased this value correspondingly. Taking into account these corrections the dotted lines in Fig. 2 represent the extrapolated susceptibility values at $T = 0$ K ($\chi_A(0) = -8.5$, $-13.4$, and $-16.4 \times 10^{-6}$ emu/atg for $AgO_{1.11}$, $AgO_{1.06}$, and $AgO_{0.99}$, respectively). For $AgO_{1.11}$ and $AgO_{1.06}$ the extrapolation was made from above the transition temperature $T_N$. For sample $AgO_{0.99}$ the extrapolated susceptibility was identical to that of sample $AgO_{0.96}$ (monoclinic modification) and close to the calculated ionic susceptibility: $\chi_A^{calc}(Ag^+Ag^{3+}(O^{2-})_2) = -17 \times 10^{-6}$ emu/atg (partly filled shell ionic susceptibility (*16*)).

## 3. Discussion

Tetragonal silver oxide, AgO, shows structural features similar to those of monoclinic silver oxide, AgO (*2*, *3*). Its metal atom arrangement forms a distorted face-centered cubic substructure which contains two nonequivalent Ag sites in equal proportions. One, Ag(I), is linear coordinated with respect to oxygen and has a bond distance of [Ag(I)–O] = 2.183(3) Å ($AgO_{mono}$: 2.18 Å), whereas the other, Ag(III), is nearly square-planar coordinated with respect to oxygen and has bond distances of [Ag(III)–O] = 2.019(1) and 2.037(3) Å ($AgO_{mono}$: 2.01 and 2.05 Å), and O–Ag(III)–O bond angles of 86.00(4)° and 88.95(4)° ($AgO_{mono}$: 88.3 and 91.6°). Both metal sites are inversion centers of the structure. The shortest Ag–Ag and O–O separations are 3.34 and 2.82 Å, respectively ($AgO_{mono}$: 3.25 and 2.83 Å, respectively). A comparison between the structures of the tetragonal and monoclinic modification is represented in Fig. 3. For

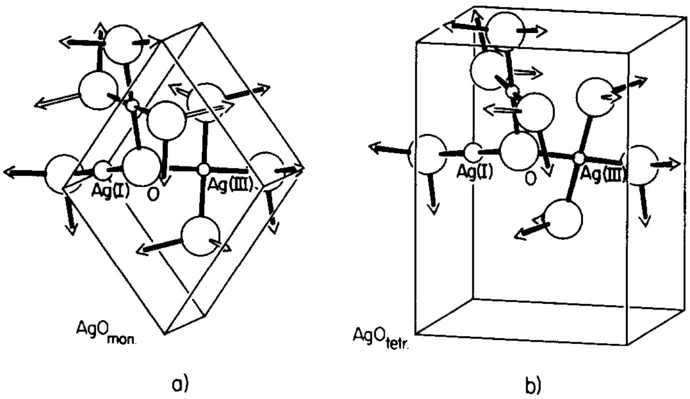

FIG. 3. Structure segment of monoclinic AgO (a) viewed approximately down the twofold axis, compared to that in tetragonal AgO (b) viewed approximately perpendicular to the fourfold axis. Unit cells indicated by solid lines. Full lines: metal–oxygen bonds. Open arrows indicate directions of third-nearest metal neighbors which differ in both structures.

clarity only the partial structure around the oxygen atom (marked by O) is represented. In both modifications the oxygen atom is coordinated by three silver atoms (two square-planar and one linear coordinated). These metal atoms occupy the corners of a slightly distorted tetrahedron of which the empty corner points toward a hole in the structure. The configuration of the nearest metal and second-nearest nonmetal neighbors is approximately the same in both structures. The structures differ mainly with respect to the directions of third-nearest metal neighbors, and the linkage of the latter via oxygen atoms to a three-dimensional network (see O–Ag bonds marked by arrows). No simple shear operation appears to exist which allows to transform one structure into the other.

Altogether, the structural features and magnetic properties of tetragonal AgO suggest that it is a silver(I,III) oxide much as monoclinic AgO. A point which remains to be clarified is the origin of the paramagnetism found in oxygen-rich samples. It could be due to an oxygen-rich impurity phase (possibly a peroxide), not seen by diffraction methods, which orders antiferromagnetically at $T_N \simeq 50$ K. The absence of a significant magnetic scattering contribution to the low-temperature neutron diffraction pattern of sample $AgO_{1.11}$, and the failure to detect both lattice parameter variations and significant deviations from stoichiometry during structure analysis support this assumption. The existence of an oxygen-rich paramagnetic silver oxide was suggested previously from interpretation of the magnetic properties of a product obtained by oxidation of $AgClO_4$ with ozone (*7*). This phase presumably differs from the recently reported silver(III) oxide $Ag_2O_3$ (*17*) which is expected to be diamagnetic.

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