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On electron pairing in superconducting cuprates

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Abstract. The superconducting properties of materials of layered structure containing copper and other metal oxides are compared with the expectations of a recently proposed electron pairing model [1]. The role of the oxygen content of samples is emphasized. Evidence is found showing that superconduction is originated only in presence of coupled layers of metal oxides holding unpaired electrons.

PACS. 74.20.-z Theories and models of the superconducting state

1 Introduction

In a previous paper, by analyzing the common features of a number of unconventional superconductors, a special electron pairing model was derived [1]. Taking into account the discontinuous structure of the materials dealt with and the presence of atoms with unpaired electrons, this model assumes that electrons running in lattice layers separated by discontinuities in the lattice structure form spin-singlet bonds. These bonds link electrons of layers placed at the opposite sides of the lattice discontinuities. The YBCO cuprate is a typical example. Its structure shows couples of copper oxide layers separated by lattice discontinuities coinciding with planes of oxygen lacunae and yttrium ions. In the following discussion, the layers spoken of will be marked with labels *a* and *b*. Wave functions of electrons running in layers *a* and *b* can be conveniently represented by linear combinations of atomic orbitals with appropriate wavy phase factors, that is, by tight-binding (TB) wave functions. Calculations show that this kind of electron pairs is quite different from the Cooper pairs in that they are characterized by electrons of like rather than opposite momenta. Moreover, while with Cooper pairs the conjugated states refer to the opposite directions of momenta, with the pairs dealt with the conjugated states refer to the coupled layers *a* and *b*. In reality, these pairs are analogous to the nucleon-nucleon pairs in nuclear matter, which are likewise characterized by like linear momenta, but show opposite signs of the angular momentum components along the quantization axis. Belyaev [2] devised a modified version of the Bogolyubov-Valatin transformation [3,4] suitable for nuclear matter. Owing to its merely formal character, it can be reutilized for the pairs at issue provided that the signs + and − of the angular momentum components are reinterpreted as labels *a* and *b*. In this way, energy of the quasi-particles is found to be

$$E_k = \sqrt{(\widetilde{\varepsilon}_k - \mu)^2 + \Delta_0^2}, \tag{1}$$

as in the BCS theory. In this equation $\widetilde{\varepsilon}_k$ is the electron energy modified by the self-consistent field due to electron pairing interaction, μ the chemical potential and Δ_0 the energy gap. As for critical temperature, it is common knowledge that a weakly interacting fermion system with attraction between particles other than phonon coupling shows normally the temperature law [5]

$$kT_{\mathrm{c}} = 0.57\mu \exp\left(-1/N_{\mathrm{F}}V_0\right), \tag{2}$$

N_{F} standing for the density of states in the energy region around the Fermi level and V_0 for the average value of pairing energy in this region. This equation differs from that of BCS theory only in that chemical potential instead of Debye temperature appears.

In reference [1] a qualitative comparison between expectations of the model spoken of and experiments was performed. By considering the YBCO cuprate, the effects on critical temperature of pressure and oxygen content were explained. It was shown, moreover, how the model allows for the *d*-symmetry of the order parameter, which is indeed the one most accredited by experiments. However, comparison with the features of unconventional superconductors other than cuprates, such as for instance perovskites of fractional stoichiometries, was less conclusive owing to uncertainties in the structure of these materials. For this reason, and in order to find further arguments useful in singling out the real nature of the electron pairs, the superconducting properties of some special cuprates are now examined. They are selected among those which, in relation to the current theoretical models, raise the most challenging questions [6]

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Table 1. Some thallium-based cuprates.

Superconductor	$Tl_2Ba_2CuO_6$	$Tl_2CaBa_2Cu_2O_8$	$Tl_2CaBa_2Cu_3O_{10}$
Number of CuO layers	1	2	3
T_c (K)	85	107	125

2 Features of some special superconductors

2.1 The TBCO superconductors

Several thallium-based cuprates are known. They are characterized by layered structures with CuO layers alternating with TlO and BaO layers [7,8]. Some of them are listed in Table 1. In the structure of $Tl_2Ba_2CuO_6$ there is a single CuO layer interposed between two BaO layers and two TlO layers on the outside of the BaO layers. In the Tl_2 $CaBa_2Cu_2O_8$ structure there are two CuO layers with a layer of Ca ions between them and, like the $Tl_2Ba_2CuO_6$ structure, above and below there are a BaO layer and two TlO layers. In the $Tl_2CaBa_2Cu_3O_{10}$ there are three CuO layers with a Ca layer between each of them.

Superconduction of the TBCO multilayered compounds does not pose serious questions about the electron pairing mechanism. On the contrary, superconduction of the $Tl_2Ba_2CuO_6$ compound with a single CuO layer represents a quite challenging question. In the proposed mechanism, superconducting pairs cannot be originated in single layered structures. Actually, and in full agreement with this forecast, the wholly oxidized $Tl_2Ba_2CuO_6$ compound is not a superconductor. Experiments have in fact shown that by enhancing oxygen stoichiometry to 6.1 superconductivity is destroyed. It is however present at 85 K in samples with a reduced oxygen content [6]. To explain this result, it should be kept in mind that a lack of oxygen causes a corresponding decrease in cation charges which means that a number of Tl^{+2} ions appears in the structure. The thallium atom and the Tl^{+3} ion show the $[Xe]4f^{14}5d^{10}6s^26p^1$ and the $[Xe]4f^{14}5d^{10}$ configurations, respectively, so that in the Tl^{+2} ion configuration an unpaired 6s electron is found. It follows that in reduced compounds the TlO layers at the sides of each CuO layer hold unpaired electrons. Consequently, superconducting electron pairs are originated between copper $3d$ and thallium $6s$ orbitals. Since the presence of a minimum quantity of superconducting material is sufficient to set sample resistance to zero, the sudden onset of superconductivity as soon as oxygen content is reduced is not surprising. This state of affairs mimics what happens with $SrTiO_3$. This compound is not a superconductor, but superconduction appears, although only at 0.3 K, in the reduced samples $SrTiO_{3-\delta}$ owing to the presence of Ti^{+3} ions bearing unpaired electrons [9].

2.2 The Sr_2RuO_4 superconductor

This compound, like the first discovered superconducting cuprate La_2CuO_4, is characterized by a layered K_2NiF_4 structure. In spite of its low critical temperature of 0.93 K, it is interesting because it confirms that the presence of copper is not essential for the existence of superconduction in perovskite-like materials [10]. With the formal stoichiometry Sr_2RuO_4, ruthenium ions assume valence four. The ruthenium atom configuration is $[Kr]4d^75s^1$ so that Ru^{+4} ions show a $[Kr]4d^4$ configuration devoid of unpaired electrons. This prevents the formation of electron pairs between the RuO layers. But trivalent ruthenium showing one unpaired electron in the $4d$ shell is also known. It should be found in compounds of stoichiometry $Sr_2RuO_{4-\delta}$. It follows that electron pairs can be originated in these compounds, thus allowing for superconduction. In reality, the samples utilized in the experiments of the above cited paper were single crystals grown in air which could hardly be wholly oxidized. This explains the observed low-temperature superconductivity of this ruthenium-based material. It mimics that of $SrTiO_{3-\delta}$ as does the previously examined thallium cuprate.

2.3 The $Sr_{1-y}Nd_yCuO_2$ superconductor

Another interesting issue is that of the $Sr_{1-y}Nd_yCuO_2$ compound which shows bulk superconductivity with onset temperatures rising from 34 K for $y = 0.16$ to 40 K for $y = 0.14$. This compound is isostructural to the orthorhombic $SrCuO_2$ (S.G. Cmcm) which, however, does not show superconductivity down to 2 K [11]. Owing to the partial substitution of divalent strontium with trivalent neodymium and taking into account the possibility of ions of different degrees of oxidation, the stoichiometry of this superconductor can be written in the alternative forms α) $Sr^{II}_{1-y}Nd^{III}_yCu^{II}O_{2+y/2}$, or β) $Sr^{II}_{1-y}Nd^{III}_yCu^{II}_{1-y}Cu^{I}_yO_2$, or γ) $Sr^{II}_{1-2y}Sr^{I}_yNd^{III}_yCu^{II}O_2$. Since it was not possible to measure the actual oxygen content of the samples accurately, form α) cannot be asserted in principle. The most likely option is that of form β) showing a variable percentage of monovalent copper. It is to be pointed out, in this connection, that, according to the charge-transfer model, the superconducting CuO planes in this cuprate are electron-doped, which entails the presence of monovalent copper. The configuration of the neodymium atom being $[Xe]4f^4\ 5d^06s^2$, the Nd^{+3} ion is expected to show one unpaired $4f$ electron. It follows that, with any stoichiometry, a number of electron pairs can be originated between unpaired $3d$ electrons of divalent copper and $4f$ electrons of trivalent neodymium. This explains why the Sr_{1-y} Nd_yCuO_2 compound is a superconductor while the $SrCuO_2$ is not. What is more, if the β stoichiometry is considered, it is not surprising that superconduction appears only in a narrow range of small values of y and with the highest critical temperature, that is, 40 K, corresponding to the least y. In fact, by increasing y the content of divalent copper which is required for originating the superconducting pairs decreases. As in the perovskitic superconductors with fractional stoichiometries, a certain degree of lattice disorder is expected in this compound. This hinders the ascertainment of the precise geometry of the interacting CuO and NdO layers. It is important to note, in this connection, that the lack of superconductivity in the bulk $SrCuO_2$ compound confirms that a layered, or at least a discontinuous, lattice is essential for superconductivity. In a bulk lattice, the singling out and labelling of conjugated states is impracticable, so that the pairing correlations which allow for superconductivity cannot be active.

2.4 The $PrBa_2Cu_3O_7$ compound

This compound is an exception among the rare-earth substituted YBCO superconductors owing its lack of superconductivity [12,13]. To explain this peculiar behaviour, it must be considered that praseodymium originates both trivalent and tetravalent ions. Actually, magnetic susceptibility measurements indicate that praseodymium in this compound is tetravalent [14,15]. Taking into account cell electric neutrality, this entails a decreased degree of oxidation of barium or copper cations. In the YBCO cell the Y^{+3} ion is kept inside a perovskitic cube with eight Cu^{+2} ions at the cube vertices. Each cell holds two divalent copper ions. This originates one superconducting electron pair per cell. With the Pr^{+4} ion at the cell centre, one electron is transferred to copper so that one divalent and one monovalent copper is found within each cell. Since monovalent copper shows a $[Ar]3d^{10}$ configuration lacking unpaired electrons, the superconducting electron pairs can no longer be originated. According to the model in question, this shuts out superconductivity. In practice, substitution of yttrium with praseodymium is equivalent to converting the bilayered superconductor in a monolayered material devoid of superconducting properties.

3 Final remarks

Among the features shown by the previous superconductors the most intriguing one is perhaps the role of the oxygen content. In reality, all these unconventional superconductors consist of a blend of metal oxides. Since oxygen is kept in the form of divalent O^{-2} ions, when oxygen is removed as neutral atoms some electrons are left in the material and become bound to metal ions. In most cases, this reduction process inserts the very unpaired electrons which originate the superconducting electron pairs. The $Tl_2Ba_2CuO_6$ and $SrRuO_4$ compounds, like the classic perovskite $SrTiO_{3-\delta}$, belong to this kind of superconductors. It is to be pointed out, in this connection, that superconductors like $BaPb_{0.7}Bi_{0.3}O_3$ and $Ba_{0.6}K_{0.4}BiO_3$ are also to be regarded as reduced compounds. In fact, without reduction, their actual stoichiometries should be written as $BaPb_{0.7}Bi_{0.3}O_{3.15}$ and $Ba_{0.6}K_{0.4}$ $BiO_{3.3}$ respectively. For these compounds, the lack of room in the stiff perovskitic cells prevents oxygen from entering the lattice until metals are fully oxidized (1). With the YBCO superconductor the situation is quite different. This compound holds both divalent and trivalent copper. For $0 \leq x \leq 0.5$ its stoichiometry is indeed $YBa_2Cu^{II}_{2+2x}Cu^{III}_{1-2x}O_{7-x}$. When oxygen is removed, trivalent copper on the cell basal planes is reduced to divalent with no effect on the conjugated $Cu^{II}O$ layers facing each other at the opposite sides of the lacuna-yttrium planes. This would leave T_c unchanged. But, as shown in reference [1], oxygen removal takes place mostly at the $Cu^{II}O_5$ pyramid apexes thus weakening the polarizing field which stretches the $3d$ orbitals of copper ions lying on $Cu^{II}O$ layers toward each other. This lessens overlap of $3d$ orbitals thus reducing electron pairing energy V_0 and, as follows from equation (1), T_c. It is to be pointed out that by further on removing oxygen, that is, for $0.5 \leq x \leq 1$, YBCO stoichiometry becomes $YBa_2Cu^{II}_{4-2x}Cu^{I}_{2x-1}O_{7-x}$ showing monovalent copper with $3d^{10}$ electron configuration. The appearance of monovalent copper lacking unpaired electrons on the conjugated $Cu^{II}O$ layers might play a role in shutting out superconductivity for $x > 0.5$.

As for the $Sr_{1-y}Nd_yCuO_2$ compound considered in Section 2.3, the main conclusion is that the charge reservoir layers play a more momentous role that the one foreseen by the current interpretations of the superconduction mechanism. With this compound, in fact, reservoir layers do not merely control the doping of the $Cu^{II}O$ layers but, owing to the unpaired electrons of neodymium ions, they share directly in superconduction. The same conclusion applies to the thallium-based compound $Tl_2Ba_2CuO_6$. It is worth noting that with these compounds some amount of ionic contribution should be included in the trial function of equation (4) of reference [1] in order to account for the different kinds of orbitals coupled in the spin singlet bonds. Concerning the absence of superconductivity in the praseodimium-substituted YBCO of Section 2.4, it essentially reaffirms the conclusion attained with the thallium compound $Tl_2Ba_2CuO_{6.1}$ according to which single-layered compounds are not superconductors.

A further point worth considering is the actual nature of the atomic orbitals which form the spin-singlet bonds. In cuprates, the Cu^{+2} ions show unpaired $3d$ electrons whose charge distribution is characterized by prominent lobes lined up with the crystal axes. On the copper oxide planes, the Coulomb field of the O^{-2} ions arranged in a cross around Cu^{+2} ions cuts down the electron charge density along Cu-O directions thus increasing density along the cross diagonals. This means that the charge distribution is expected to be like that of $3d_{xy}$ orbitals. It has been shown in reference [1] that this leads to d-symmetry of the superconducting gap. However, even though cuprates are essentially ionic crystals, bonds between copper and oxygen can show a certain degree of covalent character. Thus, copper $3d_{x^2-y^2}$ orbitals and oxygen p orbitals, which are

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[1] In analogy with the ancient alchemist's phlogiston theory according to which: *earths + phlogiston → metals*, these compounds might be referred to as "phlogistic superconductors". In fact, with this theory, the reduction process originating superconduction can be reinterpreted as: *nonsuperconducting metal oxides + phlogiston → superconductors.*

lined up along the Cu-O directions, should be considered as well. This can originate a superexchange interaction between copper ions of Cu-O-Cu chains. According to some theoretical models [16], superconduction is to be ascribed to this very kind of interaction. It follows that the $3d$ orbitals of copper ions of lattice vector $\mathbf{u}_p$ should be written in the more general form

$$a\left(\mathbf{r}_1-\mathbf{u}_p\right)=c' a_{\mathrm{xy}}\left(\mathbf{r}_1-\mathbf{u}_p\right)+c'' a_{x^2-y^2}\left(\mathbf{r}_1-\mathbf{u}_p\right), \qquad (3)$$

where $(c')^2+(c'')^2=1$ and $c'>c''$ or perhaps $c'\gg c''$. Consequently, only the first contribution $c' a_{\mathrm{xy}}\left(\mathbf{r}_1-\mathbf{u}_p\right)$ is to be considered when dealing with the TB wave functions accounting for the electrons running in the conjugated a and b layers. This means that superexchange and spin-singlet interactions can readily coexist with no significant reciprocal effect.

We are aware that the previous arguments, owing to their qualitative nature, are questionable. A quantitative treatment would require the development of onerous numerical calculations which are out of place here. But a further, perhaps more convincing, qualitative argument should be considered. Indeed, the model proposed maintains that in unconventional superconductors a special kind of non-localized spin-singlet bonds capable of sliding along discontinuities of the lattice structures is present. Electrons of these bonds can be reinterpreted as quasi-particles essentially with the same formalism of the BCS theory. By keeping in mind that the formation of spin-singlet bonds is a matter of paramount consequence in all fields of condensed matter physics, it follows that it is unlikely that the "sliding-bond" mechanism considered is not active in cuprates as well as in other unconventional superconductors.

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