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The Crystalline Structure of Pt_3O_4

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By x-ray diffraction, the chemical formula and crystal structure of Pt_3O_4 have been established. The crystal lattice has a body-centered cube symmetry. The edges of the cubes are 6.226A long, and there are two molecules per unit cell. A chemical method for preparing this oxide has been given by Jörgensen but Wöhler claims that the compound thus obtained is a mixture of monoxide and dioxide rather than a separate chemical entity, see references 2 and 3.

INTRODUCTION

THE crystal structure of the platinum oxides has never yet been studied.[1] Neither has the chemical process used for their preparation been very clearly understood,[2,3] and in some cases even the existence of such platinum oxides has been doubted.[4] We have studied the crystalline structure of a compound formed on a platinum wire which has been used during 15 years in Duane's set up for the purification of radon. In this apparatus the wire was heated red hot to recombine oxygen and hydrogen. The available amount of the compound is very small and this fact makes its chemical analysis impossible, but the x-ray diffraction pattern is very neat and understandable. This compound is reduced to metallic platinum by heating it in the air. Using it as the cathode for the electrolysis of an aqueous solution of sulphuric acid, the nascent hydrogen reduces it to metallic platinum. Furthermore, in a report of Finch, Murison, Stuart and Thomson[5] it is pointed out that on some platinum plates heated in an atmosphere of oxygen, oxides were formed; and by electron diffraction they find, among the lines corresponding to platinum, other lines corresponding to spacings 4.4; 3.06; 2.06; 1.73 and 1.31A which correspond to the lines 1, 2, 5, 6, and 11 of our pattern.

These characteristics make us think that our compound is a platinum oxide. After the study of the x-ray diffraction pattern and the photometric measure of the intensities of its lines, we used Fourier's method to determine the coordinates of the oxygen atoms. On the basis of the results obtained we conclude that this compound must be Pt_3O_4, with two molecules per unit cell. The theoretical density is 8.8 g/cm³.

EXPERIMENTAL METHODS AND RESULTS

Figure 1 shows the Co-$K\alpha$ x-ray photograph made in a 28.85-mm radius Debye-Scherrer's camera. The lines 3′ and 14 only appear in some patterns and, besides being weak, their intensity

TABLE I. *Interpretation of powder photograph.*

Line No.	Indices	Spacings Obs.	Spacings Calc.	Structure Factors Obs.	Structure Factors Calc.	
1	110	4.400	4.402	− 31.3	− 37.2	
2	200	3.113	3.113	+ 77.2	+ 91.8	
3	211	2.552	2.540	− 25.8	− 33.4	
3′	—	2.275	—	—	—	111 of Pt
4	220	2.218	2.204	+110.7	+106.6	
5	310	1.987	1.967	− 28.5	− 31.0	
6	222	1.809	1.793	+ 58.5	+ 81.5	
7	321	1.653	1.662	− 24.8	− 29.1	
8	400	1.568	1.556	+ 91.0	+ 92.1	
9	{411}{330}	1.477	1.469	− 33.9	− 27.8	
10	420	1.399	1.388	+ 49.5	+ 76.4	
11	332	1.334	1.326	− 29.6	− 26.4	
12	422	1.277	1.270	+ 84.3	+ 83.2	
13	{431}{510}	1.225	1.220	− 35.0	− 25.2	
14	—	1.200	—	—	—	311 of Pt
15	521	1.140	1.139	− 21.2	− 24.3	
16	440	1.110	1.102	+ 75.9	+ 76.9	
17	{433}{530}	1.069	1.065	− 24.2	− 23.5	
18	{442}{600}	1.040	1.040	+102.1	+ 64.7	
19	{532}{611}	1.010	1.009	− 10.5	− 22.6	
20	620	0.984	.984	+ 71.9	+ 64.0	
21	541	0.959	.959	− 14.3	− 22.0	
22	622	0.936	.940	+ 37.4	+ 61.2	
23	444	0.915	.915	—	+ 68.6	

[1] W. J. Moore and L. Pauling, J. Am. Chem. Soc. **63**, 1392 (1941), reported a "highly probable" structure of PtO, by similarity with that of PdO.
[2] S. M. Jörgensen, J. prakt. Chem. **16**, 345 (1877).
[3] L. Wöhler, Zeits. f. Anorg. Chem. **40**, 423 (1904).
[4] A. Baroni, Atti Accad. Lincei **21**, 756 (1935).
[5] G. I. Finch, C. A. Murison, N. Stuart and G. P. Thomson, Proc. Roy. Soc. **A141**, 414 (1933).

FIG. 1. X-ray powder photograph of the unknown compound.

is not uniform all over their length as it is in the other lines; these spurious lines are due to the Pt of the wire on which the oxide was formed. When the oxide was scraped off, the lines of the pattern obtained showed the same characteristics as 3′ and 14, due to orientation of the platinum crystals.

All the other lines correspond to a body-centered cube structure, the length of the cube edge being 6.226A (Table I, columns 2 and 3). We have determined the relative intensities of the lines from the blackening in the photographic plate, using a recording microphotometer of the Zeiss type.

The structure factors have been computed from F. C. Blake's formula:[6]

$$I \propto p \cdot F_{hkl}^2 \cdot f(\theta) \cdot A \cdot e^{-2M},$$

where

p = multiplicity of the plane hkl

F_{hkl} = structure factor

A = absorption factor

e^{-2M} = temperature factor

$$f(\theta) = \frac{1+\cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta}.$$

We took for A and e^{-2M} the values from Blake's paper for the curves given there for Pt. With these values and the measured intensities, we computed (from Blake's formula) the relative values of F. The signs, however, still remain indeterminate.

In order to determine the arrangement of the atoms in our crystal lattice, we first resort to Wyckoff's tables[7] in which we find that the only space groups which admit a body-centered lattice are: T^3, T^5, O^5, O^8, T_h^5, T_h^7, T_d^3, T_d^6, O_h^9, O_h^{10}.

As the platinum atoms are the heaviest, we must find an arrangement of these atoms that will give for the structure factors values approaching the experimental ones. We assume

0	.04	.08	.12	.16	.20	.24	.28	.32	.36	.40	.44	.48	a/2
	564	492	294	139	111	95	100	125	112	90	142	1140	1210
.04	192	394	250	123	82	60	83		100		580		980
.08	294	230	152		62		$\bar{2}0$		44		97		470
.12	139	123		15		55		40		130		114	170
.16	111	82	62		127		136		164		77		94
.20	95	60		55		128		157		112		60	123
.24	100		$\bar{2}0$		136		158		129		$\bar{1}8$		100
.28	125	83		40		157		156		54		20	100
.32	112		44		164		129		144		46		91
.36	112	100		130		112		54		120		163	140
.40	90		97		77		$\bar{1}8$		46		80		81
.44	142	580		114		60		20		163		246	380
.48	1140		470		94		100		91		81		520
a/2	1210	980		170		123		100		140		380	568

FIG. 2. Fourier projection on (001) values of 0.263ρ.

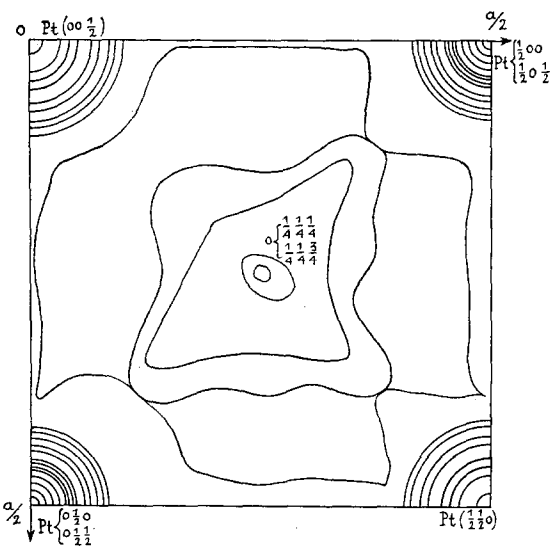

FIG. 3. Fourier projection on (001) lines of equal values of ρ.

[6] F. C. Blake, Rev. Mod. Phys. **5**, 169 (1933).

[7] R. G. Wyckoff, *Analytical Expression of the Results of the Theory of Space Groups* (1930).

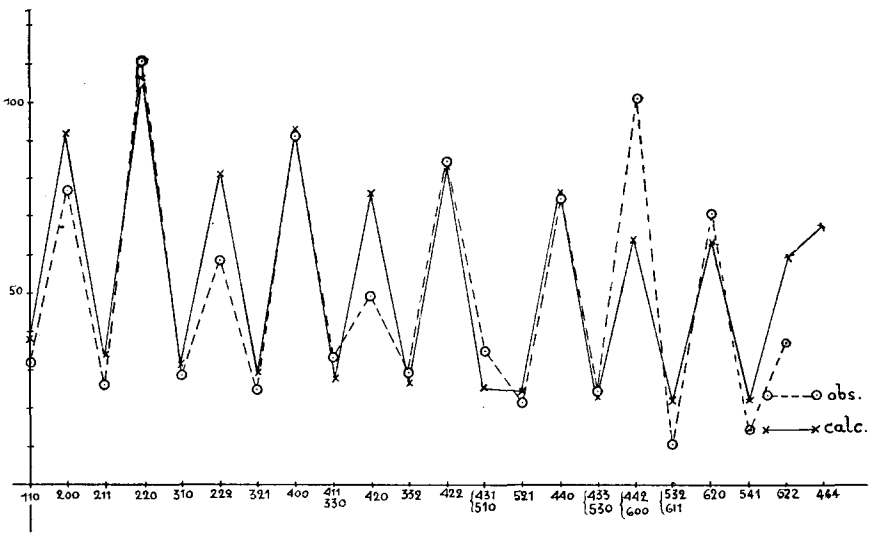

FIG. 4. Comparison of observed and calculated values of F_{hkl}.

that the presence of the oxygen atoms will only modify slightly the absolute value of the structure factor, without changing its sign. By trial, we found that the platinum atoms must occupy 6 equivalent positions in the arrangement noted as 6*e*, determined by the coordinates: $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$.

The theoretical structure factors for the assumed arrangement of the platinum atoms were calculated and the experimental values F_{hkl} were given the signs that were obtained. From the values of F_{hkl}, now known both in absolute value and sign, the values of the projections of the electron density on the 001 plane were obtained by Fourier's method.

Following Bragg and West[8] we used for our calculations the observed values F_{hk0} previously multiplied by the temperature factor $e^{-B\sin^2\theta}$, in order to increase the convergence of the series. We have chosen $n=2$. Figures 2 and 3 show the results obtained, including F_{000} which was calculated after knowing the total number of atoms per unit cell. The figures show that, besides the maxima of electron density due to the platinum atoms at 6*e*, other maxima are apparent at $\frac{1}{4},\frac{1}{4};\frac{1}{4},\frac{3}{4};\frac{3}{4},\frac{1}{4};\frac{3}{4},\frac{3}{4}$; which maxima correspond to the projection of 2 atoms of oxygen each. These atoms will therefore be located at the positions noted 8*e*, which coordinates are: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$. A final check shows that the experimental structure factors agree fairly well with the ones calculated assuming 6 Pt atoms at 6*e* and 8 oxygen atoms at 8*e* per lattice (Table I, columns 5 and 6, and Fig. 4). Therefore, we assume as the most probable for the compound, the structure shown in Fig. 5 and the chemical formula Pt_3O_4.

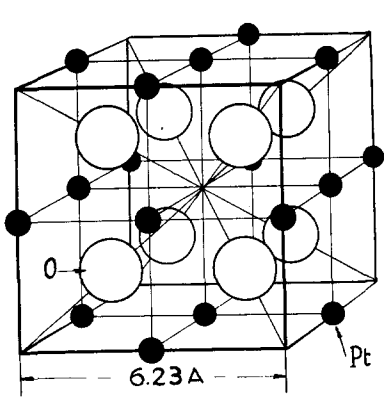

FIG. 5.

The distance between nearest atoms of Pt is 3.113A and that of Pt-O is 2.2A. From this data, the theoretical density is 8.8 g/cm^{-3}.

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[8] W. L. Bragg and J. West, Phil. Mag. **10**, 823 (1930).