

Could the oxygen superstructure in $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$ exist?

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In order to explain why the real superstructure in the basal plane of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ at $x \approx 0.35$ can exist and be observed experimentally, it is necessary to invoke simple electrostatic and charge transfer mechanisms. The numerical estimates support the assumption that the superstructure [proposed by D. Hohlwein *et al.*, Phys. Rev. Lett. **66**, 1497 (1991); Z. Phys. **B86**, 11 (1992)], which is formed by very short Cu–O–Cu chain fragments, can co-exist with the tetragonal phase which consists of short fragments arranged spatially at random.

The possibility of the existence of the real superstructure in the oxygen-deficient planes in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x \approx 0.35$ is one of the problems of the YBCO family of the high- T_c materials. Until now, it has been neither reliably theoretically explained nor regularly experimentally reproduced. The Bragg reflections due to the superstructure were experimentally observed and recently interpreted in Refs. 1 and 2. In Fig. 1 we schematically reproduce the superstructure (orthorhombic) proposed in Ref. 2. Below we refer to it as superstructure-I (s-I). It consists of very short Cu–O–Cu chain fragments arranged in a rather close configuration with the local oxygen content $x = 0.5$. This is unusual in view of the current experimental and theoretical experience: Oxygen atoms in the deficient plane [Cu(1)] are commonly believed either to be arranged in the linear ...–Cu–O–... chain fragments (orthorhombic structure) or to be randomly distributed between the so-called O(4) and O(5) sites (tetragonal state). The tetragonal behavior is typical for small x ($x < 0.3$): The interpretation of x-ray absorption spectroscopy measurements^{3,4} supports the oxygen arrangement in rather short, predominantly Cu–O–Cu chain fragments. When x is larger than 0.4, the filling of O(5) sites is negligible as compared with the filling of O(4) sites.⁵ Orthorhombicity is formed by the straight pieces of Cu–O–...–O–Cu chains. The orthorhombic state in the x range between 0.4 and 0.7 in the samples prepared by the slow-cooling technique (the so-called ortho-II phase with a double-cell periodicity across the chains) is probably not a real superstructure, because the correlation lengths along the chains and across them do not exceed 20–25 and 10–15 lattice constants, respectively⁶ (cf. Ref. 7). The (tetragonal phase)–(orthogonal phase-II) transition is believed to be driven by the effective attraction of oxygen ions in a linear coordination mediated by one copper ion between them. Such a mechanism of a chain fragment formation is due to the strong hybridization of p - and d -orbital wave functions of oxygen and copper, respectively. It could be interpreted in terms of the lattice–gas model with only few

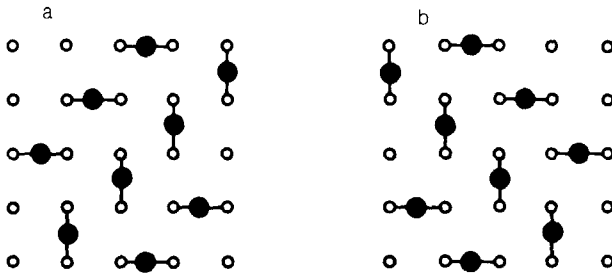


FIG. 1. Centered orthorhombic (herringbone) configurations of the chain fragments (proposed in Ref. 2); open and filled circles denote copper and oxygen atoms, respectively.

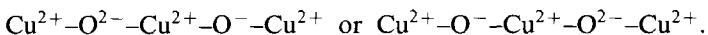
short-range coupling constants: Apart from the attraction mentioned above, there is the strong repulsion of oxygen atoms in the “corner” configurations (oxygen nearest neighbors) and also rather moderate repulsion between oxygen atoms on the opposite links of the elementary Cu–O plaquette (see Ref. 8 and the references cited there). Certainly, the s-I is in clear contradiction with the lattice–gas model description. In order to understand why such a superstructure could be stable and even competitive with the in-chain arrangement, we will briefly discuss the “intrachain” charge transfer (CT).

The CT mechanism in YBCO, as discussed in Refs. 9 and 10, can be divided into two parts. The first part is associated with the intrachain CT; i.e., the neutral oxygen, which occupies the vacant place between two copper sites, accepts two electrons if the two copper ions are in the monovalent state. This process is accompanied by a copper valence transformation which results in bivalent states of both copper ions. Such a process is dominant when x is small, i.e., when oxygen atoms are situated in the basal plane at random. It is noteworthy that in the $x=0$ limit all the copper atoms in the Cu(1) plane are monovalent. The $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$ transformation takes place if at least one of the oxygen vacancies, which is adjacent to the Cu site, is occupied. Since in the opposite limit, $x=1$, oxygen is arranged in chains, all the Cu(1) atoms are bivalent. The appearance of long chains favors the CT associated with the hole redistribution between oxygen in chains and oxygen in the regular CuO_2 planes.

At small x the “quasimolecules,” which are mainly Cu–O–Cu monomers, are therefore subjected to the charge transformation



With respect to the electrically neutral background, this is the elementary quadrupole: $1^+ 2^- 1^+$. In the dimers, Cu–O–Cu–O–Cu, the CT is probably of the intrachain type with the following charge redistribution:



Because of a strong hybridization, the oxygen hole (the O^- state) is delocalized between two oxygen sites, so the dimer behaves electrically as a quadrupole

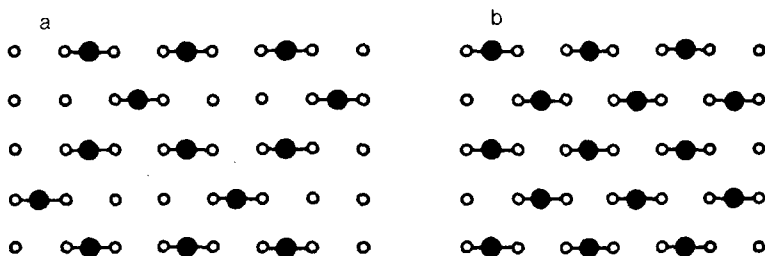


FIG. 2. Orthorhombic configurations of the chain fragments (a: proposed in Ref. 1).

$1^+(3/2)^-1^+(3/2)^-1^+$. The CT to the regular CuO_2 planes is associated with trimers and longer chain fragments. The CT mechanism proposed in Refs. 9 and 10 is in agreement with the experimental results reported in Ref. 11, where the concentration of the oxygen holes in the sufficiently long, alternating Cu–O chains was estimated to be about 30%.

Returning to the case of short chain fragments, monomers, and dimers, which do not contribute to the CT from chains into the CuO_2 planes, one performs calculations from the “first principles” for elucidating the energetically favorable configurations of “quadrupoles.” Many results concerning the possible superstructures in the oxygen-deficient planes were based on the lattice-gas model, according to which oxygen atoms must be arranged in such a way as to minimize their repulsion energy.⁸ In other words, the screening potential (see, for instance, Ref. 12) has been utilized for selection of the energetically favorable superstructures vs the oxygen content. Our “first-principle” calculations are performed for an insulating state in which screening is incomplete. According to the scheme we assume that

- all the atoms from different Cu–O–Cu chain fragments interact via the Coulomb forces: two charges, z_1 and z_2 , situated at the lattice sites \mathbf{r}_1 and \mathbf{r}_2 , interact as $z_1 z_2 / |\mathbf{r}_1 - \mathbf{r}_2|$;
- the charges of Cu and O, which form the Cu–O–Cu chain fragments, are +1 and –2, respectively;
- the lattice constant (Cu–Cu bond) is set to unity.

Under the above-mentioned conditions oxygen shows a tendency to a phase separation into the “solid” phase and a “gaseous” phase, whose roles are played by the s-I and the tetragonal phase, respectively. We remind the reader that the stability criterion of the phase at concentration c (in our case it is the oxygen content x) with respect to its separation into two phases of concentrations c_1 and c_2 is given by function $c\epsilon(c)$. The homogeneous phase is stable if $c\epsilon(c)$ vs c is concave upward. Otherwise, it separates into two phases of smaller and higher concentrations, c_2 and c_1 , respectively.

First, we check the regular configurations, which were discussed in Refs. 1 and 3. Chronologically, the first candidate proposed in Ref. 1 is the regular superstructure shown in Fig. 2a. The oxygen content, x , and the energy per oxygen atom, ϵ , are 0.375 and -0.08919 , respectively, while for the orthorhombic superstructure shown in Fig.

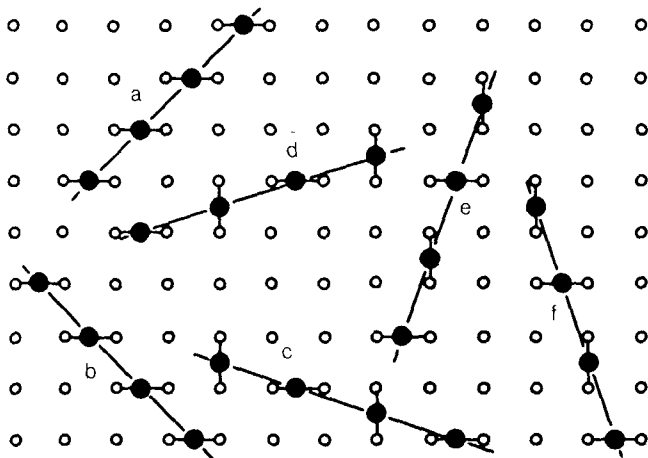


FIG. 3. Possible in-diagonal configurations of the chain fragments: "light" (a-b) and "heavy" (c-f) orientations.

2b these numbers are 0.5 and -0.13135 . Hence, these configurations are not competitive with the s-I (Fig. 1): For the latter we have $x=0.5$ and $\varepsilon_I = -0.15209$. The elementary Cu-O-Cu chain fragments in Fig. 1 are arranged in the *herringbone* structure with the axial symmetry along either (1,1) (Fig. 1a) or (1,-1) (Fig. 1b) directions. The electron diffraction measurements¹³ at small oxygen concentration have given some evidence in favor of the local diagonal configurations of the oxygen atoms in the basal planes, which can also be considered as fragments of the herringbone structure. The energy per oxygen atom in such a single diagonal is -0.11078 (Fig. 3a,b). The energy of the diagonal configuration aligned along either $(-0.5, 3.5)$ or $(-3.5, 0.5)$ directions is -0.01613 . These two diagonals consist of alternatively arranged horizontal and vertical chain fragments (Fig. 3c-f). Conclusions can therefore be drawn about the "light" and "heavy" orientations within the s-I. They could be displayed in the shape of the area formed by oxygen in the s-I state. Actually, the lines which confine such an area can be also named as "light" and "heavy." The boundary orientations, shown in Fig. 4, are analogous to the simple diagonal configurations. The linear energies are

$$e_1 = 0.03728 \quad \text{and} \quad e_2 = 0.13026$$

for the "light" and "heavy" boundaries, respectively. It is evident that the energies of the two configurations of equal areas (Fig. 4) are different: The second (Fig. 4b) minimizes the linear energy. Skipping a detail calculation, we only mention that for the optimal (with a symmetry axis parallel to the "light" orientation) macroscopic configuration, shown schematically in Fig. 4b, the linear expression $e_1 l_1 + e_2 l_2$ must be minimized at the constraint: $l_1 l_2 - l_2^2/2 = \text{const}$ (for definition of l_1 and l_2 see Fig. 4b). They result in the following proportionality:

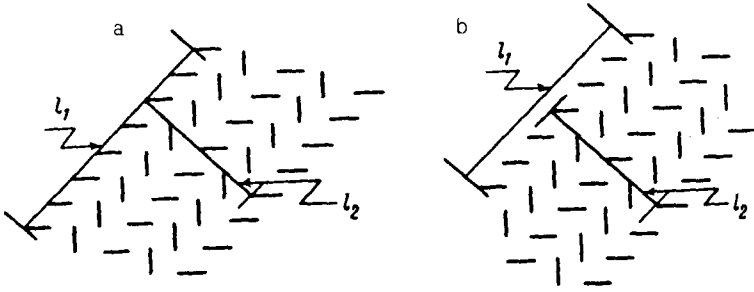


FIG. 4. Finite area arrangements of the chain fragments in s-I: symmetric configuration of b minimizes the energy at a fixed number of oxygen atoms.

$$\frac{l_1}{l_2} = \frac{e_1 + e_2}{e_1} \approx 4.5,$$

which clearly shows the anisotropy of the s-I shape.

A few words are necessary to be said about those changes which appear due to the partly screened Coulomb interaction. In the numerical calculations one employs the function

$$\left[\frac{1}{\epsilon} + e^{-\tau/\tau_0} \left(1 - \frac{1}{\epsilon} \right) \right] \frac{1}{\tau}, \quad (1)$$

instead of $1/\tau$ with the parameters τ_0 and ϵ .¹⁾ We did not find a large difference compared with the conventional Coulomb interaction, but the energy scale decreases systematically with a decrease in τ_0 (see Fig. 5, where ϵ was taken from Ref. 14). Such a behavior could influence the possible superstructures: Taking into account the scheme repulsion energy term between the nearest oxygen atoms belonging to the nearest diagonals (Fig. 1), we found that the s-I phase is energetically unfavorable compared with the simple diagonal arrangement (Fig. 3a,b).

However, the most important mechanism of the s-I instability could be connected with the competition of the s-I and tetragonal phases. In standard units ϵ_I would be on the order of 0.6 eV were it not for the partial screening. Invoking $\epsilon \sim 14.7$, according to Ref. 14, we obtain the following estimate from below: $\epsilon_I > 400$ K. Nevertheless, it may be several times larger, depending on the parameter τ_0 in Eq. (1) (see also Fig. 5). In order to find how the size of the s-I area, S , depends on the temperature T and on the oxygen content x or, equivalently, how T depends on S and x , one calculates the entropy contribution of the tetragonal phase to the free energy, assuming the simple form of the free energy of the regular s-I configuration: $\epsilon_I N_I$ (N_I is the total number of the chain fragments involved in the s-I phase). Evidently, the total number of oxygen sites which are not available for the chain fragments which form the tetragonal phase is $4N_I$; i.e., the available number $N_I^{(0)} = 2N_0 - 4N_I$ (N_0 is the total

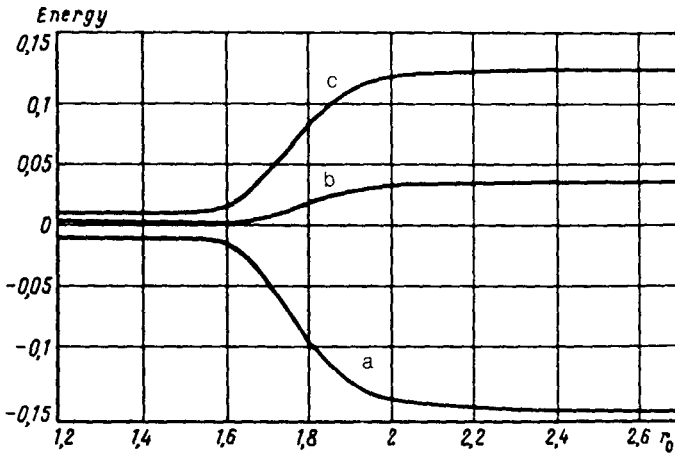


FIG. 5. a: The energy per oxygen atom of the regular s-I vs τ_0 ; b and c: the energy of "light" and "heavy" boundaries which confine the s-I.

number of copper atoms in the plane). At a fixed x , the number of constituents of the tetragonal phase is $N_t = xN_0 - N_I$. The free energy of the condensed phase, s-I, and of the gas of the N_I hard core oxygen atoms is

$$\frac{F_0}{N_0} = f_0 = \varepsilon_I z - T \left((x-z) \ln \frac{2-4z}{x-z} + (2-x-3z) \ln \frac{2-4z}{2-x-3z} \right), \quad z = \frac{N_I}{N_0}. \quad (2)$$

Expression (2) is valid asymptotically at $N_t \ll N_t^{(0)}$. However, the hard core of an oxygen atom in the basal plane must involve the nearest sites of the sublattice available for oxygen: According to the "first principle" estimate of Ref. 15, the repulsion energy of two oxygen atoms in the "corner" configuration appears to be a few times larger than a typical temperature of the oxygen equilibrium. The main order correction to Eq. (2) due to such a larger core has the form²⁾

$$\Delta f = 2T \frac{(x-z)^2}{2-4z}. \quad (3)$$

According to Ref. 2, only 12% of the oxygen atoms in the basal plane at $x=0.35$ contribute to the s-I; i.e., $z \approx 0.04$. Minimizing $f = f_0 + \Delta f$ [see Eqs. (2) and (3)] over z , we obtain $z \approx 0.04$ when the temperature of oxygen equilibrium is approximately one-half that of ε_I ($T \approx \varepsilon_I/1.88$).

In summary, the estimate performed above shows that experimental observation of the s-I phase is not impossible. On the other hand, it would be interesting to obtain more experimental evidence concerning the YBCO behavior at $x < 0.4$.

¹⁾As estimated in Ref. 14, $\epsilon \approx 14.7$.

²⁾We shall discuss this problem in a more detailed publication.

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