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著者	小池 洋二
journal or publication title	Physical review. B
volume	62
number	18
page range	R11981-R11984
year	2000
URL	http://hdl.handle.net/10097/35335

doi: 10.1103/PhysRevB.62.R11981

Giant suppression of superconductivity at $x=0.21$ in the Zn-substituted $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ single crystals

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(Received 10 July 2000; revised manuscript received 12 September 2000)

We have found a little suppression of superconductivity at $x=0.21$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals and, moreover, a giant suppression of superconductivity at $x=0.21$ through the 1% substitution of Zn for Cu. In the Zn-substituted $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ single crystal with $x=0.21$ and $y=0.01$, the resistivity exhibits an upturn at low temperatures below ~ 80 K. These results suggest that the dynamical stripe correlations of spins and holes are pinned by a small amount of Zn at $x=0.21$, leading to a static stripe order and the giant suppression of superconductivity, as in the case of $x=0.115$.

Recently, the static order of spins and holes at p (the hole concentration per Cu) $\sim 1/8$ in the La-based cuprates, which has been found from the elastic neutron-scattering experiments,¹⁻⁴ has attracted great interest. It is not only because the static order well explains the so-called $1/8$ anomaly,^{5,6} namely, the anomalous suppression of superconductivity at $p \sim 1/8$, but also because it is closely connected with the modulated dynamical correlation between Cu spins, which has been pointed out from the inelastic neutron-scattering experiments⁷⁻¹⁰ to exist in a wide range of $0.06 \leq p \leq 0.25$. At present, the static order is reasonably interpreted as a stripe-patterned one, which originates from the dynamical stripe correlations of spins and holes and is statically stabilized through the pinning by the tetragonal low-temperature (TLT) structure (space group: $P4_2/nm$) or impurities such as Zn.¹¹⁻¹³

This kind of stripe order was originally discovered in $\text{La}_2\text{NiO}_{4+\delta}$ or $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ whose crystal structure is fundamentally the same as that of the La-based cuprates. In the nickelates, the static stripe order has been found at various values of the hole concentration of $1/2$, $1/3$, $1/4$ per Ni.¹⁴⁻¹⁶ In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, it is supposed that the dynamical stripe correlation between Cu spins exists in a wide range of $0.06 \leq x \leq 0.25$.¹⁰ Therefore, there is a possibility that, besides the order at $x \sim 1/8$, another static order exists in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as well as in the nickelates. In fact, we have found anomalous behaviors of the resistivity and the thermoelectric power around $x=0.22$ in polycrystalline samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and that the superconductivity is a little suppressed around $x=0.22$. Furthermore, it has been found that the anomalies become marked through the partial substitution of Zn or Ga for Cu and that the anomalies are not related to the structural phase transition between the tetragonal high-temperature (THT) phase (space group: $I4/mmm$) and the orthorhombic mid-temperature (OMT) phase (space group: $Bmab$).^{17,18} So, we have pointed out that probably an order of spins and/or holes, such as the stripe order, is formed or fluctuates around $x=0.22$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, though this x value is neither the simply expected $1/4$ nor $1/5$.

In this paper, in order to investigate the anomalous behaviors around $x=0.22$ in detail, we have grown partially Zn-substituted ($y=0.01$) and non-Zn-substituted ($y=0$)

$\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ single crystals of good quality in the overdoped region and made measurements of the electrical resistivity and T_c .

Partially Zn-substituted ($y=0.01$) and non-Zn-substituted ($y=0$) single crystals of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $0.19 \leq x \leq 0.26$ were grown by the traveling-solvent floating-zone (TSFZ) method.¹⁹⁻²¹ Polycrystalline feed rods were prepared as follows. First, powders of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ were prepared by the solid-state reaction method. Prescribed amounts of La_2O_3 , SrCO_3 , CuO , and ZnO powders were mixed and prefired in air at 900°C for 12 h. After pulverization, the prefired materials were mixed and sintered in air at 1050°C for 24 h. This process of mixing and sintering was repeated several times to obtain homogeneous powders of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$. Next, 1 mol % CuO powders were added to the powders of $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ and mixed thoroughly in order to obtain tightly sintered feed rods in the succeeding sintering process and also to compensate for evaporated CuO in the TSFZ growth process. The powders were put into thin-wall rubber tubes and isostatically cold pressed at 2.4 kbar into rods of 7 mm in diameter and ~ 120 mm in length. They were finally sintered in air at 1250°C for 24 h to form tightly sintered feed rods of 5 – 6 mm in diameter and ~ 120 mm in length. Sintered rods used as a solvent were also prepared in a similar way, but the composition was richer in Cu and Sr than those of the feed rods, as referred in the literature.²² Typically, $\text{La}_{2-x}\text{Sr}_x\text{O}_3:\text{Cu}_{1-y}\text{Zn}_y\text{O} = 3:7$ in the molar ratio and $x = 0.35$. The final sintering was performed in air at 900°C for 12 h. The sintered rods were sliced in pieces and a piece of ~ 0.4 g was used as a solvent for the TSFZ growth. The TSFZ growth was carried out in an infrared heating furnace. The growth space was filled with flowing oxygen gas of 4 bars to suppress the evaporation of CuO .²² The zone traveling rate was 0.5 – 1.0 mm/h. The rotation speed of the upper and lower shafts was 30 rpm in the opposite direction. Crystals thus grown were in the form of cylindrical rods of ~ 5 mm in diameter. In order to fill up oxygen vacancies and to remove the strain, as-grown crystals were annealed in flowing oxygen gas of 1 bar at 900°C for 50 h, cooled down to 500°C at a rate of 8°C/h , kept at 500°C for 50 h and then cooled down to room temperature at a rate of 8°C/h .

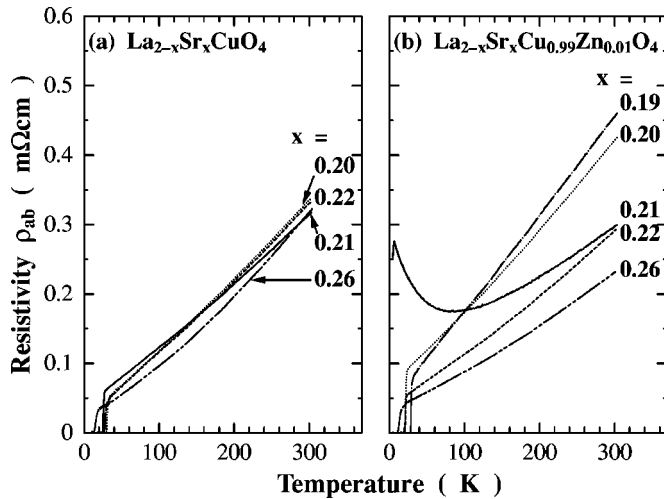


FIG. 1. Temperature dependence of the electrical resistivity ρ_{ab} in the ab plane for various x values in single-crystal $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y=0$ and (b) $y=0.01$.

These crystals were characterized by the x-ray back-Laue photography. Single-domain regions (typically 5 mm in diameter and 40 mm in length) were carefully sectioned with a diamond wheel to obtain rectangular specimens. The composition of each crystal was analyzed by inductively coupled plasma atomic-emission spectrometry (ICP-AES). The Sr content x in each crystal was almost the same as that in each feed rod within the accuracy of ± 0.01 . The Zn content y in each crystal was 0.008 ± 0.002 and tended to be a little smaller than 0.01 in each feed rod. This may be due to a little evaporation of ZnO in the TSFZ growth process. The homogeneity of the composition in each crystal was analyzed by scanning-electron microscope energy-dispersive x-ray spectroscopy to be good within the experimental accuracy.

Electrical resistivity measurements were carried out by the dc four-point probe method. Four terminals were prepared on a specimen with gold paste, which were baked in oxygen gas at 800°C for 15 min and cooled down to room temperature at a rate of $14^\circ\text{C}/\text{h}$. Lead wires of gold were attached to the terminals with silver paste. The magnetic susceptibility was measured using a superconducting quantum interference device magnetometer in a magnetic field of 10 Oe during warm up after zero-field cooling, to determine T_c .

Figure 1 shows the temperature dependence of the electrical resistivity ρ_{ab} in the ab plane for various x values in single-crystal $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $y=0$ and $y=0.01$. It is well known that the resistivity in the normal state exhibits a metallic behavior, namely, $d\rho_{ab}/dT > 0$ in the overdoped region of $x \geq 0.15$.^{23,24} In the Zn-substituted single crystal with $x=0.21$, however, the resistivity exhibits a minimum and upturn at low temperatures below ~ 80 K, and decreases with decreasing temperature below ~ 6 K, probably, on account of the filamentary superconductivity. In this crystal, the temperature dependence of the electrical resistivity ρ_c along the c axis also exhibits a minimum and upturn in the same temperature range as in the case of ρ_{ab} , as shown in Fig. 2. These anomalous upturns are analogous to those formerly found in the Zn- or Ga-substituted polycrystalline samples around $x=0.22$.^{17,18}

Figure 3 displays the temperature dependence of the mag-

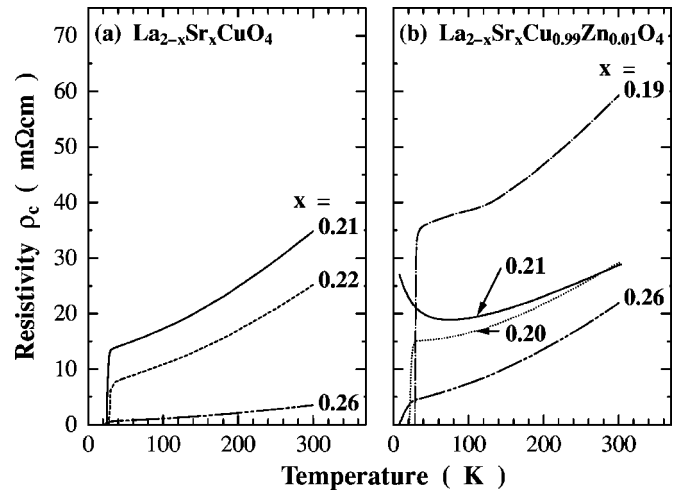


FIG. 2. Temperature dependence of the electrical resistivity ρ_c along the c axis for various x values in single-crystal $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y=0$ and (b) $y=0.01$.

netic susceptibility χ for various x values in single-crystal $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $y=0$ and $y=0.01$. It is found that the superconducting transition is very sharp for most of the superconducting crystals, suggesting that both Sr and Zn contents are very homogeneous in these crystals. It is remarkable that the Zn-substituted crystal with $x=0.21$ showing the anomalous upturn of the resistivity does not exhibit a clear superconducting transition of the bulk above 2 K. The value of T_c , defined as the temperature where the extrapolated line of the steepest part in the χ vs T plot reaches the normal-state value of χ , is shown in Fig. 4. This is in good agreement with the value of T_c defined as the midpoint of the superconducting transition curve in the ρ_{ab} vs T plot. It is found that superconductivity is drastically suppressed at $x=0.21$ in the Zn-substituted crystals, where the anomalous upturn of the resistivity occurs. This suppression of superconductivity is more striking than that observed in the Zn- or Ga-substituted polycrystalline samples.^{17,18} This may be due to better homogeneity of the Sr concentration in the single crystals than in the polycrystalline samples. It is also remark-

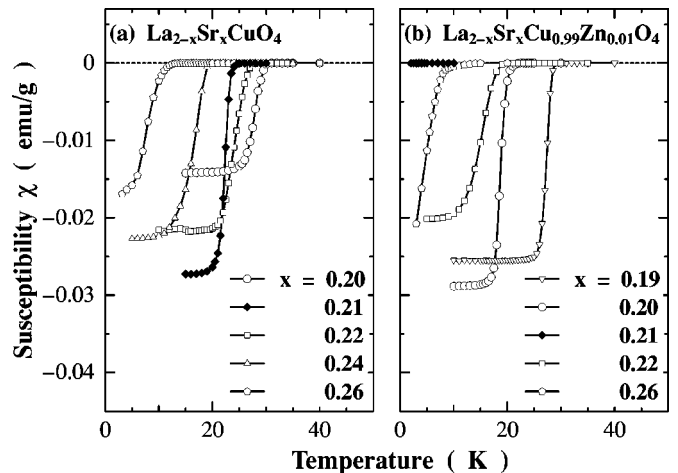


FIG. 3. Temperature dependence of the magnetic susceptibility χ , measured in a magnetic field of 10 Oe during warm up after zero-field cooling, for various x values in single-crystal $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with (a) $y=0$ and (b) $y=0.01$.

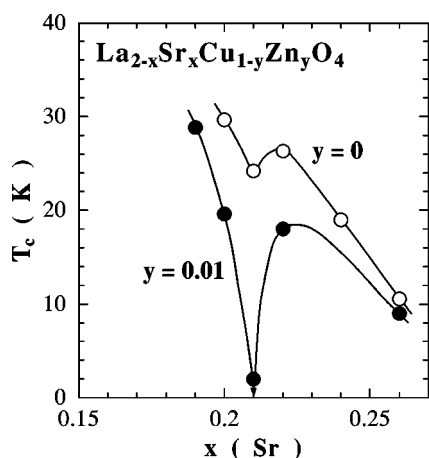


FIG. 4. Sr-concentration x dependence of T_c , estimated from the magnetic susceptibility measurements, for various x values in single-crystal $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ with $y=0$ (open circles) and $y=0.01$ (closed circles).

able that a local minimum of T_c is observed at $x=0.21$ in the non-Zn-substituted single crystals as well. Although the suppression of superconductivity is little, this local minimum of T_c is very reproducible for four single crystals which were sectioned from different rods. An analogous local minimum of T_c has also been observed at $x=0.22$ in the nonsubstituted polycrystalline samples, though the x value is slightly different from 0.21.^{17,18}

To summarize the experimental results, a little suppression of superconductivity has been found at $x=0.21$ in the non-Zn-substituted single crystals, and a giant suppression of superconductivity has been found at $x=0.21$ in the 1% Zn-substituted single-crystals. In the 1% Zn-substituted single crystal with $x=0.21$, moreover, the temperature dependences of ρ_{ab} and ρ_c have been found to be anomalous, though they are normal in the non-Zn-substituted single crystal with $x=0.21$. These results are analogous to those observed in the polycrystalline samples around $x=0.22$ and more drastic than those in the polycrystalline samples,^{17,18} which may be due to the good homogeneity of the Sr concentration in the single crystals. Therefore, it may be said that anomalies formerly found in the polycrystalline samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in the overdoped region have been reconfirmed in the single crystals. However, the x value exhibiting the anomalies in the single crystals is a little different from that in the polycrystalline samples. In the polycrystalline samples, moreover, the x value exhibiting the anomalies tends to shift to lower x values through the Zn substitution. These differences may be partly attributed to the ambiguity in the determination of the absolute values of x and y , but further experiments using single crystals with various y values will be necessary to be conclusive.

The result that the local minimum of T_c at $x=0.21$ becomes conspicuous through the 1% Zn-substitution is very

similar to the result at $x=0.115$ which was formerly reported.²⁵ As for the crystal structure, the Sr concentration of $x=0.21$ is located in close vicinity of the boundary between the OMT and THT phases at 0 K.^{17,26,27} In fact, the non-Zn-substituted crystal with $x=0.21$ is in the THT phase, while the Zn-substituted crystal with $x=0.21$ is in the OMT phase at low temperatures below 100 K though the orthorhombicity is very small.²⁸ Taking into account the result that the suppression of superconductivity is observed also in the non-Zn-substituted crystal with $x=0.21$ in the THT phase, the OMT structure does not seem to be the first driving force to the anomalies, though the OMT structure may contribute to the enhancement of the anomalies. It appears that an electronic instability resides in $x=0.21$ and that the Zn substitution enhances the instability. The stripe order is a sort of mixture of spin-density wave and charge-density wave, which are known to be easily pinned by impurities. Actually, the pinning effect of the substituted Zn has been observed at $x=0.115$,¹¹⁻¹³ and it is supported by the theoretical study.²⁹ Accordingly, there is a possibility that the dynamical stripe correlations of spins and holes tend to become static at $x=0.21$ and are statically stabilized through the pinning by Zn on analogy of the case at $x=0.115$. From the theoretical viewpoints, the stability of the stripe order in the non-Zn-substituted CuO_2 plane has been examined also in the overdoped region by several groups.³⁰⁻³² However, it seems hard to stabilize one type of stripe order among plural types, because the energy difference among the plural types of stripe order is subtle. Therefore, Zn may be helpful to stabilize one type of stripe order.

In summary, we have succeeded in growing Zn-substituted ($y=0.01$) and non-Zn-substituted ($y=0$) $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ single crystals of good quality in the overdoped region of $0.19 \leq x \leq 0.26$. We have found a little suppression of superconductivity at $x=0.21$ in the non-Zn-substituted single crystals and, moreover, a giant suppression of superconductivity at $x=0.21$ in the Zn-substituted single crystals. In the Zn-substituted single crystal with $x=0.21$, both ρ_{ab} and ρ_c exhibit upturn at low temperatures below ~ 80 K. These results suggest that the dynamical stripe correlations of spins and holes tend to become static at $x=0.21$ and are pinned by a small amount of Zn, leading to a static stripe order and the giant suppression of superconductivity, as in the case of $x=0.115$. In order to detect the possible stripe order, neutron-scattering experiments are under way.

We would like to thank Professor K. Yamada, Dr. F. Nakamura, and Dr. N. Kikugawa for their advice in the TSFZ growth and the resistivity measurements. We are indebted to Professor K. Takada and M. Ishikuro for their help in the ICP analysis. This work was supported by a Grant-in-Aid for Scientific Research of Ministry of Education, Science, Sports and Culture, Japan and also by CREST of Japan Science and Technology Corporation.

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