A Simple Model to Estimate the Optimal Doping of p-Type Oxide Superconductors

Adir Moysés Luiz*
Centro de Tecnologia, Instituto de Física – UFRJ,
Bloco A, Sala A-319, 21941-972 Rio de Janeiro - RJ, Brazil

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Oxygen doping of superconductors is discussed. Doping high-Tc superconductors with oxygen seems to be more efficient than other doping procedures. Using the assumption of double valence fluctuations, we present a simple model to estimate the optimal doping of p-type oxide superconductors. The experimental values of oxygen content for optimal doping of the most important p-type oxide superconductors can be accounted for adequately using this simple model. We expect that our simple model will encourage further experimental and theoretical researches in superconducting materials.

Keywords: high-Tc superconductors, double valence fluctuations, valence skip, optimal doping

1. Introduction

Oxide superconductors have received enormous attention since the discovery of high-Tc oxide superconductors containing copper. Recently, the synthesis of a high-Tc superconductor without copper, has opened a new discussion about the microscopic mechanisms responsible for superconductivity in high-Tc superconductors. In this work we denote by y an appropriate atomic fraction and by Tc the critical temperature of the superconductor. For a discussion of the historical development of the researches on oxide superconductors, see Cava. In Table 1 we list in chronological order the most important discoveries of oxide superconductors.

The doping procedures used for the synthesis of cuprate superconductors have been described in a review article. The first high-Tc oxide superconductor was the famous copper oxide \( \text{La}_{1.85} \text{Ba}_{0.15} \text{CuO}_4 \); this superconductor is synthesized by doping the parent material \( \text{La}_{2} \text{CuO}_4 \) with oxygen, without the introduction of any Ba atomic fraction y, it is also possible to synthesize the superconductor \( \text{La}_{1-y} \text{CuO}_y \). In this case, we conclude that the introduction of oxygen is responsible for the doping mechanism of the parent material \( \text{La}_{2} \text{CuO}_4 \). In the superconductor \( \text{GdFeAsO}_{1+y} \), a high-Tc superconductor with oxygen-deficiency, it has been shown that oxygen doping is a good and reliable procedure for the synthesis of a new family of iron-based high-Tc superconductors.

It is well known that for p-type oxide superconductors the optimal oxygen doping of high-Tc oxide superconductors corresponds to a certain critical hole content. An under-doped superconductor is synthesized when the hole content is less than this critical value and an over-doped superconductor is synthesized when the hole content is greater than this critical value. The prediction of the optimal doping is an unresolved issue. In this work we propose a simple model to estimate the optimal doping of p-type oxide superconductors.

2. Double Valence Fluctuations and Valence Skip

According to a number of tables in Lee we present in Table 2 the electron configurations and the oxidation states of some metals used in the synthesis of the oxide superconductors listed in Table 1. Examining Tables 1 and 2, we notice that: 1) In the superconductor \( \text{K}_y \text{WO}_3 \), the metal W may have the oxidation states W (+IV) and W (+VI); 2) In \( \text{LiTi}_{1+y} \text{O}_4 \) the metal Ti may have the oxidation states \( \text{Ti} (+\text{II}) \) and \( \text{Ti} (+\text{IV}) \); 3) In the superconductor \( \text{BaPb}_{4+y} \text{Bi}_y \text{O}_{8+y} \) the metal Pb may have the oxidation states: \( \text{Pb} (+\text{II}) \) and \( \text{Pb} (+\text{IV}) \) and Bi may have the oxidation states \( \text{Bi} (+\text{III}) \) and \( \text{Bi} (+\text{V}) \); 4) In all cuprate superconductors listed in Table 1, Cu may have the unstable oxidation states \( \text{Cu} (+\text{I}) \) and \( \text{Cu} (+\text{II}) \); and 5) In the new superconductor containing iron, Fe may have the oxidation states \( \text{Fe} (+\text{II}) \) and \( \text{Fe} (+\text{IV}) \) and As may have the oxidation states \( \text{As} (+\text{III}) \) and \( \text{As} (+\text{V}) \).

According to a number of authors, the existence of double valence fluctuations in oxide superconductors is very likely. Ganguly and Hegde argued that: “Apparently, the presence of double valence fluctuations is a necessary, but not sufficient, criterion for superconductivity.” Possible microscopic mechanisms for double valence fluctuations are hopping mechanisms, tunneling mechanisms, or bipolaronic mechanisms.

Jongh claims that oxide materials may become superconductors when a parent material is doped by the traditional doping mechanism with cation (or anion) substitution or by a doping mechanism due to oxygen non-stoichiometry. If a certain oxide contains a metal with mixed oxidation numbers, by increasing (or decreasing) the oxygen content, the metal may be oxidized (or reduced) in order to maintain charge neutrality. Thus, the synthesis of p-type superconductors may be obtained by doping the parent materials with an excess of oxygen atoms and the synthesis of n-type superconductors may be obtained by doping the parent materials with a deficiency of oxygen atoms.

Our basic assumption is that the existence of double valence fluctuations involving paired electrons (or paired holes) may be the key to the study of the microscopic mechanisms in oxide superconductors. Let us consider the case of an oxide superconductor containing Bi without copper (see Table 1). In this case, Bi (+III) and Bi (+V) are stable oxidation states. This element belongs to the class of elements with valence skip, that is, the valence Bi (+IV) is not present in the compounds containing Bi; only mixtures of the species Bi (+III) and Bi (+V) are possible. The same phenomenon of valence skip also occurs in the case of Pb compounds; only mixtures of Pb (+II) and Pb (+IV) are possible. About fifteen elements in periodic table skip valence in all the components they form. Varma argued that the elements with valence skip may be used in the synthesis of superconductors.
Table 1. Most important oxide superconductors in chronological order.

<table>
<thead>
<tr>
<th>Superconductor</th>
<th>Year</th>
<th>Tc (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$<em>{y}$WO$</em>{3}$</td>
<td>1967</td>
<td>6.0</td>
<td>7</td>
</tr>
<tr>
<td>LiTi$<em>{2-y}$O$</em>{4}$</td>
<td>1973</td>
<td>1.2</td>
<td>8</td>
</tr>
<tr>
<td>Ba$<em>{1-y}$Bi$</em>{y}$O$_{3}$</td>
<td>1975</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>La$<em>{2-y}$Ba$</em>{y}$CuO$_{4}$</td>
<td>1986</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>YBa$<em>{2}$Cu$</em>{3}$O$_{7-x}$</td>
<td>1987</td>
<td>90</td>
<td>6</td>
</tr>
<tr>
<td>Ba$<em>{1-y}$K$</em>{y}$BiO$_{3}$</td>
<td>1988</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Bi$<em>{2}$SrCaCuO$</em>{4+y}$</td>
<td>1988</td>
<td>105</td>
<td>11</td>
</tr>
<tr>
<td>TlBa$<em>{2}$Ca$</em>{1}$Cu$<em>{2}$O$</em>{4+y}$</td>
<td>1989</td>
<td>110</td>
<td>12</td>
</tr>
<tr>
<td>HgBa$<em>{2}$CaCu$</em>{2}$O$_{8+y}$</td>
<td>1993</td>
<td>120</td>
<td>13</td>
</tr>
<tr>
<td>GdFeAsO$_{1-y}$</td>
<td>2008</td>
<td>53.5</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2. Electron configurations and oxidation states of some metals. The symbol [Xe] means the electron configuration of Xe and [Ar] means the electron configuration of Ar.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electron configurations</th>
<th>Oxidation states</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>[Ar] 3d$^{10}$ 4s$^{2}$ 4p$^{3}$</td>
<td>+III, +V</td>
</tr>
<tr>
<td>Bi</td>
<td>[Xe] 4f$^{14}$ 5d$^{10}$ 6s$^{2}$ 6p$^{3}$</td>
<td>+III, +V</td>
</tr>
<tr>
<td>Cu</td>
<td>[Ar] 3d$^{10}$ 4s$^{1}$</td>
<td>+I, +II, +III</td>
</tr>
<tr>
<td>Fe</td>
<td>[Ar] 3d$^{5}$ 4s$^{2}$</td>
<td>+II, +III, +IV, +V</td>
</tr>
<tr>
<td>Pb</td>
<td>[Xe] 4f$^{14}$ 5d$^{10}$ 6s$^{2}$ 6p$^{3}$</td>
<td>+II, +IV</td>
</tr>
<tr>
<td>Ti</td>
<td>[Ar] 3d$^{2}$ 4s$^{2}$</td>
<td>+II, +III, +IV</td>
</tr>
<tr>
<td>Tl</td>
<td>[Xe] 4f$^{14}$ 5d$^{10}$ 6s$^{2}$ 6p$^{3}$</td>
<td>+I, +III</td>
</tr>
<tr>
<td>W</td>
<td>[Xe] 4f$^{14}$ 5d$^{10}$ 6s$^{2}$</td>
<td>+IV, +V, +VI</td>
</tr>
</tbody>
</table>

3. Optimal Doping of p-Type Oxide Superconductors

Let us now consider cuprate superconductors without Bi. In Table 2 we note that copper is not an element with valence skip. But, if one wants to apply the assumption of double valence fluctuations to a cuprate superconductor, it is necessary to assume the existence of the states Cu (+I) and Cu (+III). However, since Cu (+I) and Cu (+III) are not stable oxidation states, it is very difficult to perform reliable experiments to verify this hypothesis. Nevertheless, this assumption is supported by the possible occurrence of the following disproportionation reaction: 2Cu (+II) → Cu (+I) + Cu (+III). which has been suggested by Raveau et al. to explain the existence of the state Cu (+III).

What should be the optimal chemical doping of cuprate superconductors in order to obtain the maximum value of Tc? To answer this question we present a simple model based on the conjecture of double valence fluctuations.

According to Zhang and Sato there is a universal relationship between hole content and Tc. Examining the figure that shows this universal relationship, we observe that the optimal doping corresponds to a certain critical value of hole concentration that gives the maximum Tc. In the case of p-type cuprate superconductors this critical value corresponds to a situation of a critical oxygen content. Considering disproportionation reactions, we may suppose initially an equal probability of occurrence of the ions Cu (+I), Cu (+II) and Cu (+III). Under this hypothesis, the initial concentrations of the copper ions are: (1/3) Cu (+I), (1/3) Cu (+II) and (1/3) Cu (+III). By diffusion, it is possible to introduce in the material an excess of oxygen atoms. We know that oxygen excess may produce an oxidation reaction, converting the species Cu (+II) into the ion Cu (+III). Let us suppose a complete oxidation with conversion of all the initial (1/3) Cu (+II) ions into (1/3) Cu (+III) ions. Then, the initial concentration of (1/3) Cu (+III) ions is enhanced by the fraction (1/3) Cu (+III). Thus, the final concentration of Cu (+III) ions is given by (1/3) + (1/3) = (2/3). Therefore, applying this assumption, we conclude that for optimal doping of p-type cuprate superconductors, the final concentrations of the copper ions are given by the following proportionalities: (1/3) Cu (+I) ions and (2/3)Cu (+III) ions.

4. Results and Discussion

We apply the simple hypothesis described above to estimate the optimal doping of the famous p-type cuprate superconductor YBa$_{2}$Cu$_{2}$O$_{7-y}$, where y is the oxygen content to be calculated. Using the relative values: (1/3) for Cu (+I) and (2/3) for Cu (+III), we may write the formula unit: YBa$_{2}$Cu$_{y}$Ca$_{1}$Cu$_{1-y}$O$_{4+y}$. Considering the oxidation states Y (+III), Ba (+II), Sr (+II), Bi (+III), Ca (+II), Tl (+III), Hg (+II) and O (-II) and using the charge neutrality condition, gives:

$$3 + (2 \times x) + (1 \times 1) + (2 \times 3) - 2y = 0$$

From Equation (1) we obtain: y = 7.0. This result is in good agreement with the experimental result (y = 6.9) reported in the literature. Using the model described in the previous calculation, we may estimate the necessary oxygen content to obtain the optimal doping of a great number of p-type cuprate superconductors. It is important to note that the experimental determination of the oxygen content is a difficult task. Therefore, we have selected a number of typical works which we believe to be reliable. In Table 3 we compare the predictions based on our simple model with the oxygen content obtained in these typical works. In our model, we have used for the copper ions the following relative values: (1/3) for Cu (+I) ions and (2/3) for Cu (+III) ions. For the other elements in Table 3 we have considered the following stable oxidation states: La (+III), Y (+III), Ba (+II), Sr (+II), Bi (+III), Ca (+II), Ti (+III), Hg (+II) and O (-II). We verify that the results predicted by the simple model proposed here are in good agreement with the experimental results listed in Table 3.

The simple model suggested in this work has been applied only to the calculation of the optimal doping of superconductors doped with oxygen. To apply this model in the case of simultaneous doping with oxygen and other elements, such as in Ba$_{1-x}$La$_{x}$CuO$_{y}$, it is necessary to know the atomic fractions x and y. In the case of simultaneous doping with oxygen and other elements we have not found in the literature simultaneous measurements of the variables x and y and thus we have not compared the predictions of this simple model in this case.

Our model may be extended to estimate the optimal doping of oxide superconductors that do not contain Cu. For example, consider the superconductor $^{13}$Ba$_{2}$K$_{2}$BiO$_{3}$ with Tc approximately equal to 30 K. We shall suppose for the Bi ions the same proportionality assumed in the model just suggested for the cuprate superconductors, that is, for optimal doping, we assume that the relative concentrations should be given by: (1/3) Bi (+III) and (2/3) Bi (+V). Considering the oxidation states Ba (+II) and K (+I) and using the charge neutrality condition, we have:

$$1.2 + 0.4 + (1/3)(3) + (2/3)(5) - 2y = 0$$
Table 3. Optimal doping of p-type oxide superconductors containing copper.

<table>
<thead>
<tr>
<th>Superconductor</th>
<th>$T_c$ (K)</th>
<th>Oxygen content (Predicted)</th>
<th>Oxygen content (Experimental)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$CuO$_4$</td>
<td>30</td>
<td>$y = 4.2$</td>
<td>$y = 4.1$</td>
<td>5</td>
</tr>
<tr>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>90</td>
<td>$y = 7.0$</td>
<td>$y = 6.9$</td>
<td>26</td>
</tr>
<tr>
<td>YBa$_2$Cu$_4$O$_7$</td>
<td>80</td>
<td>$y = 8.2$</td>
<td>$y = 8.0$</td>
<td>4</td>
</tr>
<tr>
<td>Sr$_2$CuO$_3$</td>
<td>70</td>
<td>$y = 3.17$</td>
<td>$y = 3.16$</td>
<td>27</td>
</tr>
<tr>
<td>Bi$_2$CaSr$_2$Cu$_2$O$_y$</td>
<td>85</td>
<td>$y = 8.3$</td>
<td>$y = 8.3$</td>
<td>28</td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$Cu$_2$O$_y$</td>
<td>92</td>
<td>$y = 6.2$</td>
<td>$y = 6.0$</td>
<td>4</td>
</tr>
<tr>
<td>TlCa$_2$Ba$_2$Cu$_2$O$_y$</td>
<td>110</td>
<td>$y = 9.0$</td>
<td>$y = 9.0$</td>
<td>29</td>
</tr>
<tr>
<td>HgBa$_2$Ca$_2$Cu$_3$O$_y$</td>
<td>134</td>
<td>$y = 8.5$</td>
<td>$y = 8.4$</td>
<td>30</td>
</tr>
</tbody>
</table>

From equation (2) we obtain the approximate result: $y = 2.95$. This result is in good agreement with the experimental value $y = 3.0$ reported in the literature\textsuperscript{11}.

5. Conclusion

We believe that the simple model proposed in this paper in the case of p - Type oxide superconductors could also be extended to estimate the optimal doping of n-Type oxide superconductors. However, in the case of n-Type oxide superconductors, the reaction produced by oxygen doping is a reduction reaction instead of an oxidation reaction that occurs in p-Type oxide superconductors. Since we have not found in the literature any experimental determination of the oxygen content in the case of n-Type cuprate superconductors we shall not discuss this issue here. This question will be addressed in a future work.

We have proposed a simple model to estimate the relative concentrations of the ions involved to estimate the oxygen content for optimal doping of p-type oxide superconductors. It is important to know that the predictions based on this model are in good agreement with a number of reliable experimental results reported in the literature (Table 3). Thus we believe that our assumptions are helpful to the investigations of the microscopic mechanisms in oxide superconductors. We expect that this simple model will also be useful to encourage further experimental and theoretical researches in superconducting materials.

References

