Concerning order and disorder in the ensemble of Cu-O chain fragments in oxygen deficient planes of Y-Ba-Cu-O.

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Abstract

In connection with numerous X-ray and neutron investigations of some high temperature superconductors (YBa$_2$Cu$_3$O$_{6+x}$ and related compounds) a non-trivial part of the structure factor, coming from partly disordered Cu-O-...O-Cu chain fragments, situated within basal planes, CuO$_x$, can be a subject of theoretical interest. Closely connected to such a diffusive part of the structure factor are the correlation lengths, which are also available in neutron and X-ray diffraction studies and depend on a degree of oxygen disorder in a basal plane. The quantitative measure of such a disorder can be associated with temperature of a sample anneal, $T_q$, at which oxygen in a basal plane remains frozen-in high temperature equilibrium after a fast quench of a sample to room or lower temperature. The structure factor evolution with $x$ is visualized in figures after the numerical calculations. The theoretical approach employed in the paper has been developed for the orthorhombic state of YBCO.

74.70.Vy, 64.60.Cn, 64.80.Eb
I. INTRODUCTION.

While the regular CuO$_2$ planes are commonly believed to be responsible for both fascinating phenomena, the high-$T_c$ superconductivity (HTS) and high-$T_N$ antiferromagnetism, the oxygen deficient planes of the YBa$_2$Cu$_3$O$_{6+x}$ compounds play an important role too, taking a control over the mentioned phenomena. HTS is associated with the orthorhombic state of YBCO which is consistent with existence of linear chain fragments, Cu-O-...-O-Cu, in oxygen deficient planes, CuO$_x$. Even in the case of twinned crystals the substance consists of macroscopical domains where chain fragments (CFs) are arranged in chains (conventional notation is O(1) and O(5) for oxygen positions in and across the chains, respectively). There are three orthorhombic phases, Ortho-I, II and III, which have been reliably identified experimentally. Concerning the Ortho-II and Ortho-III phases, their identification in neutron and X-ray diffraction studies [1–4] has been reported. The part of the structural phase diagram in the $x$-$T$ plane is shown qualitatively in Fig.1 (cf Refs [5–7]). The $T$ coordinate plays the role of temperature of oxygen equilibrium in the basal plane. It could be of the order of room temperature, $T_R$, if a cooling procedure were done slowly. Otherwise, it would be the so-called quenching temperature, $T_q$, if a sample were annealed for a long time and then quenched rapidly from $T_q$ to room or lower temperature. The role of $T_R$ is important: Oxygen atoms in deficient planes do not diffuse below $T_R$ (cf, however, the elegant investigation by Jorgensen et al [8]). $T_q$’s have varied up to 350°C in experiments by Veal and co-workers ([9,10] and references therein). In order to prepare the Ortho-III phase the samples have been quenched at temperatures above 500°C [3].

As mentioned above the constituents which form the oxygen deficient plane are the CFs. In the tetragonal phase they are rather short and could be assumed to be situated at random were it not for evidence of a superstructure at some low oxygen content, $x \approx 0.35$, as reported in [11,12] (cf [13], however). Most likely, the origin of the herring-bone arrangement of the very short Cu-O-Cu chain pieces is simply owing to the Coulomb interaction of such fragments which are simultaneously quadrupoles (see [14]).

In the Ortho-I phase the distribution of CFs over their lengths is similar in all the chains. The single-cell structure is typical for the right part of the phase diagram ($0.75 < x < 1$ at $T_q \sim T_R$). Between Tetra and Ortho-I phases in Fig.1 there is the area of the Ortho-II phase, which simply means a double-cell structure with oxygen-poor chains alternating oxygen-rich ones. However, the phase transition lines, restricting this area, are not strictly determined up to now: There is still a question about the type of the Tetra-to-Ortho-II phase transition. Either the system could undergo the phase separation, ie, the first order phase transition with phase co-existence in the form of the ”gas” (Tetra)–”liquid” (Ortho-II) mixture or the phase transition through a growth of Ortho-II domains. More acknowledged is the first scenario, see, for instance, [15,16], but this conclusion has been done in a
frame of a lattice-gas model, the so-called ASYNNNI model, which ignores intrinsic, ie, fermionic degrees of freedom of CFs. As for the second scenario the domains of four various kinds would be locally arranged in the double-cell structures, oriented along $b-/a$-axis and shifted across the chains by a single period. Another boundary, confining the Ortho-II phase, would divide the regions of the Ortho-I and Ortho-II phases were it not for the possibility for the Ortho-III phase to exist between them. The periodicity of the latter corresponds to one oxygen-poor chain following two oxygen-rich chains. However, in order to search the Ortho-III phase experimentally the way of a sample preparation should be indirect. Actually, a slow cooling is accompanied with a formation of the Ortho-II phase, which locks the periodicity, making the kinetics of the phase transformation into the Ortho-III phase to be embarrassing. To avoid such a difficulty a slow cooling in the atmosphere of higher oxygen pressure at the first stage can be switched over to a fast quench from rather high temperature ($>500^\circ \text{C}$) at the second stage [3]. There was a theoretical conjecture concerning a possibility for long wave-length modulated structures to exist in oxygen deficient planes (see [7] and references therein). However, the afore-said impossibility of oxygen migration at low enough temperatures ($T<T_R$) makes such hypothetical modulated structures the subject of an abstract interest.

Note that the Ortho-I phase can be interpreted as a disordered Ortho-II phase with a short-range order. Certainly, the order parameter of the Ortho-I phase is of the higher symmetry than that of the Ortho-II phase.

To reveal the regions of stability of Tetra, Ortho-I and Ortho-II phases and to construct a structural phase diagram theoretically a two-dimensional lattice-gas model, the ASYNNNI model, has been used as a prerequisite by de Fontaine and colleagues. The model presented in Fig.2 (on the parameters, entering the model, see, for instance, [5,6,18]) invokes the nearest neighbor oxygen-oxygen repulsion ($V_1$, oxygen in the ”corner” configuration), the next-nearest neighbor attraction ($-V_2$, in-line configuration) and also the next-nearest repulsion without any Cu ion in between the corresponding oxygen atoms ($V_3$, ”vis-à-vis” configuration). As mentioned above the lattice-gas model ignores a fermionic origin of microscopical properties of CFs. Also this model is not the best candidate for a proper description of a structure formation: The superstructure at small $x$ is beyond the ASYNNNI model predictions. Nevertheless, the lattice-gas approach is reasonable for the orthorhombic side of the phase diagram and it can be phenomenologically generalized to incorporate the fermionic degrees of freedom into the effective interaction of oxygen atoms within CFs. Generalization is based on the result obtained in the soft X-ray absorption spectroscopy investigation of untwinned YBa$_2$Cu$_3$O$_7$ and reported in [13]: The concentration of oxygen holes in the Cu-O chains has been estimated around 30%. This experimental estimate is essential for applying the charge transfer mechanism discussed theoretically in [20] and partly based on the experimental investigations [21,22] of the monovalent Cu amount in YBa$_2$Cu$_3$O$_{6+x}$. A
short résumé of the mechanism proposed in [20] is as follows: Existence of the CF, involving $n+1$ Cu$^{2+}$ and $n$ O atoms, $m$ of which are O$^{2-}$ and $n-m$ atoms are O$^-$, is consistent with $m-1$ holes transferred from the fragment. In the limit of very long CFs ($n \gg 1$), i.e., the case investigated in Ref [19], the free energy per one oxygen site of the fragment, $f(n,m)$, depends practically of $m/n$ and has a minimum around $\xi \approx 0.70$. It allows to represent the free energy in the following form:

$$f(n,m) = f_n + \frac{a_n}{2} \left( \frac{m}{n} - \xi_n \right)^2$$

(1)

where $f_n$, $a_n$ and $\xi_n$ go to the fixed values when $n \to \infty$. One employs Eq.(1) to get a reduced information about CFs, expressed in terms of their lengths $n$:

$$e^{-n\phi(n)/T} = \sum_{m=0}^{n} e^{-nf(n,m)/T}$$

(2)

This procedure is convenient to build the statistical mechanics of the CF ensemble because the configurational entropy is associated with the lengths of CFs. The reduced free energy, $\phi(n)$, reads at $n \gg 1$:

$$\phi(n) = f_n - \frac{T}{2n} \ln \frac{2\pi n T}{a_n} \approx \phi_1 + \frac{\phi_2}{n} - \frac{T}{2n} \ln n$$

(3)

Expression (3) could be compared with the analogous one easily obtained from the lattice-gas model mentioned above. Actually, the attraction energy $-V_2(n-1)$ plays the same role as $n\phi(n)$ in formation of the CF of length $n$. So, the analogue of Eq.(3) is

$$\tilde{\phi}(n) = -V_2 + \frac{V_2}{n}$$

(4)

Deriving Eq.(4) we also include the energy loss, $V_{3-Cu}$, due to the 3-fold coordinated Cu ions at the ends of a CF, which yields the evident change $V_2/n \to \tilde{V}_2/n = (V_2 + 2V_{3-Cu})/n$. The first terms in the r.h.s. of Eqs.(3) and (4) are not relevant if oxygen atoms predominantly occupy O(1) positions: For the orthorhombic state of YBCO, prepared at moderate (not too high!) $T_q$, O(5) positions were proved [23] to be occupied poorly. This is the case for which one assumes the total amount of oxygen to be fixed, hence, the first, $n$-independent, term of Eqs.(3)-(4) does not distinguish between various configurations of CFs. The second terms in Eqs.(3)-(4) are important and their meaning is clear: CFs would show a tendency to increase their lengths were it not for the third term in Eq.(3) and, in addition, for the configurational entropy of the CF ensemble. Aforementioned temperature, $T = T_q$, is above, at least, than $T_R$.

In order to complete the scheme presented by Eq.(3) or (4) the following parts of the free energy must be involved into a theoretical consideration: First, the configurational energy term due to various configurations of CFs, and second, caused by the interaction of oxygen
atoms in different chains, i.e., the $V_3$-term. Partly, this line of attacking the problem has been realized in\cite{24, 25} and subjected to the experimental check by Boucherle et al.\cite{24}. Such a general theoretical approach as well as some important applications to the experimentally observable values, reported already and foreseen, will be presented in the following sections.

There is also a more straightforward approach to the problem of CFs in the orthorhombic phase of YBCO. Instead of employing phenomenological schemes of Eq. (3) or (4) it would be possible to start with some microscopical model for an alternating Cu-O CF, which should belong to a family of strongly correlated fermionic systems despite of its finite length. A good candidate could be the Emery model\cite{27}, or its Kondo-like version \cite{28}, or the 1d model of the Zhang-Rice type\cite{29}, derived from the original Emery model: All are well adapted to a proper description of the alternating CFs. However, to adjust such models to the reality one needs to invoke some additional short-range interactions, i.e., the nearest Cu-O and O-O interactions, the bare energy of a charge transfer from chains into CuO$_2$ planes and the energy loss because of the 3-fold coordinated Cu atoms at both ends of CFs. The problem seems to be hopeless because of too many energy parameters invoked in, however, the choice of the model parameters is based only on few relevant properties of CFs, the most important among them is a true position of the free energy minimum around $m/n \approx 0.7$. The attempt to apply the Kondo-reduced version of the Emery model has been done in Ref.\cite{20}: In addition to the above-mentioned criterium the plateau-like behavior of $n_h$ vs $x$, imitating the 60 K $T_c$ vs $x$ plateau in YBCO, has been employed as a crucial point ($n_h$ the concentration of holes leaving the chains).

Certainly, a big advantage of the microscopical model approach is in a possibility of direct calculations of such physical quantities as $n_h$, $n_{pm}$, the concentration of paramagnetically active CFs, studied by polarised neutrons\cite{26}, magnetic correlations within CFs and so on. However, the chain, consisting of more than 9 copper and 8 oxygen atoms, are not available to be treated by means of the exact numerical diagonalization algorithm by Lanczos (see the review paper\cite{30} for the technical details of the method). Nevertheless, the quantum Monte Carlo algorithm seems to be promising in studying of microscopical properties of CFs at non-zero temperature.

In this paper we mainly follow the line of the generalized lattice-gas model, whose peculiarities are expressed by Eq. (3).

The principal results of the paper are collected in Section III, while all the important spade-work is done in Section II and Appendixes. Section II starts with application of the linear programming method for selecting CFs of optimal lengths. But the method works reliably only at rather low temperatures when the contribution of the configurational entropy can be neglected. Then a more realistic situation is considered: The average lengths of chain and vacancy fragments are calculated as a function of oxygen filling in a chain vs temperature; the in-chain structure factor as well as the in-chain oxygen density-density
correlation functions are analysed. In Appendix B we represent the equations of statistical mechanics of the ensemble of CFs arranged orthorhombically by means of the distribution of CFs over their lengths. In Section III the interchain interaction is incorporated by means of the high-temperature expansion of the free energy. The final results are partly expressed in the analytical form (Section III), partly visualized after numerical calculations. They are presented in Section IV, which also includes the set of plots for some observable physical quantities, playing the role of the reference set.

Before starting the main part of the paper, let us introduce some definitions: $N_m$, the total number of chain fragments, consisting of $m+1$ Cu atoms and $m$ O atoms. It will be convenient, especially for further application to the statistical mechanics of the CF ensemble, to incorporate one of the vacant of oxygen Cu-Cu links, surrounding CF, to be certain, to the right, into it. These numbers and corresponding ”probabilities” $x_m = N_m / N_\ell$ satisfy the evident constraints:

$$\frac{1}{N_\ell} \sum_{m=0}^{\ell} (m+1) N_m = \sum_{m=0}^{\ell} (m+1) x_m = 1$$

and

$$S = \frac{1}{N_\ell} \sum_{m=0}^{\ell} N_m = \sum_{m=0}^{\ell} x_m = 1 - x$$

where $N_\ell$ is the total number of Cu atoms in a chain. $S$ is, evidently, the concentration of oxygen vacancies in a chain. Many experiments in YBCO have been performed at the fixed oxygen content: Because of a possibility for oxygen to fill the chains inhomogeneously one redefines Eq. (6) by taking a sum over the chains:

$$S = \frac{1}{N_{\text{ch}}} \sum_{\alpha} \sum_{m=0}^{\ell} x_m^{(\alpha)} = 1 - x$$

where $\alpha$ labels the chains and $N_{\text{ch}}$ is their total number.

II. IN-CHAIN DISTRIBUTION OF CFs OVER THE LENGTHS.

A. A hypothetical low-temperature case.

Using the intrinsic free energy of a CF, Eq. (3), let us elucidate an auxiliary problem, namely, what kind of CFs would be preferable if the configurational entropy as well as the interchain interaction were neglected. The free energy of the ensemble of non-interacting CFs (per one copper site) can be expressed as a linear function of the set \{$x_m$\}, which is also subjected to the linear constraints \(5\)-(\ref{eq:6}):

$$f = \sum_{m=1}^{\ell} m \phi(m) x_m = \sum_{m=1}^{\ell} (u - \tau \ln m) x_m,$$
where $u = \phi_2$, $\tau = T/2$. $f$ can be minimized by making use the linear programming method \[31\]. In the physics of the CF ensemble this procedure would reflect the properties of non-interacting constituents, ie, CFs, if they were supposed to be annealed at rather low temperature. Note, however, that such a case has no direct bearing on the YBCO behavior, because oxygen of deficient planes would be supposed to be frozen below $T_R$.

The linear programming theory says \[31\] that a function, $f$ in this case, will attain its minimum on a unique vertex of the convex polytope $P$ defined by constraints \(5\)-\(6\). Any vertex $[i,j]$ defined by Eqs.\(5\)-\(6\) can be represented by a pair of non-zero probabilities $(i < j)$:

$$x_i = \frac{(j + 1)(1 - x) - 1}{j - i}, \quad x_j = \frac{1 - (i + 1)(1 - x)}{j - i}, \quad x_m = 0 \text{ if } m \neq i, m \neq j \quad (9)$$

Certainly, not all the pairs are the candidates to be vertices, a true vertex of this particular problem is composed of two non-negative probabilities. This results in the following available set:

$$j > \kappa > i, \quad \kappa = \frac{1}{1 - x} - 1 = \frac{1 - S}{S} \quad (10)$$

True vertex $[i,j]$ defines $f\{i,j\}$, the function to be optimized, as follows:

$$f\{i,j\} = (1 - x) \left( u - \tau \left( \frac{\kappa - i}{j - i} \ln j + \frac{j - \kappa}{j - i} \ln i \right) \right) \quad (11)$$

It is proved in Appendix A that $f\{i,j\}$ attains the global minimum on the manifold of vertices, defined by Eq.\(1\) with $i$ and $j$ both non-zero, on unique vertex $[\kappa_-, \kappa_+]$ ($\kappa_\pm$ are the two nearest integers to $\kappa$):

$$f\{\kappa_-, \kappa_+\} = (1 - x) \left( u - \tau ((\kappa - \kappa_-) \ln \kappa_+ + (\kappa_+ - \kappa) \ln \kappa_-) \right) \quad (12)$$

However, Eq.\(12\) ignores the $[0,m]$ vertices: Although Eq.\(9\) is valid in this case also,

$$x_0 = 1 - \frac{m + 1}{m} x, \quad x_m = \frac{x}{m}; \quad m > \kappa,$$

the energy expression of Eq.\(8\) differs from the Eq.\(11\) form:

$$f\{0,m\} = \frac{\kappa}{m} (1 - x)(u - \tau \ln m); \quad m > \kappa \quad (13)$$

Formally, $f\{0,m\}$ as a function of a real variable $(m \to \mu)$ would achieve its minimum at

$$\mu = \exp(u/\tau + 1),$$

hence, one of the nearest integers to $\mu$, $\mu_-$ and $\mu_+\,$, is the true candidate to be the minimum point. To analyse what kind of oxygen arrangement in CFs is favorable we should compare two competing minima of Eqs.\(12\)-\(13\). Such an analysis is put into Appendix A and it says that the global minimum of the free energy $f$ is situated on the
[0, µ±] vertex if κ+ < µ and on the [κ−, κ+] vertex if κ− > µ. Switching over the vertices occurs at some µ between κ− and κ+.

Less rich is the information about ”vacancy fragments” (VF), ie, those pieces of the chains which are free of oxygen atoms. Nevertheless, one can define the average length of such VFs and express it in terms of the average length of CFs, 7, as

\[ \bar{\ell}_v = \frac{\sum_{k=0}^{\infty} N_k}{\sum_{k=1}^{\infty} N_k} = \frac{S}{S-x_0} = \frac{7}{\kappa} \approx \frac{\mu}{\kappa} \] (14)

Note, that there is a broad distribution of VFs over their lengths around µ/κ.

The conclusions of this subsection are applicable to the ensemble of non-interacting chain (and vacancy) fragments:

- If the oxygen content, x, is not close to 1, ie, in the moderate-κ case, the preferable length of CFs is determined by µ. The average length of VFs could be estimated as \( m_v \approx \mu/\kappa \).

- If κ+ exceeds µ, the average length of CFs is determined by κ. They are separated by single oxygen vacancies.

In the following sections the role of the configurational entropy will be revealed and the first conclusion of this subsection will be significantly revised.

B. The role of configurational entropy.

By the next step we incorporate the configurational entropy term into the free energy of a 1d chain. This will be done in order to estimate the average length of chain fragments, which is available in the neutron and X-ray diffraction studies (see [1–4]). A theoretical prerequisite is collected in Appendix B where the ”probability” set, \{x_m\}, is derived (recall, that the formulas below stand upon Eq.(3) (see also [24,25])):

\[ x_m = e^\Phi + \sum_{m=1}^{\sqrt{m} z^m} \sqrt{m} (m+1) z^m (m \geq 1) \] (15)

\[ x_0 = e^\Phi + \sum_{m=1}^{\sqrt{m} z^m} \sqrt{m} (m+1) z^m \] (16)

Certainly, constraint (3) is satisfied by Eqs.(15)-(16) where \( \Phi = \phi_2/T \). z plays the role of fugacity and could be determined from Eq.(3), rewritten in the following form:
We perform the summation over \( m \) by using substitution \( z = \exp -1/2m_0 \), assuming that \( m_0 \gg 1 \). Then, for example, in the main order one obtains

\[
\sum_{m=1}^{\infty} \sqrt{m} m^n z^m \rightarrow \sqrt{m_0} m_0^{n+1} \int_0^\infty dx x^n e^{-x/2} = \sqrt{2\pi} m_0^{n+1} (2n + 1)!!
\]

One may check by using the Poisson summation formula that the main order correction to Eq.(18) measured in the Eq.(18) units is expressed through Riemann’s zeta function,

\[
\frac{2}{(4\pi m_0)^{n+3/2}} \cos \left( \frac{n}{2}\pi + \frac{3}{4}\pi \right) \zeta (n + \frac{3}{2})
\]

and small at any \( m_0 \) of the real interest.

Following such a summation recipe we get from Eq.(17):

\[
S = \frac{e^\Phi + \sum_{m=1}^{\infty} \sqrt{m} m^n z^m}{e^\Phi + \sum_{m=1}^{\infty} \sqrt{m} (m + 1) z^m}
\]

Eq.(19) can be properly solved by substitution:

\[
m_0^{3/2} = \frac{1 - S}{S} \frac{e^\Phi}{3\sqrt{2\pi}}
\]

which assumes \( m_0^{3/2} \) to be neglected as compared to \( e^\Phi \) in the r.h.s. of Eq.(19). On the contrary, when \( S \ll 1 \), \( e^\Phi \ll m_0^{3/2} \) and the analogue of Eq.(20) reads

\[
m_0 = \frac{1}{3S}
\]

For the average length of CFs, \( \ell \), one assumes the following definition:

\[
\ell = \frac{\sum_{k=1}^{\infty} k \cdot N_k}{\sum_{k=1}^{\infty} N_k} = \frac{1 - S}{S - x_0}
\]

One may easily check

\[
\ell = 3m_0, \quad m_0 \gg 1
\]

independently of the \( S \)-range. The same estimate can be found after minimization of \( mx_m \) over \( m \). However, such a distribution is very broad, its half-width exceeds \( 2\ell \). This circumstance makes the situation significantly distinct of that discussed in subsection II.A.

The temperature dependence of \( \ell \) is exponential when \( S \) is not very close to 1:
\[ \ell = \left( \frac{1 - S}{3\sqrt{2\pi S}} \right)^{2/5} e^{2\Phi/5} \]  

(24)

and practically \( T \)-independent

\[ \ell = 1/S \]  

(25)

for \( S \) in a close vicinity of 1.

By using Eqs.(14),(16) and (13) the average length of VFs can be estimated as

\[ \ell_v = \frac{S}{S - x_0} = 1 + \frac{e^\Phi}{\sqrt{2\pi m_0}^{3/2}} \approx 1 + 3m_0 \frac{S}{1 - S} \]  

(26)

At \( S \ll 1 \) \( \ell_v \approx 1 \), otherwise \( \ell_v \approx 7S/(1 - S) \). This conclusion, concerning VFs, is similar to that of subsection II.A.

C. In-chain structure factor and density-density correlation functions.

Here we derive the equations and suggest the computational recipes of the in-chain correlations. Apart from the other values they allow to compute the in-chain irreducible averages which enter the high-temperature expansion of the free energy.

We start with a calculation of the Fourier components of the oxygen-oxygen correlation function, expressed through the distribution of CFs over their lengths in the following form:

\[ B(q) = S \left\{ \left( 1 - \frac{1}{S} \sum_{m=0}^\infty x_m e^{iq(m+1)} \right)^{-1} + c.c. \right\} - 1 \]  

(27)

In order to prove Eq.(27) one reminds a convention of the chain fragment definition: If \( \{m_1, m_2, m_3, \ldots \} \) is the sequence of lengths of the CFs, then the coordinates of oxygen vacant sites are \( \{m_1 + 1, m_1 + m_2 + 2, m_1 + m_2 + m_3 + 3, \ldots \} \). The Fourier component of the oxygen density (not averaged!) is simply

\[ g(q) = \sum_{n=1} \{ e^{iqn} - \{ e^{iq(m_1+1)} + e^{iq(m_1+m_2+2)} + \ldots \} \} \]  

(28)

The first sum in the r.h.s. of Eq.(28) is zero for any non-zero \( q \) and we omit it because the subject of interest is the irreducible averages. The probability to find a CF of the length \( m \) in the chain fragment ensemble is \( x_m / \sum_{k=0} x_k = x_m / S \). Averaging \( g(q) \) over the distribution of the CF lengths according to the auxiliary formula

\[ \langle e^{iqm} \rangle = \frac{1}{S} \sum_{m=0} e^{iqm} x_m \]  

one obtains:
\[ \langle g(q) \rangle = - \left( \left\{ e^{iq(m_1+1)} + e^{iq(m_1+m_2+2)} + \ldots \right\} \right) = -\frac{\frac{1}{S} \sum_{m=0} \left( e^{iq(m+1)} x_m \right)}{1 - \frac{1}{S} \sum_{m=0} e^{iq(m+1)} x_m} \] (29)

According to a definition the in-chain structure factor reads

\[ B(q) = \frac{1}{N_\ell} \left\langle \sum_{r_1, r_2} n_{r_1} n_{r_2} e^{iq(r_1-r_2)} \right\rangle = \frac{1}{N_\ell} \left\langle g(-q) g(q) \right\rangle = \left\{ e^{iq(m_1+1)} + e^{iq(m_1+m_2+2)} + \ldots \right\} \times \left\{ e^{-iq(m_1+1)} + e^{-iq(m_1+m_2+2)} + \ldots \right\} \] (30)

To evaluate Eq. (30) we introduce the auxiliary function:

\[ \Phi_k = \left\{ e^{iq(m_1+1)} + e^{iq(m_1+m_2+2)} + \ldots + e^{iq(m_1+m_2+\ldots+m_k+k)} \right\} \times \left\{ e^{-iq(m_1+1)} + e^{-iq(m_1+m_2+2)} + \ldots + e^{-iq(m_1+m_2+\ldots+m_k+k)} \right\} \] (31)

Let us define \( \xi = \langle e^{iq(m_1)} \rangle \). Evidently, \( |\xi| < 1 \) for not a regular distribution of CFs in a chain. Now \( \Phi_k \) can be rearranged as

\[ \Phi_k = \left( 1 + \xi + \ldots + (\xi^k)^{-1} \right) + \left( \xi + 1 + \xi + \ldots + (\xi^k)^{-2} \right) + \ldots + \left( \xi^k + \xi^{k-2} + \ldots + \xi + 1 \right) = k + (k-1)(\xi + \xi^*) + \ldots + (\xi^{k-1} + (\xi^*)^{k-1}) \]

\[ = k \left( \frac{1 - \xi^k}{1 - \xi} - \frac{1}{2} \right) + \frac{-\xi + k\xi^k - (k-1)\xi^{k+1}}{(1-\xi)^2} + c.c. \] (32)

Going to the \( k \to \infty \) limit according to the rule \( \lim_{N_\ell \to \infty} \frac{k}{N_\ell} = S \) we obtain

\[ B(q) = S \left( \frac{1}{1 - \xi} + \frac{1}{1 - \xi^*} - 1 \right) \]

which is simultaneously Eq. (27).

Value \( B(q=0) \) is a matter of interest, because it enters the thermally induced interaction terms of the high-temperature expansion of the second order (see Appendix B). A small-\( q \) expansion of \( B(q) \) yields a direct reminiscence to the Lorenzian shape of the structure factor:

\[ B(q) = S \left\{ \frac{Sx^{(2)}}{1 + \frac{q^2}{12} \left( 3x^{(2)} \right)^2 - 4x^{(3)} + \frac{x^{(4)}}{x^{(2)}}} - 1 \right\} \] (33)
\[ x^{(n)} = \sum_{m=0} m + 1 \] x^m \]

Hence,

\[ B(q \to 0) \to S(Sx^{(2)} - 1). \] (34)

This expression can be simply evaluated at \( S \ll 1 \). Actually, according to Eqs. (18), (21), (22)

\[ Sx^{(2)} = \frac{5!! \sqrt{2 \pi m_0^2 m_0^2}}{3!! \sqrt{2 \pi m_0^2 m_0^2}} = 5S m_0 = \frac{5}{3} \]

In this case \( B(q \to 0) \to 2S/3 \). It tends to increase with increasing \( S \):

\[ B(q \to 0) \to S^2 x^{(2)} \approx \frac{5S^2 (1 - S)}{m_0} \] (35)

where \( m_0 \) is supposed to be large and temperature dependent (see Eq. (24)).

The prefactor in the \( q^2 \)-term of Eq. (33) can be interpreted as the square of the in-chain correlation length, \( \lambda^2 \), (positive or negative!). So, after doing a simple, but tedious algebraic exercise, one obtains:

\[ |\lambda^2| = \left| \frac{25}{4} (1 - S)^2 - \frac{35}{3} (1 - S) + \frac{21}{4} \right| m_0^2 \] (36)

The interesting feature of Eqs. (33) and (36) is that the central peak at \( q = 0 \) splits when

\[ 1 - S > \frac{14 - \sqrt{7}}{15} \approx 0.757. \]

Evidently, the knowledge of \( B(q) \) allows to perform estimation of the irreducible density-density correlation function:

\[ \langle \langle n_m n_{m+r} \rangle \rangle = \langle n_m n_{m+r} \rangle - \langle n_m \rangle^2 = \int_{-\pi}^{\pi} \frac{dq}{2\pi} B(q)e^{iqr} \] (37)

Note that the important sum, \( \sigma(q) = S^{-1}e^{iq} \sum_{m=0} x_m e^{iqm} \), entering \( B(q) \), can be asymptotically evaluated in the case of oxygen-rich chains \( (m_0 \gg 1) \). It can be transformed in the Eq. (18) manner:

\[ \sigma(q) = e^{iq} \frac{1 + \sqrt{2\pi} e^{-\phi_m} m_0^{3/2} (1 - 2iqm_0)^{-3/2}}{1 + \sqrt{2\pi} e^{-\phi_m} m_0^{3/2}}, \] (38)

so, the general expression of \( B(q) \) takes the form:

\[ B(q) = S\alpha \frac{2(1 - u \cos \psi) + \alpha(1 - u^2)}{2(1 - \cos q)(1 + \alpha(1 + u \cos \psi)) + 2\alpha u \sin \psi \sin q + \alpha^2(1 + u^2 - 2u \cos(q + \psi))} \] (39)

where \( \alpha = \sqrt{2\pi} m_0^{3/2} e^{-\phi} \), \( u = (1 + 4q^2 m_0^2)^{-3/4} \) and \( \psi = \frac{3}{2} \arctan 2qm_0 \). One notes that by using Eq. (21) all the parameters, entering Eq. (33), can be expressed through \( m_0 \). Namely, \( \alpha = (1 - S)/(Sm_0) \) and small. In the \( S \to 0 \)-limit \( \alpha \) is no more small, on the contrary, \( \alpha \gg 1 \) and \( B(q) \) takes the form:

\[ B(q) = S \frac{1 - u^2}{1 + u^2 - 2u \cos(q + \psi)} \] (40)
III. STRUCTURE FACTOR OF INTERACTING CFs.

In the preceding section we were interested in the behavior of the chain fragment ensemble: First, in a hypothetical situation provided a thermal equilibrium of oxygen in a basal plane is available at rather low temperatures, second, in more realistic case when the configurational entropy is not neglected. The results obtained in the latter case seem to be reasonable as regards the in-chain correlation functions, although the interaction between the chains has been ignored. However, the role of such an interaction is important in many physical quantities which are sensitive to distinctions between Ortho-I and Ortho-II phases, such as concentration of holes leaving CFs, \( n_h \), concentration of paramagnetically active CFs, \( n_{pm} \), and so on. In this section we derive the formulas, describing that part of diffuse scattering caused directly by oxygen atoms and vacancies. We apply these formulas in numerical calculations, and visualize them in Section IV.

Treating the problem in terms of the set \( \{x_k\} \), we outline in Appendix B the method which incorporates the interaction between nearest chains into some scheme of statistical mechanics: This allows to determine the correlated set \( \{x^\alpha_k\} \), depending of the type of orthorhombic phase. The goal of this section is to develop a similar approach for correlation functions, in particular, for the irreducible part of the oxygen density-density correlation function. The latter is associated with the intensities of diffuse scattering due to a partial disorder in the CF ensemble:

\[
B(q) = \frac{1}{\mathcal{N}} \sum_{r_1, r_2} G(r_1, r_2) e^{i\mathbf{q} \cdot (r_1 - r_2)}
\]

where

\[
G(r_1, r_2) = \langle \langle n_{r_1} n_{r_2} \rangle \rangle = \langle n_{r_1} \rangle \langle n_{r_2} \rangle - \langle n_{r_1} n_{r_2} \rangle
\]

and \( \mathcal{N} = \mathcal{N}_i \mathcal{N}_ch \). It is evident, that for \( r_1 \) and \( r_2 \), both belonging to the same chain, the main order contribution into \( G(r_1, r_2) \) relates to the in-chain correlation function discussed in subsection II.C. Provided \( r_1 \) and \( r_2 \) are separated by \( n \) chains, the main order contribution appears to be

\[
G(\alpha, \mu_0; \alpha + n, \mu_n) = \left( -\frac{V_3}{T} \right)^n \sum_{m_0} \ldots \sum_{m_{n-1}} \langle \langle n^\alpha_{\mu_0} n^\alpha_{m_0} \rangle \rangle \langle \langle n^{\alpha+1}_{m_0} n^{\alpha+1}_{m_1} \rangle \rangle \ldots \langle \langle n^{\alpha+n}_{m_{n-1}} n^{\alpha+n}_{\mu_n} \rangle \rangle
\]

or, Eq.(43) can be read as

\[
G_{\alpha, n}(q_y) = \frac{1}{\mathcal{N} \mu_0 \mu_n} \sum_{\mu_0, \mu_n} G(\alpha, \mu_0; \alpha + n, \mu_n) e^{iq_y(\mu_0 - \mu_n)} = \left( -\frac{V_3}{T} \right)^n B_\alpha(q_y) B_{\alpha+1}(q_y) \ldots B_{\alpha+n}(q_y)
\]

As regards the Eq.(44) derivation we refer the reader to Appendix C. We use in Eq.(44) the \( y \) component of the wave vector following the convention about predominant orientation of chains along \( y \)-axis.
Let us perform summation in $B(q)$: For any separation $n$ between the chains the leading term of the order $(V_3/T)^n$ will be only kept.

The Ortho-I case is rather simple: All the elements $B_\alpha = B(q_\alpha)$ in Eq.(44) are $\alpha$-independent. Summation over all the elements $G_n(q_\alpha)$ in Eq.(41) yields:

$$B(q) = B \left\{ 1 + 2 \sum_{n=0}^{\infty} \cos nq_x \left( -\frac{V_3}{T} B \right)^n \right\} = B \left\{ \frac{1}{1 + \frac{V_3}{T} e^{iq_x B}} + \frac{1}{1 + \frac{V_3}{T} e^{-iq_x B}} - 1 \right\}$$

(45)

In the case of the Ortho-II phase the analogous expression is more complex ($B_\alpha$ alters from chain to chain, taking the values, say, $B_1(q_\alpha)$ and $B_2(q_\alpha)$ for oxygen-rich and oxygen-poor chains, respectively):

$$B(q) = \left\{ \frac{B_1 + B_2}{2} - 2 \frac{V_3}{T} B_1 B_2 \cos q_x + \left( \frac{V_3}{T} \right)^2 (B_1 + B_2) B_1 B_2 \cos 2q_x \right\}$$

$$-2 \left( \frac{V_3}{T} \right)^3 B_1^2 B_2^2 \cos 3q_x + \ldots \right\} = \left\{ \frac{B_1 + B_2}{2} - \frac{V_3}{T} e^{iq_x B_1 B_2} \cos \delta B \right\} + c.c. \right\} - \frac{B_1 + B_2}{2}$$

(46)

Anticipating the results of numerical calculations let us find the $B(q)$ shape in the Ortho-I phase in the vicinity of the Ortho-II Bragg peak ($\frac{1}{2} = \delta q_x, \delta q_y$): This point of the reciprocal space is a suitable candidate to be used in determination of correlation lengths along and across the chains. One simply checks that Eq.(45) can be written as

$$B(q) = B(\delta q_y) \frac{1 - \left( \frac{V_3 B(\delta q_y)}{T} \right)^2}{1 - 2 \frac{V_3 B(\delta q_y)}{T} \cos \delta q_x + \left( \frac{V_3 B(\delta q_y)}{T} \right)^2}$$

(47)

The correlation length across the chains is associated with the denominator in Eq.(47):

$$\lambda_x^2 = \frac{\frac{V_3 B(0)}{T}}{\left( 1 - \frac{V_3 B(0)}{T} \right)^2}$$

(48)

so, $\lambda_x^2$ is positively defined. The $\lambda_y^2$ expression can be also easily obtained from Eq.(47):

$$\lambda_y^2/\lambda^2 = \frac{2 \frac{V_3 B(0)}{T}}{1 - \left( \frac{V_3 B(0)}{T} \right)^2} + 1$$

(49)

For $\lambda^2$ see Eq.(36).

If $V_3 B(0)/T \ll 1$, ie, provided the high-temperature expansion holds, $\lambda_x$ is of the order of the lattice constant, whereas $\lambda_y \sim |\lambda| \sim m_0$. 14
IV. NUMERICAL CALCULATIONS.

Below some analytical results of the preceding section are visualized after numerical calculations. In order to make a selection of the fitting parameters for the theory presented above we refer to the plateau-like behavior of $n_h$ vs $x$ which should imitate the 60 K plateau of $T_c$ vs $x$ in YBCO. In Fig.3 the $n_h(x)$ dependence is shown at $V_2 = V_3 = 1$ and $T_q$, varying with interval 0.08 from 0.46 to 0.86, which seems a reasonable choice for interpretation of experimental facts. The regions of stabilities of Ortho-I and Ortho-II phases can be clearly distinguished in the set of curves of Fig.3. The curves, illustrating the monovalent copper amount vs $x$ are shown in Fig.4. À propos, monovalent copper atoms occupy 2-fold coordinated sites, which are out of CFs. This quantity, $n_{2\text{-}\text{fold}}$, is certainly not in a contradiction with the experimental data of Refs [21,22]. Closely related to $n_{2\text{-}\text{fold}}$ are the concentrations of copper ions in 3- and 4-fold coordinated positions, ie, copper atoms at the ends of CFs and within them, respectively (see Figs.5,6). According to [22] the information about distribution of copper atoms in differently coordinated positions can be obtained in NQR experiments. The quantity, which also reflects the structural peculiarities of the Ortho-I and Ortho-II phases, is the average length of chain fragments shown in Fig.7. The last physical quantity of the reference set available for checking experimentally could be the concentration of paramagnetically active chain fragments, $n_{pm}$. The theoretical curves have typical forms shown in Fig.8. The experimental research program, employing the polarized neutron technique is in the beginning (see Ref. [26]). Also the concentration of paramagnetic CFs at low temperatures could be measured due to the Shottky effect. Below we give shortly the explanations of how the afore-said concentrations can be evaluated in the frame of the generalized lattice-gas model.

A. Concentration of holes quitting the chains.

The general expression of the concentration of holes transferred from chains has a form:

$$n_h = \frac{1}{2} \sum_{n=1}^{\infty} \sum_{m=0}^{n} (m - 1) \frac{x_n \Pr(n,m)}{\langle x_n \rangle}$$  \hspace{1cm} (50)

Factor $\frac{1}{2}$ enters the equation because one oxygen deficient plane supplies holes into two CuO$_2$ planes. Function $\Pr(n,m)$ is the probability for a chain fragment of the length $n$ to have $m$ O$^{2-}$ ions within and can be obtained in the frame of some strongly correlated model. Here we accept a simplified consideration according to which the most probable configuration has to be substituted Eq.(50). For very long chains the most probable $m$ at fixed $n$ is simply $\xi n$, where $\xi = \lim_{n \to \infty} \xi_n$. Although for shorter chain fragments the relationship between $m$ and $n$ is more delicate, it could be approximately expressed as
\[
m(n) \approx \text{nint}(\xi n)
\]

where function \text{nint} denotes the nearest integer number. So, in this case we rewrite Eq. (50) as follows:

\[
n_h = \frac{1}{2} \sum_{n=1}^{n} (\text{nint}(\xi n) - 1) \langle x_n \rangle
\]

B. Concentration of paramagnetically active CFs.

Again, starting with some microscopical model for a finite CF characterized by \( n \) and \( m \), one obtains, in principle, the average value of \( \vec{S}^2 \). To simplify the scheme (see also Ref. [24]) we first recall that there is no charge transfer from short chain clusters with one or two oxygen atoms, both are spin-singlet fragments. For a cluster of three oxygen atoms, \( n = 3 \), a spin-1/2 state forms, contributing to the paramagnetic Curie constant. On the other hand, for \( n = 4 \), one expects again a singlet state, because the most probable is the \( m = 3 \) state. In the longer clusters, \( n \geq 5 \), singlet and doublet states occur with roughly the same probability, at sufficiently high temperatures. So, the paramagnetic Curie constant is proportional to the concentration of paramagnetically active CFs, \( n_{pm} \), which may be approximated by

\[
n_{pm} = \langle x_3 \rangle + \frac{1}{2} \sum_{n=5}^{n} \langle x_n \rangle
\]

C. Cu\(^{+}\) amount.

The experiments [21,22] were very important for understanding of the charge transfer mechanism in YBCO. Because only those copper site which are surrounded by oxygen vacancies give a contribution into the monovalent copper amount, their concentration coincides with \( \langle x_0 \rangle \).

D. Average lengths of CFs and concentrations of Cu atoms in 3- and 4-fold coordinations.

Acceptable in applications to the Ortho-II phase are the formulas given below and expressed by means of the \( x_0 \) values:

\[
\overline{\ell}_c = \frac{x^{(c)}}{S^{(c)} - x_0^{(c)}}
\]

where \((c)\) relates to either rich \((r)\) or poor \((p)\) chains; their average characteristic takes a form:
\[ \bar{\ell} = \frac{x}{S - \langle x_0 \rangle} \]  
\hspace{1cm} (54)

Noting that \( 2(N_1 + N_2 + \ldots) \) is the amount of copper in the 3-fold coordination in a chain, one easily obtains \( n_{3\text{-fold}} \)

\[ n_{3\text{-fold}} = 2 - 2x - 2\langle x_0 \rangle. \]  
\hspace{1cm} (55)

\( n_{4\text{-fold}} \) can be simply derived due to a sum rule:

\[ n_{4\text{-fold}} = 1 - n_{2\text{-fold}} - n_{3\text{-fold}} = 2x - 1 + \langle x_0 \rangle. \]  
\hspace{1cm} (56)

E. Structure factor: Diffuse scattering on the CF ensemble.

Figs.9(a-f) illustrate a diffuse part of the structure factor calculated numerically according to the scheme developed in this paper. Remind, that this part is due to structural imperfections in the \( \text{CuO}_x \) plane. The fitting parameters, \( \tilde{V}_2 \) and \( V_3 \), are common with the values used for the plots in Figs.3-8. Calculations were performed at \( T_q = 0.62 \): Figs.3-8 also include the curves relating to this temperature.

The following features of the structure factor shape are necessary to be mentioned:

- Its value enhances on the Brillouin zone boundary, \( (\pm 1/2, q_y) \) (in units of \( 2\pi \)), it reflects a tendency for a system to be arranged as a double period structure on a short wavelength scale. This fact would become especially pronounced if the Ortho-I phase were forced to substitute a true Ortho-II phase – in this case a short-range oxygen atom – oxygen vacancy correlation across the chain should be significant.

- The Ortho-I phase exhibits a clear down-fall behavior of the structure factor in the \( (\pm 1/2, 0) \) points of the reciprocal space. This reminds a central peak splitting discussed in subsection II.C.

- The maximum diffuse scattering intensity is displayed in the vicinity of the Ortho-I–Ortho-II phase transition.

V. CONCLUSIVE REMARKS AND SUMMARY.

This paper is devoted to the correlations in the oxygen deficient planes which are the important structural elements of HT superconductors, \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) and related compounds.

There were many experiments performed to reveal the fascinating properties of such compounds. Some of them are quoted in this paper in connection with superstructure
formations, charge transfer mechanism, magnetic behavior of CFs. There were also many attempts to describe CuO$_x$ planes theoretically. Many of them invoked into consideration the oxygen subsystem only. We already mentioned the conventional lattice-gas approach [4,15-18]: the approach based on the screened Coulomb potential [33] has been also applied to the oxygen subsystem in order to explain some hypothetical superstructures. The model utilized in this paper looks as generalization of the lattice-gas model (see also [24]), but the role of copper in formation of alternating Cu-O CFs and charge transfer mechanism is not ignored.

The statement, utilized in this paper, concerns the copper-oxygen chain fragments: Many phenomena in YBCO are caused by them. The function of the CF ensemble to control the YBCO behavior is closely connected with the charge transfer which could be conditionally subdivided into two parts: the intrachain charge redistribution and that one from chains onto CuO$_2$ planes. The former is the oxidation of monovalent Cu ions, forming the CFs, to the bivalent state According to this process almost all oxygen atoms in not very short Cu-O CFs would be subjected to transformation into the monovalent state where it not for the hole transfer to outside: Around 30% of oxygen atoms in chains persist their monovalency, the rest oxygen constituents appear to be in the bivalent state [19]. It is noteworthy, that the distribution of oxygen valencies is neither frozen, nor ordered in any charge density superstructure, but due to strong $p$-$d$ hybridization oxygen holes form strongly correlated systems of finite lengths as discussed in [20].

According to the detailed investigation by Jorgensen et al [23] of the orthorhombically arranged CuO$_x$ planes the concentration of oxygen atoms in "wrong" O(5) positions is negligibly small up to rather high temperature $\sim 600^\circ$C. The situation reminds the soft matter: Cu-O fragments behave as long molecules strongly oriented and weakly correlated to each other in chains.

Any oxygen migration stops approximately at and below room temperature. So, this circumstance does not allow to appear those CF structures whose existence could be a result of a simple energy competition. Actually, distribution described by Eq.(15) has a maximum at $m_0$, but its width is of the order $2m_0$, hence, the role of the entropy becomes decisive.

Below we resume the method and results presented in the paper.

- The principal variables over which the statistical averaging can be done are the probabilities, $\{x^\alpha_m\}$.

- The broad distribution of CFs around $3m_0$ (see Eq.(23)) can be utilized for calculation of such quantities as the hole transfer from chains, concentration of paramagnetically active chain fragments, the monovalent copper amount, etc. They evidently depend on the oxygen content, $x$, and quenching temperature, $T_q$.  

18
• The in-chain structure factor can be used for interpretation of the diffuse scattering results in the Ortho-I phase. Splitting of the 1d central peak could be a counterpart of the analogous splitting of the diffuse maximum on the Brillouin cell boundary, \((\pm 1/2, 0)\).

• Oxygen-oxygen correlations in the basal plane are illustrated in Figs 9. The maximum of diffuse scattering corresponds to the Ortho-II-to-Ortho-I transition concentration.

• Measurements of the correlation length along the chains can be employed for experimental determination of effective coupling constants.

The message of this work is clearly addressed to those experimentalists whose field of interests lies in atomic and magnetic correlations in YBCO and related compounds. Neutron and X-ray studies seem to be the most appropriate technique for this. Nevertheless, the method developed in the paper is possible for evaluation of thermodynamical quantities, such as, isothermical susceptibility, Shottky anomaly, etc.

Acknowledgement.

I thank the Léon Brillouin Laboratory at Saclay for its hospitality during the initial stage of this work. I keep in my memory a deep interest to the problem by J.Rossat-Mignod, deceased last August. I thank also V.Plakhty, L.-P.Regnault and J.Schweizer for the discussions which gave rise to this work.

I want to acknowledge Prof. J.Zittartz for his kind invitation to visit the Institute for Theoretical Physics at the Cologne University where the work has been completed.
Appendix A.

Taking the formal derivatives of $f\{i,j\}$ (see Eq.(12)) over $i$ and $j$ we get

$$\frac{\partial f\{i,j\}}{\partial j} = -\tau(1-x) \frac{\kappa - i}{(j-i)^2} \left( \frac{j-i}{j} - \ln \frac{j}{i} \right)$$  \hspace{1cm} (A.1)

$$\frac{\partial f\{i,j\}}{\partial i} = -\tau(1-x) \frac{j - \kappa}{(j-i)^2} \left( \frac{j-i}{i} - \ln \frac{j}{i} \right)$$  \hspace{1cm} (A.2)

Substituting $z = i/j < 1$ we notice that the sign of derivative (A.1) coincides with the sign of expression $z^{-1} - 1 - \ln z$ and positive. Let $i$ be fixed, hence, $f\{i,j\}$ approaches the minimum as a function of $j$ at the greater nearest integer to $\kappa$, say, $\kappa_+$. The same substitution makes the sign of derivative (A.2) identical to the sign of expression $1 - \ln z^{-1}/z$ which is negative.

The minimum of $f\{i,j\}$ as function of $i$ is situated at the lower nearest integer to $\kappa$, say, $\kappa_-$. Hence, $f\{i,j\}$ attains the global minimum on the manifold of vertices, defined by Eq.(9) with $0 < i < j$, on unique vertex $[\kappa_-, \kappa_+]$. In order to search, what kind of vertex, $[\kappa_-, \kappa_+]$ or $[0, m]$, will be realized as a proper one, we start with the case $\kappa_- > \mu = \exp(1 + u/\tau)$. Functions

$$f_1 = u - \tau((\kappa - \kappa_-) \ln \kappa_+ + (\kappa_+ - \kappa) \ln \kappa_-) \text{ and } f_2 = \frac{\kappa}{m}(u - \tau \ln m)$$

differ from those of Eqs.(12) and (13) by a common multiplier. Because in this case $m = \kappa_+$ is optimal for $f_2$ (see Eq.(13)),

$$f_1 - f_2 = u \left( 1 - \frac{\kappa}{\kappa_+} \right) - \tau \left( (\kappa - \kappa_-) \ln \kappa_+ + (\kappa_+ - \kappa) \ln \kappa_- - \frac{\kappa}{\kappa_+} \ln \kappa_+ \right)$$

$$= \tau \frac{\kappa_+ - \kappa}{\kappa_+} (\ln \mu - 1 - \kappa_+ \ln \kappa_- - \kappa_+ \ln \kappa_+)$$  \hspace{1cm} (A.3)

appears to be negative and favors the $[\kappa_-, \kappa_+]$ vertex. When deriving Eq.(A.3) we used the relation $\ln \mu = u/\tau + 1$. Contraversal, if $\kappa_+ < \mu$ we substitute $f_2$ by $\bar{f}_2$:

$$f_2 \rightarrow \bar{f}_2 = \frac{\kappa}{\kappa_+}(u - \tau \ln \kappa_+) \geq f_2$$

Then

$$f_1 - f_2 \geq f_1 - \bar{f}_2 = \tau \frac{\kappa_+ - \kappa}{\kappa_+} (\ln \mu - 1 - \kappa_+ \ln \kappa_- - \kappa_+ \ln \kappa_+) > 0$$  \hspace{1cm} (A.4)

To complete the proof we consider the last possibility, $\kappa_- < \mu < \kappa_+$. Again $\kappa_+$ substitutes for $\mu$ and the sign of $(f_1 - f_2)$ coincides with the r.h.s. of Eq.(A.3) which turns to zero at

$$\mu \approx \kappa_- + \frac{1}{2} - \frac{5}{24\kappa_-}, \kappa_- \gg 1$$
Appendix B.

Deriving the equations of statistical mechanics for oxygen in a deficient plane we suppose:

- A negligible probability for oxygen to occupy a position across the chains;
- The largest energy contribution comes from the interchain degrees of freedom;
- Apart from the entropy contribution to the total energy of the CF ensemble we take into account the oxygen-oxygen repulsion on the nearest chains, like in the lattice-gas model (cf. [3, 5, 11, 18]).
- The constraint used is the total oxygen content, $x$ (see Eq.(7)).

As regards the second supposition it denotes a preferable role of strong fermionic correlations within ...Cu-O-... chain fragments as compared with interchain interactions which are effectively screened in the metallic state of YBCO. The oxygen ordering in deficient planes reminds the soft matter case, e.g., the nematic liquid crystal. Whereas the CFs weakly correlate to each other they are strongly coupled from inside and preferably oriented in chains.

Let \( \{N_0^\alpha, N_1^\alpha, N_2^\alpha, \ldots, N_k^\alpha, \ldots\} \) be the total numbers of CFs of various lengths (for their definitions see the beginning of Section II) in the $\alpha$-th chain. A complete number of different configurations of all those CFs has a form usual for a mixture of ideal gases:

\[
\frac{(N_0^\alpha + N_1^\alpha + N_2^\alpha + \ldots + N_k^\alpha + \ldots)!}{N_0^\alpha!N_1^\alpha!N_2^\alpha!\ldots N_k^\alpha!\ldots} \quad (B.1)
\]

Before giving a definition of the partition function of the CF ensemble in the oxygen deficient plane let us omit for a while the $V_3$-term and consider the auxiliary partition function, $Z_0^\alpha$, of the $\alpha$-th chain with two constraints imposed: (5) and (6). Playing the role of the Lagrange multiplayers are the chemical potentials, $\mu^\alpha$ and $\mu_0^\alpha$, conjugated to the above mentioned constraints. With such a prerequisite $Z_0^\alpha$ takes a form:

\[
Z_0^\alpha = \sum_{\{x_k^\alpha\}} \exp \left\{ N_\alpha \ln S_\alpha - \sum_{m=0}^\alpha x_m^\alpha \ln x_m^\alpha - \frac{1}{T} \sum_{m=1}^\alpha \mu^\alpha \phi(m)x_m^\alpha + \frac{\mu_0^\alpha}{T} \sum_{m=0}^\alpha (m+1)x_m^\alpha - \frac{\mu_0^\alpha}{T} S_\alpha \right\} = \sum_{\{x_k^\alpha\}} \exp A^\alpha(\{x_k^\alpha\}) \quad (B.2)
\]

where summation runs over the possible distribution of CF lengths, $A^\alpha(\{x_k^\alpha\})$ is the corresponding ”action“.
The equilibrium distribution of "probabilities" \( \{x_k^\alpha\} \) achieves at the maximal "action" and can be expressed as follows:

\[
x_k^\alpha = \frac{e^{-k(\phi(k)-\mu^\alpha)/T}}{\sum_{m=0}^{\infty} (m+1)e^{-m(\phi(m)-\mu^\alpha)/T}}
\]

(B.3)

\[
S^\alpha = \frac{\sum_{m=0}^{\infty} e^{-m(\phi(m)-\mu^\alpha)/T}}{\sum_{m=0}^{\infty} (m+1)e^{-m(\phi(m)-\mu^\alpha)/T}}
\]

(B.4)

In principle, \( \mu_0^\alpha \) can be also expressed through \( \mu^\alpha \):

\[
e^{\mu_0^\alpha/T} = e^{\mu^\alpha/T} \sum_{m=0}^{\infty} e^{-m(\phi(m)-\mu^\alpha)/T}
\]

(B.5)

So, any \( Z_0^\alpha \) can be considered as a function of \( \mu_0^\alpha \). Substituting \( \phi(k) \) in Eqs. (B.3)-(B.4) by its approximation of Eq. (3) one obtains functions (15)-(17).

Let us include the \( V_3 \)-term into consideration:

\[
Z = \prod_{\{x_k^\alpha\}} e^{A^\alpha(\{x_k^\alpha\})} \zeta^{\alpha,\alpha+1}, \quad \zeta^{\alpha,\alpha+1} = \exp \left( -\frac{V_3}{T} \sum_{m=0}^{\infty} n_i^\alpha n_{i+1}^\alpha \right)
\]

(B.6)

Then it is suitable to expand \( \zeta^{\alpha,\alpha+1} \) over the cumulants. Such a scheme is well-known and we only outline it below (\( \eta = \prod_\alpha \zeta^{\alpha,\alpha+1} \)):

\[
Z = \sum_{\{x_k^\alpha\}} \ldots \eta = \sum_{\{x_k^\alpha\}} \ldots \left( 1 + \eta + \frac{1}{2} \eta^2 + \ldots \right) = Z_0 \left( 1 + \langle \eta \rangle_0 + \frac{1}{2} \langle \eta^2 \rangle_0 + \ldots \right)
\]

where \( \langle \ldots \rangle_0 \) an average over the ensemble of non-interacting chains, \( Z_0 = \prod_\alpha Z_0^\alpha \). For example,

\[
\langle \eta \rangle_0 = -\frac{N_i V_3}{T} \sum_\alpha n_i^\alpha n_{i+1}^\alpha.
\]

The expectation values, entering the \( \langle \eta \rangle_0 \)-term of the high-temperature expansion, can be expressed through the \( S \)-values, supposed to be known:

\[
\sum_\alpha n^\alpha n_{\alpha+1} = \sum_\alpha n^\alpha n_{\alpha+1} = \sum_\alpha (1 - S^\alpha)(1 - S_{\alpha+1}) = (2x - 1)N_{ch} + \sum_\alpha S^\alpha S_{\alpha+1}
\]

\( \langle \eta^2 \rangle_0 \) consists of the expectation values of the forth order, \( n_i^\alpha n_{i+1}^\alpha n_j^\beta n_{j+1}^\beta \), which completely decouple if \( \beta > \alpha + 1 \) or \( \beta < \alpha - 1 \). Also,

\[
\frac{n_i^\alpha n_{i+1}^\alpha n_j^\beta n_{j+1}^\beta}{n_{i+1}^\alpha n_{j+1}^{\beta+1}} \to \frac{n_i^\alpha n_{i+1}^\alpha}{n_{i+1}^{\alpha+1}} \left( n^\alpha_2 + \langle \langle n_i^\alpha n_{j}^\beta \rangle_0 \rangle \right)
\]

(B.7)
where
\[ \langle \langle n^\alpha_i n^\alpha_j \rangle \rangle_0 = n^\alpha_i n^\alpha_j - n^\alpha_i^2 \]  \tag{B.8}

According to a definition \( \langle \langle n^\alpha_i n^\beta_j \rangle \rangle_0 \equiv 0 \) at \( \alpha \neq \beta \). Note, that Eq. (B.8) is invariant under the oxygen atom \( \leftrightarrow \) oxygen vacancy transformation \( (n^\alpha_m \leftrightarrow 1 - n^\alpha_m) \).

There is another non-trivial contribution of the \( n^2 \)-term:
\[ \overline{n^\alpha_i n^\alpha_{i+1} n^\alpha_j n^\alpha_{j+1}} \rightarrow \left( n^\alpha_i^2 + \langle \langle n^\alpha_i n^\alpha_j \rangle \rangle_0 \right) \left( n^\alpha_{i+1}^2 + \langle \langle n^\alpha_{i+1} n^\alpha_{j+1} \rangle \rangle_0 \right) \]  \tag{B.9}

All the decoupled terms, coming from all the orders of the high-temperature expansion, can be recollected into
\[ \exp \left( -\frac{N_i V_3}{T} \sum_{\alpha} S^\alpha S^{\alpha+1} \right) . \]  \tag{B.10}

The terms \( \langle \langle n^\alpha_i n^\alpha_j \rangle \rangle_0 n^\alpha_i n^\alpha_{i+1} \) (see Eq. (B.7)) give rise a thermally induced interaction of the next-to-nearest chains. The recollected contribution of Eq. (B.10) is of the main order in the \( V_3/T \) expansion: It formally corresponds to the mean-field approach. The \( V_3 \)-exponential term (Eq. (B.10)) simply contributes \( Z_0 \) and does not formally influence on Eqs. (B.3)-(B.4), but Eq. (B.5) changes its form
\[ e^{\mu_0/T} = e^{\mu^\alpha/T} \sum_{m=0} \exp \left( -\frac{m(\phi(m) - \mu^\alpha)}{T} \right) \exp \left( -\frac{V_3(S^\alpha - S^{\alpha-1})}{T} \right) \]  \tag{B.11}

It is noteworthy, that Eq. (B.11) is a system of non-linear equations which couple the densities of oxygen vacancies in nearest chains. Actually, \( S^\alpha = S^\alpha(\mu^\alpha) \) (see Eq. (B.4)), hence, the r.h.s. of Eq. (B.11) is some function of \( S^{\alpha-1}, S^\alpha, S^{\alpha+1} \), whereas the l.h.s. of Eqs. (B.11) does not depend of index \( \alpha \) and contains the function of the global chemical potential, \( \mu_0 \), conjugated to the global density of oxygen atoms (vacancies).

Appendix C.

The correlation function entering the r.h.s. of Eq. (12) can be expressed through the partition function of non-interacting chains, \( Z_0 \), as follows:
\[ \langle n_{r_1} n_{r_2} \rangle = \sum_{\{x_k\}} Z_0 \exp \left( -\frac{V_3}{T} \sum_{\alpha,i} n^\alpha_i n^{\alpha+1}_i \right) = \]  
\[ \sum_{\{x_k\}} Z_0 \exp \left( -\frac{V_3}{T} \sum_{\alpha,i} n^\alpha_i n^{\alpha+1}_i \right) = 23 \]
\[
\langle n_{r_1} n_{r_2} \rangle_0 - \frac{V_3}{T} \sum_{\alpha, i} \langle n_{r_1} n_{r_2} n_{i}^{\alpha} n_{i}^{\alpha + 1} \rangle_0 + \frac{V_3^2}{2T^2} \sum_{\alpha, i} \sum_{\beta, j} \langle n_{r_1} n_{r_2} n_{i}^{\alpha} n_{i}^{\alpha + 1} n_{j}^{\beta} n_{j}^{\beta + 1} \rangle_0 + \ldots \\
= \frac{1 - \frac{V_3}{T} \sum_{\alpha, i} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} \rangle_0 + \frac{V_3^2}{2T^2} \sum_{\alpha, i} \sum_{\beta, j} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} n_{j}^{\beta} n_{j}^{\beta + 1} \rangle_0 + \ldots}{1 - \frac{V_3}{T} \sum_{\alpha, i} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} \rangle_0 + \frac{V_3^2}{2T^2} \sum_{\alpha, i} \sum_{\beta, j} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} n_{j}^{\beta} n_{j}^{\beta + 1} \rangle_0 + \ldots} \quad (C.1)
\]

In order to deal with irreducible averages one needs the \( \langle n_r \rangle \) definition:

\[
\langle n_r \rangle = \frac{\sum_{\{x_i\}} Z_0 n_r \exp \left( -\frac{V_3}{T} \sum_{\alpha, i} n_{i}^{\alpha} n_{i}^{\alpha + 1} \right)}{\sum_{\{x_i\}} \exp \left( -\frac{V_3}{T} \sum_{\alpha, i} n_{i}^{\alpha} n_{i}^{\alpha + 1} \right)} = \\
\langle n_r \rangle_0 - \frac{V_3}{T} \sum_{\alpha, i} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} \rangle_0 + \frac{V_3^2}{2T^2} \sum_{\alpha, i} \sum_{\beta, j} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} n_{j}^{\beta} n_{j}^{\beta + 1} \rangle_0 + \ldots \\
= \frac{1 - \frac{V_3}{T} \sum_{\alpha, i} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} \rangle_0 + \frac{V_3^2}{2T^2} \sum_{\alpha, i} \sum_{\beta, j} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} n_{j}^{\beta} n_{j}^{\beta + 1} \rangle_0 + \ldots}{1 - \frac{V_3}{T} \sum_{\alpha, i} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} \rangle_0 + \frac{V_3^2}{2T^2} \sum_{\alpha, i} \sum_{\beta, j} \langle n_{i}^{\alpha} n_{i}^{\alpha + 1} n_{j}^{\beta} n_{j}^{\beta + 1} \rangle_0 + \ldots} \quad (C.2)
\]

It has been known since the beginning of sixties [34] that in Ising-like systems a correlation function can be expressed as a power series over irreducible averages, the so-called cumulants. A true expansion must only contain connected diagrams. In our particular problem the interaction involves atoms of nearest chains, hence, a series expansion of the irreducible average, \( \langle n_{i}^{\alpha} n_{j}^{\alpha + n} \rangle \), starts with a term proportional to \( (V_3/T)^n \):

\[
\langle n_{i}^{\alpha} n_{j}^{\alpha + n} \rangle = \left( \frac{V_3}{T} \right)^n \sum_{m_1} \langle n_{i}^{\alpha} n_{m_1}^{\alpha} \rangle_0 \sum_{m_2} \langle n_{m_1}^{\alpha + 1} n_{m_2}^{\alpha + 1} \rangle_0 \cdots \sum_{m_n} \langle n_{m_n}^{\alpha + n} n_{j}^{\alpha + n} \rangle_0 \quad (C.3)
\]
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Figure Captions.

Figure 1. The structural phase diagram is shown qualitatively. The bottom is confined by room temperature, $T_R$: Below $T_R$ oxygen is practically frozen. Probably the Tetra-to-Ortho-II phase transition is of the 1st order and the $T-x$ phase diagram contains the phase separation area. Hypothetically, the superstructures of longer periodicities, like Ortho-III, could appear between Ortho-II and Ortho-II areas.

Figure 2. The lattice-gas model definition, involving the oxygen-oxygen interactions only (circles and crosses are for oxygen and copper atoms, respectively).

Figure 3. $n_h$ vs $x$: Six curves are shown for the equidistant set of quenching temperatures,
from 0.46 to 0.86; \( \tilde{V}_2 = V_3 = 1 \); The higher temperature, the smaller \( n_h \).

**Figure 4.** \( n_{\text{Cu}^+} (n_{2\text{-fold}}) \) vs \( x \): Six curves are shown for the equidistant set of quenching temperatures, from 0.46 to 0.86; \( \tilde{V}_2 = V_3 = 1 \); The higher temperature, the smaller \( n_{2\text{-fold}} \).

**Figure 5.** \( n_{3\text{-fold}} \) (copper in 3-fold coordination) vs \( x \): Six curves are shown for the equidistant set of quenching temperatures, from 0.46 to 0.86; \( \tilde{V}_2 = V_3 = 1 \); The higher temperature, the larger \( n_{3\text{-fold}} \).

**Figure 6.** \( n_{4\text{-fold}} \) (copper in 4-fold coordination) vs \( x \): Six curves are shown for the equidistant set of quenching temperatures, from 0.46 to 0.86; \( \tilde{V}_2 = V_3 = 1 \); The higher temperature, the smaller \( n_{4\text{-fold}} \).

**Figure 7.** Average length of CFs: \( \ell \) (solid curves), \( \ell_r \) (dashed curves), \( \ell_p \) (dotted curves); \( \tilde{V}_2 = V_3 = 1; T_q = 0.46, 0.62, 0.78 \). The higher temperature, the smaller \( \ell \)’s.

**Figure 8.** \( n_{\text{pm}} \) vs \( x \): Six curves are shown for the equidistant set of quenching temperatures, from 0.46 to 0.86; \( \tilde{V}_2 = V_3 = 1 \); The higher temperature, the larger \( n_{\text{pm}} \).

**Figure 9.** The structure factor, \( B(q) \), as defined in the text. \( \tilde{V}_2 = V_3 = 1; T_q = 0.62 \); Oxygen content changes equidistantly from \( x = 0.45 \) (a) to 0.95 (f). Chain orientation is supposed along the \( y \)-axis.