Site-selective doping and superconductivity in $(La_{1-y}Pr_y)(Ba_{2-x}La_x)Cu_3O_{7+\delta}$

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Samples in the quaternary system $(La_{1-y}Pr_y)(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ have been prepared and characterized using x-ray and neutron diffraction, thermogravimetric analysis, and transport and magnetic measurements. Pr substitutes on the oxygen-depleted La layers for y > 0.0, while La substitutes on the Ba sites for x > 0.0. The effect of doping on each site is inferred to be primarily local, affecting immediately adjacent Cu-O layers. The similar suppression of superconductivity that accompanies doping on each of the two distinct sites apparently correlates with the degree of oxidation of the Cu-O sheets (and not the chains), indicating that the sheets support the hightemperature superconductivity. Comparison of orthorhombic and tetragonal samples with similar Ba:La ratios (and y=0) demonstrates that the orthorhombic phase yields the largest Meissner signals and highest transition temperatures in the La(Ba_{2-x}La_x)Cu₃O_{7+\delta} system. The effect on superconductivity of oxygen-vacancy configuration in the Cu-O chain layers is proposed to derive, indirectly, from their influence on the Cu-O sheets. In addition, optimally superconducting La(Ba_{2-x}La_x)Cu₃O_{7+\delta} samples exhibit interesting normal-state magnetic properties, with a paramagnetic susceptibility that decreases steadily with temperature between 350 K and T_c .

I. INTRODUCTION

High-temperature superconductivity in $RBa_2Cu_3O_7$ compounds (R = trivalent lanthanides) is highly sensitive to structural and compositional modification. Materials in the La($Ba_{2-x}La_x$)Cu_3O_7+ δ system display superconducting transitions from 90 K ($x \approx 0$) down to 0 K ($x \approx 0.5$),¹⁻⁴ and are isostructural with YBa₂Cu₃O_{7- δ}, but with Y replaced by La, partial substitution of La on Ba sites, and, typically, more oxygen in the oxygendeficient O(1)-Cu(1)-O(5) layers²⁻⁸ (Fig. 1). The range of La substitution extends between $0.10 \le x \le 0.50$, with BaCuO₂ appearing as the main impurity for x < 0.10. Superconductivity and structural properties depend critically upon the La concentration x and the oxygen content δ .

We report here on the structure, oxygen content, transport, and magnetism in the more general system $(La_{1-y}Pr_y)(Ba_{2-x}La_x)Cu_3O_{7+\delta}$. Pr is indicated to substitute in a mixed-valent state $(3^+, 4^+)$ and to replace La^{3+} cations on the oxygen-depleted La layers (Fig. 1). By examining samples with various degrees of La (x) and Pr (y) doping, we compare the effect on structure and superconductivity of doping on two distinct sites in the 1:2:3 structure.

II. SAMPLE PREPARATION

Two groups of samples were prepared; one La doped $(y=0 \text{ and } 0.075 \le x \le 0.350)$, and the other Pr doped $(x=0.125 \text{ and } 0 \le y \le 0.56)$. The fixed value of x=0.125 for the Pr-doped samples was chosen, rather than x=0, to minimize BaCuO₂ impurity content.

The La-doped series consists of seven compositions, x = 0.075, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35, prepared using at least 99.99% pure La₂O₃, Ba(NO₃)₂, and CuO. The La₂O₃ was typically baked out at 900 °C for 10-72 h to remove any hydroxide or carbonate contamination.

Stoichiometric quantities of the starting powders were ground in an agate mortar and pestle until well mixed and packed into alumina crucibles. Samples were then heated slowly (over a 16-h period) to 930 °C, held at 930 °C for 15 h, thoroughly reground, pressed back into the original crucibles, and refired at 950 °C for 36 h. After regrinding, powders were pressed, at 100000 psi, into half-inch diameter pellets, sintered in air at 970 °C for 24 h, cooled to 800 °C over 24 h, and then cooled to room temperature. The sintered pellets were then either pressure annealed in oxygen (150 or 270 psi O₂), air quenched from 950 °C, or received no further heat treatment. The annealing conditions for each set of samples are given in Table I along

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FIG. 1. Representation of the crystal structure of $(La_{1-y}Pr_y)(Ba_{2-x}La_x)Cu_3O_{7+\delta}$, which is similar to YBa₂-Cu₃O_{7- δ}, with partial replacement of La on Ba sites and Pr on La sites. Oxygen atoms in O(1)-Cu(1)-O(5) layers tend to order into Cu(1)-O(1) "chains" as x and δ approach zero. Oxygen sites in the O(2)-Cu(2)-O(3) planes have, within experimental error, full oxygen-site occupancy.

with an identification label (LalOx1, LalOx2, LalA, LalQ, etc.) used to refer to each group of samples.

A second run of La-doped samples (La2Ox), with x = 0.075 and 0.150, were prepared similarly to the first run, but were heated and sintered in air over a longer period of time and at lower temperatures (powders were

heated to 900 °C over 5 days with intermediate regrindings and pressed pellets were sintered at 945 °C for 16 h and 600 °C for 5 h). These samples were pressure annealed in 150 psi of oxygen at 450 °C for 18 h.

Pr-doped samples with y = 0.0, 0.06, 0.11, 0.17, 0.22, 0.28, 0.34, 0.45, and 0.56 were made using 99.99% pure Pr_6O_{11} and either $Ba(NO_3)_2$ (Pr1 series) or $BaCO_3$ (Pr2 series). Samples made with $Ba(NO_3)_2$ had significantly better superconducting properties. Sample preparation was similar to the La-doped samples. Annealing conditions are summarized in Table I.

III. STRUCTURE

The site of Pr substitution in $(La_{1-\nu}Pr_{\nu})$ - $(Ba_{2-x}La_{x})Cu_{3}O_{7+\delta}$ was determined using powder neutron diffraction (PND). Data were collected on the powder diffractometer at the Missouri University Research Reactor facility (MURR)⁹ from three Pr2 series samples with y = 0.17, 0.34, and 0.56. In each case, approximately 5 g of sample was contained in a 6.35-mm outside diameter, 0.05-mm walled vanadium can. A wavelength of 1.2892 Å was selected from the (220) planes of a Cu monochromator at a take-off angle of 60.6°. This wavelength has been calibrated using many data sets collected on a range of materials.¹⁰ Data from five 21° spans of the linear position-sensitive detector were each accumulated over 4 h at 298(5) K and combined to yield the diffraction profile $5 \le 2\theta \le 110^\circ$, rebinned in 0.1° steps.

The PND data were analyzed by full-matrix Rietveld refinement¹¹ using the pseudo-Voigt function in a modified version of the DBW 3.2 code.¹² The background was treated by linear interpolation between a set of estimated points that were updated periodically. Scattering lengths of 8.27, 4.45, 5.25, 7.718, and 5.805 fm (or 10^{-15} m) for La, Pr, Ba, Cu, and O, respectively, were taken from Koester, Rauch, Herkens, and Schroder.¹³ Approximate initial atomic coordinates were taken from earlier work on La(Ba_{1.875}La_{0.125})Cu₃O_{7+s}.⁸ Powder x-ray

TABLE I.	Summary of	f sample j	preparation	conditions.
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Doping	Label	Annealing treatment	Comments	
Laª	LalA	None		
	LalOx1	Pressure anneal 150 psi O ₂ 700 °C/18 h; 450 °C/30 h	Prepared at higher	
LalOx2		Pressure anneal 270 psi O ₂ 450 °C/18 h	temperature (sintered at 970° C) than La2Ox	
	LalQ	Air quench 950 °C to room temperature	samples	
	La2Ox	Pressure anneal 150 psi O ₂ 450 °C/18 h	Sintered at 945°C	
Pr ^b	Prl	Pressure anneal 150 psi O ₂ 450 °C/18 h	Made with Ba(NO ₃) ₂	
	Pr2	Pressure anneal 150 psi O ₂ 450°C/18 h	Made with BaCO ₃	

 $^{a}y = 0.0; 0.75 \le x \le 0.35.$

 $b_x = 0.125; 0.0 \le y \le 0.56.$

diffraction data (described below) indicate orthorhombic symmetry for the Pr-doped samples, and, for each of the three samples, the PND data were refined to full convergence in the orthorhombic space group *Pmmm* (No. 47, Ref. 14). Permitted variables included all coordinates unconstrained by symmetry, isotropic temperature factors for each site, and site occupancies for the sites La, Ba, O(1), and O(5). There was no evidence for oxygen occupancy in the oxygen-depleted La layers for any of the samples.

Weighted profile R factors for the three fits are $R_{WP} = 4.97$ (y = 0.17), $R_{WP} = 4.48$ (y = 0.34), and $R_{WP} = 4.40 (y = 0.56)$.¹¹ The preferred site for Pr substitution was determined by refining the effective scattering lengths for the La and Ba sites with no constraint on the total lanthanum content. The refined scattering lengths (in fm) for the La site in the y = 0.17, 0.34, and 0.56 samples are 7.58(11) [7.63, 8.14], 6.73(9) [6.98, 7.63], and 5.84(9) [6.12, 6.95], respectively, where estimated standard deviations are given in parentheses. The values in the square brackets are the calculated scattering lengths assuming complete Pr occupancy on, respectively, the La and Ba sites. Comparison of observed and calculated scattering lengths indicates that Pr substitutes only on the La site. The effective scattering lengths for the Ba site are less sensitive to the Pr distribution. The results are, however, also consistent with the Pr occupancy of the La site only.

Powder x-ray diffraction data were collected for both the La(Ba_{2-x}La_x)Cu₃O_{7+ $\delta}$ and (La_{1-y}Pr_y)(Ba_{1.875}-La_{0.125})Cu₃O_{7+ δ} systems on a Huber diffractometer with a rotating anode source using Bragg-Brentano geometry, an incident beam graphite focusing monochromator and Cu K α radiation. Scans were typically $5 \le 2\theta \le 80^{\circ}$ in steps of 0.05°, with 0.70° incident beam divergence and 0.15° angular resolution. More precise scans of 0.005° steps and longer count times over relevant peaks helped identify orthorhombic splitting. No BaCuO₂ reflections were detected in the diffraction patterns for samples with $x \ge 0.10$. Lattice constants were determined by leastsquares optimization based on peak positions for 20 $\le 2\theta \le 80^{\circ}$.}

 $La(Ba_{1.5}La_{0.5})Cu_{3}O_{7+\delta}$ (x =0.5) is tetragonal, space group P4/mmm.^{1-4,7,8} (Powder-diffraction data cannot distinguish between genuine tetragonal symmetry and orthorhombic symmetry with a and b axes of effectively equal length. Samples without a detectable orthorhombic distortion are described here as tetragonal.) For compositions x < 0.50, materials have been reported with tetrago $nal^{1,5,6}$ and orthorhombic²⁻⁴ symmetry. However, we have observed that samples with x < 0.50 are often mixtures of closely related orthorhombic and tetragonal phases.⁸ Evidence of biphasic behavior is particularly noticeable in x-ray powder patterns for d spacings in the range 1.895 Å $\leq d \leq 2.058$ Å, which includes contributions from the (020), (006), and (200) reflections. In orthorhombic samples, the (020) and (006) reflections are nearly coincident because $c \approx 3b$, and are resolved from the (200) reflection. Consequently, two peaks are observed in roughly a 2:1 integrated intensity ratio (see Fig. 3, inset). In mixed-phase samples, the larger peak broadens and the (200) integrated intensity decreases as the amount of tetragonal component increases.

Results for the lanthanum-doped samples are shown in Fig. 2. In Fig. 2(a), the a and b lattice constants for samples which were annealed under 270 psi oxygen (La1Ox2) are compared with the corresponding values for the initial series of samples (La1A) which were not pressure annealed in oxygen at low temperature. The La1Ox2 series are, within instrumental resolution, orthorhombic for x < 0.25 and tetragonal for $0.25 \le x \le 0.50$. For $0.2 \le x \le 0.3$, a small contribution from a tetragonal (x < 0.25) or orthorhombic $(x \ge 0.25)$ component was also evident, indicative of the tendency towards biphasic behavior in this system. The c-axis dimension tracks closely the *b*-axis length $(\times 3)$ in all samples and is, therefore, not shown in Fig. 2. Samples in the La1Ox1 series (150 psi oxygen pressure annealed) were similar to the La1Ox2 samples, suggesting that the effect of oxygen pressure annealing saturates at or before 150 psi of oxygen pressure.

The air-annealed samples (La1A) show a similar change from orthorhombic to tetragonal symmetry as x increases, although the crossover occurs at a lower lanthanum concentration, $x \approx 0.20$. Samples in the La1A series have slightly smaller orthorhombic distortions than the corresponding pressure-annealed samples and have a and b lattice constants larger by about 0.005 Å as a result of reduced oxygen content. The reduction in the orthorhombic distortion with increased La concentration, for both the La1Ox2 and La1A samples, implies that La doping on



FIG. 2. Lattice constants, *a* and *b*, for the (1) La1A air annealed, (2) La1Ox2 orthorhombic (for $x \le \langle 0.25 \rangle$) pressure annealed, (3) La2Ox tetragonal pressure annealed, and (4) La1Q quenched samples, where *x* refers to the doping concentration in La(Ba_{2-x}La_x)Cu₃O_{7+s}. The estimated errors on the least-squares optimized lattice constants are typically ± 0.002 Å.

the Ba site progressively disrupts the $\ldots O(1)$ -Cu(1)-O(1)... linear chains (Fig. 1) in the 1:2:3 structure.

Lattice constants for the air-quenched (La1Q) and the pressure-annealed samples of the second run of La-doped samples (La2Ox) are shown in Fig. 2(b). Samples in the La1Q series are tetragonal for all compositions x and have larger unit-cell constants than the corresponding tetragonal samples in either the air-annealed or pressureannealed series. Surprisingly, the majority phase in the pressure-annealed samples (La2Ox), with x = 0.075 and x = 0.150, has, within experimental resolution, no detectable orthorhombic distortion and exhibits an a_{tetr} cell dimension intermediate between the a_{orth} and b_{orth} cell dimensions of the corresponding phase in the orthorhombic pressure-annealed samples (La1Ox2). Diffraction patterns for the orthorhombic pressure-annealed La1Ox2 sample and tetragonal pressure-annealed La2Ox sample for the composition x = 0.075 are compared in Fig. 3. The c-axis dimensions of the tetragonal La2Ox samples are smaller than those of analogous orthorhombic La1Ox1(2)samples [c = 11.773(5) vs 11.806(5) for x = 0.075 andc = 11.761(5) vs 11.796(5) for x = 0.150], implying that tetragonal La2Ox samples have larger oxygen contents than their orthorhombic counterparts. The thermogravimetric analysis (TGA) results (see below) confirm this trend. Clearly, the structural properties of the $La(Ba_{2-x}La_{x})Cu_{3}O_{7+\delta}$ system depend very sensitively on the processing conditions used during sample preparation.

The effect of Pr substitution on the lattice constants is shown in Fig. 4 for the Pr1 series of samples. Substitution of the smaller Pr for La on the La sites results in a decrease in both the *a* and *b* lattice parameters. In contrast to La doping, however, Pr doping has, at most, a small effect on the orthorhombic distortion, at least within the composition range $0 \le y \le 0.28$. Samples with no Pr have



FIG. 3. Comparison of x-ray powder diffraction data for x = 0.075 pressure-annealed (a) orthorhombic (La1Ox2) and (b) tetragonal (La2Ox) samples. Especially note the splitting of the peaks at 46° and 78°.



FIG. 4. Lattice constants for the pressure-annealed Pr-doped Pr1 samples as a function of y in $(La_{1-y}Pr_y)$ - $(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ materials. The estimated errors on the least-squares optimized lattice constants are typically ± 0.002 Å.

an orthorhombic distortion b-a = 0.034(2) Å, while for y = 0.28, b-a = 0.038(2) Å. These trends are in contrast with those found in Pr-doped YBa₂Cu₃O_{7- δ}, where replacement of Y³⁺ by larger Pr mixed-valent ions leads to a larger unit cell and a tendency towards a reduced orthorhombic distortion.^{15,16}

The different response of the unit-cell symmetry to La and Pr doping appears to be a consequence of the local cation coordinations. The La³⁺ ions, substituted on the Ba site, are coordinated in part by the O(1) and O(5) oxygen ions (Fig. 1). The difference in size and charge between La³⁺ and Ba²⁺ results in an increased tendency towards oxygen disorder in the oxygen-deficient O(1)-Cu(1)-O(5) layers. In the case of Pr substitution, however, the filled Cu-O planes, sandwiching the oxygendepleted La layers, shield the Cu-O chains from a direct influence of the Pr ions and orthorhombic symmetry is maintained.

IV. THERMOGRAVIMETRY

Thermogravimetric analysis, using a Dupont 951/9900 TGA system, was used to determine oxygen contents. The typical starting sample mass was approximately 100 mg, with a balance resolution of 2 μ g. A typical scan involved flowing forming gas (6 vol.% H₂, 94 vol.% He) through the sample chamber and ramping the temperature to 1000 °C at 12 °C/min⁻¹. Oxygen loss was observed as early as 200 °C and saturated by 980 °C. Sample oxygen content, z, was calculated assuming complete reduction of the La- and Pr-doped samples to La₂O₃/BaO/Pr₂O₃ and metallic Cu. The presence of small amounts of BaCuO₂ in samples with x < 0.1 made analysis of oxygen content in these samples less accurate.

The results for the oxygen contents determined by TGA are shown in Fig. 5 as a function of the total doping level, x + y. In the La-doped samples (y = 0), several trends are apparent. There is a clear trend toward higher oxygen content with increasing x. For example, samples in the pressure-annealed series La1Ox1 and La1Ox2 yield an oxygen content, $z \approx 7.00(3)$, for orthorhombic samples with x approaching zero, and an oxygen content that in-



FIG. 5. Oxygen content determined by TGA, z, vs total doping, x + y, in $(La_{1-y}Pr_y)(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ for (a) quenched La1Q (y = 0), (b) air-annealed La1A (y = 0), (c) orthorhombic pressure-annealed La1Ox1 and La1Ox2 (y = 0), (d) tetragonal pressure-annealed La2Ox (y = 0), and (e) air-annealed Pr1 (x = 0.125) samples. The estimated error bars on oxygen content (not shown) are ± 0.03 . The solid lines are merely guides to the eye.

creases roughly linearly to $z \approx 7.14(3)$ when x = 0.35 and samples become tetragonal. The replacement of Ba²⁺ cations by trivalent La³⁺, adjacent to the oxygen-depleted O(1)-Cu(1)-O(5) layers and the associated disordering of oxygen on the O(1) and O(5) sites (Fig. 1) allows for more oxygen to be pulled into these planes. Samples subjected to oxygen pressure annealing show a larger oxygen content than air-annealed or air-quenched samples with similar x values (although no difference was noted between samples annealed in 270 or 150 psi of oxygen). In addition, tetragonal samples in the pressure-annealed series La2Ox yield slightly larger oxygen contents than their orthorhombic counterparts with similar x values in the La1Ox1 and La1Ox2 series.

The majority phase in samples with average oxygen contents of z > 7.0 is tetragonal, implying disorder of oxygen over the O(1) and O(5) sites. Orthorhombic materials (with $z \approx 7.0$) show a barrier to further oxygen uptake (i.e., moderate increases in oxygen pressure do not increase sample oxygen content). In addition, tetragonal samples with z > 7.0 can be depleted of oxygen and remain largely tetragonal. The present data are consistent with the transition to tetragonal symmetry at $z \approx 7.0$ being driven by increasing oxygen content, with a significant barrier to initial disordering of oxygen over the O(1) and O(5) sites. Alternatively, materials with z > 7.0 that are tetragonal may have an intrinsic tendency toward this tetragonal symmetry (driven, perhaps by La-Ba ordering in the Ba planes), with the associated oxygen disorder permitting higher oxygen contents to be readily attained. Higher sintering temperatures and long anneals at a lower temperature (used for the La1Ox1 and La1Ox2 samples) appear to favor the formation of largely orthorhombic material, whereas lower temperatures (used for the La2Ox samples) yield more of the tetragonal phase.

In contrast to the behavior of the La doped samples, the oxygen contents of the Pr-doped materials are insensitive to the dopant concentration (Fig. 5). This is not unexpected, as the Pr ions are situated between stable Cu-O planes with full oxygen occupancy rather than adjacent to the oxygen-deficient Cu-O chain layers in which oxygen is considerably more mobile. The PND results on pressureannealed Pr2 samples confirm the insensitivity of oxygen content to Pr concentration yielding values of z = 7.08(6)(y = 0.17), z = 7.03(4) (y = 0.34), and z = 7.08(4)(y = 0.56).

Both x-ray and TGA results emphasize the predominantly local nature of La and Ba site substitution effects in $(La_{1-y}Pr_{y})(Ba_{2-x}La_{x})Cu_{3}O_{7+\delta}$. Pr affects the O(2)-Cu(2)-O(3) planes sandwiching the oxygendepleted La layer, whereas La substitution for Ba apparently influences both the oxygen-deficient O(1)-Cu(1)-O(5) layers (the chain layers) and the oxygensaturated O(2)-Cu(2)-O(3) planes.

The average Cu oxidation state for each sample was calculated using the oxygen contents measured by TGA and the values of the average valence of Pr ions in $(La_{1-y}Pr_y)(Ba_{1.875}La_{0.125})Cu_3O_{7+\delta}$ measured by superconducting quantum interference device (SQUID) magnetometry (described below). Oxygen is assumed to be present as O^{-2} in these calculations. While the exact distribution of charge between Cu and O in these materials remains a debated question, this problem does not directly affect the results of the present discussion, which, for convenience, is phrased in terms of a variable Cu valence state.

The calculated average Cu valence for the Pr- and Ladoped samples appears in Table II. The oxygen contents of the Pr samples are constant as a function of composition implying an average Cu valence which decreases with increasing Pr concentration. The reduction in Cu valence must primarily be accommodated in the O(2)-Cu(2)-O(3) planes, since if the O(1)-Cu(1)-O(5) layers were significantly affected, a noticeable change in sample oxygen content would be expected (given the high mobility of oxygen and abundance of vacancies in these layers). The important point here is that the present data should be considered in terms of distinct Cu valences on the O(1)-Cu(1)-O(5) and O(2)-Cu(2)-O(3) planes rather than in terms of an average Cu valence.

For the La-doped samples, oxygen uptake in the O(1)-Cu(1)-O(5) layers balances the valence difference between La and Ba cations, yielding a constant average Cu oxidation state of approximately 2.31 for the pressureannealed La1Ox1 and La1Ox2 samples. A lower constant value is obtained for the La1A air-annealed (2.20) and the La1Q quenched (2.10) samples.

Comparing the *average* Cu oxidation-state trend in the Pr- and La-doped material, there is a clear difference—in the former it decreases with doping, while in the latter it remains constant. However, in the La-doped material, when La replaces Ba the associated filling of O(1)-Cu(1)-O(5) layer oxygen vacancies surrounds Cu in this plane with more oxygen and presumably *increases* the Cu oxidation state in this plane. Since the total average Cu oxidation state remains constant, the Cu oxidation state in the O(2)-Cu(2)-O(3) planes must *decrease*, just as in the case of Pr substitution where only the O(2)-Cu(2)-O(3) planes are influenced. Consequently, although the effects of Pr and La doping on the O(1)-Cu(1)-O(5) chain layers are clearly different, the effects on the O(2)-Cu(2)-O(3) planes are expected to be similar.

TABLE II. Average Cu valence in La- and Pr-doped samples.

Sample			ce	
x	y	Quenched	Air annealed	Pressure annealed
0.10	0.00	2.09	2.19	2.31
0.15	0.00		2.20	2.31
0.25	0.00	2.08	2.19	2.30
0.35	0.00	• • •	2.22	2.32
0.125	0.00		2.26	2.44ª
0.125	0.11	• • •	• • •	2.36ª
0.125	0.17		2.23	
0.125	0.22			2.30ª
0.125	0.28		2.21	

^aPressure-annealed Pr-doped samples are from Pr2 series. Air-annealed are from Pr1 series.

V. TRANSPORT

Four-point resistance versus temperature measurements were performed over the temperature range 5-290 K for the Pr- and La-doped samples (Fig. 6). Pressureannealed samples consistently had higher transition temperatures and sharper transitions compared with the corresponding air-annealed or air-quenched samples. Doping with either Pr or La depresses T_c^{onset} for pressure-annealed orthorhombic samples. The observed suppression of the transition to zero resistance with increasing Pr concentra-



FIG. 6. Resistance vs temperature for pressure-annealed (a) $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ (La1Ox2) and (b) $(La_{1-y}Pr_y)$ -(Ba_{1.875}La_{0.125})Cu₃O_{7+ δ} (Pr1) samples. Curves have been multiplied by scale factors to clarify the figure.

tion is consistent with trends reported for Pr-doped YBa₂Cu₃O_{7- δ}.¹⁵ Broadening of the superconducting transitions may result from an inhomogeneous distribution of dopant ions or oxygen as sample parameters move further from the fully ordered x=0 and z=7.0 orthorhombic configuration.

Room-temperature resistivities are of the order 500 $\mu \Omega$ cm in both La- and Pr-doped samples, with no clear trend appearing as a function of doping. Despite attempts to suppress the semiconductorlike behavior above T_c by varying annealing and sintering conditions, samples in the Pr-doped series demonstrate a more pronounced trend toward semiconducting behavior as Pr concentration increases, whereas this tendency develops more slowly in the La-doped pressure-annealed samples.

Despite having orthorhombic symmetry, air-annealed La1A samples all displayed semiconductorlike resistance versus temperature curves. The reduced oxygen contents and larger a and b cell parameters in these samples, as compared to the orthorhombic pressure-annealed samples, could account for the suppressed superconductivity, although YBa₂Cu₃O_z samples with z = 6.85 are superconducting.¹⁷ Air-quenched samples were also entirely semiconducting.

VI. MAGNETIC MEASUREMENTS

Meissner effect, shielding, and normal-state magnetic measurements were obtained between 2 and 350 K using a Quantum Design SQUID magnetometer. Meissner effect and shielding measurements were collected in a 50-Oe field. Normal-state properties were measured using fields ranging from 1 to 50 kOe.

Samples doped with Pr display Curie-Weiss law behavior between 10-80 K in samples where superconductivity has been suppressed by the applied magnetic field or by doping¹⁸ (Fig. 7). Above 80 K, significant curvature away from linear Curie-Weiss χ^{-1} vs T results. Other rare-earth compounds exhibit similar behavior, which is attributable to crystal-field effects.¹⁹

Values for the effective magnetic moment p, Curie-Weiss law constant Θ , and the calculated Pr oxidation state v appear in Table III. Localized f-electron moments



FIG. 7. Inverse magnetic susceptibility (per mole Pr ions) vs temperature showing Curie-law behavior below 80 K for nonsuperconducting samples and distinct slopes for air-annealed (y=0.56, 0.34), and pressure-annealed (y=0.56, 0.45, 0.34, 0.23) samples.

are assumed and crystal-field interactions are neglected. In addition, localized Cu moments are assumed to be absent in the Pr-doped samples. This assumption is based on our data (discussed below) for pressure-annealed samples with no Pr (y = 0.0, x = 0.125) which indicate the absence of localized Cu moments (at least within the detection level of our magnetic measurements). A small contribution from localized Cu moments would, in any event, not affect the conclusions of this study.

Two distinct slopes of the $[x \text{ (per mole Pr)}]^{-1}$ vs T curves are noted (Fig. 7), one for air-annealed and one for pressure-annealed samples. The average Pr oxidation state, calculated within the framework of the abovementioned assumptions, varies between $v \approx 3.5$ and $v \approx 3.8$, depending on annealing conditions. The higher oxidation state becomes more prevalent with oxygen pressure annealing. Pr ions appear in a mixed oxidation state $(3^+, 4^+)$, as in the initial starting material Pr₆O₁₁. The value of v = 3.8 for pressure-annealed La-Pr-Ba-Cu-O agrees with that reported for Y-Pr-Ba-Cu-O.¹⁶ In addition, a negative Curie-Weiss temperature of approximately -10 K suggests antiferromagnetic correlations between Pr ions.

Meissner effect data are shown in Fig. 8 for the La- and Pr-doped samples. Both La doping on the Ba site and Pr doping on the La site depress T_c and the magnitude of the Meissner signal. Furthermore, the rate of depression of the Meissner signal or transition temperature does not depend on which doping site is considered but depends only on the total doping concentration x + y (Fig. 9). It is not

TABLE III. Magnetic properties of Pr ions in $(Pr_{1-y}La_y)$ $(Ba_{1,875}La_{0,125})Cu_3O_{7+\delta}$.

Sample	р	Valence	θ
y = 0.56; air annealed	3.06	3.54	-9.9
y = 0.34; air annealed	3.07	3.53	-9.6
y = 0.56; pressure annealed	2.86	3.73	-10.9
y = 0.45; pressure annealed	2.83	3.75	-9.6
y = 0.34; pressure annealed	2.79	3.79	-10.5
y = 0.22; pressure annealed	2.79	3.79	-9.7



FIG. 8. Meissner effect in a 50-Oe field for (a) $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ and (b) $(La_{1-y}Pr_y)(Ba_{1.875}La_{0.125})-Cu_3O_{7+\delta}$ pressure-annealed samples with the indicated compositions.

clear why the magnitude of the Meissner signal should correlate with T_c . However, this correlation of T_c and the magnitude of the Meissner effect appears in several of the high-temperature superconducting systems, including $La_{2-x}Sr_xCuO_{4-\delta}$ (Ref. 20) and $YBa_2Cu_3O_{7-\delta}$ for $\delta > 0.3$.¹⁷ Since the coherence length is small (15-25 Å,



FIG. 9. (a) Meissner signal vs total doping, x+y, and (b) temperature at which 10% and 90% of the Meissner transition has been completed vs x+y. La and Pr are indicated to be equally effective at suppressing superconductivity in this system.

in plane), sample inhomogeneity, even over length scales of only a few unit cells, could lead to a mixture of superconducting and nonsuperconducting regions, with the volume fraction of superconducting material depending on oxygen content and ordering, and dopant concentration and homogeneity.

The Meissner data in Fig. 10 also demonstrate a difference between orthorhombic and tetragonal samples with the same Ba:La ratio (although different δ) in $La(Ba_{2-x}La_{x})Cu_{3}O_{7+\delta}$. Orthorhombic samples with x = 0.075 yield Meissner and shielding signals which are 36% and 71%, respectively, of complete diamagnetism (compaction 0.80 assumed) with a relatively sharp onset of 80 K (defined as the point at which 10% of the Meissner transition is attained). The tetragonal sample has 17% and 40% of full diamagnetism with an onset of 60 K. A tail which extends between 60-70 K is associated with a small fraction of the sample which is orthorhombic, consistent with the analysis of the power x-ray diffraction data. This direct comparison between tetragonal and orthorhombic samples demonstrates that the highesttemperature superconductivity occurs in orthorhombic samples in the $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ system. This is consistent with earlier work^{2-4,8} on orthorhombic $La(Ba_{2-x}La_{x})Cu_{3}O_{7+\delta}$ samples. However, while we cannot rule out the existence of an orthorhombic distortion below the level of our resolution, these data indicate the existence of a $T_c \approx 60$ K phase with tetragonal symmetry and higher oxygen content.

Samples with no paramagnetic impurities also have interesting normal-state magnetic properties, with χ paramagnetic, but *decreasing* as a function of temperature from 350 K down to T_c (Fig. 11). An empty sample holder was measured to confirm that this behavior arises in the sample. Similar susceptibility behavior has been reported for La_{1.85}Sr_{0.15}CuO_{4- δ} (Ref. 21) and, recently in YBa₂Cu₃O_{7- δ} after a C/T contribution had been subtracted.¹⁷ The magnitude of the magnetic susceptibility is very small (~10⁻⁴ emu/mole La-Ba-Cu-O), consistent, at least in magnitude, with Pauli paramagnetism. Clearly, Cu valence electrons must essentially all be delocalized since, otherwise, the paramagnetic signal from the localized Cu moments would swamp the tiny decreasing χ signal. Actually, in the x = 0.35, $z \approx 7.15$ sample, a small, Curie law-type contribution appears at low temperatures



FIG. 10. Comparison of Meissner signals observed in orthorhombic and tetragonal pressure-annealed $La(Ba_{1.925}La_{0.075})-Cu_3O_{7+\delta}$ samples.



FIG. 11. Anomalous temperature dependence of the magnetic susceptibility above the superconducting transition temperature in x = 0.10 and x = 0.35, pressure-annealed La1Ox2 samples.

(Fig. 11), consistent with a tendency toward localization with increased doping [or with increased oxygen occupancy in the O(1)-Cu(1)-O(5) layers].

One explanation of this normal-state magnetic behavior is a Pauli susceptibility with a temperature-dependent density of states at the Fermi level, $g(E_F)$. Using the formula $\chi_{\text{Pauli}} = \mu_B^2 g(E_F)$ and correcting for core diamagnetism²¹ such that $\chi_{\text{Pauli}} = \chi_{\text{meas}} - \chi_{\text{core}}$, we get $g(E_F) \approx 5.2$ and 4.8 states/[eV (Cu atom)] for the x = 0.10 and x = 0.35 samples, respectively, at room temperature. These values are larger than the value 3.0 states/[eV (Cu atom)] calculated by Mattheiss and Hamann²² for $YBa_2Cu_3O_{7-\delta}$ but smaller than the value 6.7 states/[eV (Cu atom)] measured in YBa₂Cu₃O_{7- δ}.²¹ We do not include a correction for Landau diamagnetism due to the relatively large effective mass²³ (we calculate $m^* \approx 4m_e$ based on the measured density of states at the Fermi level and modeling the system as a series of free 2D carriers) and the random orientation with respect to the applied magnetic field of the two-dimensional planes in the many crystallites of the ceramic pellets.²¹

For a gas of free carriers, a temperature-independent Pauli susceptibility is expected for $kT \ll E_F$ (or a 1/Tdependence for high temperature). Since we observe a strong temperature dependence in the opposite direction over a wide range of temperature, the free-carrier picture appears to be inadequate and interactions are expected to be important in this system. At present, the nature of these interactions has not been determined although short-range antiferromagnetic correlations have been suggested.¹⁷

VII. DISCUSSION AND CONCLUSION

The system $(La_{1-y}Pr_y)(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ allows for selective doping on two distinct sites in the 1:2:3 structure. For Pr doping on the La site, oxygen content and orthorhombic distortion remain essentially unchanged, indicating that the state of Cu in the O(1)-Cu(1)-O(5) layers remains essentially unaffected. The decreasing average Cu valence with increasing Pr concentration is, therefore, primarily accommodated by a decrease in the oxidation state of the O(2)-Cu(2)-O(3) planes. Despite the undisturbed character of the one-dimensional chains in the O(1)-Cu(1)-O(5) layers, T_c and Meissner effect are both reduced by the introduction of Pr.

In the La-doped samples, as La replaces Ba, oxygen content increases and the orthorhombic distortion disappears for $x \ge 0.25/z > 7.0$. This effect has also been observed when Ba is replaced by Nd, Sm, Eu, or Gd.²⁴ Here, doping occurs on a site in close proximity to the oxygen-deficient, O(1)-Cu(1)-O(5) layers which, when ordered, yield one-dimensional chains. Oxygen uptake typically balances La substitution and is coupled with a tendency towards a disordering of oxygen over the O(1)and O(5) sites. The average Cu valence remains unchanged. However, introducing oxygen into the O(1)-Cu(1)-O(5) oxygen-deficient layers increases the oxidation state of Cu in those planes and to compensate, the oxidation state of Cu in the O(2)-Cu(2)-O(3) planes must decrease, as in the Pr-doped samples, to maintain the constant average Cu valence.

Observation of a similar progression of superconducting properties with doping, independent of whether Pr for La or La for Ba substitution is considered, implies that the suppression of superconductivity is correlated with the state of the O(2)-Cu(2)-O(3) planes and not directly with the O(1)-Cu(1)-O(5) planes (the chain layers). This strongly suggests that superconductivity is supported by the O(2)-Cu(2)-O(3) planes and not the Cu-O chains. The recent discovery of superconductivity in the Bi-Sr-Ca-Cu-O system,²⁵ with $70 \le T_c \le 120$, and subsequent reports on structure,^{26,27} which indicate the presence of Cu-O sheets but no Cu-O chain layers, further supports our conclusion that superconductivity is supported by the Cu-O sheets. In addition, this discussion explains why $La_{1.5}Ba_{1.5}Cu_{3}O_{7+\delta}$ (x = 0.5) is not superconducting despite having the same average Cu oxidation state as $YBa_2Cu_3O_{7-s}$.⁷ Rather than deriving from an absence of linear Cu-O chains,² the lack of superconductivity can be interpreted in terms of the reduced state of the O(2)-Cu(2)-O(3) planes.

Local structural distortions accompanying Pr and La substitution may also contribute a small reduction in both T_c and Meissner signal, in addition to the doping effect. In YBa_{2-x}Sr_xCu₃O_{7- δ}, ^{28,29} doping on the Ba site with an ion of similar valence but different size slightly reduces both T_c and the magnitude of the Meissner signal. However, in the case of Sr for Ba substitution, replacement of 50% of Ba by Sr yields a transition-temperature decrease

of approximately 10% and only little change in Meissner signal, 28,29 whereas in the case of replacing Ba with La, 25% replacement completely disrupts superconductivity. Hence, the effect of local structural distortions that accompany doping is expected to be small compared with the direct effect of doping itself.

While the superconductivity appears to be supported by the Cu-O planes, the present data also demonstrate that orthorhombic samples yield the highest T_c 's and the largest Meissner signals in the $(La_{1-y}Pr_y)(Ba_{2-x}La_x)$ - $Cu_3O_{7+\delta}$ system. Oxygen-vacancy ordering in the O(1)-Cu(1)-O(5) layer is accompanied by subtle changes in the bonding geometry in the O(2)-Cu(2)-O(3) planes.¹⁰ Introducing disorder into the O(1)-Cu(1)-O(5) layers reduces the a-axis compression and presumably results in local fluctuations (on a unit-cell scale) in oxygen content. These local variations presumably also influence the local bond geometry in the O(2)-Cu(2)-O(3) planes. Consequently, the effect of oxygen vacancy ordering [O(1),O(5)]sites] on superconductivity can be understood in terms of the subtle relation between oxygen vacancy configuration in the O(1)-Cu(1)-O(5) layers and structure of the O(2)-Cu(2)-O(3) planes, rather than in terms of the direct electronic implications of the existence of onedimensional chains.

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