Generic superconducting phase behavior in high-T_c cuprates: T_c variation with hole concentration in YBa$_2$Cu$_3$O$_{7-\delta}$

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A direct determination of the relationship between T_c and hole concentration p for Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ is obtained by investigating the properties of the fully oxygen-deficient ($\delta \approx 1.0$) compound for which $p = x/2$. Measurements of T_c, the thermoelectric power S, and bond-valence sums calculated from neutron-diffraction refinements for various values of x and δ allow the full determination of the relations $p = p(\delta)$, $T_c = T_c(p)$, and $S = S(T,p)$ confirming that YBa$_2$Cu$_3$O$_{7-\delta}$ satisfies the same universal relations in these quantities as the other high-T_c superconducting cuprates.

Several years passed following the discovery of YBa$_2$Cu$_3$O$_{7-\delta}$ (123) before it was realized that the variation of T_c with oxygen deficiency δ was just the underdoped to optimally doped region[1] of a generic phase diagram for the high-T_c superconducting cuprates (HTSC's) in which T_c is seen to follow an approximately parabolic dependence[2] upon the doped hole concentration p. Specifically, p is the fraction of holes per Cu atom in the CuO$_2$ sheet. This generic behavior is seen most clearly in La$_{2-x}$Sr$_x$CuO$_4$ which can be doped across the entire superconducting phase diagram. Other such, though less studied, compounds include[3,2] Bi$_2$Sr$_{1-x}$La$_x$CuO$_{6+\delta}$ and Tl$_{0.5+x}$Pb$_{0.5-x}$Sr$_2$Ca$_{1-y}$Y$_y$Cu$_2$O$_7$ and these, also, display the same generic parabolic dependence upon p. In oxygen stoichiometric La$_{2-x}$Sr$_x$CuO$_4$ there exists a one-to-one correspondence between x and p. T_c appears to be maximized at $p \approx 0.16$, falls to zero on the underdoped and overdoped sides at $p \approx 0.05$ and $p \approx 0.27$, respectively, and is conveniently represented by the curve[2]

$$T_c / T_{c,\text{max}} = 1 - 82.6(p - 0.16)^2. \qquad (1)$$

In the neighborhood of $p \approx 0.125$ $T_c(p)$ dips to lower values[4] (in La$_{2-x}$Ba$_x$CuO$_4$ it traces a deep cusp) due to a possible structural change or Sr ordering. This need not concern us further in the present work. In most other HTSC both cation and oxygen nonstoichiometry make it difficult to determine p, and hence the p dependence of T_c, accurately. However, if this nonstoichiometry is determined accurately, by, e.g., resonant synchrotron x-ray diffraction, then the composition of near optimally doped Tl-2223 and Tl-1223 has

been found to be (Tl$_{1.72}$Cu$_{0.28}$)Ba$_2$(Ca$_{1.86}$Tl$_{0.14}$)Cu$_3$O$_{10}$ and (Tl$_{0.47}$Pb$_{0.53}$)(Sr$_{1.58}$Ca$_{0.42}$)(Ca$_{1.936}$Tl$_{0.064}$)Cu$_3$O$_9$, respectively, giving $p \approx 0.14$ in both cases.[5,6] Optimally doped Tl$_{0.5}$Pb$_{0.5}$Sr$_2$Ca$_{0.8}$Y$_{0.2}$Cu$_2$O$_7$ also has $p \approx 0.15$[2] and several other HTSC's point to similar values. It appears therefore that many of the HTSC's have similar phase curves and possibly there is a single universal phase curve $T_c(p)$ for all HTSC's which scales only with $T_{c,\text{max}}$.[7]

In this spirit, the temperature-dependent thermoelectric power (TEP), $S(T)$, of a large number of HTSC's was examined and a universal relationship was found between the room-temperature TEP, $S(290)$ and the ratio $T_c/T_{c,\text{max}}$.[8] Inasmuch as Eq. (1) is generally applicable to the HTSC's this implied a universal relationship between $S(290)$ and p which has since been used extensively to determine the doping state of HTSC's. (Notably, the p values for 123 in this correlation were determined, not from the ratio $T_c/T_{c,\text{max}}$, but from an independent method using bond valence sums as discussed below.) Moreover, $S(T,p)$ in the normal state appears to be a universal function of both T and p the only exceptions being 123 and 124 because of additional contributions to the TEP from the metallically conducting CuO chains. It is the existence of these chains, in 123 in particular, which makes it difficult to determine p in terms of the oxygen deficiency δ. While the total doping state of the compound is determined by δ the doped charge is distributed nontrivially between the CuO$_2$ planes and the CuO$_{1-\delta}$ chains. Tokura *et al.*[9] made an important step towards establishing the relationship between p and δ in 123 by examin-

ing the systematics of the hole-doping and hole-filling solid solutions $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and $YBa_{2-y}La_yCu_3O_{7-\delta}$ but their analysis is flawed by the assumption that the chains are insulating and that the metal/insulator transition coincides with $p \approx 0$ (rather than 0.05 as, e.g., in $La_{2-x}Sr_xCuO_4$). An alternative approach has been developed which uses a combination of copper and oxygen bond valence sums (BVS's), determined from structural bond lengths, to estimate p.[1,10] This showed an almost exact correspondence to Eq. (1) and it was these p values which were used in the TEP correlation noted above.[8] These results taken together are reasonably compelling, but not rigorously persuasive, of a universal phase curve for the HTSC's, including 123 in particular. To date there has been no direct measure of the absolute value of p for 123 and its dependence upon δ. The issue is of prime importance for understanding the phase behavior of HTSC's, the interplay between magnetism and superconductivity, and, indeed, the origins of superconductivity in these compounds. For example, Batlogg and co-workers[11,12] have uncovered from the transport properties a possibly universal p-dependent temperature scale $T^*(p)$ extending across the superconducting domain. This has clearly important implications but the applicability to the 123 compound is dependent upon establishing a reliable relationship between p and the oxygen deficiency δ. By investigating bond valence sums, thermoelectric power and T_c values particularly in the oxygen-deficient system $Y_{1-x}Ca_xBa_2Cu_3O_6$, i.e., with $\delta \approx 1.0$, we establish an absolute scale for $p = p(\delta)$ and show that indeed 123 has identical phase behavior to $La_{2-x}Sr_xCuO_4$ as well as the broad range of other HTSC's.

The central idea here is that the oxygen-deficient 123 material $Y_{1-x}Ca_xBa_2Cu_3O_6$ provides a link between 123-type compounds having both planes and chains and the remaining HTSC materials with CuO_2 planes only. When all oxygen is removed from the chain layer the copper atoms are in the $+1$ valence state and p for the planes is just $x/2$, i.e., the hole concentration can be directly determined from the Ca content. However, ideal samples with Ca substituting exclusively for Y are not easy to synthesize. Typically, a fraction substitutes on the Ba site, the excess Ba appearing as residual $BaCuO_2$ impurity.[13] We have found that this can be substantially suppressed by relatively high-temperature synthesis in air, although lower-temperature synthesis in lower PO_2 is also effective.

Stoichiometric precursors made from decomposing a mixture Y_2O_3, $Ba(NO_3)_2$, $CaCO_3$, and CuO were repeatedly reacted in air, then ground, milled and die-pressed and re-reacted starting from 900 °C and working up to a final temperature of 970 °C. The samples were finally reacted overnight at 1000 °C in flowing oxygen at 1 bar then slow cooled to 350 °C. At these high reaction temperatures the $BaCuO_2$, which was present for the lower-temperature reactions, is eliminated while for higher temperatures the impurity $Ba_4CaCu_3O_8$ appears. The window for synthesis is narrow, but reproducible, from one batch to the next. By this means Ca is forced to substitute primarily on the Y site and heavily overdoped samples can be obtained. The limiting composition for single-phase material is about $x = 0.2$ and even here neutron-diffraction refinements[14] indicate that the substituent on the Y site is only 0.16. Compositions below
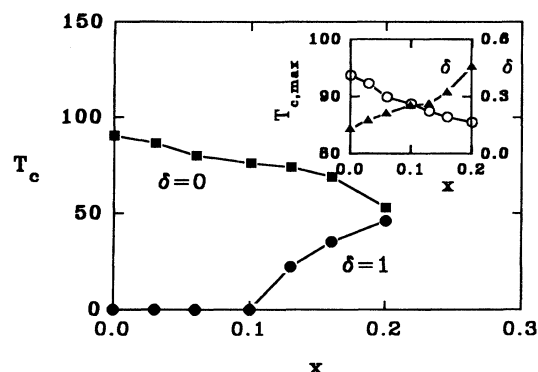

FIG. 1. T_c values for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ plotted as a function of x for $\delta \approx 0.04$ (overdoped) and $\delta \approx 0.98$ (underdoped). Inset: $T_{c,max}$ and δ values for optimum doping versus x.

$x = 0.13$ appear to be stoichiometric. Samples with $x = 0$, 0.03, 0.06, 0.10, 0.13, 0.16, and 0.2 were thus prepared and finally oxygen loaded by further annealing for 3 to 5 days at 350 °C in oxygen at 60 bars pressure. Neutron-diffraction structural refinements[14] showed occupancies yielding $\delta = 0.04$ for each of the samples investigated consistent with titration measurements. T_c values were determined using four-terminal resistivity, ac susceptibility, and vibrating-sample-magnetometer measurements and those values quoted herein are the diamagnetic onsets extrapolated from the steepest diamagnetic part of the curve, $\chi(T)$. These T_c values were 1 K below the onset temperatures at optimum doping and up to 4 K below for both the most overdoped samples and most underdoped. Bulk superconductivity throughout the under- and overdoped regions was confirmed by muon spin relaxation[15] and heat-capacity[16] studies. The maximally overdoped T_c values for these samples with $\delta = 0.04$ are plotted in Fig. 1 as a function of x. These range down to as low as 51 K for $x = 0.2$.

Samples were then successively annealed and quenched in a range of temperatures and PO_2 values to achieve optimal doping by plotting the resultant T_c against $S(290)$ and locating the position of the (sharp) peak. $S(290)$ values at the peak were all between 2.0 and 2.9 $\mu V/K$ typical of all optimally doped HTSC samples. δ values were determined from mass changes of 1.5 g samples and in some cases were confirmed by titration measurements. The $T_{c,max}$ values and their accompanying optimized δ values obtained for each x value are plotted in the inset of Fig. 1. These range from 93.5 K for $x = 0$ to 85.5 K for $x = 0.2$.

By annealing samples at 770 °C in 0.2% oxygen mixed with nitrogen then quenching into liquid nitrogen, oxygen deficiencies of the order of 0.95 were achieved and with further annealing at 550 °C in a vacuum of about 10^{-7} torr δ was increased to 0.97 or 0.98. These δ values were confirmed by neutron-diffraction structural refinements.[14] The small fraction (0.02 or 0.03) of oxygen remaining in the chain layer proved to have no effect on the relationship $p = x/2$. For δ values between 0.9 and 0.98 there was essentially no further change in $S(290)$ or, for those samples for which $p > 0.05$ ($x > 0.10$), no further change in T_c. Isolated
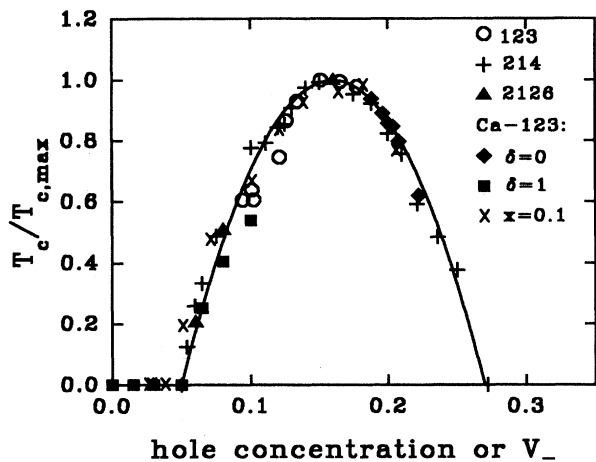
FIG. 2. T_c, normalized to $T_{c,\max}$, plotted as a function of hole concentration, p determined (i) from $p = x/2$ for $Y_{1-x}Ca_xBa_2Cu_3O_6$ (solid squares), (ii) from $p = V_-$ for $YBa_2Cu_3O_{7-\delta}$ with different δ (open circles), (iii) from $p = V_-$ for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with $\delta \approx 0.04$ and different x (solid diamonds), and (iv) from $p = V_-$ for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with $x = 0.1$ and different δ (crosses, $\times$). The solid curve is Eq. (1), the "plus" symbols ($+$) are T_c vs x data for $La_{2-x}Sr_xCuO_4$ and solid triangles for $La_{2-x}Sr_xCaCu_2O_6$.
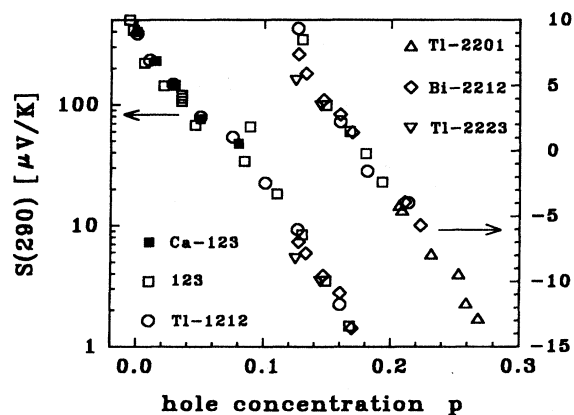
FIG. 3. Room-temperature thermoelectric power plotted as a function of hole concentration for various HTSC's as reported in Ref. 8 and for oxygen-deficient ($\delta \approx 0.98$) $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ for which $p = x/2$. The underdoped side has a logarithmic scale and the overdoped side a linear scale.

$$S_{290} = 372 \ \exp(-32.4p) \quad \text{for } 0.00 < p < 0.05,$$
$$S_{290} = 992 \ \exp(-38.1p) \quad \text{for } 0.05 < p < 0.155, \quad (2)$$
$$S_{290} = -139p + 24.2 \quad \text{for } p > 0.155.$$

oxygen atoms inserted into the chain layer appear to convert the two adjacent Cu^+ atoms to Cu^{2+} with no overall doping effect. This will be more apparent in the BVS estimate of p which will be discussed below.

Figure 2 shows $T_c/T_{c,\max}$ plotted against the absolute hole concentration $p = x/2$ for all of the fully oxygen depleted samples (solid squares). The threshold of superconductivity occurs at $x = 0.1$ and only the 0.13, 0.16 and 0.2 samples superconduct. We have used the nominal x value for each sample but for $x = 0.2$ the data point would clearly fit better if $x_{\text{effective}}$ is taken to be 0.16 as shown by the neutron-diffraction refinements. Also plotted are the data for $La_{2-x}Sr_xCuO_4$ (plus symbols) and $La_{2-x}Sr_xCaCu_2O_6$ (solid triangles), and the solid curve is Eq. (1). These data confirm that the threshold value for onset of superconductivity is the same for 123, $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Sr_xCaCu_2O_6$, namely $p = 0.05$. Moreover, the initial development of the phase curves for the three systems is the same in spite of the very different $T_{c,\max}$ values.

We used these values of $p = x/2$ to check on the previously reported correlation with the room-temperature thermoelectric power.[8] Values of $S(290)$ for the $Y_{1-x}Ca_xBa_2Cu_3O_6$ samples (i.e., with $\delta \approx 1.0$) are plotted in Fig. 3 as a function of $x/2$ (solid squares) together with the previously reported data, $S(290)$ versus p, for a range of other HTSC's. In particular, $S(290)$ versus $x/2$ for $Y_{1-x}Ca_xBa_2Cu_3O_6$ matches precisely the data for $YBa_2Cu_3O_{7-\delta}$ where p was previously estimated using BVS. This gives further confirmation of the reliability of the universal correlation between the TEP and the hole concentration, and also confirms that the BVS estimates of p correspond closely to the absolute values of $p = x/2$. The correlation may be conveniently parametrized by the relation

There appears to be a discontinuity in $S(290,p)$ in the neighborhood of the superconductor/insulator transition at $p = 0.05$.

We turn finally to determining the relation $p = p(\delta)$ using the above results in combination with BVS estimates of p. BVS's have been used extensively to estimate qualitative changes in charge distribution in a variety of HTSC's. Most notably Cava et al.[17] have determined copper BVS's for a series of oxygen-deficient 123 samples and shown that the copper BVS's have two plateaus roughly corresponding to the 90 and 60 K plateau in T_c versus δ. The two plateaus could therefore be interpreted in terms of local lags in the charge transfer from chains to planes due, for example, to oxygen vacancy ordering. The 90 K "plateau" is, however, clearly the peak in the parabolic curve of T_c versus p and fully loaded, 123 ($\delta = 0$) is overdoped.[18] It has elsewhere been argued that, as the hole carriers in HTSC's have both copper and oxygen character, it is more appropriate to assess the charge distribution in terms of a combination of oxygen and copper BVS's, V_O and V_{Cu}, respectively.[1,10] The excess charge on the Cu site is $V_{Cu} - 2$ while that on the oxygen site is $2 - V_O$ so the total charge on the CuO_2 plane was then estimated by $p \approx V_- \equiv 2 + V_{Cu(2)} - V_{O(2)} - V_{O(3)}$. The BVS's are calculated as described previously[10] and V_{Cu}, in particular, is calculated using the scheme proposed by Brown.[19] The parameter V_- is shown plotted as a function of δ in Fig. 4 for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ for $x = 0$ and $x = 0.1$. The $x = 0$ data were determined from bond lengths reported by Cava et al.[17] and the shape of the solid curve through the data was fitted guided by additional data from Jorgensen et al.[20,1] The $x = 0.1$ bond lengths are from the unpublished thesis of Radaelli.[21] Interestingly there is no plateau corresponding to either the "60 K plateau" or the "90 K plateau." Rather the charge transfer is quite linear over the superconducting do-
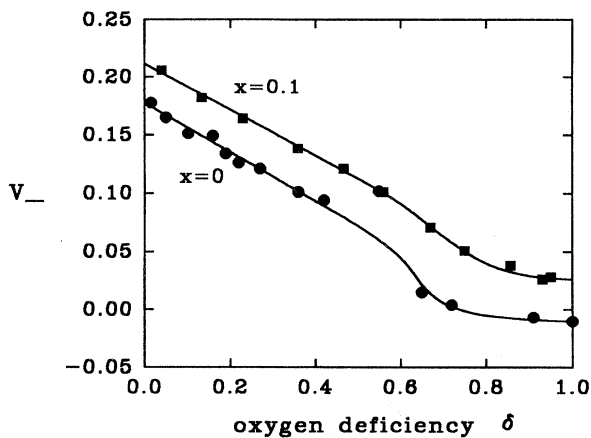
FIG. 4. The bond valence sum parameter $V_- = 2 + V_{Cu} - V_{O(2)} - V_{O(3)}$ plotted versus δ for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with $x = 0$ and $x = 0.1$.

main but clearly shows the δ-independent region near $\delta \approx 1.0$, to which we have already referred. Here T_c, the TEP, and evidently p change only weakly or not at all with δ. We focus first on the $x = 0$ curve. If, at $\delta = 1.0$, the chain copper atoms are all in the $+1$ valence state then p for the planes must be zero and this is borne out by the V_- values. Indeed, the values of V_- appear to be a remarkably good measure of p. If the entire curve is shifted up by only 0.01 then V_- is zero at $\delta = 1.0$, as it should be, and $V_- = 0.16$ when $\delta = 0.13$. This last point ($\delta = 0.13$) coincides with optimum doping and concurs with our view that $p = 0.16$ there. We therefore take this displaced curve to be our best estimate of $p = p(\delta)$ and for $\delta \leq 0.55$ it has the linear form $p = 0.187 - 0.21\delta$. For $x = 0.1$, apart from the fact that the δ-independent region appears to be less broad, the curve of $V_-(\delta)$ is roughly displaced upwards by 0.036 from the $x = 0$ curve although one would expect for $x = 0.1$ an upwards displacement of 0.05. This small discrepancy could be attributed in part to the tendency of the O(1) oxygens to partially disorder onto the O(5) sites with increasing Ca substitution,[14,21] thus reducing the charge transfer to the planes.

For $x = 0$ T_c is plotted in Fig. 2 (open circles) as a function of the V_- values shown in Fig. 4 extending across the underdoped to slightly overdoped region. For the more heavily overdoped region the set of fully oxygen-loaded Ca-substituted samples (annealed at 350 °C in oxygen at 60 bars pressure) were investigated by neutron diffraction and V_- values were calculated from the structural refinements.[14] For these samples T_c is also plotted in Fig. 1 as a function of these V_- values (solid diamonds). The collective data for doped and undoped 123 (solid and open circles and solid diamonds) follow the solid phase curve given by Eq. (1) remarkably well providing strong confirmation that this phase curve is quite universal to the HTSC's. In addition, the crosses in Fig. 2 show T_c values plotted against the $V_-(\delta)$ values for 0.1 Ca shown in Fig. 4. Again, these data match the phase curve shown in Fig. 2 very well. This illustrates that, irrespective of substituents which induce substantial disorder, $T_c/T_{c,max}$ remains the same function of hole concentration. Moreover, the fact that this function is the same for 123 and $La_{2-x}Sr_xCuO_4$ having very different $T_{c,max}$ values (93.5 and 39 K) is compelling evidence that a single process or excitation is responsible for both the underdoped and overdoped decline in T_c. Otherwise with two distinct and independent processes on either side of optimum doping, while the underdoped behavior may be identical the overdoped behavior could, in general, be expected to be different, or vice versa.

In summary the hole concentration in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ is estimated from $p = x/2$ when δ is close to 1.0 and also from bond valence sums. It is found that the correlation of room-temperature thermoelectric power with hole concentration observed for other HTSC's is preserved for 123 and that the p dependence of T_c is identical to that found for $La_{2-x}Sr_xCuO_4$. This clearly has important implications for interpreting the phase behavior of HTSC's in general.

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