Physics/Solids, fluids: magnetic and electrical properties

A spatial interpretation of emerging superconductivity in lightly doped cuprates

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Abstract

The formation of domains comprising alternating 'hole rich' and 'hole poor' ladders recently observed by Scanning Tunneling Microscopy by Kohsaka et al., on lightly hole doped cuprates, is interpreted in terms of an attractive mechanism which favors the presence of doped holes on Cu sites located each on one side of an oxygen atom. This mechanism leads to a geometrical pattern of alternating hole-rich and hole-poor ladders with a periodicity equal to 4 times the lattice spacing in the CuO plane, as observed experimentally. ***To cite this article: G. Deutscher, P.-G. de Gennes, C. R. Physique 8 (2007).***
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Résumé

Cuprates supraconducteurs peu dopés : une interprétation des structures spatiales. Des arrangements électroniques réguliers ont été détectés récemment par Kohsaka et al. dans des cuprates sous dopés (via une sonde tunnel locale). Certaines paires Cu–O–Cu sont « actives », et forment une échelle. Les autres sites sont peu actifs. Pour expliquer ces structures, nous postulons que, lorsqu'une liaison Cu–O–Cu est occupée par deux trous, la distance (Cu–Cu) rétrécit et l'intégrale de transfert (t) est fortement augmentée. Ceci peut engendrer des paires localisées (réelles ou virtuelles). Aux taux de dopage étudiés, la période de répétition vaudrait 4 mailles élémentaires. ***Pour citer cet article : G. Deutscher, P.-G. de Gennes, C. R. Physique 8 (2007).***
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Cette Note est le dernier article de Pierre Gilles de Gennes. Il s'était passionné pour ce retour à la supraconductivité, abandonnée après 1970. Sa disparition soudaine l'a empêché de répondre aux commentaires des rapporteurs. L'avenir dira si ses suggestions sont ou non pertinentes. Par respect pour sa mémoire ce texte est publié en l'état, mises à part quelques clarifications de détail apportées par son coauteur Guy Deutscher pour en préciser la lecture.

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Version française abrégée

On voit par effet tunnel, sur des cuprates peu dopés, des domaines rectangulaires de largeur $4a$ (où a est la maille du réseau plan CuO). Le centre du rectangle est formé par une colonne d'atomes O et deux cuivres voisins, qui apparaît comme « active » en effet tunnel, et est entourée de colonnes inactives.

Nous proposons une interprétation de ces arrangements à partir du postulat suivant : si deux trous occupent deux sites Cu voisins, il se produit une contraction de la liaison Cu–O–Cu. Celle-ci augmente significativement l'intégrale de transfert t entre les Cu, car t fait intervenir deux fois le recouvrement des orbitales d du Cu et p de l'oxygène, et est donc très sensible à la distance. Nous montrons, par une méthode variationnelle, que l'énergie d'une paire est notablement abaissée (Eq. (2)). Si cet abaissement dépasse la demi-largeur de bande pour des trous isolés, on arrive à une paire liée. Si il est un peu inférieur, on aura un état lié virtuel, avec une durée de vie finie. On arrive à une conclusion similaire si l'on considère des segments O–Cu–O–Cu–O avec deux trous localisés de préférence sur les oxygènes, comme indiqué Fig. 2.

Les conséquences de ce modèle apparaissent sur la Fig. 3 où la paire active est formée par les atomes $2'$–1–2. La distance suivante (entre 3 et $3'$) est augmentée : donc cette colonne doit avoir une faible intégrale de transfert, et sera inactive.

La propagation de paires ne peut alors se faire que dans la direction perpendiculaire. Pour un taux de dopage voisin de la moitié du dopage optimum, comme c'est le cas dans les expériences, on engendre ainsi des rectangles, de largeur $4a$, dont la longueur est probablement conditionnée par des défauts. Avec le taux de dopage utilisé ($\sim$10%), le nombre minimum de Cu requis pour avoir une paire active est de l'ordre de 20. La concentration locale sur les colonnes actives est alors comparable à l'optimum de supraconductivité.

Y-a-t-il des excitations, de type quasi particule, mobiles ? La conduction à l'état normal est faible. Si une certaine cohérence entre domaines subsiste, elle porterait probablement sur des excitations orientées à 45° des domaines. On sait que les cuprates peu dopés ont une surface de Fermi incomplète formée de petits arcs autour de la direction (11).

La supraconductivité macroscopique n'est pas asservie à la structure interne des domaines : on attendrait plutôt un paramètre d'ordre Δ fort dans les directions (01).

1. Introduction

Recent imaging of Scanning Tunneling Spectroscopy (STM) of lightly doped superconducting cuprates has revealed the existence of rectangular domains of width $4a$, where a is the lattice spacing in the CuO plane [1]. Inside each domain the carrier concentration is non-uniform, with a sharp contrast between a central ladder consisting of a column of oxygen atoms and the two neighboring Cu–O–Cu columns where the carrier concentration is high, while it is low on similar ladders at the edges of the domain. The general aspect of the images shows domains having two possible orientations at right angles to each other, with less well organized domains spread randomly across the surface. Tunneling characteristics measured at sites belonging to the central ladder show at low bias a structure reminiscent of a superconducting density of states, with pronounced peaks particularly on the Cu–O–Cu columns, while at the edge ladders only a small conductance dip is visible.

In this communication we wish to point out that this geometrical pattern can be easily understood if one assumes the existence of a mechanism that favors the presence of a pair of doped holes on Cu–O–Cu, or perhaps O–Cu–O–Cu–O segments, accompanied by a small contraction of the Cu–O distances. This mechanism can be due to an increase of the transfer integral t_{OCu}. t_{OCu} depends critically on the overlap between Cu(d) orbitals and O(p) orbitals. If the energy gained by contraction is sufficient, a bound state of the hole pair can be formed.

2. The model

Our interpretation of the pattern observed in [1] proceeds in three steps: (i) Pair formation; (ii) Formation of hole-rich and hole-poor regions; (iii) Pair propagation.

2.1. Pair formation

We discuss on Fig. 1 the binding energy of a hole pair on a Cu–O–Cu segment. We estimate it by a variational function containing four states α, β, γ', and γ'' as defined in Fig. 1(b). We are interested here in the spin singlet,
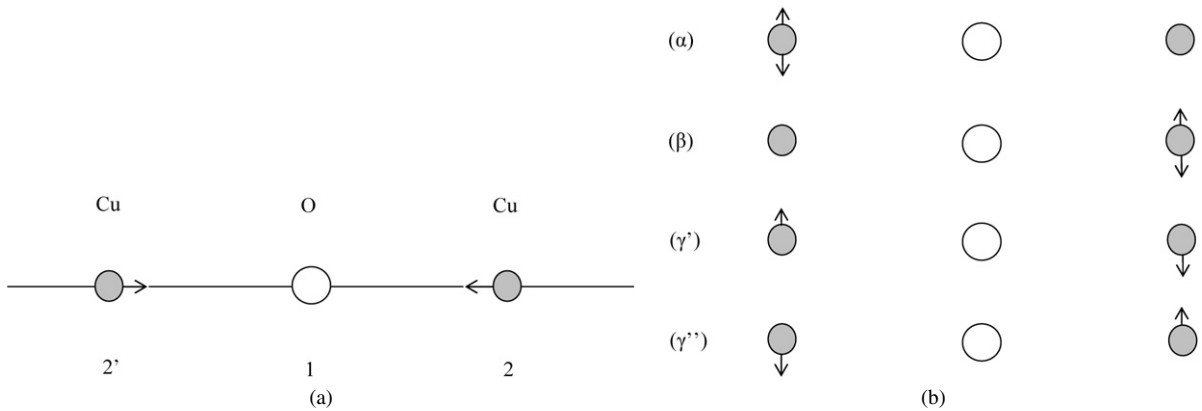
Fig. 1. (a) A two hole pair on two copper atoms (2) and (2′), around one oxygen atom (1). We assume here that the two coppers move in when each of them carries a hole: the transfer integral between 2 and 2′ is increased. (b) The four states participating in the construction of a spin singlet pair.

Fig. 1. (a) Une paire de trous sur deux atomes de cuivre (2) et (2′), autour d'un même atome d'oxygène (1). On suppose ici que les deux suivres se rapprochent de l'oxygène (quand chacun porte un trou) : l'élément de matrice de transfert entre (2) et (2′) est alors augmenté. (b) Les quatre états quantiques participant à la construction d'un singulet de spin.

Fig. 2. (a) An oxygen centered O–Cu–O–Cu–O segment with holes located on the edge oxygens. Energy is lowered by admixture with states as shown in Fig. 2b.

Fig. 2. (a) Un segment O–Cu–O–Cu–O centré sur un atome d'oxygène, avec un trou sur les oxygènes aux extrémités du segment. L'énergie est réduite par mélange avec des états comme montrés Fig. 2b.

for which the amplitudes are even ($\alpha = \beta$, $\gamma' = \gamma''$). The unperturbed energy of (α) and (β) is U and is large. The eigenvalue equation for the energy ϵ is then:

$$\epsilon(\epsilon - U) = 4(t_{\text{OCu}})^2 \tag{1}$$

This leads (for large U) to an energy:

$$\epsilon_{\text{pair}} = -4(t_{\text{OCu}})^2/U \tag{2}$$

(We are indebted to W. Harrison for pointing out the factor 4 showing up in the singlet energy.) We must compare this to the energy of two independent holes, both at the bottom of the band, $2\epsilon_0$, where $\epsilon_0 = 4t_0$ is the half band width. The pairs win if:

$$t_{\text{OCu}} > (Ut_0/2)^{1/2} \tag{3}$$

On the whole, this idea is very tentative but it has one merit: the ratio t_{Ocu}/t_0 is very sensitive to the (Cu d)(O p) overlap; this could explain why ions which are isoelectronic to Cu cannot compete with the cuprates.

There is, however, a difficulty with holes residing on copper atoms, in view of the high ionization potential of the Cu^{++} ion [2]. Holes may reside preferentially on oxygen atoms. This can be achieved if we consider a O–Cu–O–Cu–O segment, with holes on the edge oxygen atoms (Fig. 2). Here, energy can be gained by admixture with states where a hole is transferred from one of the coppers to the central oxygen. The energy gained is still proportional to $(t_{\text{OCu}})^2$.

2.2. Formation of hole-rich and hole-poor regions

So let us assume that two holes have formed a bound state, and let us examine the consequences for the neighboring sites, as shown in Fig. 3. Following Kohsaka et al. we label 1 the site of the central oxygen atom; 2 and 2′ the neighboring copper sites; 3 and 3′ the following copper sites, followed by the oxygen sites 4 and 4′. Since the contraction, or dimerisation, of the segment (2–2′) goes hand in hand with a local increase of the hole density, it follows that the

```
     Insulating              Metallic              Insulating
       ladder                ladder                 ladder


  3    4'   3'          2'    1    2          3    4    3'

  Cu – O – Cu – O – Cu – O – Cu – O – Cu – O – Cu
  |         |         |         |         |         |
  O         O         O         O         O         O
  |         |         |         |         |         |
  Cu – O – Cu – O – Cu – O – Cu – O – Cu – O – Cu


         <              Domain width 4a            >
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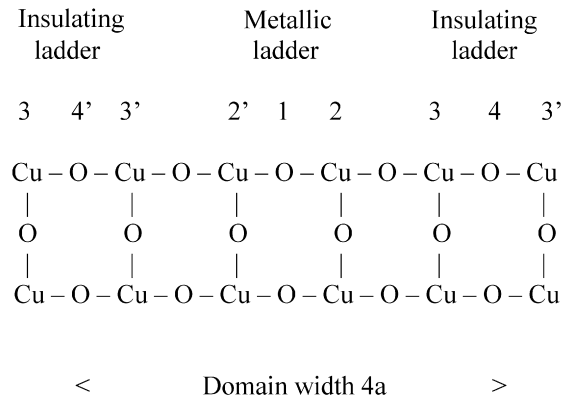
Fig. 3. The pattern of hole concentration in a domain consisting of one high concentration central ladder centered on a column of oxygen atoms with two low concentrations ladders on each side. The pattern leads to a periodicity of 4 times the lattice parameter of the CuO plane.

Fig. 3. Répartition des trous dans un domaine : une échelle centrale riche en trous et deux échelles pauvres de part et d'autre. Ceci engendre une maille multipliée par 4.

hole density on neighboring sites such as copper sites 3 and $3'$ is decreased. A charge density wave can be triggered by local pair formation, dimerisation and the charge density wave being coupled phenomena, the two reinforcing each other. We then arrive at the following sequence: the central Cu–O–Cu bond ($2'$–1–2) is hole-rich, the neighboring bonds (3–4) and ($4'$–$3'$) are hole-poor. Over a distance of $4a$, there are two hole-rich and two hole-poor Cu sites. Defects, due primarily to independent nucleation of other dimers at right angles with the one under consideration, will pin the charge density wave. The pair on $2'$–2 cannot propagate along its axis. These conclusions still hold if the hole pair is localized on a five site segment.

2.3. Pair propagation

There is nothing to prevent pair propagation in the perpendicular direction, which will reduce the kinetic energy. This will lead to the formation of domains consisting of one central hole-rich and two lateral hole-poor ladders, the central ladder being centered on an oxygen column. Pair propagation on the central ladder can lead to incipient superconductivity. A periodicity of $4a$ (1), as has been observed, with alternating conducting (and may be superconducting), and insulating (and may be antiferromagnetic) domains can be favorable in some range of doping, see below a discussion of this point.

Domain formation is the result of a nucleation process of the first bound state. This nucleation process occurs randomly along the (10) and (01) directions, resulting in domains at right angles randomly distributed, again as observed. There is no long range order in this pattern.

3. Discussion

The essential difference between the proposed model and that of stripes [3–5] is that ours is not a purely electronic one reflecting the competition between AF and superconducting orders, where the lattice plays no role (or only a very secondary one). Rather, the contraction of Cu–O bonds plays here a central role. Both models predict oxygen centered structures, in agreement with experiments [1,6], but differ in some important ways. While stripes are basically one dimensional (namely their length should be much longer than their width), our model being based on a local bond contraction leads to a pattern of domains, at right angles to each other, that are not necessarily very long, in better agreement with what is observed [1], and with several pieces of experimental evidence for an Electronic Cluster Glass in underdoped samples ([7] and references therein), rather than one dimensional stripes. Lattice disorder below the temperature of formation of the domains is a natural consequence of our local pair formation model, since bond contraction is local and occurs randomly in two different directions. Lattice disorder has indeed been found to increase below a temperature of about 150 K, which we surmise is that of formation of the domains [8,9].

The hole doping level of the samples studied by Kohsaka et al. is of the order of 0.1 per Cu site. The minimum number of Cu sites necessary to have at least one hole pair per domain is then 20, which means that slightly elongated

domains as observed do contain a few hole pairs. Conduction can take place along the central ladder. If we assume that the hole concentration is peaked on the central ladder and is negligible on the edge ladders, the hole concentration on the central ladder is then of the same order as the average concentration at optimum doping. The edge ladders are then at a concentration near that of the pure antiferromagnetic phase. Barring complications due to the one-dimensional character of the central ladders, one may also expect the formation of a superconducting gap of the same order of magnitude as that of the gap at optimum doping, i.e. of a few 10 meV, again as observed.

The emerging picture of a lightly doped cuprate is then that it is composed of conducting and superconducting ladders weakly coupled together, either laterally through insulating ladders or at right angles. Conduction and super-conduction on the macroscopic scale will necessarily require coupling between ladders oriented at right angles. Since translational and rotational symmetry are broken in the ladder pattern, which is highly disordered, it is not obvious that quasi-particles can exist with a well defined wave vector formed in lightly doped cuprates. Indeed, the normal state is known to be weakly insulating. If some degree of coherence can be achieved, one may expect that it will be for quasi-particles having their momentum at 45 degrees from the ladders directions, which is the (11) orientation and equivalent. Clearly, there is no possibility of propagation along the (10) and equivalent directions because of the interruption of the domains. This is in agreement with the known fact that lightly doped cuprates have an incomplete Fermi surface consisting of small arcs around the (11) directions [10]. We note that strong renormalization effects near the Fermi level around the (11) direction over an energy range of the order of 100 meV have recently been attributed to electron–phonon interaction [11].

Superconductivity on the macroscopic scale can be very different from that in the individual domains, again because it requires coupling between domains that are at right angles from each other. A gap anisotropy is to be expected, with the strongest gap values being along the (10) and equivalent directions. It may be that this coupling is also at the origin of the d-wave symmetry of the macroscopic superconducting order parameter.

Note added by Guy Deutscher at the time of submission of the final version

Pierre-Gilles de Gennes passed away a few days before we were to have a final discussion of the manuscript. He had left clear instructions that I was to take care of the final version. It is under these very sad circumstances that this revised version is being submitted. Had we met as planned, the final version might of course have been somewhat different but in view of the intense correspondence that we had in the period of several weeks preceding his death, I feel reasonably sure that this version is close to what he wanted it to be. In any case, I have done the best I could. Warm thanks are due to Philippe Nozières for a critical reading of the manuscript.

Acknowledgements

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