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Superconducting cuprates: A simple model of coupling between electronic holes through apical ions

L. Cianchi [a], P. Moretti [a], F. Piazza [b]

[a] *Istituto di Ricerca sulle Onde Elettromagnetiche, C.N.R., I-50127 Firenze, Italy*

[b] *Dipartimento di Fisica, Università di Firenze, I-50139 Firenze, Italy*

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Abstract

An intuitive description is given of a phenomenological model for the formation of Cooper pairs in cuprate superconductors. In this model, coupling is mediated by large lattice strains connected to anharmonic oscillations along $\hat{c}$ of the apical ions. A pair binding energy of the order of several hundred kelvin was obtained. © 1998 Elsevier Science B.V.

1. Introduction

Superconducting cuprates have structures and electronic properties that are much more complicated than those of ordinary metals and, perhaps precisely for this reason, in spite of the great amount of research carried out, the origin of high-T_c superconductivity is still unknown.

Metals have high symmetry and few atoms per unit cell. Moreover, their conduction properties are well described by low energy excitations of an electronic Fermi liquid, and lattice vibrations are harmonic at not very high temperatures. By virtue of these characteristics, it has been possible to work out a fairly accurate theory of metal superconductivity which is able to account for the various aspects of the phenomenon [1]. Much work has been carried out in order to extend the theory to situations in which high-temperature superconductivity could be expected [2]. The result is a deeper knowledge of the phenomenon, but no new superconducting material has been discovered as a consequence of such research. Superconducting cuprates are the result of experimental studies on materials belonging to the family of perovskites, the concealed superconducting properties of which could not have been foreseen [3].

Unlike metals, cuprates have many atoms per unit cell and are highly anisotropic. Current carrier properties are still being debated [4–6], particularly the role played by electronic correlations and antiferromagnetic magnons. On the other hand, in the case of high doping, the so-called t–J Hamiltonian describing the electronic properties of the CuO_2 planes is largely intractable [7]. Lastly, some calculations and several experiments carried out using different techniques give evidence of low-temperature anharmonic lattice vibrations [8–12]. Because of these complicated features, an accurate theory of cuprate superconductivity seems to be premature at the moment.

In metals, supercurrent carriers are electronic Cooper pairs. In cuprates, they are usually pairs of electronic holes [13]. The pairs in metals have a spherical shape, the diameter of which is of the order of 10^4 Å, while in cuprates they form a flat,

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disk-like structure, the diameter of which is about 20–30 Å [14]. But small pairs mean high bond energy and, consequently, high T_c. So, if we hypothesize that coupling is mediated by lattice strains due to the electrostatic action of the holes, very large strains are necessary in order to obtain a high bonding energy, which, in cuprates, could be connected to anharmonic lattice modes.

In this paper, we will describe a simple phenomenological model of the coupling of holes in the CuO_2 planes through the mediation of the polarization of the facing AO planes (A = Ba, Sr) due to the actions of the holes themselves. For this, we will suppose that the apical site ions perform large amplitude anharmonic oscillations in the $\hat{c}$ direction.

Although it seemed that materials with high T_c had been found with no apical ion [15], subsequent experiments have shown that these materials also have apical ions [16], although the apical sites are irregularly occupied. On the other hand, the doped antiferromagnetic spin-ladder compound $(La, Sr)CuO_{2.5}$ has no apical ion, and does not show any superconducting transition down to 5 K [17], although, in common with superconducting cuprates, it has an insulator-to-metal transition with increased doping. This fact suggests that apical ions actually play an important role in cuprate superconductivity.

Coupling models based on the existence of anharmonic modes have already been considered in the past and in more recent literature [18–21]. In particular, the possibility of obtaining high T_c in cuprates has been discussed using the strong coupling theory for metal [18–20]. However, as we have already noted, cuprates are much more complicated than metals, and T_c changes very greatly from one compound to another: e.g. changing the reservoir layers and/or the number of CuO_2 planes per cell. In other words, the superconducting state is determined by several structural factors, not just by the coupling mechanism, which is presumably the same in all cuprates. A different approach was presented in Ref. [21], where Monte Carlo calculations for a system of strongly-correlated fermions coupled to anharmonic phonons were carried out.

In this paper our aim is to present a simple, very intuitive phenomenological description of the pairing in cuprates through the anharmonic vibrations of the apical ion.

For this, we have followed the Weisskopf treatment for Cooper pair formation in metals [22]. This intuitive treatment makes it easier to see the role played by the different characteristic factors of cuprates that could determine superconductivity. In our opinion this is very useful at the present state of knowledge.

2. Basic facts and hypotheses of the model

Our model is based on certain facts and hypotheses that will now be briefly described.

First, let us consider the electronic properties of the CuO_2 planes. They have been widely discussed both qualitatively, by means of tight-binding approximation, and by more accurate band calculations [23]. However, the description in terms of single-electron states cannot explain the insulating antiferromagnetic state of the non-doped materials. It is a consequence of electronic correlations due to the strong Coulomb repulsion between two opposite spin electrons on the same site, and these correlations are not taken into account in band calculations. Nevertheless, for highly-doped materials, the Fermi surface calculated by the tight-binding method surprisingly agrees with the ARPES experiments [24]. On the other hand, the experimental dispersion curve has a slope of about one half of the calculated one [24,25]: i.e. the effective mass is about twice the band mass.

In our phenomenological description then, we will suppose that: (a) Holes behave as itinerant particles of mass $m \approx 2m_e$ and charge $+e$ suitably shielded by the in-plane charges. The physical properties of these particles are assumed to be mainly determined by the complicated interactions with the ions and the electrons of the CuO_2 plane in which they lie. (b) All the holes created by doping form a fermion gas that occupies single-hole states close to the Fermi surface within an energy range that is a small fraction of ε_F and corresponding to a satisfactorily defined wave vector. Their Wannier functions will be a hybrid between the Cu $d_{x^2-y^2}$ and its immediate neighbor O $p_{x,y}$ orbitals.

One condition for hole coupling is that, at $T = 0$, excitation energies in order to reach free states – i.e. the states immediately below the Fermi surface – are comparable to or smaller than the bonding energy, which can be presumed to be of the order of several hundred kelvin (see Section 5). For optimized doping,

this condition is practically verified for all the holes [24]; consequently, the Cooper pair density is about one half of the hole density. This conclusion agrees with the dependence of T_c on doping, as a number of experiments show [26].

Lattice vibrations and in particular those of the apical ions is another very important characteristic of cuprates. These ions are normally O^{-2}, but in some cases they can be other negative ions, for example Cl^- or F^- [27].

EXAFS measurements on oriented YBCO powder have shown a strong anharmonicity in apical O^{-2} motion along the $\hat{c}$ axis. A similar anharmonicity has also been revealed by Raman [11] and ion channeling [9] experiments. Although, to our knowledge, experiments on the apical ion motion have only been carried out on YBCO, the interatomic distances of this ion from its immediate neighbors are similar in the different compounds [28]. Consequently, we will suppose that the above-mentioned anharmonicity is present in all cuprates.

3. Interaction between holes

For the sake of simplicity, we will suppose that the apical ions move independently of each other, subjected to a potential which is strongly anharmonic in the $\hat{c}$ direction. Ion displacements in the directions along which the potential is harmonic should result in a coupling energy that is comparable to that of the Cooper pairs in metals, i.e. much smaller than that expected for cuprates. Then, in order to evaluate the coupling energy for cuprates, these displacements can be disregarded and only the apical ion motion in the $\hat{c}$ direction will be considered.

Now, let us consider a moving hole in a CuO_2 plane. Its electric field changes the average position of the surrounding ions. This field increases when the hole approaches a site, and decreases when the hole moves away from it. From the moment at which the field becomes negligible, a certain amount of time is necessary for the ion to come back to the previous position. Consequently, a moving hole leaves behind it a "wake" of apical ions shifted toward the CuO_2 facing plane in which the hole lies (Fig. 1).

A second hole that finds itself under the influence of the bipolar electric field due to the displaced ions, i.e. practically just below the wake of the first hole, has a lesser energy than when it is outside of such influence.

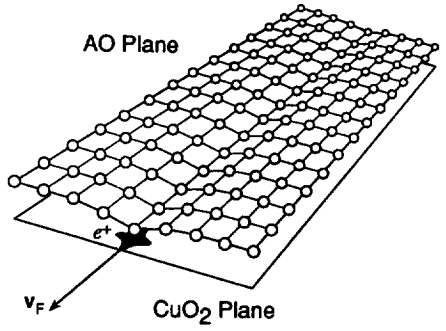

Fig. 1. Schematic representation of the wake of shifted apical ions that a hole leaves behind it because of its electrostatic action on the ions. Only the apical ions (generally O^{-2}) of the AO plane are indicated.

If the angle between the trajectories of two holes is not zero, one of the holes that crosses the wake of the other hole is subjected for a short time to the bipolar field of the wake ions. It will then undergo only a small scattering (Fig. 2a). But if the trajectories are parallel, each of the two holes may experience the influence of the wake of the other hole for a long time (Fig. 2b). In this case, if the wave vectors have opposite directions, the *relative motion* is strongly influenced by hole interaction and a bonding state can be formed. On the other hand, if the wave vectors have the same direction, there is no relative motion; therefore, there is no coupling, since interaction is constant.

Let $\Psi(\boldsymbol{x} - \boldsymbol{R}_n)$ be the Wannier function of a hole in the nth cell of a CuO_2 plane, where $\boldsymbol{x}$ denotes the position of a point of the plane and $\boldsymbol{R}_n$, that of the nth cell. The corresponding planar charge density of the bare hole is: $\rho(\boldsymbol{x} - \boldsymbol{R}_n) = e|\Psi(\boldsymbol{x} - \boldsymbol{R}_n)|^2$.

The screening action of the plane charge will be described by the dielectric function of the Fourier components of the field. In the spirit of the tight binding approximation, a hole stays on a site for a sufficiently long time to "acquire" the Wannier state of that site. In the same spirit, we shall suppose that the screening charges have time to conform themselves to the $\rho = e|\Psi|^2$ charge density. This means that we can consider the dielectric function for $\omega = 0$: $\varepsilon(\boldsymbol{k}, 0) \equiv \varepsilon(\boldsymbol{k})$. Then, the $\hat{c}$ component $E_z(\boldsymbol{x}_i - \boldsymbol{x}_n)$ of the electric field created by a hole at $\boldsymbol{x}_n$ at the point $\boldsymbol{x}_i$ of the AO plane is

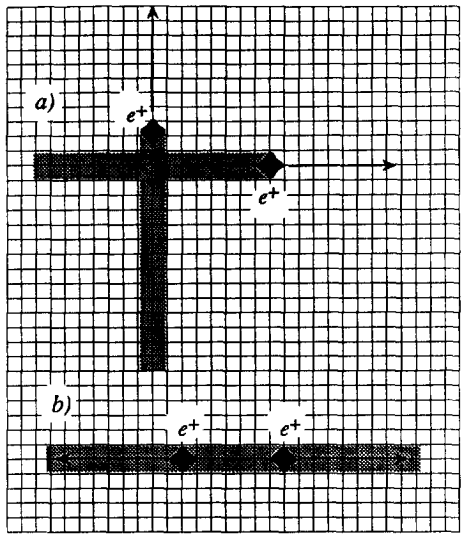

Fig. 2. Two different kinds of interaction between hole + wake entities. (a) The trajectories of the holes are not parallel. A hole crossing the wake of the other hole interacts with the bipolar field of the ion of the wake for only a short time, and undergoes a small scattering. (b) The trajectories of the holes are parallel, and the movement directions are opposite. Both the holes interact simultaneously with the wake of the other hole for a long time, and the coupling may occur.

$$E_z(\boldsymbol{x}_i - \boldsymbol{x}_n) = \frac{1}{4\pi\varepsilon_0}\frac{d}{(2\pi)^2} \times \int \mathrm{d}^2\boldsymbol{x}' \int \mathrm{d}^2\boldsymbol{k}\, \frac{\phi(\boldsymbol{k})}{\varepsilon(\boldsymbol{k})}\, \frac{\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}' - \boldsymbol{x}_n)]}{[(\boldsymbol{x}_i - \boldsymbol{x}')^2 + d^2]^{3/2}} = \frac{1}{4\pi\varepsilon_0}\frac{d}{2\pi} \times \int \mathrm{d}^2\boldsymbol{k}\, \frac{\phi(\boldsymbol{k})}{\varepsilon(\boldsymbol{k})} \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}_i - \boldsymbol{x}_n)] \exp(-kd)\,, \tag{1}$$

where $\phi(\boldsymbol{k})$ is the Fourier transform of ρ and d is the distance of the AO plane from the CuO_2 contiguous plane.

Since Ψ is not known, in order to work out a semi-quantitative estimation – but one that is sufficiently accurate to catch the order of magnitudes – ρ will be approximated to a Gaussian function, the standard deviation of which is of the order of a fraction of the side length a of the square cell:

$$\rho \approx \frac{e}{2\pi\sigma^2} \exp\left(-\frac{|\boldsymbol{x} - \boldsymbol{x}_n|^2}{2\sigma^2}\right). \tag{2}$$

Moreover, we will assume for $\varepsilon(\boldsymbol{k})$ a Thomas–Fermi expression with screening length $k_s = \lambda_s^{-1}$ of the order a^{-1}: $\varepsilon(\boldsymbol{k}) \approx 1 + (k_s/k)^2$.

With the position $x_{in} = |\boldsymbol{x}_i - \boldsymbol{x}_n|/a$, we obtain

$$E_z(x_{in}) \approx \frac{e}{4\pi\varepsilon_0 a^2}\, I(x_{in})\,, \tag{3}$$

where

$$I(x_{in}) = \int_0^\infty \mathrm{d}\xi\, \frac{\xi^3}{\xi^2 + \xi_s^2} \exp(-\tfrac{1}{2}s^2\xi^2 2 - \xi\delta) \times J_0(x_{in}\xi)\,, \tag{4}$$

with $s = \sigma/a$, $\xi_s = ak_s = a/\lambda_s$ and $\delta = d/a$. J_0 denotes the Bessel function of order zero.

Now, let us examine a hole moving along a certain direction, e.g. the direction of the $\hat{a}$ axis. The average time of its stay at each site is $\tau_s = a/v_F$. Since $v_F = \hbar k_F/m$, $k_F \approx 1.3/a$ [29] and $m \approx 2m_e$, $\tau_s \approx 5 \times 10^{-15}$ s is obtained. During this time, the force $ZeE_z(x_{in})$ acts on the ion at position x_{in} with respect to the hole in which Ze is the ion charge. If z is the displacement of the apical ion from the AO plane, the total potential energy of the ion is given by the sum of the non-perturbed potential energy – represented by a symmetrical function with respect to the AO plane – and of the term $ZeE_z(x_{in})z$. The latter, which is negligible for large x, increases when the hole approaches the ion and decreases, again becoming negligible, when the hole moves away from it. In the end, the average displacement $\langle z \rangle$ of the ion will be different from zero and its value will remain unchanged for a time of the order ω_T^{-1}, where ω_T is the tunneling frequency for a double-well potential. More generally, ω_T is a characteristic frequency of the ion. The length L of the wake left behind it by a hole moving at velocity v_F will then be given by $L \approx v_F\omega_T^{-1}$. But this is true only if the mean life τ_F of the hole state is of the order of or greater than ω_T^{-1}. τ can be estimated starting from the in-plane conducibility data by means of the simple Drude formula: $\tau_F = \sigma m/e^2 n$, where n is the hole density. For the best single crystals of YBCO, at $T = 100$ K, $\sigma \approx 5 \times 10^5\ \Omega\mathrm{m}^{-1}$; moreover, $n \approx 2.5 \times 10^{27}\ \mathrm{m}^{-3}$. Then $\tau \approx (1.5\text{–}2) \times 10^{-14}$ s, i.e. a value of the same order of magnitude as ω_T^{-1} obtained for YBCO by EXAFS measurements [10].

In metals coupling can be formed, in spite of interaction weakness, because of long range interaction.

In fact, in order to have a bonding state in a three-dimensional potential of depth U and width L, the relation

$$U > \frac{\pi^2\hbar^2}{8mL^2} = U_0 \tag{5}$$

must be satisfied.

If the mean life τ_F of the electron states with Fermi energy is greater than ω_D^{-1} (ω_D is the Debye frequency), $L \approx v_F\omega_D^{-1}$ is of the order of 300–400 Å, so that U_0 is of the order of a few kelvin. However, if $\tau_F < \omega_D^{-1}$, L decreases proportionally to τ_F and U_0 increases like τ_F^{-2}. In other words, if $\hbar\tau_F^{-1}$ is of the order of or greater than $\hbar\omega_D$, since for metals $\hbar\omega_D \gg \Delta$, the energy indetermination of the quasi particles is much greater than Δ. In this case, Cooper theory is no longer meaningful. But for superconductor cuprates, $\Delta > \hbar\omega_T$; therefore, in order to estimate the bonding energy, the hole state can be considered adequately definite also for $\tau_F \approx \omega_T^{-1}$.

Let us now evaluate the attractive interaction between two holes. Firstly, we observe that the average displacement $\langle z\rangle$ of the wake ions depends on the characteristics of the anharmonic potential. In any case, $\langle z\rangle$ is maximum for the ions lying in the row just over the hole trajectory (*central row*) and decreases as row distance increases (Fig. 1). We will denote with $\langle z\rangle_0$ the average displacement for the central row, with $\langle z\rangle_1$ those of the two nearest neighboring rows, and so on.

As we explained in Section 3, a hole with wave vector $\boldsymbol{k}$, staying under the wake of a second hole with wave vector $-\boldsymbol{k}$, "sees" a negative potential. At the same way, the second hole, moving under the wake of the former, "sees" the negative potential due to this wake. Since L is the length of the polarization wake, the relative motion of the two holes is determined by a potential energy extending over a range L. The strength of this potential energy can be obtained by evaluating the interaction of the holes with the wake dipoles, or, equivalently, the interaction of the wake dipoles with the field of the holes. If $\boldsymbol{x}_l$ and $\boldsymbol{x}_m$ are the position vectors of the holes, such an interaction energy is given by

$$U = -Ze\sum_i [E_z(x_{li}) + E_z(x_{mi})]\langle z_i\rangle\,, \tag{6}$$

where $\langle z_i\rangle = \langle z\rangle_0$ if the ith ion belongs to the central row, $\langle z_i\rangle = \langle z\rangle_1$ if it belongs to one of the two nearest neighboring rows, and so on.

The significant terms of the sum in (4) are those for which x_{li} and x_{mi} are small ($x_{li}, x_{mi} = 0, 1$). In this case, U is practically independent of the sites occupied by the holes below one row of the wake; otherwise, $U = 0$. In general, U will depend on the motion direction and on the distance λ between the trajectories of the holes:

$$\begin{aligned} U &= U_{k,\lambda}\,, \quad \text{for } x < L\,,\\ &= 0\,, \quad\quad \text{for } x > L\,. \end{aligned} \tag{7}$$

Lastly, let us consider the Coulomb interaction between holes. Since the hole charges are shielded by the in-plane charges, the range of this interaction will be much smaller than L. Thus, Coulomb interaction should not prevent the formation of the bonding state.

According to our assumptions, a direct calculation can be performed for the Coulomb interaction between holes, taking into account that the screened-charge density ρ_s of a hole at the site $\boldsymbol{x}_n$ has the form [30]

$$\rho_s(\boldsymbol{x} - \boldsymbol{x}_n) = \frac{e}{(2\pi)^2}\int \mathrm{d}^2\boldsymbol{k}\,\frac{\phi(\boldsymbol{k})}{\varepsilon(\boldsymbol{k})}\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x} - \boldsymbol{x}_n)]\,. \tag{8}$$

Evaluating the Coulomb interaction between a charge distribution centered at the site $\boldsymbol{x}_1$ and another charge distribution centered at the site $\boldsymbol{x}_2$, one easily obtains

$$U_c(x_{12}) = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2\pi}\int \mathrm{d}^2\boldsymbol{k}\,\frac{\phi^2(\boldsymbol{k})}{\varepsilon^2(\boldsymbol{k})}\,\frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}_{12})}{k}\,. \tag{9}$$

With the usual approximations, Eq. (9) can be written in the form

$$U_c(x_{12}) \approx \frac{e^2}{4\pi\varepsilon_0 a}\,I_c(x_{12})\,, \tag{10}$$

where x_{12} is the distance between the holes in a and

$$I_c(x_{12}) = \int_0^\infty \mathrm{d}\xi\,\frac{\xi^4}{(\xi^2 + \xi_s^2)^2}\exp(-s^2\xi^2)\,J_0(x_{12}\xi)\,. \tag{11}$$

For s and ξ of the order of unity, the numerical evaluation of the integral (11) shows that I_c is significantly

different from zero for $x_{12} \approx 1 \ll L$. Then, in order to perform an estimation of the bonding energy of the Cooper pairs in cuprates, the Coulomb energy can be disregarded.

4. Wave function of a Cooper pair

The general form of the wave function of a Cooper pair is

$$\Psi = \psi(X)\,\Phi(r)\,\chi(\sigma_1,\sigma_2)\,, \tag{12}$$

where $X = \frac{1}{2}(x_1 + x_2)$ denotes the center of mass position, $r = x_1 - x_2$ the relative position of the holes, and σ_1 and σ_2 the spin coordinates.

Here, pairs with center of mass at rest will be considered, i.e. $\psi(X) = \text{const}$. Moreover, since the Fermi surface has a quasi circular shape, the interaction between holes can be assumed to be independent of the r direction. In this case, the component of the relative angular moment of the pair along $\hat{c}$ is conserved: $l = v_F\lambda = \text{const}$ and

$$\Phi(r) = \mathcal{R}(r)\exp(il\varphi)\,, \quad l = 0, \pm 1, \pm 2, \ldots\,, \tag{13}$$

where the radial part satisfies the equation

$$\frac{d^2\mathcal{R}}{dr^2} + \frac{1}{r}\frac{d\mathcal{R}}{dr} + \left(\frac{m}{\hbar^2}(E-U) - \frac{l^2}{r^2}\right)\mathcal{R} = 0\,. \tag{14}$$

For $U = 0$, the solutions of this equation, normalized and orthogonal in a large circle of radius R, are given by $(\mathcal{R}^{(l)}(R) = 0)$,

$$\mathcal{R}_k^{(l)}(r) = \sqrt{\frac{k}{2R}}\,J_l(kr)\,, \quad k = \sqrt{\frac{mE}{\hbar}}\,. \tag{15}$$

Then, we will try to solve Eq. (13) in the form

$$\mathcal{R}^{(l)}(r) = \sum_k \alpha(k)\,\mathcal{R}_k^{(l)}(r)\,. \tag{16}$$

By inserting this expression into Eq. (14), multiplying with $\mathcal{R}_{k'}^{(l)}(r)$ and integrating on the circle of radius R, we obtain

$$\alpha(k)\left(\frac{\hbar^2k^2}{m} - E\right) = -\sum_{k'}\alpha(k')\,U_{kk'}^{(l)}\,, \tag{17}$$

where

$$U_{kk'}^{(l)} = \sqrt{kk'}\,\frac{\pi}{R}\int_0^R J_l(k'r)\,UJ_l(kr)\,r\,dr$$
$$= \frac{\pi}{R}U_l\frac{L\sqrt{kk'}}{k'^2 - k^2}\left[J_l(kL)\,J_{l+1}(k'L)\,k' - J_l(k'L)\,J_{l+1}(kL)\,k\right]. \tag{18}$$

Since $k \approx k' \approx k_F \approx a^{-1}$ and $L \gg a$, is also $kL \gg 1$. So J_l $(l = 0, 1, \ldots)$ can be replaced by their asymptotic expressions. The result is

$$U_{kk'}^{(l)} \approx \frac{LU_l}{R}\,\frac{\sin[(k-k')L]}{k-k'}\,. \tag{19}$$

Finally, we can write in a good approximation

$$U_{kk'}^{(l)} = \frac{L}{R}U_l\,, \quad \text{for } |k-k'| < 1/L\,,$$
$$= 0\,, \quad \text{for } |k-k'| > 1/L\,. \tag{20}$$

We note that the ranges of the wave numbers and of the energies forming the bonding state of the pair are respectively given by L^{-1} and

$$\Delta\varepsilon \approx \left|\frac{d\varepsilon}{dk}\right|\Delta k = \frac{2\hbar^2k_F}{m}\,\frac{m\omega_T}{\hbar k_F} = 2\hbar\omega_T\,, \tag{21}$$

i.e. these ranges are independent of the interaction strength.

If we assume the Fermi level as zero energy, and treat Eq. (17) in the usual way [22], the bonding energy Δ_l is finally found:

$$\Delta_l = \frac{2\hbar\omega_T}{\exp(2\pi\hbar\omega_T/|U_l|) - 1}\,. \tag{22}$$

This expression is formally equal to the one that was obtained for metals [22]. But for metals $\hbar\omega_T \approx |U|$, so that $\Delta \ll \hbar\omega_T$, while for cuprates, at least for $l = 0$, we will show that $\hbar\omega_T \ll |U|$, so that $\Delta > \hbar\omega_T$.

The diameter of the pairs is defined by the relation

$$\varrho^2 = \langle r^2\rangle = \int_0^R \mathcal{R}^2(r)\,r^2\,d^2\boldsymbol{r}\,. \tag{23}$$

By developing the integral in Eq. (22) the usual expression is obtained,

$$\varrho = \alpha\frac{\hbar v_F}{\Delta}\,, \quad \alpha \approx 1\,. \tag{24}$$

5. Numerical estimates

The value of $\Delta_{l=0}$ can be evaluated starting from the experimental data on the coherence length: $\xi_{ab} \approx 20$–30 Å [3]. Since $\rho = \xi_{ab}$ and $v_F \approx 10^5$ ms^{-1}, Eq. (24) gives $\Delta \approx 300$ K.

On the other hand, the value of $\Delta_{l=0}$ can be obtained by Eq. (22), once $U_{l=0}$ has been determined. In order to evaluate $U_{l=0}$, the potential of the apical ion has to be known. The only data at our disposal are the EXAFS data on YBCO. As suggested in Ref. [10] this potential has the form (Fig. 3a)

$$V(z) = k_e(z - z_0)^2, \quad \text{for } z \geqslant 0,$$
$$= k_e(z + z_0)^2, \quad \text{for } z \leqslant 0. \tag{25}$$

In Fig. 3b we have the total potential energy, which is obtained by adding the term $ZeE_z(x_{in})z$ to the non-perturbed potential energy. Here the ion displacement z is assumed to be negative if it is directed toward the CuO_2 planes. The average displacement of the ion in the time in which the hole electric field acts on it is then given by

$$\langle z \rangle = (p_{12} - p_{21})z_0, \tag{26}$$

where p_{12} and p_{21} represent, respectively, the probabilities that the ion tunnels from well I to well II and vice versa. Obviously, for $E_z = 0$, $p_{12} = p_{21}$ and then $\langle z \rangle = 0$. On the other hand, for $E_z \neq 0$, $p_{21} > p_{12}$ so that $\langle z \rangle < 0$.

With the data of Ref. [10] $\Delta_{l\neq 0}$ is completely negligible. This is why, for $x_{in} \geqslant 1$, the potential $ZeE_z(x_{in})z_0$ is much smaller than the potential barrier between the two wells, so that $p_{12} \approx p_{21}$ and $\langle z \rangle \approx 0$. Then, the polarization wake of each hole consists of only the central row and, if two holes have parallel but not coincident trajectories, their interaction is negligible. Concerning the case $l = 0$, by assuming that s and k_s, respectively, are in the 0.2–0.4 and 0.5–1 ranges, Δ_0 is of the order of several hundred kelvin (Fig. 4): i.e. the values agree with the one evaluated starting from ξ_{ab}. Since the bonded state of the pairs has $l = 0$, the corresponding wave function will have circular or s symmetry.

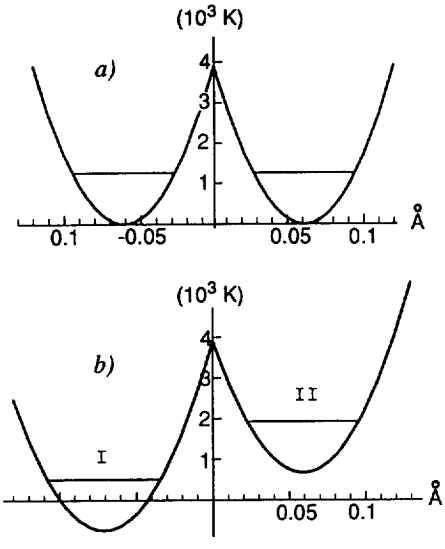

Fig. 3. (a) Potential energy of the apical oxygen at low temperatures as has been determined by EXAFS measurements [10]. (b) Potential energy perturbed by the field of a hole at $x_{in} = 1$.

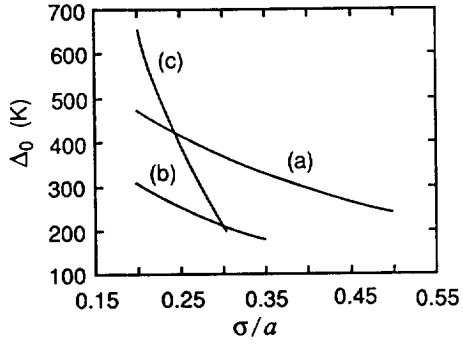

Fig. 4. Bonding energy as a function of the standard deviation s of the hole charge distribution for different shielding constant ξ_s and double-well potential parameters k_e and z_0: (a) $\xi_s = 0.5$, $k_e = 1.5 \times 10^6$ K/Å^2 and $z_0 = 0.055$ Å. (b) $\xi_s = 1$, $k_e = 1.5 \times 10^6$ K/Å^2 and $z_0 = 0.055$ Å. (c) $\xi_s = 0.5$, $k_e = 1.85 \times 10^6$ K/Å^2 and $z_0 = 0.065$ Å.

6. Conclusions

It is worthwhile to observe that, although the coupling mechanism between holes in cuprates can be qualitatively similar to that between electrons in superconducting metals, two important differences arise. First, the Cooper pairs in cuprates are much smaller than in metals, so that their overlap is small.

Second, according to our scenario, practically all

holes are coupled so that they form an interacting gas of bosons, moving in a nearly two-dimensional way.

Our estimation of the bonding energy of a pair gives a value Δ_0 of an order of some hundreds. Consequently, if the Cooper pair condensation is the main cause of superconductivity in cuprates [31], it can happen that above T_c free holes are also present.

However, in order for this conclusion to be true, two essential facts should be verified. First, that the apical ions carry out large amplitude anharmonic oscillations. As we mentioned above, this has only been confirmed by experiments on YBCO, therefore an extension of the experimental studies on the apical ion motion in all cuprates is necessary.

Second, at least for doping corresponding to the metallic phase, that the hole states in the CuO_2 planes can be roughly represented according to the tight-binding method. ARPES measurements would seem to confirm this [24], but the question is still being debated.

According to our model, the ground state of the pair has s symmetry, while in the case of coupling mediated by spin waves, pairs have $d_{x^2-y^2}$ symmetry [32,33]. Consequently, the two different mechanisms cannot contribute together to the coupling. However, at the moment, even the question of pair symmetry has not been made clear by experiments [34,35].

But our model leaves open the possibility that an excited bonding state with $l = 1$, i.e. an orbital doublet with $S = 1$, exists. However, the barrier between the two wells of the apical ion potential has to be at least two orders of magnitude smaller than that given by EXAFS measurements for YBCO. Again, the need for further accurate experiments on apical ion motion is evident.

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