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Room Temperature Superconductivity

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1. Introduction

Superconductivity was discovered by Kamerlingh Onnes in 1911. For one century superconductivity has been a great challenge to theoretical physics. The first successful set of phenomenological equations for superconducting metals was given by F. London in 1935. Yet, in 1950, almost 40 years after the discovery of this phenomenon, there was not any adequate microscopic theory of superconductivity. However, by 1935, single elements necessary to a successful theory to explain superconductivity was known to theorists. The peculiar condensation of a Bose-Einstein gas was predicted by Einstein in 1925. The idea that pairs of fermions can combine to form bosons has been known since 1931. In 1950 the most relevant ideas of superconductivity has been summarized by F. London in his famous book "Superfluids", volume 1. At last, BCS theory (Bardeen et al., 1957) was the first successful theory to explain the microscopic mechanisms of superconductivity in metals and alloys.

Practical applications of superconductivity are steadily improving every year. However, the actual use of superconducting devices is limited by the fact that they must be cooled to low temperatures to become superconducting. For example, superconducting magnets used in most particle accelerators are cooled with liquid helium, that is, it is necessary to use cryostats that should produce temperatures of the order of 4 K. Helium is a very rare and expensive substance. On the other hand, because helium reserves are not great, the world's supply of helium can be wasted in a near future. Thus, because liquid nitrogen is not expensive and the reserves of nitrogen could not be wasted, it is important to use high-T_c superconductors cooled with liquid nitrogen. Superconductors with critical temperatures greater 77 K may be cooled with liquid nitrogen.

We know that BCS theory (Bardeen et al., 1957) explains the microscopic mechanisms of superconductivity in metals. According to BCS theory, electrons in a metallic superconductor are paired by exchanging phonons. According to many researchers (De Jongh, 1988; Emin, 1991; Hirsch, 1991; Ranninger, 1994), BCS theory is not appropriate to be applied to explain the mechanisms of superconductivity in oxide superconductors. Nevertheless, other models relying on a BCS-like picture replace the phonons by another bosons, such as: plasmons, excitons and magnons, as the mediators causing the attractive interaction between a pair of electrons and many authors claim that superconductivity in the oxide superconductors can be explained by the conventional BCS theory or BCS-like theories (Canright & Vignale, 1989; Tachiki & Takahashi, 1988; Takada, 1993).

Copper oxide superconductors are the most important high-T_c superconductors. The discovery of a room temperature superconductor should trigger a great technological revolution. There are claims of synthesis of a room temperature superconductor (see, for example, www.superconductors.org, 2011). But these claims are not accepted by the scientific community. It is generally accepted in the scientific literature that the highest T_c is approximately equal to 135 K at 1 atm in the Hg-Ba-Ca-Cu-O system (Schilling & Cantoni, 1993). However, T_c in this system can be raised up to 180 K using high external pressures. We believe that the discovery of a room temperature superconductor would be possible only when the microscopic mechanisms of oxide superconductors should be clarified. However, up to the present time, the microscopic mechanisms responsible for high-T_c superconductivity are unclear. In a recent article (Luiz, 2010), we have discussed a simple model to study microscopic mechanisms in high-T_c superconductors. The objective of this chapter is to present new studies in order to give new theoretical support for that simple model. We also discuss the possibility of room temperature superconductivity.

2. Possibility of room temperature superconductivity

It is well known that the superconducting state is characterized by a quantum macroscopic state that arises from a Bose-Einstein condensation (BEC) of paired electrons (Cooper pairs). Initially, it is convenient to clarify some concepts regarding BEC. It is well known that a collection of particles (bosons) that follows the counting rule of Bose-Einstein statistics might at the proper temperature and density suddenly populate the collections ground state in observably large numbers (Silvera, 1997). The average de Broglie wavelength λ_{dB} which is a quantum measurement of delocalization of a particle, must satisfy this condition. We know that $\lambda_{dB} = h/p$, where h is Planck's constant and p is the momentum spread or momentum uncertainty of the wave packet. In the other extreme, for particles in the zero momentum eigenstate, the delocalization is infinite; i.e., the packet is spread over the entire volume V occupied by the system. It is generally accepted that BEC occurs when the interparticle separation is of the order of the delocalization λ_{dB} (Silvera, 1997).

The thermal de Broglie wavelength λ_{dB} is a measure of the thermodynamic uncertainty in the localization of a particle of mass M with the average thermal momentum. Thus, λ_{dB} is given by

$$\lambda_{dB} = h/[3MkT]^{1/2} \tag{1}$$

where k is Boltzmann's constant. Equation (1) shows that at a certain low temperature T or/and for a small mass M, λ_{dB} may be spread over great distances. In order to determine the critical temperature T_c at which the addition of more particles leads to BEC it is sufficient to calculate a certain critical density $n = N/V$, where N is the number of bosons. This calculation is performed using Bose-Einstein statistics; according to (Silvera, 1997) and considering the mass of the boson (Cooper pair) $M = 2m^*$, where m^* is the effective mass of the electron, we obtain

$$T_c = 3.31h^2n^{2/3}/(4\pi^2kM) \tag{2}$$

The first application of BEC theory to explain ^{4}He superfluidity was realized in 1938 (London, 1938). In an important paper (Blatt, 1962), the BEC approach has been extended to give the same results predicted by BCS theory. Thus, it is reasonable to conclude that the conventional n-type superconductivity in metals (explained by BCS theory) is a special case that can also be considered as a phenomenon of BEC of Cooper pairs.

There are three possibilities of occurrence of BEC: (a) BEC involving just bosons, (b) BEC involving just fermions, and (c) BEC involving bosons and fermions simultaneously. In (a) there is a direct BEC without the need of an interaction to bind the bosons. However, in the cases (b) and (c) BEC is possible only indirectly in two steps: in the first step it occurs the binding between pairs of fermions giving rise to bosons and, in the second step, BEC of these bosons may occur.

Because liquid ^{4}He is a system of bosons, the condensation of ^{4}He is a BEC of type (a). Superfluidity of ^{3}He (Lee, 1997) is an example of BEC of type (b). Because liquid ^{3}He is a system of fermions, in order to occur BEC, two particles must be binded to form a boson and, in he next step, a BEC of these bosons may occur. Another example of BEC of type (b) is the phenomenon of superconductivity in metals and alloys. In the last case, BCS theory (Bardeen et al., 1957) is a successful theory to explain the microscopic mechanisms of superconductivity in metals, and in this case, Equation (2) is not appropriate to calculate the critical temperature T_c because we cannot predict the density n of the bosons formed exchanging phonons. In BCS theory, the critical temperature T_c is the temperature at which a great number of Cooper pairs are formed by exchanging phonons. When the density n of pairs formed are sufficiently high it is possible to occur a Bose-Einstein condensation. For example, in pure copper the density n of Cooper pairs formed are not sufficiently high, thus pure copper cannot become superconductor even at temperatures in the neighborhood of 0 K.

We study now the possibility of occurrence of a Bose-Einstein condensation in an oxide material. If possible, this phenomenon should be a BEC of type (c) just mentioned, that is, the mechanism should involve bosons and fermions simultaneously. In order to verify if BEC is possible in oxide superconductors, it is sufficient to calculate the order of magnitude of the critical temperature T_c using Equation (2). According to Table 1 in the reference (De Jongh, 1988), in a p-type copper oxide superconductor, a typical order of magnitude of the carrier density is given by $n = 10^{21}/\text{cm}^3$. Considering an effective mass $m^* = 12m$, where m is the rest mass of the electron, we obtain by Equation (2) the following approximated value: $T_c = 100$ K. This calculation is very crude because Equation (2) is based on an isotropic model of an ideal Bose gas. However, oxide superconductors are not isotropic; on the other hand, pair of electrons (bipolarons) in oxide materials are not an ideal Bose gas because we must consider Coulomb interactions. But the crude calculation based on Equation (2) is sufficient to show that BEC in oxide superconductors cannot be ruled out. A more appropriate formula to calculate T_c (supposing BEC) has been derived in (Alexandrov & Edwards, 2000).

On the basis of the crude calculation based on Equation (2) we will now discuss the possibility of room temperature superconductivity. Using the same above mentioned values and considering a carrier density greater than $n = 10^{21}/\text{cm}^3$ we conclude that the critical temperature T_c could be enhanced. For example, considering $m^* = 12m$ and a carrier density $n = 3 \times 10^{21}/\text{cm}^3$, we obtain a critical temperature $T_c = 300$ K. Thus, if we apply Equation (2), it is reasonable to conclude that room temperature superconductivity is possible.

According to the type of charge carriers, superconductors can be classified in two types: n-type superconductors, when the charge carriers are Cooper pairs of electrons and p-type superconductors, when the charge carriers are Cooper pairs of holes.

We claim that only p-type materials should be considered in the researches to synthesize a room temperature superconductor. We claim that n-type materials are not qualified to obtain a room temperature superconductor, because in an n-type material the carriers are electrons and these electrons should be binded in order to form bosons. On the other hand, due to Coulomb interactions, it is very difficult to accept a situation of an ideal Bose gas of electrons pairs in order to apply Equation (2). However, considering p-type materials, there are two types of interactions: Coulomb repulsions between electrons, but Coulomb attractions between electrons and holes. Thus, it is reasonable to accept an approximation considering an ideal Bose gas of Cooper pairs of holes in order to apply Equation (2). On the other hand, Bose-Einstein condensation is not restricted only to an ideal Bose gas of bosons (Blatt, 1962). The phenomenon of Bose-Einstein condensation could also be extended to a real Bose gas. It is worthwhile to develop a complete theory to extend the predictions of BEC to a real Bose gas. A fermion-boson mixture of unpaired electrons coexisting and interacting with Cooper pairs treated as real two-electrons and two-holes has been proposed in a letter (Tolmachev, 2000). Finally, considering the simple calculation based on Equation (2) we conclude that the possibility of room temperature superconductivity cannot be ruled out.

3. Superconductors containing oxygen

The most relevant metallic superconductors are pure metals and alloys. BCS theory is appropriate to explain the microscopic mechanisms of superconductivity in pure metals and alloys. However, a great number of oxide materials may become non-metallic superconductors. It seems that BCS theory is not appropriate to explain the microscopic mechanisms in superconductors containing oxygen. An interesting review about oxide superconductors is found in the references (Cava, 2000). The history of oxide superconductors begins in 1933 with the synthesis of the superconductor NbO; with T_c = 1.5 K (Sleight, 1995). In 1975 it was discovered the oxide superconductor $BaPb_{0.7}Bi_{0.3}O_3$ (Sleight et al., 1975) with T_c = 13 K.

Superconductor	Year	T_C	Reference
NbO	1933	1.5	Sleight, 1995
K_xWO_3	1967	6.0	Remeika et al., 1967
$LiTi_{2+x}O_4$	1973	1.2	Johnston et al., 1973
$BaPb_{1-x}Bi_xO_3$	1975	13	Sleight et al., 1975
$La_{2-x}Ba_xCuO_4$	1986	30	Bednorz & Müller, 1986
$YBa_2Cu_3O_{7-x}$	1987	90	Wu et al., 1987
$Ba_{1-x}K_xBiO_3$	1988	30	Cava et al.,1988
$BiSrCaCu_2O_{6+x}$	1988	105	Maeda et al., 1988
$Tl_2Ba_2Ca_2Cu_3O_{9+x}$	1988	110	Shimakawa et al., 1988
$HgBa_2Ca_2Cu_3O_{8+x}$	1993	130	Schilling & Cantoni, 1993
$NdFeAsO_{1-x}$	2008	54	Yang et al., 2008

Table 1. List of the most relevant superconductors containing oxygen in chronological order.

In 1986, the oxide superconductor $Ba_{0.15}La_{1.85}CuO_4$ with T_c = 30 K has been discovered (Bednorz & Müller, 1986). The expression "high-T_c superconductors" has been generally used in the literature to denote superconductors with critical temperatures higher than 30 K. After this famous discovery many cuprate high-T_c superconductors have been synthesized. The cuprate superconductor $HgBa_2Ca_2Cu_3O_{8+x}$ (Hg-1223) has the highest critical temperature (T_c = 135 K) at 1 atm (Schilling & Cantoni, 1993). In 2008, a new type of high-T_c

superconductor containing iron (without copper) has been discovered (Yang et al., 2008). In Table 1, we list in chronological order the most important discoveries of superconductors containing oxygen. In Table 1, T_c is expressed in Kelvin and x is a variable atomic fraction of the doping element.

4. Valence skip and double valence fluctuations

What is the principal feature observed in all superconductors listed in Table 1? It is easy to verify that all metals used in the synthesis of superconductors containing oxygen have mixed oxidation states. For example, we can verify that in the superconductor NbO, Nb may have the oxidation states Nb(+III) and Nb(+V). In the bronze superconductor K_xWO_3, W may have the oxidation states W(+IV) and W(+VI). In the superconductor $LiTi_{2+x}O_4$, Ti may have the oxidation states Ti(+II) and Ti(+IV). In the superconductor $BaPb_{1-x}Bi_xO_3$, Pb may have the oxidation states: Pb(+II) and Pb(+IV) and Bi may have the oxidation states Bi(+III) and Bi(+V). Finally, we verify that in the copper oxide superconductors listed in Table 1, Cu may have the oxidation states Cu(+I) and Cu(+III).

Note also that in the superconductor $NdFeAsO_{1-x}$, an example of the recent discovery of iron-based superconductors (Yang et al., 2008), we can verify that Fe may have the oxidation states Fe(+II) and Fe(+IV) and As may have the oxidation states As(+III) and As(+V).

According to a number of authors the probable existence of double charge fluctuations in oxide superconductors is very likely (Callaway et al., 1987; Foltin, 1988; Ganguly & Hegde, 1988; Varma, 1988). Spectroscopic experiments (Ganguly & Hegde, 1988), indicate that double charge fluctuations is a necessary, but not sufficient, criterion for superconductivity. We argue that these charge fluctuations should involve paired electrons hoping from ions (or atoms) in order to occupy empty levels. That is, our basic phenomenological hypothesis is that the electrons involved in the hopping mechanisms might be paired electrons coming from neighboring ions or neighboring atoms.

The discovery of Fe-based high-T_c superconductors (Yang et al., 2008) has reopened the hypothesis of spin fluctuations for the microscopic mechanisms of high-T_c superconductivity. However, it is interesting to note that Fe may have the oxidation states Fe(+II) and Fe(+IV). Thus, the conjecture of double charge fluctuations cannot be ruled out in the study of the microscopic mechanisms in all Fe-based high-T_c superconductors. It is worthwhile to study the competition between double charge fluctuations and spin fluctuations in order to identify which phenomenon is more important in the microscopic mechanisms responsible for the condensation of the superconducting state of Fe-based materials.

What is valence skip? About fifteen elements in the periodic table skip certain valences in all compounds they form. For example, it is well known that the stable oxidation states of bismuth are Bi(+III) and Bi(+V). The oxidation state Bi(+IV) is not stable. If the state Bi(+IV) is formed, it occurs immediately a disproportionation, according to the reaction: 2Bi(+IV) = Bi(+III) + Bi(+V). In the compound $BaBiO_3$, the formal valence Bi(+IV) is understood as an equilibrium situation involving a mixture of equal amounts of the ions Bi(+III) and Bi(+V). Other important examples of elements with valence skip are As, Pb and Tl. In (Varma, 1988) there is an interesting discussion about the microscopic physics responsible for the phenomenon of valence skip. The electronic states of valence-skipping compounds are described in a conference paper (Hase & Yanagisawa, 2008). Elements with valence skip, like Bi and Pb, are the most appropriate elements to study the hypothesis of double charge fluctuations proposed in this chapter. It has been claimed that all elements with valence skip may be used in the synthesis of superconductors (Varma, 1988).

5. Oxygen doping by diffusion

The most relevant doping procedures used for the synthesis of cuprate superconductors have been described in a review article (Rao et al., 1993). Historically, the first synthesis of a high-T_c oxide superconductor was the copper oxide $Ba_xLa_{2-x}CuO_4$ (Bednorz & Muller, 1986). This superconductor is synthesized by doping the parent material La_2CuO_4 with Ba atoms. Soon after this discovery, it was realized (Schirber et al., 1988) that doping the parent material La_2CuO_4 with oxygen, without the introduction of any Ba atomic fraction x, it is also possible to synthesize the superconductor La_2CuO_{4+x}. Thus, in this case, we conclude that the introduction of oxygen is responsible for the doping mechanism of the parent material La_2CuO_4 (Schirber et al., 1988).

Oxide materials may become superconductors when a parent material is doped by the traditional doping mechanism with cation substitution or by a doping mechanism based on oxygen nonstoichiometry (De Jongh, 1988). 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. Therefore, 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.

The most famous example of oxygen doping is provided by the family of p-type oxide superconductors Y-Ba-Cu-O. It is well known that $YBa_2Cu_3O_{6+x}$, considering compositions x between x = 0.5 and x = 0.9, are superconductors, and with a maximum T_c corresponding to a composition x = 0.9. An important example of n-type superconductor is provided by the recent discovery of the superconductor $GdFeAsO_{1-x}$, a high-T_c 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-T_c superconductors (Yang et al., 2008).

In the present chapter we shall study only oxygen doping of p-type oxide superconductors. It is well known that high-T_c superconductors are generally synthesized when a parent material is doped by the traditional doping mechanism with cation (or anion) substitution. But it seems that doping mechanisms based on oxygen nonstoichiometry are more appropriate than doping mechanisms based on cation (or anion) substitutions. However, doping mechanisms based on oxygen nonstoichiometry are not completely clear. In this chapter we give some ideas to study the microscopic mechanisms associated with oxygen doping of p-type oxide superconductors.

A normal atmosphere contains about 21% of O_2, 78% of N_2, and 1% of other gases. Consider an oxide material. When it is heated in a furnace containing atmospheric air at ambient pressure or containing an oxygen reach atmosphere, due to diffusion, some O_2 molecules may be absorbed in the bulk of the solid material. Thus, oxygen nonstoichiometry is a necessary consequence of heating processes of oxide materials submitted to ambient pressure or submitted to atmospheres containing an oxygen excess. The diffusion of oxygen in binary metal oxides has been studied in a book (Kofstad, 1983).

According to molecular orbital (MO) theory (Petrucci et al., 2000), to obtain the molecular orbital electronic configuration of O_2 molecule it is necessary to combine the atomic orbitals of two O atoms. We obtain the following molecular orbital electronic configuration of O_2 molecules:

[MO configuration of O_2]: [inner electrons]$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2(\pi^*_{2p})^2$

Considering the above MO configuration of O_2 we conclude that there are two unpaired electrons in the orbital π^*_{2p}. By diffusion and solid state reaction, O_2 molecules may oxidize metal atoms or ions in the bulk material. Because there are two unpaired electrons, the O_2 molecule may pick two electrons in the neighboring metal ions, becoming a peroxide ion O_2(-II) species. Our hypothesis of formation of peroxide ion species in oxide superconductors is supported by a great number of spectroscopic measurements (Rao et al., 1987; Sarma et al., 1987; Dai et al., 1988; Mehta et al., 1992).

In order to understand the microscopic mechanisms of oxygen doping, we give an example. Consider an oxide material containing bismuth (without copper); for instance, consider $BaBiO_3$. As we have stressed in Section 4, the bismuth stable oxidation states are Bi(+III) and Bi(+V). When an oxygen molecule reacts with a Bi(+III) ion, it is reasonable to suppose that this ion gives two electrons to the O_2 molecule, that is, we may write the following reaction:

$$O_2 + \mathrm{Bi(+III)} \rightarrow O_2\mathrm{(-II)} + \mathrm{Bi(+V)}$$

Considering this oxidation reaction we conclude that the formation of the peroxide species O_2(-II) corresponds to the creation of a double hole. In many oxide compounds the electrons or holes may be considered to be localized at lattice atoms forming lattice defects. In such a case, we may suppose that p-type conduction may involve hopping of electrons from site to site (Kofstad, 1983). Therefore, in the bismuth example just mentioned, we claim that conductivity (and superconductivity) may be explained by hopping of electron pairs that jump from neighboring sites to occupy hole pairs.

It is well known that for p-type superconductors the optimal oxygen doping of high-T_c 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 the next Section we propose a simple model to estimate the optimal doping of p-type oxide superconductors.

6. Optimal doping of p-type oxide superconductors containing bismuth without copper

Our basic hypothesis is that the existence of double charge fluctuations involving paired electrons may be a key to study the microscopic mechanisms in oxide superconductors. The essential concept in this hypothesis is that the hopping mechanism involves two paired electrons, instead of the hopping of a single electron. Our hypothesis may be easily applied in the oxide superconductors containing Bi (without Cu) because, in this case, it is well known that Bi (+III) and Bi (+V) are the only stable oxidation states for the Bi ions. Thus, double charge fluctuations may occur between the ions Bi (+III) and Bi (+V). In this Section we propose a simple method to calculate the optimal doping of oxide superconductors containing bismuth without copper and in the next Section we consider oxide superconductors containing copper without bismuth.

What should be the ideal chemical doping of oxide p-type superconductors containing bismuth without copper in order to obtain the maximum value of T_c? This optimal doping should be obtained by cation substitution or by increasing the oxygen content in the material.

Let us first suppose equal amounts of the ions Bi (+III) and Bi (+V). In this case the formal oxidation state of bismuth should be Bi (+IV). Thus, charge fluctuations should be balanced and the formation of holes is very difficult.

For example, it is well known that $BaBiO_3$ is an insulator because in this material the formal oxidation state of bismuth is Bi (+IV). However, by doping $BaBiO_3$ by cation substitution or by increasing the oxygen content a superconductor may be obtained. Chemical doping may destroy the balance between the ions Bi (+III) and Bi (+V). If the ions Bi (+V) are increased, it is possible to create holes. It is reasonable to suppose that the maximum concentration for optimal doping should correspond to a ratio [(Bi(+V) ions)/(Bi(+III) ions)] = 2, that is, the optimal concentration of the ions Bi (+V) should be the double of the concentration of the ions Bi (+III). Why we have proposed the ratio [(Bi(+V) ions)/(Bi(+III) ions)] = 2 for optimal doping? It is well known that T_c decreases when the hole concentration is higher than a certain critical concentration (Zhang & Sato, 1993). This important property is the nonmonotonic dependence of T_c on the carrier concentration, a high-T_c characteristic feature of all oxide superconductors. If the concentration of the ions Bi (+V) are further increased (and the concentration of the ions Bi (+III) are further decreased), the material becomes overdoped and T_c decreases. Thus, for optimal doping, the bismuth ion concentrations should be: (2/3)Bi (+V) and (1/3)Bi (+III). In the next section we propose an analogous simple model to estimate the optimal doping of p-type copper oxide superconductors (without bismuth).

Now we apply the above simple model to estimate the optimal doping of p-type oxide superconductors containing bismuth without copper. As an example, we apply our hypothesis to the material $Ba_{0.6}K_{0.4}BiO_x$, a famous oxide superconductor without copper, with T_c approximately equal to 30 K (Cava et al., 1988).

We shall suppose for the Bi ions the proportionality assumed in the model just suggested, that is, for optimal doping, we assume that the relative concentrations should be given by: (2/3)Bi(+V) and (1/3)Bi(+III). Considering the oxidation states Ba(+II) and K(+I) and using the charge neutrality condition, we have:

$$1.2 + 0.4 + (1/3)(3) + (2/3)(5) - 2x = 0 \qquad (3)$$

From Equation (3) we obtain the result:

$$x = 2.97 \qquad (4)$$

The result (4) is in good agreement with the value (x = 3) reported in the reference (Cava et al., 1988).

In the next section we extend the simple model just proposed to estimate the optimal doping of p-type oxide superconductors containing copper without bismuth.

7. Optimal doping of p-type oxide superconductors containing copper without bismuth

To apply our hypothesis to a copper oxide superconductor (without Bi) it should be necessary to suppose the existence of Cu (+I) because we are assuming double charge fluctuations between the states Cu(+I) and Cu(+III). In p-type Cu oxide superconductors, the existence of the oxidation state Cu(+III) is obvious by the consideration of charge neutrality. Thus, from an experimental point of view, it is very important to verify if the oxidation state Cu(+I) is present in the high-T_c Cu oxide superconductors. The probable existence of the states Cu(+I) and Cu(+III) has been verified in the works (Karppinen et al., 1993; Sarma & Rao, 1988).

It is generally believed that the microscopic mechanisms in a cuprate superconductor depends only on the ions Cu(+II) and Cu(+III), without the presence of the ions Cu(+I). Let us suppose that the hopping mechanism involves just a single electron between Cu(+II) and Cu(+III); if this single charge fluctuation would be responsible for superconductivity, we should conclude that the enhancement of Cu(+III) ions should produce a continuous enhancement of the critical temperature T_c. However, it is well known that T_c decreases when the hole concentration is higher than a certain concentration (Zhang & Sato, 1993). This important property is the nonmonotonic dependence of T_c on the carrier concentration, a high-T_c characteristic feature of all oxide superconductors. Thus, by this reasoning and considering the experimental results (Karppinen et al., 1993; Sarma & Rao, 1988), we can accept the presence of the mixed oxidation states Cu(+I), Cu(+II) and Cu(+III) in the copper oxide superconductors. On the other hand, this conjecture is supported if we consider the copper disproportionation reaction (Raveau et al, 1988): 2Cu(+II) = Cu(+I) + Cu(+III).

What should be the optimal chemical doping of Cu oxide superconductors in order to obtain the maximum value of T_c? Initially, considering the disproportionation reaction (Raveau et al, 1988): 2Cu(+II) = Cu(+I) + Cu(+III), we may suppose an equal probability for the distribution of the copper ions states Cu (+I), Cu (+II) and Cu (+III). Thus, the initial concentrations of these ions should be (1/3)Cu(+I), (1/3)Cu(+II) and (1/3)Cu(+III). However, we may suppose that by oxidation reactions, (1/3)Cu(+II) ions may be completely converted to (1/3)Cu(+III) ions. In this case, the maximum concentration of the Cu(+III) ions should be: (1/3) + (1/3) = (2/3). Thus, the optimal doping should correspond to the following maximum relative concentrations: (1/3)Cu(+I) ions and (2/3)Cu(+III) ions. That is, the optimal doping, should be obtained supposing the following concentration ratio: [(Cu(+III) ions)/(Cu(+I) ions)] = 2.

We apply this hypothesis to estimate the optimal doping of the famous cuprate superconductor $YBa_2Cu_3O_x$, where x is a number to be calculated. Using the relative values: (1/3) for Cu(+I) ions and (2/3) for Cu(+III) ions, we may write the formula unit: $YBa_2Cu_1(+I)Cu_2(+III)O_x$. Considering the oxidation states Y(+III), Ba(+II) and O(-II) and using the charge neutrality condition, we get:

$$3 + (2 \times 2) + (1 \times 1) + (2 \times 3) - 2x = 0 \tag{5}$$

From Equation (5) we obtain:

$$x = 7.0 \tag{6}$$

The result (6) is in good agreement with the result (x = 6.9) reported in (Kokkallaris et al., 1999).

Using the simple model just described, we estimate the necessary oxygen content to obtain the optimal doping of the most relevant p-type cuprate superconductors. It is important to note that the experimental determination of the oxygen content is a very difficult task. In Table 2 we have selected a number of works containing this experimental information.

Superconductor	Predicted	Measured	REFERENCE
$Ba_{0.15}La_{1.85}CuO_x$	x = 4.1	x = 4.0	Bednorz & Müller, 1986
La_2CuO_x	x = 4.2	x = 4.1	Schirber et al., 1988
$YBa_2Cu_3O_x$	x = 7.0	x = 6.9	Kokkallaris et al.,1999
$YBa_2Cu_4O_x$	x = 8.2	x = 8.0	Rao et al., 1993
Sr_2CuO_x	x = 3.17	x = 3.16	Hiroi et al., 1993
$HgBa_2Ca_2Cu_3O_x$	x = 8.5	x = 8.4	Hung et al., 1997

Table 2. Comparison between the values of oxygen content of copper oxide superconductors (not containing Bi) predicted by our simple model and the experimental values reported in the literature.

According to 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 2, we have considered the following stable oxidation states: La(+III), Y(+III), Ba(+II), Sr(+II), Ca(+II), 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 2.

8. Discussion

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 oxide 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. The predictions based on this model are in good agreement with experimental results reported in the literature (Table 2). However, we emphasize that the model proposed in this chapter is not a complete theoretical model, it is just a simple phenomenological model.

Our conjectures can be used to explain some remarkable properties of high-T_c superconductors: (a) the anisotropy is explained considering that the electrons involved in the hopping mechanisms are 3d-electrons (in the case of copper oxide superconductors); (b) the order of magnitude of the coherence length (the mean distance between two electron pairs) is in accordance with the order of magnitude of the distance between the electron clouds of two neighboring ions; (c) the nonmonotonic dependence of T_c on the carrier concentration is explained by the hypothesis of double charge fluctuations and the optimal doping model proposed in this chapter.

The theory of bipolaronic superconductivity (Alexandrov & Edwards, 2000) is similar to our phenomenological model. In the theory of bipolaronic superconductivity, bipolarons are formed supposing a mechanism to bind two polarons. However, by our hypothesis, it is not necessary to suppose the formation of bipolarons by the binding of two polarons. We have assumed that the preformed pairs are just pairs of electrons existing in the electronic configurations of the ions or atoms involved in double charge fluctuations. These pairs should be, for example, lone pairs in atoms or ions or pairs of electrons in the electronic configurations obtained when Hund's rule is applied.

9. Concluding remarks

In this chapter we have studied the most relevant questions about the microscopic mechanisms of superconductivity in oxide materials. Parts of our arguments may be found in the list of references in the next Section. However, we believe that our ideas have been expressed in a clear form for the questions at hand.

The simple model described here is not a theoretical model and cannot be used to account quantitatively for the microscopic mechanisms responsible for superconductivity in oxide materials. However, 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. It is worthwhile to study the details of the role of double charge fluctuations in the microscopic mechanisms responsible for superconductivity in oxide materials.

We have stressed in Section 2 that in p-type materials there are two types of interactions: Coulomb repulsions between electrons, but Coulomb attractions between electrons and holes. Thus, considering the possibility of a Bose-Einstein condensation, we claim that only p-type materials are qualified to be considered in the researches to obtain a room temperature superconductor.

Finally, we suggest some future researches. It is worthwhile to make experiments to verify if this model is correct. Supposing that this simple model works, it would be possible to calculate stoichiometric compositions in order to obtain the optimal doping in the researches to synthesize new oxide superconductors. It is well known that the most important method in semiconductor technology is obtained by ion implantation techniques. Similarly, we believe that ion implantation techniques probably will be important in superconductor technology as well. Thus, we hope that future researches based on ion implantation techniques could open a new route in the synthesis of high-T_c superconductors. These future researches, using ion implantation, should take advantage of the possibility of double charge hoping mechanisms, instead of single charge hoping mechanisms existing in the case of ion implantation in the semiconductor technology.

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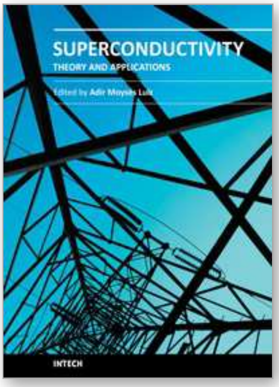

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Superconductivity was discovered in 1911 by Kamerlingh Onnes. Since the discovery of an oxide superconductor with critical temperature (Tc) approximately equal to 35 K (by Bednorz and Müller 1986), there are a great number of laboratories all over the world involved in research of superconductors with high Tc values, the so-called â€œHigh-Tc superconductorsâ€. This book contains 15 chapters reporting about interesting research about theoretical and experimental aspects of superconductivity. You will find here a great number of works about theories and properties of High-Tc superconductors (materials with Tc > 30 K). In a few chapters there are also discussions concerning low-Tc superconductors (Tc < 30 K). This book will certainly encourage further experimental and theoretical research in new theories and new superconducting materials.

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