Extended Superconducting Concentration Range Observed in $Pr_{2-x}Ce_xCuO_{4-\delta}$

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We report magnetic susceptibility, electrical resistivity, and Hall-effect measurements on single crystals from the n-type high-T_c superconducting system $Pr_{2-x}Ce_xCuO_{4-\delta}$. Using an improved reduction technique, we find that bulk superconductivity can be established over the broad Ce concentration range $0.04 \leq x \leq 0.17$. The new superconducting phase diagram and the systematics of the electronic transport properties resemble those observed in the overdoped concentration range of the p-type high-T_c superconductors.

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Even after eight years of intense international research, the basic mechanism of high-T_c superconductivity seems far from being well understood. However, due to enormous experimental efforts, the family of high-T_c superconductors has grown continuously and essential progress in the characterization of their properties has been achieved [1].

All high-T_c compounds are structurally strongly related with the CuO_2 planes being the essential superconducting units. The majority of the high-T_c superconductors are obtained by doping of an antiferromagnetic insulator by holes, as in $La_{2-x}Sr_xCuO_4$ where in an ionic picture Sr^{2+} substitutes for La^{3+} [2]. There exists only one well-established high-T_c system with an electron type of doping, namely $Ln_{2-x}Ce_xCuO_{4-\delta}$ (Ln = Pr, Nd, Sm, Eu) with Ce^{4+} substituting for Ln^{3+} [3]. The existence of high-T_c superconductivity for both hole and electron doping has very important implications for theoretical models [4].

However, there still are open questions concerning n-type high-T_c superconductivity. Whereas all p-doped systems exhibit a very similar generic phase diagram with superconductivity existing over a broad concentration range from the metal-insulator transition at a charge carrier concentration of about 0.02 hole/Cu atom to about 0.3 hole/Cu [5], superconductivity in the n-doped systems occurs only in a very narrow concentration range close to a doping level of about 0.15 electron/Cu atom [6–9]. Intimately connected with this phenomenon is the role of the reduction process for the occurrence of superconductivity in the n-doped systems, which is not completely understood. In contrast to the situation for p-type superconductors, the oxygen stoichiometry not only determines the charge carrier concentration but has a more complex influence. It seems that even very small amounts of oxygen at the interstitial apical position above the CuO_2 layers are very detrimental for superconductivity [10,11]. A very effective pair-breaking scattering process of the interstitials could be the possible origin of this phenomenon [12].

In other important properties, too, there are essential differences between the hole-doped and electron-doped

systems. The symmetry of the superconducting order parameter seems to be of conventional s type in the electron-doped systems [13], whereas for the hole-doped systems the d symmetry is favored [14]. The variation of the electrical resistivity with temperature at optimum doping is linear for the p-type [15] and quadratic for the n-type systems [16]. Recent detailed investigations of the electron-doped high-T_c superconductors revealed a crossover of the sign of the Hall coefficient from negative to positive at low temperatures, thus casting doubts on the sign of the superconducting charge carriers [17–19].

The main aim of this Letter is to demonstrate that by using an improved reduction technique it is possible to induce bulk superconductivity in $Pr_{2-x}Ce_xCuO_{4-\delta}$ over a much broader concentration range than previously reported. The resulting new superconducting phase diagram and the variation of the transport properties with the Ce concentration fits much better into the systematics known for the hole-doped superconductors.

Single crystals of the system $Pr_{2-x}Ce_xCuO_{4-\delta}$ with different Ce concentrations were grown in Al_2O_3 crucibles following the standard method using a CuO-rich flux [20].

The quality of the platelet-shaped crystals with dimensions of typically $2 \times 2 \times 0.05$ mm^3 was checked by x-ray Laue patterns. The width of the x-ray rocking curves determined on the (0014) Bragg peak was typically $0.5°$. The Ce concentration varies slightly even among crystals from the same batch and was determined individually for each crystal by quantitative wavelength dispersive electron microprobe analysis (WDX). The Ce concentration in the a-b plane of each crystal was found to be constant within experimental resolution of $\Delta x = \pm 0.01$. $Pr_{2-x}Ce_xCuO_{4-\delta}$ single crystals tend to develop a slight gradient of the Ce concentration along the c axis [21], but for the crystals of the present study this gradient could be neglected as evidenced by a comparison of the Ce concentration on both sides of the crystals. Table I gives the composition and the lattice parameters for the crystals of the present study. The c-axis lattice parameters of the crystals increase continuously with decreasing Ce concentration in good agreement with results determined for polycrystalline materials [22].

TABLE I.   Composition, lattice parameters, annealing temperature, and annealing time of the single crystals of the present study. The capital letters in the first column are used to identify the crystals in the figures below.

No.	Pr	Nd	Ce (x)	Cu	c (Å)	a (Å)	T_{an} (°C)	t_{an} (h)
A	1.96(1)		0.04(1)	0.99(3)	12.229(1)	3.96(1)	1080	80
B	1.93(1)		0.07(1)	0.97(3)	12.194(1)	3.96(1)	1080	80
C	1.91(1)		0.09(1)	0.97(3)	12.175(1)	3.96(1)	1080	80
D	1.86(1)		0.14(1)	0.98(3)	12.142(1)	3.96(1)	1080	80
E	1.83(1)		0.17(1)	0.96(3)	12.117(1)	3.96(1)	1080	80
F		1.78(3)	0.22(3)	0.99(3)	12.040(1)	3.95(1)	980	80

The standard oxygen reduction procedure used for the induction of superconductivity in the n-type superconductors in an annealing in Ar at a temperature of 950 °C for about 10 h [6–9,22]. This procedure is known to be rather unsatisfactory even for the optimum Ce concentration $x \approx 0.15$. It often results in an oxygen gradient along the c axis, giving an incomplete superconducting transition for the resistivity measured along the c axis. This shows that the reduction process is rather ineffective, probably due to a limited oxygen mobility. A higher reduction temperature or a longer reduction time, however, usually cannot be applied, since the crystals then decompose at the surface, probably triggered by the evaporation of Cu [23]. With our crystals subjected to this standard reduction procedure, we recover the superconducting phase diagram known from the literature, namely a very narrow superconducting range close to Ce concentrations $x = 0.15$ (see dashed line in Fig. 4) [6–9].

In order to overcome this problem, we covered the single crystals on the top and bottom with two polycrystalline pellets of the same composition. This provides an effective diffusion barrier for the evaporation of Cu. Using this protection of the surfaces, we could increase the reduction temperature to 1080 °C and the reduction time to 3 days without any observable destruction of the crystal surfaces. The higher temperature and longer time make the reduction process much more effective in removing oxygen and establishing an equilibrium of the oxygen content along the c axis. The crystals of Table I have been reduced using this method. The total oxygen content of the crystals after the reduction process could not be determined, since the total mass of the crystals of about 1–2 mg is too low.

The in-plane electrical resistivity of the crystals was measured by a four-point low frequency ac technique with silver-painted contacts. The normal state Hall resistivity was measured by the standard five-contact geometry with the applied dc current in the a-b plane and a magnetic field of 4 T oriented along the c axis. The Hall voltage was determined from the voltage difference measured after rotating the crystal by 180° in the magnetic field. The low field dc susceptibility was measured using a noncommercial SQUID magnetometer [24].

In Figs. 1(a) and 1(b) we present our results of the a-b plane resistivity measurements on the crystals from Table I. Contrary to the results reported in the literature [25], we obtain metallic conductivity in the whole Ce concentration range down to a Ce concentration $x = 0.04$. All crystals except the overdoped one with $x = 0.22$ exhibit a superconducting transition above 20 K with some broadening for the samples with lower Ce concentrations. Measurements with a superimposed magnetic field of 4 T parallel to the c axis shift the transition below 10 K [dotted lines in Figs. 1(a) and 1(b)]. It is evident that the low-temperature logarithmic upturn in $\rho_{ab}(T)$ observed for the majority of the crystals reported in the literature [26–28] is absent, except for the crystal with the lowest Ce concentration $x = 0.04$. This upturn indicates weak localization behavior [29] and is attributed to strong conduction electron scattering at the residual interstitial oxygen atoms [30].

The resistivity was fitted using the empirical formula $\rho(T) = \rho(0) + bT^n$ [see drawn lines in Fig. 1(a)]. The exponent n changes from $n \approx 1.7$ for high Ce concentrations to $n \approx 1.3$ for lower Ce concentrations. A similar systematic change is well known for the overdoped concentration range of the p-doped high-T_c superconductors [15].

In Fig. 2 we show the zero-field-cooled magnetic susceptibility curves at different magnetic fields for the crystals with the magnetic field parallel to the c axis. The demagnetizing factors of the crystals (given in the figure caption) have been calculated from the ratio of the measured susceptibility at 1 Oe and the theoretical susceptibility for full screening. The fact is that full screening is obtained for applied fields of up to 50 Oe, and that the susceptibility curves shift with applied field in a similar manner, clearly showing the bulk nature of the superconductivity. Further evidence comes from a study of isothermal magnetization hysteresis loops at low temperature which gave the highest critical current density of 2×10^6 A/cm^2 [31] for the crystal with the lowest Ce concentration $x \approx 0.04$ (crystal A).

The results of our measurements of the Hall coefficient are plotted in Fig. 3. The Hall coefficient shifts systematically from negativelike to positivelike with increasing Ce concentration. All crystals except the one
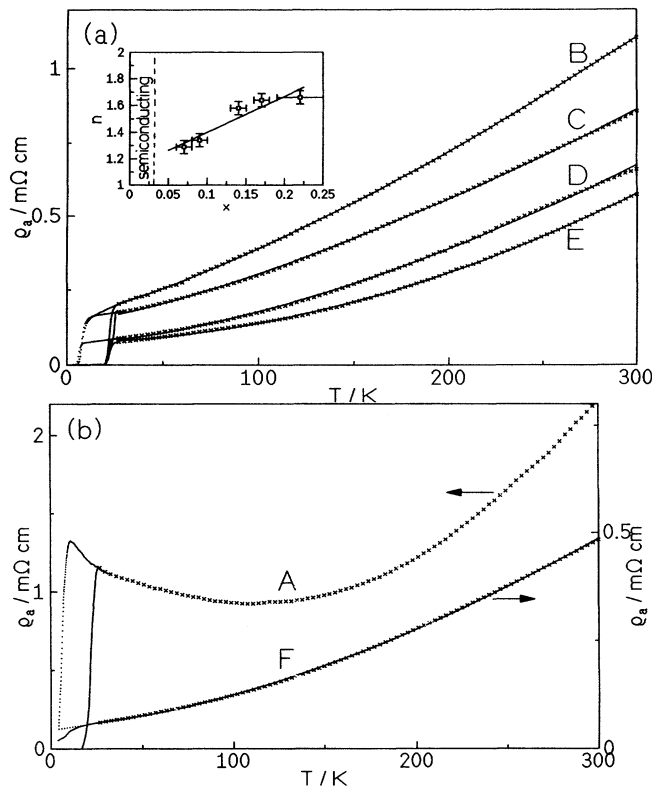
FIG. 1. (a,b) In-plane resistivity vs temperature for the crystals of Table I. The dotted lines give $\rho_a(T)$ in a superimposed perpendicular field of 4 T. The drawn lines above 30 K represent a fit by the formula $\rho(T) = \rho(0) + bT^n$ (see main text) with the exponent n given in the inset.
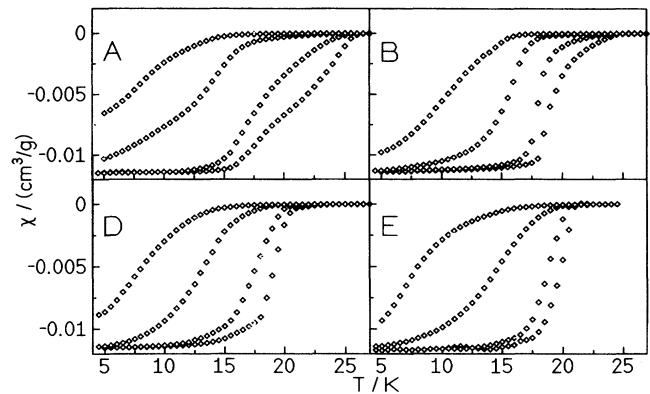

FIG. 2. dc zero-field-cooled susceptibility of the single crystals of Table I in an applied field of 1, 5, 50, and 300 Oe (from the right to the left). The demagnetizing factors for the crystals were $N = 0.89, 0.92, 0.94, 0.86$, and 0.87 (SI units) for samples A, B, C, D, and E, respectively.

with $x = 0.04$ (crystal A) exhibit the characteristic upturn in $R_H(T)$ toward positive values at low temperatures. Similar systematics of $R_H(T)$ have been observed in $Nd_{2-x}Ce_xCuO_{4-\delta}$ and in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ with changing δ [19]. The observation that for the superconducting sample with $x = 0.04$ (sample A in Fig. 3) the upturn at low temperatures is absent suggests that the existence of hole-type charge carriers is not a prerequisite for the occurrence of superconductivity in $Pr_{2-x}Ce_xCuO_{4-\delta}$.

In Fig. 4 we have plotted our results in a superconducting phase diagram after the improved reduction process and the same crystals after the standard, unprotected lower temperature reduction process. For low Ce concentrations there is a dramatic change: Bulk superconductivity is found down to the metal-semiconductor transition at $x \approx 0.04$, very similar to $La_{2-x}Sr_xCuO_4$. Although the superconducting transition broadens with decreasing Ce concentration, indicative of an increasing difficulty in getting chemically homogeneous samples, there is a clear tendency of an increasing T_c value with decreasing Ce concentration. The diamagnetic onset temperature of 27 K obtained for the crystal with $x \approx 0.04$ actually rep-

resents the highest transition temperature ever reported for n-type superconductors.

An essential question now concerns the origin of the change of the phase diagram with the reduction method as shown in Fig. 4. There are two possible explanations.

First, it might be that the more effective reduction technique induces charge carriers by creating vacancies at the regular O2 position in the T'-type lattice [32]. Then the total charge carrier number could be higher than calculated from the Ce content alone and a decreasing Ce content could be compensated by an increasing number of vacancies on the O2 position.

Second, it might be that only with the more effective reduction technique is it possible to remove the interstitial oxygen for lower Ce concentrations completely. As mentioned in the introduction, this seems to be a prerequisite for the occurrence of superconductivity.
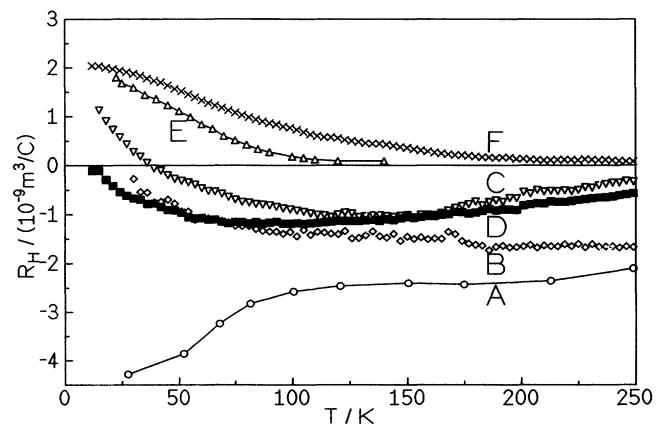

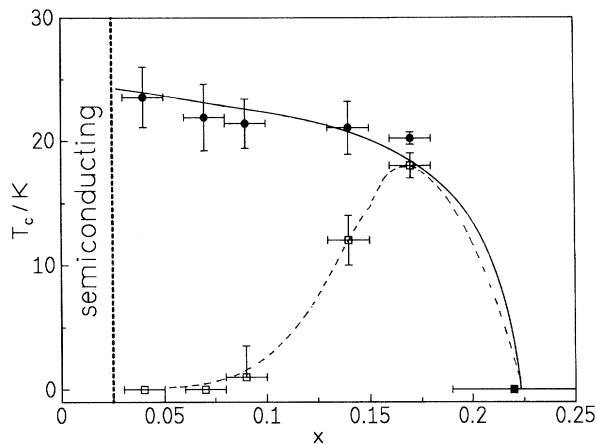FIG. 3. Hall coefficient vs temperature for the crystals of Table I.

FIG. 4. Superconducting transition temperatures vs Ce concentration for single crystals from Table I after the high-temperature reduction process (full line and full circles) and after reduction using the standard procedure (dashed line and empty squares). The upper and lower limits of the vertical error bars give the susceptibility onset and the 50% diamagnetic screening value in an applied field of 1 Oe, respectively.

We think the latter explanation is more plausible. The main argument in favor of this is the similarity of the two phase diagrams at the right-hand side in Fig. 4 and our observation that pure Pr_2CuO_4 subjected to the same reduction process remains semiconducting with a resistivity at room temperature about 5 orders of magnitude above that of the crystal with the Ce concentration $x = 0.04$. These observations suggest that additional electron doping of the CuO_2 layer by the creation of oxygen vacancies in the regular T' lattice is not most important.

The revised superconducting phase diagram in Fig. 4 resembles the overdoped part of the generic phase diagram of the p-type superconducting systems [5]. We find the maximum of T_c, i.e., the optimum doping in $Pr_{2-x}Ce_xCuO_{4-\delta}$ at the lowest Ce concentration $x = 0.04$. The underdoped part of the phase diagram is suppressed by the intervening metal-semiconductor phase boundary.

Actually there are striking similarities in the evolution of the transport properties in $Pr_{2-x}Ce_xCuO_{4-\delta}$ and in the overdoped concentration range of the p-type superconductors. First, the temperature dependence of the resistivity with increasing doping level changes similarly from approximately linear in T to approximately quadratic in T. The T^2 behavior of the resistivity reported for the n-type superconductors having a Ce concentration $x \approx 0.15$ then appears to be only due to the fact that this composition belongs to the overdoped concentration range in $Pr_{2-x}Ce_xCuO_{4-\delta}$. Second, the low values of the Hall coefficient in Fig. 3 compared to the values calculated from a single parabolic band model is characteristic of

the overdoped concentration range of the p-type superconductors [33].

The model of high-T_c superconductivity based on a van Hove singularity at ϵ_F for optimum doping provides a reasonable explanation for the change of the T dependence of the resistivity in the overdoped range of the p-type superconductors [34]. In superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ crystals, angular-resolved photoemission spectroscopy (ARPES) gave no evidence for a van Hove singularity at ϵ_F [35]. From our results the intriguing possibility exists that at lower Ce concentrations $x \approx 0.04$ the Fermi energy might coincide with the flat part of the conduction band resolved by ARPES slightly below ϵ_F for $x = 0.15$ [34], thus giving rise to a van Hove-type singularity at ϵ_F and joining the n-type superconductors to the same phenomenological systematics which have been established for p-type systems.

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