Acta Cryst. (1953). **6**, 661

The Structure of PdO

By Jürg Waser

Department of Chemistry, The Rice Institute, Houston, Texas, U.S.A.

and Henri A. Levy and S. W. Peterson

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

(*Received* 19 *December* 1952)

On the basis of neutron and X-ray diffraction data, the structure of PdO is confirmed to be based on the space group D_{4h}^9–$P4_2/mmc$ with two PdO per unit cell. The cell dimensions are $a = 3{\cdot}03 \pm 0{\cdot}01$, $c = 5{\cdot}33 \pm 0{\cdot}02$ Å and the atomic positions are 2 Pd at $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and 2 O at $\frac{1}{2}, 0, \frac{1}{4}$; $\frac{1}{2}, 0, \frac{3}{4}$.

Introduction

The structure of PdO has been described on the basis of a tetragonal unit cell with 2 Pd at $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and 2 O at $\frac{1}{2}, 0, \frac{1}{4}$; $\frac{1}{2}, 0, \frac{3}{4}$. X-ray evidence favoring this structure was presented by Moore & Pauling (1941) after Huggins (1932; see also Pauling & Huggins, 1934) had advanced it as being compatible with data reported by Zachariasen (1927) and as providing the bond configuration expected for bivalent palladium. Moore & Pauling found that all reflections but one satisfied the criterion $h+k+l = 2n$, the exception being the very weak form (100). As they point out, the above structure fits these results since in it the palladium atoms, which do most of the scattering, form a body-centered grating. In the placement of the two oxygen atoms only positions $\frac{1}{2}, 0, z$; $\frac{1}{2}, 0, z+\frac{1}{2}$ were considered by them, and they chose the value $z = \frac{1}{4}$ essentially on the basis of the intensity of the (112) reflection. However, any pair of oxygen parameters permitting a (100) reflection is a potential candidate for a fit to the observed X-ray pattern. This entails a far wider latitude in the choice of positions than is covered by the above set since any tetragonal space group must be examined which contains besides the positions $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$—either as a twofold set or as two onefold sets—two further positions for which the (100) reflection is permitted. The structure supported by Moore & Pauling is nevertheless very satisfactory in crystal chemical respects, and is indeed confirmed by the present investigation involving the diffraction of neutrons as well as X-rays.

Experimental procedure

The oxide was prepared by a method suggested by Frampton, Edwards & Henze (1951), which results in a product that is free of metallic palladium. About 1 g. of palladium chloride is finely ground together with 9 g. dry $NaNO_3$. This mixture is added in one batch to a melt of about 100 g. $NaNO_3$ at 520° C. The reaction mixture is left to cool, after which the $NaNO_3$ is washed away with water.

The X-ray data were obtained with a Norelco High-Angle Spectrometer, using Cu K radiation filtered with nickel foil. The spectrometer utilized in collecting the neutron-diffraction data is to be described elsewhere (Levy & Peterson, 1954). The neutron wavelength was 1·16 Å. Both types of data were recorded two ways: (1) as counting rate, measured by an electronic rate meter and strip-chart recorder, and (2) as direct counts, suitably scaled down and printed on paper tape.

Fig. 1 shows the neutron and below it the X-ray diffraction patterns, the latter against a non-linear

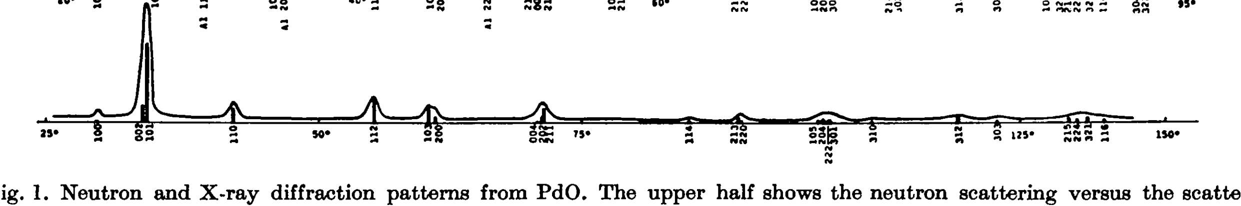

Fig. 1. Neutron and X-ray diffraction patterns from PdO. The upper half shows the neutron scattering versus the scattering angle 2θ. A much weaker line represents the scattering due to the aluminum sample holder. The lower half represents the X-ray scattering of PdO with a non-linear scale of 2θ adjusted so that the two curves can be directly compared. Calculated intensities are indicated by narrow black vertical rectangles.

Table 1. *Calculated spacings and calculated and observed intensities*

		X-rays			Neutrons		
hkl	*d* (Å)	$I_c \times 10^{-3}$		$I_o \times 10^{-3}$	I_c		I_o
100	3·04	4		3	74		94
002	2·68	41	261	(261)	0·2	133	(133)
101	2·64	220			133		
110	2·15	43		37	0·3		—
102	2·005	2		—	67		92
112	1·672	66		67	205		211
103	1·537	39	62	63	47	132	128
200	1·520	23			85		
210	1·360	0·4			32	138	135
004	1·338	7	70	71	34		
202	1·319	18			0·2		
211	1·318	45			72		
104	1·223	0·2		—	27	80	99
212	1·209	0·4		—	53		
114	1·133	12		12	0·2		
213	1·080	26	34	34	44	91	80
220	1·073	8			47		
300	1·013	0·1			10	140	132
105	1·008	12	48	44	23		
204	1·002	14			84		
222	0·996	10			0·1		
301	0·995	12			23		
310	0·961	10		9	0·1	54	24
214	0·952	0·2			36		
302	0·948	0·1			18		
312	0·902	30	33	28	146	165	177
006	0·896	3			0		
303	0·880	13		12	19		
106	0·854	0·1			16	283	204
320	0·843	0·1			16		
215	0·840	33	110	81	37		
224	0·836	20			67		
321	0·831	35			36		
116	0·823	22			66		
304	0·807	—			15		
322	0·803	—			30		
314	0·779	—					

scale of the scattering angle 2θ, which was adjusted so that the X-ray reflection of a given form would have the same position as the corresponding neutron reflection. Calculated intensities are represented by solid vertical lines. Both patterns could be indexed on the basis of the tetragonal cell reported by Moore & Pauling (1941) and by Zachariasen (1927). The cell dimensions providing the best fit with the X-ray data were

$$a = 3{\cdot}03\pm0{\cdot}01,\ c = 5{\cdot}33\pm0{\cdot}02\ \text{Å}\,.$$

Derivation of structure

The neutron pattern is seen to satisfy the extinction criterion that *hhl* occurs only if $l = 2n$. This leads to the probable space groups C_{4v}^7–$P4mc$, D_{2d}^2–$P\bar{4}2c$, D_{4h}^9–$P4_2/mmc$, which all contain a body-centered set of positions suitable for the palladium atoms. Appropriate placement of the origin permits description of this set by the parameters 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Furthermore, provided the a axis is properly oriented, all non-body-centered twofold sets in the above three space groups are embraced by the parameters $0, \frac{1}{2}, z$; $0, \frac{1}{2}, z+\frac{1}{2}$. The value of z is general for the hemihedral space group but must be either 0 or $\frac{1}{4}$ for the two holohedral space groups. This is precisely the set considered by Moore & Pauling (1941). Indeed it is evident that these two sets call for the more stringent extinction conditions that only reflections can occur for which either $h+k+l = 2n$ or $l = 2n$. This is fully compatible with observations, as may be seen in Fig. 1

The value of the parameter z which is in best agreement with the neutron-diffraction pattern was found to be $z = \frac{1}{4}$. In particular, the absence of the neutron reflection (114) is in agreement with this value, as with it there is near cancellation of the scattering amplitudes due to oxygen and to palladium. (A deviation of about 0·025 from $z = \frac{1}{4}$ would give rise to a (114) peak amounting to about 10% of either of the two adjoining peaks, (104)+(212) or (213)+(220).) Table 1 contains the calculated spacings of the PdO grating and calculated and observed intensities for X-ray as well as neutron scattering. The following formulas, with the usual meaning of symbols, were used for the calculated intensity values:

For X-rays (flat sample),

$$I = \frac{1+\cos^2 2\theta}{2\sin\theta\sin 2\theta} j|F|^2 .$$

For neutrons (cylindrical sample),

$$I = \frac{j|F|^2}{\sin\theta\sin 2\theta} .$$

The X-ray atom form factor for palladium was obtained by averaging the Pauling–Sherman (1932) values with those of Thomas–Fermi (*Internationale Tabellen*, 1935), while for oxygen the scattering factor based on Hartree's model was used. The neutron scattering amplitudes taken were $0{\cdot}58 \times 10^{-12}$ cm. for oxygen and $0{\cdot}63 \times 10^{-12}$ cm. for palladium, as determined by Shull & Wollan (1951). The absorption correction was a constant factor in the X-ray case and negligible for the neutron experiment. The observed intensities were found by summing the counts recorded on the paper tape for a given peak and subtracting the background. The neutron data were corrected for the effect of the sample holder, which was made of thin aluminum. Its scattering is shown in Fig. 1 by a thin line. The observed data were brought to an absolute scale by matching the values for the peak due to the (002) and (101) reflections.

The agreement between observed and calculated values is satisfactory, allowing for the large background observed which is probably caused by small particle size and by amorphous material present. The tendency of the observed intensity I_o to be low at large scattering angles is doubtless due to a temperature effect. The poor agreement for the neutron reflections (214) and (302) is probably due to the background being estimated too high in this neighborhood.

The neutron pattern contains four peaks due to oxygen scattering alone: (100), (102), and the unresolved peaks (104)+(212) and (214)+(302). For the first three of these peaks the observed intensity is some 25% too large (the last one being unreliable as just discussed). This may be an indication that the scattering amplitude used for palladium was perhaps too large (the peak utilized to establish the scale factor for the observed values being essentially due to palladium scattering) or that for oxygen too small, the latter being less probable. We may remark that this discrepancy does not depend on the exact value of the parameter z.

This work was performed at the Oak Ridge National Laboratory under the auspices of the Atomic Energy Commission. Our thanks are due to Mr B. S. Borie for the use of a Norelco High-Angle Spectrometer. One of us (J. W.) gratefully acknowledges the hospitality of the Oak Ridge National Laboratory for the summer 1951.

References

FRAMPTON, V. L., EDWARDS, J. D. & HENZE, H. R. (1951). *J. Amer. Chem. Soc.* **73**, 4432.

HUGGINS, M. L. (1932). *Chem. Rev.* **10**, 427.

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Bornträger.

LEVY, H. A. & PETERSON, S. W. (1954). To be published.

MOORE, W. J. & PAULING, L. (1941). *J. Amer. Chem. Soc.* **63**, 1392.

PAULING, L. & HUGGINS, M. L. (1934). *Z. Krystallogr.* **87**, 205.

PAULING, L. & SHERMAN, J. (1932). *Z. Krystallogr.* **81**, 1.

SHULL, C. G. & WOLLAN, E. O. (1951). *Phys. Rev.* **81**, 527.

ZACHARIASEN, W. H. (1927). *Z. phys. Chem.* **128**, 412.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1953). **6**, 663

A technique for testing the piezoelectric properties of crystals.

By YOICHI IITAKA, *Mineralogical Institute, University of Tokyo, Hongo, Tokyo, Japan*

(*Received* 24 *March* 1953)

Bergmann (1935) examined piezoelectric substances by subjecting them to a periodic pressure at audio-frequency and measuring the charge produced. We likewise impress a periodic pressure by means of a vibrator coupled with an oscillator circuit (1,000 c./sec.) but the charge generated, instead of being measured directly, is led through the vibrator to a cathode-ray oscillograph after appropriate amplification. The abscissa of the oscillograph is synchronized with the oscillator circuit. This device renders piezoelectricity visible and provides a very convenient means for testing the piezoelectric properties of crystals.

A small slip of crystal set upon a flat electrode is pressed by the needle electrode of the vibrator which is capable of a fine vertical movement for adjustment. Best results are obtained by inserting sheets of insulating paper between the crystal to be tested and the electrodes.

A feature of the device is that we can not only detect