

## Correlation of $T_c$ with hole concentration in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ superconductors

M. W. Shafer, T. Penney, and B. L. Olson

*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*

(Received 8 June 1987)

The electron deficiency (hole concentration) in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  system is determined by a chemical method. Our results show a direct correlation between  $T_c$  and hole concentration. The hole concentration equals the Sr concentration to about  $x=0.15$ . For  $x > 0.15$ , the hole concentration decreases and oxygen vacancies are formed. These results strongly support an all-electronic mechanism for superconductivity in this system.

Since the discovery of superconductivity in the La-Ba-Cu oxides by Bednorz and Müller<sup>1</sup> a number of similar copper-oxide-type materials have been shown to be high-temperature superconductors. For example,  $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$  with a transition temperature  $T_c \approx 90$  K (Ref. 2) is of intense current interest. However, from a purely scientific point of view, the  $\text{La}_{2-x}(\text{Ba},\text{Sr})_x\text{CuO}_{4-\delta}$  series has a major advantage over the 90-K system because of the large solubility of divalent ions such as Ba and Sr, whose concentrations can be systematically varied to control the state of the copper-oxygen interactions, and hence the physical properties.

The series  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  with the  $\text{K}_2\text{NiF}_4$ -type structure, was studied in considerable detail even before they were known to be superconductors.<sup>3-5</sup> Pure  $\text{La}_2\text{CuO}_4$  is orthorhombic but the substitution of Sr for La stabilizes a tetragonal phase and forces an equivalent number of  $\text{Cu}^{2+}$  to be converted to  $\text{Cu}^{3+}$ . It is generally accepted that the transport properties are strongly a function of the  $\text{Cu}^{3+}$ - $\text{Cu}^{2+}$  ratio. The Sr-doped samples for  $x > 0.06$  were shown to be superconductors with a maximum transition temperature at about 36–38 K when  $x \approx 0.15$ .<sup>6-9</sup>

The work we report here is an extension of these earlier studies and shows that the superconductivity is related to the electron deficiency (hole concentration) in the copper-oxygen layer. These results are consistent with recent nonphonon theories of oxide superconductivity based on strongly correlated electrons<sup>10</sup> or dynamic peroxide formation.<sup>11</sup>

The  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  compounds were prepared from the nitrates. Copper metal (99.9999% purity), assayed  $\text{La}_2\text{O}_3$ , and  $\text{SrCO}_3$  were each dissolved in nitric acid and combined in the desired proportions by standard volumetric techniques. The solutions were evaporated and converted to oxides by heating in oxygen. Although the reaction to the  $\text{K}_2\text{NiF}_4$ -like phase was essentially complete at 850°C, they were again reground and pressed into pellets and sintered at 1140–1180°C in oxygen, then annealed at 550–600°C. In order to avoid crucible contamination during the high-temperature sintering, the pellets were supported on powders of identical composition in high-density alumina boats. The resulting materials were characterized as follows: by x-ray diffraction, microprobe analysis, and phase-contrast microscopy. The total copper

was determined by inductively coupled plasma atomic emission spectroscopy. The electron deficiency, which we call the hole concentration and refer to as a  $[\text{Cu-O}]^+$  complex rather than  $\text{Cu}^{3+}$ , was determined by wet chemistry according to the reaction  $[\text{Cu-O}]^+ + \text{Fe}^{2+} = \text{Cu}^{2+} + \text{Fe}^{3+} + \text{O}^{2-}$ . For the La-Sr-Cu oxides, the finely powdered materials were dissolved in 6N  $\text{H}_2\text{SO}_4$  containing standardized 0.04N  $\text{Fe}^{2+}$ . After the addition of  $\text{H}_3\text{PO}_4$  the remaining  $\text{Fe}^{2+}$  was determined by titrating with standard 0.04N  $\text{KMnO}_4$ .<sup>12</sup>

The fact that these materials are metals, even in the nonsuperconducting state, implies nonionic-type bonding without well-defined  $\text{Cu}^{3+}$  species on any given lattice site. Therefore, we assume the electron deficiency to be distributed between the copper and oxygen ions to form a complex of the type  $[\text{Cu}^{3+}\text{-O}^{2-}]^+ \leftrightarrow [\text{Cu}^{2+}\text{-O}^{1-}]^+$ . The latter can be thought of as a peroxide complex.<sup>11</sup> This electron-deficient complex, which we write as  $[\text{Cu-O}]^+$ , like a  $\text{Cu}^{3+}$  ion, is a good oxidant and easily oxidizes ferrous iron to ferric. On the other hand, the  $\text{Cu}^{2+}$  ion will not do so. Attempts to determine the accuracy of this analytical procedure were hampered because of the lack of a good  $\text{Cu}^{3+}$  standard. However, based on favorable reduction oxidation potentials and using stable volumetric solutions, we believe that the actual hole concentration is being measured. Supporting evidence for the reliability of our analysis in determining the concentration of the  $[\text{Cu-O}]^+$  complex is based on a total oxygen determination as done by Nguyen.<sup>5</sup> Here, dry hydrogen is used to reduce the copper in the La-Sr-Cu oxides to the metal. The La and Sr are assumed to remain as their stoichiometric oxides, i.e.,  $\text{La}_2\text{O}_3$  and  $\text{SrO}$ , so that the weight loss is due to the oxygen associated with the copper. When we compare these results for total oxygen with our chemical method, there is good agreement. For example, the sample with  $x=0.06$  had an oxygen content of  $3.99 \pm 0.02$  and  $3.98 \pm 0.03$  for the solution and  $\text{H}_2$  reduction methods, respectively.

At room temperature the orthorhombic  $\text{La}_2\text{CuO}_4$  transforms to tetragonal at  $x \approx 0.06$ , in general agreement with previous work.<sup>5,8</sup> Further, for the tetragonal phase,  $a_0$  decreases with  $x$  while  $c_0$  increases. The small difference between the values we obtained for the lattice constants and those reported earlier<sup>5,7</sup> are likely due to a different preparation procedure and subsequent thermal

history. It is clear from Fig. 1 that the cell volume  $V_0$  does not change linearly with Sr doping. There is a sharp decrease around the  $x(\text{Sr})=0.15$  composition. In Fig. 1 (closed triangles), we show the variations in oxygen stoichiometry obtained from our compositional analysis. It is seen that an oxygen stoichiometry of  $\text{O}_4$  is essentially maintained, meaning there are few, if any, oxygen vacancies for compositions from  $x=0$  to about  $x=0.15$ . For compositions with  $x > 0.15$ , the measured decrease in the  $[\text{Cu-O}]^+$  concentration indicates a decrease in the oxygen content—and therefore an increase in the number of oxygen vacancies. Also given in Fig. 1 are the data of Nguyen, Choisnet, Hervieu, and Raveau<sup>5</sup> (open triangles). The rather sharp decrease in the cell volume at  $x=0.15-0.20$  (Fig. 1) can be correlated with the oxygen-vacancy content, determined from the  $[\text{Cu-O}]^+$  concentration, which increases sharply above  $x=0.15$ . This decrease is due to both the oxygen vacancies and the presence of the  $[\text{Cu-O}]^+$  complex, whose size is undoubtedly smaller than the  $\text{Cu}^{2+}$  ion. It appears that when about 15% of the “octahedral” sites are occupied by  $[\text{Cu-O}]^+$ , in order to maintain the  $\text{K}_2\text{NiF}_4$  structure, oxygen vacancies are formed, rather than additional  $[\text{Cu-O}]^+$  complexes.

Figure 2 shows  $T_c$  vs the  $\text{Sr}^{2+}$  concentration (closed triangles) and the  $[\text{Cu-O}]^+$  concentration versus the  $\text{Sr}^{2+}$  (closed squares). This clearly shows that up to about  $x=0.15$  a  $[\text{Cu-O}]^+$  is formed for each  $\text{Sr}^{2+}$  that substitutes for  $\text{La}^{3+}$ . Surprisingly, however, for  $\text{Sr}^{2+}$  concentrations greater than 0.15, a decrease in the  $[\text{Cu-O}]^+$  concentration is seen and the number of oxygen vacancies increases sharply. In this range we see a similar decrease in  $T_c$ .

In Fig. 3 we plot  $T_c$  vs  $[\text{Cu-O}]^+$  concentration and see a strong dependence of  $T_c$  on the  $[\text{Cu-O}]^+$  concentration with a maximum  $T_c$  of 35 K for  $[\text{Cu-O}]^+$  concentration of 15% of the total copper. It is clear that the  $[\text{Cu-O}]^+$  concentration and not the Sr doping determines the  $T_c$ .  $T_c$  increases rapidly above a  $[\text{Cu-O}]^+$  threshold, i.e., about 5%, and reaches a maximum at roughly 15%. It appears

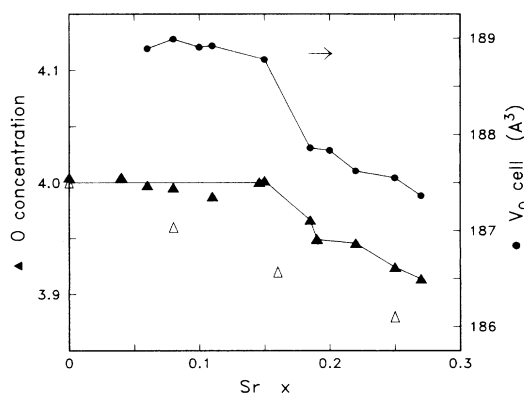


FIG. 1. Cell volume (closed circles) and oxygen content determined from our analysis of  $[\text{Cu-O}]^+$  (closed triangles) vs strontium concentration ( $x$ ). The open triangles are data from Nguyen *et al.* (Ref. 5) as determined by hydrogen reduction.

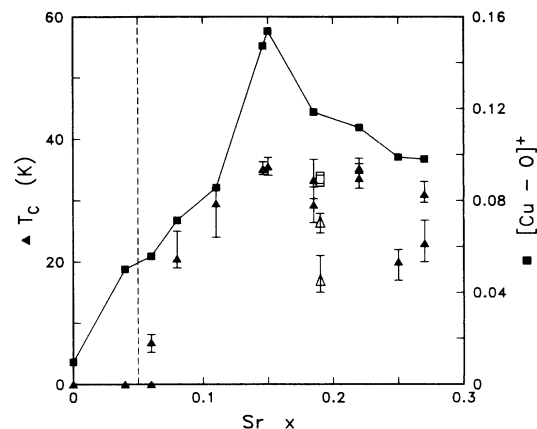


FIG. 2.  $T_c$  (closed triangles) and  $[\text{Cu-O}]^+$  concentration (closed squares) vs strontium concentration ( $x$ ). Error bars indicate transition widths. Points without error bar did not show a transition down to 5 K.

that 15%–16%  $[\text{Cu-O}]^+$  concentration is the maximum that this structure will accept.

In order to see if the relationship between  $T_c$  and  $[\text{Cu-O}]^+$  concentration in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system can be extended to the  $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$  system, we have replotted the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  system data together with the results for one  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$  sample (dot in Fig. 3 inset). In the  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$  structure there are two different copper layers, one between the barium planes and two between yttrium and barium planes. If only one or two layers are active then the ratio of  $[\text{Cu-O}]^+$  to active Cu is given by the crosses labeled 1 and 2, respectively, in the inset. An

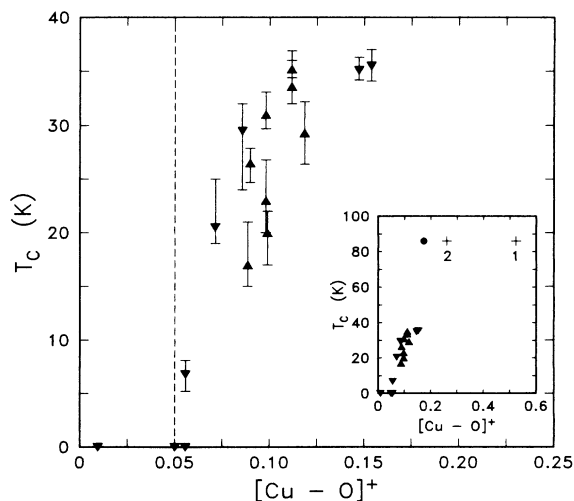


FIG. 3.  $T_c$  vs the hole concentration  $[\text{Cu-O}]^+$ , as a fraction of total copper. Down triangles are for compositions with  $x < 0.15$ , up triangles are for  $x > 0.15$ . Inset shows same data plus points for a single  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$  sample with three normalizations. See text.

extrapolation of the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  data does pass within the range of values for  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ , indicating that the same relation between  $T_c$  and hole concentration might apply in this system too.

Our samples with strontium concentrations of  $x$  up to  $\sim 0.15$  and containing a corresponding amount of  $[\text{Cu-O}]^+$  were more reproducible and stable than those for  $x > 0.15$ . Because of increased diffusion rates in the vacancy-containing samples, the  $[\text{Cu-O}]^+$  complex is less stable and is perhaps reduced in dry air by the loss of oxygen or by the reaction with water under ambient conditions. For example, the sample with  $x = 0.27$ , which when measured 12 h after preparation had a  $T_c$  and  $[\text{Cu-O}]^+$  concentration of 31 K and 9.8% respectively. After standing in He gas for 64 h,  $T_c$  dropped to 23 K and  $[\text{Cu-O}]^+$  concentration to 7.4%.

$\text{La}_2\text{CuO}_4$  contains a small concentration (1%–5%), of  $[\text{Cu-O}]^+$ . More detailed analysis of samples prepared close to the nominal composition  $\text{La}_2\text{CuO}_4$  showed a strong preference to form with La deficiencies and to have intragranular concentration gradients similar to  $\text{La}_2\text{CoO}_4$ .<sup>13</sup> Our microprobe and wet chemical analysis of several samples showed the total La concentration to be less than two and the La/Cu ratio within the larger grains to vary between 2.06 and 1.95. Thus, it is easy to explain the presence of 5%  $[\text{Cu-O}]^+$  in a composition corresponding to  $\text{La}_{1.95}\text{Cu}_{1.0}\text{O}_{3.96}$ . The fact that superconductivity has been observed in  $\text{La}_2\text{CuO}_4$ ,<sup>14,15</sup> presumably as a filamentary grain boundary phase, or as intergrowths of the Ruddlesden-Popper type,<sup>16,17</sup> is understandable because of the inhomogeneities which are likely to produce regions where the  $[\text{Cu-O}]^+$  concentration exceeds the 5%–6% we think is necessary for superconductivity.

In a simple one-band metal the Hall constant  $R_H$  is temperature independent. The number of carriers per formula unit is the Hall number  $V_0/R_{He}$  where  $V_0$  is the volume of the formula unit. We find that for  $x < 0.15$  all the samples have  $p$ -type Hall constants nearly temperature independent. The Hall number (Fig. 4) tracks the hole concentration  $[\text{Cu-O}]^+$  and the Sr concentration (dashed line), showing that the Sr substitution creates holes in and otherwise filled band and that one band dominates the transport. In the all electronic model, this is a highly correlated Hubbard band.<sup>10</sup> The situation changes for  $x > 0.15$ . The breaking away of the Hall number from the Sr concentration (dashed line in Fig. 4) signals a qualitative change in behavior. Detailed interpretation of the Hall effect in this range is ambiguous. A small Hall constant, large Hall number, may result from either a large number of carriers or the cancellation of hole and electron bands. A temperature-dependent Hall effect would suggest the latter since the mobilities of the different bands usually have different temperature dependences. In our case the Hall constants for  $x > 0.15$  are only weakly temperature dependent, consistent with either picture. How-

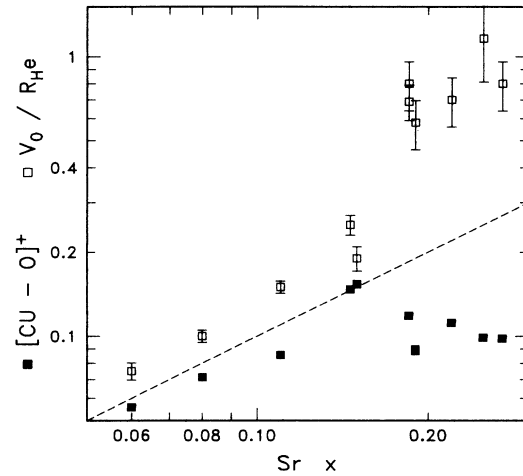


FIG. 4.  $[\text{Cu-O}]^+$  concentration and Hall number  $V_0/R_{He}$  at 50 K vs strontium concentration ( $x$ ). The Hall number is the number of holes per formula unit if only one band contributes.

ever, our wet chemical results which directly measure the holes in the Cu-O band, resolve the ambiguity in the Hall effect and show that the number of holes decreases for  $x > 0.15$ . The Hall effect has been measured previously in this system at one temperature with similar results.<sup>18</sup> Various other workers have measured the Hall constant for a single composition.<sup>19–22</sup>

In summary, we have prepared a series of samples in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  system and studied the superconducting and transport properties as a function of composition. A unique wet chemical analytical technique is used to determine the electron deficiency (hole concentration) in the copper-oxygen layer, which we define as a  $[\text{Cu-O}]^+$  complex. From this analysis we obtain a value for the oxygen stoichiometry and contrary to previously published results, we find few if any oxygen vacancies for  $0 \leq x \leq 0.15$ . The  $[\text{Cu-O}]^+$  concentration is approximately equal to the Sr concentration and the Hall number to about  $x = 0.15$ . Conduction is therefore due to holes in a single band. For  $x > 0.15$  the  $[\text{Cu-O}]^+$  concentration decreases and the number of oxygen vacancies increases. The Hall effect is qualitatively different in this range. It does not measure the number of carriers but rather indicates hole and electron conduction or other exotic behavior. A strong correlation between the  $[\text{Cu-O}]^+$  concentration and  $T_c$  is shown. This dependence has been found theoretically in an all electronic model with strong electron-electron correlations.<sup>10</sup>

We thank R. A. Figat, C. F. Guerci, and J. M. Rigotty for technical assistance and A. Malozemoff, R. A. deGroot, and D. M. Newns for valuable discussions.

- <sup>1</sup>J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986); J. G. Bednorz, M. Takashige, and K. A. Müller, *Europhys. Lett.* **3**, 379 (1987).
- <sup>2</sup>M. K. Wu, J. R. Ashburn, C. J. Torng, D. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).
- <sup>3</sup>J. M. Longo and P. M. Racciah, *J. Solid State Chem.* **6**, 526 (1973).
- <sup>4</sup>N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, *J. Solid State Chem.* **39**, 120 (1981).
- <sup>5</sup>N. Nguyen, F. Studer, and B. Raveau, *J. Phys. Chem. Solids* **49**, 6389 (1983).
- <sup>6</sup>J. M. Tarascon, L. H. Green, W. R. McKinnon, G. W. Hull, and T. H. Geballe, *Science* **235**, 1373 (1987).
- <sup>7</sup>R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, *Phys. Rev. Lett.* **58**, 408 (1987).
- <sup>8</sup>S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, *Jpn. J. Appl. Phys. Lett.* **26**, 443 (1987).
- <sup>9</sup>R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, *Phys. Rev. B* **35**, 7191 (1987).
- <sup>10</sup>D. M. News (unpublished).
- <sup>11</sup>R. A. de Groot, H. Gutfreund, and M. Weger, *Solid State Commun.* **63**, 451 (1987).
- <sup>12</sup>A slightly different technique was used for the Y-Ba-Cu oxides since they could not be dissolved in H<sub>2</sub>SO<sub>4</sub>.
- <sup>13</sup>J. T. Lewandowski, R. A. Beyerlein, J. M. Longo, and R. A. McCauley, *J. Am. Ceram. Soc.* **9**, 699 (1986).
- <sup>14</sup>J. Beille, R. Cabanel, C. Chaillout, B. Chevallier, G. Demazeau, F. Deslandes, J. Etourneau, P. Lejay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J. L. Tholence, and R. Tournier, *Phys. Condens. Matter* (to be published).
- <sup>15</sup>P. M. Grant, S. S. P. Parkin, R. L. Green, V. Y. Lee, E. M. Engler, M. L. Ramirez, J. E. Vasquez, G. Lim, and R. O. Jacowitz, *Phys. Rev. Lett.* **58**, 2482 (1987).
- <sup>16</sup>S. N. Ruddlesden and P. Popper, *Acta Crystallogr.* **11**, 54 (1958).
- <sup>17</sup>A. H. Davies and R. J. Tilley, *Nature* **326**, 859 (1987).
- <sup>18</sup>N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. McKinnon, *Phys. Rev. B* **35**, 8807 (1987).
- <sup>19</sup>M. F. Hundley, A. Zettl, A. Stacy, and Marvin L. Cohen, *Phys. Rev. B* **35**, 8800 (1987).
- <sup>20</sup>A. J. Panson, G. R. Wagner, A. I. Braginski, J. R. Gvaler, M. A. Janocko, H. C. Phol, and J. Talvacchio, *Appl. Phys. Lett.* **50**, 1104 (1987).
- <sup>21</sup>M. Suzuki and T. Murakami (unpublished).
- <sup>22</sup>S. Uchida, H. Takagi, H. Yanagisawa, K. Kishio, K. Kitazawa, K. Fueki, and S. Tanaka (unpublished).