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Ordered Pd^{2+}–Cu^{2+} Substitution in 1.2.3 Superconductor: The Oxide $YBa_2Cu_{(3-x)}Pd_xO_y$ ($x \sim 0.5$) with Pd^{2+} in Square Planar Coordination*

G. FEREY,† A. LE BAIL, AND Y. LALIGANT

Laboratoire des Fluorures, UA CNRS 449, Faculté des Sciences, route de Laval, 72017 Le Mans Cedex, France

M. HERVIEU AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, Campus 2, Boulevard du Maréchal Juin, Université, 14032 Caen Cedex, France

AND A. SULPICE AND R. TOURNIER

CRTBT-CNRS, 25 avenue des Martyrs, 38042 Grenoble Cedex, France

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The substitution of copper by palladium II in $YBa_2Cu_3O_7$ leads to a new compound $Yba_2Cu_{2.5}Pd_{0.5}O_y$ with orthorhombic symmetry ($a = 3.841(1)$ Å, $b = 3.883(1)$ Å, $c = 11.671(3)$ Å; space group *Pmmm*) in which Pd exclusively occupies (1a) sites of the structure, corresponding to cations in square planar coordination. A resistive transition occurs at 49 K; magnetic measurements indicate less than 5% of the full Meissner effect. © 1988 Academic Press, Inc.

Introduction

After several months of investigation of the mixed valence copper oxides, it appears that the difference between the critical temperatures of the superconductors $YBa_2Cu_3O_{7-\delta}$ (*1–3*) and $La_{2-x}A_xCuO_4$ (*4–8*) is at least as spectacular as that observed between $La_{2-x}Ba_xCuO_{4-y}$ and Nb_3Ge. There is no doubt that for both families of oxides the mixed valency of copper plays an important role in the onset of superconductivity. Another factor which may give rise to the superconducting properties of these materials concerns the low dimensionality of their structure (*9–12*). The difference in behavior between La_2CuO_4-type oxides and $YBa_2Cu_3O_{7-\delta}$ could result from their structure: only one crystallographic site with an octahedral symmetry is observed for copper in La_2CuO_4, whereas $YBa_2Cu_3O_{7-\delta}$ exhibits two different sites which can be described in terms of CuO_5 pyramids and

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† To whom correspondence should be addressed.

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CuO_4 planar groups, respectively. Moreover it has been shown recently (*13*) that the apparent $3d^8$ configuration of Cu(III) in oxides could better be interpreted by considering a $3d^9$ ligand hole state ($3d^9L$), where L indicates a hole in the oxygen-derived band. In this respect, the study of the selective replacement of copper by Pd(II) which only adopts square planar coordination (see Refs. (*14–16*) and references therein), could provide information about the mechanism giving rise to superconductivity in these oxides, owing to its $4d^8$ configuration. A recent paper (*17*) claimed that small amounts (0.001%) of Pd^{2+} in 1.2.3 superconductor slightly increased its T_c. The present work deals with the structural study of Pd-rich oxide $YBa_2Cu_{3-x}Pd_xO_{7-\delta}$ ($x \sim 0.5$) and its electric and magnetic properties.

Experimental

Syntheses were carried out in silica crucibles (to prevent contamination from extraneous cations) according to the following equation:

$$BaCO_3 + BaO_2 + 2CuO + \tfrac{1}{2}Y_2O_3 + Pd.$$

BaO_2, which decomposes at high temperature into BaO and $\tfrac{1}{2}O_2$, is used to ensure *in situ* oxidation of $Pd^0 \rightarrow Pd^{2+}$.

Optimizing conditions for the synthesis were sought by using different temperatures and reaction times, together with numerous grindings and systematic X-ray investigation. Whatever the reaction conditions, two phases coexist with the 1.2.3 derived phase; at low temperature ($T <$ 800°C), they are $BaCuO_2$ (major phase) and Y_2BaCuO_5 (*18*). The 1.2.3 phase of interest exists only as a minor phase. Above 800°C, the latter progressively becomes predominant, whereas Y_2BaCuO_5 disappears. The maximum yield (~90%) of 1.2.3 is obtained at 815°C after heating for 22 hr. At higher temperatures ($T >$ 850°C), 1.2.3 is decomposed into $BaCuO_2$ and Y_2BaPdO_5 (*15*) whose structure was recently solved from single-crystal X-ray data.

The Cu^{3+} content was determined from chemical analysis with Fe^{2+} solutions whose excess was titrated by manganimetry. This leads to an oxygen content of 6.8(1).

Structure Analysis

The structure determination of $YBa_2Cu_{3-x}Pd_xO_y$ was carried out from an X-ray powder diffraction pattern using a modified Rietveld method (*19*) and SHELX program (*20*), with space group *Pmmm*.

Atomic scattering factors for Y^{3+}, Ba^{2+}, Cu^{2+}, and Pd^{2+} and anomalous-dispersion corrections were taken from "International Tables for X-ray Crystallography" (*21*) and for O^{2-}, from (*22*).

The structure, solved by direct method facilities of the SHELX program, immediately specifies the positions of barium [site (2t)], palladium only on the square site (1a), yttrium [site (1h)], and finally copper [site (2q)] within a square pyramid. A least-squares refinement of these positions and a difference Fourier map yield the coordinates of the four oxygen atoms. A new refinement of all the above positions corresponding to $YBa_2Cu_2PdO_7$ leads to a conventional R value of 8.88%, but an unrealistic isotropic thermal parameter for paladium is found.

The occupancy factor of Pd^{2+} was then refined using different hypotheses:

(i) a statistical distribution of Cu and Pd on (1a) [square planes] and (2q) [pyramids] sites;

(ii) a (1a) site with only Cu, and a Cu–Pd distribution on (2q);

(iii) no palladium in the structure;

(iv) Pd and Cu on (1a) and Cu on (2q).

The first three cases lead to high isotropic thermal parameters and to R values of 9.58, 9.02, and 8.88%, respectively, whereas R drops to 7.02 in the last hypothesis, Pd and Cu being equally distributed over (1a) site, after refinement. This result agrees with the formulation $YBa_2Cu_{2.5}Pd_{0.5}O_7$.

Further refinement of occupancy factors K of oxygen positions shows that they do not deviate significantly from their ideal value. Therefore, neutron diffraction measurements are required to obtain more accurate values of K which could correspond to the oxygen content determined from chemical analysis.

At this stage, the modified multipattern Rietveld method was once more applied using this structural model. This was necessary because some of the values of the intensities previously obtained are doubtful owing to their very close overlap with other Bragg peaks. With isotropic B factors on all atoms, conventional Rietveld reliability factors are $R_i = 5.77\%$, $R_P = 11.74\%$, and $R_{wP} = 11.01\%$. The atomic coordinates and thermal parameters are reported in Table I, together with the profile parameters. The observed and calculated profiles are presented in Fig. 1.

Electric and Magnetic Measurements

The resistivity of the sample versus temperature was measured between 4 and 300 K (Fig. 2). At room temperature, the resistivity is close to 0.2 Ω · cm. The compound exhibits semimetallic behavior between 80 and 300 K; a broad transition is then observed with an onset of 77 K, the zero value of the resistance being reached below 49 K. However, this palladium oxide is metastable: similar measurements, carried out 1 month after on the same sample stored in a moisture-free system show values of the

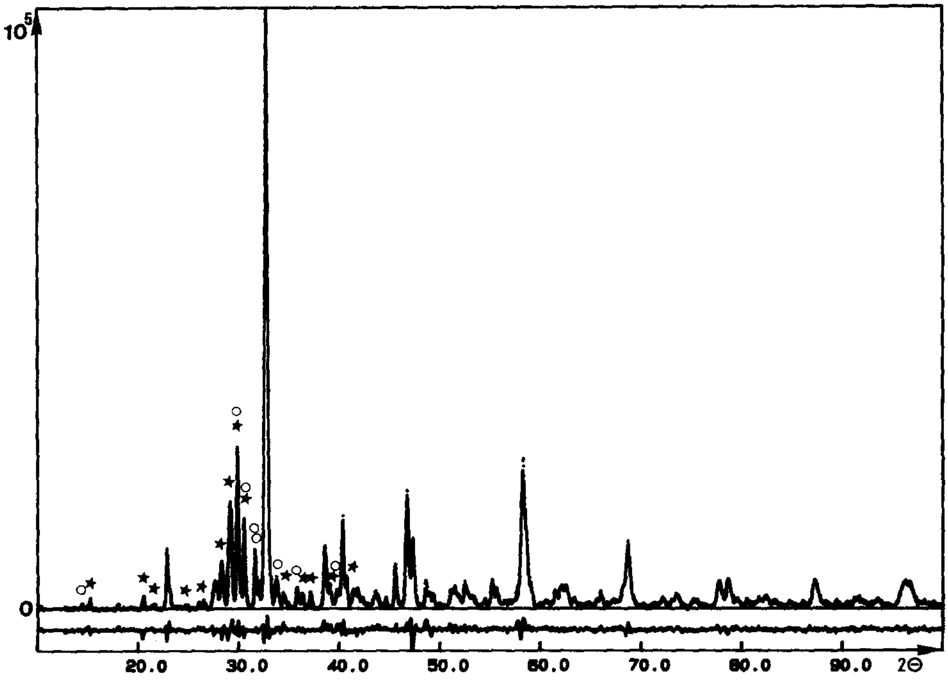

FIG. 1. Observed and calculated X-ray diffraction patterns of a multiphase synthesis involving $YBa_2Cu_{2.5}Pd_{0.5}O_{6.8}$ as a major phase. Asterisks and open circles correspond to $BaCuO_2$ and Y_2BaCuO_5 impurities, respectively.

TABLE I

STRUCTURE AND PROFILE PARAMETERS

Cell parameters	$a = 3.841(1)$ Å, $b = 3.883(1)$ Å, $c = 11.671(3)$ Å
Space group	*Pmmm*
Volume (Å^3)	174.04(3)
2θ range (°)	10–100
Step scan (°2θ)	0.02
Time/step (sec)	15
No. of reflections	132
No. of parameters (total)	19
Zero point (°2θ)	0.035(4)
Profile parameters for $a = 80$, $l = 39$	$U_1 = 0$, $V_1 = 0.14(1)$, $W_1 = 0.003(5)$ $U_2 = 0$, $V_2 = 0.05(3)$, $W_2 = 1.60(5)$ $C = -0.002$, $D = -0.002$
Reliability factors (%)	$R_i = 5.77$, $R_P = 11.74$, $R_{wP} = 11.01$, $R_{exp} = 3.28$

Atom	x	y	z	B (Å^2)	
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.17(7)	
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.1841(3)	0.21(6)	
Cu	0	0	0.3582(7)	0.25(5)	
Cu	0	0	0	0.25(5)	$K = 0.50(9)$
Pd	0	0	0	0.25(5)	$K = 0.50(9)$
O1	0	0	0.158(3)	1.3(2)	
O2	0	$\frac{1}{2}$	0.367(2)	1.3(2)	
O3	$\frac{1}{2}$	0	0.388(2)	1.3(2)	
O4	$\frac{1}{2}$	0	0	1.3(2)	

original resistivity multiplied by 100 and no transition to the superconducting state.

Magnetization measurements were carried out, as previously described (*23*), for two samples, before and after annealing in an oxygen flow, in the temperature range 1.5–90 K. Typical magnetization curves versus H (at $T = 2$ K) and versus T ($H = 100$ oe) are shown in Fig. 3. These results show that the behavior of the material is not strongly modified by the thermal treatment and that less than 5% of the matrix volume exhibits superconducting behavior. So, it appears that the zero resistance reached at $T < 49$ K is only an effect due to the existence of some copper-rich particles which provide a percolation path.

Discussion and Conclusion

The results clearly show that the replacement of copper by palladium in the "1.2.3" oxide kills the superconductivity. This effect, which can be correlated with the preferential replacement of copper by palladium in the CuO_4 groups, suggests that the $[CuO_2]_\infty$ files play a predominant role in the superconductivity of this oxide. On the other hand, the oxygen content observed for this composition, close to $YBa_2Cu_{2.5}$

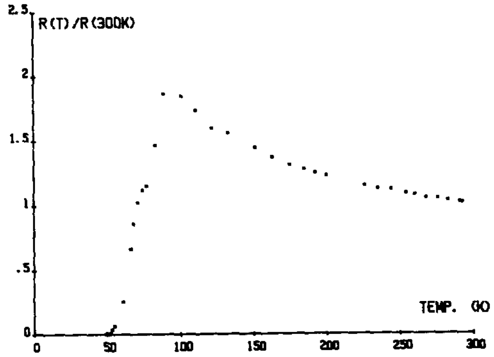

FIG. 2. Reduced resistivity of $YBa_2Cu_{2.5}Pd_{0.5}O_{6.8}$ as a function of temperature.

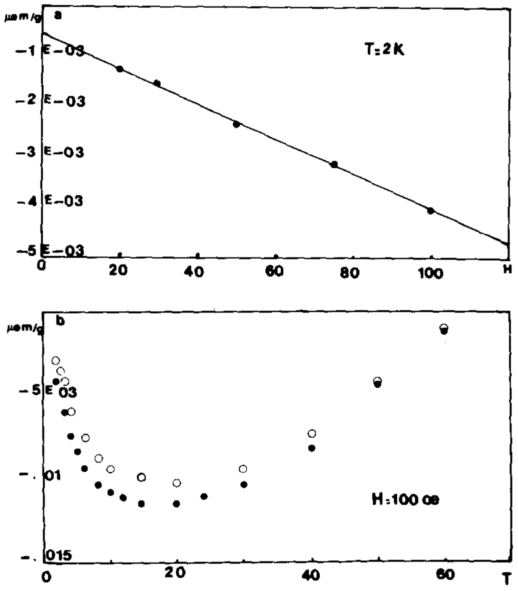

FIG. 3. (a) $M(H)$ curve at 2 K. (b) $M(T)$ curve under 100 oe. Open and full circles correspond to decreasing and increasing T, respectively.

$Pd_{0.5}O_{6.8}$, involves a rather high Cu(III) content, which should lead to superconductivity at least at low temperature, unless palladium was present in higher oxidation states. Further investigations, especially by neutron powder diffraction and EXAFS, will be necessary to understand the behavior of palladium in this structure.

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