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Evaluation of CuO_2 plane hole doping in $YBa_2Cu_3O_{6+x}$ single crystals

Ruixing Liang, D. A. Bonn, and W. N. Hardy
Department of Physics and Astronomy, University of British Columbia, 6224 Agricultural Road,
Vancouver, British Columbia V6T 1Z1, Canada

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The electron hole concentration p in the CuO_2 planes of $YBa_2Cu_3O_{6+x}$ (YBCO) has been evaluated using the unit cell length in the c direction together with a simple estimation for p in the chain oxygen-ordered phases. The empirical relationship between p and c obtained allows the calculation of p from the c-axis lattice parameter for the entire doping range of YBCO. It is also suggested that the empirical parabola describing the relationship between T_c and p in $La_{2-x}Sr_xCuO_4$ is reasonably correct for YBCO except for the region around $p=1/8$ ($x=0.67$), where the T_c of YBCO is suppressed by as much as 17 K. A plot of p vs x and a correction of the parabola for the $p=1/8$ effect are presented, allowing convenient determination of p from x and T_c.

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The parent compounds of all high T_c cuprates are antiferromagnetic insulators where the CuO_2 plane Cu $d_{x^2-y^2}$ orbital is exactly half filled. When holes are doped into the planes, the antiferromagnetic ordering weakens and eventually gives way to high T_c superconductivity. The doping p, the number of holes per copper atom in the CuO_2 planes, is a parameter that appears in all theories of high T_c superconductivity and is the single most important parameter that determines the properties of high T_c cuprates. The doping dependence of various physical properties provides key insights into the problem of high T_c superconductivity and has been a major focus of high T_c research.

The determination of the doping dependence requires accurate values of p. This is not a problem for some cuprates such as $La_{2-x}Sr_xCuO_4$ (LSCO), where p is simply equal to the substitution concentration x. It has been found that the superconducting transition temperature T_c and the doping p in LSCO have a parabolic relationship:[1–3]

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

where $T_{c,\max}$ is the maximum T_c for the compound. However, for most other cuprates p is not obvious from their chemical formula. $YBa_2Cu_3O_{6+x}$ (YBCO), the most widely investigated cuprate, has two different Cu sites, the chain site Cu(1) and the plane site Cu(2), and the calculation of p from the chemical formula requires knowing how holes are distributed between the two Cu sites, which depends not only on the oxygen content x but also the degree of oxygen ordering at the chains. The experimental determination of p is also very difficult. For oxygen content x between 0.35 and 0.55 the Hall coefficient R_H gives very reasonable values of p.[4] For other values of oxygen content, however, R_H is strongly temperature dependent. In any case, it is the hole density in the CuO_2 planes alone, that is of greatest interest. Conduction of the chains will contribute to R_H and complicate the situation. Presumably, at low oxygen content the chains conduct poorly, which may account for the observed behavior of R_H. X-ray absorption spectra (XAS) are useful in the determination of the oxidation status of copper and oxygen atoms,[5] but the quantitative interpretation of the spectra is difficult. Another method for determining p is the phenomenological bond valence sum (BVS) approach.[6–10] BVS for an ion is calculated from its bonding lengths to the nearest neighbors. It has been found that a combination of BVS for Cu(2) and oxygen ions in the CuO_2 planes gives a very good estimation of p.[9,10] However, the calculation of BVS requires detailed and precise structural parameters that are not conveniently measurable.

Due to the difficulty in measuring p, it is now a widely adopted practice to calculate p for YBCO (and other cuprates) from the superconducting T_c using the empirical Eq. (1). However, Eq. (1) was obtained from data for LSCO with the data near $p=1/8$ excluded from the regression. Although it may also be correct overall for other cuprates[1,10] including YBCO, it is inaccurate near $p=1/8$. At this doping, T_c is suppressed by the tendency of charge stripe formation and does not follow Eq. (1).[1–3] The magnitude of T_c suppression is sensitive to structural details. For example, a much more pronounced T_c suppression was observed in $La_{2-x}Ba_xCuO_4$ (LBCO) (Ref. 11) and a substrate-dependent T_c suppression is observed for LSCO thin films.[12] Therefore, before applying Eq. (1) to YBCO one ought to ask the question if, and to what extent, the T_c of YBCO is also suppressed around 1/8 doping. Furthermore, in the very underdoped region where $T_c=0$, Eq. (1) is certainly not applicable, and an alternative method is needed to evaluate p.

In YBCO, each Cu(2) atom in the CuO_2 planes has an apical oxygen O(4) above it. This oxygen moves toward the plane when p increases, that is, when positive charge in the plane increases. Properties related to the Cu(2)-O(4) bonding, such as the Raman frequency of the O(4) A_g mode[13–15] and the Cu(2)-O(4) bond length[8,16] have been found to be sensitive to the change in oxygen content x that is closely related to hole doping p. However, neither Raman frequencies nor bond lengths are conveniently measurable. Another quantity sensitive to the change in oxygen content is the c-direction unit cell length, which is a sum of bond lengths, $c=2d_{\mathrm{Cu(1)\text{-}O(4)}}+d_{\mathrm{Cu(2)\text{-}Cu(2)}}+2d_{\mathrm{Cu(2)\text{-}O(4)}}$. The change in c is mainly caused by the change in $d_{\mathrm{Cu(2)\text{-}O(4)}}$ because it is much more sensitive to change in the oxygen content than other bond lengths. The lattice parameter c can be easily measured for high precision by diffraction techniques, and there has been considerable work[15–19] on the relationship between c and the oxygen content of YBCO. However, by examining the data for our single crystals, we have found that the dependences of p and c on the oxygen content are not unique:

both p and c depend not only on the oxygen content but also on the degree of oxygen *ordering* in the Cu(1)-O chains. However, we argue that there is a unique relationship between p and c.

The lattice constant c was studied in high-purity (99.995%) YBCO crystals grown in barium zirconate crucibles.[20] Crystals with oxygen content $x=0$ were prepared by annealing the crystals at 660 °C under oxygen partial pressure 1×10^{-5} Pa. Crystals with x between 0.09 and 0.99 were prepared using procedures reported elsewhere.[21,22] The oxygen content was determined by weight analysis[22] to a precision of ±0.002. The chain oxygen-ordered ortho-II, ortho-VIII, and ortho-III phases were prepared with $x=0.50$, 0.67, and 0.75, respectively, by annealing the crystals at 10 °C below the corresponding ordering temperatures,[23] 105 °C, 40 °C, and 75 °C, respectively. The superconducting T_c of the crystals was determined by measuring the in-field cooling magnetization at 1 Oe applied parallel to the c axis, with T_c being chosen as the midpoint of the transition. The lattice parameter c was determined from $(00l)$ x-ray diffraction lines measured at room temperature (22 °C) using CuKα radiations. To minimize systematic errors only diffraction lines with 2θ greater than 100° were used. The data was extrapolated to $2\theta=180°$ to yield c.

The Cu(1)-O chain segments promote holes to the planes only when they are at least the critical length of three Cu atoms (two oxygen atom in between).[24] When the oxygen content is increased from $x=0$, where YBCO is tetragonal, initially hole doping increases slowly since oxygen ions in the chain sites are far apart and only a small fraction of them are in Cu(1)-O chain segments at or longer than the critical length. Therefore, c should change slowly with oxygen content near $x=0$ if the change in c is dominated by the change in doping in the planes. We have confirmed this is indeed the case: when the oxygen content x is increased from 0 to 0.10, c changes from 1.18447 to 1.18403 nm or by only 0.037%. In comparison, when x changes from 0.35 to 0.45, c changes from 1.17833 to 1.17631 nm or by 0.17%.

Figure 1(a) shows the superconducting transition temperature, T_c, of YBCO as a function of oxygen content. This curve, with a tendency toward a plateau near $x=0.66$ and a maximum near $x=0.9$ is well known. The reason for the $T_c \cong 60$ K quasiplateau between $x=0.5$ and 0.75 is not yet well understood. One explanation is that when the oxygen content is increased from $x=0.50$, where YBCO forms the ortho-II phase with alternating full (means the chain oxygen site is fully occupied) and empty (means the chain oxygen site is empty) chains, additional oxygen ions fill the empty chains and make a relatively small contribution to hole doping, since they are far apart from each other and only a small fraction of them are in Cu(1)-O chain segments at or longer than the critical length.[24] However, this model fails to explain why the quasiplateau extends smoothly beyond the ortho-II phase region and into regions of ortho-VIII (ordering in sequence of full-empty-full-full-empty-full-full-empty) and ortho-III (full-full-empty) phases.[23]

A major complication of Fig. 1(a) is that the dependence of T_c on the oxygen content is not unique because the doping p also depends on the oxygen order in the Cu(1)-O chain layer. This is particularly obvious for $x<0.50$ as shown in Fig. 1(a), where the lower dashed line shows T_c for the ortho-I phase, which has equal average oxygen occupancy for *every* Cu(1)-O chain, and the upper dashed line shows T_c for the ortho-II phase that has alternating empty and partially filled chains. When T_c is plotted against c, as shown in Fig. 1(b), the data fall onto a single curve. This indicates that c is more uniquely related to the doping than the oxygen content. A striking feature of the plot is that the curve is very similar in shape to the curve of T_c vs oxygen content and also has the $T_c \cong 60$ K quasiplateau. It seems unlikely that the slope of c vs p is suddenly changing in this regime, so Fig. 1(b) suggests that the 60 K "plateau" in T_c is an *intrinsic* doping effect, and not caused by oxygen ions entering the empty chain sites. That is, it is T_c itself that plateaus for some other reason, not the doping.

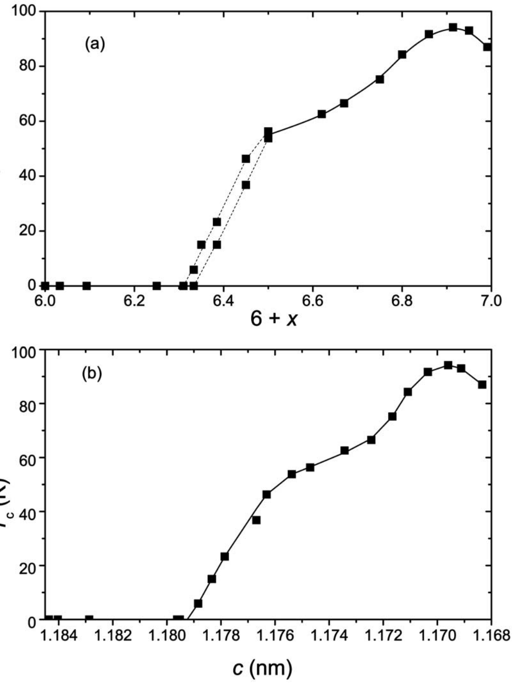

FIG. 1. Superconducting T_c of YBCO as functions of (a) oxygen content and (b) c-axis lattice parameter. The shape of the two curves is quite similar, but the relation between T_c and c is more unique.

As a first step in determining the relationship between p and c, the doping p was calculated from the superconducting T_c using Eq. (1), and $T_{c,\max}=94.3$ K for high-purity crystals, and plotted against the lattice parameter c, as shown in Fig. 2. The data between $p=0.05$ and 0.09, corresponding to T_c between 0 and 52 K, show linearity between p and c. In particular, the linearity extrapolates to the data point for $p=0$. This suggests that Eq. (1) generates reasonable values of p for YBCO in the low-doping region, as is also confirmed by the measurements of Hall coefficient[4] and studies of calcium-doped YBCO.[10] However, in the intermediate doping region between $p=0.09$ and 0.15, corresponding to T_c between 52 and 90 K, the data unexpectedly fall below the extrapolation from the low-doping region. Since this intermediate doping region is around $p=1/8$, a natural explanation for this deviation is that T_c is depressed by a tendency

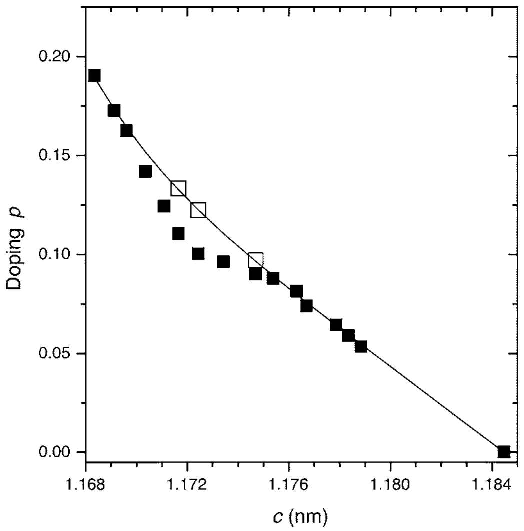

FIG. 2. The doping p of YBCO as a function of the lattice parameter c. Solid squares represent p values obtained using Eq. (1). Open squares are p values estimated for the chain oxygen-ordered phases (see text). The solid line is the fit to the data of $p > 0.15$ and $p < 0.09$ obtained using Eq. (1) in conjunction with values estimated for the ordered phases.

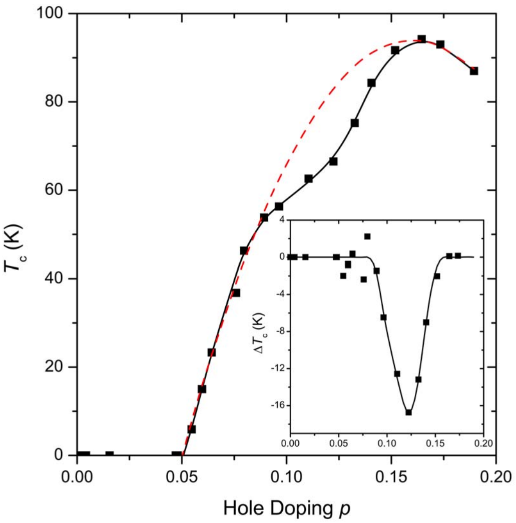

FIG. 3. (Color online) The actual critical temperature $T_{c,act}$ (solid squares) as a function of p obtained from Eq. (2). Also plotted is the parabolic relationship Eq. (1) (dashed line). The inset shows ΔT_c, the difference between $T_{c,act}$ and the parabolic relationship. The line is a guide to the eye. The T_c suppression reaches a maximum very close to $p=1/8=0.125$.

toward stripe formation, which Eq. (1) does not account for, causing the p value calculated using Eq. (1) to be lower than it actually is.

We now make use of the fact that the chain oxygen-ordered phases ortho-II, ortho-VIII, and ortho-III happen to fall in the median-doping region around $p=1/8$. Using simple arguments we can determine p for the ordered phases relative to that for $x=1$. In particular, we assume that each oxygen ion in a full Cu(1)-O chain makes the same contribution to the doping regardless of whether the neighboring chain is empty or full, so that p in these phases is essentially proportional to the fraction of the Cu(1)-O chains that are full. This assumption is reasonable if the coupling between the chains is very weak. It has been reported that the chains show very strong one-dimensional characteristics.[4] For $x=1$ where every chain is full, we obtained $p=0.194$ by inserting $T_c=85.3$ K [see Fig. 1(a)] into Eq. (1). A calculation using the BVS model has found $p \cong 0.2$ for fully oxygenated YBCO ($x=1$). In particular, Tallon *et al.*[10] have concluded $p=0.187$ for $x=1$ after detailed analysis of BVS and thermoelectric power of calcium-doped YBCO samples. Our $x=1$ crystals are slightly more overdoped than early YBCO samples, as indicated by a 2 K lower T_c, possibly due to better chain oxygen order. Therefore, $p=0.194$ appears to be a very reasonable number for our $x=1$ crystals. Based on this number, for ortho-II YBCO ($x=0.50$) where half of the chains are full, the doping $p=0.097$ is half of that for $x=1$. Next, the ortho-III phase has two thirds of the chains full. However, the best ortho-III ordering occurs at $x=0.75$,[23] higher than the theoretical oxygen content $x=0.667$, which requires that the "empty" chains have a finite oxygen occupancy $\upsilon=0.25$. Such an empty chain also makes a small contribution to the doping. Based on the calculation by Zaanen *et al.*[24] it should be a good approximation that a chain segment of n oxygen ions makes the same contribution to the doping as $n-1$ oxygen ions in full chains. Thus, the doping contribution by an empty chain is υ^2 times the contribution by a full chain if oxygen ions distribute randomly in the empty chain, which should be the case when υ is small. Therefore, the doping in the ortho-III YBCO is $p=0.194 \times (2/3+\upsilon^2/3)=0.133$. Similarly, for the ortho-VIII (five eighths of the chains are full and $x=0.67$) we obtained $p=0.122$. It should be pointed out that the p values estimated for ortho-II and ortho-III are in excellent agreement with the results of BVS calculation[9] for similar oxygen content using the structural parameters from Jorgensen *et al.*[16]

The p values estimated for the chain oxygen-ordered phases are plotted in Fig. 2 as open squares. We see that the data fall exactly on the extension of the linear low-doping region and smoothly connect to data points for $p > 0.15$. This suggests the p values estimated by the simple method are very reasonable. Combination of the data by Eq. (1) for the low-doping region ($p < 0.09$), optimal doping region ($p > 0.15$), and the data estimated for the chain oxygen-ordered phases suggests a smooth relationship between p and c. Fitting these data yields:

$$p = 11.491y + 5.17 \times 10^9 y^6, \qquad (2)$$

where $y=1-c/c_0$ and $c_0=1.18447$ nm (at 22 °C) is the c-axis lattice parameter at zero doping ($x=0$). The second term is negligible for the low-doping region ($p < 0.1$). This empirical formula enables calculation of p from the easily measurable lattice parameter c over the entire oxygen content range for YBCO.

In Fig. 3, the actual measured values of critical temperature $T_{c,act}$ are plotted against the p values obtained using Eq. (2). Also plotted in Fig. 3 is $T_{c,cal}$ calculated using the parabolic Eq. (1). $T_{c,act}$ is lower than $T_{c,cal}$ between $p=0.1$ and

0.15. The difference $\Delta T_c = T_{c,\mathrm{act}} - T_{c,\mathrm{cal}}$, as shown in the inset, peaks at very close to $p=1/8$ (corresponding to $x=0.67$). If one believes that the T_c suppression in YBCO originates from the same physics as in the LSCO system, that is, the tendency of charge stripe formation, the suppression should occur at the same doping $p=1/8$ as seen in the LSCO system. There is evidence that indicates this is indeed the case. A minimum in the coherence length[25] and a change in dependence of T_c on the superfluid density[26] have been observed for YBCO at $p=1/8$. In particular, evidence of charge stripes has been observed by μSR measurements in Zn-doped YBCO at $p=1/8$.[27] Therefore, the fact that we found the maximum T_c suppression at $p=1/8$ lends further confidence to the accuracy of our determination of p from the c-axis lattice constant. The maximum T_c suppression, 17 K or about 20%, is similar to the 20% observed for LSCO.[2]

For convenient reading of p from oxygen content x, the doping p is plotted as a function of x in Fig. 4(a). As stated earlier, the dependence of p on x is not unique since p depends also on chain oxygen ordering. This is particularly apparent in the low oxygen content region where the upper dashed line is for samples of the ortho-II phase with the best oxygen ordering achievable at ambient pressure and the lower dashed line is for samples of the ortho-I phase quenched from above the ortho-II transition temperature. The p values for samples with short-range chain oxygen ordering should fall between the two dashed lines. Furthermore, when T_c is finite it is very convenient to calculate p from T_c using Eq. (1). Therefore, we provide a correction to Eq. (1) in Fig. 4(b) where the T_c suppression data are plotted as a function of T_c. The plot allows correcting for the 1/8 doping-related T_c suppression before applying Eq. (1) to calculate p for the underdoped YBCO.

In summary, we have evaluated the doping p in YBCO using the c-axis lattice parameter and a simple method for estimating p in chain oxygen-ordered phases. The relationship between p and c, Eq. (2), allows calculation of p from c for the entire doping region of YBCO, including the region where $T_c=0$. The relationship calibrates well against the characteristic doping $p=1/8$, which is found to occur at oxygen content $x=0.67$. Our data also suggest that Eq. (1) obtained from data for LSCO is reasonably correct for YBCO in the low-doping region ($p<0.09$) and near the optimal doping ($p>0.15$). This, together with the early study on Bi- and Tl-based cuprates,[1] suggests that the parabolic Eq. (1) is universal for hole-doped cuprates except near $p=1/8$ where Eq. (1) is incorrect due to T_c suppression by the tendency of charge stripe formation. The magnitude of the T_c suppression is compound specific and depends on structural details. For YBCO, our data suggest the suppression occurs between $p=0.09$ and 0.15 with a maximum suppression of 17 K, or about 20%, at $p=1/8$. The correction to Eq. (1) for the effect of $p=1/8$ has been generated, which allows convenient use of Eq. (1) for underdoped YBCO when T_c is finite.

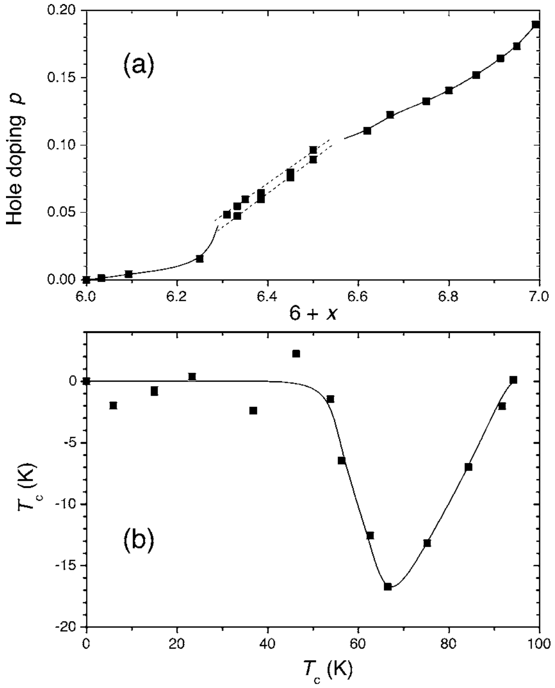

FIG. 4. Plots for convenient determination of p. The lines are guides to the eye. (a) Plot of p as a function of oxygen content. (b) Plot of $p=1/8$ related T_c suppression vs T_c.

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