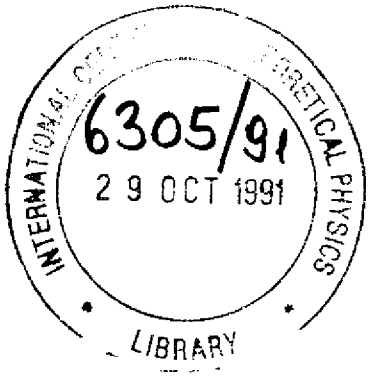
IC/91/217



INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ON THE COMBINATION OF THE COOPER PAIR AND THE OGG PAIR IN THE HIGH-T_c OXIDE SUPERCONDUCTOR

Zhang Li-yuan

INTERNATIONAL ATOMIC ENERGY AGENCY

UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

MIRAMARE-TRIESTE

IC/91/217

International Atomic Energy Agency

and

United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ON THE COMBINATION OF THE COOPER PAIR AND THE OGG PAIR IN THE HIGH–T_c OXIDE SUPERCONDUCTOR

Zhang Li–yuan *

International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

In this paper it is argued that the superconductivity of the high–T_c oxide superconductor (HTOS) can be explained by the combinating mechanism of the Cooper pair and the Ogg pair. The properties of the superconducting state of the HTOS have been calculated under this mechanism, and the theoretical results are overall consistent with the experiment.

MIRAMARE – TRIESTE

August 1991

* On leave of absence from: Department of Physics, Peking University, Beijing 100871, People's Republic of China.

1. INTRODUCTION

Five years have passed since the discovery of $La - Ba - Cu - O$ superconductor [1]. Much effort has been made to reveal the mechanism of the high–T_c superconductive oxide material [2)–8)]. Unfortunately, until now a clear picture has still not been achieved. In 1987, we suggested the free carrier–negative U centre (or the localized bipolaron) interacting mechanism to the high–T_c superconductive system [4)–5)]. Theoretical work has also been done independently in 1987 by Robaszkiewicz *et al.* [8)] in a similar way. We emphasize here two essential points among others: (a) the localization–delocalization competition and (b) the existence of some kind of local pair correlation in the high–T_c oxide superconductor (HTOS). There is considerable evidence from various sources that the oxide superconductors possess these two essential factors, and thus they should impose some restrictions on the Hamiltonian of superconductivity for HTOS. Combining these with some theoretically related models we will see from our discussion that it is necessary to bring up again an old controversy which is the Ogg pairs against the Cooper pairs [9),10)].

First of all, there are many experimental evidences for the existence of two kinds of carriers in HTOS, one is the itinerant carriers and the other is the localized carriers (or nearly localized), and there is an evolutive process of the competition between the itinerant and the localized carriers when the doping in these systems changes. Bianconi *et al.* have given evidence for the itinerant holes in the oxygen derived band (ligand hole) in $Y\ Ba_2\ Cu_3\ O_{7-x}$ and $La_{1.85}\ Sr_{0.15}\ Cu\ O_4$ [11),12)]. They have also indicated that strong correlation between the local $Cu\ 3d$ and itinerant ligand holes and large hybridization between the oxygen $2p$ and $Cu\ 3d$ orbitals exist. Ando *et al.* [13)] have suggested from the transport properties that there are electrons in the hybridized $Cu\ 3d - O\ 2p\sigma$ states of $La_{2-x}\ Sr_x\ Cu\ O_{4-y}$, which are localized for $x < 0.30$ and delocalized for $x > 0.3$, and there are mobile holes on the $O\ 2p\pi$ orbitals. It is also well known that as the content of some component in HTOS changes, the metal–insulator transition appears. This phenomenon is a reflection of the competition between the delocalization and the localization of the carriers in these systems. Therefore, in my opinion, the first condition for the Hamiltonian which can be chosen for the high–T_c oxide systems is that the delocalization–localization competition between the two kinds of carriers must be inherently involved in the Hamiltonian.

The second condition which must be considered for the Hamiltonian of HTOS is that it must contain the essential factor of the existence of some kind of local pair correlation. With regard to this, the most direct evidence is the recent work by S. Sugai *et al.* [14], in which the coexistence of the itinerant large polarons and localized bipolarons has been shown from the detailed analysis of Raman spectra in $Ba_x K_{1-x} Bi O_3$, and the strong interactions between these two states have been suggested as the origin of the superconductivity in the HTOS. Another well–known unique feature in HTOS is the shortness of the superconductive coherent length, which is of the order of lattice parameter or somewhat larger. This is no doubt a reflection that the extent of some pair correlation on the spatial scale is very different from the BCS picture. From the theoretical standpoint, the arguments of the existence of the bipolaron are multiform. In Ref.15, Mila *et al.* have pointed out that a strongly bound singlet ground state exists in the vicinity of the same *Cu* atom in HTOS. Similar point has been pointed by the author [4]. The other arguments of forming the bipolaron are: the local distortion of the lattice [4], the "magnetic confinement" [16], the chemical stability [16] and the electronic originated attractive potential [4),17].

Combining the first aspect with the second, both aspects mentioned above make us remember naturally the old controversy which is the Ogg pair against the Cooper pair. Here, the term of the Ogg pair is used in the sense that it means the localized pair. There is no doubt about Ogg's priority of the suggestion [10]. My idea is that for HTOS we must combine these two kinds of pair correlations into one expression of the Hamiltonian potentially. Consequently, it is appropriate at this point to involve two subsystems in the Hamiltonian. One of them is assumed to be the free–carrier (or nearly free carrier) subsystem (electrons or holes), in which there is BCS coupling constant (λ_s), no matter how weak it is. The other subsystem is the bound pairs or bipolarons. Besides, it is important to stress an additional point that the mixing term between the free carrier and the bipolaron must be added to the Hamiltonian for describing the HTOS so that two functions can operate automatically on the concrete calculation. The first function is that the mixing between the free carriers and the carriers in the bipolarons results in an effective hopping of bipolarons, so it is better to say the nearly localized pairs. The second is that the mixing strength

can change as the doping changes and as a result the extent of localization of the carriers changes simultaneously [18].

2. THE HAMILTONIAN AND THE COUPLING EQUATIONS OF THE ENERGY GAP FUNCTIONS

The Hamiltonian is

$$H = H_s + H_u + H_{mix} \tag{1}$$

$$H_s = \sum_{\vec{k},\sigma} \varepsilon_{\vec{k}} c^+_{\vec{k}\sigma} c_{\vec{k}\sigma} - \lambda_s \sum_{\vec{k}} c^+_{\vec{k}\uparrow} c^+_{-\vec{k}\downarrow} c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow} \tag{2}$$

$$H_u = \sum_{i\sigma} E_b b^+_{i\sigma} b_{i\sigma} - U \sum_{i\sigma} n_{i\uparrow} n_{i\downarrow} \ (U > 0) \tag{3}$$

$$H_{mix} = h \sum_{i,\vec{k},\sigma} (e^{i\vec{k}\cdot\vec{R}_i} c^+_{\vec{k}\sigma} b_{i\sigma} + H.C.) \tag{4}$$

$c^+_{\vec{k}\sigma}$ and $b^+_{i\sigma}$ are the creation operators of the free carrier with momentum $\vec{k}$ and spin σ and the local carrier on the site i. $\varepsilon_{\vec{k}}$ and E_b are the one–particle energies of the free and local carrier, respectively, and h is the mixing potential between them. $-U(U > 0)$ describes the negative correlation energy between the two local carriers with opposite spin on the same site, or, as well known a singlet state of bipolarons is usually formed between different site (nearest neighbours), in this sense the "site" is referred to the bipolaron site.

Here, we want to make three annotations on the above mentioned Hamiltonian. First, direct hopping of the bipolarons has been neglected. Secondly, according to our earlier papers [19),20)], provided λ_s exists, no matter how weak it is, there are induced nondiagonal self energy and the corresponding induce energy gap for the nearly localized carriers, which are due to the mixing interaction. Consequently, the Cooper pairs of the itinerant carriers and the nearly localized pairs interact and induce each other to generate the superconductivity, which may be a function of the superconductive correlation length. This is a combining picture of the Cooper pair and the Ogg pair. Thirdly, we can discuss the limit $\lambda_s \to 0$, which means that the value of λ_s is so small that

the contribution of the Cooper pairs has only the function of inducing the superconductive energy gap of the nearly localized carriers, and the enhancement of T_c comes decisively from the latter.

As for the distribution of bipolarons, three cases can be suggested. (a) the random distribution in a bulk sample; (b) periodic distribution expressed as a periodic Anderson model with negative correlation energy; (c) a sandwich of two layers. One layer (U layer) is a metal thin film randomly containing negative correlation energy regions (bipolarons) and the other (S layer) is the BCS superconducting thin film layer (as mentioned above, λ_s may be very small).

In case (c), linearizing the negative correlation part of the Hamiltonian and making the Dyson expansion of the mixing term, then up to the second power of the mixing parameter, we have obtained the coupling equations of the energy gap functions as follows,

$$\Delta_s(\omega_n) = \frac{\left(1 + n\frac{g_b(\omega_n)}{N(0)} + \frac{\Gamma_u}{|\omega_n|}\right)\Delta_s^{ph} + n\frac{g_b(\omega_n)}{N(0)}\frac{\Gamma_s}{|\omega_n|}\Delta_b^{in}}{1 + \frac{\Gamma_1}{|\omega_n|} + n\frac{g_b(\omega_n)}{N(0)}\left[1 + \frac{\Gamma_s}{|\omega_n|}\right]} \tag{5}$$

$$\Delta_u(\omega_n) = \frac{\frac{\Gamma_s}{|\omega_n|}\Delta_s^{ph} + n\frac{g_b(\omega_n)}{N(0)}\left(1 + \frac{\Gamma_s}{|\omega_n|}\right)\Delta_b^{in}}{1 + \frac{\Gamma_1}{|\omega_n|} + n\frac{g_b(\omega_n)}{N(0)}\left[1 + \frac{\Gamma_s}{|\omega_n|}\right]} \tag{6}$$

$$(T \sim T_c)$$

where $\omega_n = (2n+1)\pi T_c$, $(n = 0, \pm 1, \pm 2 \ldots)$. The quantities Γ_U, Γ_S are the interlayer tunnelling parameters introduced by McMillan [21]. $\Gamma_1 = \Gamma_U + \Gamma_S$, $N(0)$ is the density of states (DOS) at E_F of the free carriers, $g_b(\omega_n)$ is the DOS of the localized carriers, and n is the concentration of the bipolarons. In Eqs.(5) and (6), Δ_S^{ph} and Δ_b^{in} are the measures of the superconducting strength originated from the BCS electron–phonon and the negative correlation energy regions respectively. The importance of Eqs.(5) and (6) lies in their internal physical content that the Cooper pair (represented by Δ_S^{ph}) and the Ogg pair (represented by Δ_b^{in}) are interdependent and support each other to contribute to superconductivity. In the following we make some preliminary numerical calculations to argue that this picture fits in with the experiments of the HTOS.

3. NUMERICAL RESULTS

A. Results of $La_{2-x}Sr_xCuO_4$ system

In the paper of Tang *et al.* [22] the Ginzburg–Landau equation in the above mentioned bulk model has been derived, and the formulas for calculating penetration depth, superconductive coherence length, thermodynamic critical field and the specific heat jump at T_c have been given. We have used this bulk model with randomly distributed bipolarons, assuming there being very weak BCS phonon mediated pairing potential in the bulk. It has been shown from our early experience of numerical calculations that the results of this model are semi–quantatively consistent with the two–layer model (case c).

The lattice parameters are $a = 3.791$ Å, $b = 3.791$ Å, $c = 11.279$ Å[23]. There are two copper atoms per unit cell. Using the experimental value of the charge carrier density, $0.3 \times 10^{22} cm^{-3}$ [24], the effective mass of a carrier $m^* = 4.7\, m_e$ [25] and $N(E_F) = 3$ states/eV·Cu atom · spin [26], and taking $|h| = 0.15$ eV, $U = 1.25$ eV and the concentration of the bipolarons $n_u = 2$ per cell, we obtain $T_c = 37$ K

$$\frac{\Delta c}{T_c} = 9.8\ mJ/\mathrm{K}^2 - mol\ Cu$$

$$\lambda = 8600\ \mathring{A} \quad \text{at} \quad T = 34\,\mathrm{K}$$

$$\xi = 49\ \mathring{A} \quad \text{at} \quad T = 34\,\mathrm{K}$$

$$H_c(T = 0\,\mathrm{K}) = 0.38 \text{ Tesla}\ .$$

The corresponding experimental values are 37 K, $10\,mJ/\mathrm{K}^2 - mol\ Cu$ [27], 2500 Å at $T = 6$ K [24], 30 Å at $T = 0$ K [28] and 0.3 Tesla [26]. These theoretical values are overall consistent with experiments. In the calculation we have assumed that the energy level of the localized carrier is near the Fermi energy. This is in general agreement with the experiment [29].

It is also worth noting that the isotope effect exponent of $La_{1.85}Sr_{0.15}CuO_4$ has been calculated to be 0.17 with the same values of h, U, n_u as mentioned above. The experimental value of the isotope effect of $La - Sr - Cu - O$ is between 0.1 and 0.37 with diversity of values by different authors.

B. Results of YBa_2, Cu_3, O_7

With the method as mentioned in A, we have calculated the properties in the superconducting state of $YBa_2\,Cu_3\,O_7$. The lattice parameters are taken to be $a = 3.856$ Å, $b = 3.870$ Å, $c = 11.666$ Å[30]. There are three copper atoms per unit cell. Using the experimental value of the charge carrier density $1.0 \times 10^{22} cm^{-3}$ [31], $m^* = 7\ m_e$ [31] and $N(E_F) = 1.5$ states/eV-Cu atom–spin [26] and taking $|h| = 0.20$ eV, $U = 1.77$ eV, $n_u = 4$, we obtain,

$$T_c = 93\mathbf{K}$$

$$\frac{\Delta c(T_c)}{T_c} = 13\ mJ/\mathbf{K}^2 - mol\,Cu$$

$$\lambda = 5.2 \times 10^3\ \mathring{A} \quad \text{at} \quad T = 83\mathbf{K}$$

$$\xi = 21\ \mathring{A} \quad \text{at} \quad T = 83\mathbf{K}$$

$$H_c(T = 0) = 1.4 \text{ Tesla}\ .$$

The corresponding experimental values are $92.2\,K$, $13 mJ/\mathbf{K}^2 - mol\,Cu$ [32], 1065 Å at $T = 6\mathbf{K}$ [31], 15.6 Å at $T = 0\mathbf{K}$ [33] and 1.6 Tesla [33].

C. Results of $Bi_2\ Sr_2\ Ca_2\ Cu_3\ O_{10}$

The superconductive properties of $Bi_2\ Sr_2\ Ca_2\ Cu_3\ O_{10}$ have also been calculated with the above–mentioned method. The lattice parameters are $a = 3.779$ Å, $b = 3.834$ Å, $c = 37.150$ Å[34]. There are six copper atoms per unit cell. The charge carrier density is $2.5 \times 10^{21} cm^{-3}$ [35]. $N(E_F)$ was calculated to be 2.45 states/eV-Cu atom spin from the experimental value of γ [34] by $\gamma = \frac{2}{3}\pi^2 k_B^2 N(E_F)$. From $N(E_F)$ we estimated $m^* = 7\,m_e$. Taking $|h| = 0.185$ eV, $U = 4.45$ eV, $n_u = 3.2$ per cell, we obtain

$$T_c = 110\ \mathbf{K}$$

$$\frac{\Delta c(T_c)}{T_c} = 16.6\ mJ/\mathbf{K}^2 - mol\,Cu$$

$$\lambda = 8.03 \times 10^3\ \mathring{A} \quad \text{at} \quad T = 80\mathbf{K}$$

$$\xi = 4.22\ \mathring{A} \quad \text{at} \quad T = 80\mathbf{K}$$

$$H_c = 1.46 \text{ Tesla} \quad \text{at} \quad T = 0\mathbf{K}\ .$$

The corresponding experimental values are $110\,K$, $16.5 mJ/\mathbf{K}^2 - mol\,Cu$, 4000 Å at $T = 79\,K$, 7 Å at $T = 79\,K$ and 2.00 Tesla [34),36].

D. The superconducting energy gap

Solving the coupled equations of the energy gap functions at $T < T_c$, which are derived from the two–layer model within the framework of the combination mechanism, using the formula for calculating the quasi–particle density of states at $T = 0\mathbf{K}$,

$$N(\omega) = \text{Re}\left\{\frac{\omega}{[\omega^2 - \Delta^2(\omega)]^{1/2}}\right\}\ . \tag{7}$$

We have calculated the energy gap as the value of ω at which the $N(\omega)$ sharply grows to the appreciable value.

For $La - Sr - Cu - O$ system, with the same values of U, $|h|$, n_u as mentioned in paragraph A, we obtained

$$\frac{2\Delta(0)}{k_B\,T_c} = 4.00\ .$$

Similarly, for $Y - Ba - Cu - O$, we have

$$\frac{2\Delta(0)}{k_b\,T_c} = 4.22\ .$$

It is very interesting to mention that within the combination mechanism, the value of $2\Delta(0)/(k_B T_c)$ is near or somewhat larger than 4 in the case of basically non BCS electron–phonon case (i.e. $\Delta_s^{ph} \approx 0$), and that the practical value of it for a sample can be somewhat varied about 4 depending on the details of the electronic structure expressed by h, U, n_u etc.

4. DISCUSSION

In all the above numerical calculations it has been found that the direct phonon induced superconductivity (measured by λ_s, Δ_s^{ph} etc.) is very small. Certainly, there may be contribution to the strength of negative correlation energy from some local distortion of the lattice, so, the local phonons can make some contribution to the superconductivity indirectly through U. Anyhow, the

overall picture is that provided there is some BCS phonon mediated attractive potential between the itinerant carriers, no matter how weak it is, there are induced nondiagonal self energy and the corresponding induced superconducting energy gap for the nearly localized carriers (Δ_k^{in}), which are due to the mixing interaction. Consequently, the mixing will enhance the effective pairing potential, the Cooper pair and the Ogg pair combine and induce each other.

One of the most interesting features predicted by the combination mechanism is that even at $T = 0\,K$ a very small density of states due to the mixing interaction exists within the region of the energy gap. This prediction comes from our early calculation of the excitation spectra for quasiparticles at $T = 0\,K$. For further details please see Ref.20. This result is consistent with the experiment of S.L. Cooper *et al.* [37]. Moreover, this remnant density of states must lead to contribution to the residual electronic specific heat near 0 **K**, which can be tentatively calculated with the formula

$$\gamma' = \frac{2}{3}\,\pi^2 k_B^2\,\tilde{N}_R$$

where $\tilde{N}_R$ is the remnant density of states inside the energy gap averaged over the energy gap region. The coefficient of the residual electronic specific heat at $T = 0$ **K** have been estimated from numerical calculations of $\tilde{N}_R$. They are 2.25 and 3.04 $mJ/mol\,\mathbf{K}^2$ for $La - Sr - Cu - 0$ and $Y - Ba - Cu - 0$ system respectively. These can be compared with the experiments.

Finally, I want to point out another interesting result here. For the two–layer model, we have calculated the excitation spectra for quasiparticles. It is found that the energy gaps for the quasiparticles in the U layer and S layer are somewhat different, although the difference is small as expected from the existence of mixing interaction. Moreover, the difference in magnitude of these two gaps varies with the values of some parameters, e.g. U, n_u and Γ_u. When U and Γ_u increase, the difference of the two gaps decreases. Therefore, in the combining picture of the Cooper pair and the Ogg pair, there may be two gaps, or in some cases in which the difference between them is so small that it is difficult to measure from experiment, they appear like one. It depends to a large extent on the details of the crystal and the electronic structures of the materials, which can be reflected by U, n_u, Γ_u etc.

5. CONCLUSION

In summary, we make an extensive report here to suggest the mechanism of the combination of the Cooper pair and the Ogg pair for the high–T_c oxide superconductor. Using some simple concrete models within the framework of this combination mechanism, we have explained a variety of the properties in the superconducting state of some high–T_c oxide superconductors. We also emphasize that there are many interesting results inherent in the combination mechanism, e.g. the very small density of states due to the mixing interaction within the energy gap region, the isotope effect exponent being smaller than 0.5 and the two gap structure in some cases etc. We believe that at least there is a reasonably physical kernel in our theory.

Acknowledgments

The author would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.

REFERENCES

1) J.G. Bednorz and K.A. Müller, Z. Physik **B64**, 189 (1986).

2) P.W. Anderson, Science **235**, 1196 (1987).

3) C.M. Varma and S. Schmitt–Rink, Solid State Commun **62**, 681 (1987).

4) Zhang Li–yuan, Solid State Commun. **62**, 491 (1987).

5) Chen Changfeng and Zhang Li–yuan, Physica **147B**, 175 (1987).

6) V.J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

7) J.R. Schrieffer, X.G. Wen and S.C. Zhang, Physica **C153–155**, 21 (1988).

8) S. Robaszkiewicz, R. Micnas and J. Ranninger, Phys. Rev. **B36**, 180 (1987).

9) R.A. Ogg, Phys.Rev. **69**, 243 (1946).

10) J.M. Blatt, *Theory of Superconductivity* (Academic Press, New York and London, 1964) pp.86–87.

11) A. Bianconi et al., Solid State Commun. **63**, 1135 (1987).

12) A. Bianconi et al., Phys. Lett. **127**, 285 (1988).

13) Y. Ando et al., Solid State Commun. **63**, 1135 (1987).

14) S. Sugai, Y. Enomoto and T. Murakami, Physica **B165, 166**, 1241 (1990).

15) F. Mila, F.C. Zhang and T.M. Rice, Physica **153–155**, 1221 (1988).

16) L.J. De Jongh, Physica **C152**, 171 (1988).

17) Zhang Li–yuan, Solid State Commun. **71**, 1065 (1989).

18) Chen Changfeng and Zhang Li–yuan, Acta Physics Sinica **34**, 1442 (1985).

19) Zhang Li–yuan, Chinese Phys. (Amer. Inst. Phys.) **4**, 318 (1984).

20) Tang Hui and Zhang Li–yuan, Chinese Phys. (Amer. Inst. Phys.) **5**, 606 (1985).

21) W.L. McMillan, Phys. Rev. **175**, 537 (1968).

22) Tang Hui and Zhang Li–yuan, Solid State Commun. **54**, 1 (1985).

23) C. Politis et al., Z. Phys. **B66**, 141 (1987).

24) G. Aeppli et al., Phys. Rev. **B35**, 7129 (1987).

25) W.J. Kossler et al., Phys. Rev. **B35**, 7133 (1987).

26) S. Tanaka et al., Proc. of the Beijing Int. Workshop on HTS (World Scientific, Singapore, 1987) p.219.

27) A.P. Ramirez et al., Phys. Rev. **B35**, 8833 (1987).

28) D.K. Finnemore ta al., Phys. Rev. **B35**, 5319 (1987).

29) T. Takahashi et al., Nature **334**, 691 (1988).

30) T. Siegrist et al., Phys. Rev. **B35**, 7137 (1987).

31) D.R. Harshman et al., Phys. Rev. **B36**, 2386 (1987).

32) A. Junod et al., Jpn. J. of Appl. Phys. **26**, Supplement 26–3, 1021, 1119 (1987).

33) Wang Jun et al., Low Temp. Phys. (China) **10**, 12 (1988).

34) F. Shi et al., Phys. Rev. **B41**, 6541 (1990).

35) M. Rateau et al., Phys. Rev. **B41**, 857 (1990).

36) W. Schnelle et al., Physica **C161**, 123 (1989).

37) S.L. Cooper et al., Phys. Rev. **37**, 5920 (1988).