Electron and hole doping in Nd-based cuprates with single-layer CuO$_2$ sheets: Role of doped Ce ions and 30-K superconductivity

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We have attempted electron and hole doping in Nd-based cuprates with single-layer sheets of Cu-O squares and pyramids. It was found that partial substitution of Nd^{3+} sites with Ce^{4+} ions introduces mobile electrons into the Nd$_2$CuO$_4$ structure which shows two-dimensional (2D) sheets of Cu-O squares with no apical oxygens. With further Sr doping into Nd$_{2-x}$Ce$_x$CuO$_4$, the crystalline lattice undergoes a structural transformation into the new hole-conductive compound with 2D sheets of Cu-O pyramids, which is identical with the superconducting phase discovered recently by Akimitsu *et al.* [Jpn. J. Appl. Phys. **27**, L1859 (1988)]. The hole concentration in Nd$_{2-x-y}$Ce$_x$Sr$_y$CuO$_{4-\delta}$ can be increased by controlling the composition (x,y) of non-copper cations and filling oxygen vacancies (δ) as well, which give rise to superconductivity with T_c up to 30 K.

It has been generally accepted that the introduction of holes into CuO$_2$ planar sheets is required for high-temperature superconductivity (high T_c) in cuprate compounds. High-T_c cuprates are thus far known to exhibit four types of Cu-O sheets, namely, Cu-O networks of (a) octahedra, (b) pyramids, (c) squares, and (d) chains. For example, the first discovered high-T_c compound[1] La$_{2-x}$A$_x$CuO$_4$ (A = Ca,Sr,Ba) has sheets of Cu-O octahedra, whereas YBa$_2$Cu$_3$O$_y$-like compounds[2] exhibit Cu-O pyramids and chains. Furthermore, it is believed that triple or quadrupole CuO$_2$-layer compounds Bi(Tl)-Ca-Sr(Ba)-Cu-O with above 100-K T_c (Ref. 3) show both Cu-O square- and pyramid-type sheets within a unit cell. All of these high-T_c cuprates possess, as a common unit, the CuO$_2$ sheets with apical oxygens in either side of the sheet, forming a two-dimensional (2D) array of Cu-O octahedra or pyramids, which are doped with mobile holes. Nevertheless, there is still controversy over where the doped holes are dominantly located, or more specifically whether the apical oxygens above and/or below Cu sites are necessary or not for high T_c. Furthermore, it should be tested experimentally whether *electron* doping, if possible, can produce high-T_c superconductivity in a class of cuprate compounds with various types of Cu-O sheets.

To address these questions, it is desirable to use simple compounds having a *single* Cu-O sheet per repeated unit as model systems. Figure 1 shows typical structures with single-layer CuO$_2$ sheets; (a) the T phase with Cu-O octahedra as observed in La$_2$CuO$_4$, (b) the T' phase with squares as in L_2CuO$_4$ (L=Pr, Nd, Sm, Eu, and Gd),[4] and also (c) the newly discovered T^* phase with pyramids as in (Nd,Ce,Sr)$_2$CuO$_4$ (Refs. 5–8) (*vide infra*). The hole

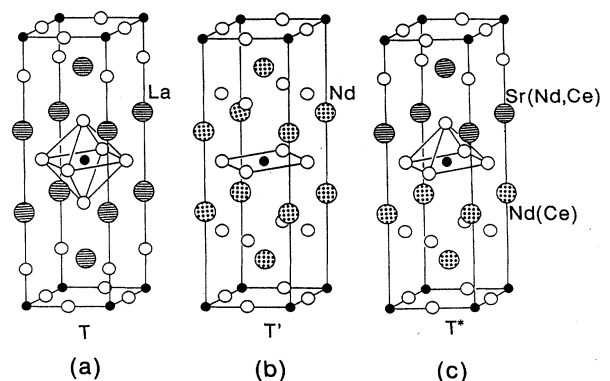FIG. 1. Crystal structures of (a) La$_2$CuO$_4$ (T-phase), (b) Nd$_2$CuO$_4$ (T' phase), and (c) Nd$_{2-x-y}$Ce$_x$Sr$_y$CuO$_4$ (T^* phase).

doping into the T-phase structure has been investigated extensively since the discovery of high T_c in this material.[1] In this Rapid Communication, we report our attempts at electron and hole doping in Nd-based cuprates with two-dimensional sheets of Cu-O squares and pyramids [as shown in Figs. 1(b) and 1(c)] to make the compounds conducting and hopefully superconducting.

Related to the present approach, Akimitsu, Suzuki, Watanabe, and Sawa[5] reported the discovery of superconductivity around 20 K in Ce, Sr-doped Nd-based cuprates with composition formula of $Nd_{2-x-y}Ce_xSr_yCuO_4$. They presented the possibility that its structure might be of the T' phase with Cu-O square sheets [Fig. 1(b)]. Very recently, the structure of this new phase was determined by means of electron[6] and neutron diffraction[7,8] measurements. The structure is essentially a hybrid of the T and T' structures with a pyramid-type Cu-O network, that is, the T^* phase shown in Fig. 1(c). Therefore, there still remains the question of whether the 2D sheets of Cu-O squares, for example, in the Nd_2CuO_4 structure shown in Fig. 1(b), can be doped with electrons and/or holes and can be made superconducting or not. If the Nd_2CuO_4-type cuprate could be made to be a high-T_c compound, it will be quite decisive concerning the position of doped carriers. In this paper, we focus our investigation on the effect of chemical doping of tetravalent (Ce^{+4}) and divalent (Sr^{2+}) ions in Nd_2CuO_4.

Materials were synthesized from mixtures of rare-earth oxides ($CeO_2, Nd_2O_3, Pr_6O_{11}$), $SrCO_3$ ($CaCO_3$), and CuO. The mixtures were first calcined at 950°C, and then pressed into pellets, and finally fired in air at 1100–1150°C. The pellets were quenched or furnace cooled to room temperature and subsequently annealed under various pressures (10^{-3}–85 atm) of oxygen at 550°C.

Let us first describe our attempts to dope the T' phase Nd_2CuO_4 with electrons and holes. Until now, all of our attempts to introduce an appreciable density of holes to the T' phase Nd_2CuO_4 have been unsuccessful: For example, Sr doping into Nd_2CuO_4 causes rapid phase separation, where the *dominant* secondary phase is a double CuO_2-layer compound (e.g., $Nd_2SrCu_2O_6$). A small amount of Ca (less than 5%) can be doped into the T' phase, yet the hole concentration remains nearly zero due to compensating oxygen deficiencies. On the other hand, Ce can be dissolved in the T' lattice up to approximately 10% of the Nd sites. In Fig. 2 we show temperature dependence of resistivities in $Nd_{2-x}Ce_xCuO_{4-\delta}$. In the figure we also plot the result for the Ce undoped but highly oxygen-deficient ($\delta \sim 0.04$) sample which was obtained by quenching from air atmosphere at 1150°C. The Ce-doped or oxygen-deficient samples show reduced resistivity and are semimetallic. Preliminary measurement on the Hall coefficient (R_H) in these compounds indicate that the charge carriers are of the electron type; for example, $R_H = -4 \times 10^{-4}$ cm^3/C for the $x = 0.10$ sample at 300 K. This clearly shows that oxygen vacancies as well as the tetravalent Ce ions embedded in T' Nd_2CuO_4 introduce mobile electrons into the compounds. This is in contrast with the case of La_2CuO_4 (K_2NiF_4 structure) where holes, not electrons, can be introduced by chemical doping

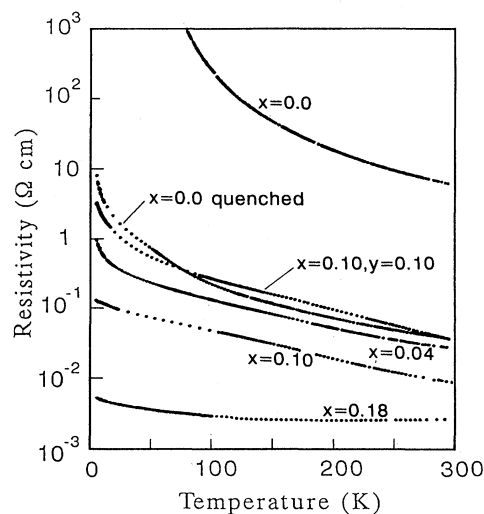FIG. 2. Temperature dependence of resistivity in T'-phase compounds, $Nd_{2-x}Ce_yCuO_4$ ($x = 0.0$–0.18) and $Nd_{2-x-y}Ce_x$-Sr_yCuO_4 ($x = 0.10$, $y = 0.10$).

of divalent alkaline-earth ions or by La deficiencies.

The nominal density of doped electrons in the T' phase $Nd_{2-x}Ce_xCuO_{4-\delta}$ could be determined by an iodomeric titration method,[9] taking into consideration the reductive reaction to convert Ce^{4+} into Ce^{3+} in the titration process. It was found that the Ce doping with $x = 0.18$ could increase the electron density (q) per [Cu—O] unit up to 0.20 (or effectively $Cu^{+1.80}$). Superconductivity has not been found for electron densities below 0.20 per [Cu—O] unit, though we have yet to explore further electron-rich (high-q) regions.[10]

Contrary to the parent compound, the Ce-doped T' compound $Nd_{2-x}Ce_xCuO_4$ with $x = 0.1$–0.2 can be doped with Sr and Ca ions. However, this procedure makes the samples less conducting, as shown in Fig. 2 for the T'-phase sample $Nd_{1.80}Ce_{0.10}Sr_{0.10}CuO_4$ ($x = 0.10$, $y = 0.10$). This indicates that the doped divalent ions partly compensate the charge and hence reduce the number of mobile electrons. When the concentration (y) of Sr is further increased, particularly beyond that of Ce, the lattice of $Nd_{2-x-y}Ce_xSr_yCuO_4$ undergoes a distinct transformation from the T' phase to the new tetragonal phase (T^* phase). The new phase[8] is identical to the superconducting phase which Akimitsu et al.[5] recently discovered. Since the divalent Sr (Ca) ion overcompensates the increased cation-site charge by Ce^{4+} in the Nd^{3+} lattice, the above observation implies again that the T' lattice cannot sustain holes, but that the T^* lattice can. The lattice parameters in this T^* phase are 3.85 Å ($=a$) and 12.48–12.51 Å ($=c$), which should be compared with the values in the T' phase $Nd_{2-x}Ce_xCuO_4$ ($a = 3.96$ Å, $c = 12.1$ Å) and in the T phase $La_{2-x}Sr_xCuO_4$ ($a = 3.78$ Å, $c = 13.2$ Å).

A similar phase transformation is observed in $Pr_{2-x-y}Ce_xSr_yCuO_4$ systems with increasing Sr concentration (y) when $x = 0.1$–0.2. In the case of Ca doping in $Nd_{2-x}Ce_xCuO_4$, the partial T' to T^* transformation

takes place, but the fraction of the transformed T^* phase is less than 10% according to the rough estimate of peak intensities in the powder x-ray diffraction pattern. It appears to be difficult to substitute Sr sites with smaller Ca ions in the T^* phase. According to structural studies,[6-8] Nd and Sr ions in the T^* phase show sequential ordering along the axis normal to the CuO_2 basal planes, as shown in Fig. 1(c). Very recently, Tokura *et al.*[11] discovered a class of new compounds having the similar T^* structure shown in Fig. 1(c) Sr-doped La*L*CuO$_4$ (L = Eu and Sm) compounds, where large La ions and comparatively small L ions show the sequential ordering (-La-La-*L*-*L*-). This observation shows that the T^*-phase structure is not restricted to (Nd,Ce,Sr)$_2$CuO$_4$, but is a widely observed structure characterized by the 2D sheets of pyramids and ordered A-site cations.

The T^*-phase compounds $Nd_{2-x-y}Ce_xSr_yCuO_{4-\delta}$ can be superconducting, as Akimitsu *et al.* first pointed out.[5] Superconductivity in the T^*-phase compounds was observed to appear in a rather narrow composition region; $x = 0.15 - 0.20$, $y = 0.4 - 0.5$. We further observed that the properties of the T^*-phase compounds are quite sensitive to annealing atmosphere. Figure 3 shows the Meissner data (field cooled) on the samples $Nd_{1.4}Ce_{0.2}Sr_{0.4}CuO_{4-\delta}$ which were prepared by different thermal treatments. The sample quenched from air atmosphere at 1150 °C down to room temperature shows no Meissner effect (no superconductivity) and the temperature dependence of the resistivity is semiconducting (not shown). Annealing the same sample in an oxygen atmosphere leads to much reduced resistivity and gives rise to superconductivity. In particular, extensive annealing for 12 h in 85-atm oxygen appears to fill oxygen vacancies and greatly improve the superconducting properties: By this procedure the onset of T_c in resistivity (shown in the right part of Fig. 3) increases above 30 K. The substantial magnitude of the Meissner signal in this sample—more than 30% of the ideal value—guarantees the bulk nature of the superconductivity with T_c above 28 K.

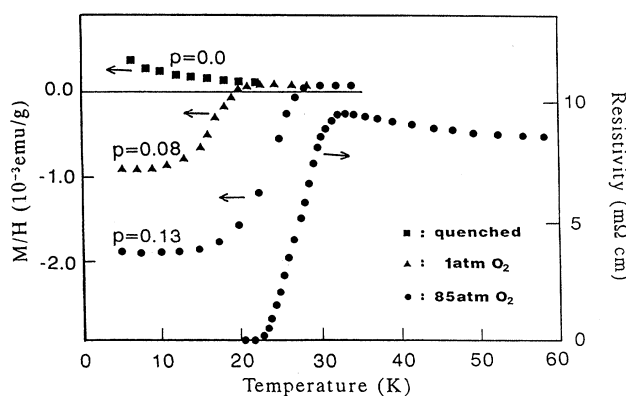As is evident from such a remarkable dependence on oxygen deficiencies, the charge carriers in these T^*-phase

compounds are holelike. Measurements of the Hall coefficient were also carried out on several superconducting samples, which always showed positive values of $(2-3) \times 10^{-3}$ cm^3/C at room temperature, supporting the above conclusion. We tried further to determine the average $[Cu-O]^{+p}$ charge, or the concentration of chemically doped holes with use of the iodometric titration technique.[9] We obtained the approximate values of p which are indicated in Fig. 3 for each sample. There is uncertainty in the Ce concentration dissolved in the T^* phase owing to a small amount (less than 5%) of secondary phases (mainly $Nd_2Ce_2O_7$). Therefore, the p values indicated in the figure have an experimental error of approximately ± 0.03, yet the relative change of p in the course of oxygen treatments is considered to be accurate. The increase in p observed in these series of samples corresponds to a decrease in oxygen vacancies as much as 0.07. As in $La_{2-x}Sr_xCuO_4$ (Ref. 12) and $YBa_2Cu_3O_y$-like compounds,[13] it appears that the hole concentration (p) is the major variable strongly correlated with T_c, although in the present case it is difficult to separate the contribution of oxygen vacancies from that of the hole concentration.

It is to be noted here that the superconducting T^* phase is stabilized by a subtle balance of electronic charge on the cation sites. Crystallographically, the concentration of Sr ions included in the T^* phase must be high enough because the sequential ordering of Nd and Sr is essential for realizing the T^* phase. With too high a Sr concentration, however, the sample would have a substantial amount of oxygen vacancies, as in the case of highly Sr-doped La_2CuO_4 (Ref. 12); it may even destabilize the T^* structure. Tetravalent Ce ions dissolved in the Nd lattice compensate for the over-decreased charge on the noncopper cation sites and hence serve to prevent oxygen vacancies or phase separation. The tetravalency of Ce ions
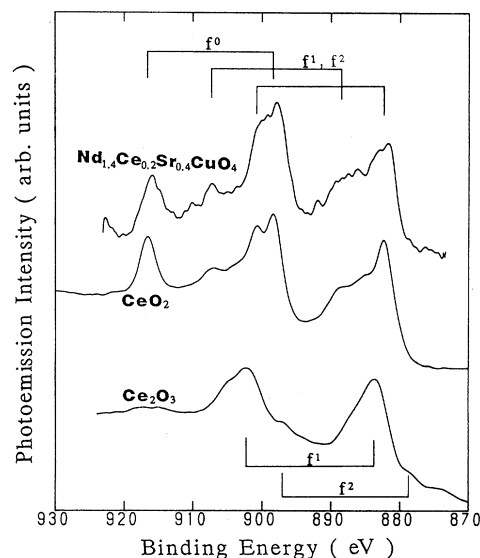

FIG. 3. Meissner effect (field cooled) in the T^*-phase compounds $Nd_{1.6}Ce_{0.2}Sr_{0.4}CuO_{4-\delta}$. The oxygen-annealing conditions: 1 atm O_2 at 400 °C for 48 h and 85 atm O_2 at 550 °C for 12 h.

FIG. 4. X-ray photoemission spectra of Ce core levels in the superconducting T^*-phase compound $Nd_{1.6}Ce_{0.2}Sr_{0.4}CuO_{4-\delta}$ in comparison with those in CeO_2 (Ce^{4+}) and Ce_2O_3 (Ce^{3+}) (Ref. 14).

in the superconducting T^* phase was confirmed by photo-emission spectroscopy. Figure 4 shows x-ray photoemis-sion spectra of the Ce core level in the superconducting sample with $p = 0.13$ shown in Fig. 3, in comparison with those for CeO_2 (Ce^{4+}) and Ce_2O_3 (Ce^{3+}).[14] As is evident from the close similarity between the spectra of the T^*-phase compound and of CeO_2, almost all Ce ions involved in the specimen are assigned to Ce^{4+} and not to Ce^{3+}.

Finally, let us briefly mention the properties of some T^*-phase compounds other than $Nd_{2-x-y}Ce_xSr_yCuO_4$. First, the Ca-containing compound $Nd_{2-x-y}Ce_xCa_y$-CuO_4 could not be obtained in the form of a single phase, as mentioned before, which is composed of the major T' phase and the minor T^* phase and pyrochrore-phase ($Nd_2Ce_2O_7$) compounds. The mixed-phase compounds were observed to show a resistivity drop at 10–20 K. Con-sidering that there is no possible superconducting com-pound other than the T^*-phase in this combination of cat-ions, we suppose that a small fraction of the T^* phase is supposed to be superconducting. On the other hand, Pr-based T^*-phase compounds, for example, $Pr_{1.4}Ce_{0.2}$-$Sr_{0.4}CuO_4$, can be obtained as a single-phase material, yet its resistivity behavior is typical of a semiconductor. The samples investigated had various composition ratios of Pr to Ce and Sr within the nearly single-phase region and were further extensively annealed in 80 bar oxygen, but never showed metallic nor superconducting behavior. Such a situation in Pr-containing cuprates also has been observed in $PrBa_2Cu_3O_7$ (isostructural with

$YBa_2Cu_3O_7$),[15] in which Pr ions show the mixed valence between 3^+ and 4^+. The same situation is supposed to occur in this Pr-containing T^* phase. This is in contrast with the case of the T' phase Pr_2CuO_4 where the valence of the Pr ion is fixed at 3^+.

In conclusion, we have demonstrated from the results on Nd-based single-layer cuprates that the 2D sheets of Cu-O squares with no apical oxygen can support mobile electrons, but not holes. The electron-doped cuprates are conducting, but not superconducting above 4 K for an electron density less than 0.20 per [Cu−O] unit. The mobile holes can be doped into *single-layer* sheets of Cu-O pyramids, like the 2D sheets of octahedra in La-based cuprates, and make the compound superconducting with T_c up to 30 K. It appears that apical oxygens are neces-sary for CuO_2-layered compounds to be doped with mobile holes. However, it does *not necessarily* mean that doped holes are mainly positioned on the apical oxygens. We should further pursue the real role of the apical oxy-gen: How does it affect the electronic structures of the ground state and low-lying excited states?

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the ideal value. Except for slight differences in lattice con-stants, the solved structure is essentially identical with that re-ported in Ref. 7, which was obtained on the clean single-phase compound, but with less Meissner signal and lower T_c.

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[10]After completion of this manuscript, Y. Tokura, H. Takagi, and S. Uchida discovered bulk superconductivity in highly re-duced $Nd_{2-x}Ce_xCuO_{4-\delta}$ with $x = 0.15$ and $\delta = 0.07$; Nature (London) (to be published).

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