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Broader perspective on the high-temperature superconducting $YBa_2Cu_3O_y$ system: The real role of the oxygen content

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A series of new $YBa_2Cu_3O_y$-like materials are reported in which the oxygen content and the average [Cu-O] charge (or Cu valence) are separately varied over a wide range. We find a distinct boundary between samples showing anomalous insulating behavior and those with high T_c. These data are interpreted to demonstrate that the [Cu-O] charge in the sheets largely determines T_c and that the variable oxygen content and the chains merely provide an insulating reservoir of charge.

High-temperature superconductivity[1,2] has generated an enormous amount of interest and research over the last two years, but has so far eluded theoretical understanding.[3] Some of the most valuable clues to this mystery come from the dramatic dependence[4-6] of the superconducting properties of $YBa_2Cu_3O_y$ on the oxygen content y. Upon decreasing the oxygen concentration, the material transforms from a 93-K superconductor, to a 60-K superconductor, and finally to an insulator. By decreasing the oxygen content, what changes are induced in the material that might so strongly affect the superconducting properties? Important modifications of the structure occur. The copper-oxygen chains, prominent[7] when $y = 7$ are no longer present[8] near $y = 6$. Correspondingly, the oxygen coordination of the copper atoms in this layer decreases from 4 to 2. In addition, the average effective valence of copper decreases from +2.33 at $y = 7$ to +1.67 at $y = 6$. Furthermore, this valence is distributed in an unknown way among the two copper sites: in the sheets and in the inter-Ba plane. Since these three factors are intimately coupled, it has not been possible to untangle which of them is most responsible for the changes in the superconducting behavior observed.

We have succeeded in finding a way to decouple these aspects and better understand their respective roles in superconductivity. This involves synthesizing a series of new $YBa_2Cu_3O_7$-like compounds, each having a different total charge Q on the noncopper cations. A different Q gives rise to differences in the effective copper valence, in addition to those induced by variations in the oxygen concentration. In order to synthesize such compounds with varying Q, we must recognize that an essential feature of their structure is the three sites per unit cell: one small Y site and two larger Ba sites. Using the guideline of one small and two large ions per unit cell, we have made the new systems $Y(La_xBa_{1-x})_2Cu_3O_y$ and $(Y_xCa_{1-x})Ba_2Cu_3O_y$. For these two solid solutions, the range of solid solubility is indicated at the top of Fig. 1 where it is represented in terms of the total charge Q of the noncopper metals. By substituting the small Ca^{2+} ion for Y^{3+}, Q has been reduced from 7 to 6.5. Substitution of the large La^{3+} for the large Ba^{2+} yields compounds with large values of Q, up to $Q = 7.8$. The solid solution systems $(L_xBa_{1-x})_3Cu_3O_y$ (L = La,Nd) also offer the possibility of varying Q. However, the experimental results are often strongly dependent on the sample preparation and annealing conditions.[9-11] We attribute these problems partially to the difficulties of trying to place the relatively large La^{3+} and Nd^{3+} ions onto the smaller Y^{3+} site. Another example of the success of this guideline is the new compound $CaLaBaCu_3O_y$, where Ca^{2+} is substituted for Y^{3+} and a La^{3+} ion is substituted for one of the Ba^{2+} ions. The resultant compound[12] is isostructural with the tetragonal form of $YBa_2Cu_3O_y$ and for $y \sim 7$ is superconducting with

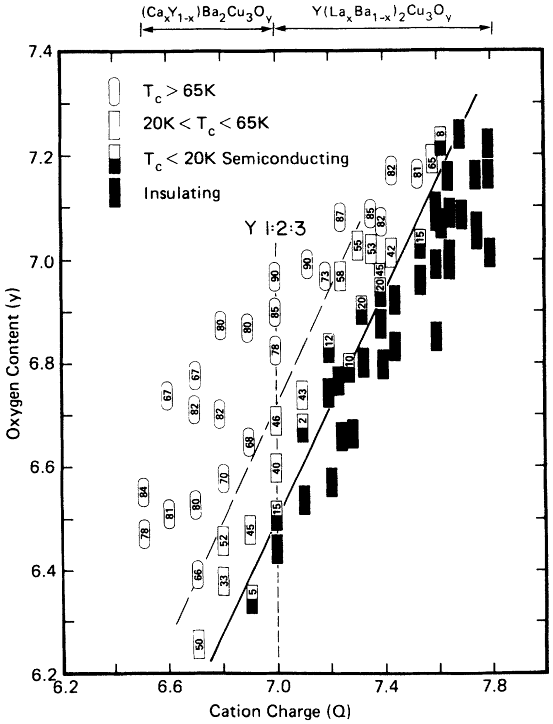

FIG. 1. The oxygen content (±0.03) measured for a series of isostructural samples made with different total charge Q on the noncopper metals. The short dashed line labeled Y1:2:3 is for $YBa_2Cu_3O_y$. The solid line is drawn to separate insulating and superconducting phases, while the long dashed line is drawn to separate high-T_c phase from that with $20 < T_c < 65$ K, where T_c is temperature of zero resistance.

$T_c = 80$ K.

Samples from a batch of any given composition (and, hence, any given Q) can be annealed in different partial pressures of oxygen. Thus, several samples with differing oxygen content have been obtained for each Q and are shown in Fig. 1. Samples of $YBa_2Cu_3O_y$ are included along the short dashed vertical line at $Q = 7$. It is seen that this new series of more than 80 samples spans a rather wide range of both Q and oxygen content. Note that there is a tendency for compounds with higher cation charge Q to have higher oxygen content. The samples were prepared by solid-state reaction in alumina crucibles from appropriate mixtures of $BaCO_3$, $CaCO_3$, La_2O_3, and Y_2O_3. The powders were mixed and ground in an alumina mortar and pestle, then fired in air at 900 °C for 6 h. This was followed by three cycles of regrinding and firing for 15 h in air at a temperature (920–1020 °C) which was experimentally optimized for each compound. For the final firing, pellets of these powders were usually heated at 500 °C in flowing oxygen for 15 h. Two methods were used to control the oxygen content: annealing at 500–650 °C in variable oxygen pressure (0–200 bars) or quenching from a high-temperature (400–900 °C) air atmosphere to 300 or 77 K. X-ray powder diffraction showed that each sample has the $YBa_2Cu_3O_y$ structure, with less than 3% of other phases.

One of the most important variables[13] in these materials is the degree of oxidation or, equivalently, the average charge p per $[\text{Cu-O}]^{+p}$ unit. We use this more general description, rather than the effective copper valence $(2+p)$ or the concentration of Cu^{3+}, or O^-, etc. For these samples, we have measured this average charge using an iodometric titration technique.[14] This measurement of the chemical hole concentration can be correlated with, but should not be confused with, the Hall effect measurement of the electronic hole concentration. From Q and this measurement of p, we have determined the oxygen content y using the condition of electrical neutrality: $Q+3(2+p) = 2y$. The same samples (Fig. 1) may each be characterized by their oxygen content and the average $[\text{Cu-O}]^{+p}$ charge and replotted as shown in Fig. 2. Large differences are observed in the conductivity behavior of samples in this series and are included in Figs. 1 and 2 by classifying these data into four types of behavior: (1) metals showing $T_c > 65$ K (open ellipses); (2) metals or semimetals showing $65 > T_c > 20$ K (open rectangles); (3) semiconductors, but having 20 K $> T_c$ (half-open/half-solid rectangles); and (4) insulators (with fairly large activation energies ~0.1 eV) showing no superconductivity (solid rectangles). The superconducting transitions measured by ac conductivity had widths 1–10 K and T_c was defined as the temperature of zero resistance (included inside the ellipse or rectangle in Fig. 2).

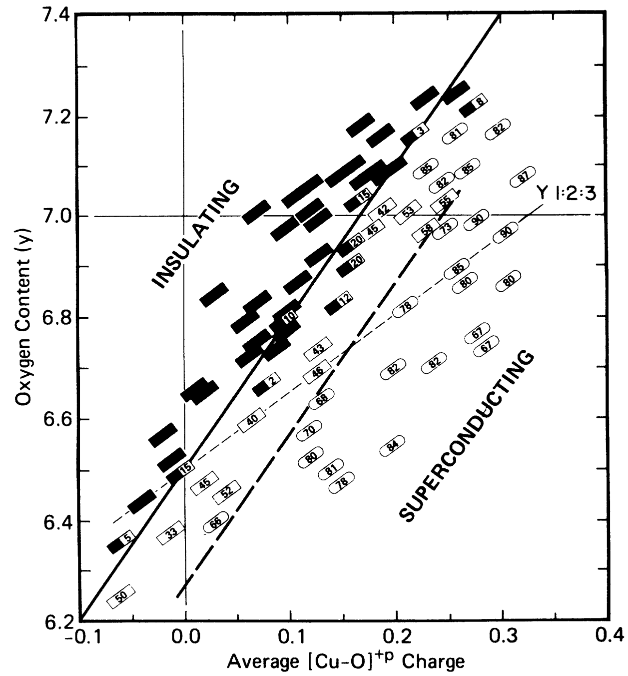

FIG. 2. Data of Fig. 1 plotted vs the average $[\text{Cu-O}]^{+p}$ charge (± 0.02) using the relation $Q+6+3p = 2y$. Same symbols as in Fig. 1.

The data in Figs. 1 and 2 show a consistent and well-defined pattern of behavior for this series of new materials. In the "space" shown, there is a large region of compounds with high T_c ($T_c > 65$ K), but more surprisingly, a large region where the samples are insulating. In between the high-T_c and insulating phases, is a smaller region in which we observe intermediate T_c ($65 > T_c > 20$ K) in samples which do not show metallic behavior. There is thus a strong correlation of superconducting behavior with normal-state conductivity behavior, i.e., they disappear together. The $YBa_2Cu_3O_y$ system is seen to be a narrow slice in this broader picture of these phases and its behavior[4–6] is consistent with that observed for this larger series. The data for the samples in Figs. 1 and 2 may be used to study the effects of y and p (or Q) separately. For example, Fig. 3 shows the behavior of a series of samples with approximately constant oxygen content of $y \sim 7.0$ as a function of the average $[\text{Cu-O}]^{+p}$ charge (corresponding to a horizontal scan in Fig. 2). The boundary between insulating and superconducting phases is evident near $p = +0.17$ and T_c exhibits the two plateaus behavior as

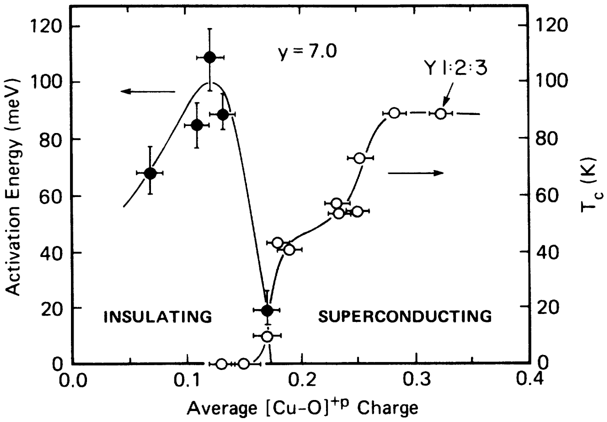

FIG. 3. Activation energy and T_c for series of samples with $y \sim 7.0 \pm 0.1$ as a function of the average $[\text{Cu-O}]^{+p}$ charge. $YBa_2Cu_3O_7$ is indicated as Y1:2:3.

seen[5,6] in $YBa_2Cu_3O_y$ observed by varying y. Since the boundaries in Fig. 2 are neither horizontal nor vertical, we can conclude that neither y nor p is the single relevant variable (which must be a combination of y and p). Some of these samples are orthorhombic and some tetragonal. In general, the orthorhombic-tetragonal boundary[15] does not follow the superconductor-insulator boundary. Furthermore, the $Ca(La_{1-x}Ba_x)_2Cu_3O_y$ system[12] has a very similar superconductor-insulator boundary, but is tetragonal.

The most surprising feature of the data (Fig. 2) is the presence of a broad series of insulating samples. The insulating phase found for $y < 6.5$ in the $YBa_2Cu_3O_y$ system can be reasonably understood as a Mott insulator, since $p \leq 0$. Such a simple explanation cannot be generalized to account for the insulating phase in the broader range of samples. For example, there are samples with a $[Cu\text{-}O]^{+p}$ charge as high as $p = +0.25$ (corresponding to an average valence of $Cu^{+2.25}$), yet they are insulating. Similar insulating phases are also found adjacent to superconducting phases in the $BaPb_{1-x}Bi_xO_3$ system[16] and in some organic superconductors.[17]

We believe that there is one simple and reasonable explanation for the pattern of behavior of this system: samples with $p > 0$ can be insulating only if the holes in *both* the sheets and the inter-Ba plane were insulating. The sheets would be insulating only if they were Mott insulators, with $p_{sh} = 0$. All of the $[Cu\text{-}O]^{+p}$ charge (or holes) must then be in the inter-Ba plane. These holes would be insulating only if they were localized. The behavior for $y = 7$ in Fig. 3 is then described as follows: for small p, all of this charge resides on the chains and these hole states are localized, giving rise to an activated conductivity among the holes in the chains. As the charge p is increased, a threshold is reached beyond which increased conductivity and superconductivity occur. We interpret this threshold as the point at which charge begins to appear on the sheets, which can sustain metallic conductivity and superconductivity. The measured $[Cu\text{-}O]^{+p}$ charge in Fig. 2 is an average over the charge in the sheets and that in the inter-Ba plane: $p = \frac{1}{3}(2p_{sh} + p_{Ba})$. At threshold (and below), $p_{sh} = 0$ and the measured charge at the threshold is $p_c = p_{Ba}/3$. The experimental boundary in Fig. 2 is approximately given by $3p_c = y - 6.5 = p_{Ba}$. At threshold for $y = 7$, $p_{Ba} = +0.5$, meaning that *every other* [Cu-O] in the chains is charged. This is a reasonable charge for a threshold, since it should be easier to begin to put holes in the sheets than to further increase the charge in the chains beyond this value. For smaller oxygen content, the threshold charge decreases, as expected. This analysis can be continued beyond threshold into the region of superconducting samples if we assume that the charge in the inter-Ba plane cannot be increased beyond the threshold value, so that beyond threshold all of the increased charge comes from the sheets. That is, for $p > p_c$, $p_{sh} = \frac{3}{2}(p - p_c)$.

Applying these conclusions to $YBa_2Cu_3O_y$, for example, we find that the holes are distributed among the Cu sites as follows: $p_{sh} = \frac{1}{2}(y - 6.5)$ and $p_{Ba} = y - 6.5$. Thus, for $y = 7$ (the average charge $p = +0.33$), the charge on the chains is $p_{Ba} = +0.5$ and the sheet charge $p_{sh} = +0.25$, in agreement with other estimates.[18] Using this analysis to determine p_{sh} for the superconducting sample in Fig. 2, we plot T_c vs p_{sh} in Fig. 4, which shows plateaus of T_c near 40 and 80 K. The fact that the same well-defined behavior is obtained for samples with oxygen contents ranging from 6.25 to 7.00 and with Q ranging from 6.5 to 7.6 demonstrates that the principal variable correlated with the T_c in this system is the [Cu-O] charge on the sheets. However, a few samples (open squares in Fig. 4) do not have the same behavior for small p_{sh}, perhaps because they have $y > 7$.

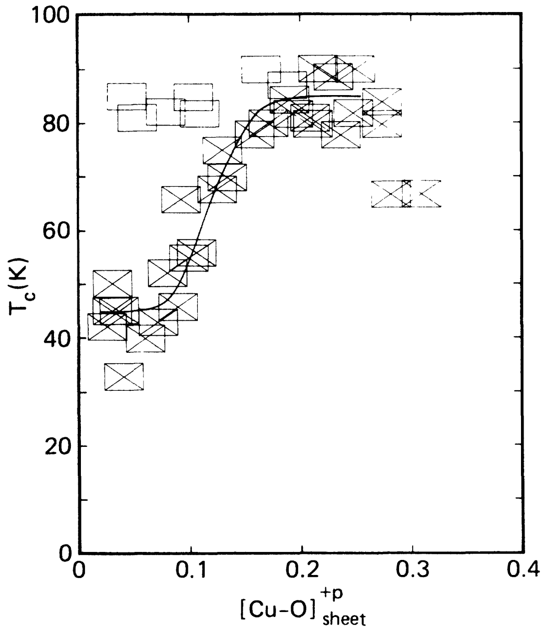

FIG. 4. Temperature (T_c) of zero resistance for all samples in Fig. 2 vs the $[Cu\text{-}O]^{+p}$ charge on the sheets. $YBa_2Cu_3O_7$ is indicated as Y1:2:3. The open squares are for samples with $y > 7$.

In summary, a series of new materials with a wide range of both oxygen content and [Cu-O] charge has given a much broader view of the properties of $YBa_2Cu_3O_y$-like systems. A large number of samples exhibit unexpected insulating behavior, while others are high-T_c superconductors. From the existence of these insulating samples, we conclude that the holes associated with the $[Cu\text{-}O]^{+p}$ charge in the inter-Ba plane (chain region) are localized and merely provide an insulating reservoir of charge. From the well-defined boundary between these insulating samples and the superconductors, we determine the [Cu-O] charge in this plane and, hence, that in the sheets, i.e., p_{sh}. For a series of samples having a large variety of oxygen contents and values of the average [Cu-O] charge, their T_c is correlated with p_{sh}. We conclude that superconductivity occurs in these sheets and that p_{sh} is the principal variable governing the superconducting properties. For $YBa_2Cu_3O_y$ itself, the general analysis above indicates that the hole concentration in the sheets is given by $p_{sh} = (y - 6.5)/2$. Thus, the observed[4-6] changes in T_c upon varying the oxygen content are caused by the associated changes in p_{sh}.

Note added. After completion of this work, we became aware of other recent work[19–21] on the two solid solutions discussed here. These data are consistent with ours, but are not analyzed in the same way.

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