Anomalous Disappearance of High-T_c Superconductivity at High Hole Concentration in Metallic $La_{2-x}Sr_xCuO_4$

J. B. Torrance, Y. Tokura,[a] A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin

IBM Research Division, Almaden Research Center, San Jose, California 95120

(Received 28 June 1988)

Samples of $La_{2-x}Sr_xCuO_{4-\delta}$ have previously shown a maximum concentration of $p=0.15$ holes per $[CuO_2]$ unit, because increasing $x>0.15$ normally induces compensating oxygen vacancies. Annealing samples in 100 bars of oxygen pressure fills the oxygen vacancies and greatly increases the range of accessible hole concentrations, up to $p=0.40$ (or effectively $Cu^{+2.40}$). We find that T_c is constant at $\simeq 36$ K from $p=0.15$ to 0.24, where it begins to decrease. Beyond $p \simeq 0.32$, superconductivity disappears, even though the samples are more conducting.

PACS numbers: 74.70.Vy, 74.60.Mj

Extensive studies[1-19] have been carried out on the system $La_{2-x}Sr_xCuO_{4-\delta}$, potentially the simplest example of the new high-temperature superconductors.[20] Its structure[21] contains neither the Cu-O chains found in $YBa_2Cu_3O_7$, nor the additional, modulated sheets of BiO and TlO present in the most recently discovered members.[22-25] Rather, the K_2NiF_4 structure of $La_{2-x}Sr_xCuO_{4-\delta}$ contains isolated sheets of CuO_2, believed to be the essential structural feature of this remarkable phenomenon. The attractiveness of this system as a prototype material system for the study of high T_c is further enhanced by the fact that the system maintains the same structure over the composition range $0 \le x \le 1.33$, potentially allowing the study of wide variations in hole concentration and their effects on superconductivity. This potential is, however, largely unfulfilled, because in samples with $x \gtrsim 0.15$, oxygen vacancies start to appear[2,6,7,13,15] and there is often evidence of phase separation.[5,9,15] In addition, samples in this range show degraded superconducting behavior,[6,7,9,13-15] anomalous decreases in Hall constant,[11,13] and decreases in infrared oscillator strength[14] when compared with the behavior of samples with $x<0.15$. These experiments indicate that oxygen vacancies greatly complicate the properties of this potentially simple system and have previously limited the range of accessible hole concentrations to less than $\simeq 0.15$. By preparing a set of samples at 600 °C in 100 bars of oxygen pressure, we have been able to inhibit the formation of oxygen vacancies and hence extend the range of hole concentrations,[26] up to $p=0.40$. In this set of samples, the hole concentration is measured directly, as are the lattice constants, resistivity, and Meissner susceptibility. This well-characterized set of samples allows a reliable determination[26] of the superconducting behavior as a function of hole concentration, up to $p=0.40$ holes per CuO_2 unit, or equivalently to an effective valence of $Cu^{+2.40}$, on samples without oxygen vacancies.

The samples were prepared by solid-state reaction in alumina crucibles from appropriate mixtures of La_2O_3, $SrCO_3$, and CuO. The powders were mixed and ground in an alumina mortar and pestle, then fired at 900 °C for 15 h, at 950 °C for 15 h, at 1000 °C for 30 h, and at 1010 °C (1100 °C for $x>0.2$) for 62 h in 1 bar oxygen, with regrinding between firings. For this final firing, powders had been pressed into pellets and were cooled slowly to room temperature over 6 h. For the additional anneal at high oxygen pressure, pellets of the above powders were placed in a high-pressure reaction vessel, heated from 20 °C (60 bars O_2) to 900 °C for 1 h, cooled to 600 °C over 2 h, then held at 600 °C (about 100 bars O_2) for 12 h, and finally slowly cooled to room temperature over a period of 5 h.

Samples of Sr-doped La_2CuO_4 generally contain oxygen vacancies, so that the general formula is given by $La_{2-x}Sr_xCuO_{4-\delta}$. These compounds have the K_2NiF_4 structure which contains covalent CuO_2 sheets, embedded within a lattice of ionic charges which we will represent as

$$La^{3+}_{2-x}Sr^{2+}_x[CuO_2]^{+p-2}O^{2-}_{2-\delta}. \qquad (1)$$

Here the concentration, p, of holes in the covalent CuO_2 network is given by conservation of charge:

$$p=x-2\delta. \qquad (2)$$

The compound La_2CuO_4 has $p=0$ and is an insulator. For $La_{2-x}Sr_xCuO_{4-\delta}$, the hole concentration is increased by doping with Sr, but can be decreased because of compensation by oxygen vacancies, as seen in Eq. (2). For this reason and because the values of δ depend strongly on the sample preparation and annealing conditions, the knowledge of the Sr content, x, alone is insufficient to determine p; it must be measured directly. This was first done by Nguyen *et al.*[2] and by Shafer, Penney, and Olson[13] and is extended to higher hole concentrations in this work. The concentration of holes is measured by our dissolving the sample in an acid solution and measuring the charge on the $[CuO_2]$ unit by a titration technique.[13,27] This measurement yields the number of holes, but cannot distinguish how they are

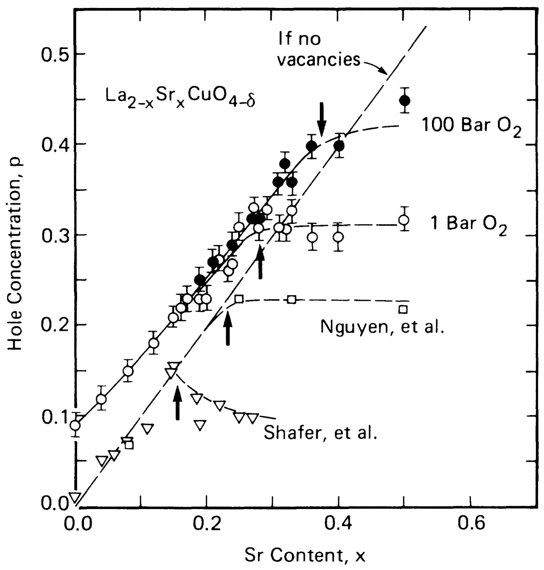

FIG. 1. The measured hole concentration, p, is plotted vs the Sr content for four sets of samples. In each case the arrow marks the concentration above which oxygen vacancies first appear.

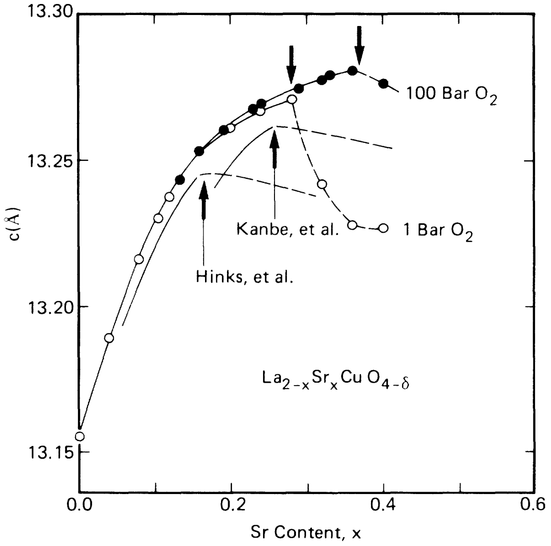

FIG. 2. The c-axis lattice constant plotted vs Sr content for four sets of samples. As in Fig. 1, arrows indicate the initial occurrence of oxygen vacancies.

distributed over the copper and oxygen atoms in the covalent network in the solid. Hence, following Shafer *et al.*,[13] we will not speak of Cu^{3+} or peroxide, etc., just the hole concentration, which is equivalent to an effective copper valence of Cu^{+2+p}.

The concentration of holes can be varied by varying the Sr doping concentration. A solid solution has been shown[2] to form over the range $0 \leq x \leq 1.3$, with a high concentration of oxygen vacancies known to be present for large x. The oxygen vacancy concentration can be controlled to some extent by the conditions of annealing, especially the partial pressure of oxygen. In Fig. 1 the measured hole concentration is shown versus x for a series of samples from Shafer, Penney, and Olson,[13] Nyugen *et al.*,[2] and the present work. For reference, the dashed line is $p = x$, that is, the contribution to the hole concentration coming from the Sr doping alone. The trend is clear: The hole concentration increases as the samples are doped with higher concentrations of Sr until the onset of oxygen vacancies. Beyond this point, the hole concentration tends to level off at a maximum value, $p_{\max}$. The value of x at the onset and $p_{\max}$ both depend on the preparation and annealing conditions. For the samples of Shafer, Penney, and Olson,[13] $p_{\max} = 0.15$, whereas a few of the samples of Nyugen *et al.*[2] appear to have $p_{\max} = 0.23$. Our preparation procedure give $p_{\max} = 0.31$ for samples prepared in 1 bar of oxygen and $p_{\max} = 0.40$ for those annealed at 600 °C in 100 bars of oxygen.[28] With our procedure, the range of hole concentrations has clearly increased up to $p = +0.40$.

Evidence of the onset vacancies is also seen in measurements of the lattice constants. Data for the c-axis lattice constant, for example, are shown in Fig. 2 and are seen to increase strongly with Sr content until this onset. In the data of Hinks *et al.*[15] (Fig. 2), direct neutron measurements of the oxygen concentration confirm that the change in $c(x)$ near $x = 0.15$ corresponds to the onset of an increasing oxygen-vacancy concentration. Similarly, the anomalies evident in our data for $c(x)$ at $x = 0.28$ and 0.37 directly correspond to the onsets of oxygen vacancies evident from $p(x)$ in Fig. 1 for 1 and 100 bars oxygen pressure, respectively. There is evidence for an onset near $x = 0.26$ in the data of Kanbe *et al.*[5] (Fig. 2) and near $x = 0.30$ in $c(x)$ of Tarascon *et al.*[6] The a-axis lattice constant shows an increase at the onset. There is often evidence of phase separation in samples with oxygen vacancies, corresponding to variations in oxygen concentration. In samples without such vacancies, this problem is less severe. In addition, phase separation in Sr content would not be expected and there is not evidence for it in the Meissner data (below).

For the remainder of this paper, we shall discuss only samples having *no oxygen vacancies*, i.e., samples from the literature with $x < 0.15$ and our samples made under 100 bars of oxygen for $x < 0.37$. The latter series of samples exhibits monotonically increasing conductivities with increasing doping from $x = 0.15$ to 0.31, or from $p = 0.25$ to 0.36. Over this entire range, the conductivity is always metallic, with a constant resistivity ratio of $R(300\text{ K})/R(50\text{ K}) \sim 4.5$. The superconducting behavior is most reliably determined from the set of Meissner susceptibility data shown in Fig. 3. For $p = 0.21$, 0.23, 0.24, and 0.26, the maximum Meissner signal was approximately the same, $-0.3/4\pi$. This value appears to be the characteristic maximum value for this set of samples. It is clear from the data in Fig. 3 that increasing

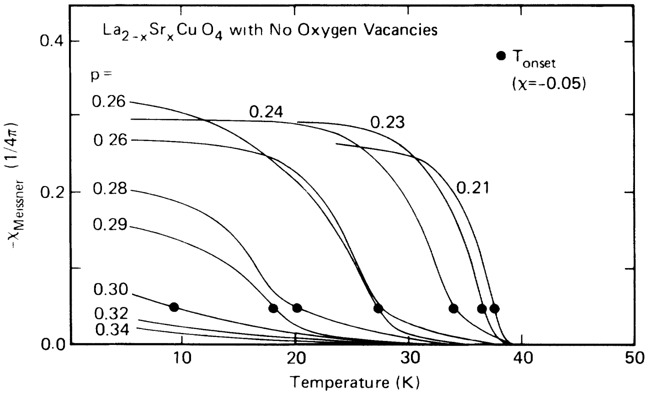

FIG. 3. The Meissner susceptibility measured on a vibrating-sample magnetometer (with $H=20$ Oe), showing the superconducting transition temperature decreasing with increasing hole concentration.

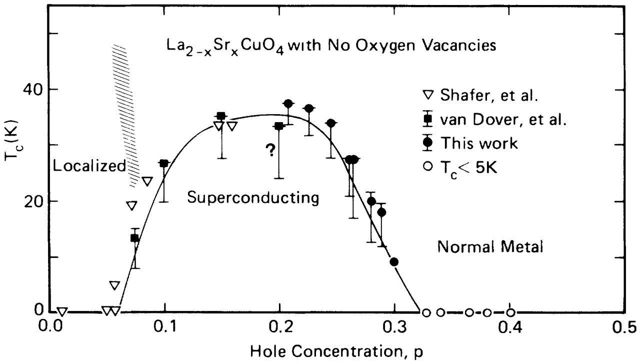

FIG. 4. The dependence of T_c on hole concentration, including resistance measurements of Shafer *et al.* and magnetic measurements of present work and van Dover *et al.* Symbols and T_c are defined in text and the question mark refers to the concern that this sample may have some oxygen vacancies.

the hole concentration results in an eventual decrease in the temperature at which superconductivity occurs in these samples. Since these transitions are not sharp, it is difficult to define a single "T_c," so we shall use two somewhat arbitrary measures in order to plot "T_c" versus hole concentration in Fig. 4. First, the onset temperature (filled circles in Figs. 3 and 4) is arbitrarily defined as the temperature when χ_M has increased to $-0.05/4\pi$. Second, the bar in Fig. 4 represents the temperature width over which χ_M is between 20% and 80% of its observed low-temperature value. In addition to these data, we show for low hole concentrations the Meissner data of van Dover *et al.*[7] (plotted like ours) and resistance data of Ref. 13 (when resistance is equal to 10% of value just above T_c). (We assume that the low-x samples of van Dover *et al.*[7] have no oxygen vacancies, but their $x=0.20$ sample can be questioned.)

A very significant feature of the Meissner data in samples of $La_{2-x}Sr_x CuO_{4-\delta}$ (Fig. 3 and in the literature) is the broad width of the transitions observed. A consistent understanding of these widths can be obtained by the assumption that they originate in part from local variations in Sr concentration. With use of the $T_c(p)$ curve in Fig. 4, the widths in T_c correspond to local variations of $\Delta x/x \sim \Delta p/p \sim 10\%$. Such variations are normally averaged out by delocalized electrons, but would be felt by a pair of superconducting holes which had a coherence length as small as 10 Å, as they do in these materials. Thus, it is reasonable to attribute the broad Meissner transitions in Fig. 3 not to poor sample quality, but rather to a distribution of local Sr concentrations. Hence, the bars in Fig. 4 are a reasonable representation of the widths of the distribution of local T_c. (Note also that the sharper Meissner transitions observed in $YBa_2Cu_3O_7$ would be expected due to the lack of such local compositional fluctuations in that material.)

In summary, holes in two-dimensional sheets of CuO_2 are the superconducting elements in the new phenomenon of high T_c. The concentration of these holes is the principle experimental variable, as shown by Shafer, Penney, and Olson[13] for $La_{2-x}Sr_xCuO_{4-\delta}$ and by Tokura *et al.*[29] for the $YBa_2Cu_3O_y$-like systems. The behavior of T_c versus hole concentration for the simple model system of $La_{2-x}Sr_xCuO_4$ is shown in Fig. 4, including the new data for $p > 0.15$ reported here. Evidently, high transition temperatures are found in a somewhat narrow window of hole concentrations. At low p, the onset of superconductivity is probably a complex phenomenon[17-19,30,31]: Holes go from being localized, in complex magnetic environment, to a delocalized superconductor. This change may not easily be explained by simple theories. For $p > 0.15$ (in samples *without* oxygen vacancies), the situation is much less complex, since samples in this region are always metallic and show a clear characteristic behavior of T_c: it appears *independent* of hole concentration from $p \sim 0.13$ to ~ 0.24, but above this value, T_c falls toward zero. Above $p \sim 0.32$, superconductivity disappears and the mechanism of high T_c ceases to be effective, even though the conductivity is higher. This clear behavior, in this simplest of systems, is a fundamental feature of the experimental data and provides a key test of theories of high T_c. A few theories[32-34] appear to have begun to address this issue.

We gratefully acknowledge on-going discussions with our colleagues, especially M. W. Shafer, E. M. Engler, S. J. LaPlaca, A. P. Malozemoff, and B. Batlogg, as well as technical assistance from R. Karimi. We also wish to thank IBM-Japan and the Swiss National Foundation for generously supporting two of us (Y.T. and A.B., respectively) during their stay at Almaden.

---

[a] Present address: Physics Department, University of Tokyo, Tokyo, Japan.

[1] I. S. Shaplygin, B. G. Kakhan, and V. B. Lazarev, Russ. J.

Inorg. Chem. **24**, 820 (1979).

[2] N. Nguyen, J. Choiset, M. Hervieu, and B. Raveau, J. Solid State Chem. **39**, 120 (1981); N. Nguyen, F. Studer, and B. Raveau, J. Phys. Chem. Solids **44**, 389 (1983).

[3] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Reitman, Phys. Rev. Lett. **58**, 408 (1987).

[4] K Kishio *et al.*, Chem. Lett. **1987**, 429.

[5] S. Kanbe *et al.*, Chem. Lett. **1987**, 547.

[6] J. M. Tarascon *et al.*, Science **235**, 1373 (1987).

[7] R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Reitman, Phys. Rev. B **35**, 5337 (1987); R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Reitman, Phys. Rev. B **35**, 7191 (1987).

[8] C. Politis, J. Geerk, M. Dietrich, and B. Obst, Z. Phys. B **66**, 141 (1987).

[9] T. Fujita *et al.*, Jpn. J. Appl. Phys. Pt. 2 **26**, L368 (1987).

[10] J. E. Schirber *et al.*, J. Mater. Res. **2**, 421 (1987).

[11] N. P. Ong *et al.*, Phys. Rev. B **35**, 8807 (1987).

[12] W. Kang *et al.*, J. Phys. **48**, 1181 (1987).

[13] M. W. Shafer, T. Penney, and B. L. Olson, Phys. Rev. B **36**, 4047 (1987).

[14] S. Etemad *et al.*, Phys. Rev. B **37**, 3396 (1988).

[15] D. G. Hinks *et al.*, Mater. Res. Soc. Symp. **99**, 9 (1987).

[16] A. R. Moodenbaugh, Y. Xu, and M. Suenaga, Mater. Res. Soc. Symp. **99**, 427 (1988).

[17] M. Kato, Y. Maeno, and T. Fujita, Physica (Amsterdam) **152C**, 116 (1988).

[18] K. Kamagai *et al.*, Physica (Amsterdam) **148B**, 480 (1987).

[19] R. J. Birgeneau *et al.*, to be published.

[20] J. G. Bednorz and K. A. Müller, Z. Phys. **64**, 189 (1986).

[21] H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Pt. 2 **26**, L123 (1987).

[22] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Pt. 2 **27**, L209 (1988).

[23] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 55 138 (1988).

[24] J. B. Torrance *et al.*, Solid State Commun. **66**, 703 (1988).

[25] S. S. P. Parkin *et al.*, to be published.

[26] These results were first reported in J. B. Torrance, Y. Tokura, A. I. Nazzal, and T. C. Huang, Bull. Am. Phys. Soc. **33**, 689 (1988).

[27] A. I. Nazzal *et al.*, Physica (Amsterdam) **153–155C**, 1367 (1988).

[28] Note that our samples generally have p above the dashed line in Fig. 1, which we attribute to the presence of La vacancies, or possibly oxygen interstitials. In our sample with $x=0$, for example, $p=0.09$, which corresponds to 1.5% La vacancies.

[29] Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, Phys. Rev. B (to be published).

[30] Y. Kitaoka, K. Ishida, S. Hiramatsu, and K. Asayama, J. Phys. Soc. Jpn. **57**, 734 (1988).

[31] A. Aharony *et al.*, Phys. Rev. Lett. **60**, 1330 (1988).

[32] H. Fukuyama and K. Yosida, Jpn. J. Appl. Phys. Pt. 2 **26**, L371 (1987).

[33] M. Inui, S. Doniach, P. J. Hirschfeld, and A. E. Ruckenstein, Phys. Rev. B **37**, 2320 (1988).

[34] J. E. Hirsch, private communications.