A model for the chain-to-plane charge transfer in $YBa_2Cu_3O_{6+x}$*

V. M. Matic†, N. Dj. Lazarov, and M. Milic

Laboratory of Theoretical Physics, Institute of Nuclear Sciences "Vinca", Belgrade University, Belgrade 11001, *Serbia*

(Received 26 April 2012; revised manuscript received 26 May 2012)

A model for the chain-to-plane charge transfer is proposed to account for the two plateaus, at 60 K and at 90 K, of the $T_c(x)$ characteristics of the $YBa_2Cu_3O_{6+x}$ high-T_c superconductor. It is assumed that the number of holes transferred from a CuO chain of length l to two nearby CuO_2 sheets is proportional to l (that is, to the number of oxygen atoms in the chain), if the chain length is greater than, or equal to, a certain critical chain length, l_{cr}, that is required to trigger the charge transfer process. No holes are assumed to have been transferred from chains of length $l < l_{cr}$. The calculated $T_c(x)$ dependence is found to be in excellent agreement with the experimentally reported $T_c(x)$. The critical chain length parameter is estimated to be equal to $l_{cr} = 11$ (eleven oxygen atoms in a chain), which is a greater value than that obtained in the previously proposed model for the chain-to-plane charge transfer ($l_{cr} = 4$). The results obtained out of the proposed model are briefly discussed.

Keywords: YBCO, oxygen ordering, critical temperature, doping

PACS: 74.62.En, 74.72.Gh, 74.62.Bf, 64.60.Cn **DOI:** 10.1088/1674-1056/21/11/117401

1. Introduction

The two plateaus, at 60 and 90 K, of the $T_c(x)$ characteristics of the $YBa_2Cu_3O_{6+x}$ high-T_c superconductor comprise a well-known phenomenon. Although the latter plateau is commonly associated with the x dependence of doping ($p(x)$) passing through the optimal doping level of about 0.16, there is still an ongoing debate over the cause for the 60-K plateau: is it the stripe induced decline of T_c from a parabolic (universal) $T_{c,univ}(p) = T_{c,max}(1-82.6\cdot(p-0.16)^2)$ dependence (around $p = 1/8$), or peculiarities associated with the statistics of CuO chain ordering of the OII phase? Since the doping cannot be convincingly measured experimentally between $p \approx 0.09$ ($T_c \approx 60$ K) and $p = 0.15$, due to the system's local scale non-homogeneity driven by the OII phase and other orthorhombic phases like OV, OVIII, and OIII,[1,2] the stripe effect on $T_c(p)$ cannot be mapped accurately enough onto the $T_c(x)$ through $p(x)$. Thus, the issue of how much stripes affect $T_c(x)$ is still largely unresolved. On the other hand, within the OII concept, the doping $p(x)$ is presumed to stay constant over the regime of the 60-K plateau at a level of about 0.095 (corresponding to $T_c \approx 60$ K through the $T_{c,univ}(p)$), which is half of the doping at $x = 1$ ($p \approx 0.19$).[1,2]

Recently, a model for the charge transfer from CuO chains to CuO_2 planes has been proposed, which results in $p(x)$ dependence with exactly such properties.[3] According to this model, a chain of length l is assumed to have created $h(l) = \mu(l-l_{cr}+1)$ holes in two nearby CuO_2 sheets, where $\mu \approx 0.19$ and l_{cr} is the critical chain length parameter defined so that no holes are transferred from a chain of length $l < l_{cr}(h(l) = 0)$, but the charge transfer takes place only when l is equal to, or, greater than, l_{cr}. The number of created holes per in-plain Cu (aka doping) is then equal to

$$p = \frac{n_1}{4}\sum_{l=1_{cr}}^{\infty}\mu(l-l_{cr}+1)f_1(l) + \frac{n_2}{4}\sum_{l=l_{cr}}^{\infty}\mu(l-l_{cr}+1)f_2(l), \quad (1)$$

where n_1 and n_2 are the fractions of 3-fold coordinated Cu(1) ions on two respective oxygen chain sublattices of the OII phase; $f_1(l)$ and $f_2(l)$ are the corresponding length distributions of CuO chains. The model (1) has successfully explained both 60 K and 90 K plateaus of the $T_c(x)$, with the parameter l_{cr} estimated to be equal to 4 ($l_{cr} = 4$).[3] It should be noted, however, that the exact details of the charge transfer mecha-

*Project supported by the Ministry of Education and Science of the Republic of Serbia (Grant No. 171027).

†Corresponding author. E-mail: vladimir_matic@vektor.net; vmatic@vin.bg.ac.rs

© 2012 Chinese Physical Society and IOP Publishing Ltd

nism are not in fact known, so that proposing that $h(l) = \mu(l - l_{\rm cr} + 1)$, or, possibly, some other form of the $h(l)$ dependence, would be just a manifestation of what is conventionally termed a phenomenological approach to the problem. The fact that $h(l)$ is a linear function reflects a generally accepted viewpoint that the main source which attracts electrons from CuO_2 sheets (thereby creating holes in them) is the electronegativity of chain ordered oxygen. Thus, the more oxygen in a chain, the more holes will be created in the sheets, and, consequently, $h(l)$ is to be a linear function. One could speculate, for instance, that each in-chain O^{1-} atom creates a sort of a potential at the points of the CuO_2 sheets positioned above (below) the chain (whatever the nature of this potential might be), so that the transfer of electrons would be initiated only after the combined potential of all of the chain's oxygen atoms has reached a certain threshold value. In other words, all of the chain's oxygen might be expected to participate in creating a strong enough condition (potential) that is needed for the charge transfer to take place. However, from the doping expression (1) it follows that not only the short chains ($l < l_{\rm cr}$) are cut-off, but also the effect of the first $l_{\rm cr} - 1$ oxygen atoms from long chains ($l \geq l_{\rm cr}$) is eliminated. Practically, the effect of a long chain having, for example, a length l ($l \geq l_{\rm cr}$), reduces to that of a shorter chain of the length $l - (l_{\rm cr} - 1)$, which might raise some controversies over what particular mechanisms the $l_{\rm cr}$-concept should in principle be a reflection of.

2. Doping model

Led by such thoughts, we arrived at a notion that reducing long chains by $l_{\rm cr} - 1$ might not be at the core of the $l_{\rm cr}$-concept, and for this reason we propose here a new model to calculate doping in $YBa_2Cu_3O_{6+x}$. The model is given by

$$p = \frac{n_1}{4} \sum_{l=l_{\rm cr}}^{\infty} \mu l f_1(l) + \frac{n_2}{4} \sum_{l=l_{\rm cr}}^{\infty} \mu l f_2(l), \qquad (2)$$

where the sums run from $l_{\rm cr}$ to ∞, implying that the contribution of short chains, $l = 1, 2, \ldots, l_{\rm cr} - 1$, is again cut-off entirely, but the effect of long chains has not been reduced by $l_{\rm cr} - 1$. Since the average chain lengths, $l_{\rm av,1}$ and $l_{\rm av,2}$, on two respective oxygen atom sublattices of the OII phase are given by

$$l_{\rm av,1} = \frac{2x_1}{n_1} = \sum_{l=1}^{\infty} l f_1(l), \; l_{\rm av,2} = \frac{2x_2}{n_2} = \sum_{l=1}^{\infty} l f_2(l), \qquad (3)$$

expression (2) can be written in the following form:

$$p = \mu x + \frac{\mu}{4} \left[n_1 \sum_{l=1}^{l_{\rm cr}-1} l f_1(l) + n_2 \sum_{l=1}^{l_{\rm cr}-1} l f_2(l) \right], \qquad (4)$$

where x_1 and x_2 in $x = (x_1 + x_2)/2$ are concentrations of oxygen atoms on the two oxygen chain-site sublattices. This expression is suitable for numerical calculations because the infinite summations in Eq. (2) are now included in the first term, μx, on the right-hand side and the finite number of terms in two sums of Eq. (4) can be calculated numerically in a straightforward manner.

3. Results of numerical calculations

The theoretical model that has been commonly used to describe the CuO chain ordering of the OII phase is the two-dimensional asymmetric next-nearest neighbour Ising (ASYNNNI) model.[4] For given x and T, and for the values of the ASYNNNI model interactions, V_1, V_2 and V_3, that were proposed in Ref. [5], we use the Monte Carlo method (MC) to calculate concentrations of oxygen atoms, x_1 and x_2, on two respective oxygen chain site sublattices (sometimes referred to as α_1 and α_2) and the corresponding fractions, n_1 and n_2, of 3-fold coordinated Cu(1) ions (these correspond to unlike V_2 bonds). We also calculate the CuO chain length distribution functions $f_s(l)$ ($s = 1, 2$), $l = 1, \ldots, l_{\rm cr}$, in a way that in each MC step the total numbers of chains, $N_{\rm ch,1}$ and $N_{\rm ch,2}$, are counted, and also the numbers of chains of the particular lengths $N_{\rm ch,1}(l)$ and $N_{\rm ch,2}(l)$ for $l = 1, \ldots, l_{\rm cr}$. The ratios $N_{\rm ch,1}(l)/N_{\rm ch,1}$ and $N_{\rm ch,2}(l)/N_{\rm ch,2}$ are then calculated and their equilibrated values (through the MC process) are finally identified with the chain length distributions $f_1(l)$ and $f_2(l)$. The system size that the calculations were made on consists of 200.×400 oxygen sites on the α sublattice (comprised of both α_1 and α_2) and the same number of sites is attached to the β sublattice (the one that interlaces α sites). The fixed-chemical potential scheme (Glauber dynamics) is used at practically all calculated points with just a few exceptions made by using the Kawasaki dynamics (fixed-x scheme) mainly to check the consistency of the obtained results.

The values of doping are calculated from Eq. (4) at different isotherms (T = const) for several characteristic values of oxygen content x within the interval of the 60 K plateau of the $T_{\rm c}(x)$ (that is, at

$0.50 < x < 0.60$). In addition, doping is also calculated for a number of values of the cut-off parameter $l_{\rm cr}$ from Eq. (4), and these $l_{\rm cr}$-dependences of p are shown in Fig. 1 (for different values of x and at three isotherms).

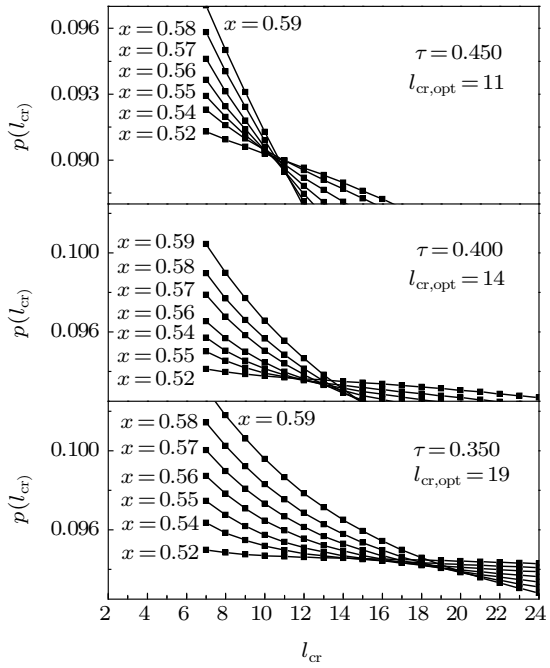


Fig. 1. Calculated curves of $p(l_{\rm cr})$ dependences at three isotherms ($\tau = k_{\rm B}T/V_1 = {\rm const}$) for several values of oxygen concentration x, which span the interval $0.50 < x < 0.60$. Calculated values of $p(l_{\rm cr})$ at $\tau = {\rm const} = 0.45$ are shown in the top plot, at $\tau = {\rm const} = 0.35$ in the middle, and at $\tau = {\rm const} = 0.40$ at the bottom section.

It can be seen from the three plots in Fig. 1 that at a given $T = {\rm const}$ (or, at $\tau = k_{\rm B}T/V_1 = {\rm const}$) the $p(l_{\rm cr})$ curves of all $x \in (0.50, 0.60)$ intersect at a well defined value of $l_{\rm cr}$; we call this value the optimal critical chain length, $l_{\rm cr,opt}$, for the particular isotherm. It also follows from Fig. 1 that the so-defined parameter $l_{\rm cr,opt}$ depends on the temperature in a way that it increases with temperature lowering. In Fig. 2 are shown the values of the $l_{\rm cr,opt}(\tau)$ dependence, which are calculated in the same way as in Fig. 1. It can be inferred from Fig. 1 that the relevance of the $l_{\rm cr,opt}$ quantity lies in the fact that, when at a certain isotherm $\tau = {\rm const}$ the $l_{\rm cr}$ parameter of Eq. (4) is taken to be equal to $l_{\rm cr,opt}(\tau)$, then the resulting $p(x)$ will display a constant section over the interval $0.50 < x < 0.60$. As the critical temperature $T_{\rm c}$ and doping p are inter-connected by the empirical relation $T_{\rm c}(p) = T_{\rm c,max}(1 - 82.6 \cdot (p - 0.16)^2)$,[2] the constant doping $p(x) = {\rm const}$ at $0.50 < x < 0.60$ inevitably implies the constant $T_{\rm c}(x)$ over the same interval. This kind of $p(x)$ and/or $T_{\rm c}(x)$ behaviour is shown in Fig. 3 for the case $\tau = {\rm const} = 0.45$, $l_{\rm cr} = 11$ ($= l_{\rm cr,opt}(\tau)$), and $\mu = 1.192$. From the bottom graph of Fig. 3 it can be seen that the obtained $T_{\rm c}(x)$ reproduces fairly well both plateaus, at 60 K and at 90 K, of the experimental $T_{\rm c}(x)$ given by Jorgensen *et al.*[7] (with the latter plateau being obviously related to the $p(x)$ passing across the optimal doping level $p = 0.16$). As for the parameter μ it should be noted that it is nothing but the doping at $x = 1$, i.e. $p(x = 1)$, as it can be inferred from Eq. (4), so the obtained $\mu = 0.192$ is in a very good correlation with the experimental findings in Refs. [1] ($p(x = 1) = 0.194$) and [2] ($p(x = 1) = 0.187$). On the other hand, that the $\tau = {\rm const} = 045$ isotherm can be taken as a very good representative of the room temperature (≈ 290 K, or so), it can be seen from the fact that $\Delta\tau = 0.1$ corresponds to $\Delta T \approx 100$ K.[5] Furthermore, the experimental results point to the top of OII phase to be lying somewhere between ~ 120 °C and ~ 140 °C,[8] while theoretically it corresponds to $\tau = 0.58$.[9] Therefore, the difference $\Delta\tau = 0.13$ ($= 0.58 - 0.45$) corresponds to ~ 130 °C, which is in accordance with the experimental findings in Ref. [8]. In addition, on the right-hand side from $x = 0.50$ experimental results show that the OII phase disappears at $x = 0.62$.[8] That is again in a very good correlation with the theoretical phase diagram according to which the edge of the OII phase occurs at $x \approx 0.63$[9] (at $\tau = 0.45 = {\rm const}$).

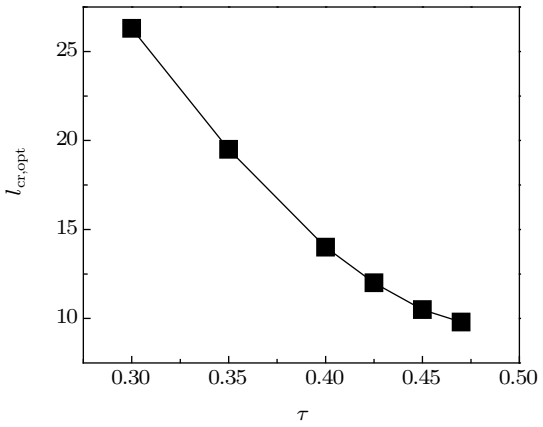


Fig. 2. Calculated values of the $l_{\rm cr,opt}(\tau)$ dependence for the ASYNNNI model interactions from Ref. [5].

Perhaps the most important aspect of what is presented in Fig. 3 is the obtained result $l_{\rm cr} = 11$. The relevance of this result will be expounded in the following section.

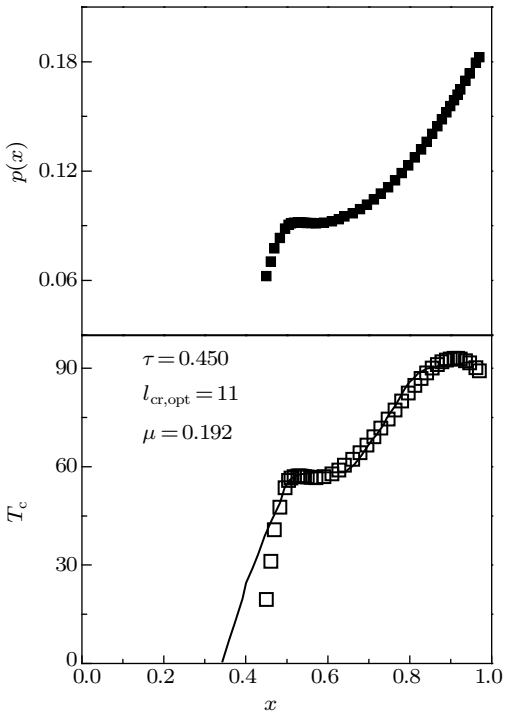


Fig. 3. Calculated $p(x)$ (top graph) and $T_{\rm c}(x) = T_{\rm c,univ}(p(x))$ (bottom graph) dependences at $\tau = {\rm const} = 0.45$ for $l_{\rm cr} = l_{\rm cr,opt}(\tau) = 11$ and $\mu = 0.192$. The solid line stands for the experimental $T_{\rm c}(x)$ of Ref. [7].

4. Discussion and conclusions

The shortest CuO chain that can exist in the basal Cu–O plane is the one that consists of a single oxygen atom. Due to its well defined tendency to become O^{2-} the oxygen will then take away two electrons from two nearest neighbours Cu(1) ions (transferring them from Cu^{1+} into Cu^{2+}), so there would be no need for any additional charge to be taken from some more distant part of the structure. When another oxygen atom is brought in to form a chain of length $l = 2$ there is only one electron available in the neighbouring Cu(1) ion, so there is a potential for attracting an electron from a remote region of the lattice (presumably from one of two nearby CuO_2 layers). Generally, a chain of length l would thus comprise $l-1$ O^{1-} ions (this is of course a simplified picture, as there is still an ongoing debate over what might be the true nature of the missing electron (or, a hole), i.e. whether it is of O $2p$ character, or of Cu $3d$, but such a description is nonetheless useful for plain chemical-like reasoning that will be employed below). Therefore, the electronegativity of chain-ordered O^{1-} is the actual source that attracts electrons from CuO_2 layers (thereby creating holes in them), but the problem here is that they are not 100% effective. We know that from the measured doping at $x = 1$ ($p(x = 1) \approx 0.19$,[1,2]) at which concentration practically, each oxygen atom is O^{1-} (very long (infinite) CuO chains along b axis with no vacant segments between them). This means that an average efficiency of O^{1-} in dragging down an electron from the CuO_2 layer above, or, bringing it up from the layer below, is around $\sim 38\%$. However, as the details of the charge (electron) transfer mechanism are basically not known, the only remaining option is to address the problem in a phenological way. With this kind of thinking kept in mind it is surely not a strange idea that a chain of length $l = 2$ (including one O^{1-} in it) might still not have enough capability to initiate the electron transfer. A chain of length $l = 3$ (two O^{1-}) would be probably closer to the threshold of the charge transfer to be triggered, but whether it is enough is an open question. A similar reasoning can be applied as well to chains with $l = 4, 5, \ldots$, so that a widely accepted estimate for what $l_{\rm cr}$ would be equal to is, generally speaking, yet to be achieved.

It should be pointed out, however, that some theoretical work on $l_{\rm cr}$ has nonetheless been done. In Ref. [10] it was suggested that the charge transfer would already start from chains of length $l = 3$ (i.e. $l_{\rm cr} = 3$), while in previous publications it was obtained $l_{\rm cr} = 4$.[3,6] It should be noticed that the latter result is obtained by use of model (1), according to $p \sim \mu(l - l_{\rm cr} + 1)$, so that the present result $l_{\rm cr} = 11$ (obtained by $p \sim \mu l$, for $l \geq l_{\rm cr}$) can be viewed as pointing to a conclusion that the estimate for $l_{\rm cr}$ is, at least, model dependent. Secondly, a rather large value $l_{\rm cr} = 11$ gives a very accurate prediction of both 60 K and 90 K plateaus of the $T_{\rm c}(x)$, and, moreover, the whole calculated $T_{\rm c}(x)$ (the bottom part in Fig. 3) accords well with the experimentally reported one.[7] Therefore, the main result of this study would be that the critical number of oxygen atoms linked in a chain, which is required to trigger the chain-to-plane charge transfer, could be as high as $l_{\rm cr} = 11$.

References

[1] Liang R, Bonn D A and Hardy W N *Phys. Rev.* B 2006 **73** 180505

[2] Tallon J L, Bernhard C, Shaked H, Hitterman R L and Jorgensen J D *Phys. Rev.* B 1995 **51** 12911

[3] Matic V M and Lazarov N D 2007 *Solid State Commun.* **142** 165

[4] Wille L T and de Fontaine D, 1988 *Phys. Rev.* B **37** 2227

[5] Sterne P A and Wille L T 1989 *Physica* C **162-164** 223
[6] Matic V M and Lazarov N D 2007 *J. Phys. Cond. Matt.* **19** 346230
[7] Jorgensen J D, Beno M A, Hinks D G, Soderholm L, Volin K J, Hitterman R L, J D Grace, Schulle J K, Segre C U, Zhang K and Kleefisch M S 1987 *Phys. Rev.* B **36** 3608
[8] Zimmermann M V, Schneider J R, Frelo T, Andersen N H, Madsen J, Kall J, Poulsen H F, Liang R, Dosanjih P and Hardy W N 2003 *Phys. Rev.* B **68** 104515
[9] Matic V M 1992 *Physica* A **184** 571
[10] Gawiec P, Grempel D R, Uimin G and Zittartz J 1996 *Phys. Rev.* B **53** 5880