Unusual T_c variation with hole concentration in $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$

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We have investigated the T_c variation with the hole concentration p in the La-doped Bi-2201 system, $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$. It is found that the Bi-2201 system does not follow the systematics in T_c and p observed in other high-T_c cuprate superconductors (HTSC's). The T_c vs p characteristics are quite similar to those observed in Zn-doped HTSC's. An exceptionally large residual resistivity component in the in-plane resistivity indicates that strong potential scatterers of charge carriers reside in CuO_2 planes and are responsible for the unusual T_c variation with p, as in the Zn-doped systems. However, contrary to the Zn-doped HTSC's, the strong scatter in the Bi-2201 system is possibly a vacancy in the Cu site.

Many high-T_c cuprate superconductors (HTSC's) display an approximately parabolic dependence of T_c upon the hole concentration p with the maximum T_c at $p \approx 0.16$.[1,2] (p is defined as the hole concentration per Cu atom in CuO_2 planes.) This behavior was observed first in $La_{2-x}Sr_xCuO_4$.[1] Then other HTSC's, such as $YBa_2Cu_3O_{7-y}$,[2] $Bi_2Sr_2CaCu_2O_{8+\delta}$,[3] and $TlSr_2CaCu_2O_{7+\delta}$,[1] were also found to show approximately the same relation between T_c and p which scales only with the maximum T_c, $T_{c,max}$. Though not studied for the full range of p, several other HTSC's are also known to have $T_{c,\ max}$ at $p \approx 0.14 \sim 0.15$.[4,5] Therefore one might expect that there possibly exists a universal relation between T_c and p which all HTSC's satisfy.[2]

Existence of a universal parabolic relation between T_c and p for all HTSC's, despite the different combinations of constituent atoms, the presence of various charge-carrier reservoir layers, and a variety of interplane coupling strengths, cannot be common but is believed to be related to a noble nature of high-temperature superconductivity. It is therefore not strange that the recent observations in Zn-doped HTSC's of departure from the universal relation have drawn particular interest.[6–9] Much attention has focused on the function of Zn. Within a HTSC, Zn substitutes for Cu in the CuO_2 plane and behaves as a nonmagnetic impurity without altering the carrier concentration. In this paper, we show that a similar nonuniversal T_c-p relation holds also for the La-doped Bi-2201 system, $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$, which contains strong disorders in CuO_2 planes differing from impurities.

We have obtained the hole concentration p of the samples from the thermopower (S) measurements. The room-temperature thermopower S(290 K) of HTSC's was found to be a universal function of p over the whole range of doping,[1,3] which has since been used widely to determine the p of HTSC's. The superconducting-transition temperature T_c was determined at half the normal-state resistivity. The conventional solid-state reaction of stoichiometric oxides and carbonates was adopted in preparing polycrystalline samples of $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$. The x-ray diffraction (XRD) analysis shows all the samples to be single phase to the threshold of detection. The oxygen content in the sample of $x=0.1$ could be varied by annealing the same sample in vacuum for 6 h at different temperatures (400 °C, 500 °C, and then 600 °C). S was measured by employing the dc method described in Ref. 10. The resistivity ρ was measured through the conventional low-frequency ac four-probe method.

Figure 1 shows the temperature dependences of S and ρ of $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ (BSLCO) with $0.1 \leqslant x \leqslant 0.8$. The temperature and doping dependences of S in Fig. 1(a) are typical of HTSC's. S (290 K) increases with doping x from -15.5 to 60 μV/K. Corresponding p determined from the relations between S (290 K) and p in Ref. 3 varies from 0.286 to 0.073 with doping. The ρ measurements in Fig. 1(b) display that the T_c of BSLCO has its maximum at $x \sim 0.5$ or $p \sim 0.22$. The appearance of $T_{c,max}$ at $x \sim 0.5$ agrees with the previous measurements.[11] $T_c/T_{c,max}$ against p is plotted in

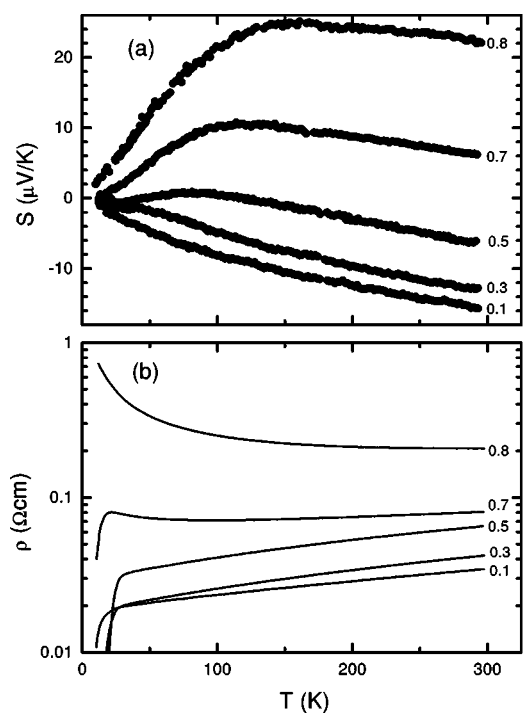

FIG. 1. (a) The thermopower S and (b) the resistivity ρ of $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ as functions of temperature. The numbers next to the curves denote the La content x in the materials.

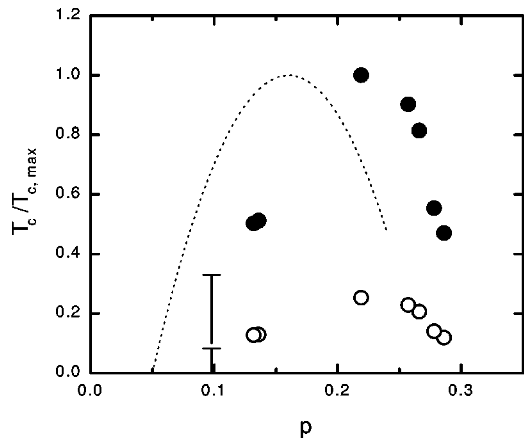

FIG. 2. T_c of $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$, normalized to $T_{c,max}$, plotted as a function of the hole concentration p determined from the S data in Fig. 1 and the S-p relations in Ref. 1. $T_{c,max}=21.5$ K for closed circles and 85 K for open circles. The error bars show the upper limit of T_c for the sample of $x=0.8$ with $p=0.098$. The dotted curve is a plot of the ''universal'' relation in Ref. 1.

Fig. 2. The T_c (=21.5 K) of $x=0.5$ is used as $T_{c,max}$ for solid circles. The dotted curve is of the ''universal'' relation, $T_c/T_{c,max}=1-82.6(p-0.16)^2$, in Ref. 1. The relation has not yet been fully tested in the overdoped region of $p>0.25$. Figure 2 clearly displays that BSLCO does not follow the systematics. Superconductivity in the underdoped region is deeply suppressed and the $T_{c,max}$ appears at an overdoped hole concentration $p\sim0.22$ rather than 0.16. Besides, the $T_{c,max}$ of $\sim$21.5 K is also unusually low, which is only $\frac{1}{4}$ the T_c of $Tl_2Ba_2CuO_{6+\delta}$, isostructural of BSLCO.[12] Taking the maximum T_c of $Tl_2Ba_2CuO_{6+\delta}$ as $T_{c,max}$, BSLCO has much lower $T_c/T_{c,max}$'s, as represented by open circles in Fig. 2.

Unusual T_c variation with p is exposed more dramatically in the vacuum-annealed sample of $x=0.1$ which superconducts at $T\leqslant10$ K without being vacuum annealed. Vacuum annealing reduces the content of oxygen atoms interstitial between Bi-O planes and consequently p in CuO_2 planes.[13–15] Figure 3(a) shows that successive vacuum annealings at 400 °C, 500 °C, and then 600 °C enhance S of $Bi_2Sr_{1.9}La_{0.1}CuO_{6+\delta}$ from -15.5 to -9.3 μV/K. The corresponding variation of p is from 0.286 to 0.240. We expect from the observed T_c-p relation of BSLCO in Fig. 2 that T_c of the sample of $x=0.1$ rises with annealing from 10 to 20 K. The ρ measurements in Fig. 3(b), however, show that the superconductivity observed in the as-grown sample disappears with annealing in vacuum. We observed similar behaviors also in $Bi_2Sr_2CuO_{6+\delta}$ which had been prepared from the nominal composition of Bi:Sr:Cu=2:2:1.5. The semiconducting as-grown sample of $Bi_2Sr_2CuO_{6+\delta}$ having $p=0.282$ exhibited a superconducting-transition onset at 11.5 K when vacuum annealed at 400 °C. And yet subsequent vacuum annealings at 500 and 600 °C put the sample back in the semiconducting states. The p's of the $Bi_2Sr_2CuO_{6+\delta}$ sample annealed at 400, 500, and 600 °C were 0.256, 0.250, and 0.216, respectively, all of which are located in the superconducting region of Fig. 2.

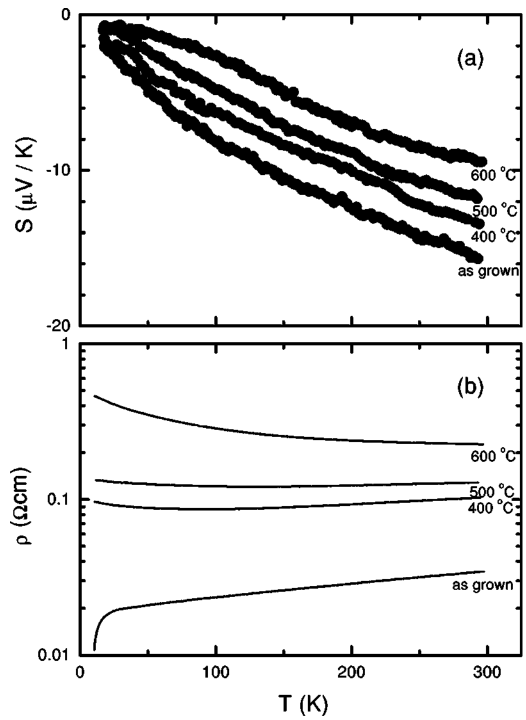

FIG. 3. (a) S and (b) ρ of vacuum-annealed $Bi_2Sr_{1.9}La_{0.1}CuO_{6+\delta}$ as functions of temperature. The numbers next to the curves denote the annealing temperatures.

The T_c vs p characteristics of as-grown samples represented by the open circles in Fig. 2 resemble those of Zn-doped HTSC's in Refs. 6 and 7. It has been suggested that the primary effect of Zn impurities is to produce a large residual resistivity as a nonmagnetic potential scatterer in the unitary limit and that the more rapid depression of T_c in the underdoped region is related to the large residual resistivity reaching the universal two-dimensional resistance $h/4e^2\approx6.5$ k$\Omega/\square$ per CuO_2 plane at the edge of the underdoped superconducting region.[8] Unlike most HTSC's, the Bi-2201 superconductor is found to have an exceptionally large residual resistivity.[16,17] The corresponding two-dimensional residual resistance per CuO_2 plane ranges from 0.3 k$\Omega/\square$ at an overdoped hole concentration to 10 k$\Omega/\square$ at an underdoped concentration with 50% uncertainties.[18] The large residual resistivity indicates that BSLCO contains strong scatterers of charge carriers in the planes. The strong scatterer in BSLCO is, however, not an impurity but most likely a vacancy in the Cu site, since any of Bi, Sr, and La can hardly substitute for Cu and disorders in the noncopper sites have little effect on superconducting properties but changing the hole concentration. Nevertheless, a vacancy in the CuO_2 plane is expected to act as a nonmagnetic potential scatterer, just like the Zn impurity in the planes. Vacuum annealing may cause extra vacancies in CuO_2 planes as well as expelling interstitial oxygen atoms. Thus the same argument in terms of disorder in the CuO_2 plane can be adopted for an explanation of the deeper suppression of T_c in vacuum-annealed samples.

Although the above discussion does not provide a full account for the origin of the nonuniversal T_c vs p characteristics, it may be concluded that similarity between the Bi-

2201 HTSC with disorders differing from impurities and other HTSC's with Zn impurities seem to strengthen the argument that a strong potential scattering in the planes and a large residual resistivity at an underdoped hole concentration are closely related to the strong suppression of high-temperature superconductivity and the more rapid T_c depression in the underdoped region.

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[18] Hole concentrations of the samples in Refs. 16 and 17 are estimated from the in-plane resistivity at room temperature, ρ_{ab} (300 K), and the temperature dependence of ρ_{ab}. A ρ_{ab} (300 K)$\approx$5 mΩ cm and a semiconductorlike temperature dependence at low temperatures of ρ_{ab} usually appear in a sample with an underdoped hole concentration.