Superconductivity Produced by Electron Doping in CuO$_2$-Layered Compounds

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We have discovered that the Ce^{4+} doping and subsequent annealing in reducing atmosphere give rise to 24-K superconductivity in the Nd$_2$CuO$_4$-type structure with sheets of Cu-O squares. In contrast to the previously reported high-T_c cuprates, the charge carriers in the new superconductors are doped electrons, not holes; this was confirmed by the measurements of Hall and Seebeck coefficients as well as by chemical analysis of the effective copper valence. An anomalous dependence of T_c on the concentration of doped electrons is shown for these electron-doped superconducting cuprates.

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Since the discovery of high-temperature superconductivity (high T_c) in cuprate compounds,[1] extensive unprecedented studies have been carried out to elucidate what is required for high-T_c superconductivity. At present, the empirical view has come to the following consensus on the requirement for high-T_c superconductivity (Ref. 2): All high-T_c cuprates so far discovered have Cu-O layers with apical oxygens, forming the two-dimensional arrays of Cu-O pyramids or octahedra. The charge carriers are holes doped into the parent compounds which are antiferromagnetic insulators as a consequence of strong correlation between Cu $3d$ electrons. In contrast to these features, new superconducting cuprates, L_{2-x}Ce$_x$CuO$_{4-y}$ (L=Pr, Nd, and Sm), have been discovered very recently,[3] which are composed of two-dimensional sheets of Cu-O squares with no apical oxygen.[4] The new compounds were considered to be doped with electrons as charge carriers. The fact that high-T_c superconductivity is observed in CuO$_2$-layered cuprates with both types of charge carriers, electrons and holes, will provide a crucial test of the proposed theories for the mechanism of high-T_c superconductivity, many of which stand on the view of the pairing of O $2p$ holes mediated by some spin or charge fluctuation.[5] In this Letter, we present experimental evidence for the electron character of carriers in Nd$_{2-x}$Ce$_x$CuO$_{4-y}$ and new features in its electron-doped superconductivity, in particular the anomalous dependence of T_c on the electron concentration. We observe an abrupt onset and a subsequent disappearance of superconductivity with increasing concentration of electrons, which is to be compared with the continuous behavior of T_c against the hole concentration in La$_2$CuO$_4$-type compounds.[6]

The introduction of mobile electrons was achieved by doping Nd$_2$CuO$_4$ (or Pr$_2$CuO$_4$) with Ce. The samples used in the study were prepared by the solid-state reaction technique. Prescribed amounts of Nd$_2$O$_3$ (or Pr$_6$O$_{11}$), CeO$_2$, and CuO were mixed and prereacted at

950 °C for 10 h in air with two intermediate pulverizations. Then the powders were pressed into pellets and sintered at 1100 °C for 15 h in air. The pellets were cooled down to room temperature at the cooling rate of 300 °C/h. (We will denote these pellets as "as-grown" samples hereafter.) To produce superconductivity in Ce-doped Nd$_2$CuO$_4$, it was necessary to anneal the sample in the reducing atmosphere. We annealed the pellets at 1050 °C for 10 h under Ar-O$_2$ gas mixture flow with the oxygen partial pressure of 1×10^{-4} atm, and then quenched to room temperature in the same atmosphere. Finally, the sample was further annealed at 550 °C for 10 h in the same atmosphere, although the result of this annealing procedure was rather insensitive to the oxygen partial pressure (10^{-4}-1 atm) of the atmosphere. This final annealing procedure was necessary to improve the width of the superconducting transition and also to reduce the normal-state resistivity, supposedly by eliminating harmful effects arising from grain boundaries within the reduced ceramics.

The as-grown samples were confirmed to be of the single phase of the Nd$_2$CuO$_4$ structure (shown schematically in the inset of Fig. 1) by measurements of powder x-ray diffraction. After the reducing treatment, however, a tiny trace of Nd$_2$O$_3$ and Cu$_2$O impurity phase (less than 2%) was sometimes discernible in the diffraction pattern. The systematic variation of the lattice parameters upon Ce composition, as shown in Fig. 1, indicates that Ce ions are certainly dissolved into the compounds up to x =0.20. No remarkable difference was observed in the lattice parameters between the samples before and after the annealing.

The oxygen content was determined by an iodometric titration technique,[7] which is also plotted against Ce concentration (x) in Fig. 1. After the heat treatment under the reducing condition, the oxygen content appears to decrease from about 3.99 (y ~0.01) to 3.96 (y ~0.04), though the data points were somewhat scat-
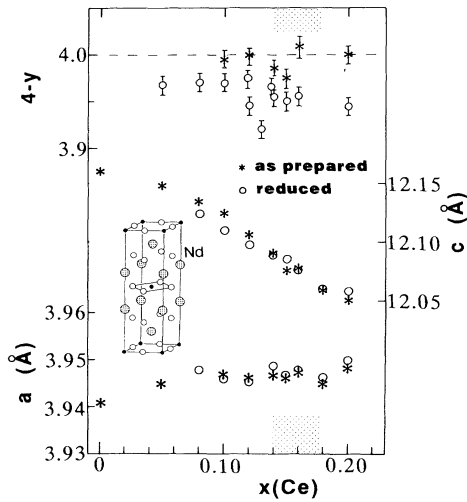
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FIG. 1. Ce-concentration (x) dependence of the oxygen content $(4-y)$ and the lattice parameters a and c of the tetragonal Nd_2CuO_4 structure in as-grown (asteriks) and reduced (open circles) samples of $Nd_{2-x}Ce_xCuO_{4-y}$.

tered, possibly due to the presence of a small amount of secondary phase. According to the measurements of Ce core-level photoemission spectra by Fujimori, all Ce ions dissolved in Nd sites are existing in tetravalent (Ce^{4+}) ionic states.[8] Later, we will show further evidence for the tetravalency of Ce ions from the transport measurements. Then, we can represent the compound as $(Nd^{3+})_{2-x}(Ce^{4+})_xCu^{(2-q)+}(O^{2-})_{4-y}$. Here, the concentration of the chemically doped electrons is given by the conservation of charge: $q = x + 2y$. On this basis, the results shown in Fig. 1 indicate that the electrons are chemically introduced by the Ce doping and oxygen vacancies as well as up to the concentration $q \sim 0.3$ in the reduced samples of $Nd_{2-x}Ce_xCuO_{4-y}$ $(y \sim 0.04)$.

So far, superconductivity in $Nd_{2-x}Ce_xCuO_{4-y}$ has been observed only for the samples with $y \sim 0.04$ which were annealed under the reducing atmosphere. Hereafter we will present the results on such reduced samples. In the inset of Fig. 2, we show the temperature dependence of the resistivity as well as the Hall coefficient for the typical superconducting sample $Nd_{1.85}Ce_{0.15}CuO_{3.96}$ with T_c above 20 K. The resistivity is nearly temperature independent above T_c. The onset temperature of the superconductivity in resistivity is as high as 24 K and zero resistance is achieved below 20 K. The substantial amount of the Meissner signal in this sample (see Fig. 3)—more than 25% of the ideal value—guarantees the bulk nature of the superconductivity.

The transport measurements give clear evidence that the charge carriers are *electrons* introduced by the substitution of Nd^{3+} ions with Ce^{4+} ions. The Hall coefficient in the superconducting sample is negative, as shown in the inset of Fig. 2, over the whole temperature
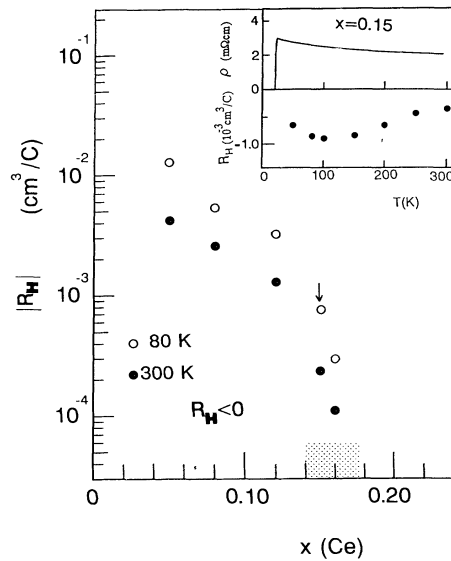
FIG. 2. Ce-concentration (x) dependence of the absolute value of the Hall coefficient R_H at 80 and 300 K for $Nd_{2-x}Ce_xCuO_{4-y}$ annealed under the reducing atmosphere. The sign of R_H is negative for all the samples shown in the figure. Inset: The temperature dependence of the resistivity and the Hall coefficient R_H for the superconducting compound $Nd_{1.85}Ce_{0.15}CuO_{3.96}$.

region investigated (below 300 K), indicating that the dominant charge carriers are electrons. We have also observed that the Seebeck coefficient of the same sample is negative and is almost temperature independent $(-2\mu V/K)$ between 80 and 300 K. This contrasts sharply with the case of the high-T_c cuprates known so far, where positive Hall and Seebeck coefficients were always observed.[2]

In Fig. 2, we plot the Ce-concentration (x) dependence of the Hall coefficient measured for the reduced
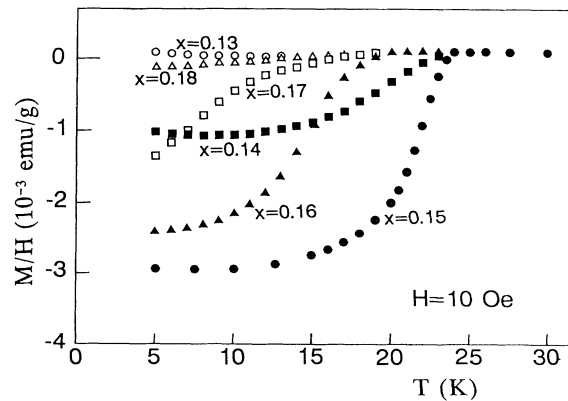
FIG. 3. Temperature dependence of the Meissner signal measured by cooling the sample under a constant field of $H = 10$ Oe for $Nd_{2-x}Ce_xCuO_{4-y}$ annealed under the reducing atmosphere.

samples of $Nd_2Ce_xCuO_{4-y}$ with various Ce contents. The rapid decrease in the absolute value of the negative Hall coefficient is clearly seen with decreasing x. This undoubtedly indicates that the number of the mobile electrons increases with Ce^{4+} doping in the Nd^{3+} sites. Apart from the different sign of the carriers, the dependence of the Hall coefficient on x is quite similar to the case of the hole-doped superconductor $La_{2-x}Sr_xCuO_4$, in which the mobile holes are introduced by substituting trivalent La ions with divalent Sr ions.[9]

Superconductivity was observed in a very limited Ce-concentration range, as seen from Fig. 3, which demonstrates the temperature dependence of the Meissner signal (field-cooling run) measured by a SQUID magnetometer. Based on the Meissner data shown in Fig. 3, we plot in Fig. 4 the dependence of T_c on the concentration of Ce (x) in the reduced sample of $Nd_{2-x}Ce_xCuO_{4-y}$ $(y \sim 0.04)$. The "bulk" T_c was arbitrarily defined as the 20% of the saturated magnetization at low temperatures for the sample showing the Meissner signal of more than 10% of the ideal value at 5 K. On the upper abscissa in Fig. 4, we tentatively draw the scale of q, that is the number of chemically doped electrons per Cu-O unit, which was determined from the relation $q = x + 2y$. There is some ambiguity in the measured value of the oxygen content $(4 - y)$ as shown in Fig. 1. On adjusting the scale of q, we assumed that the oxygen content was kept constant (3.96 or $y \sim 0.04$) in the Ce-concentration range of $x = 0.10$–0.20 when the annealing was performed under the same reducing condition. Figure 4 demonstrates an anomalous dependence of T_c on the Ce-concentration x (or on $[Cu-O]^{-q}$ charge). The bulk superconductivity with T_c above 20 K abruptly emerges at around $x = 0.14$. From $x = 0.14$ to 0.15, the magnitude of the Meissner signal rapidly grows as shown in
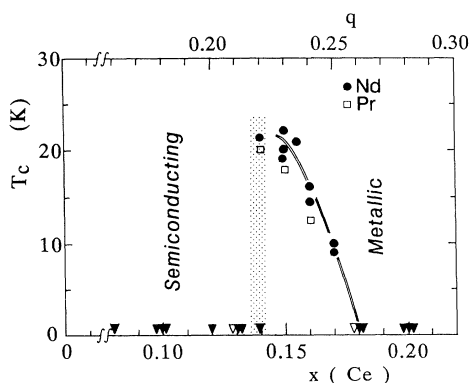

FIG. 4. Dependence of the transition temperature T_c on the Ce concentration (x) in reduced $Nd_{2-x}Ce_xCuO_{4-y}$ (circles) and in $Pr_{2-x}Ce_xCuO_{4-y}$ (squares). (For the definition of T_c, see text.) The closed and open triangles indicate that bulk superconductivity is not observed above 5 K for Nd and Pr systems, respectively. The determined scale of effective charge q per Cu-O unit is shown on the upper abscissa.

Fig. 3, without remarkable change of the onset temperature. This shows that the 24-K superconducting and the nonsuperconducting regions are coexisting in this very narrow composition range, supposedly due to the compositional inhomogeneity of the dopant distribution. With further increase of x beyond $x = 0.15$, T_c begins to decrease continuously and the superconductivity disappears at around $x = 0.18$ (or $q \sim 0.26$).

Characteristic temperature dependence of resistivity is observed to be strongly correlated with the superconductor-nonsuperconductor phase change shown in Fig. 4. Below $x = 0.14$ (or $q \sim 0.2$), its temperature dependence is semiconducting $(d\rho/dT < 0)$, though the resistivity still steadily decreases with increase of x. Therefore, the observed abrupt onset of the superconductivity at $x = 0.14$ seems to be associated with the semiconductor-metal transition. When x exceeds 0.14 at which superconductivity appears, the resistivity becomes nearly temperature independent above T_c. At present, we have no definite explanation for the observed abrupt semiconductor-to-metal, or nonsuperconductor-to-superconductor transition. We can speculate that the system may undergo some magnetic or structural phase transition induced by Ce doping.

When x exceeds 0.18, the superconductivity disappears as shown in Figs. 3 and 4, where the system shows a typical metallic behavior in resistivity. The resistivity still decreases with increasing x and its temperature coefficient becomes positive $(d\rho/dT > 0)$. Such a superconductor-to-nonsuperconductor metal transition observed at high *electron* concentration was quite analogously observed at the high *hole* concentration $(x \sim 0.3)$ in the hole-doped $La_{2-x}Sr_xCuO_4$.[6]

Here we should stress that quantitatively the same behaviors of T_c and resistivity against the Ce concentration have been observed in the $Pr_{2-x}Ce_xCuO_{4-y}$ system. In Fig. 4, we also plotted T_c (defined in the same way) against x in the reduced $Pr_{2-x}Ce_xCuO_{4-y}$ system, which falls on almost the same T_c vs x curve as observed for $Nd_{2-x}Ce_xCuO_{4-y}$. This is a strong indication that the observed electronic phase diagram is general for the single CuO_2-layered compound with the Nd_2CuO_4-type structure and that there must be an underlying common mechanism for the doping-induced semiconductor-to-superconductor and superconductor-to-nonsuperconductor metal phase transition.

There remain some urgent problems to be tackled experimentally. First, the real role of the annealing in the reducing atmosphere should be clarified. The present annealing procedure produces the oxygen vacancy $y \sim 0.04$ (see Fig. 1), which corresponds to the increase of q by $2y \sim 0.08$. However, superconductivity has not been observed so far in the as-grown samples $(y \sim 0.01)$ up to $x = 0.20$ (and hence $q \sim 0.22$). The absence of superconductivity in the as-grown samples might be due to the insufficient electron number needed in order to produce the superconductivity. We speculate, however, that

the oxygen vacancies introduced by this procedure do not only add the electrons to the system, but also may play a more active role in producing the superconductivity. Relating to this, it should be clarified as to why the compound remains a semiconductor up to the rather high concentration of electrons ($q \sim 0.2$). Do oxygen deficiencies produced by the reducing procedure serve to destroy the magnetic or structural order in the semiconducting region?

Another important question concerns the location of the doped electrons. If the electrons are situated primarily within CuO_2 sheets, the electrons will be Cu $3d$ character (Cu^{1+} in the local picture). At present, we cannot rule out other possibilities such as doped electrons existing mainly in Nd layers, which needs to be checked experimentally and theoretically.

In conclusion, the electron doping in the CuO_2-layered compound can give rise to the high-temperature superconductivity as well as hole doping. The abrupt onset of above 20-K superconductivity with the semiconductor-metal transition induced by electron doping has been commonly observed in $Nd_{2-x}Ce_xCuO_{4-y}$ and $Pr_{2-x}Ce_xCuO_{4-y}$. Further electron doping makes the system more metallic, but not superconducting.

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