PHYSICAL REVIEW B VOLUME 55, NUMBER 10 1 MARCH 1997-II

Concentration range for superconductivity in high-quality $Pr_{2-x}Ce_xCuO_{4-y}$ thin films

J. L. Peng, E. Maiser,* T. Venkatesan, and R. L. Greene
Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742

G. Czjzek
Forschungszentrum Karlsruhe Institut fur Nukleare Festkorperphysik, Postfach 36 40, D-76021 Karlsruhe, Germany

(Received 19 August 1996)

We report ac susceptibility, electrical resistivity, and structural measurements on crystalline $Pr_{2-x}Ce_xCuO_{4-y}$ (PCCO) thin films prepared by pulsed laser deposition. We find superconductivity occurs within a narrow Ce concentration range ($0.13<x<0.20$) similar to that found for ceramic samples of this "electron-doped" material. Our results are quite different than those recently reported [Phys. Rev. Lett. **74**, 4927 (1995)] on PCCO single crystals where superconductivity near 20 K was found for Ce concentration as low as $x=0.04$. Possible reasons for this difference will be discussed. [S0163-1829(97)50610-2]

The "electron-doped" high-T_c system $R_{2-x}Ce_xCuO_{4-y}$ ($R=$Nd, Pr, etc.)[1,2] continues to be actively studied (in spite of its modest $T_c \cong 20$ K) because it has unusual properties compared to the "hole-doped" high-T_c copper oxides. Most current theories of high-T_c superconductivity do not distinguish between electron or hole doping in the CuO_2 planes and the observed experimental differences are not presently understood. Some of the anomalous features of $R_{2-x}Ce_xCuO_{4-y}$ are (i) an apparent s-wave symmetry[3] for the superconducting wave function; (ii) a normal-state resistivity proportional to T^2 and evidence for both electron and hole carriers in the transport properties;[4] (iii) a narrow Ce doping range for the occurrence of superconductivity.

The latter result has been questioned recently by Brinkmann *et al.*,[5] who reported that single crystals of $Pr_{2-x}Ce_xCuO_{4-y}$ (PCCO) are superconducting over a much wider Ce concentration range than previously found in ceramic samples of PCCO or in single crystals of $Nd_{2-x}Ce_xCuO_{4-y}$ (NCCO). For example, they found a $T_c=20$ K for Ce = 0.04 in PCCO. The T_c vs x phase diagram determined by Brinkmann *et al.* was similar to that found in "hole-doped" $La_{2-x}Sr_xCuO_4$,[6,7] although the high T_c observed at low x near the antiferromagnetic state was rather unusual. Since results on single crystals are usually considered to be more reliable than results on ceramic samples, and the implications of the Brinkmann *et al.* results are quite significant for the theory of high-T_c superconductivity, we attempted to verify their new phase diagram with high-quality thin films. In the case of NCCO, films, crystals, and ceramics all give the same phase diagram even though they are prepared under different conditions. PCCO films have not been previously prepared over a wide Ce concentration range to our knowledge. We find that our c-axis oriented films of PCCO have a phase diagram similar to that found originally in ceramic materials of PCCO and NCCO.[2] Later we will discuss the possible origin of the different phase diagram found by Brinkmann *et al.*

Systematic studies of $R_{2-x}Ce_xCuO_{4-y}$ compounds have been hindered by the difficulties in preparing well-characterized single phase samples because of two distinct features of these materials. First, the doping range of Ce for superconductivity is very narrow: for example, $0.14<x<0.17$ in $Nd_{2-x}Ce_xCuO_{4-y}$ (Ref. 2) as compared to $0.05<x<0.3$ in $La_{2-x}Sr_xCuO_{4-y}$.[6] Second, the appearance of superconductivity in $R_{2-x}Ce_xCuO_{4-y}$ is extremely sensitive to the oxygen stoichiometry. As-grown samples are not superconducting and a high-temperature reduction process is required to obtain superconductivity—usually a difficult and complicated procedure. High-quality and homogeneous ceramics, single crystals or thin films of these materials are necessary to ensure reliable experimental data. Unfortunately, these are difficult to prepare. Ceramic samples often contain phases with different Ce concentrations as evidenced by broad superconducting transition widths ($\Delta T_c>2$ K) in both magnetic and resistivity measurements. Single crystals are ideal for studying many physical properties, but careful investigation has shown that the Ce concentration is often not uniform inside crystals with thickness greater than 20 μm.[8,9] Another possible problem associated with crystals is oxygen inhomogeneity. Since the diffusion coefficient[10] of oxygen in Nd_2CuO_4 is lower than that of Y-Ba-Cu-O, for example, at 900 °C, $D=2.39\times10^{-5}$ cm^2 sec^{-1}, it is difficult to remove oxygen uniformly from the interior of NCCO crystals.

An alternative is to fabricate thin-film samples. The thermodynamics of epitaxial growth of thin films on single-crystalline substrates is very different from that of the bulk samples. The deposition temperature of thin films ($\sim$800 °C) is much lower than the sintering temperature of bulk samples ($\sim$1100 °C). Phase separation is less likely in a thin-film sample since its thickness (normally $<$500 nm) is much smaller than the thickness range ($\sim$20 μm) over which Ce concentration was found to be fairly uniform in single-crystal samples. The thin films are easier to reduce uniformly because of their large surface-to-volume ratio and much shorter diffusion length.

The fabrication of NCCO thin films has drawn considerable effort during the past years. As demonstrated by Gupta *et al.*[11] and Mao *et al.*,[12] pulsed laser deposition (PLD) is a suitable technique for making NCCO thin films since it reproduces the target composition. In this work PCCO films

0163-1829/97/55(10)/6145(4)/$10.00

were deposited in 200 mTorr of N_2O gas at a deposition rate of 0.3 A/pulse on $LaAlO_3$ substrates using the PLD technique. The pellets used for targets were made from PCCO ceramic samples. During the deposition the substrates were held at temperatures varying from 750 to 840 °C depending upon the Ce composition (we prepared films for $0<x<0.24$). After the deposition the deposition chamber was evacuated to 10^{-5} Torr and the films were cooled to room temperature within 2 h. The thickness of the films reported in this work varied from 300 to 600 nm. The films were characterized for structural and superconducting properties using x-ray diffraction, ac susceptibility, and resistivity measurements. We attempted to anneal PCCO films for $x<0.1$ at the temperature (1050 °C) used by Brinkmann *et al.* for their crystal growth. Such films were found to be inhomogeneous (see below).

X-ray diffraction shows that the PCCO films are grown primarily with the c axis perpendicular to the substrate surface with a small fraction of (110) orientation. No impurity peaks from any secondary phases were detected within the resolution of x-ray diffraction. Rocking curve analysis through the (006) planes of the films gives a full width at half maximum (FWHM) of 0.11°, indicating a superior growth characterized by a narrow mosaic distribution. The lattice parameters were determined from the peak values of 2θ by indexing to a tetragonal Pr_2CuO_4-type structure (space group $I4/mmm$). Since the size of a Ce^{4+} ion ($r=0.92$ A) is smaller than that of a Pr^{3+} ion (1.013 A), a substitution of Pr^{3+} by Ce^{4+} in Pr_2CuO_4 causes a change in the lattice parameters. The variation in the lattice parameter c is consistent with that of PCCO crystals and ceramic[13] as a function of Ce concentration.

ac susceptibility is a stringent test of the superconducting properties. In this work, the thin film was placed between two coils separated coaxially by several millimeters. One of the coils was driven by an ac current, typically at 70 kHz, and the other coil picks up a signal which is detected by a lock-in amplifier. The inductive coupling between driving and pick-up coils is strongly modified by the self-inductance of the film, especially when the film goes superconducting. In Fig. 1, we plot both the real part and the imaginary part of the ac susceptibility data as a function of temperature for different Ce concentrations. Superconductivity occurs, within a narrow Ce concentration range, $0.13<x<0.20$, with a maximum T_c of 21 K and a transition width ΔT_c (FWHM of the imaginary part) as sharp as 0.15 K at $x=0.15$. The transition temperature decreases quickly with both increasing and decreasing Ce content. No superconductivity was observed above 4.2 K for $x<0.12$. In the higher Ce doping range we observe superconductivity up to $x=0.20$. This is higher than previously reported in the ceramics[2] and may be a result of our improved sample quality.

PCCO films annealed under the same conditions as used by Brinkmann *et al.* for their crystals showed no evidence of bulk superconductivity for $x<0.10$. Films prepared this way most likely have oxygen or Ce inhomogeneities since no signal is seen in ac susceptibility but the resistivity decreases below ~13 K. However, the resistivity never goes to zero even at 4 K, the lowest temperature we measured. This suggests there are some small superconducting regions in films prepared this way—regions where the Ce or oxygen concentration is sufficient to give the number of carriers found in a homogeneous superconducting sample with $x=0.15$. We also annealed $x=0.15$ PCCO films under the Brinkmann *et al.* conditions. We found these films to have a lower T_c and a broader transition width as compared to films prepared by our technique.

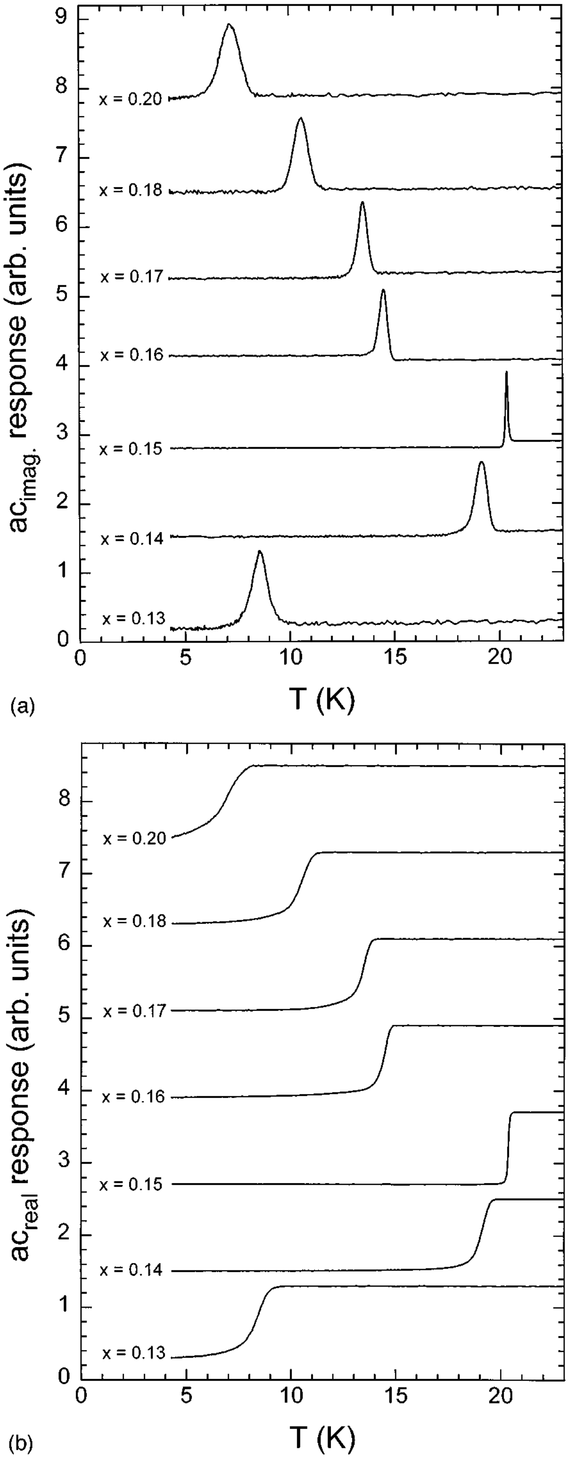

FIG. 1. Imaginary part (a) and real part (b) of the ac susceptibility signal of $Pr_{2-x}Ce_xCuO_{4-y}$ films, normalized and offset for clarity of presentation, for a range of cerium doping.

It is commonly accepted that ceramic samples of $R_{2-x}Ce_xCuO_{4-y}$ have the highest T_c at an optimal doping

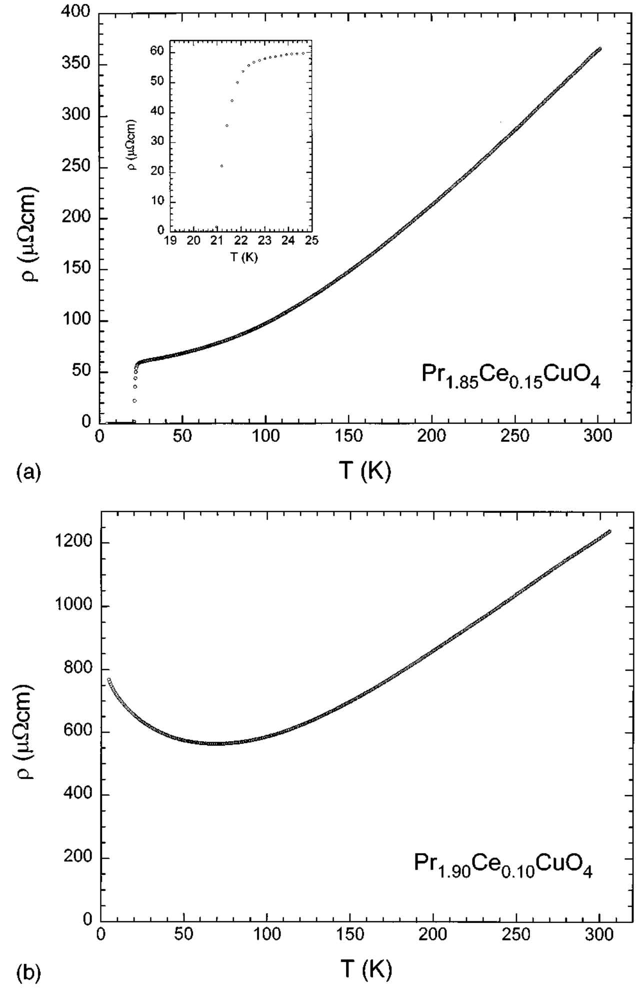

FIG. 2. Temperature dependence of the resistivity for $Pr_{2-x}Ce_xCuO_{4-y}$ thin films of $x=0.15$ (a) and $x=0.10$ (b). The inset shows the resistivity data near T_c for $x=0.15$ film.

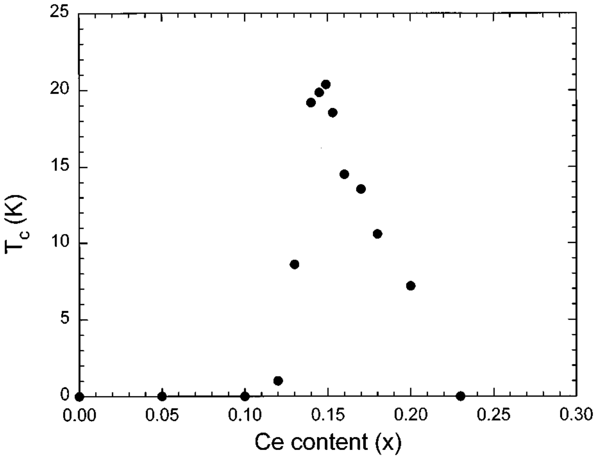

FIG. 3. Superconducting transition temperature vs cerium concentration for $Pr_{2-x}Ce_xCuO_{4-y}$ thin films. T_c was determined by the peak position of the imaginary part of ac susceptibility. Since the superconducting transitions are sharp the error of T_c is less than 0.5 K.

near $x=0.15$.[1,2] When the superconducting transition temperature decreases by moving away from $x=0.15$, the transition width is broadened. It is not unusual to see traces of superconductivity above 20 K when x is not at the optimal value and the midpoint of the transition is at a lower temperature. In our thin-film work, as demonstrated in Fig. 1, the superconducting transitions are shifted with only a slight broadening of the transition widths when changing x. Therefore, T_c vs x has been determined for the ‘‘electron-doped’’ materials *without ambiguity*. Based on our experience with film preparation in NCCO (Ref. 12) we believe our films have the same oxygen content for all Ce doping levels. Therefore, our data give a true representation of T_c versus CuO_2 plane carrier density, which is the phase diagram of relevance to theory.

Electrical resistivity using a standard four-probe method was measured on these same PCCO films. The normal-state resistivity shows a metallic behavior except for $x<0.13$. Generally the absolute value of the resistivity at room temperature decreases with increasing x. The temperature dependence of the normal-state resistivity of these thin films is nonlinear, and is similar to the NCCO crystals and thin films previously reported.[14] Detailed transport properties will be published separately. For the present study, more than two films were measured for each x and the results are reproducible. Here only the resistivity data for $x=0.10$ and 0.15 are presented. The temperature dependence of the resistivity for a superconducting film at $x=0.15$ is shown in Fig. 2(a). The corresponding resistivity ratio $\rho(300\text{K})/\rho(T_c)$ is 6.2. The residual resistivity near T_c is 60 $\mu\Omega$ cm. As shown in the inset, there is a sharp transition at $T_c=21.5$ K with $\Delta T_c=0.5$ K. These parameters indicate that our films have a higher quality than any previously reported on ‘‘n-type’’ materials. The temperature dependence of resistivity for an $x=0.10$ film is shown in Fig. 2(b). Superconductivity was not observed down to 4.2 K. At low temperature this film shows an upturn in resistivity, similar to that found in crystals, which most likely originated from localization effects.[15]

In our resistivity measurements, the variation of T_c with changing Ce concentration is consistent with the ac susceptibility data. We note that the temperature of zero resistance corresponds to the onset of the transition in the ac susceptibility measurements. Since the ac susceptibility, particularly the imaginary part, provides a sensitive means to detect inhomogeneities (such as Ce and oxygen distributions) in the films, the ac susceptibility measurements were adopted to determine the T_c’s for these PCCO films. The results of T_c vs x are shown in Fig. 3.

Clearly our results on the PCCO films are consistent with the earlier work on NCCO (Refs. 1 and 2) that superconductivity can only occur in the narrow range of Ce doping (near 0.15). We are convinced this is the intrinsic behavior of the $R_{2-x}Ce_xCuO_{4-y}$ system and represents the true dependence of T_c versus CuO_2 plane carrier concentration (as discussed earlier). This raises the question of the origin of the different results obtained by Brinkmann *et al.* There could be two possibilities: either oxygen or Ce inhomogeneity in their crystals. Brinkmann *et al.* argue against both of these based on their crystal-growth method.[16] However, our experience with NCCO crystal growth[8,9,17] suggests that crystals with transition widths greater than 2 K are inhomogeneous. In an earlier work[8] we reported that Ce phase segregation occurs in thick (>20 μm) single crystals and polycrystalline samples of

$Nd_{2-x}Ce_2CuO_{4-y}$ with nominal composition $x=0.15$. The crystals showed segregation into sharply defined ab plane sheets of material with different cerium concentrations. In a later experiment,[9] energy-dispersive diffraction of synchrotron-produced x rays was used to study microscopic structural inhomogeneities in the same crystals. Small changes in the lattice parameter c were detected over a spatial scale of 10 or 20 μm along the c axis. These changes were interpreted as evidence of variations in the cerium content inside the crystals. Since the dimensions of the crystals studied by Brinkmann *et al.* were typically $2\times2\times0.05$ mm^3, it is possible that these crystals (50 μm thick) contain cerium inhomogeneity along the c axis. The broad superconducting transitions in Fig. 2 of their paper[5] also suggest that their crystals with $x<0.1$ were inhomogeneous. One possible explanation for their results is that for low x the Ce concentration in the middle of the crystal is much higher (say, $x>0.10$) than near the outside. Under a normal reduction procedure, only the outside layers might be reduced which would result in a nonsuperconducting crystal. When the new annealing technique is used to reduce the crystals, more oxygen could be taken out of the middle region of the crystals, such that the middle layers become superconducting. This may explain why they observe such a very different T_c vs x behavior.

In summary, we fabricated high-quality thin films of $Pr_{2-x}Ce_xCuO_{4-y}$ by pulsed laser deposition. No superconductivity was observed in any low Ce doped films ($x<0.12$) above 4.2 K. Superconductivity only occurs within a narrow Ce concentration range $0.13<x<0.20$ with $T_{c\max}=21$ K and ΔT_c as sharp as 0.15 K at the optimal doping ($x=0.15$). When the cerium concentration is changed from this optimal doping the superconducting transition is shifted to a lower temperature with minimal broadening of the transition. We were thus able to determine the T_c vs x phase diagram more accurately than in prior work.

The authors wish to thank S. N. Mao and Z. Y. Li for their help with the experiments and Z. Trajanovic and P. Fournier for helpful discussions. This work was supported by the National Science Foundation under Grant No. DMR-9510475 and the German Academic Exchange Service (DAAD) from Hochschulsonderprogramm II funds under Grant No. D/95/09140.

---

[*] Also at Forschungszentrum Karlsruhe Institut fur Nukleare Festkorperphysik, Postfach 36 40, D-76021 Karlsruhe, Germany.

[1] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).

[2] H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).

[3] D. Wu *et al.*, Phys. Rev. Lett. **70**, 85 (1993).

[4] W. Jiang *et al.*, Phys. Rev. Lett. **73**, 1291 (1994).

[5] M. Brinkmann *et al.*, Phys. Rev. Lett. **74**, 4927 (1995).

[6] J. B. Torrance *et al.*, Phys. Rev. Lett. **61**, 1127 (1988).

[7] M. B. Maple, MRS Bull. **15**, 60 (1990).

[8] A. R. Drews *et al.*, Physica C **200**, 122 (1992).

[9] E. F. Skelton *et al.* , Science **263**, 1416 (1994).

[10] Y. Idemoto, K. Fueki, and M. Sugiyama, J. Solid State Chem. **92**, 489 (1991).

[11] A. Gupta, G. Koren, C. C. Tsuei, A. Segmueller, and T. R. McGuire, Appl. Phys. Lett. **55**, 1795 (1989).

[12] S. N. Mao *et al.*, Appl. Phys. Lett. **61**, 2356 (1992).

[13] M. Matsuda *et al.*, Physica C **179**, 347 (1991).

[14] X. Q. Xu *et al.* , Phys. Rev. B **53**, 871 (1996).

[15] S. J. Hagen *et al.*, Phys. Rev. B **45**, 515 (1992).

[16] M. Brinkmann *et al.*, J. Cryst. Growth **163**, 369 (1996).

[17] J. L. Peng, Z. Y. Li, and R. L. Greene, Physica C **177**, 79 (1991).