Hole concentrations, Hall number, and T_c relationships in substituted YBa$_2$Cu$_3$O$_y$

M. W. Shafer, T. Penney, B. L. Olson, R. L. Greene, and R. H. Koch

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

(Received 29 September 1988)

One of the fundamental questions involving the high-temperature copper oxide containing superconductors is to understand the relationship between hole concentration and the superconducting transition temperature, T_c. We help resolve this question by a study of Nd-, La-, Ga-, Ca-, and Zn-substituted YBa$_2$Cu$_3$O$_y$ with controlled oxygen stoichiometry. The total hole concentration is determined by a chemical method and trends in the mobile hole concentration by Hall measurements. By considering T_c to be a function of the mobile sheet holes only, there is a maximum in T_c (92 K) at a sheet-hole concentration of about 0.20–0.25 per Cu site.

The importance of the hole concentration in Cu oxide containing superconductors is widely recognized and its relationship to the superconducting transition temperature (T_c) has been the object of numerous studies.[1−12] The hole concentration, which we call p, is an electron deficiency and can be determined chemically, as well as by Hall measurements. Although it is generally accepted that it is associated with the oxygen rather than the copper, i.e., O$^-$, the chemistry of its determination is identical to that of Cu^{3+} or a hole in the copper-oxygen band. The Hall measurement is complimentary to the chemical measurement since it measures only the mobile holes. Previously, using both techniques we showed a rather linear relationship existed between T_c and p in the La$_{2-x}$Sr$_x$CuO$_4$ system (for $p < 0.15$) and discussed the possible T_c vs p relationship in the 1:2:3-type materials, e.g., YBa$_2$Cu$_3$O$_y$.[1] Our data suggested a possible relationship between the two systems if similar hole concentrations per sheet (CuO$_2$), which we showed reached a maximum at about 0.15 in the one-sheet La$_{2-x}$Sr$_x$CuO$_4$ system, could be produced in each of the two sheets of the 1:2:3 materials. Torrance *et al.*[10] further studied the La$_{2-x}$Sr$_x$CuO$_4$ system for $0.2 < x < 0.4$ and showed that p can be increased above 0.15 but T_c drops from about 30 K at $p = 0.25$ to 0 K at about $p = 0.30$. From these results they[10] concluded that there is a broad maximum in T_c vs p, with $T_c = 0$ when $p < 0.05$ and $p > 0.30$.

In this paper we describe our recent work on substituted YBa$_2$Cu$_3$O$_y$, where we combine the results of chemical, Hall, and T_c measurements. We show that the trends in hole concentrations, determined chemically, agrees well with that determined by Hall measurements if we use the prescription of Tokura, Torrance, Huang, and Nazzal[9] to distinguish the mobile from the localized holes. Further, we find that a maximum occurs in T_c when plotted versus the mobile sheet holes, indicating qualitatively similar behavior to the La$_{2-x}$Sr$_x$CuO$_4$ system.

We discuss five substitutional systems: Nd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$, YBa$_2$Cu$_{3-x}$$M_xO_y$ (M = Ga and Zn), La$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$, and Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$. We prepared samples in the Nd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ and YBa$_2$Cu$_{3-x}$$M_xO_y$ systems from nitrate solutions as previously described.[1] In these solid-solution-type systems, special care was taken to insure homogeneity by repeated grindings and firings. All samples were single phase, as determined by a combination of x-ray diffraction and standard metallographic techniques. The overall chemical composition was obtained from inductively coupled plasma (ICP) atomic-emission spectrometry and the hole concentration by iodometric titration, which was also used to obtain the oxygen content.[13] In addition, further information on the oxygen content was obtained from thermogravimetric analysis (TGA). The Hall measurements were made in the van der Pauw configuration in a field of 1 T. Transition temperatures were taken from the midpoints of the resistive transitions. The data we present for the La$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ (Ref. 14) and Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$ (Refs. 9 and 15) systems are taken from the literature.

Nd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$

We see, as did Takita and co-workers,[5,8] a rather linear decrease in T_c from 92 to about 20 K as x increases from 0 to 0.40, suggesting a corresponding decrease in the number of holes p. However, our chemical determination clearly shows p to be constant and independent of x, which appears to contradict the idea of a strong dependence of T_c on holes. Since the holes are constant as Nd replaces Ba, the oxygen content y must increase, even as T_c decreases, also opposite to what is seen in YBa$_2$Cu$_3$O$_y$ where T_c decreases when y decreases. Our results do indeed show an increase in y as the Nd concentration is increased.

The solution to this apparent nondependence of T_c on p is likely to be found in the works of Tokura *et al.*[9] and Mitzi *et al.*[14] They make the assumption that the number of holes, as determined by wet chemistry (Ref. 9) or TGA (Ref. 14), may be divided between localized holes in the Cu-O chains and the mobile holes on the CuO$_2$ sheets. The justification for this assumption is based on their study of many samples in the Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$ (hole doping) and YBa$_{2-x}$La$_x$Cu$_3$O$_y$ (electron doping) systems. They showed that, for all samples in these systems, by plotting the oxygen content y vs p they could clearly separate the insulators from the metals by a straight line. In Fig. 1, we redraw their plot, without all their data
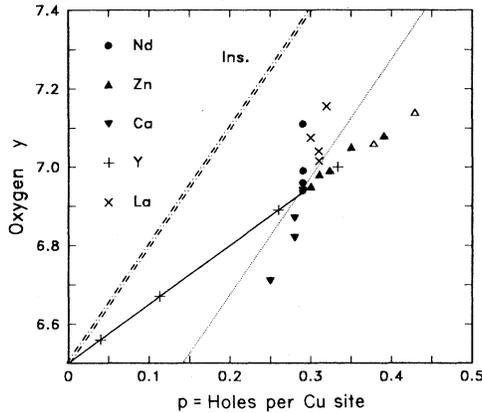
FIG. 1. Oxygen content vs hole concentration for various substitutions in $YBa_2Cu_3O_y$. The double dashed line separating the insulating from the metallic samples is from Tokura et al. (Ref. 9). The dotted line is our proposed T_c max curve. See text for further explanation.

points, showing this straight line (double-dashed). Here, all samples to the left are insulators and those to the right are metals. This line is called p_c, and is defined as

$$p_c = (y - 6.5)/3 .$$

Since p_c, the boundary between the insulators and metals, is neither horizontal or vertical, they concluded that neither y nor p is singularly relevant. Furthermore, for both the electron and hole doped materials, their data show that for the metals T_c tends to increase with the distance $p - p_c$ from the critical line. Since all samples to the left p_c are insulating with a finite number of holes $(0 < p < p_c)$, the holes must be localized, presumably on the chains. If the localized chain holes cannot be increased beyond p_c, additional holes will form on the sheets. These sheet holes, in excess of p_c, are mobile and are what one is likely to see by the Hall measurements. Since there are two sheet Cu atoms for each one on the chain, their concentration is given as $p_{sh} = 3/2(p - p_c)$. We also show in Fig. 1 the data for $YBa_2Cu_3O_y$ (solid line), which is consistent with this model and intersects the p_c at $y = 6.5$ and $p = 0$.[12] Our $Nd_{1-x}Ba_{2-x}Cu_3O_y$ points (filled circles) and the $La_{1+x}Ba_{2-x}Cu_3O_y$ points of Mitzi et al.[14] (crosses) are seen to have very similar y vs p behavior. Since the total hole concentration p, as determined chemically, was shown to be constant and y increased with x, we move vertically upward toward the p_c line. As we do this, the number of mobile sheet holes decrease and T_c drops despite the fact that p remains unchanged. This is further evidence that the mobile holes on the CuO_2 sheets p_{sh} largely determines T_c, in the same manner as Tokura et al. and Mitzi et al.[14] This is more clearly seen in Fig. 2, where we plot sheet holes per Cu site p_{sh} vs T_c. The Nd and La points (filled circles and crosses, respectively) show similar behavior. There is a strong increase of T_c with p_{sh} for p_{sh} values up to about 0.225. Comparison with Takita et al.[5] is difficult because their hole concentration was determined from the assumption of constant oxygen composition, contrary to our re-
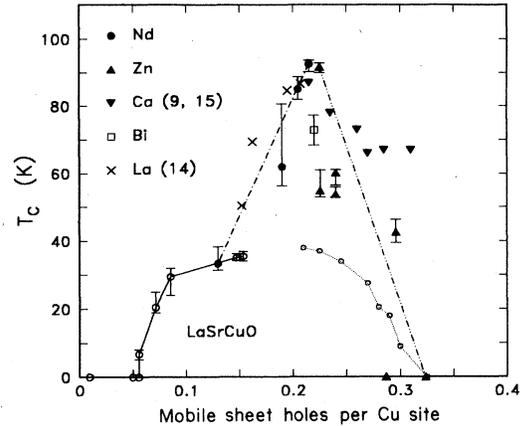
FIG. 2. Superconducting transition temperatures T_c vs chemically determined sheet holes per Cu site for various substitutions in $YBa_2Cu_3O_y$ and for $La_{2-x}Sr_xCuO_4$. The open circles connected by the solid line are from Shafer et al. (Ref. 1) and those connected by the dotted line from Torrance et al. (Ref. 10). The Ca points, down triangles, are from Manthiram et al. (Ref. 15) and Tokura et al. (Ref. 9) while the La points, crosses, are from Mitzi et al. (Ref. 14). The dash-dot line illustrates the strong increase in T_c with p_{sh} while the dash-dot-dot line illustrates how T_c decreases as p_{sh} increases beyond about 0.22.

sults, and no separation between sheet and chain holes was made.

Our Hall measurements show that the Hall number V_{Cu}/R_He gives the correct trend of the number of mobile carriers on the sheets (Fig. 3). Here R_H is the Hall constant, e is the electronic charge, and V_{Cu} is the volume per Cu ion. In a simple metallic system with one parabolic band partially occupied, the Hall number would be the temperature-dependent carrier density. In the case of
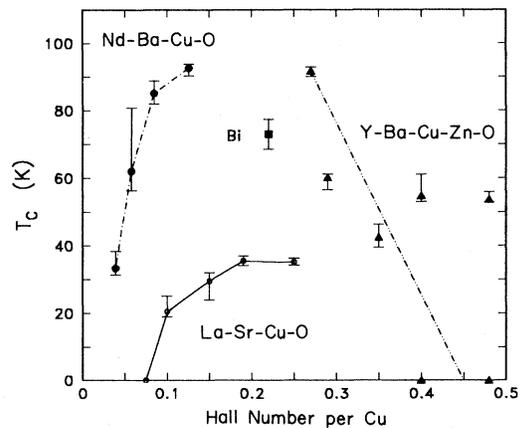
FIG. 3. Superconducting transition temperatures T_c vs Hall number, V_{Cu}/R_He (defined in text) measured at 50 K for the $La_{2-x}Sr_xCuO_4$ system (solid line) and at 125 K for the Nd (dash-dot line) and for the Zn (dash-dot-dot line) substituted $YBa_2Cu_3O_y$. These lines illustrate the trend of T_c vs the number of mobile holes.

$YBa_2Cu_3O_y$ and $Nd_{1+x}Ba_{2-x}Cu_3O_y$, the Hall number is strongly temperature dependent and its interpretation is not known.[16] However, the trend on Hall number increasing with T_c in the Nd system probably indicates an increase in the concentration of mobile holes as suggested by Wang et al.[12] for $YBa_2Cu_3O_y$, and in agreement with what we determine chemically. It should be noted that these 125 K values, which we show in Fig. 3, are in rather good agreement with p_{sh} determined chemically (Fig. 2).

$YBa_2Cu_{3-x}Zn_xO_y$ and $Y_{1-x}Ca_xBa_2Cu_3O_y$

Structurally the Zn substituted samples remained orthorhombic to our highest doping level ($x = 0.28$) and, as has been reported by others,[17–21] T_c is reduced rapidly with x. Both the resistive and magnetic transitions in this system were sharp indicating good homogeneity and bulk superconductivity.

Our chemical data clearly show that there is an increase in p but a decrease in T_c with x. The Hall data are somewhat scattered. However, all of the Hall data lie to larger Hall numbers and smaller T_c's than the undoped $YBa_2Cu_3O_y$. The dash-dot-dot line in Fig. 3, connecting $YBa_2Cu_{3x}O_y$ and the nonsuperconducting Zn-doped samples, shows this trend. Clearly, the correlation with the chemically determined p_{sh} is not as good as it is in the Nd or $La_{2-x}Sr_xCuO_4$ systems. Recently, Zhenhui et al.[21] reported Hall measurements on zinc-substituted 1:2:3 which showed the Hall number varying nonmonotonically between 0.25 and 0.4. In Fig. 1 (y vs p), the up triangles, which are the points for the $YBa_2Cu_{3-x}Zn_xO_y$ system, extend diagonally upward and to the right from $YBa_2Cu_3O_y$ with $y > 7$ and $p > \frac{1}{3}$. In Figs. 1 and 2, we plot data (down triangles) for samples in the $Y_{1-x}Ca_xBa_2Cu_3O_y$ system as reported by Tokura et al.[9] and Manthiram, Lee, and Goodenough.[15] In the y vs p plot (Fig. 1), these points are somewhat parallel to the p_c line extending downward from $YBa_2Cu_3O_7$ with $y < 7$ and $p < \frac{1}{3}$. The maximum in T_c vs x we observe on these two trajectories (Zn, up triangle; and Ca, down triangle) may indicate a ridge of T_c max that runs parallel to the p_c line at a distance slightly less than $\frac{1}{4}$ hole per sheet Cu (shown as the dotted line in Fig. 1). Tokura et al.[9] observe a plateau at $T_c = 80$–90 K in the range of 0.15–$0.25p_{sh}$ and show two Ca-substituted samples with T_c's of 67 and p_{sh} of 0.3. We believe, in view of the Zn and Ca results, that these samples are probably beyond the maximum and indicate that the ridge of maximum T_c extends down to oxygen values of 6.7. Thus, there is a maximum in the T_c vs p curve in the 1:2:3 structures similar to that seen in the $La_{2-x}Sr_xCuO_4$ system.[10] This is more evident in Fig. 2, where the chemically determined p_{sh} vs T_c are plotted. Both the Zn (up triangles) and the Ca (down triangles) points show that T_c decreases rather sharply with Zn and Ca substitutions as seen by the dash-dot-dot line we draw through these points. This maximum, which occurs at about $0.22p_{sh}$ is not too different to that found in the $La_{2-x}Sr_xCuO_4$ system. Our earlier data for the $La_{2-x}Sr_xCuO_4$ system are also shown here

(open circles). The dotted line in Fig. 2, data from Torrance et al.,[10] shows this maximum to be rather broad and centered around a p_{sh} of 0.18–0.22. Clearly when p_{sh} exceeds about 0.30, superconductivity is not seen in either system. An intriguing difference between the two systems is that in the 1:2:3 materials, semiconducting behavior is seen in those samples with high p_{sh} concentrations which are nonsuperconductors while the corresponding samples in the $La_{2-x}Sr_xCuO_4$ system are good metals.

A question remains as to why zinc substitutions are unique in increasing p since it has a charge of $+2$. Xiao and co-workers[17] suggested that it substitutes on the Cu(2) site where it reduces the number of holes resulting in a sharp drop in T_c with x. Our results show the opposite in that there is a slight increase in y and a corresponding increase in p_{sh} beyond the maximum in the p_{sh} vs T_c curve and that is the reason for the sharp drop in T_c. Whether all the substituted zinc goes on the Cu(2) site is still unclear because a recent neutron study by Kitijani et al.[22] showed the Cu(1) site to contain 80% of that substituted. Since the neutron results are not definitive, the fact that the oxygen content y remains high may indicate that there is some Zn located on positions other than those normally occupied by the regular metals. If zinc substitutes on the yttrium site it would be a mechanism for increasing p. It is clear more work is necessary to determine where zinc substitutes and why it increases p. Calcium substitutions, on the other hand, are more easily understood since it presumably replaces yttrium. Although, as expected, there is an overall decrease in y, the number of sheet holes p_{sh}, in fact, increases resulting in a similar drop in T_c.

In addition to the zinc-substituted materials, we prepared a series of samples in the $YBa_2Cu_{3-x}Ga_xO_y$ system. Their behavior was similar to that reported by others[17,23] in that at $x = 0.25$ they transform to tetragonal and the T_c dependence on x is rather linear and small when compared to zinc. Although we do not show it in Fig. 2, their T_c vs p_{sh} behavior is very similar to that of the Nd samples.

We also measured a single-phase ceramic of a bismuth containing superconductor with the 2:2:1:2 structure. Our sample had a composition of $Bi_{2.2}Sr_{1.6}Ca_{1.3}Cu_{1.95}O_{8.5}$ and a transition temperature 73 K. The chemically determined p was 0.22, in excellent agreement with the Hall at 100 K, i.e., 0.22. Since there are no chains, these holes are presumably all mobile on the two CuO_2 sheets. These data, when plotted in Figs. 2 and 3 (squares), fall very close to the two-sheet 1:2:3 curve but well above the one-sheet $La_{2-x}Sr_xCuO_4$ curve. Takigi et al.[24] have measured the Hall number on a 2:2:1:2 single crystal which had a T_c of 80 K with H perpendicular to the planes. Our results are similar to theirs.

In conclusion, by determining the total hole concentration chemically and the mobile hole concentration by Hall measurements and using the ideas of Tokura et al.[9] and Mitzi et al.[14] to distinguish between localized chain holes and mobile sheet holes, we show there is a maximum in the T_c vs mobile sheet hole curve in the 1:2:3-type materials just as there is in the $La_{2-x}Sr_xCuO_4$ system. This maximum in T_c, which occurs at a hole concentration of about 0.22 per Cu site, appears to be independent of how

the holes are produced, e.g., dopant species, and strongly suggests that the sheet-hole concentration is the singularly most important factor in determining T_c.

Note added. We recently became aware of a paper by Okazaki *et al.*[25] where they report results on the hole T_c relationships of Fe-, Co-, Ni-, and Zn-substituted 1:2:3. Their hole concentration and Hall data for the Zn system are in agreement with ours. Further, they also strongly conclude that T_c is universally determined by the hole concentration, regardless of how the holes are produced.

ACKNOWLEDGMENTS

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

[2]T. Penney, M. W. Shafer, B. L. Olson, and T. S. Plaskett, Adv. Ceram. Mater. **2**, 577 (1987).

[3]M. W. Shafer, T. Penney, and B. L. Olson, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 771.

[4]Y. Saito, T. Naji, K. Hirokawa, A. Edno, N. Matsuzaki, M. Katsumata, and N. Higuci, Jpn. J. Appl. Phys. **26**, 838 (1987).

[5]K. Takita, H. Akinaga, H. Katah, H. Asano, and K. Masuda, Jpn. J. Appl. Phys. **27**, L67 (1988).

[6]H. Uwe, T. Sakudo, H. Asano, T. Han, K. Yagi, R. Harada, M. Iha, and Y. Yokoyama, Jpn. J. Appl. Phys. **27**, 577 (1988).

[7]H. Akinaga, H. Katah, K. Takita, H. Asano, and K. Masuda, Jpn. J. Appl. Phys. **27**, 610 (1988).

[8]K. Takita, H. Akinaga, H. Katah, and K. Masuda, Jpn. J. Appl. Phys. **27**, 5731 (1987).

[9]Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, Phys. Rev. B **38**, 7156 (1988).

[10]J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988).

[11]T. Penney, M. W. Shafer, and B. L. Olson, in *Towards a Theoretical Understanding of High Temperature Superconductivity,* edited by S. Lundqvist, E. Tosatti, M. Tosi, and Yu Lu, Progress in High Temperature Superconductivity, Vol. XIV (World Scientific, Singapore, 1988), p. 699.

[12]Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, Phys. Rev. B **36**, 7222 (1987).

[13]A. I. Nazzal, Y. V. Lee, E. M. Engler, R. O. Jacowitz, Y. Tokura, and J. B. Torrance, Physica C **153–155**, 1367 (1988).

[14]D. B. Mitzi, P. T. Feffer, J. M. Newsam, D. J. Webb, P. Klavins, A. J. Jacobson, and A. Kapitulnik, Phys. Rev. B **38**, 6667 (1988).

[15]H. A. Manthiram, S. J. Lee, and J. B. Goodenough, J. Solid State Chem. **73**, 278 (1988).

[16]T. Penney, S. von Molnar, D. Kaiser, F. Holtzberg, and A. W. Kleinsasser, Phys. Rev. B **38**, 2918 (1988).

[17]Gang Xiao, M. Z. Cieplak, A. Gavrin, F. H. Streitz, A. Bakhsai, and C. L. Chien, Phys. Rev. Lett. **60**, 1446 (1988); Gang Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, F. H. Streitz, C. L. Chen, J. J. Rhyne, and J. A. Gotaas, Nature **322**, 238 (1988).

[18]Y. Oda, H. Fugita, T. Ohmichi, T. Kohara, I. Nakada, and K. Asayama, J. Phys. Soc. Jpn. **57**, 1548 (1988).

[19]J. M. Tarason, P. Barboux, P. F. Micelli, L. H. Greene, and G. W. Hull, Phys. Rev. B **37**, 7458 (1988).

[20]B. Jayaran, S. K. Agarwal, C. V. Narasimha Rao, and A. V. Narlikar, Phys. Rev. B **38**, 2903 (1988).

[21]H. Zhenhvi, Z. Han, S. Shifang, C. Zuyao, Z. Qirui, and X. Jiansheng, Solid State Commun. **66**, 1215 (1988).

[22]T. Kajitani, K. Kusaba, M. Kikuchi, Y. Syono, and M. Hirabayashi, Jpn. J. Appl. Phys. **27**, 354 (1988).

[23]M. Hiratani, Y. Ito, K. Miyauchi, and T. Kudo, Jpn. J. Appl. Phys. **26**, 1997 (1987).

[24]H. Takagi, H. Eisaki, S. Uchida, A. Maeda, S. Tajima, K. Uchinokura, and S. Tanaka, Nature **332**, 236 (1988).

[25]N. Okazaki, S. Kambe, A. Kishi, N. Kanazawa, A. Ohtomo, A. Fukuoka, T. Hasegawa, K. Kishio, K. Kitazawa, and K. Fueki, Proceedings of the Materials Research Society International Meeting, Tokyo, Japan, 1988 (unpublished).