

LaPd₂O₄, a Novel Mixed Valent Oxopalladate

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A novel ternary oxide of palladium, LaPd₂O₄, has been synthesized by the solid-state reaction of La₂O₃ and PdO, apply high pressure (2 GPa) and KClO₃ as an oxidizing agent. The black crystals of LaPd₂O₄ belong to space group *I4₁/a* of the tetragonal crystal system with four formula units per unit cell which has the dimensions *a* = 5.9140(5) Å and *c* = 10.289(1) Å. The crystal structure (determined and refined to a final *R* value of 2.48% using 392 unique reflections) consists of square planar PdO₄ units which are stacked to form columnar arrangements along [1 0 0] and [0 1 0], respectively. Despite the oxidation state of 2.5, the palladium atoms occupy the same crystallographic site and thus are structurally indistinguishable. Consequently, LaPd₂O₄ has to be classified as mixed valent of type III according to Robin and Day (*Adv. Inorg. Chem. Radiochem.* 10, 247 (1967)). Lanthanum is coordinated dodecahedrally by eight oxygen atoms. The structural relationship between LaPd₂O₄ and lanthanum palladates described previously is discussed. The title compound shows temperature-independent paramagnetism down to 5 K. © 1995 Academic Press, Inc.

INTRODUCTION

Since the initial report on high-*T_c* superconductivity in substituted lanthanum cuprate (1), there have been considerable efforts in improving the critical properties of ceramic superconductors. Most of this research has been concentrated on the parent compound La_{2-x}M_xCuO₄ (*M* = Sr, Ba) of high-*T_c* superconductors or on its derivatives, multinary layered copper oxides. Part of our work in this field is aiming at novel alternative superconducting compounds without copper. In our view promising candidates in this respect are those oxides which exhibit high electrical conductivity in the normal state and contain mixed valent cations in identical coordination by oxygen. A prototype situation is realized in BaBiO₃ (2) which turns into a superconducting state after doping with potassium (3) or lead (4). There are plausible concepts to explain the superconductivity by a periodical localization (Bi³⁺) and delocalization (Bi⁵⁺) of two electrons of the mixed valent cation coupled with an active mode in the

crystal. This can be interpreted as a mechanism for the formation of Cooper pairs in the sense of the Bardeen-Cooper-Schrieffer (BCS) theory (5).

According to these considerations mixed valent palladium oxides with an oxidation state between two and four may represent promising candidates for the occurrence of superconductivity. At least, there are two obstacles to be overcome in synthesizing such compounds. First, palladium in an oxidation state between two and four is rather unstable and tends to disproportionate into Pd²⁺ and Pd⁴⁺. Furthermore the synthesis of high valent oxopalladates requires extremely oxidizing conditions. Besides Na₂PdO₃, K₂PdO₃ (6), and Rb₂PdO₃ (7), which form at ambient oxygen pressure, Zn₂PdO₄ (8) and Ln₂Pd₂O₇ (*Ln* = Gd, Dy, Er, Yb, Sc, Y) (9) are known, so far. The latter have been synthesized applying high hydrostatic pressures (up to 7 GPa) and KClO₃ as an oxidizing agent. By the same technique we have investigated the system La₂O₃/PdO/"PdO₂" and identified the novel ternary oxopalladate LaPd₂O₄.

EXPERIMENTAL

Synthesis, starting materials. As starting materials for the synthesis of LaPd₂O₄ reactive La₂O₃, PdO, and KClO₃ (Riedel de Haën, 99%) have been used. The oxides were prepared by decomposition of the respective nitrates (La(NO₃)₃ · 6 H₂O: 600°C, 0.2 Pa, 3d; Pd(NO₃)₂: 450°C, 101 Pa, 1d). Pd(NO₃)₂ was synthesized as described in (10) from elemental palladium (Heraeus, 99.99%) and the lanthanum nitrate by dissolution of reagent grade La₂O₃ (Aldrich, 99.9%) in nitric acid and evaporating to dryness. All starting materials were proven to be single-phased by X ray powder diffraction (STOE-Stadi P diffractometer, germanium monochromator on the primary beam and CuKα radiation (λ = 1.54056 Å)).

Stoichiometric amounts of La₂O₃ (93 mg, 0.285 mmol), PdO (140 mg, 1.144 mmol), and KClO₃ (210 mg, 1.716 mmol) were intimately mixed in an inert atmosphere (glove box), encapsulated gas tight in palladium tubes (length, 12 mm; diameter, 3 mm) and pressurized under 2

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GPa using a piston–cylinder apparatus modified by Johannes (11). Heat treatment under pressure was carried out at 900°C with a heating rate of 600°C/hr. After a reaction time of 3 hr the samples were quenched to room temperature within approximately 2 min. To remove KCl, the crude product was washed with 250 ml water and subsequently dried in a desiccator over P₂O₅ for 5 days.

Structure determination. For data collection a crystal of LaPd₂O₄ with the dimensions 0.05 × 0.06 × 0.08 mm was mounted on an Enraf–Nonius CAD4 automatic four-circle diffractometer supplied with a graphite monochromator using MoK α radiation ($\lambda = 0.71069$ Å). Essential crystal data and experimental details of the structure determination are listed in Table 1.

The cell parameters used in all calculations were determined by indexing and least-square refinement of an X ray powder diagram (cf. Table 2, STOE-Stadi P diffractometer, germanium monochromator on the primary beam, CuK α radiation ($\lambda = 1.54056$ Å), Si as external standard, and STOE-Stadi P software).

The program SHELXS-86 (12) was used for data reduction and structure solution by direct methods. Scattering factors for La and Pd were taken from "International Tables for X-Ray Crystallography" (13), for oxygen implemented in the program. The final refinements were performed by full matrix-least-squares methods using SHELXL-93 (14). Structure plots were generated using the programs KPLOT (17) and ORTEP (16).

TABLE I
Experimental Details of the Structure Determination
for LaPd₂O₄

Molecular weight [g · mol ⁻¹]	415.71
Crystal system	Tetragonal
Space group	I4 ₁ /a
Unit cell dimensions [Å]	$a = 5.9140(5)$
(from powder data)	$c = 10.289(1)$
Volume [Å ³]	357.78(6)
Z	4
D_{calc} [g · cm ⁻³]	7.718
Wavelength [Å]	0.7107
θ -range for data collection [°]	$4 \leq \theta \leq 35$
h, k, l range for data collection	$-5 \leq h \leq 9$ $-9 \leq k \leq 9$ $-16 \leq l \leq 16$
Scan mode	ω/θ
Scan width	$0.7 + 0.35 \tan \theta$
$F(0\ 0\ 0)$	724
Corrections	Lorentz polarization
Crystal size	$0.05 \times 0.06 \times 0.08$ mm
$\mu_{\text{MoK}\alpha}$ [cm ⁻¹]	215.22
Number of reflections measured	2070
Number of unique reflections	392
Number of parameters	19
R value	0.0248
wR value	0.0529
Weighting scheme ($P = (F_0^2 + F_2^2)/3$)	$(\sigma^2(F_0^2) + (0.0249 \times P)^2 + 2.6026 \times P)^{-1}$
Maximum height in difference	0.826
Fourier map [e · Å ⁻³]	

TABLE 2
X Ray Pattern of LaPd₂O₄, Miller Indices, Relative Intensities, Observed d_0 [Å] and Calculated d_c [Å] Spacing

$h\ k\ l$	I_0/I_{max}	d_0	d_c
1 1 2	33.4	3.2463	3.2449
1 0 3	64.6	2.9671	2.9668
2 0 2	49.9	2.5651	2.5637
1 2 1	100.0	2.5602	2.5615
1 0 5	27.8	1.9434	1.9435
2 0 4	6.7	1.9411	1.9407
3 1 2	9.1	1.7577	1.7576
3 0 3	11.8	1.7094	1.7091
2 2 4	19.0	1.6229	1.6225
2 3 1	20.1	1.6205	1.6198
1 1 6	4.3	1.5868	1.5866
2 0 6	10.0	1.4834	1.4834
4 0 0	9.6	1.4786	1.4785
3 0 5	5.3	1.4237	1.4235
3 3 2	1.0	1.3449	1.3454
4 1 3	7.6	1.3233	1.3233
2 4 0	1.3	1.3219	1.3224
0 0 8	8.4	1.2859	1.2861
2 1 7	8.2	1.2846	1.2847
4 2 2	6.6	1.2809	1.2808
1 3 6	3.5	1.2640	1.2639

Analyses. The cation composition of the crystals was determined by energy dispersive X ray analysis using an electron microscope (Zeiss DSM 940) equipped with EDX (EDAX PV9800). EDX spectra from different points of the sample were registered at an acceleration energy of 25 kV. Integrations of the La and Pd L-lines were used to calculate the respective concentrations. The magnetization of LaPd₂O₄ was recorded by a SQUID magnetometer (Quantum Design MPMS; 5–300 K). Differential thermal analysis (DTA) was carried out on a Netsch STA 429 (heating rate, 5 K/min; reference, high purity α -Al₂O₃), the decomposition products having been characterized by X ray powder diffraction (STOE-Stadi P diffractometer, germanium monochromator, and CuK α radiation ($\lambda = 1.54056$ Å)).

RESULTS

Black crystals of the novel ternary palladium oxide LaPd₂O₄ have been prepared by solid state reaction between La₂O₃ and PdO, applying high pressure (2 GPa) and KClO₃ as an oxidizing agent. LaPd₂O₄ is stable in air and, with the exception of concentrated HBr, insoluble in acids. It decomposes at 945°C to La₂O₃ and elemental palladium. The composition was confirmed by EDX analyses (La:Pd = 1:1.96, average of 20-point analyses, no impurities of K or Cl were observed) and X ray structure determination. The magnetic measurement shows a

TABLE 3
Fractional Coordinates and Equivalent Thermal Parameters^a
for LaPd₂O₄

Atom	Wyckoff notation	Atomic parameters			Thermal parameters <i>U</i> _{eq} [Å ²]
		<i>x</i>	<i>y</i>	<i>z</i>	
La	4a	0	0	0	0.006(1)
Pd	8d	0	0.25	0.625	0.006(1)
O	16f	0.2050(6)	0.3535(6)	0.0495(3)	0.007(1)

^a $U_{eq} = 1/3 (U_{11} + U_{22} + U_{33})$.

nearly temperature-independent paramagnetism (TIP) with a slight field dependence. The latter could be caused by ferromagnetic impurities. After ferromagnetic¹ and diamagnetic² corrections an experimental susceptibility of $2.72 \times 10^{-4} \text{ mol} \cdot \text{cm}^{-3}$ is obtained. The results of the crystal structure determination (atomic parameters, equivalent thermal parameters, and interatomic distances) are documented in Tables 3 and 4.³

DISCUSSION

The crystal structure contains one crystallographically independent position for Pd which has the site symmetry $\bar{1}$. Pd is coordinated by four oxygen atoms forming approximately square planar PdO₄ groups with Pd–O bond lengths of 2.001 and 2.009 Å; the observed O–Pd–O angles are close to 90° ($\angle_{\min} = 86^\circ$, $\angle_{\max} = 94^\circ$). This corresponds well to the values found for La₂Pd₂O₅ and La₄PdO₇ (18). The PdO₄ units are stacked along [1 0 0] and [0 1 0], respectively, in a staggered manner in both directions. Figure 1 shows one of the PdO₄ columns in the [0 1 0] direction. The planes through the square units are tilted by 24.1° out of the *a/c* and *b/c* planes (cf. Fig. 2). The arrangement of the oxygen atoms can be looked upon as consisting of distorted antiprisms, the base planes of which are occupied by Pd. The staggered sequence of the PdO₄ units as found in LaPd₂O₄ is not uncommon, e.g., it is realized in Bi₂PdO₄ (19) or La₄Au₂O₉ (20), too. In these latter oxides the MO₄ groups are isolated, while they are connected to a three-dimensional framework via common vertices in LaPd₂O₄.

¹ The ferromagnetic correction was performed by linear extrapolation to $H = \infty$ over the temperature range of 5–300 K by the magnetic fields 0.5, 1, 1.5, and 2 T.

² Diamagnetic correction from (17).

³ Further details of the structure determination have been deposited as Supplementary Publication CSD-58140. Copies may be obtained through Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, W-7514 Eggenstein-Leopoldshafen, Germany.

TABLE 4
Important Distances [Å] and Angles [°] in LaPd₂O₄

La–O	2.465(4)	× 4
La–O	2.539(3)	× 4
La–Pd	3.5402(2)	× 4
Pd–O	2.001(4)	× 2
Pd–O	2.009(3)	× 2
Pd–Pd	2.9509(2)	× 2
O–La–O	156.1(2)	
O–La–O	137.6(1)	
O–La–O	131.1(1)	
O–La–O	92.45(3)	
O–La–O	66.3(1)	
O–La–O	77.2(1)	
O–La–O	83.50(1)	
O–La–O	83.5(1)	
O–La–O	71.7(2)	
O–Pd–O	180.0(1)	
O–Pd–O	94.0(1)	
O–Pd–O	86.0(1)	
O–Pd–O	94.0(1)	

Lanthanum is located on the special site 4a and surrounded by eight oxygen atoms. The La–O bond lengths are comparable to those in La₂Pd₂O₅ and La₄PdO₇. The LaO₈ polyhedron represents a dodecahedron which may be described as a distorted square antiprism or a dibisphenoid (cf. Fig. 3). Each dodecahedron is connected to four neighboring dodecahedra by four of its edges, thus forming a three-dimensional network.

A more extended section of the structure is shown in Fig. 4. The three-dimensional framework is constituted by the distorted square antiprisms of oxygen, two faces of which are occupied by Pd. Sharing these faces

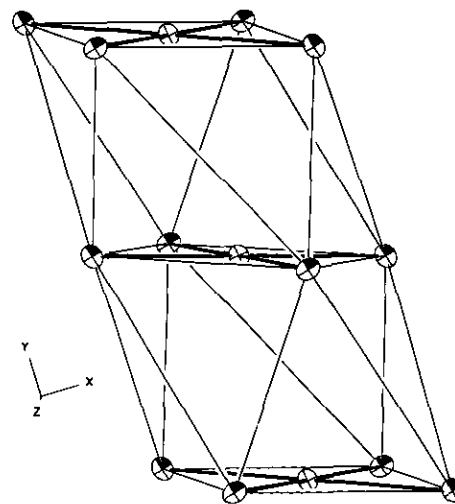


FIG. 1. The coordination of palladium by oxygen in LaPd₂O₄ and the stacking along [0 1 0].

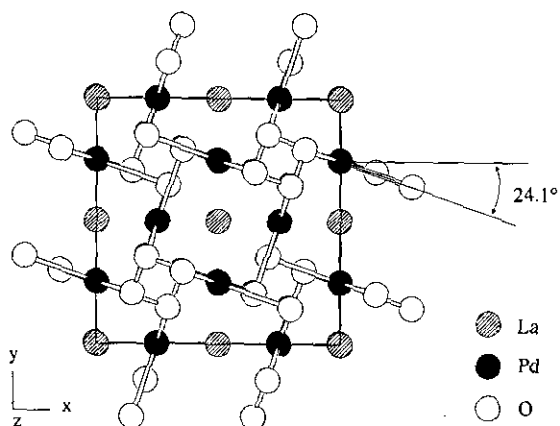


FIG. 2. The crystal structure of LaPd₂O₄ projected on (0 0 1).

columns along [1 0 0] and [0 1 0] result. The columns are linked to each other by some of the remaining faces. Lanthanum is located in the dodecahedral spaces resulting from cross-linking the columns. The structure can be related to the known lanthanum palladates which for their part can be derived from the CsCl structure as was reported by Attfield and Ferey (21). The compositional relationship may be expressed by the formula (La□Pd₂)O₄ (□: vacancies) and is illustrated in Figs. 4 and 5. The structural relationship becomes apparent when rotating all PdO₄ squares in the original structure of LaPd₂O₄ by 22.5° against each other. This procedure results in the formation of a primitive cubic grid of oxygen atoms. After shifting lanthanum by 0, 0, 0.125 it is located in the center of some of the cubes, while Pd occupies the faces of those not centered by La (cf. Fig. 5).

By deriving structures containing square planar units in this manner from the CsCl structure, they may be related to each other. This has been done for the structures of LaAuO₃ (22), the lanthanum palladates La₄PdO₇ and La₂Pd₂O₅, as well as for some platinum bronzes (21). Only the platinum bronzes and LaPd₂O₄ form columnar structures and consequently contain chains of noble

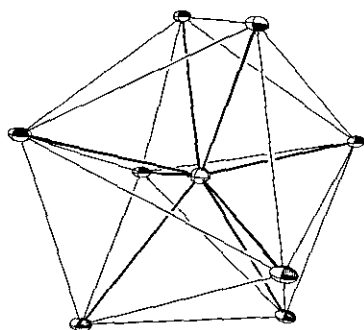


FIG. 3. The eightfold coordination of lanthanum by oxygen.

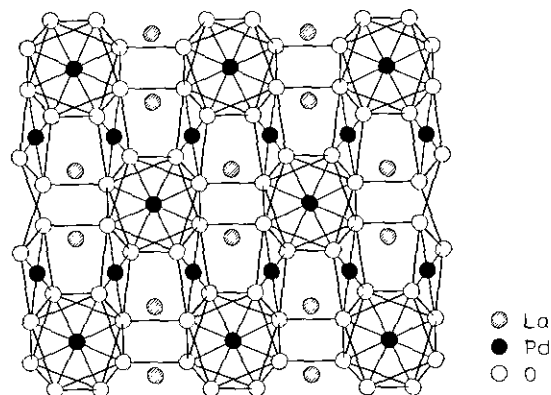


FIG. 4. A view of the three-dimensional framework of LaPd₂O₄ along [0 1 0].

metal ions. The metal-metal distances in the bronzes vary from 2.79 to 2.84 Å, which can be compared to the Pt-Pt bond length in pure metal. The Pd-Pd distance of 2.95 Å in LaPd₂O₄ is considerably larger than that in the metal (2.751 Å) and is at most indicative of weak metallic interactions, particularly since the *d*_{z² orbitals are not pointing directly toward each other. We are currently investigating the electronic conductivity of the title compound and the result will be the subject of a future publication.}

The average oxidation state of the palladium atoms in LaPd₂O₄ amounts to 2.5. As all palladium atoms occupy the same crystallographic site and thus are structurally indistinguishable, LaPd₂O₄ has to be classified as mixed valent of type III according to Robin and Day (23). A comparable situation is found in the platinum bronze CaPt₂O₄ (24, 25) which has an average oxidation state of 3+ for platinum, and which in addition is structurally related to LaPd₂O₄. These similarities are reflected in similar magnetic properties in both oxides.

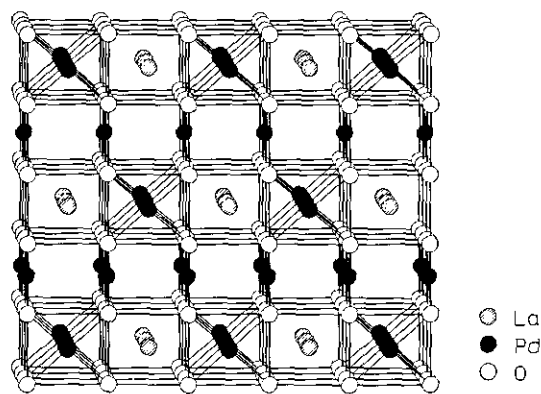


FIG. 5. The structural relationship of LaPd₂O₄ to the CsCl structure (see text).

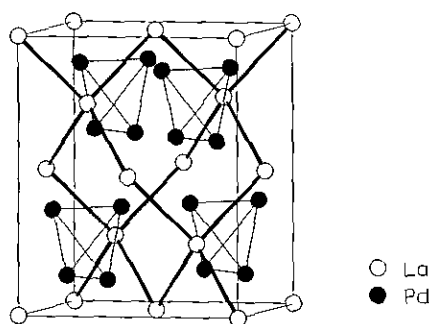


FIG. 6. The cation arrangement in LaPd_2O_4 resembling the MgCu_2 structure.

An alternative way of looking at collective structures is by examining the cation partial structure. O'Keeffe and Hyde have reported on a widespread crystal chemical feature according to which many cation arrangements in oxides correspond to the crystal structure of metals or alloys (26). We have investigated this concept for validity, and analyzing the ternary silveroxides Ag_3BiO_3 and Ag_5BiO_4 (27), and now LaPd_2O_4 . In both cases the cation arrangements are identical to the Laves phase MgCu_2 (28). Figure 6 shows the cation partial structure of LaPd_2O_4 after performing a suitable cell transformation ($a^* = a\sqrt{2}$, $b^* = b\sqrt{2}$, $c^* = c$). Lanthanum occupies the position of magnesium in the Laves phase, forming a tetragonal distorted diamond structure ($a = 8.364 \text{ \AA}$, $c = 10.289 \text{ \AA}$). Palladium, like copper in MgCu_2 , forms tetrahedra which are located in the tetrahedral spaces of the lanthanum network and are linked by common corners. The concept of O'Keeffe and Hyde may be particularly helpful to describe in a simple manner the arrangement of different cations in complex structures.

CONCLUSION

Single crystals of LaPd_2O_4 have been synthesized by applying high pressure. The novel oxopalladate contains mixed valent palladium with identical coordination by oxygen for all palladium atoms. Thus the preconditions we estimated necessary for the occurrence of superconductivity are realized; however, no superconducting properties down to 5 K have been observed. This may be explained by the arrangement of the PdO_4 units. In contrast to the ceramic superconductors based on copper, which contain layers of copper and oxygen, a three-dimensional network of square planar PdO_4 units is formed in LaPd_2O_4 . Furthermore the d_{z^2} orbitals of adjacent pal-

ladium atoms are not pointing directly at each other. This is expected to affect the electronic conductivity crucially.

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