Chain-site versus plane-site Cu substitution in $YBa_2Cu_{3-x}M_xO_7$ ($M = Co, Ni$): Hall and thermopower studies

J. Clayhold, S. Hagen, Z. Z. Wang, and N. P. Ong

Joseph Henry Laboratories, Princeton University, Princeton, New Jersey 08544

J. M. Tarascon and P. Barboux

Bell Communications Research, Redbank, New Jersey 07701

(Received 26 August 1988)

Substitution of Cu by Ni at Cu(2) (plane) sites in $YBa_2Cu_3O_7$ has a weak effect on the Hall constant, but turns the thermopower negative. In contrast, substitution at Cu(1) (chain) sites by Co decreases the Hall number exponentially. The suppression of T_c is due to different mechanisms in the two cases. We discuss how doping affects the carrier density, and the evidence in favor of a filling factor of $\frac{1}{2}$ in the undoped system.

Recently, several groups[1-6] have shown that isomorphous substitution of Cu in $YBa_2Cu_3O_{7-y}$ by Fe, Co, Ni, Zn, Al, and Ga systematically suppresses the transition temperature for superconductivity T_c. Thermogravimetric analysis (TGA) evidence on the binding energy of the O(1) (chain) oxygen suggest that Ni and Zn enter the Cu(2) sites (in the planes) whereas Co and Al substitute into the Cu(1) sites (on the chains).[4] Fe appears to enter both Cu(1) and Cu(2) sites, depending on x. Co, Fe, and Ga doping[4,6] induce an orthorhombic-to-tetragonal transition near $x = 0.1$, whereas Zn and Ni-doped $YBa_2Cu_3O_7$ remain orthorhombic[4,6] up to $x = 0.4$. A suggestive correlation has been established between the Cu(1)−O(4) bond length and T_c in the Co-doped samples.[7] [O(4) is the apical oxygen between Cu(1) and Cu(2); O(1) is at the chain site.] Hall and thermopower measurements are useful complementary tools to structural and chemical techniques because they provide a measure of the carrier density n, which is one of the major factors affecting T_c. From the transport data on $YBa_2Cu_3O_7$ ceramics doped with Co and Ni, we show that there is a striking difference in the transport properties, depending on the site preference [Cu(1) or Cu(2)]. While the Hall number is little affected by Ni substitution, it is decreased exponentially by Co dopants. This implies that the observed suppression of T_c in the two cases is most probably due to different causes. We also discuss the evidence from the transport, chemical, and structural data supporting a hole density of $\frac{1}{2}$ per Cu(2) for undoped $YBa_2Cu_3O_7$.

Thermogravimetry and iodometric analysis show that the oxygen content in the Ni-doped samples is roughly unchanged from the undoped compound. In the Co-doped samples the oxygen content remains constant up to $x = 0.2$, then *increases* slightly as x approaches 1.0, consistent with an extra oxygen being bound by two Co ions.[4] The Hall measurements on the Ni-doped samples were carried out in a fixed field of 8 T by rotating the sample. The Hall measurements on Co-doped samples were performed in a 15-T Bitter magnet.

Figure 1 shows the variation of the thermopower S with temperature (T) in three of the Ni-doped samples. We find that the magnitude of S (negative) rises monotonically as T decreases from 290 K, attaining a maximum ~ 20 K above T_c. At small x, S is apparently very sensitive to the dopant level. This is brought out in Fig. 2 where S is plotted versus x at three fixed T's. The most interesting features are the steep increase of S (to larger negative values) at low x, and the very broad maximum at higher x. The thermopower of undoped $YBa_2Cu_3O_7$ (both ceramic and single-crystal samples) has been studied by many groups.[8-11] All studies find a small, weakly T-dependent thermopower ($|S| < 4$ μV/K). However, there are conflicting reports on the sign of S in ceramics[8-10] (and of the in-plane component S_{ab} in single crystals[11]). Figure 1 clearly shows that S is very sensitive to very low concentrations of Ni. A slight increase in x from 0 to 0.1 is sufficient to change S from ~ 0 to -8 μV/K at 100 K. (The trend in our data implies that S is either close to zero or slightly positive in the $x = 0$ sample.) For $x > 0.1$, S saturates to the value -8 μV/K at 100 K. The sensitivity of S to very light doping may account for the disagreements in sign. Apparently, very slight doping levels or changes in sample processing are sufficient to alter its sign.
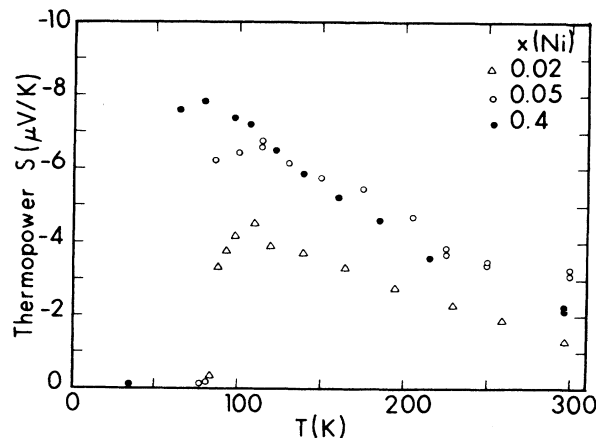

FIG. 1. The thermopower vs temperature of Ni-doped $YBa_2Cu_3O_7$ for three Ni concentrations.

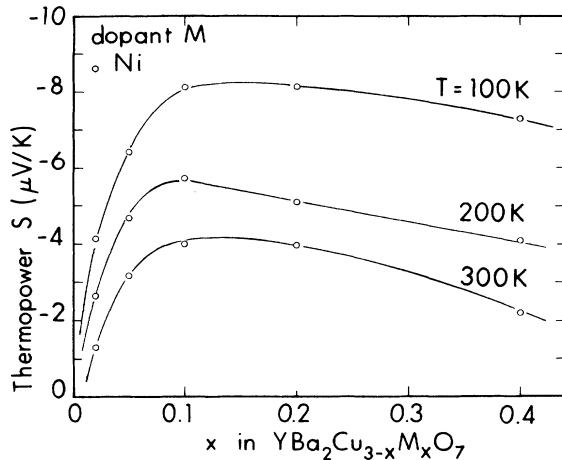FIG. 2. Variation of the thermopower S with Ni context x in $YBa_2Cu_3O_7$ at 100, 200, and 300 K. The magnitude of S increases rapidly with x for $x < 0.1$, before saturating. The trend as $x \to 0$ suggests that S is close to zero or slightly positive in the undoped system.

FIG. 3. Solid circles: the Hall number [defined as $V/(R_H e)$, where V is the unit-cell volume, 174 Å^3] at 100 K vs Ni content in $YBa_2Cu_3O_7$. Note the sensitive variation of n_H at low x, and the saturation to the value ~ 1 hole/cell at high x. The solid triangles indicate the temperature for the onset of the superconducting transition measured resistively while the open triangles indicate the highest zero-resistance temperature for the Ni-doped samples. The dashed line indicates the variation of T_c with x for the Co-doped samples as reported in Refs. 4 and 7.

We discuss next the Hall effect of the Ni-doped samples. At the lowest doping level ($x = 0.02$) the temperature variation of R_H is closely similar to that observed[10,12,13] in undoped ceramics ($n_H = 1/R_H e$ is linear in T). Further increase in x suppresses the slope of n_H vs T, so that at the highest Ni-doping level (0.4), n_H is only weakly T dependent, increasing by less than 20% between 100 and 200 K. (A full discussion of the T dependence of R_H appears elsewhere.[14]) In Fig. 3 we have plotted the variation of the Hall number, defined as $n_H V$ (V is volume of a unit cell) with x at 100 K. As x increases from 0, n_H increases rapidly before reaching a maximum near $x = 0.05$. For x larger than 0.2, n_H saturates to a value close to 1 hole/unit cell.

The anomalous $1/T$ dependence[12,13] of R_H is observed in undoped $YBa_2Cu_3O_7$. R_H also decreases with increasing T in $Tl_2Ca_2Ba_2Cu_3O_x$ (Ref. 15) and $La_{2-x}Sr_xCuO_4$ (Ref. 14) ($x = 0.15$) although more weakly than $1/T$. In Ref. 14 it is proposed that in $YBa_2Cu_3O_7$ the Hall resistivity is dominated by anomalous scattering which obscures the conventional Hall effect. This precludes a simple inference of the actual carrier density n from R_H. However, as the Ni content increases both the superconductivity and the anomalous scattering are suppressed, leaving the normal component which is insensitive to T. As in Ref. 14, we make the reasonable assumption that in highly doped samples, in which R_H is only weakly T dependent, it is justified to identify n_H with the carrier density n. With this assumption we deduce that n approaches 1 hole/unit cell as x increases beyond 0.4.

Photoemission experiments[16] indicate that in $YBa_2Cu_3O_7$ the holes reside in orbitals $d^9\underline{L}$ with predominantly O $2p$ character. The $d^9\underline{L}$ combination is equivalent to a formal valence of $3+$ on the Cu site. If Ni substitutes into Cu(2) sites as a divalent impurity it cannot alter the total ligand hole population (assuming the oxygen content remains at seven per cell).[14] Therefore, the Hall results
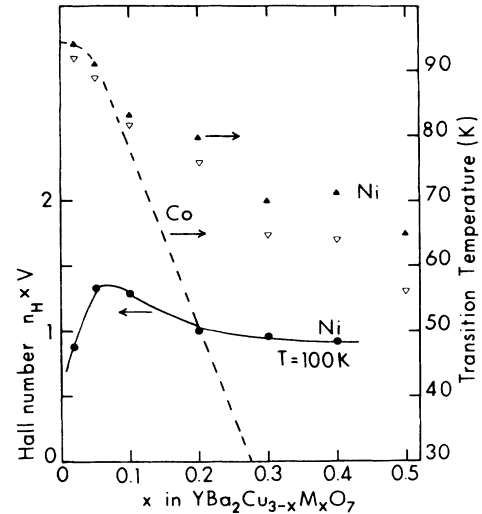
are consistent with assuming (i) that Ni is in the $2+$ oxidation state, and (ii) the ligand holes remain itinerant up to $x = 0.4$. However, the singlet state, which is formed from the hybridization of $3d_{x^2-y^2} - 2p\sigma$ orbitals and thought to be crucial to superconductivity,[17] cannot occur at the Ni site. Thus, the observed suppression of superconductivity with Ni content may be caused by the effective removal of these sites, rather than from a decrease in available itinerant holes.

Next we compare these results with the Hall data in Co-doped samples. The TGA and neutron-diffraction results confirm that Co substitutes into the Cu(1) sites.[4,7] Furthermore, the Cu(1)−O(4) bond length shrinks from 1.845 to 1.830 Å as x increases from 0 to 0.3. Over this range, T_c decreases from 93 to 22 K (see Fig. 3). Both the sharp decrease in T_c and the contraction in the bond length suggest that the carrier density is greatly decreased. Figure 4, which displays the variation at two temperatures of n_H vs x for $YBa_2Cu_{3-x}Co_xO_7$ ($0.02 < x < 0.5$), confirms this inference. As in the Ni case, n_H is linear in T at small x. At large x, however, the T dependence becomes negligible, so that we again identify n_H with n. The data at large doping levels ($x > 0.2$) in Fig. 4 suggest that n, in fact, decreases exponentially with x. This is to be contrasted with the large-x behavior of n_H in the Ni case (Fig. 3). The striking difference between the two cases is consistent with the conclusion that Ni substitutes for a Cu site different from Co. In view of the neutron diffraction results, we conclude that Ni enters into Cu(2) sites, in agreement with the TGA results.

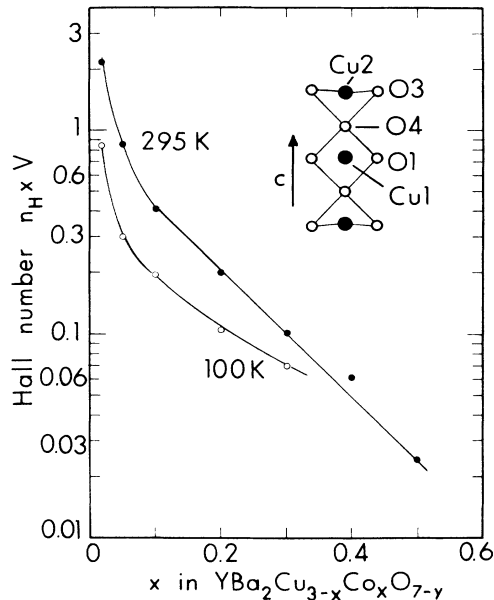The exponential decrease of n with x ($x > 0.2$) in Fig. 4

FIG. 4. The Hall number at 100 and 295 K vs Co content in $YBa_2Cu_3O_7$. The exponential decreases of n_H at large x is compared with the Ni case in the text. The lines are drawn to guide the eye. We expect both curves to show a maximum between $x = 0.0$ and 0.02, as in the Ni case. The inset shows the designation of the Cu and O sites.

may seem surprisingly rapid. Simple valence counting suggests that each trivalent Co dopant decreases the hole density in the CuO_2 planes by 1 hole/cell. However, this is not valid because of the additional oxygen bound by every two Co ions.[7] The increased oxygen content compensates for the extra electrons donated by Co. The other important factor is the dramatic change in the Cu(1)− O(4) bond length.[7] As x increases, the oxygen O(4) at the apical site (see inset of Fig. 4) is pulled away from the CuO_2 planes. (Ba is pulled towards the planes, but its filled states are far from the Fermi level.) If we assume that the increased Cu(2)-O(4) separation induces an electron transfer back to the CuO_2 planes, we may anticipate a dramatic decrease in the itinerant hole population. Because the Cu(2)-O(4) separation is large (2.305 Å), the overlap integral between the Cu(2) $3d_{z^2}$ and O(4) $2p_z$ states decreases exponentially with the separation. Since the energy level of O(4) $2p_z$, in relation to the Fermi level, depends on this overlap, the electron transfer increases exponentially with x. We propose this scenario to explain the observed exponential decrease in n_H with x. The strong decrease in n implies that in the Co-doped system the reduction in T_c is primarily due to carrier reduction, similar to the case in $La_{2-x}Sr_xCuO_4$ ($x < 0.15$.)

One of the important parameters in undoped $YBa_2Cu_3O_7$ is the carrier concentration, or filling factor δ [δ is defined as the fraction of Cu(2) in the formal 3+ state]. Are all the ligand holes confined to the CuO_2

planes [i.e., all Cu(1) are 2+], or are they uniformly distributed between Cu(2) and Cu(1) sites? The former case would correspond to $n = 1$ hole/cell (filling factor $\delta = 0.5$), whereas the latter should correspond to $n = 0.67$ (in-plane) holes/cell ($\delta = 0.33$). From neutron scattering results, Miceli et al.[7] infer that all the Cu(1) are in the 2+ state. Hall studies[12] on oxygen-doped $YBa_2Cu_3O_{7-y}$ indicate a sharp transition in R_H when the oxygen deficiency y exceeds 0.50 per cell, suggesting that the itinerant hole population at $y = 0$ is 1 hole/cell. Thus, both experiments are in favor of $\delta = 0.5$.

This conclusion is corroborated by the transport data presented here. As discussed above, it is hopeless to derive n from n_H in the strongly superconducting samples because of the linear T behavior. However, the suppression of high-T_c behavior in the Ni-doped samples leads to a number for the ligand holes also approaching (approximately) 1 hole/cell. Within the assumptions stated above,[14] we propose that this is a more reliable way to determine the actual carrier density in the undoped system. (Hall measurements on one $YBa_2Cu_3O_7$ single crystal with the field aligned in the a-b plane shows a weakly T-dependent Hall number close to 1 hole/cell as well.[18])

The very small thermopower measured in good ceramics and the sharp increase to large positive values when $YBa_2Cu_3O_7$ is doped with Pr, Ga, or by oxygen removal has been suggested by Anderson[19] as evidence for midband filling of the lower Hubbard band. (This picture assumes a large U and a δ of 0.5.) The demonstration that S can be driven negative with systematic doping of Ni is consistent with midband filling, and lends support to the broad picture of a large U and a value of $\delta = 0.5$. It is well known that thermopower of a metal is generally a very difficult quantity to calculate. The relative contributions of phonon drag, many-body corrections, and impurities (especially magnetic) still remain to be sorted out for most simple metals. Nonetheless, the present data show that there are two distinct classes of behavior in doped $YBa_2Cu_3O_7$. In one class [doping with Pr (Ref. 10) and oxygen[20]] S increases rapidly to very large positive values (> 50 μV/K), indicating that these oxides have an intrinsically large S (because of correlation). The large S is suppressed as we approach the pure system because of cancellations, arising from electron-hole symmetry in the midband situation. The rapid change in S vs x is a band-filling effect. In the second class (Ni doping) $|S|$ remains small (< 10 μV/K) because the chemical potential is not strongly affected by the impurity content. The variation of the Hall coefficient is quite consistent with this classification.

[1]Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. A. Oki, K. Hoshino, A. A. Minami, and T. Fujita, Nature **328**, 512 (1987); Y. Maeno, M. Kato, Y. Aoki, and T. Fujita, Jpn. J. Appl. Phys. **26**, L1982 (1987).

[2]J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. McNiff, Phys. Rev. B **36**, 8393 (1987).

[3]G. Xiao, F. H. Streitz, A. Garvin, Y. W. Du, and C. L. Chien, Phys. Rev. B **35**, 8782 (1987).

[4]J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).

[5]T. Siegrist, L. F. Schneemeyer, J. V. Waszczak, N. O. Singh, R. L. Opila, B. Batlogg, L. W. Rupp, and D. W. Murphy, Phys. Rev. B **36**, 8365 (1987).

[6]G. Xiao, M. Z. Cieplak, A. Garvin, F. H. Streitz, A. Bakhshai, and C. L. Chien, Phys. Rev. Lett. **60**, 1446 (1988).

[7]P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, F. J. Rotella, and J. D. Jorgensen, Phys. Rev. B **37**, 5932 (1988).

[8]C. Uher and A. B. Kaiser, Phys. Rev. B **36**, 5680 (1987); A. Mawdsley, H. J. Trodahl, J. Tallon, J. Sarfati, and A. B. Kaiser, Nature **328**, 233 (1987); S. C. Lee, J. H. Lee, B. J. Suh, S. H. Moon, C. J. Lim, and Z. G. Khim, Phys. Rev. B **37**, 2285 (1988); N. Mitra, J. Trefny, M. Young, and B. Yarar, ibid. **36**, 5581 (1987).

[9]S. W. Cheong et al., Phys. Rev. B **36**, 3913 (1987).

[10]A. P. Goncalves, I. C. Santos, E. B. Lopes, R. T. Henriques, M. Almeida, and M. O. Figueiredo, Phys. Rev. B **37**, 7476 (1988).

[11]Z. Z. Wang and N. P. Ong, Phys. Rev. B **38**, 7160 (1988); R. C. Yu, M. J. Naughton, X. Yan, P. M. Chaikin, F. Holtzberg, R. L. Greene, J. Stuart, and P. Davies, ibid. **37**, 7063 (1988).

[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]P. Chaudari et al., Phys. Rev. B **36**, 8903 (1987).

[14]J. Clayhold, N. P. Ong, Z. Z. Wang, J. M. Tarascon, and P. Barboux (unpublished).

[15]J. Clayhold, N. P. Ong, P. H. Hor, and C. W. Chu, Phys. Rev. B **38**, 7016 (1988).

[16]N. Nucker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, Phys. Rev. B **37**, 5158 (1988).

[17]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[18]S. W. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1768 (1987).

[19]P. W. Anderson, in Proceedings of the International Conference on High Temperature Superconductors and Materials and Mechanisms of Superconductivity, edited by J. Muller and J. L. Olsen [Physica C **153–155**, 527 (1988)].

[20]H. Takagi, S. Uchida, H. Iwabuchi, S. Tajima, and S. Tanaka, Jpn. J. Appl. Phys. Ser. 1, Supercond. Mat. 6 (1988).