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The Structure of the Ag (I, III) Oxide Phases

By I. Náray-Szabó and G. Argay

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

and P. Szabó

Central Research Institute for Physics of the Hungarian Academy of Sciences, Budapest, Hungary

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The cubic, magnetite-like, octahedral crystals produced on the anode when silver nitrate or silver fluoride solutions are electrolysed have been investigated with X-ray and neutron diffraction. For Ag_7NO_{11}, $a=9·890$ Å, $Z=4$, space group $Fm3m$. There are Ag^+ and Ag^{3+} ions in the structure. The oxygen ions form a network with cubo-octadodecahedral and small cubic cages, with silver ions in the centres of the dodecahedron planes and in the centers of the small cubes. The oxygen atoms of the NO_3^- ions are distributed statistically over twelve sites of the position $96(k)$. The electrical conductivity and the magnetic behaviour are discussed.

The formula of the well-known magnetite-like black octahedra growing on the anode during the electrolysis of silver nitrate solution is Ag_7NO_{11}, as found by earlier authors and confirmed by us. From silver fluoride solution we obtained similar crystals with the approximate composition Ag_7O_3F (Náray–Szabó & Popp, 1963).

Several authors have investigated the structure of the Ag_7NO_{11} crystals (Braekken, 1934; Zvonkova & Ždanov, 1948; Chou Kung-Du, 1963). The short publication by Chou Kung-Du came to our knowledge only after the completion of our own work. None of these publications gives a structure satisfactorily proven by intensity data and no intensity calculations are given. Cho Kung-Du gives no intensities or calculations at all. The determination of the sites of oxygen and nitrogen atoms as well as silver ions is hardly possible with X-rays alone. We therefore made a new determination of the structure with the aid of X-rays and neutron diffraction.

Experimental

Our crystals were prepared as described by Náray–Szabó & Popp. Small octahedral crystals of about 0·1 mm size have been used with Mo $K\alpha$ radiation for Weissenberg diagrams. Fine powder was used for X-ray and neutron diffractograms.

The X-ray diffractograms have been made with Cu $K\alpha$ and Mo $K\alpha$ radiation. The intensities of single-crystal reflexions have been measured with a Zeiss type microphotometer. The diffractogram intensities were estimated from the areas under the peaks. The neutron diffractograms were made with the apparatus described by Szabó, Krén & Gordon (1963), with a wavelength of 1·15 Å.

Deduction of the structure

The cell edge of the Ag_7NO_{11} crystals was $a=9·890 \pm 0·002$ Å, $Z=4$. Since only reflexions with $h+k$, $k+l$ (and $l+h$) $=2n$ appear, the lattice is face-centred. No other absences occur; the space group is therefore $Fm3m$, $F432$ or $F\bar{4}3m$. There are 28 Ag, 44 O and 4 N atoms in the cell; all of these must be in special positions in the above three space groups.

The special positions (a) and (b) are the same in all three space groups, (c) is the same in $Fm3m$ and $F432$, but it can be composed from (c)+(d) of $F\bar{4}3m$; (d) is the same in $Fm3m$ and $F432$ and it is identical with (g) of $F\bar{4}3m$ if $x=0$. The position (e) is the same in $Fm3m$ and $F432$ and it is identical with (f) in $F\bar{4}3m$, and lastly the position (f) of $Fm3m$ is the same in $F432$ whilst it can be composed from two 16-fold positions (e) xxx and $\bar{x}xx$ in the space group $F\bar{4}3m$.

Therefore we can start from $Fm3m$.

The general position of the space group $Fm3m$ is 192-fold. If we do not wish to place the ions in incompletely filled positions, then according to *International Tables for X-ray Crystallography* (1952) only the following possibilities exist for the 28 Ag, 4 N and 44 O atoms:

$4(a)$ 000; $4(b)$ $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $8(c)$ $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $24(d)$ $0\frac{1}{4}\frac{1}{4}$; $24(e)$ $x00$; $32(f)$ xxx.

The case of incompletely filled positions will be discussed later.

Considering only the case of completely filled positions, the 4 N atoms can be only in (a) or (b), the 28 Ag atoms in $4(a)+24(d)$, $4(a)+24(e)$, $4(b)+24(d)$, or $4(b)+24(e)$.

From the zero layer line of the Weissenberg photographs we made a Patterson projection perpendicular to [100] (Fig. 1). This shows very strong vectors from the zero point to $\frac{1}{4}, \frac{1}{4}$; $0, \frac{1}{4}$; and $\frac{1}{4}, 0$; this corresponds to the filling up of the positions $24(d)+4(a)$ or $4(b)$ with Ag atoms. A much weaker vector is ending in about $\frac{1}{8}, \frac{1}{8}$; this comes evidently from the oxygen atoms.

Calculating the contributions of Ag and N atoms on the basis of either possibility we obtain the signs of all F's; an electron-density projection made in this way (Fig. 2) gave peaks on the face diagonals. These are 32 O atoms lying in 32(f) xxx with $x=0{\cdot}161$.

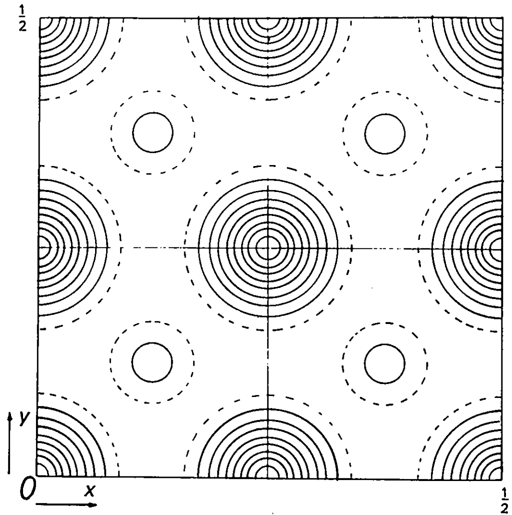

Fig. 1. Patterson projection along [001].

Twelve O^{2-} ions are still not placed. All anions must lie on mirror planes, since in a cell of the edge $a=9{\cdot}890$ Å and space group $Fm3m$ every O^{2-} ion not lying on a mirror plane would be asymmetrically intersected by another mirror plane. Only the points of the general position 192(l) do not lie on mirror planes in the space group $Fm3m$; therefore the O^{2-} ions cannot lie in (l).

All X-ray reflexions with $h+k$, $k+l$ and $l+h=4n$ (n integral), *e.g.* 222, 400, 622, are very strong or strong and all other reflexions are very weak. This is in accordance with the positions 4(a) and 24(d) for the silver ions. The 4 NO_3^- ions would not have enough place in (a); they are therefore in (b) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. We cannot assign a definite position for the oxygen atoms of the NO_3^- ions from the X-ray diffractograms; these have been determined from neutron diffraction.

The positions of the 12 O^{2-} ions of the NO_3^- groups can be determined by the following considerations. The general 192-fold positions not being on symmetry planes, from the possible positions only 96(k) (xxz) gives the possibility of having trigonal plane NO_3^- groups,

Table 1. *Diffractogram of* Ag_7NO_{11} (Cu $K\alpha$)

hkl	F_o	F_c	I_o	I_c
111	145	+153	7·5	
200	132	−171	3·5	
220	78	−106	1	
311	57	+72	1	
222	1103	+1108	100	
400	1008	+924	46	
331	209	+209	6·5	
420	92	−106	1	
422	145	−152	2	
511		+153	4	3·87
333		+16		0·01
440	1020	+1021	41	
531	170	+246	4	
600		−26	3	0·02
442		−104		2·08
620	157	−158	1·5	
533	146	+127	1	
622	824	+866	36	
444	738	+774	9	
711		+158	3	1·89
551		+113		0·97
640	201	−177	2	
642	119	−142	1	
731		+64	1	0·53
553		+109		0·77
800	820	+805	6	
733	188	+173	1	
820		−127	1	0·90
644		−59		0·19
822		−87	1	0·40
660		−58		0·09
751		+95	1	0·93
555		+93		0·09
662	749	+768	17	
840	678	+706	23	
911		+117	2	0·66
753		+92		0·83
842	101	−102	1	
664	102	−134	0·5	
931	126	+119	1·5	
844	685	+656	22	
755		+100	2	0·47
771		+137		0·89
933		+75		0·26
860		−67	1	0·21
1000		−169		0·34
862		−87	1	0·73
1020		−80		0·31
951		+86	1	0·72
773		+40		0·08
666		+702	25	8·0
1022		+669		21·8
953	70	+94	0·5	
1040		−34	1	0·08
864		−109		1·25
1042	136	−71	3	
11,1,1		+73	0	0·31
775		+84		0·40
880	700	+649	14	
11,3,1		+111	4	1·56
955		+87		0·48
971		+72		0·66
1044		−90		0·52
882		−89		0·52
1060		−120	1	1·05
866		−72		0·37
11,3,3		+49	2	0·18
973		+103		1·64
1062	556	+599	48	
1200		+605	30	7·9
884		+602		31·2
11,5,1		+82	2	1·29
777		+134		0·44
1220	72	−86	0·5	
12,2,2		−80	1	0·71
1064		−50		0·55
11,5,3		+84	2	1·78
975		+84		1·78
1240	560	+584		

which are present without doubt in the lattice, since they can be extracted slowly from the substance by shaking the powder with water, We suppose therefore that the oxygen ions of the NO_3^- groups are filling statistically one eighth of the position (*k*) with $x=0{\cdot}546$ and $z=0{\cdot}592$. Then the distance N–O will be 1·258 Å and O–O 2·25 Å, as in the well-known nitrates.

We compared our calculated *F* values with those experimentally determined from diffractograms and from Weissenberg photographs. The observed intensities have been taken on the absolute scale by Wilson's method and the isotropic temperature factor was found to be $B=2{\cdot}0$ Å^2. The oxygen positions are in accordance with the neutron diffraction measurements (see below). Table 1 contains the data of the X-ray diffractograms. For 31 non-coinciding reflexions we obtained $R=0{\cdot}064$ and for the coinciding 22 reflexions $R=0{\cdot}124$ (intensities!). Of 97 reflexions on Weissenberg photographs (Table 2) 21 had the intensity 0; for the non-zero reflexions $R=0{\cdot}124$, for all reflexions $R=0{\cdot}177$. Since *F* values below 40 to 70 are not observable (depending on the glancing angle) on our Weissenberg photographs, the real *R* value is better than the last given figure.

The sequence of the neutron reflexion intensities is quite different from that of the X-ray reflexions (Table 3). The intensities of 400 and 444 are nearly zero with neutrons, while they are very strong on the X-ray diffractograms. The scattering factors for neutron diffraction are: Ag 0·61; N 0·940 and O 0·577. If the oxygen contribution is opposite to that of silver, very small or zero intensities can arise; with X-rays the

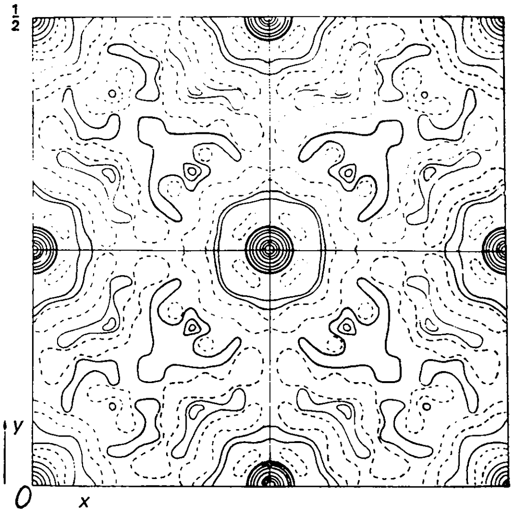

Fig. 2. Electron-density projection along [001]. Contour lines are drawn on an arbitrary scale.

Table 2. *Observed and calculated F values of* Ag_7NO_{11}

(Weissenberg diagrams, layer lines 0, 1, 2)

The F_c values were calculated for Ag and O^{2-} after *International Tables* (1952), for N after *International Tables* (1962).

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	—	−171	12,12,0	445	+457	022	—	−106
220	—	−106	16,6,0	116	−82	222	1100	+1108
400	1006	+924	14,10,0	116	−101	422	229	−152
420	154	−106	16,8,0	405	+436	622	984	+866
440	1004	+1021	18,0,0	120	−86	822	76	−86
600	64	−26	18,2,0	0	−52	10,2,2	627	+669
620	146	−158	18,4,0	0	−38	12,2,2	102	−80
640	162	−177	14,12,0	0	−53	14,2,2	451	+535
800	795	+805	16,10,0	0	−27	042	115	−106
820	131	−127	18,6,0	0	−79	442	126	−104
660	79	−58	18,8,0	0	−68	642	143	−142
840	649	+706	14,14,0	0	−21	842	120	−102
10,0,0	164	−169	20,0,0	495	+460	10,4,2	90	−71
860	106	−67	16,12,0	382	+408	12,4,2	110	−86
10,2,0	108	−80	20,2,0	0	−69	14,4,2	130	−81
10,4,0	40	−34	20,4,0	402	+358	16,4,2	150	−51
880	830	+649	18,10,0	0	−25	062	132	−158
10,6,0	128	−120	20,6,0	0	−30	662	803	+768
12,0,0	505	+605	16,14,0	0	−72	862	88	−87
12,2,0	129	−86	20,8,0	422	+385	10,6,2	566	+599
12,4,0	487	+584	18,12,0	0	−52	12,6,2	110	−68
10,8,0	109	−101	22,0,0	0	−32	14,6,2	561	+513
12,6,0	87	−69	20,10,0	0	−92	082	104	−127
14,0,0	0	−39	22,4,0	0	−53	882	100	−89
10,10,0	150	−125	16,16,0	428	+373	10,8,2	110	−85
14,2,0	87	−92	20,12,0	390	+345	12,8,2	130	−74
12,8,0	396	+534	22,8,0	0	−53	0,10,2	88	−80
14,4,0	128	−110	24,0,0	390	+307	10,10,2	456	+546
14,6,0	0	−33	20,14,0	0	−16	12,10,2	140	−77
12,10,0	83	−77	20,16,0	340	+284	14,10,2	392	+447
16,0,0	431	+452				0,14,2	132	−97
14,8,0	0	−43	511	148	+153	14,14,2	500	+409
16,2,0	0	−64	711	181	+158			
16,4,0	445	+498	911	110	+117			

oxygen contributions can never compensate the silver contribution.

The maximal negative contribution for the 32 oxygen atoms in position (*f*) would occur with $x=0{\cdot}125$ or $0{\cdot}375$; this would give poor agreement with the observed *F* values and improbable Ag–O distances. We have got satisfactory agreement with $x=0{\cdot}147$. Table 3 shows the observed and the calculated neutron diffraction intensities, the latter for $x=0{\cdot}147$ and $0{\cdot}152$ (Chou Kung-Du). Our *x* value (0·147) gives a markedly better agreement, *i.e.* $\Sigma(I_o-I_c)/\Sigma I_o$ is 0·232 for $x=0{\cdot}147$ and 0·297 for $x=0{\cdot}152$. The experimental conditions of the powder method do not permit a high enough resolution for determining whether all square-coordinated Ag–O distances are equal or some difference in bond length occurs. Both the X-ray and the neutron intensity series can be satisfactorily interpreted by the above structure.

Table 3. *Neutron diffraction data of* Ag_7NO_{11}

hkl	F_o^2	F_c^2, $x=0{\cdot}152$	F_c^2, $x=0{\cdot}147$
111	3·7	7·4	5·5
200	4·6	0·2	0·5
220	24	33·4	26·6
311	93	73·0	77·0
222	460	460	460
400	0	32·5	27·2
331	110	50·0	46·5
420		27·5	22·3
422	0	1·4	0·6
511	202	1·8	0
333		283	237
440	1320	970	1100
531	428	0·6	1
600		188	135
442		10·4	9·5
620	0	37·5	21·5
533	430	0	5
622		444	418
444	0	135	82
711	110	49	52
551		2	2
640		120	90
642	0	29·4	18·8
731	239	115	128
553		2	2
800	2020	—	—
733			
820			
644			
		$R=29{\cdot}7\%$	$R=23{\cdot}2\%$

The skeleton of the structure is a cubo-octadodecahedral oxygen lattice (Fig. 3) with an O–O separation of 2·90 Å. Two kinds of Ag ions are present: 4 with 8 oxygen neighbours on the apices of a cube, Ag–O 2·52 Å, and 24 with 4 oxygen neighbours at the corners of a square with a distance Ag–O 2·05 Å. Eight-coordinated Ag^+ ions are present in the $AgClO_3$ lattice (Náray-Szabó & Pócza, 1942), with Ag–O 2·52 and 2·55 Å. The radius of Ag^+ is 1·26 Å – according to Ahrens (1952) – which gives with 1·32 Å for the radius of O^{2-} Wasastjerna, 1923) an Ag^+-O^{2-} distance of 2·58 Å. We can conclude that the 8-coordinated cations are Ag^+ ions. According to the chemical formula the other kind of Ag ions which are square-coordinated must be for the greater part ($\frac{5}{6}$) trivalent; but there is no published value for the Ag^{3+} radius. The difference between the radii of the Au^+ and Au^{3+} ions (which have a similar electron shell structure to the corresponding silver ions) is 0·52 Å after Ahrens. Subtracting this from the radius of Ag^+ we get 0·74 Å for the radius of Ag^{3+} and 2·06 Å for the $Ag^{3+}-O^{2-}$ distance, which is in good agreement with our value of 2·05 Å.

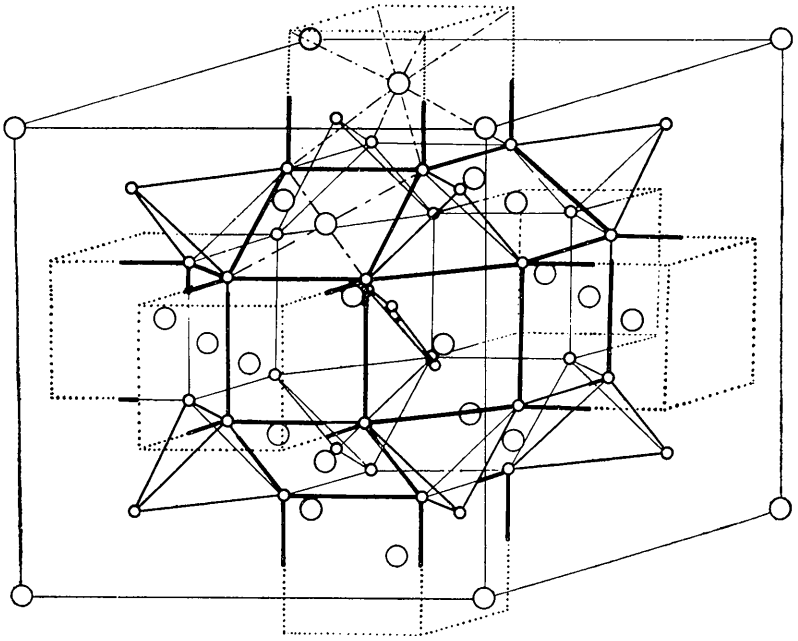

Fig. 3. The unit cell of Ag_7NO_{11}. Small circles are oxygen ions, larger circles silver ions; nitrogen is marked by a cross in the center of the cell.

Comparing our structure with that of Zvonkova & Ždanov we see that the sites of the 4 Ag are different, as well as those of the NO_3^- ions, which according to their supposition should be rotating. The parameter of the 32 O ions in (*f*) would be $\frac{3}{8}$ according to them. Neither of these conclusions is valid: the F values calculated for their structure are not in agreement with the observed ones.

The structure of Chou Kung-Du is, apart from the small difference in the parameter x, identical with ours. It came to our knowledge only after completion of our experimental work. Our neutron diffraction results are in any case a very desirable support for the oxygen positions.

The unit cell of the fluorine-containing products has the cell edge $a=9\cdot842\div9\cdot860$ Å, the fluorine content being variable. The cell contains 44–45 anions (O+F). As in the case of Ag_7NO_{11}, it seems that the cages must contain about 12 anions, otherwise they would collapse. At any rate the fluorine-containing samples are more disordered than Ag_7NO_{11}. The relative intensities of the reflexions are somewhat different, but they have not been worked out thoroughly.

Discussion of properties

The crystals show an electrical conductivity similar to that of semiconductors (McMillan, 1962). They are feebly paramagnetic (Prof. Dr W. Klemm, Münster, private communication).

Both these properties can be explained qualitatively by the fact that the structure is defective in anions (oxygen). It is well-known that many oxides, *etc.*, which are good insulators when stoichiometrically correct, are turned into semiconductors by a stoichiometric excess of one constituent. With excess metal, as in the present case, a semiconductor of *n*-type arises.

Some of the electrons are raised from the donor levels to the conduction band, as a result of interaction with the thermally oscillating lattice. This explains the electrical conductivity. The black colour is also explained: absorption of visible light may raise the electrons from the donor levels into the conduction band.

The electrons of the valency bands form a system with compensated spins and thus they cause diamagnetism. At the same time the electrons in the conduction band can be considered as a classical electron gas which contributes a larger paramagnetic and a smaller diamagnetic part to the susceptibility. Thus a very weak (either para- or dia-)magnetism is to be expected.

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The Crystal Structure of Rhombohedral $PuAl_3$

BY O. J. C. RUNNALLS AND R. R. BOUCHER
Research Metallurgy Branch, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada

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The crystal structure is reported for $PuAl_3$ single crystals extracted from aluminum–6 at.% plutonium alloys which had been slow-cooled to 930 °C and then quenched to 20 °C. The structure is rhombohedral with $a_r=7\cdot879\pm0\cdot003$ Å and $\alpha_r=45\cdot94°$, $Z=3$ units of $PuAl_3$ per unit cell and probable space group $R\bar{3}m$. The structure can be described as an assembly of close-packed layers each with an Al:Pu atomic ratio of 3:1 and stacked in the sequence *ABABCBCACA* · · · Thus the stacking sequence is appreciably different from that of the earlier-reported hexagonal configuration, *ABCACBA* · · ·, which is produced on heating rhombohedral $PuAl_3$ to 1027 °C.

Recent studies of the aluminum–plutonium binary system have revealed that several polymorphic transformations occur on heating the intermetallic compound $PuAl_3$ (Runnalls, 1962; Runnalls & Boucher, 1965). Earlier work (Runnalls, 1956; Larson, Cromer & Stambaugh, 1957) had indicated that the only stable configuration was hexagonal with small deviations from an ideal $6H$ structure of stacking sequence