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Structure of Solid α' -Oxygen

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Abstract

A monoclinic unit cell for solid α' -O₂ was determined. Its dimensions are: $a = 9.225 \pm 0.006$, $b = 6.668 \pm 0.004$, $c = 3.414 \pm 0.004$ Å and $\beta = 85.05 \pm 0.1^\circ$. A triangular net of O₂ molecules in an ab projection may be expected with the centers of the molecules near the ab positions 00, $\frac{1}{3}0$, $\frac{2}{3}0$, $\frac{1}{6}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}$ and $\frac{5}{6}\frac{1}{2}$.

Introduction

In previous publications of electron diffraction work on solid oxygen (Hörl, 1962, 1969) one of us reported on a modification of solid oxygen called α' which was formed in the temperature range of the α phase when oxygen gas was deposited as a thin film on a cold substrate at a low gas-flow rate. This modification was also observed in due course by a number of other groups, but up to now its crystal structure could not be determined.

In spite of many attempts it was not possible to produce single crystals of this modification for a structure determination. One of the reasons was the transition of the α' to the β and/or γ phase during attempts to recrystallize the condensed layers (Hörl, 1969). On the other hand there were found new α' -O₂ diffraction rings on our plates obtained in these

numerous experiments and, in addition, it was possible to measure some of the d values of the rings already known, with higher accuracy than before. In this way our powder pattern data on α' -O₂ increased substantially and the application of our computer programs (Kohlbeck & Hörl, 1976, 1978) for indexing ring patterns of triclinic, monoclinic and orthorhombic crystals promised to yield the dimensions of the unit cell. Furthermore, a special graphical technique was expected to provide also the cell parameters and to confirm the computer data. In addition, the estimated ring intensities made it possible for us to perform a Patterson analysis to obtain information on the positions of the O₂ molecules within the unit cell.

Features of the α' -O₂ powder patterns

The experiments were performed with the aid of a liquid-helium cooling stage (Hörl, 1974) in a transmission electron microscope (Siemens Elmiskop I). Formvar substrate mounted on a copper specimen holder was used. Large-area as well as selected-area diffraction patterns were obtained together with images of the specimens (see Hörl, 1969). All experiments were carried out at a specimen-holder temperature of 4.2 K; the temperature of the α' deposit may have been a few degrees higher.

Most of our α' -O₂ electron diffraction patterns (see Table 1) consisted of rings with two kinds of profiles: sharp ones which showed in many cases a slightly

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Table 1. *Experimental electron diffraction data on α' -O₂ together with their theoretical interpretation by two orthorhombic cells (80 keV electrons, temperature of copper specimen holder on which the Formvar substrate for the O₂ condensation was mounted: 4.2 K)*

For all other experimental parameters see Hörl (1969).

Ring No.†	Observation			Interpretation			
	<i>d</i> (Å) measured‡	Relative <i>FF</i> * estimated§	Relative ring width estimated	<i>hkl</i>		Δd (Å)¶	
				Cell I	Cell II	Cell I	Cell II
1 ^a	~9.3	~1	1	100			
2	6.634	10	1	010		-0.024	
3	5.407	4	1	110		+0.010	
4	4.599	7	1	200		+0.004	
5 ^b	3.775	4	1	210		-0.009	
6	3.400	70	1	001	201	-0.001	0.000
7, (2), [1]	3.336	270	1	020		+0.002	
8 ^c	3.270	~1	1	101	$\bar{2}01$	-0.013	+0.018
9, (3), [2]	3.133	200	1	120		-0.001	
10, [3]	3.070	160	1	300		+0.006	
11	3.028	110	1.5-2	011	211	-0.002	+0.001
	2.970						
12 ^d , (4), [4]	to	120	3-4	111	$\bar{2}11$	+0.004	+0.009
	2.910						
13 ^e	2.850	~1	1	201		-0.001	
14 ^f , (5), [5]	2.782	200	1	310		-0.002	
15 ^g , [6]	2.707	70	1	220		+0.006	
16 ^h , [7]	2.623	70	1.5-2	{ 211 201	$\bar{1}21$	-0.001 -0.004	-0.001
17	2.389	15	1.5-2	{ 301 021	$\bar{3}11$	+0.008 +0.008	-0.003
18	2.297	45	1	400		-0.001	
19	2.264	~1	1	320		+0.008	
20, (6), [8]	2.222	100	1	030		0.000	
21 ⁱ	2.170	50	1	221	410	+0.002	-0.002
22 ⁱ	2.154						
23	2.087	35	1.5-2	$\bar{3}11$	212	+0.011	-0.013
24	2.008	20	3-4	230	411	+0.003	+0.004
25	1.948	20	3-4	321	302	+0.008	-0.010
26	1.895	30	1	420		+0.003	
27, (9)	1.799	150	1	330		0.000	
28	1.776	15	1	510		+0.004	
29	1.666	90	1	040		-0.001	
30	1.640	150	1	140		0.000	
31	1.601	40	1.5-2	{ 3 groups 430	2 groups	0.000 to +0.007	-0.005 to +0.007
32	1.563	20	1	240		+0.003	
33	1.532	85	1	600		-0.004	
				610		0.000	
34	1.487	90	1.5-2	{ 2 groups $\bar{1}41$	$\bar{2}41$	+0.001 to +0.006	0.000
35 (12)	1.459	150	1.5-2	340	023	+0.010	-0.005
36	1.417	25	1.5	530			0.000
37	1.387	260	1	620		+0.005	

Remarks: (a) Only on one plate. (b) Position close to strong 001 peak ^g of α -O₂. (c) Position of main peak of α -N₂. (d) Diffuse band, center at *d* = 2.940 Å. (e) Only on one plate. (f) Position of strong 111 peak ^c of α -O₂. (g) Weak diffuse line could be superimposed. (h) Positions of strong $\bar{2}01$ and 110 peaks ^g of α -O₂. (i) Never observed together.

† The numbers in parentheses are from Hörl (1962), in square brackets from Hörl (1969).

‡ Probable errors of sharp lines are usually ± 0.007 Å, of diffuse lines up to ± 0.025 Å.

§ The numbers given have large errors up to 100% (in some cases even more, since the intensities of a number of diffraction rings were found to depend significantly on the deposition parameters and were changing from experiment to experiment considerably). They were obtained by dividing the observed averaged intensities by the plane multiplicity factor and eliminating all the factors depending on scattering angle.

|| Group of reflecting planes (two or four planes in each group).

¶ +/-: Empirical value higher/lower than theoretical one.

^c Indices of α -O₂ according to Barrett *et al.* (1967a).

dotted appearance and diffuse rings with a width 1.5 to 4 times that of the sharp rings.

The diffraction rings of the first type were generally found to be caused by the reciprocal-lattice vectors of one single reciprocal-net plane. The rings of the second category were mainly caused by reciprocal-lattice vectors not belonging to this plane. They were broadened probably by rather small dimensions of the microcrystals perpendicular to this reciprocal-net plane and/or by stacking faults or other kinds of defects.

Unit-cell dimensions

Having determined for this reciprocal-net plane its two-dimensional cell with reciprocal-lattice vectors of $0.1088_0 \text{ \AA}^{-1}$ and 1.499_7 \AA^{-1} and an angle of 90° between them we thought it a rather simple task to find the dimensions of the complete cell. However, this turned out to be very complicated since the computer programs and also the graphical analysis had produced quite a large number of similar solutions for the cell dimensions. This had its cause firstly in the small number and secondly in the diffuseness of the reflections not belonging to this reciprocal-net plane. Finally, on the basis of the most precise experimental d values two monoclinic cells were found to be most probable: (1) a cell (I) with $a = 9.225 \pm 0.006$, $b = 6.668 \pm 0.004$, $c = 3.414 \pm 0.004 \text{ \AA}$ and $\beta = 85.05 \pm 0.1^\circ$, having six molecules and a density of 1.524 Mg m^{-3} close to the density of $\alpha\text{-O}_2$ (1.530 Mg m^{-3} at 23 K according to Barrett, Mayer & Wasserman, 1967*a*) and (2) a cell (II) with $a = 9.196 \pm 0.006$, $b = 6.668 \pm 0.004$, $c = 4.873 \pm 0.004 \text{ \AA}$ and $\beta = 88.08 \pm 0.1^\circ$ having eight molecules and a density of 1.423 Mg m^{-3} close to the density of $\gamma\text{-O}_2$ (1.387 Mg m^{-3} at 44 K according to Barrett, Mayer & Wasserman, 1967*b*).

The ring indices for both cells are given in the columns 'Interpretation' of Table 1. The reflections with $l = 0$ are those belonging to the reciprocal-lattice plane mentioned above. They are common to both cells. The deviations Δd of the experimental d values from the theoretical ones (last three columns of Table 1) are all within the experimental errors to be expected for the kind of electron diffraction patterns taken.

The choice of cell I was made on the following grounds:

(1) On the basis of the experimental observation (see Hörl, 1969) that in warming-up α' deposits the β phase was sometimes formed together with the γ phase. This in turn suggested that the density of α' -oxygen should be higher than that of β -oxygen. Since cell II would give a density lower than the $\beta\text{-O}_2$ density (1.495 Mg m^{-3} according to Hörl, 1962), cell II has to be excluded.

(2) By taking into account the fact that Patterson maps calculated for cell II did not give maxima suitable for eight molecules, while maps for cell I (see below) produced a satisfactory pattern for six molecules.

(3) On account of a comparison of the M_{20} values, introduced by de Wolff (1968) for evaluating the probability of calculated cells from powder patterns. These values were 10.8 for cell I and 6.9 for cell II, indicating a higher probability for cell I.

Patterson analysis

To determine the molecular arrangement within cell I we tried to obtain FF^* values of the reflections from our numerical estimates of the intensities of the diffraction rings and calculated maps of the Patterson function $P(uvw)$. These FF^* values are presented in the third column of Table 1. They have very large errors (up to 100% or even more) since the intensities of a number of diffraction rings were found to depend significantly on the gas deposition parameters used in preparing the thin-film specimens. In spite of these large errors we calculated Patterson maps for 12 planes through the unit cell using mainly strong reflections. They showed for $w = 0$ ($c = 0$ plane) six relative maxima at the positions $00, \frac{1}{3}0, \frac{2}{3}0, \frac{1}{6}\frac{1}{2}, \frac{1}{2}\frac{1}{2}$ and $\frac{5}{6}\frac{1}{2}$. The three-dimensional Patterson function exhibited maxima on lines parallel to the c axis through these positions at the points $000, \frac{1}{3}0\frac{1}{3}, \frac{2}{3}0\frac{1}{3}, \frac{1}{6}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$ and $\frac{5}{6}\frac{1}{2}\frac{1}{2}$. There occurred also a weak maximum at $0\frac{1}{2}\frac{1}{2}$.

The Patterson maps therefore suggest a structure in which the molecules are arranged in a kind of triangular net if viewed in the c direction. The centers of the molecules seem to lie close to the lines parallel to the c axis through the points $00, \frac{1}{3}0, \frac{2}{3}0, \frac{1}{6}\frac{1}{2}, \frac{1}{2}\frac{1}{2}$ and $\frac{5}{6}\frac{1}{2}$ of the ab plane. They may, for example, be situated near the points $000, \frac{1}{3}0\frac{1}{3}, \frac{2}{3}0\frac{1}{3}, \frac{1}{6}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$ and $\frac{5}{6}\frac{1}{2}\frac{1}{2}$. The exact positions of the centers as well as the directions of the molecular axis unfortunately cannot be determined from the intensity data of our powder patterns (see comment for the third column of Table 1).

Nitrogen impurity

Krupskii, Prokhvatilov, Freiman & Erenburg (1979) made a study of the exchange interaction acting together with the van der Waals forces in solid oxygen. For this investigation they introduced small quantities of nitrogen with the effect of the appearance of $\alpha'\text{-O}_2$ reflections in their X-ray patterns.

These observations raise the question whether $\alpha'\text{-O}_2$ in our experiments is also caused by an N_2 impurity. The oxygen gas used by us was very pure (99.999 vol%), but in introducing the gas into our system adsorbed air was certainly released from the walls of

the cryostat. In addition there was certainly a very thin layer of solid air on the Formvar substrate on which oxygen gas was condensed, which could have had an influence on the formation of the oxygen deposit. Even though such an air layer was not detectable* by electron diffraction, a slight diffusion of nitrogen from an extremely thin air layer into the oxygen film might have occurred during deposition since by this process the surface temperature of the substrate certainly was raised. We therefore cannot exclude the existence of small impurities of nitrogen in our samples.

It may be interesting to note that Barrett, Mayer, Greer & Wasserman (1968) in their work on the nitrogen–oxygen phase diagram found an unknown phase which they called x phase between 34.0 and 45.0 K and between 18 and 37% N₂. For smaller N₂ concentrations a mixture of β -O₂ and the x phase occurred. Since Krupskii *et al.* (1979) have observed that for N₂ concentrations > 1% the lines of α' -O₂ persisted up to the transition temperature of the β - to the γ -O₂ phase, the x phase may be identical with α' -O₂.

Argon impurity

Bostanjoglo & Goertz (1969) reported that a phase, very similar or identical to α' -O₂ (called ε -O₂ by these authors), exists for oxygen–argon mixtures in the range from 20 to 40% argon besides β -O₂. This phase may also be identical with the δ phase in the argon–oxygen phase diagram of Barrett, Mayer & Wasserman (1966).

* The main peak of α -N₂ ($d = 3.259 \dots 3.268$ Å) should appear at the position of ring No. 8. Therefore a contribution of this peak to this ring cannot be excluded. The peak of second highest intensity of α -N₂ ($d = 2.822 \dots 2.831$ Å) might give some contribution to ring No. 13.

It is unlikely that the formation of our α' -O₂ layers were caused by an argon impurity, since the argon content of air is only 0.9%, while nitrogen amounts to 78.1%.

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