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The dependence of critical temperature on oxygen concentration in $YBa_2Cu_3O_{6+x}$ in terms of the fragmented chain model

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Abstract: An extended ASYNNNI model, that beside nearest-neighbour and next-nearest neighbour O-O interactions in the basal plane also includes interactions between the three nearest oxygen atoms, is used to describe the statistics of CuO chain fragmentation and to calculate doping and T_c in $YBa_2Cu_3O_{6+x}$. Calculations were made by the Monte Carlo method employing the recently proposed charge transfer model that assumes only chains whose length is equal to, or exceeds, a characteristic (critical) length, l_{cr}, can provide holes to the layers and contribute to doping p. The obtained $p(x)$ is then combined with a universal T_c versus p relation to yield $T_c(x)$ characteristics that correlate remarkably with those reported in recent experiments. The best coordination between theoretical and experimental $T_c(x)$ characteristics has been achieved for $l_{cr} = 2$, implying that only isolated basal plane oxygen atoms (trivial chains) do not contribute holes to CuO_2 layers.

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1. Introduction

The problem of oxygen ordering in the oxygen deficient CuO_x (basal) planes and its influence on doping p (number of holes per one Cu(2) ion) of the superconducting CuO_2 layers, and thus on the superconducting properties of the high-T_c $YBa_2Cu_3O_{6+x}$ material, has been extensively studied for more than two decades [1–6]. By now it has been widely accepted that not only the variable oxygen concentration x, but also the degree of oxygen order in CuO_x planes, controls the crystallographic structure as well as the electronic properties of the system, leading to an insulating antiferromagnetic state for approximately $x < 0.4$, while for $x > 0.4$ the material starts becoming a superconductor. As a function of oxygen concentration x the critical temperature T_c exhibits a rather peculiar behavior, characterized by the existence of two plateaus at 60 K and 90 K [7–14]. While the formation of the 90 K plateau is explained in terms of optimal doping of CuO_2 planes [15], appearance of the 60 K plateau is still the subject of scientific debates [6, 16]. The first theories, that were suggested in order to account for the emergence of

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the 60 K plateau, associated this plateau with the formation of the Ortho II structural phase (characterized by long CuO chains) and peculiarities of the accompanying charge transfer [5, 16], while some later theories involved other mechanisms [6, 15, 17].

Dependence of superconducting properties on the oxygen chain ordering was initially noticed in experiments with sample aging, in which room temperature annealing was followed by an increase of T_c. Since this process was accompanied by an enhancement of oxygen ordering and the sample's orthorombicity, the T_c increase was explained as a result of the lengthening of CuO chains and accompanying increase of the hole concentration in superconducting CuO_2 plains [18]. Namely, it is known that long chains are more effective hole donors than short ones, and it has often been thought that there should exist a threshold (critical) chain length l_{cr} that has to be achieved in order for the charge transfer from the chain to take place [19, 20]. Even before the experimental results indicated the possible existence of such a critical chain length, this concept had been used by Zaanen and coauthors [2] in an attempt to explain the appearance of the two plateaus in $T_c(x)$ dependence. By the use of an *ad hoc* suggested structural model, characterized by the so-called "fragmented–chain structure" of the chain planes, and employing a relatively simple band structure reasoning, they managed to obtain two plateaus in the T_c vs. x dependence. This was one of the first attempts to provide an explanation, plausible up to a certain point, for the two–plateaus in $T_c(x)$ behavior, though the model itself was strongly criticized since the suggested chain plane structure did not follow from any Hamiltonian known up to that time, and particularly not from that of the ASYNNNI model (two dimensional asymmetric next–nearest neighbour Ising model) which had already been successfully applied to explain a number of properties of the $YBa_2Cu_3O_{6+x}$ structural phase diagram [21, 22].

Though the model of Zaanen and co-workers [2] is usually mentioned mainly for historical reasons, research interest in this model has been revived recently [23–25]. It was shown that if it is assumed that the effective O-O interaction mediated by the Cu ion (superexchange) depends not only on the occupancy of two interacting oxygen sites, but also on occupancy of surrounding oxygen sites, a new Hamiltonian can be constructed. This Hamiltonian stabilizes in the range of oxygen concentrations $0.5 < x < 1$, exactly the fragmented chain structure, which was stated in Ref. [2] as the ground state. It was also shown that the derived Hamiltonian for $x = 0.5$ and $x = 1$ stabilizes two main orthorhombic structural phases OII and OI, and that it produces a structural phase diagram which agrees fairly well with the general topology of the experimentally established phase diagram [24].

In the present work the Hamiltonian of the fragmented chain model is employed to calculate doping p of superconducting CuO_2 planes in terms of the recently proposed charge transfer model that, besides assuming holes can be transferred only from chains longer than some critical length l_{cr}, also proposes that only a part of the overall number of holes created in these long-enough chains can be transferred out of the chain plane, thus making a contribution to superconductivity [26–28]. Calculated values for $p(x)$ and the well known empirical relation between p and T_c [29], are used here to obtain the T_c vs. x dependence. The paper is organized as follows: in Section 2 the charge transfer model is presented, while in Section 3 the main aspects of the fragmented chain model are outlined. In Section 4, the numerical results obtained are presented and the T_c vs. x dependence is discussed. Summaries and final remarks are outlined in Section 5.

2. The charge transfer model

The process of doping of the CuO_2 layers by holes that were created in CuO_x planes has been thoroughly addressed in many theoretical studies [19, 20, 30–33]. It is usually explained in the frame of simple charge transfer models, that assume the degree of oxygen order in the CuO_x planes crucially determines the number of the holes doped [2, 31, 32]. Depending on the occupancy of six neighbouring oxygen sites the Cu(1) ions located in the chain planes can be found in two different oxidation states. The Cu(1) ions coordinated by two oxygen atoms (located at apical sites) are in the $+1$ electronic state, while threefold Cu(1) ions (Cu(1) ions located at the end of chains) and fourfold coordinated Cu(1) ions (located within the chain fragments) are assumed to be in the $+2$ electronic state. In the process of adding oxygen to the chain planes no holes will be created if the chain fragment of length one (consisting of one oxygen ion and two Cu ions) is formed, since both holes provided by the added oxygen will be used to oxidize two neighboring Cu^{+1} ions to the Cu^{+2} state. One hole along the chain is produced if the oxygen atom is added to form the chain of length two, since one of the holes provided is to oxidize the neighboring Cu atom (the other ion is already oxidized), while the second hole may in principle either stay localized around the oxygen atom or become transferred to the CuO_2 plane. Therefore, it follows that chain of length $l = 1$ will transfer no holes, chain of length 2 has a potential to transfer one hole, and so on [2]. On the other hand, Gawiec *et al.* [31, 32] suggested that in the chain of length l a certain number of oxygen ions can exist in the O^- state, so that in

this model the number of holes created is reduced imply-ing that chains of length $l = 1, 2$ transfer no holes, chains of length $l = 3$ and $l = 4$ can transfer 1 and 2 holes, respectively, while the number of holes transferred from longer chains has been roughly estimated to be $\sim 0.7\,l$ [31]. Furthermore, some authors suggested that holes can be transferred only out of the chains that comprise more than three oxygen atoms ($l_{cr} = 4$) [8, 34].

Recently a simple charge transfer model was proposed in order to obtain the 60 K plateau in the $T_c(x)$ de-pendence in terms of the well known two dimensional ASYNNNI model [26–28]. The model assumes the exis-tence of a threshold (critical) length, l_{cr}, of CuO chains, so that chains of length $l < l_{cr}$ are not able to provide any holes to CuO$_2$ sheets, but only those with $l \geqslant l_{cr}$ are. The number of holes that are potentially transfer-able from a chain of length $l \geqslant l_{cr}$ is therefore equal to $(l-1) - (l_{cr} - 1) = l - l_{cr} + 1$, and their concentration in the basal (chain) plane can accordingly be expressed by [27]

$$h = \frac{n}{2} \sum_{l=l_{cr}}^{\infty} (l - l_{cr} + 1) f(l), \qquad (1)$$

where n is concentration of three fold coordinated Cu(1) ions and $f(l)$ is the probability for a chain to have length l. The proposed charge transfer model also suggests the doping p of the superconducting planes is proportional to h [27]

$$p = \left(\frac{\chi}{2} \right) h, \qquad (2)$$

where the factor χ, as extracted from available experimen-tal data for $p(x)$ in the nearness of $x = 1$, is estimated to be around $\chi \approx 0.39$ [29]. Incidentally, this estimate also correlates very well with the doping level $p \approx 0.095$ at $x = 0.5$ through the universal T_c versus p relation [29]

$$\frac{T_c}{T_{c,\max}} = 1 - 82.6 \times (p - 0.16)^2. \qquad (3)$$

Here, $T_{c,\max}$ is the maximal critical temperature that corre-sponds to optimal doping. Equation (1) can be straightfor-wardly applied for the case of the Ortho I (OI) structural phase, while it has to be somewhat modified in the case of the Ortho II phase (as explained in the Appendix) when the oxygen chain site lattice decomposes into two sublat-tices, usually denoted by α_1 and α_2 [27]. These two basal plane oxygen site sublattices are characterized by differ-ent chain length probability distributions, $f_{\alpha1}(l)$ and $f_{\alpha2}(l)$ [26, 27] (they also have different 3-fold Cu fractions, $n_{\alpha1}$ and $n_{\alpha2}$, and different oxygen occupancies, $x_{\alpha1}$ and $x_{\alpha2}$). Applying the model as described by (1)-(2) means that for a set of values of x at $T = const$ ($=$ room temperature) the values of $p(x)$ are calculated by (1) and (2), and then used

in $T_c(p)$ (3) to obtain the $T_c(x)$ characteristics. The statis-tics of oxygen ordering enters into these calculations via Equation (1), through the 3-fold Cu fractions $n_{\alpha1}$ and $n_{\alpha2}$ and length distributions $f_{\alpha1}(l)$ and $f_{\alpha2}(l)$. These are single-parameter distributions of the form $f_{\alpha s}(l) = m_{\alpha s}(1 - m_{\alpha s})^{l-1}$ (geometric distribution), where $m_{\alpha s}$ equals the inverse of the average chain length,

$$l_{av,\alpha s} = 2 \frac{x_{\alpha s}}{n_{\alpha s}},$$

on the corresponding α sublattice ($s = 1$, or $s = 2$) [24]. Therefore, the particular model of oxygen ordering reveals its impact through the equilibrium values of four quanti-ties: $n_{\alpha1}$, $n_{\alpha2}$ and $x_{\alpha1}$, $x_{\alpha2}$, so that though the charge trans-fer model (1)-(3) has been initially developed in relation to the ASYNNNI model [26, 27], it is also applicable for other models of oxygen ordering and is accordingly used below for the case of the fragmented chain model.

3. The fragmented chain model

Originally, the fragmented chain model was introduced by Zaanen and co-workers as a specific spatial arrangement of oxygen atoms in the chain planes of YBCO material [2]. When x starts increasing beyond $x = 0.5$ the model as-sumes a structure in which very long, almost intact, chains exist on every even row of α oxygen sites (α_1 sublattice), while on the rows that lie between them (these make the α_2 sublattice) the formation of isolated oxygen atoms, or eventually short chain fragments, is favoured. Thus, when x increases beyond $x = 0.5$ (at which concentration α_1 sites are completely occupied and α_2 completely empty (OII phase)), only isolated oxygen atoms are created on α_2 sites and, consequently, no additional charge trans-fer takes place causing the $T_c(x)$ to remain constant at 60 K. The structure of the chain planes as predicted by the ground state of the fragmented chain model for $x = 0.75$ is shown in Figure 1. However, the proposed structure raises an ambiguity as to the real nature of the O-O in-teraction with the Cu ion in between: while it seems the interaction is attractive for oxygen pairs on α_1 sites, it appears as if it turns into becoming repulsive for pairs on α_2? Such a pronounced nonhomogeneity on the local microscopic level of the Cu mediated NNN interaction be-tween basal plane oxygen atoms has raised a controversy about whether it is at all possible to construct a Hamil-tonian out of which the fragmented chain structure would follow in compliance with the laws of statistical physics. Accordingly, the fragmented chain structure has been crit-icized for being artificial, as it was proposed in an *ad hoc* manner merely to account for the constant T_c in the OII
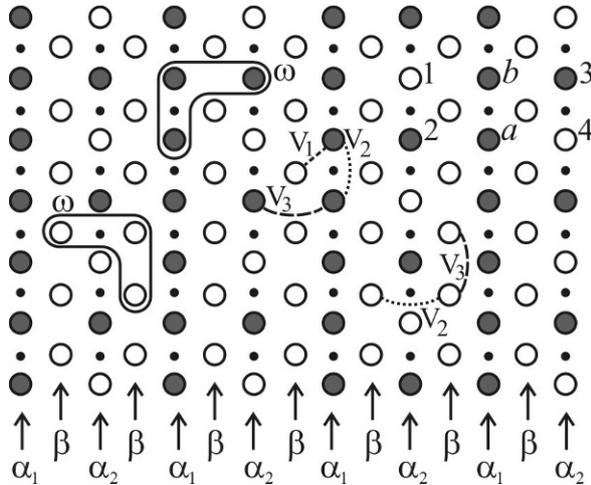
Figure 1. Spatial arrangement of oxygen atoms in the chain plane as predicted by the fragmented chain model. Large empty (black) circles denote unoccupied (occupied) oxygen sites, while small black circles denote Cu atoms. Sublattices α_1, α_2, and β are also shown (the latter is almost always empty because of the strong repulsive NN interaction $V_1 > 0$). The NN and NNN interactions, as well as the three atom interaction ω of the model Hamiltonian (6), are also shown. In the up-right corner are depicted sites a and b, that are connected by the NNN copper-mediated interaction $V_2 < 0$, together with the four nearest α sites (denoted by numbers from 1 to 4).

phase [21], and interest in the model has therefore gradually faded out. It has been subsequently shown, however, that an Ising type Hamiltonian that would favour, on one hand, the formation of isolated oxygen atoms on α_2 sites only (every second α column) while, on the other hand, still being able to allow for long copper-oxygen chains to be developed on columns that lie in-between (comprising the α_1 sublattice), can nonetheless be constructed starting from the Hamiltonian of the ASYNNNI model

$$H = V_1 \sum_{NN} \sigma_i \sigma_j + V_2 \sum_{NNN'} \sigma_i \sigma_j + V_3 \sum_{NNN} \sigma_i \sigma_j + \mu \sum_i \sigma_i.$$
(4)

In the above expression V_3 is the direct Coulomb NNN O-O interaction (repulsive, $V_3 > 0$) while V_2 is the NNN O-O interaction through the Cu ion (superexchange). $V_1 > 0$ is the interaction that couples NN sites, one on sublattices α_1 or α_2 and the other on the β sublattice, as it is shown in Fig. 1. Also, $\sigma_i = +1$ means that the site i is occupied by an oxygen atom, while $\sigma_i = -1$ means the site is empty, and μ is chemical potential. In a broader sense, the effective interaction energy between two oxygen atoms coupled by a V_2 bond can be thought of as depending not only on population of the two oxygen sites, but on occupancy of surrounding oxygen sites as well. Given that β

sites are always empty because of the very strong repulsive NN interaction V_1, the most relevant impact comes from the four α sites that are closest to the considered pair (the sites denoted by a and b, shown in up-right corner of Fig. 1; the four nearest α sites are labelled by numbers from 1 to 4). Therefore, in this extended approximation the parameter V_2 from (4) modifies into

$$V_2^{\text{eff}} \to V_2 + \omega \left(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 \right),$$
(5)

where the quantity ω characterizes the impact of surrounding sites. Inserting (5) into (4) the latter assumes the following form

$$H = V_1 \sum_{NN} \sigma_i \sigma_j + V_2 \sum_{NNN} \sigma_i \sigma_j + V_3 \sum_{NNN} \sigma_i \sigma_j$$
$$+ \omega \sum_{ijk} \sigma_i \sigma_j \sigma_k - \mu \sum_i \sigma_i.$$
(6)

The above Hamiltonian differs from the standard ASYNNNI model in that it includes three-atom interactions in addition to those pair-wise interactions that already exist in (4), so in this view Hamiltonian (6) can be regarded as a further approximation of (4). A detailed ground state analysis of the model Hamiltonian (6) points towards a conclusion that the parameter ω must satisfy the condition $\omega > \frac{1}{4}|V_2|$, in order for the fragmented chain structure to be stabilized as its ground state, i.e. in that case it favours formation of long CuO chains on every second α column (α_1 sites) and, simultaneously, as many as possible isolated oxygen atoms on columns that lie in-between [24, 25].

4. Results and discussion

The relations (1) and (2) have been used to calculate doping p at various oxygen concentrations x that span the region of stability of both major orthorombic phases, OI and OII. All calculated points corresponded to the same temperature and the so-obtained $p(x)$ dependence at $T = const$ was then combined with the universal $T_c(p)$ relation (3) to yield the $T_c(x)$ characteristics. The single spin flip Monte Carlo (MC) algorithm has been applied on a lattice consisting of 400×400 spins on α sites subject to the periodic boundary condition (consequently, there were as many spins on the β sublattice). The Glauber dynamics scheme has been employed with oxygen concentration x being a function of temperature T and chemical potential μ. The values of the interaction parameters were taken to be: $V_2 = -0.37\,V_1$, $V_3 = 0.17\,V_1$ [35], and $\omega = 0.105\,V_1$ (with the latter being only slightly greater

than the required $\frac{|V_2|}{4} = 0.0925\,V_1$). As temperature enters into calculations via the so-called *scaled temperature*,

$$\tau = \frac{k_B T}{V_1},$$

the constant temperature at which the doping was calculated was set at $\tau = 0.45$, in accordance with previous estimations of the value of the parameter τ that is in best correlation to room temperature [27]. The doping p has been calculated for a set of oxygen concentrations $0 < x < 1$ in order to obtain the $p(x)$ dependence. As a result of the MC run, for each value of x equilibrium values of $x_{\alpha 1}$, $x_{\alpha 2}$, $n_{\alpha 1}$, $n_{\alpha 2}$ were obtained, and also length distributions $f_{\alpha 1}(l)$ and $f_{\alpha 2}(l)$, $l = 1, \ldots, 300$ which were then employed in (1). Instead of Equation (1) the somewhat modified expressions (A2), or (A3), have been used in the case of the OII phase, as described in the Appendix. In order to get a deeper insight into how large the chain length needs to be for the charge transfer to be triggered (i.e. to estimate the value of parameter l_{cr}), for each x from the region of the 60 K plateau of T_c the basal plane hole concentration h was calculated for a range of values of l_{cr}, and all these $h(l_{cr})$ dependences were then shown on the same plot (Fig. 2). As can be seen from Fig. 2, all of these $h(l_{cr})$ functions intersect at a well-defined value $l_{cr} = 3$, which implies that when this value is inserted into (1) the corresponding x-dependence of h will be constant over the regime of the 60 K plateau (with a value that is a little less than 0.5). Furthermore, from Fig. 2 it also follows that if l_{cr} is set to be $l_{cr} < 3$ the $h(x)$ function will be monotonically increasing over the 60 K plateau (OII phase), while for $l_{cr} > 3$ it will decrease. It should be noted that although some earlier experimental results have pointed to the $T_c(x)$ dependence as being strictly constant in the regime of the 60 K phase [5, 7] (implying that both $h(x)$ and $p(x)$ functions are constant as well), a recent experimental study indicated that the 60 K plateau of $T_c(x)$ is not exactly a strictly horizontal plateau, but rather a sort of "quasi plateau", so that $T_c(x)$ in fact increases monotonically, though at a slow rate, over the regime of the plateau [9]. With this in mind we therefore used $l_{cr} = 2$ (< 3) to be inserted into (1) (i.e. into (A2), or (A3)) for that would yield slowly increasing $h(x)$, $p(x)$, and, consequently, $T_c(x)$, when x increases beyond $x = 0.50$. As for the parameter χ that has been introduced in (2) its value was varied within a narrow interval around ~ 0.39, which is a value that is not disputable – at least for $x \approx 1$ [9, 29]. In Fig. 3 are shown the calculated values of T_c as a function of x at $\tau = 0.45 = const$, for $\chi = 0.374$ and $l_{cr} = 2$. The calculated $T_c(x)$ is shown in three plots in order to make a clear comparison with three experimental $T_c(x)$ dependences from Refs. [7–9], respectively. From
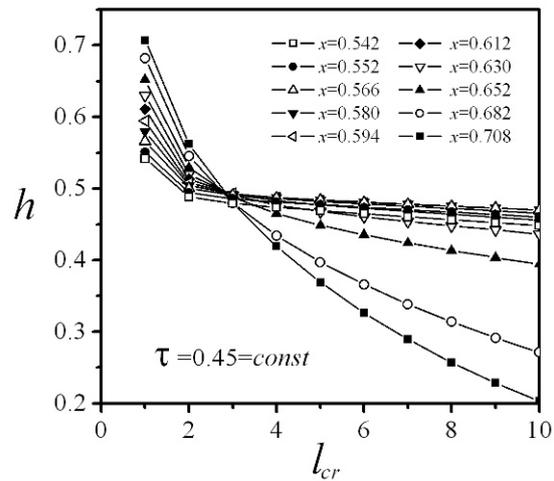

Figure 2. Concentration of active holes h as a function of the cut-off parameter l_{cr} calculated at $\tau = 0.45 = const$ for several values of oxygen concentration that span the region over which the 60 K plateau extends (OII phase - $0.50 < x < 0.63$ (5)). Note that all $h(l_{cr})$ curves intersect at a single, well-defined, value $l_{cr} = 3$.

Fig. 3 it can be seen that the calculated $T_c(x)$ does not agree well with the old result of Jorgensen *et al.* [7]. The reason for this discrepancy is obvious: the 60 K section of Ref. [7] is strictly horizontal, while here it has been chosen $l_{cr} = 2$ (< 3) with a primary intention to exactly avoid such a striking horizontality. A better agreement is achieved with the $T_c(x)$ of Manca *et al.* [8], as in that study the plateau obtained was slightly angled with respect to the horizontal direction, and thence attributed, for the first time up to that moment, with a qualifier "quasi". Besides that, there is some discrepancy, though not very large, with the $T_c(x)$ of Ref. [8] in the transition region between the two plateaus, immediately before the optimal doping (maximal T_c). However, a remarkable degree of correlation has been achieved with the most recent result for $T_c(x)$ of Liang *et al.* [9] (right plot in Fig. 3), which further confirmed the absence of an ideal horizontality in the 60 K sequence of $T_c(x)$. The two curves almost completely coincide, in the region of the 60 K "quasi" plateau and in the transition section between two plateaus, and also around the optimal doping and in the small region of the overdoped phase. Such a remarkable agreement with the results of Ref. [9] points to the conclusion that the fragmented chain model, as given by (6), can successfully account not only for the statistics of CuO chains in basal planes, but also for the wholeness of the charge transfer process from chains towards CuO$_2$ planes.

The most important aspect of the presented results is that

chains do not supply holes to CuO_2 sheets only in the ele-mentary case when they consist of only one oxygen atom. This is consistent with the commonly accepted opinion according to which an isolated oxygen takes away two electrons from two nearest neighbour Cu^{1+} ions (transfer-ring them into Cu^{2+}), so that in this way the local charge balance is maintained and, consequently, there is no need for electrons from more distant parts of the structure to be attracted (primarily, from CuO_2 sheets). As for the chains of non-trivial length ($l > 1$) the result $l_{cr} = 2$ points to a notion that there will be $l - l_{cr} + 1 = l - 1$ holes in a chain of length $l > 1$ that are in principle transferable, which is no less than the total number of holes that one generally expects to find in a chain comprising l oxygen atoms. Therefore, all of the $l-1$ holes created in a chain of length l can attract electrons from two CuO_2 sheets (lying just above and below the basal plane), but, according to (2), it is only a little less than 40% of all these basal plane holes (organized along CuO chains) that will eventually succeed in achieving this goal. It should be pointed out that the obtained result $\chi = 37.4\%$ (Fig. 3) is in remark-able correlation with experimental estimation for doping, $p \approx 0.187$, at $x \approx 1$ [29], as at this concentration all α_1

and α_2 sites are fully occupied (the chains are very long, nearly infinite) and there would be one basal plane hole per oxygen atom. Thus, $x = 1$ (OI stoichiometry) implies $h = 1$, which, when combined with (2), gives exactly the same $p = 0.187$ as in Ref. [29]. In addition to that, even though the doping is not convincingly obtainable in ex-periments between $x \approx 0.4$ and $x \approx 0.6$, the obtained estimate $\chi = 0.374$ seems to be in very good coordina-tion with what one might expect that the doping would have been equal to at $x = 0.50$ (OII stoichiometry). At this concentration only α_1 columns are completely occu-pied by oxygen with infinite chains developed along them (no oxygen exists at all on the α_2 sites), so, given that each oxygen has created one hole as there is no fragmen-tation of chains, it follows that $h = 0.5$, which by virtue of (2) points to $p = 0.093$ and to $T_c = 60$ K (through the universal empiric T_c versus p relation (3)). It should also be mentioned that below $p \approx 0.091$ (2) any effect of stripes on the universal $T_c(p)$ relation (3) has already faded away, as was shown on unequivocal grounds in Ref. [9], so that (3) can be considered a reliable connection between T_c and p for at least as long as the doping does not substantially exceed the level $p \approx 0.091$.
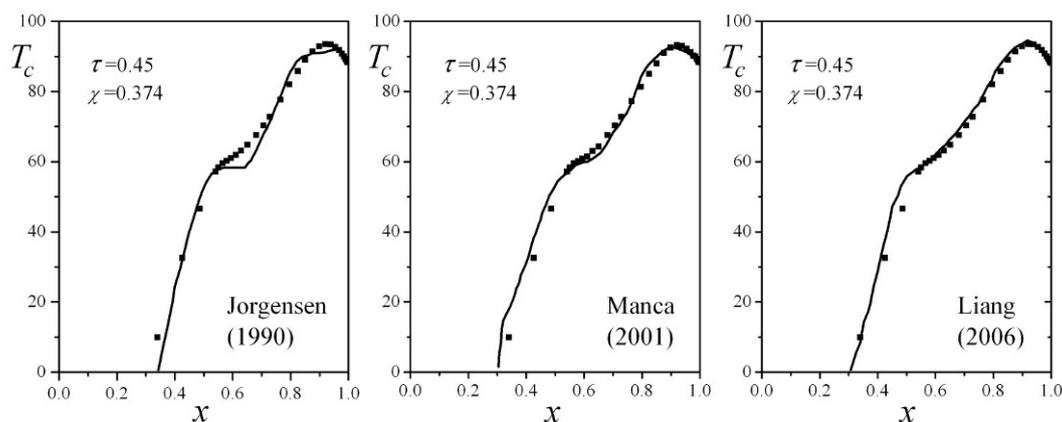

Figure 3. Calculated $T_c(x)$ dependence at $\tau = 0.45 = const$ for $l_{cr} = 2$ and $\chi = 0.374$ (black square symbols) shown in three figures in which it is compared with three experimentally obtained $T_c(x)$ characteristics from References [7–9].

The obtained $l_{cr} = 2$ is the lowest value of the critical chain length, introduced as a threshold for the onset of charge transfer, that is in principle possible (the option $l_{cr} = 1$ is senseless, as it has been explained above). That is the most important difference between the fragmented chain model (6) and the ASYNNNI model (4). The latter

doesn't predict a large number of isolated oxygen atoms as the former does, and thence its threshold parameter l_{cr} appears to be greater, ranging around $l_{cr} = 4$ [26, 27]. The $l_{cr} = 2$ brings down the whole concept of the threshold (critical) chain length to trigger the charge transfer to its trivial form in which only isolated oxygen atoms are cut

from the expression (A2). Given that no compelling mechanism has been offered yet as to why the chains of, for example, lengths $l = 2$, or $l = 3$, would give no holes to the layers whatsoever, it therefore appears that the fragmented chain model (6) gives an explanation for the charge transfer process in the YBa$_2$Cu$_3$O$_{6+x}$ compound in a way that is probably more direct and simpler then the one provided by the ASYNNNI model. That is why we believe the model (6) deserves due consideration in future analyses as a useful tool for quantifying the processes of charge transfer in YBa$_2$Cu$_3$O$_{6+x}$.

5.   Conclusions

The key results that have been exposed here can be summarized as follows: a new Hamiltonian has been introduced, that besides the nearest neighbour and next–nearest neighbour pair–wise interactions also includes the three–atom interactions. The new Hamiltonian stabilizes the fragmented chain structure in the basal planes of the YBa$_2$Cu$_3$O$_{6+x}$ system, that is characterized by an abundance of isolated oxygen ions, but only on every second column of α oxygen sites. A model has been proposed (as given by (1)) to obtain how many holes are generated in CuO$_2$ sheets from a chain of a given length l, and the number of these holes per in–plane Cu (doping) has been calculated by expression (2). The obtained p versus x dependence at $T = const$ is then combined with the universal T_c versus p (empirical) relation (3) and the resulting $T_c(x)$ characteristics have been found to be in remarkable correlation with the experimental ones [9]. The obtained $l_{cr} = 2$ points to a conclusion that only isolated oxygen ions of the basal planes do not cause a large enough effect at the two nearby CuO$_2$ planes to drag an electron down from them. Only chains that include two or more oxygen atoms are long enough to instigate the charge transfer in terms of the fragmented chain model.

Acknowledgment

Appendix A

The length distributions of CuO chains on sublattices α_1 and α_2 are given respectively by

$$f_{\alpha 1}(l) = \frac{1}{l_{av,\alpha 1}} \left(1 - \frac{1}{l_{av,\alpha 1}} \right)^{l-1},$$
$$f_{\alpha 2}(l) = \frac{1}{l_{av,\alpha 2}} \left(1 - \frac{1}{l_{av,\alpha 2}} \right)^{l-1}, \tag{A1}$$

where $l_{av,\alpha 1}$ and $l_{av,\alpha 2}$ stand for the average chain lengths on the corresponding sublattices. The above length distributions hold for practically the whole (x, T) space of the phase diagram, in the case of the bare ASYNNNI model [24], and also for the fragmented chain model [25], with the only departure being detected in a narrow region around second order phase transition lines in accordance with theoretical predictions [36]. When (A1) is inserted into (1) the expression for doping (2) attains the following form

$$p = \frac{\chi}{8} \left[\frac{n_{\alpha 1}}{l_{av,\alpha 1}} \sum_{l=l_{cr}}^{\infty} (l - l_{cr} + 1) \left(1 - \frac{1}{l_{av,\alpha 1}} \right)^{l-1} \right.$$
$$\left. + \frac{n_{\alpha 2}}{l_{av,\alpha 2}} \sum_{l=l_{cr}}^{\infty} (l - l_{cr} + 1) \left(1 - \frac{1}{l_{av,\alpha 2}} \right)^{l-1} \right]. \tag{A2}$$

The above summations satisfy general conditions for convergence and employing some mathematics the doping can be expressed in an integrated form

$$p(x) = \frac{\chi}{4} x_{\alpha 1} \left(1 - \frac{1}{l_{av,\alpha 1}} \right)^{l_{cr}-1} + \frac{\chi}{2} x_{\alpha 2} \left(1 - \frac{1}{l_{av,\alpha 2}} \right)^{l_{cr}-1}, \tag{A3}$$

where the first term gives the doping $p_{\alpha 1}(x)$ that originates from CuO chains on the α_1 sublattice, while the second term is the contribution to doping, $p_{\alpha 2}(x)$, from the chains residing on α_2 sites. In this study the doping $p(x)$ at $T = const$ was calculated in two ways: by calculating the first 300 terms of (A2) and by use of (A3), and the calculated values of $p(x)$ were in both cases practically identical. That was so even in the proximity of critical lines, signifying that a slight disagreement between calculated length distributions $f_{\alpha 1}(l)$ and $f_{\alpha_2}(l)$ and geometric probability distributions (A1) was of no significant effect in the calculation of $p(x)$.

The closed–form expression for doping (A3) is convenient when one analyses the issue of why the value of l_{cr}, for which $p(x)$ in the regime of the OII phase is a constant function ($\approx \frac{\chi}{4}$) at any $T = const$, is so well–defined (as illustrated in Fig. 2). It is well known that starting from $x = 0.5$ ($x_{\alpha 1} \approx 1$, $l_{av,\alpha 1} \sim \infty$, and $x_{\alpha 2} \approx 0$, $l_{av,\alpha 2} \approx 1$) both

$x_{\alpha 1}(x)$ and $l_{av,\alpha 1}(x)$ are monotonically decreasing functions at $T = const$, while $x_{\alpha 2}(x)$ and $l_{av,\alpha 2}(x)$ are monotonically increasing (such behaviour has been confirmed for the fragmented chain model in reference [25]). The corresponding expressions in brackets of (A3) are then also decreasing (increasing) functions of x as long as $l_{cr} > 1$ (the case $l_{cr} = 1$ is senseless, for isolated oxygen does not create holes – as has been explained above), and, as a product of two decreasing (increasing) functions, $p_{\alpha 1}(x)$ $(p_{\alpha 2}(x))$ is also a decreasing (increasing) function. The rate of $p_{\alpha 1}(x)$ decrease (or, of $p_{\alpha 2}(x)$ increase) obviously depends on l_{cr} through the exponent and the problem of finding the value of l_{cr} for which $p(x)$ stays at a constant level is simply equivalent to finding the exponent for which the increase of $p_{\alpha 2}(x)$ is exactly compensated by the decrease of $p_{\alpha 1}(x)$ (in Fig. 2, this occurs for $l_{cr} = 3$ at an estimated temperature $T = \frac{0.45 V_1}{k_B} = const$).

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