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# Extra oxygen and carrier distribution in $CuO_2$ layers in $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ compounds (n=1,2,4)

R.V.Lutciv, Ya.V.Boyko

Chair of Radio-electronic Material Sciences, Physics Department, Ivan Franko State University of Lviv, 50 Dragomanov Str., 290005 Lviv, Ukraine

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It is proposed to determine the equilibrium state of the crystal lattice by minimizing the total energy in order to elucidate the role of electrostatic interactions as well as to determine the nonstoichiometry in Hg-contained high temperature superconductors (HTSC). The approximation of non-interacting holes is used to evaluate the band energy. Such an approach enables us to satisfactorily describe the changes of oxygen nonstoichiometry and to indicate the preferred localization of the carriers on oxygen sites in $CuO_2$ layers.

**Key words:** *HTSC, carrier distribution, nonstoichiometry*

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While investigating the high-temperature superconductors (HTSC) there is still an important problem to elucidate the role of different interactions in the formation of their physical characteristics. Superconducting properties of all HTSC types are determined by the concentration of carriers and their distribution in the lattice cell. In many works which are dedicated to the investigation of LSCO, YBCO, BiSrCaCuO and TlBaCaCuO systems it is pointed out that the electrostatic (Madelung) energy is the most important factor which determines the distribution of carriers. Other factors, such as the ionization potentials of metallic ions and the electron affinity of the oxygen, are not essential or remain stable with changes of doping levels [1].

In this work it is proposed to study the distribution of the carriers in Hg-HTSC among atomic positions determining an equilibrium state of the crystal lattice by minimizing the total energy, the latter including $E_{\mathrm{M}}$ (electrostatic energy) and $E_{\mathrm{b}}$ – band energy:

$$E_{\mathrm{tot}} = E_{\mathrm{M}} + E_{\mathrm{b}}.$$

Using this method it is possible to determine the contents of the excessive oxygen which can be compared to the experimental data. The inter-ion Coulomb energy was calculated using Evald's method which was generalized for a random number of ions in the lattice cell:

$$E_{\mathrm{M}} = \frac{e^2}{2}\frac{4\pi}{V_0}\Big[\sum_{\vec{K}\neq 0}|S(\vec{K})|^2\frac{\exp(-K^2/4\eta^2)}{K^2}$$

$$-\frac{\pi}{V_0K^2}(\sum_n q_n)^2 + \sum_{\vec{R}}\sum_{n,n'}\frac{q_nq_{n'}\mathrm{erfcc}(\eta R_{nn'})}{R_{nn'}} - \frac{2\eta}{\pi}\sum_n q_n^2\Big], \qquad (1)$$

where $S(\vec{K}) = \sum_n q_n \mathrm{e}^{\mathrm{i}\vec{K}\vec{r}}$, $\eta$ is the width of Gauss distribution; $\vec{R}, \vec{K}$ are vectors of the direct and reciprocal lattice, respectively; $V_0$ is the volume of the lattice cell. Environment screening effects were accounted for by introducing a dielectric constant [2]. The following approach is suggested to estimate the band energy. Let $p_{\mathrm{h}}$ be the number of holes per one $CuO_2$ plane. The hole energy in the system L x L which is formed by a number of planes can be presented as

$$\varepsilon_k = \frac{\hbar^2k^2}{2m^*}, \qquad (2)$$

where $m^*$ is a hole effective mass in the parabolic band. Then $p_{\mathrm{h}} = \frac{a^2}{2\pi}k_{\mathrm{F}}^2$ ($a$ is the lattice parameter) or $k_{\mathrm{F}} = \sqrt{(2\pi/a^2)p_{\mathrm{h}}}$ (Fermi wave vector) and Fermi energy $\varepsilon_{\mathrm{F}} = \frac{\pi\hbar^2}{m^*a^2}p_{\mathrm{h}}$.

Thus, the densities of states will be presented as

$$D(\varepsilon) = \frac{m^*a^2}{\pi\hbar^2}.$$

A band energy per one $CuO_2$ plane is expressed as:

$$E_{bi} = \int_0^{\varepsilon_{\mathrm{F}}} D(\varepsilon)\varepsilon\mathrm{d}\varepsilon = \frac{\pi\hbar^2}{2m^*a^2}p_{\mathrm{h}}^2.$$

Then we shall consider a band energy per one lattice cell as a sum over planes [2]:

$$E_{\mathrm{b}} = \frac{\pi\hbar^2}{2m^*a^2}\sum_i p_{hi}^2.$$

A one-electron band energy (2) can also be considered as an a eigenvalue of Hubbard hamiltonian in the approximation of completely non-interacting holes U=0, where U is a parameter of Coulomb repulsion at one site. Then the effective mass is connected with intra-plane transfer integral $t_{||}$: $m^* = \hbar^2/(2t_{||}a^2)$. According to Cyrot's model [3] there is a connection between the temperature of the superconducting transition and the parameters of the Hubbard hamiltonian which for U=0 is expressed as $T_{\mathrm{c}} = tn_{\mathrm{h}}$, where $n_{\mathrm{h}}$ is the total number of holes in the lattice cell. Finally, a band energy is expressed as:

$$E_{\mathrm{b}} = \frac{\pi T_{\mathrm{c}}}{n_{\mathrm{h}}}\sum_i p_{hi}^2. \qquad (3)$$

**Table 1.** Ionic charge in $HgBa_2CuO_{4+\delta}$

| Atom | x/a | y/b | z/c | q |
|---|---|---|---|---|
| Hg | 0 | 0 | 0 | 2 |
| Ba | 1/2 | 1/2 | 0.298 | 2 |
| Cu | 0 | 0 | 1/2 | $2+2y\delta$ |
| O(1) | 1/2 | 1/2 | 0 | $-2+\delta(1-y)$ |
| O(2) | 0 | 0 | 0.2076 | $-2$ |
| O(3) | 1/2 | 1/2 | 0 | $-2\delta$ |

**Table 2.** Ionic charge in $HgBa_2Ca_3Cu_4O_{10+\delta}$

| Atom | x/a | y/b | z/c | q |
|---|---|---|---|---|
| Hg | 0 | 0 | 0 | 2 |
| Ba | 1/2 | 1/2 | 0.142 | 2 |
| Ca(1) | 1/2 | 1/2 | 0.324 | 2 |
| Ca(2) | 1/2 | 1/2 | 1/2 | 2 |
| Cu(1) | 0 | 0 | 0.2502 | $2+\delta xy$ |
| Cu(2) | 0 | 0 | 0.4160 | $2+\delta(1-x)y$ |
| O(1) | 1/2 | 0 | 0.248 | $-2+(\delta/2)x(1-y)$ |
| O(2) | 1/2 | 0 | 0.4174 | $-2+(\delta/2)(1-x)(1-y)$ |
| O(3) | 0 | 0 | 0.102 | $-2$ |
| O(4) | 1/2 | 1/2 | 0 | $-2\delta$ |

In order to make the analysis according to the above scheme the authors used structural data and properties of the sample series from [4]. In the structure with four $CuO_2$ planes the nonequivalence of external and internal planes was taken into account [2] by introducing $x$-parts of the holes which go into internal planes. Tables 1, 2 show the examples of choice distribution of ionic charges between atoms for determining the Madelung energy.

The total energy minimization was effected relating to the excessive oxygen contents (figure 1).

The calculations were carried out as follows. At different values of $y$ those values of $x$ were determined for which at the given magnitude of an index $\delta$ the energy had the minimum value. Then using the received values $x(\delta)$ dependencies $E_{\mathrm{tot}}(\delta)$ for one of the samples of a series were determined. At the $\delta$ minimizing energy coinciding with that experimentally determined (such $\delta$ are marked in the table 3 by asterisks) an appropriate value of $y$ was used for minimizing the $E_{\mathrm{tot}}$ in relation to $\delta$ on structural data of the other examples of a series. It means that relative changes of nonstoichiometry were determined. It should be noted, that experimental measurements of $\delta$ also determined only relative changes of nonstoichiometry because $\delta$ values which were determined by different methods do not coincide. As it is shown

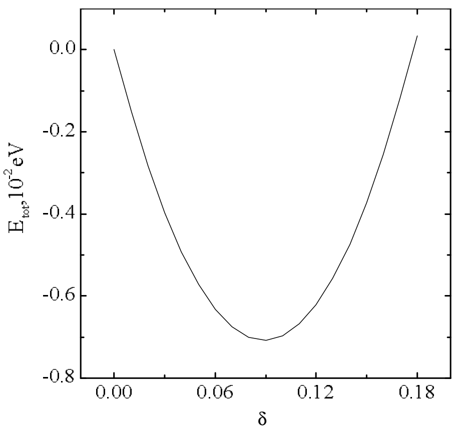


**Figure 1.** The total energy $E_{\mathrm{tot}}$ as a function of the nonstoichiometry $\delta$ for Hg-1201 compound (the sample with $T_c$=53 K)

**Table 3.** Results of calculations

| Compounds | $y$ | $\delta_{\mathrm{xp}}$ | $\delta_{\mathrm{calc}}$ | $T_c$, K |
|---|---|---|---|---|
| Hg-1201 | 0.16 | 0.18* | 0.18* | 95 |
| | | 0.08 | 0.09 | 53 |
| | | 0.04 | 0.11 | 0 |
| | | 0.23 | 0.29 | 30 |
| | | 0.21 | 0.22 | 80 |
| | | 0.18 | 0.16 | 94 |
| Hg-1212 | 0.14 | 0.08* | 0.08* | 92 |
| | | 0.22 | 0.23 | 126 |
| | 0.17 | 0.22* | 0.22* | 112 |
| | | 0.38 | 0.36 | 120 |
| | 0.21 | 0.35* | 0.35* | 104 |
| | | 0.28 | 0.32 | 123 |
| | 0.21 | 0.33* | 0.33* | 122 |
| | | 0.21 | 0.29 | 126 |
| Hg-1234 | 0.25 | 0.4* | 0.4* | 125 |
| | | 0.47 | 0.56 | 120 |

* – values through which $y$ were chosen.

in table 3, the calculated values give a very good description of $\delta$ changes. $\delta_{\mathrm{calc}}$ are always present in the same doping area (insufficient or excessive doping) with experimentally determined values.

In addition, the calculations show a predominant localization of the holes at the oxygen position which matches experimental data for other HTSC types.

Thus, it is possible to make a conclusion on the similarity of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ homological series and other HTSC families by the type of the chemical link and by the characteristics of the charge carrier distribution among the structural elements (nonequivalence of internal and external $CuO_2$ planes, a preferred localization on the O2$p$ orbitals).

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# Надлишковий кисень і розподіл носіїв у площинах $CuO_2$ у сполуках $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1,2,4)

Р.В.Луців, Я.В.Бойко

Львівський державний університет, фізичний факультет,
кафедра радіоелектронного матеріалознавства,
290005 Львів, вул. Драгоманова, 50

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Для з'ясування ролі електростатичних взаємодій і визначення нестехіометрії у Hg-вмісних високотемпературних надпровідниках (ВТНП) пропонується визначати рівноважний стан кристалічної гратки шляхом мінімізації загальної енергії. Для обчислення зонної енергії використовується наближення повністю невзаємодіючих дірок. Такий підхід дає змогу добре описати зміни нестехіометрії за киснем і показує переважне розміщення носіїв на позиціях кисню у площинах $CuO_2$.

**Ключові слова:** *ВТНП, розподіл зарядів, нестехіометрія*

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