Письма в ЖЭТФ, том 58, вып.2, стр.139 - 144 ©1993 г. 25 июля

COULD THE OXYGEN SUPERSTRUCTURE IN $YBa_2Cu_3O_{6.35}$ EXIST?

M.Schreckenberg[+], *G.Uimin*[*]

[+] *Institut für Theoretische Physik, Universität zu Köln,*
W-5000 Köln, Federal Republic of Germany

[*] *Laboratoire Léon Brillouin, CEA-CNRS, C.E.Saclay,*
91191 Gif-sur-Yvette Cedex, France

[*] *Landau Institute RAS*
142432 Chernogolovka, Moscow District, Russia

Submitted 24 June 1993

In order to explain why the real superstructure in the basal plane of $YBa_2Cu_3O_{6+x}$ at $x \approx 0.35$ can exist and be observed experimentally the simple electrostatic and charge transfer mechanisms are invoked. The numerical estimates support a possibility for the superstructure (proposed by Hohlwein *et al*), formed by very short Cu-O-Cu chain fragments, to co-exist with the tetragonal phase, consisting of the short fragments arranged spatially at random.

The possibility for the real superstructure in $YBa_2Cu_3O_{6+x}$ at $x \approx 0.35$ to exist in the oxygen deficient planes is one of the problems of the YBCO family of the high T_c materials. Up to date 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 [1,2]. In Fig.1 we schematically reproduce the superstructure (centred orthorhombic) proposed in [2], below we refer to it as superstructure-I (s-I). It consists of the 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 behaviour is typical at 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 practically negligible as compared with the filling of O(4) positions [5]. Orthorhombicity is formed by the straight pieces of Cu-O-...-O-Cu chains. Probably, 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 not a real superstructure, because the correlation lengths along the chains and across them do not exceed 20–25 and 10–15 lattice constants, respectively [6] (cf, however, [7]). The Tetra–Ortho-II transition is believed to be driven by the effective attraction of oxygen ions in a linear coordination mediated by one copper ion in 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 short-range coupling constants: Apart from the attraction mentioned above there is the strong repulsion of oxygen atoms in the "corner" configurations (oxygen nearest neighbours) and also rather moderate repulsion between oxygen atoms on the opposite links of the elementary Cu-O plaquette (see [8] and references therein). Certainly, the s-I is in evident contradiction with a lattice-gas model description. In order to understand why such a superstructure could be stable and even competitive with the in-chain arrangement we shortly discuss the "intrachain" charge transfer (CT).

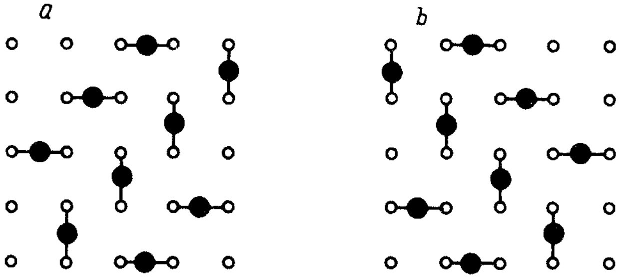

Fig.1. Centred orthorhombic (herring-bone) configurations of the chain fragments (proposed in Ref.[2]), open and dark circles denote copper and oxygen atoms, respectively

The CT mechanism in YBCO as discussed in [9,10] can be divided into two parts. The first part is associated with the intrachain CT, ie, the neutral oxygen, occupying the vacant place between two copper sites, accepts two electrons, if both copper ions are in monovalent states. 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, ie, 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 $Cu^+ \rightarrow Cu^{2+}$ transformation takes place if at least one of the oxygen vacancies, neighbouring to the Cu site, is occupied. In the opposite limit, $x = 1$, oxygen is arranged in chains, hence all the Cu(1) atoms are bivalent. The appearance of long chains favours the CT associated with the hole redistribution between oxygen in chains and oxygen in the regular CuO_2 planes.

So, at small x the "quasimolecules", which are mainly monomers Cu-O-Cu, are subjected to the charge transformation

$$Cu^+ - O - Cu^+ \rightarrow Cu^{2+} - O^{2-} - Cu^{2+}.$$

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

$$Cu^{2+} - O^{2-} - Cu^{2+} - O^{-} - Cu^{2+} \quad \text{or} \quad Cu^{2+} - O^{-} - Cu^{2+} - O^{2-} - Cu^{2+}$$

Due to a strong hybridyzation the oxygen hole (the O^- state) is delocalized between two oxygen sites, so the dimer behaves electrically as a quadrupole $1^+(3/2)^-1^+(3/2)^-1^+$. The CT to the regular CuO_2 planes is associated with trimers and longer chain fragments. The CT mechanism proposed in [9,10] is in correspondence with the experimental results reported in [11] where the concentration of the oxygen holes in the sufficiently long Cu-O alternating chains has been estimated around 30%.

Going back 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 favourable 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 situated in such a way to minimize their repulsion energy [8]. In other works the screening potential (see, for instance, [12]) has been utilized for selection the energetically favourable superstructures vs the oxygen content. Our "first principle" calculations are performed for an insulating state, where screening is incomplete. According to the scheme we suppose 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 r_1 and r_2, interact as $z_1 z_2/|\mathrm{r}_1 - \mathrm{r}_2|$;
- the charges of Cu and O, forming the Cu-O-Cu chain fragments, are $+1$ and -2, respectively;
- the lattice constant (Cu-Cu bond) is put to unity.

Under the abovementioned conditions oxygen shows a tendency to a phase separation into the "solid" and "gaseous" phases, whose roles are played by the s-I and the tetra-phase, respectively. We remind the reader that the stability criterium 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 $c\varepsilon(c)$. The homogeneous phase is stable if $c\varepsilon(c)$ vs c is concave upward. Otherwise, it separates into two phases of smaller and higher concentrations, c_2 and c_1, respectively.

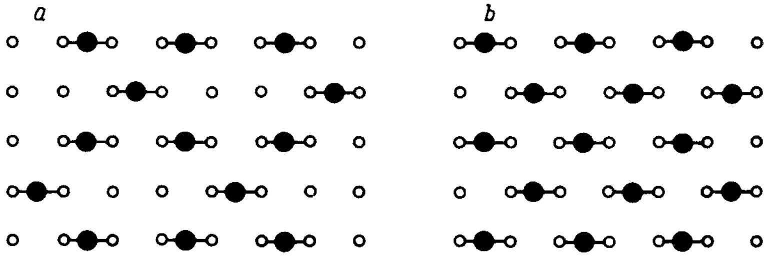

Fig.2. Orthorhombic configurations of the chain fragments (a: proposed in Ref.[1])

First, we check the regular configurations, which have been discussed in [1,2]. Chronologically, the first candidate proposed in [1] is the regular superstructure shown in Fig.2a. The oxygen content, x, and the energy per one oxygen atom, ε, are 0.375 and − 0.08919, respectively, whereas for the orthorhombic superstructure shown in Fig.2b these numbers are 0.5 and -0.13135. Hence, these configurations are not competitive with the s-I (Fig.1): For the latter $x = 0.5$ and $\varepsilon_I = -0.15209$. The elementary Cu-O-Cu chain fragments of Fig.1 are arranged in the *herring-bone* structure with the axial symmetry along either (1,1) (Fig.1a) or (1,-1) (Fig.1b) directions. The electron diffraction measurements [13] at rather small oxygen amount have given some evidence in favour of the local diagonal configurations of

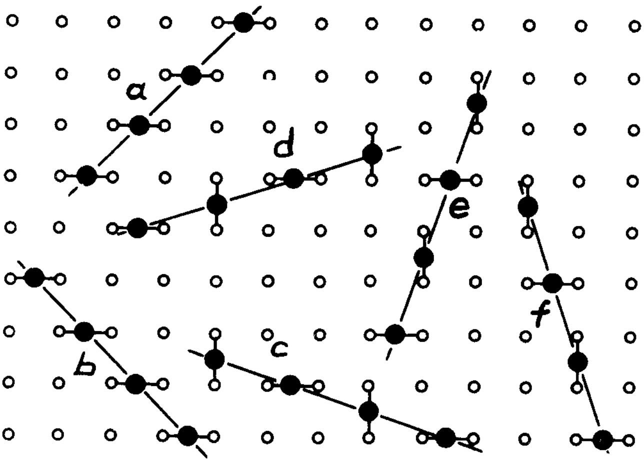

Fig.3. Possible in-diagonal configurations of the chain fragments: "light" $(a-b)$ and "heavy" $(c-f)$ orientations

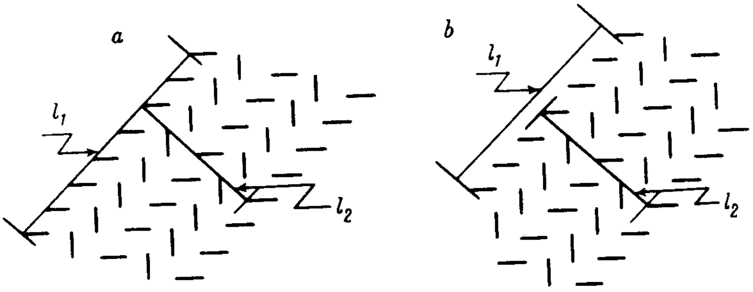

Fig.4. Finite area arrangement of the chain fragments in s-I: symmetric configuration of b minimizes the energy at fixed number of oxygen atoms

the oxygen atoms in the basal planes, which can be also considered as fragments of the herring-bone structure. The energy per one 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 both diagonals consist of alternatively arranged horizontal and vertical chain fragments (Fig.3$c-f$). It gives a possibility to conclude 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, confining such an area, can be also named as "light" and "heavy". The boundary orientations as 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 two configurations of the equal areas shown in 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) macroscopical configuration, shown schematically in Fig.4b, the linear expression

$e_1\ell_1 + e_2\ell_2$ must be minimized at the constraint: $\ell_1\ell_2 - \ell_2^2/2 = \text{const}$ (for definition of ℓ_1 and ℓ_2 see Fig.4,*b*). They result in the following proportionality:

$$\frac{\ell_1}{\ell_2} = \frac{e_1 + e_2}{e_1} \approx 4.5$$

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

A few words is necessary to be said about those changes, appearing due to the partly screened Coulomb interaction. In the numerical calculations one employs the function

$$\left(\frac{1}{\epsilon} + e^{-r/r_0}\left(1 - \frac{1}{\epsilon}\right)\right)\frac{1}{r} \tag{1}$$

instead of $1/r$ with parameters r_0 and ϵ[1]. We did not find a large difference as compared with the conventional Coulomb interaction, but the energy scale decreases systematically with r_0 decreasing (see Fig.5 with ϵ taken from [14]). Such a behaviour could influence on the possible superstructures: By including into the scheme a repulsion energy term between the nearest oxygen atoms belonging to the nearest diagonals (see Fig.1), one obtains the s-I phase to be energetically unfavourable as compared with the simple diagonal arrangement (Fig.3*a*, *b*).

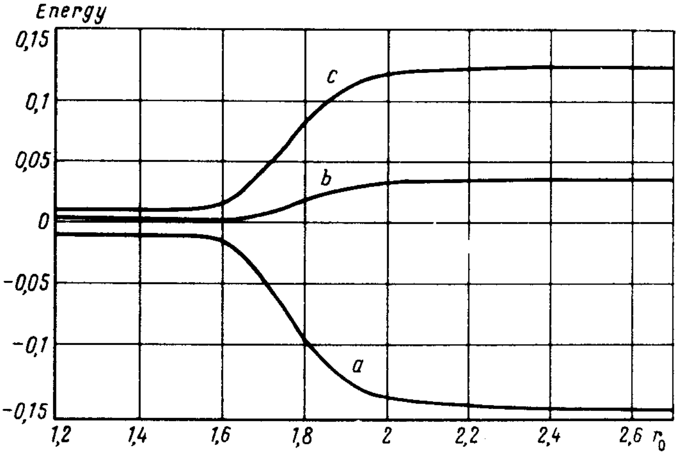

Fig.5. *a* - the energy per oxygen atom of the regular s-I vs r_0; *b* and *c* - the energy of "light" and "heavy" boundaries, confining the s-I

However, the most important mechanism of the s-I instability could be connected with the competition of the s-I and tetragonal phases. In usual units ε_I would be of the order 0.6 eV were it not for the partial screening. Invoking $\epsilon \sim 14.7$, according to Ref.[14], we get the following estimate from below: $\varepsilon_I > 400$ K. Nevertheless, it may be several times larger, it depends on the parameter r_0 of Eq.(1) (see also Fig.5). In order to find, how the size of the s-I area, S, depends on temperature, T, and the oxygen content, x, or, equivalently, how T depends on S and x, one calculates the entropy contribution of the tetragonal phase into the free energy, assuming the simple form of the free energy of the regular s-I configuration: $\varepsilon_I N_I$ (N_I is the total number of the chain fragments involved in

---

[1] As estimated in Ref.[14] $\epsilon \approx 14.7$.

the s-I phase). Evidently, the total number of oxygen sites which are not available for the chain fragments, forming the tetragonal phase, is $4N_I$, ie, the available number $N_t^{(0)} = 2N_0 - 4N_I$ (N_0 the total number of copper atoms in the plane). At fixed x the number of constituents of the tetragonal phase $N_t = xN_0 - N_I$. The free energy of the condensed phase, s-I, and the gas of the N_t hard core oxygen atoms reads:

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

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 following form2):

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

According to Ref.[2] only 12% of the oxygen atoms in the basal plane at $x = 0.35$ contribute to the s-I, ie, $z \approx 0.04$. Performing minimization of $f = f_0 + \Delta f$ (see Eqs.(2),(3)) over z one obtains that $z \approx 0.04$ is achieved when temperature of oxygen equilibrium is approximately twice less than ε_I ($T \approx \varepsilon_I/1.88$).

So, the estimate performed above shows that the experimental observation of the s-I phase is not impossible, on the contrary, it would be interesting to get more experimental evidence concerning the YBCO behaviour at $x < 0.4$.

1. R.Sonntag, D.Hohlwein, T.Brückel, and G.Collin, Phys. Rev. Lett. **66**, 1497 (1991).
2. Th.Zeiske, D.Hohlwein, R.Sonntag, et al., Z. Phys. **B 86**, 11 (1992).
3. J.M.Tranquada, S.M.Heald, A.R.Moodenbaugh, and Y.Xu, Phys. Rev. **B 38**, 8893 (1988).
4. H.Tolentino, F.Baudelet, A.Fontaine, et al., Physica **C 192**, 115 (1992).
5. J.D.Jorgensen, B.W.Veal, A.P.Paulikas, et al., Phys. Rev. **B 41**, 1863 (1990).
6. P.Burlet, V.P.Plakhty, C.Martin, and J.Y.Henry, Phys. Lett. **A 167**, 401 (1992).
7. Th.Zeiske, R.Sonntag, D.Hohlwein, et al., Nature **353**, 542 (1991).
8. L.T.Wille, A.Berera, and D.de Fontaine, Phys. Rev. Lett. **60**, 1065 (1988); D.de Fontaine, G.Ceder, and M.Asta, Nature **343**, 544 (1990); G.Ceder, R.McCormack, and D.de Fontaine, Phys. Rev. **44**, 2377 (1991).
9. G.Uimin and J.Rossat-Mignod, Physica **C 199**, 251 (1992).
10. G.Uimin Int. J. Mod. Phys. **B 6**, 2291 (1992).
11. A.Krol, Z.H.Ming, Y.H.Kao, et al., Phys. Rev. **B 45**, 2581 (1992).
12. A.A.Aligia, Phys. Rev. Lett. **65**, 2475 (1990); A.A.Aligia, H.Bonadeo , J.Garcés, Phys. Rev. **B 43**, 542 (1991).
13. J.Reyes-Gasga, T.Krekels, G.van Tendeloo, et al., Physica **C 159**, 831 (1989); T.Krekels, T.S.Shi, J.Reyes-Gasga, et al., Physica **C 167**, 677 (1990).
14. G.A.Samara, W.F.Hammetter, and E.L.Venturini, Phys.Rev **B 41**, 8974 (1990).
15. P.A.Sterne and L.T.Wille, Physica **C 162**, 223 (1989).

---

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