

Fig. 5. The surroundings of the NH_3^+ group as viewed along the bond N-C(1).

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Modifications and Transitions of Solid Oxygen

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Thin films of solid oxygen were investigated by electron diffraction and electron microscopy. New information was obtained about the formation of the modifications of solid oxygen and the transitions between the modifications. In particular, the phase which is formed on helium-cooled substrates by deposition of oxygen gas at a low flow rate was examined.

Introduction

The author has shown in previous papers (Hörl, 1959, 1962; Hörl & Marton, 1961) how electron diffraction can be applied to problems of crystal structure, crystal growth and crystal faults of solidified permanent gases. The present paper presents a further study of the modifications of solid oxygen with the aim of investigating the transitions between these modifications in thin films.

The technique described in the previous papers (see also Hörl & Marton, 1958) was extended by the use of an electron microscope as diffraction apparatus. A special stage (Hörl, 1968) for cooling specimens with liquid helium was constructed, which also allowed magnetic studies (not discussed in this paper) by the application of a transverse magnetic field. With this stage it

was possible to obtain, in addition to the electron diffraction patterns, electron micrographs of the deposits of interest. Direct observation of the crystals also allowed selected area diffraction.

Oxygen modifications

Ten years ago there were three known modifications of solid oxygen: an α modification, stable up to 23.9°K, a β modification stable between 23.9° and 43.6°K and a γ modification stable between 43.6°K and the melting point at 54.4°K. Today we have to add two additional modifications, one (we will call it α') which is formed in the temperature range of the α phase when oxygen gas is deposited in the form of a very thin film on a cold substrate, and an amorphous phase, which can be ob-

tained from the β phase under the conditions described below.

α and α' oxygen

Very divergent statements about the structure of the α phase of solid oxygen can be found in the papers published prior to 1960. For this reason the author (Hörl, 1962) tried to clarify the situation by investigating thin films of solid oxygen by electron diffraction. By the use of a low flow rate during the deposition of the oxygen gas, diffraction patterns were obtained which did not resemble patterns of either the β or the γ structure. It was therefore assumed that these patterns belonged to the α structure. Later Alikhanov (1963) and Barrett, Meyer & Wasserman (1967a) were able to analyse X-ray diffraction patterns of bulk samples of solid oxygen, obtained by cooling β phase crystals, in terms of a monoclinic structure of space group $C2/m$. The patterns obtained by these authors were completely different from our α patterns, but identical with patterns previously observed by others.

We had therefore to draw the conclusion that oxygen crystallizes in two different modifications in the temperature range below 23.9°K: (1) thin films, deposited from the gas phase at a low flow rate, have a crystal structure which we called the α structure in our 1962 paper and which we will call the α' -structure in future (in order to avoid confusion with the structure found for bulk samples); (2) bulk samples, obtained by cooling β phase crystals, exhibit the structure of space group $C2/m$ determined by Alikhanov and by Barrett, Meyer & Wasserman, which was called the α structure by a number of authors and which we will in future also call the α structure.

Since 1962 the author has observed many powder patterns of the α' phase which were identical with that described in the 1962 paper, except for the fact that usually additional rings were visible and closely spaced lines could be resolved [see Fig. 1(a)]. In addition, more accurate d values than the ones reported in 1962 could be obtained (Table 1). An electron micrograph of an

α' deposit is shown in Fig. 2(a). The crystals are of irregular shape.

In spite of a great effort to find the dimensions of the α' cell we were not successful; no fit of the observed d values with the d values of cubic, tetragonal, hexagonal and rhombohedral cells could be detected. In addition, orthorhombic cells with $\log c/a$ between 0.1 and -0.1 and $\log b/a$ between 0.1 and -0.1 were checked in the neighbourhood of the 200, 210 and 211 reflexions without success. The very large number of the lines of the α' patterns [see Fig. 1(a)] seems to indicate a cell of low symmetry, possibly a triclinic or monoclinic cell.

The α' phase was recently also observed by Bostanjoglo & Lischke (1967) and by Boersch, Bostanjoglo, Goertz & Lischke (1968). These authors have also found this phase or a similar one in O_2 -Ar mixtures (private communication). In their 1967 paper they have called it α phase, in their 1968 paper, ϵ phase.

β oxygen

The structure of the β modification was determined by the author (Hörl, 1962). A rhombohedral cell was found containing one O_2 molecule with its axis parallel to the trigonal axis. This structure was confirmed by Alikhanov (1963), who assumes a precession of the O_2 molecules around the trigonal axis with an angle of $\sim 30^\circ$ at the top.

Diffraction patterns recently obtained by the author for the β phase exhibited a better agreement between the experimental and theoretical intensities than the patterns originally used for the structure determination. In addition the 10.4 reflexion could be observed [see Fig. 1(b)], which was absent in previous patterns (Hörl, 1962).

The rhombohedral structure did not influence the external shape of the β crystals. Electron micrographs of β deposits showed deposits of α' -like crystals of irregular shape [Fig. 2(b)]. In some of the crystals faults could be seen at high magnification, which might be interpreted as faults in the stacking of the (00.1) layers.

Table 1. d -values $> 1.9 \text{ \AA}$ and relative intensities of the observed α' oxygen diffraction rings of the pattern shown in Fig. 1(a)

Ring No.	d (Å)*	Intensity†	Ring No. (Hörl, 1962)	Remarks
1	3.333	80	2	
2	3.125	30	3	
3	3.057	5		Resolved in dots. Absent in other patterns.
4	2.964 to 2.898	150	4	Band may consist of two or more rings not resolved
5	2.787	50	5	Resolved in dots. Continuous intensity along this ring in other patterns.
6	2.702	50	}	Very faint in other patterns
7	2.609	50		
8	2.218	40		

* The d values have probable errors of 0.007 Å.

† Eye estimates of the integrated intensities.

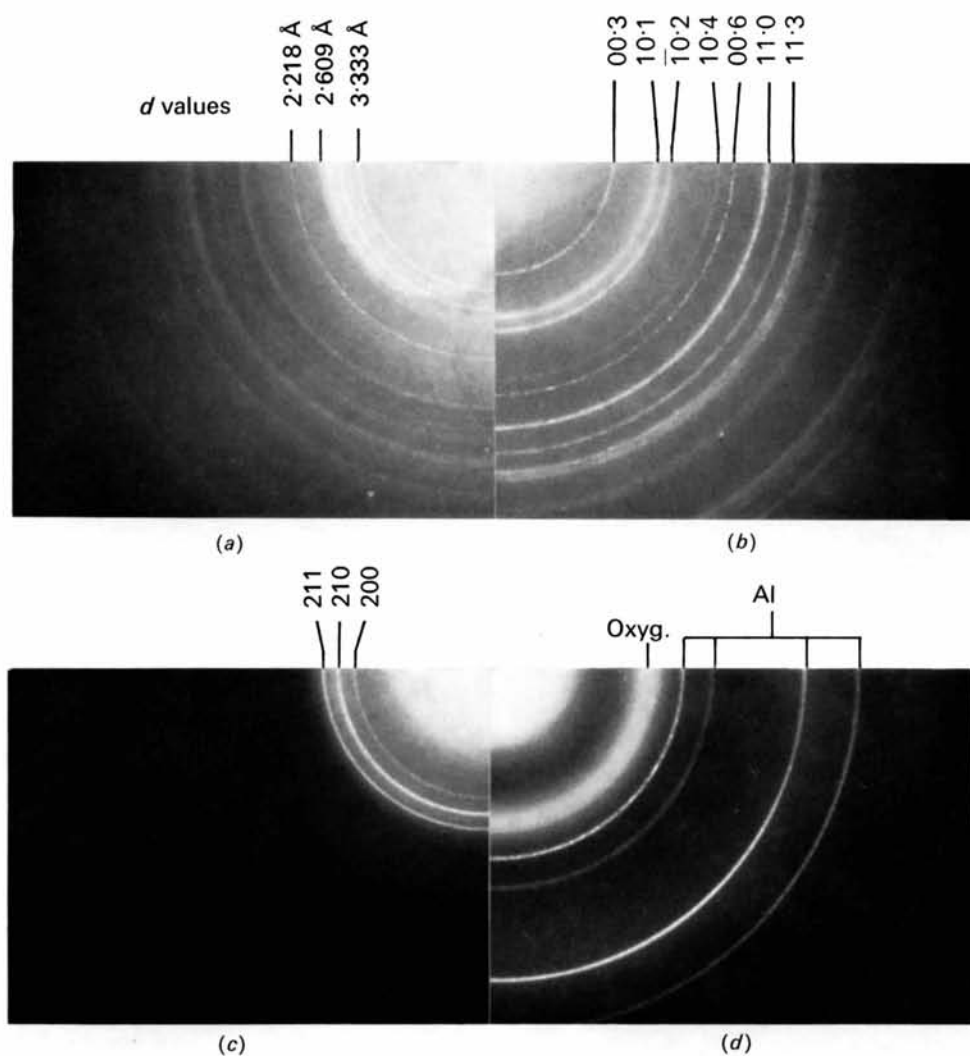


Fig.1. Electron diffraction patterns of the oxygen modifications observed by the author by electron diffraction. The apparatus constant λL is the same for all four patterns. (a) α' phase; d values are indicated for three rings in order to assign the d values given in Table 1 to the lines. A very large number of faint rings with $d < 1.9 \text{ \AA}$ is visible. Substrate: Formvar. (b) β modification; the hexagonal indices are given. Substrate: Formvar. (c) γ pattern; only rings corresponding to the cubic 200, 210 and 211 reflexions are clearly visible. Substrate: Formvar. (d) Amorphous oxygen. Substrate: aluminum.

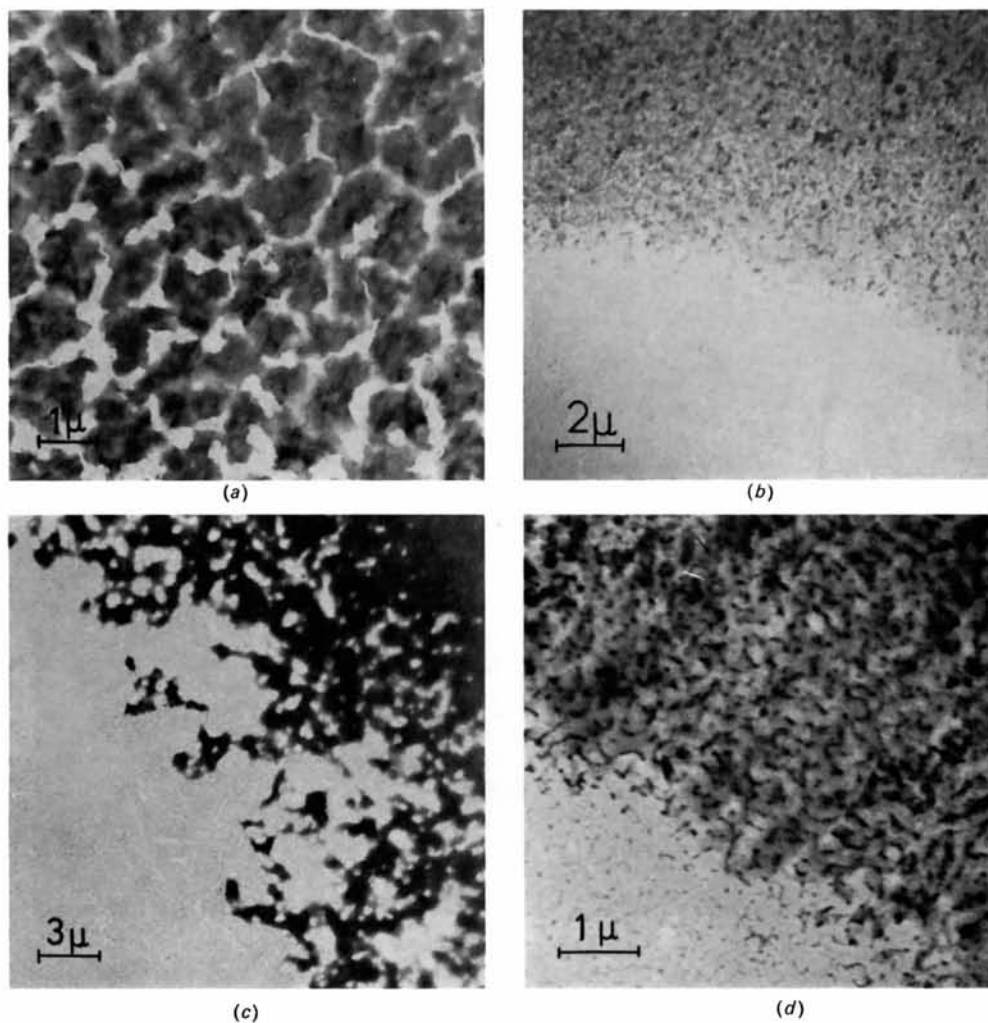


Fig. 2. Electron micrographs of solid oxygen deposits. (a) α' phase crystals; (b) β oxygen crystals; (c) γ phase crystals; (d) amorphous oxygen deposit. In the left lower corner of (b), (c) and (d) the oxygen deposit has already evaporated because of the high beam-current density used for taking the micrographs.

In our 1962 paper (Hörl, 1962) we assumed growth faults in the stacking of the (00·l) layers in order to explain the different widths of the diffraction lines. This assumption can be proved by the direct observation of 10·1 and 10·2 streaks in some β patterns. Fig. 3 shows a diffraction pattern of strongly faulted β crystals on an aluminum substrate. Streaks are clearly visible in the regions where 10·1 and 10·2 spots should appear in the case of perfect crystals. The angles between the streaks and the tangents to the Debye-Scherrer circles agree within the experimental error with the theoretical ones.

It should be noted that β films exhibited a preferred alignment of their crystals if deposited on single crystal molybdenite foils. The alignment was such that the (00·l) planes of a large number of the crystals were nearly parallel to the substrate and the (11·0) planes more or less parallel to the (10·0) planes of molybdenite.

γ oxygen

A cubic cell with eight O_2 molecules was found for γ oxygen (Vergard, 1935). The positions of the centres of the molecules were determined by Jordan, Streib, Smith & Libscomb (1964) to be: 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{4}\frac{1}{4}0$, $0\frac{1}{4}\frac{1}{4}$, $\frac{1}{2}0\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}0$, $0\frac{3}{4}\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$. This cubic structure can equally well be described by the hexagonal cell shown in Fig. 4. The letters A, B, C, . . . etc. represent centres of O_2 molecules with z coordinates equal to $c/12$, $2c/12$, $3c/12$, . . . etc. This hexagonal description of the γ structure will be of advantage in the discussion of the $\beta \rightarrow \gamma$ transformation (see below), since the hexagonal (00·l) layers of β oxygen can be related to the cubic (111) layers of γ oxygen.

The γ phase was obtained in transitions of α' and β oxygen (see below) and by the heating of extremely thick deposits with already very low electron transmission capacity. Polycrystalline γ films could be recrystallized quite readily by heating. In this way single

crystals of a few microns average size could be obtained.

An electron diffraction pattern of a polycrystalline γ deposit is shown in Fig. 1(c) and a single crystal pattern in Fig. 5. The powder pattern shows only rings corresponding to the 200, 210, 211, and 321 reflexions. The 321 ring is barely visible on the plate and does not show up on the print. The single-crystal pattern exhibits two strong reflexions of the 300 type. This is a very remarkable fact, since reflexions of this type are forbidden by the space group and can only be explained by double diffraction. A micrograph of a γ film is shown in Fig. 1(c). The microcrystallites are again of irregular shape.

Amorphous oxygen

Solid oxygen could also be observed in an amorphous phase by Bostanjoglo & Lischke (1967) and by the author. After irradiation with an electron beam of high current density ($>10^{-3}$ A.cm $^{-2}$ at 80 kV) of β deposits on substrates cooled with liquid helium a very broad and diffuse ring appeared in the diffraction pattern. The intensity maximum occurred at a d value of 2.85 Å [Fig. 1(d)]. It is believed that this disordered phase represents an amorphous phase; its formation even from a crystalline solid is hard to understand.

Oxygen transitions

In a number of papers transitions between the modifications of solid oxygen have been described and the transformation characteristics analysed (Barrett & Meyer, 1967; Barrett, Meyer & Wasserman, 1967b; Bostanjoglo & Lischke, 1967; Boersch, Bostanjoglo, Goertz & Lischke, 1968). In the following we will report on transitions which we have observed and which had not previously been observed, to our knowledge, in thin films by other investigators.

$\alpha' \rightarrow \gamma$ and $\alpha' \rightarrow \gamma + \beta$ transitions

The most remarkable transition observed was the transition from α' to γ oxygen without an intermediate β phase. When an α' film was heated by increasing the current density of the electron beam to $\gtrsim 10^{-3}$ A.cm $^{-2}$ (at 80 kV) a very sudden change in the electron diffraction pattern occurred. Within a fraction of a second the α' pattern changed to the γ pattern. In some cases the γ pattern did not show any trace of α' lines, indicating a complete transition; in other cases, the γ pattern did still show weak α' lines. In this case only part of the α' crystals underwent the transition. Since heating by an electron beam is nonuniform it could very well have been that the transition temperature was reached only in a part of the α' film.

$\alpha' \rightarrow \gamma$ transitions, were also observed, in which the diffraction pattern of the resulting phase showed lines of β oxygen together with γ lines. In one experiment the transition took place in such a way that the crystals of the γ phase were not preferentially aligned, while the

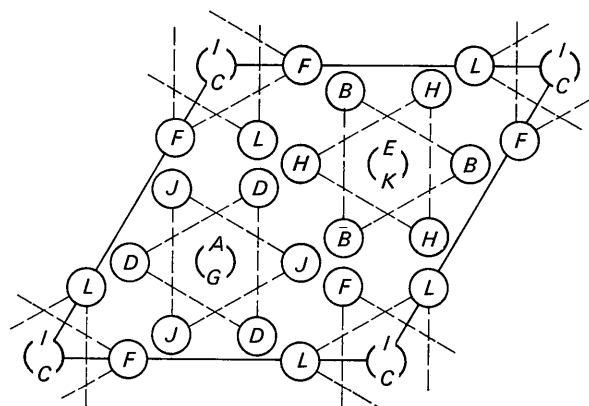


Fig. 4. Hexagonal cell for γ oxygen. The centres of the O_2 molecules are marked by letters. The letter A represents a centre with a z coordinate equal to $c/12$, the letter B a centre with a z coordinate equal to $2c/12$, the letter C a centre with a z coordinate equal to $3c/12$ etc.

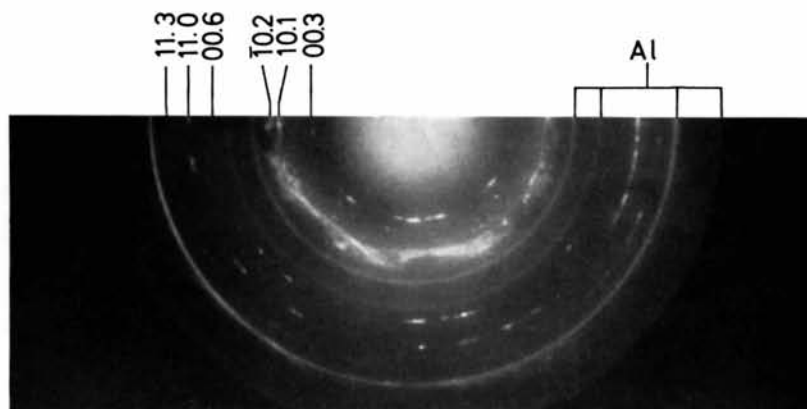


Fig. 3. Diffraction pattern of strongly faulted β oxygen crystals on an aluminum substrate. Streaks can be seen in the region where the 10.1 and $\bar{1}0.2$ ring should be visible in the case of perfect crystals.

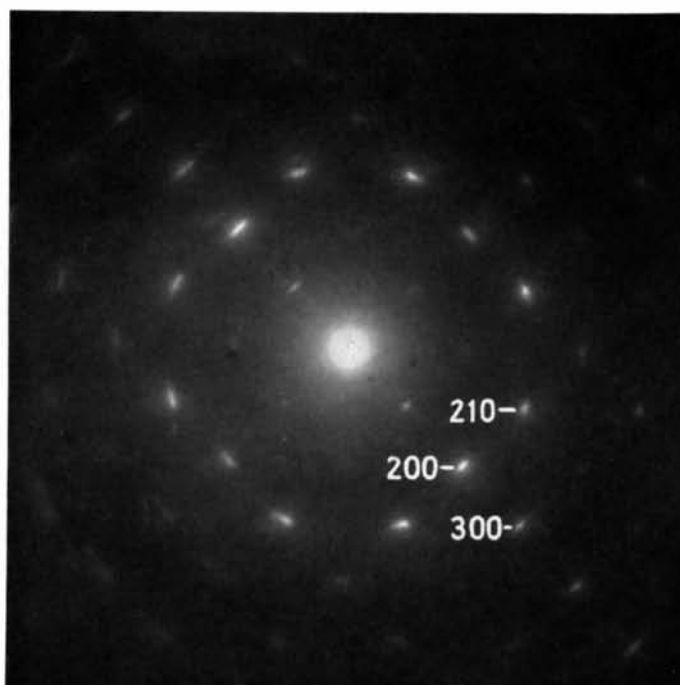


Fig. 5. Diffraction pattern of a single crystal of γ oxygen. $(100) \perp$ electron beam. Slight arcs are visible as a result of the mosaic structure of the crystal.

crystals of the β phase showed the preferred alignment already discussed above for β deposits on molybdenite substrates.

Since we have no information at present on the dimensions and structure of the α' cell we cannot make any suggestions on the transformation kinetics. Since the $\alpha' \rightarrow \gamma$ transition can take place without an intermediate β -phase being observed however, we might assume a similarity between the α' structure and the γ structure. This assumption of a similarity is also supported by the fact that the strong lines of the α' diffraction pattern lie within the same narrow range of d values as the strong lines of the γ phase (see Fig. 1).

$\beta \rightarrow \gamma$ transitions

Thick β oxygen layers could be transformed into γ layers by heating the layers with an electron beam of high current density. For the transition to occur it was necessary for the layer to be a few thousand Ångström units thick at the beginning so that it did not evaporate completely before the transition had taken place.

It should be noted that the transition occurred very readily (with only slight heating necessary) in strongly faulted β oxygen crystals with a diffraction pattern as shown in Fig. 3. This behaviour may be explained by the faults in the stacking of the $(00\cdot l)$ layers of the β crystals which increase the internal energy and favour the transition.

The transition itself may be understood in terms of a splitting of a single $(00\cdot l)$ layer of O_2 molecules of a β crystal into four (111) layers of molecules D, E, F and G for instance, of the γ phase crystal (see Fig. 6). Since the distances between the (111) layers of the γ phase are all equal and approximately equal to one fourth of the distance between the $(00\cdot l)$ layers of the β phase, the O_2 molecules do not have to be shifted by large amounts in order to form the γ structure.

The author would like to express his sincere thanks to Dr P. Koss for his continuous interest in this work and to Mr G. Groboth for his assistance in preparing the low temperature experiments.

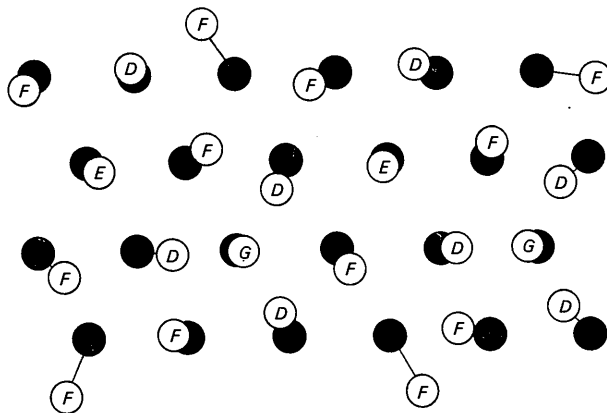


Fig. 6. Transformation of the β into the γ structure. The layers of O_2 molecules, D, E, F and G for instance, of the γ structure (see Fig. 4) can be formed from a single $(00\cdot l)$ layer of O_2 molecules of the β structure (black circles).

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