Structural behavior of palladium (II) oxide and a palladium suboxide at high pressure: An energy-dispersive x-ray-diffraction study

Andrew G. Christy

Daresbury Laboratory, Warrington WA4 4AD, England and Department of Chemistry, University of Leicester, Leicester LE1 7RH, England

> Simon M. Clark Daresbury Laboratory, Warrington WA4 4AD, England (Received 2 May 1994)

The behavior of PdO at high pressure was studied by energy-dispersive x-ray diffraction of samples contained in diamond anvil cells. PdO undergoes a first-order transition at about 12 GPa. The new phase is tetragonal and of similar cell dimensions to the low-pressure phase. However, it is more compressible along c and much harder along a. The volume change is 1.7%. It is likely that the new phase has the rocksalt structure, tetragonally elongated due to the low-spin d^8 electron configuration of palladium (II). The zero-pressure cell parameters and bulk moduli are (low pressure phase) a = 3.042(1) Å, c = 5.351(3) Å, $K = 280\pm52$ GPa; (high pressure phase) a = 2.982 Å, c = 5.383 Å, $K = 545\pm20$ GPa. One sample prepared was found to be a mixture of PdO with a cubic material [Fm 3m, a = 4.043(5) Å at ambient], deduced to be a suboxide PdO_x with x approximately 0.21-0.27. Under pressure, the two phases reacted reversibly: PdO was consumed and x increased with increasing pressure. This led to expansion of the suboxide unit cell with pressure up to 1.73 GPa, above which pressure the calculated value of x remained approximately constant and the lattice constant decreased in the usual fashion. It is evidently possible to construct mixtures of these two phases which show zero total change in the lattice constant of the cubic phase over a selected range of pressure.

I. INTRODUCTION

The stereochemistry of palladium and platinum (II) is dominated by their preference for square planar coordination, which leads to the adoption of unusual structures by their compounds. This effect arises because the lowspin d^8 electronic configuration of their divalent ions renders regular octahedral coordination unstable with respect to large tetragonal elongations. The increased repulsion of paired spins in the d_{z^2} orbital, as opposed to equally occupied d_{z^2} and $d_{x^2-y^2}$ orbitals, is more than compensated by the lowering in energy of d_{z^2} due to crystal-field splitting, and by the possibility of using the unoccupied $d_{x^2-y^2}$ orbital to form four strong dsp^2 hybrid σ orbitals to ligands. This phenomenon is in some respects the inverse of the well-known Jahn-Teller effect in that inequivalent occupation of the two e_g levels is not intrinsic, but is driven by the potential for stronger bonding in a low symmetry environment. For d^4 or d^9 species showing the Jahn-Teller effect, such as Cu(II), the loss of degeneracy is inherent in the electronic configuration, and drives the distortion.

PdO adopts a simple tetragonal structure under ambient conditions, with a=3.03 Å, c=5.33 Å, space group $P4_2/mmc$, and Z=2, in which the Pd atoms are approximately square planar and the oxygens are approximately tetrahedrally coordinated¹ (Fig. 1). An interesting feature of the structure is that linkage of the coordination polyhedra is such that the ideal symmetries cannot be adopted simultaneously: squares are flattened and tetrahedra elongated along z, and the observed O-Pd-O angle is intermediate between the ideal values of 90° and 109.5°. There is some spectroscopic evidence that thin films of PdO on Pd metal adopt the litharge structure (P4/nmm) with cell parameters similar to those of the $P4_2/mmc$ phase,² but with Pd in a square-pyramidal en-



FIG. 1. The PdO structure under ambient conditions, viewed down [110].

52 9259

vironment. Both structures can be regarded as containing expanded and distorted versions of the Pd arrangement found in Pd metal, which is face-centered cubic, but the pattern of occupation of tetrahedral interstices by oxygen differs.

Given the distinctive stereochemistry of Pd under ambient conditions, an x-ray-diffraction study was conducted of PdO at high pressure, in order to investigate its compression and phase transition behavior. An early attempt to synthesize PdO produced a cubic material, probably a suboxide PdO_x , which displayed apparent negative compressibility up to 1.7 GPa. Results from this sample are also reported and discussed.

II. EXPERIMENT

Palladium oxide was synthesized by a method similar to that of Waser, Levy, and Peterson.¹ One 0.5 g batch of PdCl₂ powder was reacted with a large excess of molten KNO₃ in a ceramic crucible for 6 h at 550 °C. A blackbrown solid was separated from potassium salts by dissolution of the latter in water and filtration. X-ray diffraction of the water-insoluble residue gave PdO peaks plus some additional reflexions, implying incomplete reaction between PdCl₂ and the nitrate melt. A second batch was prepared by reaction of PdCl₂ with NaNO₃ at 550 °C for two days. Again, the product was a fine black powder with a brownish tinge. Some slow gas evolution (either desorbed air or exsolved oxygen) was noticed when the powder was suspended in water. Therefore, after filtration and drying, the sample was roasted in air at 550 °C for another 6 h to ensure full oxidation. X-ray

diffraction showed no peaks that did not belong to PdO.

Samples were ground with NaCl, which acted as an internal pressure calibrant, and loaded into diamond anvil cells with nujol as a quasihydrostatic pressure medium. For the first sample, a short-piston diamond anvil cell was used, with 0.5 mm anvil faces. The gasket was of inconel, approx. 250 μ m thick, with a gasket hole approx. 200 μ m in diameter. The maximum pressure attained was about 10.6 GPa, at which the gasket showed signs of incipient failure. In order to extend the accessible pressure range, the second sample was loaded in to a long-piston diamond anvil cell with 0.3 mm anvil faces, using a 100 μ m gasket hole.

Energy-dispersive diffraction data were collected at Station 9.7 of the Daresbury Synchrotron Radiation Source, using a diffraction angle 2θ of about 10°. This angle was refined using a silicon standard as 9.5386° for the first sample and 9.8583° for the second. The data collection time was 1000 s per spectrum. Unit cells were refined with the REFCEL program using the 002, 101, 110, 112, 103, and 200 reflexions for PdO, and the 111, 200, and 220 reflexions of the cubic phase. Sample pressures were estimated using the lattice parameter of NaCl to an accuracy of ± 0.05 GPa for low pressures, ± 0.1 GPa at 10 GPa, and ± 0.5 GPa at the highest pressure of this study (27.3 GPa).

III. RESULTS

The first sample under ambient conditions gave a complex pattern containing peaks from tetragonal PdO and

(b)





FIG. 2. Energy-dispersive xray spectra at atmospheric pressure. F indicates Pd K fluorescence peaks; C indicates calibrant Bragg peaks. (a) The initial spectrum from the suboxide-bearing sample. Peak clusters indicate inhomogeneity. (b) After high-pressure data collection. The indices of the Pd peaks are shown. (c) Pure PdO. The indices of the PdO peaks are shown. (d) Pd metal with Bragg peaks from PdO indicated by X.



FIG. 3. Variation of cell edge with pressure for PdO_x . Squares indicate data obtained on decreasing pressure.

others which did not belong to that phase. The strongest of these were at slightly lower energy (larger d spacing) than would be expected for the 111 reflexion of Pd metal. Very slight pressurization (0.6 GPa) resulted in the disappearance of the PdO reflexions, and the merger of groups of the strong additional reflexions so as to produce isolated broad peaks, which indexed as belonging to a facecentered cubic cell with a = 4.04 - 4.09 Å (cf. 3.889 Å for Pd metal). Unusually, the peak energies decreased with pressure up to 1.73 GPa, implying "negative compressibility," and then began to increase normally. This behavior was found to be completely reversible, except that a homogeneous cubic phase remained when the sample was taken back to atmospheric pressure-the PdO peaks did not reappear. The cell parameter of the cubic phase at ambient was 4.043(5) Å.

The initial state of the sample was interpreted to be a mixture of PdO with an inhomogeneous and nonstoichiometric suboxide, PdO_x , which could be regarded as Pd metal with some oxygen in interstitial solid solution, leading to the increased lattice parameter. Pressuri-

TABLE I. Zero-pressure cell parameters and compressibilitydata for the phases of PdO.

	Low pressure	High pressure
<i>a</i> (Å)	$3.042(1)^{a}$	2.982 ^b
<i>c</i> (Å)	5.351(3) ^a	5.383 ^b
$K (GPa)^c$	280(52)	545(20)
$-(10^{3}/a)da/dP (GPa^{-1})^{d}$	4.6(9)	2.9(10)
$-(10^{3}/c)dc/dP (GPa^{-1})^{d}$	2.1(7)	1.3(2)

^aMeasured.

^bExtrapolated.

^cThird-order Birch-Murnaghan equation of state with K'=4. ^dReciprocals of moduli obtained by Birch-Murnaghan fit to *a* or *c* rather than $V^{(1/3)}$.



FIG. 4. Variation of a and c with pressure for PdO.

zation was deduced to cause homogenization of the PdO_x , and increase in its oxygen content by consumption of the PdO. The volume increase due to compositional change more than compensated for the pressure-induced compression, leading to the unusual observed behavior of the cell parameter. It should be noted that the expansion of the unit cell with increasing pressure cannot be iso-chemical, since this would imply spinodal instability with respect to decomposition into a mixture of high-density and low-density phases. Migration of oxygen into the lattice with pressure is therefore the only plausible explanation for this phenomenon.

Energy-dispersive x-ray spectra for sample 1 at atmospheric pressure are shown before and after compression in Figs. 2(a) and 2(b), respectively. These may be compared with that for the second sample [Fig. 2(c)] and a mixture of sample 2 with Pd metal [Fig. 2(d)]. The anomalous compression of PdO_x may be seen in Fig. 3.

The second sample showed no evidence of any Pd-rich phases other than tetragonal PdO. Cell parameters decreased with pressure in the normal fashion, but a reversible discontinuity in a and break in the slope of c were noted between 10.2 and 13 GPa.

This was interpreted as a first-order tetragonaltetragonal phase transition with a volume change of about 1.7%. Data for the low- and high-pressure phases were fit to the third-order Birch-Murnaghan equation of



FIG. 5. Variation of unit cell volume with pressure for PdO.

state with the pressure derivative of the bulk modulus fixed at 4, since attempts to refine this parameter gave badly constrained results. The zero-pressure cell parameters, cell volumes axial compressibilities, and bulk moduli for the two phases are given in Table I. The compression behavior of the cell parameters and cell volume may be seen in Figs. 4 and 5, respectively.

Palladium metal was prepared from sample 2 by heating in air at 950 °C for two days. The metal was mixed with sample 2 and compressed in order to investigate whether Pd and PdO would react to form the suboxide. No such behavior was observed: the PdO behaved as before, and the Pd cell parameters decreased as expected from published equation of state data.³ The suboxide is clearly metastable with respect to Pd+PdO on the time scale of the experiment.

IV. DISCUSSION

The suboxide

The variable composition, cubic cell parameter, and anomalous compression behavior all imply that the new phase is PdO_x . It is noteworthy that whereas coexistence of the cubic suboxide with stoichiometric, tetragonal PdO was observed in this study, a tetragonal suboxide has been documented previously, but only as tails on powder rings in an electron diffraction study of thin films.⁴ The observation of such a phase in a thin film but not in the bulk solids of this study lends credence to the possibility that the PdO structures are different: the PdO_{1-x} phase of Ref. 4 may be an oxygen-deficient variant of PdO with the litharge structure, analogous to mackinawite, FeS_{1-x} , which has the antilitharge structure.⁵ The suboxide of this study, with a variable amount of oxygen dispersed in a slightly expanded Pd lattice, is more reminiscent of the hydride α -PdH_x. This is one of two related palladium hydride phases: α -PdH_x, best regarded as an interstitial solid solution of H in Pd with x = 0-0.02 and metastably to 0.08, and β -PdH_x with the rocksalt structure, in which x = 0.6 - 1. There is a miscibility gap between these phases.⁶ The continuity of the $Pd-\alpha PdH_x$ solid solution allows Pd metal to absorb up to several hundred times its volume of gaseous hydrogen. A nonstoichiometric PdO_x phase would have considerable potential as a solid-state oxygen reservoir, although the lack of reaction between Pd and PdO implies both that the suboxide is metastable and that the solid solution to Pd metal is not continuous.

The coexistence of PdO with the suboxide implies that it is at its oxygen-rich solid solution limit. The observed reversibility of the cell parameter evolution with pressure indicates that oxygen exchange between the two phases is very rapid. However, the abrupt change in sign of compressibility near 1.8 GPa may be due to one of two causes: either (i) all the PdO is consumed, and the composition remains constant at higher pressures, or (ii) PdO is still present, but the uptake of oxygen by PdO_x becomes too slow to compensate for the pressure-induced volume decrease. It was not possible to distinguish the two unequivocally, but estimates of x suggest that the first alternative is more likely.

The oxygen content x was estimated by two different methods. First, it was assumed that the all Pd-O phases obeyed Vegard's Law. That is, that the volume per formula unit varied linearly with x. Interpolation from the known volume data for Pd and PdO then gave x as 0.18 at ambient, 0.25 at 1.73 GPa, and 0.27 at 10.56 GPa. There is therefore almost no change in x above the change in slope. A second, more complex method of estimated x was also employed. PdO_x was treated as an ideal solid solution between two hypothetical end members Pd*, and PdO*, which were permitted to be energetically different from the real Pd and PdO in order to take account of possible nonidealities in solid solution behavior. The reaction can be modelled

 $(1-x)Pd^*(solid soln.) + xPdO(tetrag.) = PdO_x(cubic)$,

which, since the solid solution is ideal for the chosen end-member standard states, is energetically equivalent to

$$x PdO(tetrag.) = x PdO^*(solid soln.)$$
.

The free energy for this reaction is $G(PdO^*)$ - $G(PdO) + RT \ln x$, and at equilibrium

$$\ln x = \{G(PdO) - G(PdO^*)\} / RT$$

Taking pressure derivatives

$$(1/x)(dx/dP) = \{V(PdO) - V(PdO^*)\}/RT$$

The term on the left can be calculated directly from the measured cell data with only the assumption that Henry's Law applies between Pd and PdO_x, i.e., that x is small enough for Pd=Pd*. An analytical curve of the form $\Delta a = (c_1 + c_2 P)/(c_3 + P)$ was empirically found to give the best fit to the difference between the measured cell parameter for PdO_x, and the corresponding parameter for Pd calculated using the Birch equation from³

$$a = a_0 / \{1 + K' / [\ln(1 + P/K)]\}$$

where $a_0 = 3.889$ Å, K' = 16.1, and K = 34.35 GPa. Differentiation of the Δa curve then allowed calculation of $[V(PdO)-V(PdO^*)]$ and x. The values of V in Å³ per formula unit were 2.01, 0.26, and 0.01 at 0, 1.73, and 10.56 GPa, respectively. The corresponding values of x were 0.23, 0.26, and 0.27. Values obtained by averaging those from the two methods are 0.21(3), 0.26(1), and 0.27. The increase in x is clearly insignificant above 1.73 GPa, supporting the conclusion that all the PdO is consumed at this pressure.

It is clear that for PdO_x in reversible equilibrium with PdO, the limiting value of x is close to 0.25, and increases with pressure up to at least 1.73 GPa. Establishing the true solid solution limit at higher pressures would require study of a PdO_x -PdO mixture with a greater proportion of PdO. No evidence of ordering was seen, although stoichiometric compounds Pd_4S and Pd_4Se are known (albeit with a very different structure).⁷

It should be noted that the total volume of $PdO+PdO_x$ solid decreases normally with pressure, since $V(PdO^*) < V$ (PdO). Only the lattice constant of the cubic phase shows the apparent negative compressi-







FIG. 7. Variation of O-Pd-O bond angle with pressure for PdO. The same caveat applies as for Fig. 6.

bility behavior. Nevertheless, it should be possible in principle to prepare mixtures of a PdO_x phase plus trace of PdO that display zero total lattice parameter change in the cubic phase over a chosen range of pressure. It is likely that the same buffering effect on lattice spacing will be observed in other two-phase mixtures. An obvious potential application is the maintenance of coherent interfaces over a wide range of applied stresses.

The low-pressure PdO phase

Since both Pd and O atoms are on fixed special positions in the $P4_2/mmc$ structure, the Pd-O bond length and O-Pd-O bond angle can be calculated directly as $\sqrt{(a^2/4+c^2/16)}$ and $2\tan^{-1}(2a/c)$, respectively. The variation of these parameters with pressure is shown in Figs. 6 and 7. It is clear that the PdO₄ rectangle becomes more square in shape with pressure, implying that the Pd contribution to the bonding orbitals becomes more nearly ideal dsp^2 , whereas the oxygen contribution becomes less ideal sp^3 . This in turn suggests a shift in electron density toward Pd with pressure, i.e., increasing covalency. The very low compressibility along c (Table 1) is a consequence of the very short O-O distance in that direction $(c/2 \approx 2.67 \text{ Å})$.

While considering interatomic distances, it is notable that there are no short Pd-O distances other than the four coplanar ones at 2.02 Å (at atmospheric pressure). The next nearest neighbors of Pd are 2 Pd at 3.03 Å (compare 2.75 Å in Pd metal), 8 Pd at 3.42 Å, and then 8 O at 3.64 Å.

High-pressure phase of PdO

The new high pressure phase of PdO could have one of a number of crystal structures with the litharge structure, the CuO structure and a tetragonally distorted rocksalt 9264



FIG. 8. The simplest transformation mechanism from PdO through the tenorite structure to a rocksaltlike structure.

structure being good candidates.

The high-pressure phase is tetragonal with similar cell dimensions to the low-pressure phase. It is possible that the structural change is electronic in nature with no atomic displacements, as in the case of Ce metal.⁸ However, the increased compressibility along c in the high-pressure phase suggests otherwise. If the structure is assumed to remain the same, then the decrease of O-Pd-O bond angle with pressure also ceases, as can be seen in Fig. 7.

One possibility is the litharge structure. This is derived from the $P4_2/mmc$ structure if one of the oxygens in the cell is displaced by (a+b+c)/2, thus producing a layer structure with Pd-Pd bonds between layers. The indices of the observed reflexions are compatible with both space groups, and the relative compressibilities along **a** and **c** axes are compatible with a structure built from (001) layers. However, the compressibilities are an order of magnitude smaller than for litharge-structure oxides such as PdO and SnO.⁹

An alternative structure that accounts for the very large bulk modulus (545 GPa) for this phase is a tetragonally elongated version of the rocksalt structure, with space group I4/mmm, produced by movement of the oxygens along [101] and [011] into octahedral sites. The Pd-O bond lengths would be 4×2.11 Å and 2×2.69 Å at zero pressure, comparable with those observed in the Jahn-Teller distorted octahedra of CuO [4×1.96 Å and 2×2.78 Å (Ref. 10)]. If bond length r and bond strength s are assumed to be related by the power law

TABLE II. PdO and NaCl structures described as special cases of the tenorite structure.

	PdO ^a	CuO	NaCl(cubic) ^b NaCl(tetrag.) ^{b, c}		
c/a	1.24 obs ^e	1.09 obs	1	1	
β/deg	90	99.5 obs	109.5	109.5	
$(c/a)\cos\beta$	0	-0.18 obs	-0.33	-0.33	
b/a	1	0.73 obs	0.57	0.48 obs	
y ^d	0.5	0.42 obs	0.25	0.25	

^aPdO structure in $C4_2/mcm$ setting (note that C2/c is a subgroup of this).

^b[100]_{Cu0}||[11-2]_{NaCl}; [010]_{Cu0}||[1-10]_{NaCl}; [001]_{Cu0}||[112]_{NaCl}. ^cNaCl(tetrag.) is the tetragonally elongated rocksalt structure, using the cell parameters for the high pressure phase of PdO. ^dy is the oxygen y coordinate.

^eobs indicates measured values that are not constrained by symmetry.

 $s = (r_0/r)^{n,11}$ and r = 2.02 Å for s = 0.5 in the lowpressure phase, then the bond strengths in this phase are 4×0.42 and 2×0.16 , totaling 2, for $r_0 = 1.70$ Å and the small but reasonable value n = 4.0 (*n* would be expected to be 6 for a closed-shell 4*d* cation).

Although the oxygen displacements required to transform to the rocksalt structure are simple, they cannot occur in one step if each step utilizes one of the available lattice vibrational modes, as in the transformation model of Christy.¹² If the departures from tetragonal symmetry are kept small, then at least five discrete steps are needed. A C2/c intermediate involved in several of the pathways is in fact the tenorite (CuO) structure, however, and it was shown by Zemann¹³ that this becomes either the PdO structure or the rocksalt structure with appropriate values of those structural parameters that are not constrained by symmetry (Table II). Considerable monoclinic distortion is involved in converting one high symmetry structure to the other, but the only displacive change is in the unconstrained y coordinate of the oxygen in the C2/cstructure. The displacement involved can be described on rocksalt axes as movement of alternate (111) planes of oxygen atoms along $\pm [1-10]$, which corresponds to a lattice vibration at the Brillouin zone boundary symmetry point (0.5, 0.5, 0.5) for cubic or tetragonally distorted rocksalt. Therefore, the transformation can be accomplished in two steps (Type 2 of Ref. 12) with the tenorite structure as a mechanistic as well as a geometric intermediate between PdO and rocksalt structures (Fig. 8).

The CuO structure is intermediate between cubic rocksalt and PdO in its geometry, and allows elongated octahedral coordination of the Cu atom. Madelung energy calculations suggest that for CuO, the distortion pattern giving C2/c symmetry should be slightly more stable than a tetragonally elongated rocksalt structure.¹³ However, this appears not to be the case for high-pressure PdO, where the distortion of the coordination octahedron that is required by the electron configuration of Pd(II) is accommodated by tetragonal elongation of the structure.

In view of the above considerations we conclude that the high pressure phase of PdO probably has a tetragonally elongated version of the rocksalt structure.

ACKNOWLEDGMENTS

This study was initiated under Science and Engineering Council Grant No. GR4/04844 to S.M.C. and Dr. D. M. Adams (University of Leicester). ¹J. Waser, H. A. Levy, and S. W. Peterson, Acta Crystallogr. 6, 661 (1953).

Manchester, J. Less-Common Met. 49, 67 (1976).

- ⁷F. Grønvold and E. Røst, Acta Crystallogr. 15, 11 (1962).
- ²S. G. Gargarin, Yu. A. Teterin, A. P. Kovtun, and A. L. Gubskii, Russ. J. Inorg. Chem. 28, 1561 (1983).
- ³W. F. Sherman and A. A. Stattmuller, *Experimental Techniques in High Pressure Research* (Wiley, Chichester, 1987).
- ⁴S.Yamaguchi, Fresenius Z. Anal. Chem. **303**, 409 (1980).
- ⁵L. A. Taylor and L. W. Finger, Carnegie Inst. Washington Pap. Geophys. Lab. Ann. Rep. **69**, 318 (1970).
- ⁶G. C. Libowitz, *The Solid State Chemistry of Binary Metal Hydrides* (Benjamin, New York, 1965); J. K. Jacobs and F. D.
- ⁸A. W. Lawson and T. Tang, Phys. Rev. **76**, 301 (1949); A. F. Schuch and J. H. Sturdivant, J. Chem. Phys. **18**, 145 (1950).
- ⁹D. M. Adams, A. G. Christy, J. Haines, and S. M. Clark, Phys. Rev. B 46, 11 358 (1992).
- ¹⁰S. Åsbrink and L.-J. Norby, Acta Crystallogr. B 26, 8 (1970).
- ¹¹I. D. Brown and R. D. Shannon, Acta Crystallogr. A 29, 266 (1973).
- ¹²A. G. Christy, Acta Crystallogr. B 49, 987 (1993).
- ¹³J. Zemann, Canad. Mineral. 16, 495 (1978).