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Geometric distribution of CuO chains in $YBa_2Cu_3O_{6+x}$

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Abstract

Statistics of CuO chains in basal planes of $YBa_2Cu_3O_{6+x}$ high-T_c superconductor has been studied in terms of two dimensional asymmetric next-to-nearest-neighbor Ising (ASYNNNI) model, with accentuation on distribution of CuO chains per different chain lengths. It has been shown that the fraction $p(l)$ of CuO chains containing l oxygen ions (i.e., having the length equal to l), satisfies so-called "law of geometric distribution" $p(l) = \omega(1-\omega)^{l-1}$, where the quantity ω is equal to the inverse of average chain length l_{av} in the system, for given values of oxygen content x and temperature T. In the case of ortho-II (OII) structural phase, the geometric chain probability distribution is shown to hold separately for each of two different sublattices of oxygen sites, commonly known as α_1 and α_2, with respectively defined $l_{av}^{\alpha_1}(x,T)$ and $l_{av}^{\alpha_2}(x,T)$. The theoretically derived result of the chain probability distribution $p(l)$ is shown to be in a remarkable agreement with the results obtained out of extensive Monte Carlo calculations that were made within region of stability of orthorhombic structural phases in (x, T) space. The relevance of chain length distribution for accurate count of the number of transferred electronic holes to superconducting CuO_2 layers has been pointed out and expression for hole concentration has been derived. The concept of critical chain length for charge transfer mechanism was briefly discussed.

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Keywords: CuO chains; Distribution of CuO chains; Oxygen ordering

1. Introduction

One of the most intriguing properties of the high-temperature superconductor $YBa_2Cu_3O_{6+x}$ is nonlinear variation of its superconducting transition temperature T_c when oxygen content changes from $x = 0$ to $x = 1.0$. As it has been shown in numerous experimental studies (eq. in references [1,2]) the $T_c(x)$ exhibits well-known two-plateaus like behavior maintaining at nearly 60 K for $x = 0.5$–0.7 and showing another, somehow less emphasized, plateau at $T_c \approx 90$ K when x changes from $x \approx 0.82(3)$ to $x = 1$. It is also known that transition from antiferromagnetic to superconducting state at $x \approx 0.35(0.40)$ coincides with symmetry breaking $a \neq b$, that is manifested by tetragonal-to-orthorhombic structural phase transition [3]. Within the interval $0.35 \leqslant x \leqslant 1$ a number of orthorhombic structures have been detected with different alternation schemes of "full" CuO chains and "empty" Cu-vacancy chains along a crystallographic axis [4–6]. Generally accepted opinion is that the CuO chains act as donors of electronic holes to CuO_2 sheets, and the number of transferred holes originating from a given chain, depends crucially on the chain length. It is believed that diversity of chain statistics associated with different orthorhombic structures is laying at the root of unusual behavior of $T_c(x)$.

The common feature of orthorhombic phases is that CuO chains alternate with empty Cu-vacancy fragments along columns of α oxygen sites in basal plane (Fig. 1). The chains may have variety of lengths ranking from $l = 1$ to comprising tens, or even hundreds of oxygen ions. By now, several scenarios have been suggested about how

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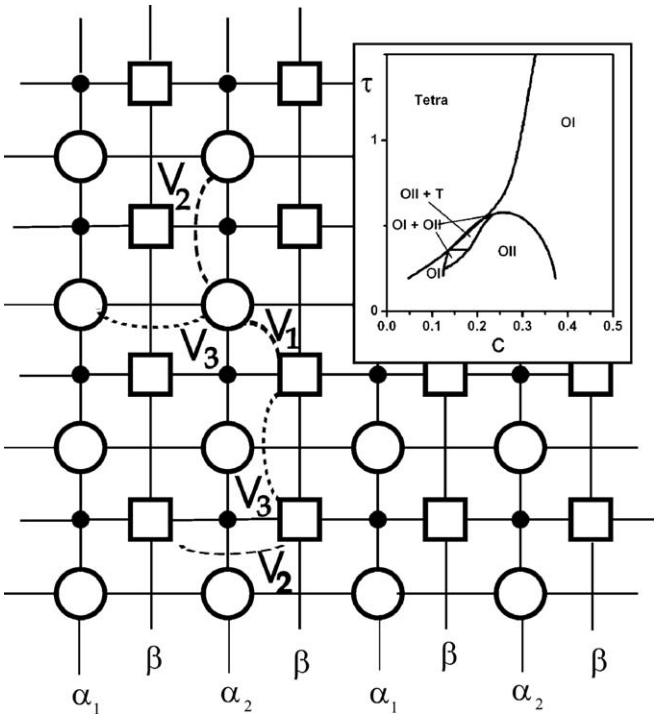

Fig. 1. The basal plane lattice of $YBa_2Cu_3O_{6+2c}$ with repulsive interactions V_1, $V_3 > 0$ and the Cooper mediated superexchange interaction $V_2 < 0$ (attractive). Open circles and squares represent oxygen sites on α (α_1 and α_2) and β sublattices, respectively, while small black circles denote Cu(1) ions. In OI phase both α_1 and α_2 sites are equally populated by oxygen atoms. The phase diagram, obtained by cluster variation method, is shown in the inset.

many holes can be transferred from the chain of particular length l. According to Gawiec et al. [7,8] some oxygen ions involved in chain may depart from being O^{2-}, so that state of chain having the length l is given by $Cu^{2+}_{l+1}O^{2-}_{m}O^{-}_{l-m}$ implying only $m-1$ electronic holes ($m < l$) must have been transferred from such a chain. The authors estimated that no holes should be transferred from chains with $l = 1, 2$, and that the chain should transfer respectively one hole if $l = 3$ and two holes if $l = 4$. For $l > 4$ it was estimated the number of transferred holes is equal to the nearest integer of $0.7l$ [7]. On the other hand, Zaanen et al. were first who introduced concept of so-called *the critical chain length* l_{cr} proposing that no charge transfer should occur from chains with $l < l_{cr}$ [9], while Manca et al. [3] and Lutgemeier et al. [10] have estimated that l_{cr} might be equal to four.

Beside the model for charge transfer mechanism from chains to plains, it is also necessary to resolve the problem of how many chains are in the system containing given number of oxygen ions, i.e., have the length l. In that case it is possible to accurately count the concentration of transferred holes. If $p(l)$ stands for the fraction of CuO chains containing l oxygen ions, in other words, $p(l)$ equals to the probability for chain to have length l, the hole concentration should be proportional to $\sum_{l=1}^{\infty} h(l)p(l)$, where $h(l)$ stands for the number of holes transferred from chains with length l. The $h(l)$, that has been introduced in this way, is expected to depend on the particular model describing mechanism of charge transfer. As different orthorhombic structures are distinguished among themselves by number of nonequivalent sublattices of oxygen α sites, and also by their mutual disposition along a-axis, it is obvious that any of these nonequivalent sublattices should have its own distribution $p(l)$.

The most widely used theoretical model to describe thermodynamics of oxygen ordering in $YBa_2Cu_3O_{6+x}$ compound is two dimensional asymmetric next-to-nearest neighbor Ising (ASYNNNI) model proposed long ago by Wille and de Fontaine [11]. The model has proven itself as reliable tool for explaining almost all basic experimental facts related to structural phase transformations in the material. Beside the fact that it stabilizes major orthorhombic structural phases (so-called orthorhombic I (OI), and orthorhombic II (OII)) as ground states, it also fairly accurately reproduces general topology of the phase diagram and the nature of phase transition curves between them (see inset in Fig. 1). A number of other chain-ordered structures have been reported (for example OIII, OIV, etc.), which can be stabilized if interactions of longer range than NNN are added to the ASYNNNI model. However, these structures were observed only in small patches embedded within large domains of one of the major phases (ortho-I, ortho-II, or tetragonal) and it is still not definitely clear if they are really thermodynamically stable. In spite of its success in describing many of the most important properties of the $YBa_2Cu_3O_{6+x}$ system, the bare ASYNNNI model have so far failed to provide decisive evidence for existence of plateaus in $T_c(x)$. Further, various extensions of the model, stabilizing other chain-like structures, were also unsuccessful in achieving this goal. One of possible explanations for a such development can be attributed to the fact that certain aspects of the model thermodynamics have not been yet fully understood and therefore need to be clarified up to more satisfactory degree. This is particularly the case with the CuO chain statistics which is the most directly expressed by form of chain length probability distribution $p(l)$.

From the above mentioned facts it is obvious that clarifying exact form of $p(l)$ marks itself to be one of key steps in establishing connection between thermodynamics of oxygen ordering and density of superconducting carriers in $YBa_2Cu_3O_{6+x}$. This is exactly the main objective of this study: to determine the chain probability distribution $p(l)$ in terms of the ASYNNNI model at different points of (x, T) space. This paper is organized as follows: in Section 2 the model Hamiltonian is briefly introduced and the chain probability distribution $p(l)$ is derived on the grounds of theoretical considerations. The obtained theoretical result on $p(l)$ is then certified showing it to be in remarkable agreement to numerical results obtained out of Monte Carlo simulations (Section 3), while discussion of results, together with some conclusions, is exposed in Section 4.