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On the nature of antiferromagnetism in the CuO_2 planes of oxide superconductors

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Abstract. Recent results regarding electron- and hole-doped CuO_2 planes can be rather easily explained by the marked covalency of CuO bonding, suggesting a band picture of long and short range antiferromagnetism. The maxima of superconductive T_c *versus* doping can be related to the crossing by the Fermi level of the edges of the pseudogap due to antiferromagnetic short range order (bonding edge for hole-doping, antibonding for electron-doping). The symmetry of the superconductive gap can be related to the Bragg scattering of electronic Bloch states near the edges of the antiferromagnetism (AF) pseudogap. Assuming a standard phonon coupling, one then predicts for commensurate AF a pure $d_{x^2-y^2}$ symmetry for the superconductive gap for underdoped samples and $d_{x^2-y^2}$ symmetry plus an imaginary contribution of s or d_{xy} symmetry contribution increasing linearly with overdoping. This seems in agreement with recent measurements of gap symmetry for YBCO, but should be more fully tested, especially for electron-doped samples. Incommensurate AF, as in LSCO, is not considered here. The simple Hartree-Fock band approximation used could no doubt be made more realistic by specific inclusion of electron correlations and by a better description of the AF short range order. This weak atomic repulsion U model, standard in transitional metals, is complementary to the strong U models usually assumed in oxides. It considers specifically the possible effects, in doped samples, of a short range AF which could be slowly dynamical or static, possibly including in that case recent evidences of nanostructures of two different phases.

PACS. 74.72.-h High-T_c compounds

Recent studies of oxide superconductors have been dominated by strong correlation models relating to large atomic repulsion U on copper atoms. From that point of view, if all such models derive from the Zhang and Rice tJ model [1], and as such have some measure of covalency, as defined below, it is useful to distinguish Zhang and Rice's work and its derivatives on AF phases of undoped samples such as [2], which assume a large covalency and ensuing strong delocalisation of the holes on oxygen ions, from recent weak covalency models such as in [3] and [4], applied to non magnetic phases assumed valid for doped samples. The latter models are assumed to be on the covalent side of the Brinkman and Rice critical point, but near enough to it to have a very small renormalised transfer integral t, coherent with the assumption of a large value of U [5].

With this background in mind, the purpose of this paper is to propose an approximate but original description of superconductivity in the cuprates. It uses a number of concepts which were successively considered by one of the authors in this field, as shown in references [6] to [9]. These concern the covalency in the CuO_2 planes and the pseudogap due to antiferromagnetic short range order. We feel it is the simplest if not the only way to explain recent experiments, which have stimulated anew our interest in the field: they confirm the qualitative symmetry of the phase diagrams of electron- and hole-doped compounds [4,10, 11] and the symmetry of the superconductive gap as a function of doping [12]. They assume a short range Antiferromagnetism which could be slowly dynamical or static, therefore possibly including in the latter case recent evidences of nanostructures of two different phases [13]. The essential conclusion is that the maxima of the critical superconductive temperature occur where the Fermi level crosses one of the peaks of the density of states associated with the AF pseudogap. This suggestion was made privately some years ago by the authors to D. Pines, but never published as will subsequently be explained. Finally, for many reasons, although crude, this model can be developed to include various specific characteristics of some of the cuprates.

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1 Three types of LCAO pictures [6] to [9]

In the simplest linear combination of atomic orbitals (LCAO) picture for the CuO_2 planes common to all cuprates, three parameters are involved: the transfer integral t between neighbouring Cu $3d$ and O $2p$ atomic functions, their energy difference $\Delta = E_{3d} - E_{2p}$ and the intra-atomic repulsion U between electrons on a Cu ion. This simple approach neglects small possible distortions from a square lattice. It also neglects interactions of a given CuO_2 plane with its surroundings, especially the coupling between parallel planes responsible for three dimensional (static) superconductivity. This essential part [7] will have to be introduced as a correction which will not be discussed here.

Three situations have been envisaged within these limits.

1.- Ionicity: $\Delta \gg U \gg t$ This starting point in many early discussions does not fit with the presence of holes in O $2p$ shells, increasing in number with hole-doping, as shown by X-rays and NMR techniques [14].

2.- Charge transfer: $U \gg \Delta \gg t$ This fits better with the doping of holes in O $2p$ shells, and agrees with the electronic structure of small clusters [15]. However it does not fit with the observation of holes in O $2p$ shells in non doped samples [14]. It is also difficult to explain in this way the qualitative but striking symmetry observed in the phase diagrams for electron-and hole-doping of the CuO_2 planes (Fig. 1). It would indeed be difficult to explain the symmetry observed in antiferromagnetism and superconductivity (S) [10,11], as well as the change from holes to electrons in Hall conductivity beyond the optimum dopings (z_0, z_0') for maximum superconductive T_c [11,15]. The basic electronic structures are very different in this charge transfer model: less than one hole per Cu ion in the electron-doped samples; while, in the hole-doped samples, one hole per Cu ion and the excess holes are distributed on the O ions. The observed qualitative symmetry is especially clear in recent experiments where carriers are introduced by an electric voltage [11], thus avoiding possible distortions of phase diagrams due to differences in chemical dopings for holes and electrons. Finally, if $U \gg \Delta$, the presence of one hole on each Cu ion in hole-doped samples would block effectively the motion of O $2p$ holes if other types of transfer between O $2p$ orbitals were not invoked in a somewhat artificial way [5].

3. Covalency: $U \gtrless w = \gamma t \geq \Delta$ *with* $\gamma \gg 1$

w is here the effective width of the covalent band built with the Cu $3d$ and O $2p$ orbitals. This condition is actually fulfilled by the studies on clusters mentioned above [16], owing to the fact that each Cu has more neighbours in a CuO_2 plane than in the clusters considered by [8].

In this case, O $2p$ holes should be present in sizeable amounts for zero doping and also for reasonable amounts in the case of electron- or hole-doping. The qualitative symmetry of phase diagrams for electron- and hole-doped compounds results naturally from the near symmetry of the Cu $3d$-O $2p$ bonding developed in this limit.

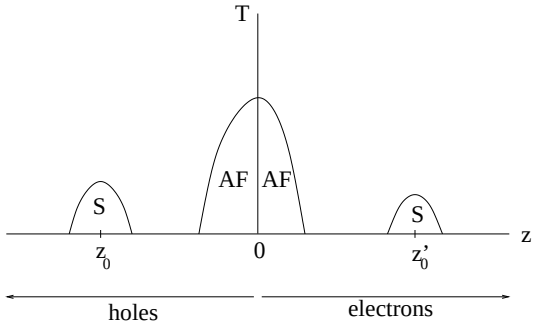

Fig. 1. Qualitative symmetry of AF and superconductive (S) phases *versus* doping z in cuprates.

We shall use this picture as the most reasonable at present. It fits with the fact that, in Pauling's electronegativity scale, copper, at the end of the $3d$ transitional series, is not very far from oxygen. This scheme would obviously be usefully confirmed if O $2p$ holes were also observed in electron-doped compounds (*e.g.* by X-ray absorption spectra) or if the qualitative symmetry observed for magnetism, superconductivity and antisymmetry for Hall transport was extended as we expect to other properties discussed below, namely AF short range order, the pseudogap and changes in symmetry with doping of the superconductive gap.

2 Ionocovalency. Correlation effects [7,8]

First, in the *uncorrelated* picture where U is neglected, the general tight binding equations give, for the partially filled antibonding band:

$$E_{\underset{\sim}{k}} = E_d + \frac{1}{2}\left[\Delta + \left\{\Delta^2 + 16t^2\left(\sin^2\frac{k_x a}{2} + \sin^2\frac{k_y a}{2}\right)\right\}^{1/2}\right] \quad (1)$$

with a width:

$$w = \frac{1}{2}\left[(\Delta^2 + 32t^2)^{\frac{1}{2}} - |\Delta|\right]. \quad (2)$$

The Fermi level for zero doping lies along the square

$$\cos k_x a + \cos k_y a = 0 \quad (3)$$

For a pure covalent limit $\Delta = 0$

$$E_{\underset{\sim}{k}} = E_d + 2t\left(\sin^2\frac{k_x a}{2} + \sin^2\frac{k_y a}{2}\right)^{1/2} \quad (4)$$

and

$$w = 2\sqrt{2}t. \quad (5)$$

The Cu $3d$ and O $2p$ states play equivalent roles, so that the holes are equally distributed between them. For zero

doping, each Cu ion has 0.5 holes and each O ion 0.25. This is to be compared with the ionic limit $\Delta \gg w$, where:

$$E_{\underset{\sim}{k}} \cong E_d + \Delta + \frac{4t^2}{\Delta}\left(\sin^2\frac{k_x a}{2} + \sin^2\frac{k_y a}{2}\right)^{1/2}$$

with a (smaller) width:

$$w \cong \frac{4\sqrt{2}t^2}{\Delta}\,.$$

Computations on clusters suggest an *approximate covalent* limit, where Δ is positive and of the order of at most $2t$ and therefore, according to (2), less than w [7,16]. Equation (1) then shows that the equirepartition of holes between Cu and O is still approximately preserved near the middle of the antibonding band, thus practically near the Fermi level. Near the edges of that band, pure $2p$ character prevails at the bottom and pure $3d$ at the top, over a width $\delta ka \cong \Delta/2t$. As the area $4\pi^2/a^2$ corresponds to one hole per cell in undoped compounds, the pocket of $2p$ character at the bottom of the band contains $\pi\delta k^2 a^2/4\pi^2 \cong \Delta^2/16\pi t^2$ Cu $3d$ holes per cell. For $\Delta \cong 2t$, this is a small fraction. There shall therefore be a *small and constant shift of the holes from O to Cu, independent of doping* when Δ increases from 0 to its likely value of $2t$.

We should now include *electron correlations* by considering $U \neq 0$, but shall at the moment neglect the (important) magnetic consequences, to be discussed later. The effect of U will be to reduce the charge fluctuations on the Cu ions. In the covalent limit considered here, this will decrease somewhat the effective width of the band considered, without however changing the *delocalised electron* picture. In fact, these electron correlations should have small consequences.

The same applies to the d band of transitional metals such as Ni, Pd, Pt, with also a fraction of d holes per atom. In the limit of a small number of d holes per atom, it is known that the intraatomic Coulomb repulsion cannot, as such, create a Mott-Verwey insulator and that the correlations only reduce the large charge fluctuations without much changing the conductive and cohesive properties. Indeed, the correlations can be described in terms of an effective S matrix [17]:

$$U_e \cong U/(1 + U/w_0)$$

always smaller than the band width w_0 of the holes. U is itself strongly reduced from its pure Hartree-Fock value by intra-atomic correlations and cohesion and magnetic properties can be satisfactorily described in small power developments in U [18], neglecting the weak interatomic exchange J at the root of magnetic couplings in the initial tJ model.

This is the weak correlation approach which we shall consider here for the CuO_2 planes, with an effective U of the order of a few t's.

These qualitative considerations have been recently confirmed by computations of the model considered here (Δ, t, U and $t' =$ or $\neq 0$), in the limit of infinite U [3].

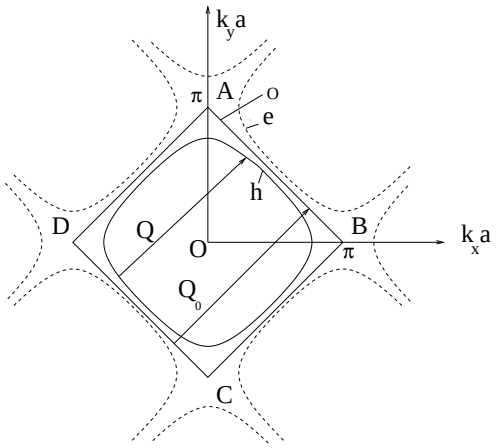

Fig. 2. Fermi surface for non magnetic compounds. 0 zero doping (square ABCD); e electron- doping; h hole-doping.

The band structure is preserved below the Brinkman and Rice critical point $\Delta = 5t$ and, for $\Delta = 2t$, the renormalisation of t is not much more than the classical value $1/\sqrt{2}$ obtained for $\Delta = 0$. Indeed, the limit of infinite U, valid of course near the Brinkman and Rice limit, has no obvious application in the covalent limit (Δ small).

3 Long range antiferromagnetism [7]

We consider now the long range antiferromagnetism observed for small dopings of holes or electrons (Fig. 1).

For *zero doping*, we shall assume with Lomer that the effect of U_e is to stabilise an antiferromagnetism of wave vector $\underset{\sim}{Q}_0$ with a magnitude equal to the size of the Fermi surface (Fig. 2). This antiferromagnetism commensurate with the lattice will induce a gap in the density of states, thus producing a band insulator. The perfect nesting of the Fermi sheets by the $\underset{\sim}{Q}_0$ translation corresponds to a strong instability and thus *a priori* to rather large moments on the copper ions. The total atomic moments developed cannot be larger than the average number of holes on the copper ions, which is itself not much larger than 0.5. Observed atomic moments μ of order 0.5 μ_B are therefore not surprising. In the approximation of our model and within an extended Hartree-Fock scheme, such moments lead to corrections $\pm U_e\mu/\mu_B$ to the copper atomic potential, depending on the relative directions of the electronic spin and the atomic moment considered [30]. Indeed the observed Néel temperature T_N and the AF gap are compatible with $U_e \lesssim w$ and a perturbation treatment of U_e. The situation above T_N probably involves AF fluctuations and possibly an Anderson localisation by magnetic disorder [7], but this range has been little explored.

For *finite doping*, Lomer's argument would lead to a static incommensurate antiferromagnetism, with a wave vector $\underset{\sim}{Q}$ varying essentially linearly with doping, so as to follow the size of the Fermi surface. However in most cases, the antiferromagnetism remains *commensurate* with the lattice, with the wave vector $\underset{\sim}{Q}_0$. This will be the only case

discussed here. It can be understood as arising from the very sharp and quasionedimensional feature of the peak in density of states at the edges of the AF gap, near the square of size $\underset{\sim}{Q}_0$ (Figs. 2 and 3). For this commensurate AF, increasing numbers of carriers due to doping should shift the Fermi surface away from the AF gap. However, because of the large gap and its very sharp peaks in the density of states, one can expect the carriers in this range to be preferentially captured by doping imperfections and not to carry current. In the recent experiments of doping by electrical voltage, one can similarly think of the injected carrier as captured by imperfections or of the applied voltage being smaller than the AF gap. In both cases, the doped AF phase should again be insulating.

More precisely, in the presence of an antiferromagnetism with a magnetic potential alternating from Cu to Cu ion, the energy of the band electrons becomes:

$$E_{\underset{\sim}{K}} = \frac{1}{2}\left(E_{\underset{\sim}{k}} + E_{\underset{\sim}{k}-\underset{\sim}{Q}_0}\right) \pm \frac{1}{2}\left[\left(E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}-\underset{\sim}{Q}_0}\right)^2 + 4|v|^2\right]^{1/2} \tag{6}$$

where $v = \langle \underset{\sim}{k}|v|\underset{\sim}{k}-\underset{\sim}{Q}_0\rangle$ is the matrix element of the atomic potential $\pm U_e\mu/\mu_B$ due to antiferromagnetism. The corresponding wave function is:

$$|\underset{\sim}{K}\rangle = \alpha_{\underset{\sim}{k}}|\underset{\sim}{k}\rangle + \beta_{\underset{\sim}{k}}|\underset{\sim}{k} - \underset{\sim}{Q}_0\rangle \tag{7}$$

with:

$$\frac{\beta_{\underset{\sim}{k}}}{\alpha_{\underset{\sim}{k}}} = -\frac{E_{\underset{\sim}{K}} - E_{\underset{\sim}{k}}}{\langle \underset{\sim}{k}|v|\underset{\sim}{k} - \underset{\sim}{Q}_0\rangle}\cdot \tag{8}$$

Using the remarks above that only states near to the Fermi level are involved in the magnetic perturbation and that these states are not very sensitive to Δ (*i.e.* U_e and Δ small), we can compute $E_{\underset{\sim}{K}}$ in the extreme covalent limit $\Delta = 0$.

The AF gap, of width $2|v|$, is centred at energy

$$E_0 = E_d + 2$$

as pictured in Figure 3. Development along the side AB, Figure 2, gives with:

$$\begin{aligned} k_x a + k_y a &= \pi - \varepsilon \quad , \varepsilon \to 0 \\ k_x a - k_y a &= u \end{aligned} \tag{9}$$

$$E_{\underset{\sim}{K}} \cong E_0 \pm |v| \pm \frac{t^2}{|v|}\varepsilon^2 \cos^2\frac{u}{2}\cdot \tag{10}$$

The corresponding density of states diverges at the gap edges. Thus, if δE is the distance of E to the gap,

$$n(E) \cong \text{const} \times \left(\frac{|v|}{t^2|\delta E|}\right)^{1/2} \ln\left(\frac{\text{const} \times t^2}{|v||\delta E|}\right)\cdot \tag{11}$$

The dominating contribution comes from the Van Hove anomaly at the corners A and B of the square, Figure 2.

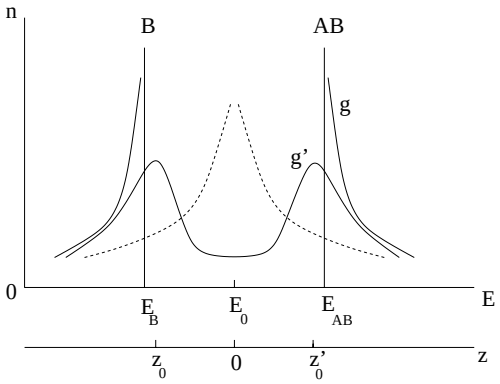

Fig. 3. Antiferromagnetic gap g and pseudogap g'. B bonding and AB antibonding peaks in the density of states. Dotted curve: Van Hove singularity of non magnetic state. Abscissae: energy E and doping z. $E < E_o$ hole-doping; $E > E_o$ electron-doping.

Thus, near A:

$$E_{\underset{\sim}{K}} \cong Eo \pm |v| \pm \frac{t^2}{4|v|}\left[k_x^2 a^2 - (\pi - k_y a)^2\right]^2 . \tag{12}$$

This van Hove anomaly is much flatter in energy than that at the corners A and B for non magnetic phase when the density of states only diverges logarithmically in δE [19]. The divergence in $|\delta E|$ is also somewhat larger than the contributions to $n(E)$ along the side AB of the square where, as in a one dimensional problem [20], they diverge as $|\delta E|^{-1/2}$. This striking result comes from the square geometry of the Fermi surface of non doped samples; it is also found in the ionic limit, if one assumes electrons to be delocalised. Finally, on either side of the AF gap, the surfaces of constant energy have the same form in reciprocal space as in the case of no gap (Fig. 2) but repeated in all the squares neighbouring ABCD and with a reduced energy scale.

The stability of the AF gap can be approximately measured by summing up the one electron energies of the occupied states:

$$\Delta E = \int^{E_F} n(E)E\mathrm{d}E - \int^{E_{F_0}} n_0(E)E\mathrm{d}E \tag{13}$$

where E_F and E_{F_o} are the Fermi levels in the presence and in the absence of antiferromagnetism respectively; $n(E)$ and $n_0(E)$ are the corresponding densities of states counted per CuO_2 in a plane [4]. In (13), a self energy term in U_e is counted twice and should be subtracted. This affects the absolute stability of the AF phase, but not the relative stability of magnetic phases with similar magnetic moments.

The average number of doping electrons per CuO_2 is:

$$z = \int^{E_F} n(E)\,\mathrm{d}E - \int^{E_{F_0}} n_0(E)\,\mathrm{d}E\cdot \tag{14}$$

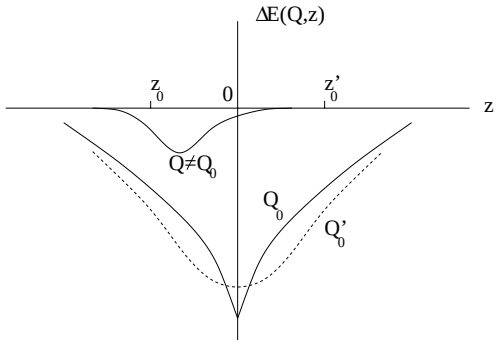

Fig. 4. Stability *versus* doping z of commensurate ($\underset{\sim}{Q}_0$) and incommensurate ($\underset{\sim}{Q} \cong \underset{\sim}{Q}_0$) AF long range order. Dotted curve: stability of commensurate short range AF (the position of z_0 and z_0' for short range commensurate order $\underset{\sim}{Q}_0'$ marked on the abscissa).

This gives:

$$\frac{\mathrm{d}\Delta E}{\mathrm{d}z} = E_F - E_{F_0} \tag{15}$$

$$\frac{\mathrm{d}^2\Delta E}{\mathrm{d}z^2} = \frac{1}{n(E_F)} - \frac{1}{n_0(E_{F_0})}\,. \tag{16}$$

It is then easy to check that, for a commensurate AF $\underset{\sim}{Q}_0$, $\Delta E(\underset{\sim}{Q}_0, z)$ has a minimum at zero doping, with a break in slope $\mathrm{d}\Delta E/\mathrm{d}z$ (related to the gap $2|v|$, thus to $U_e\mu/\mu_B$) and a negative curvature (due to the peak in $n(E)$ near the gap edges). The near symmetry of $\Delta E(\underset{\sim}{Q}_0, z)$ for electron- and hole-doping is related to that of $n(E)$, Figure 3. This is related to the quasi one dimension of $E_{\underset{\sim}{k}}$ near zero doping and to the slow variation with doping of the magnetic moment μ.

For an *incommensurate* AF at $\underset{\sim}{Q} \cong \underset{\sim}{Q}_0$, the gap of $n(E)$ is expected to be smaller and therefore also the stability of the corresponding AF phase, owing to the increasingly two dimensional nature of $E_{\underset{\sim}{k}}$. This gives obviously a stability $\Delta E(\underset{\sim}{Q}_0, z)$ less marked and more asymmetrical, which can be expected to usually be above $\Delta E(\underset{\sim}{Q}_R, z)$ in the region of stable AF order (Fig. 4).

4 Short range antiferromagnetic order [7, 8]

Ever since a strong antiferromagnetic short range order was observed by neutron scattering and the Mössbauer effect in a large range of *hole-doped* oxide superconductors such as YBCO, it has been thought that this phenomenon should play an important role in the phase diagram of these materials. In particular, up to the optimum doping z_0 and beyond, this short range is strong at temperatures well above the maximum of T_c and its possible effect on superconductivity must be taken into account. We shall restrict ourselves here to compounds with *commensurate* short range AF and thus will not consider the somewhat exceptional case of LSCO.

The first idea along these lines has been to consider a coupling scheme of the electrons via AF fluctuations [21]. The observation of a superconductive gap with d symmetry was apparently in agreement with this picture [22].

We shall take a different point of view, stressing first the special properties and structures associated with this short range AF. Discussion of the effect on the superconductive gap will be delayed until the last paragraph.

The main idea, first proposed in this field by one of the authors [6] to [8] is that, when a long range AF is replaced by a short range one of similar strength, the gap g in the density of states should be replaced by a *pseudogap g'*, as pictured Figure 3: the disorder should round off the peaks B and AB of the density of states and if the disorder is sufficient, a continuous trail of states, with a density decreasing towards the middle of the gap should appear. Such states in the pseudogap should be primarily made of parts of evanescent Bloch functions of the real gap connected together in the regions of disorder, in such a way that, except possibly for Anderson localisation near the middle of the pseudogap, such states should be conducting. Such a qualitative picture of a pseudogap and indeed its name were first evolved by Mott in the early fifties, in connection with static atomic short range order.

Indeed Mott's suggestion of the localisation of evanescent Bloch waves in the middle of the pseudogap could explain the non conductive behaviour of undoped samples above T_N if, as likely, a well defined local AF subsists in that range. This would hold in all covalent models where a Mott Verwey blocking is not possible in disordered AF, neither in our model nor in that of Zhang and Rice [1].

A rough image of this pseudogap can be obtained by considering a localised AF (commensurate) spin wave. Looking for simplicity's sake at the one dimensional problem, it is easy to compute the phase shifts produced in a non magnetic matrix by the presence of a given length of the commensurate AF phase. These phase shifts give a good idea of the variation of the density of states produced locally along the AF phase if this is much longer than the Fermi length of the matrix, *i.e.* more than several interatomic units. The coherence length of the short range AF order fulfils this condition and one finds indeed a pseudogap as sketched in Figure 3. A similar result would be obtained for one-dimensional antiphase domains of random sizes.

The existence of such a pseudogap should be retained even for AF fluctuations, as long as they are slow compared with the speed of Fermi electrons in the absence of AF. A very similar situation has been experimentally and theoretically studied for static and dynamical CDW and SDW in quasione-dimensional organic compounds [23].

The decrease of the Y Knight shift in YBCO, when underdoping increases below z_0 [24], was first attributed to the progressive opening of a pseudogap due to AF fluctuations of increasing strength for decreasing doping z below z_0 [6]. Because of the geometry of the lattice, the Y nuclei are indeed not very sensitive to the Cu moments as long as these are coupled in commensurate (alternating) antiferromagnetism. The Knight shift then measures directly the

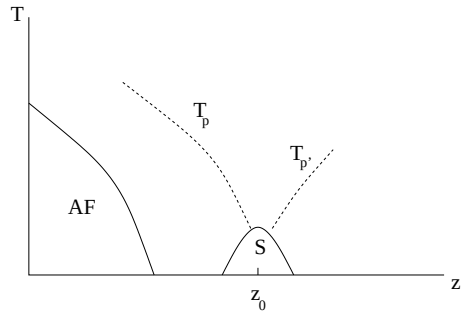

Fig. 5. Schematic phase diagram for hole-doped cuprates. AF and S: long range antiferromagnetic and superconductive phases (as in Fig. 1); z_0 optimum doping; T_p (and possibly $T_{p'}$): temperatures of characteristic excitations from (and to) the pseudogap binding peak associated with the short range AF.

density of delocalised Fermi states and is little sensitive to the paramagnetism of the Cu moments. As expected in such a picture, a peak in the density of states was observed later at an excitation energy increasing from zero with z decreasing from z_0; and a corresponding anomaly was observed at an increasing temperature T_p, Figure 5 [31]: this excitation energy could be considered as measuring the energy distance between the bonding peak B, Figure 3 and the Fermi level, assumed above E_B for $z < z_0$.

It is however clear in compounds with commensurate short range AF that this AF short range order does *not* decrease to zero at z_0, but remains strong at low temperatures well beyond this limit [34]. The crossing of the binding peak B by the Fermi level at $z = z_0$ is therefore not so much due to a closing of the pseudogap with increasing doping as to a *shift of the Fermi level associated with increasing hole-doping*. It is this (new) point of view that we wish to develop in this paper.

If we neglect the variation with doping of the amplitude of magnetic moments, an analysis of stability based on equations (13) to (16) for a density of states as sketched Figure 3, leads to a stability of the pseudogap $\Delta E(Q_0, z)$ as pictured qualitatively Figure 4. The pseudogap should be less stable than the gap for small dopings but, owing to the finite density of states in this pseudogap, this should become more stable than the gap at higher dopings, and before the Fermi level reaches the peak B of the pseudogap. There should therefore be a spontaneous transition from long range to short range order beyond a certain doping, through a first order transition. This model does not rely on increasing entropy by disorder; and thus it applies at low temperatures. It explains the otherwise surprisingly *large extent in doping of the short range AF*. Finally it does not make any specific and detailed prediction about the fine structure of short range order and is valid whether this is a static or a slowly fluctuating order.

The similarity of long range AF and superconductivity phase diagrams for electron- and hole-doped compounds suggests that the same general characteristics should apply to *electron-doped* samples. Thus, *short range AF* should be present beyond the long range AF (Fig. 1), with atomic moments similar to those in the long range AF phase, decreasing with increasing electron-doping. The characteristic features of an AF pseudogap should be observed, with a Knight shift increasing with doping up to the optimum doping z'_0 with maximum T_c; a peak in the density of states crossing at z'_0 the Fermi level should be observed, corresponding to the AB peak of the pseudogap.

From Figure 3, it is clear that the excitation energy from the Fermi level to the peak B of the pseudogap corresponds to hole excitations for underdoped samples $z < z_0$ and to electron excitations for the overdoped samples $z > z_0$ in the case of hole-doping, while the reverse should be true for electron-doped samples ($z \lesseqgtr z'_0$). This analysis suggests that, for overdoped samples, a (weaker) anomaly at a temperature $T_{p'}$ increasing with doping from $z = z_0$ (or z'_0) should be observed (*cf.* Fig. 5).This is in agreement with the general picture given for hole-doped samples by Varma [25].

5 Superconductive coupling and gaps

Let $V(\underset{\sim}{K}, \underset{\sim}{K}')$ be the effective superconductive coupling between electrons of opposite spins, such that the superconductive gap $\Delta_{\underset{\sim}{K}}$ is given in the BCS approximation by:

$$\Delta_{\underset{\sim}{K}} = -\sum_{\underset{\sim}{K}'} \frac{V_{\underset{\sim}{K}\underset{\sim}{K}'}\Delta_{\underset{\sim}{K}'}}{2\sqrt{\Delta^2_{K'} + \varepsilon^2_{K'}}} \tan h \sqrt{\frac{\Delta^2_{\underset{\sim}{K}'} + \varepsilon^2_{\underset{\sim}{K}'}}{2k_B T}} \cdot \quad (17)$$

As usual, $\epsilon_{\underset{\sim}{K}'}$ is the one particle energy measured from the Fermi level; and in the usual singlet pairing, $\Delta_{\underset{\sim}{K}} = \Delta_{-\underset{\sim}{K}}$. Because of the Bragg scattering of the Bloch functions $|\underset{\sim}{k}\rangle$ by the short range AF order, the wave functions $|\underset{\sim}{K}\rangle$ to be used are combinations of such Bloch functions. We shall assume, in this order of magnitude estimate, that they are the same combinations (7, 8) as in the long range order.

From (7)

$$\langle \underset{\sim}{K}'|V|\underset{\sim}{K}\rangle = \alpha^*_{\underset{\sim}{k}'}\alpha_{\underset{\sim}{k}}\langle \underset{\sim}{k}'|V|\underset{\sim}{k}\rangle + \beta^*_{\underset{\sim}{k}'}\alpha_{\underset{\sim}{k}}\langle \underset{\sim}{k}' - \underset{\sim}{Q}_0|V|\underset{\sim}{k}\rangle + \alpha^*_{\underset{\sim}{k}'}\beta_{\underset{\sim}{k}}\langle \underset{\sim}{k}'|V|\underset{\sim}{k} - \underset{\sim}{Q}_0\rangle + \beta^*_{\underset{\sim}{k}'}\beta_{\underset{\sim}{k}}\langle \underset{\sim}{k}' - \underset{\sim}{Q}_0|V|\underset{\sim}{k} - \underset{\sim}{Q}_0\rangle \cdot \quad (18)$$

Near the peak of the pseudogap (Fig. 3), one can assume that the main contribution to $|\underset{\sim}{K}\rangle$ will be the same as at the peak of the gap in the long range AF.

For the binding peak B, this gives:

$$\alpha_{\underset{\sim}{k}} = \beta_{\underset{\sim}{k}} = 1/\sqrt{2} \quad \text{for spin up}$$
$$\alpha_{\underset{\sim}{k}'} = -\beta_{\underset{\sim}{k}'} = 1/\sqrt{2} \quad \text{for spin down} \quad (19)$$

if the moment developed at the origin is up.

If then the coupling V is through phonons, one can assume $\langle \underset{\sim}{k}'|V|\underset{\sim}{k}\rangle \cong 0$ except for $\underset{\sim}{k}' \cong \underset{\sim}{k}$, where it is negative. It is then easy to check from (18) that:

$$\langle \underset{\sim}{K}|V|\underset{\sim}{K}\rangle \cong 0 \quad (20)$$

$$\langle \underset{\sim}{K}|V|\underset{\sim}{K} - \underset{\sim}{Q}_0\rangle \cong -\frac{1}{2}\langle \underset{\sim}{k}|V|\underset{\sim}{k}\rangle \cdot \quad (21)$$

This means that the phonon attractive coupling leads to an apparent repulsive coupling due to AF fluctuations $|\underset{\sim}{K}\rangle$ developed by Bragg scattering of the short range AF. From equation (17), one expects a gap $\Delta_{\underset{\sim}{K}}$ with $d_{x^2-y^2}$ symmetry [4,29] and since the effective density of $|\underset{\sim}{K}\rangle$ states is expected to be large along the hole side AB of the square, Figure 2, the corresponding T_c is expected to be *optimal*, *i.e.* $z \cong z_0$ (Fig. 3). It is also easy to check from (18) that a coupling V through AF fluctuations, where $\langle \underset{\sim}{K}'|V||\underset{\sim}{K}\rangle \cong 0$ except for $|\underset{\sim}{K}'\rangle = |\underset{\sim}{K} \pm \underset{\sim}{Q}_0\rangle$ (where it is positive) leads to no appreciable coupling between the dynamical functions $|\underset{\sim}{K}\rangle$.

For overdoped compounds where the Fermi level shifts below the peak B of the pseudogap (Fig. 3), and again using the wave functions $|\underset{\sim}{K}\rangle$ of long range AF as an approximation, the energy $E_{\underset{\sim}{k}}$ varies linearly with ε (Eqs. (4) and (9)) while $E_{\underset{\sim}{K}}$ varies quadratically (Eq. (10)). To first order in ε,

$$E_{\underset{\sim}{K}} - E_{\underset{\sim}{k}} \cong -|v| + \gamma\varepsilon$$

where

$$\gamma = \frac{1}{\sqrt{2}} t \cos\frac{u}{2} \cdot$$

Thus, from (8),

$$\beta_{k'}/\alpha_{k'} = -\beta_k/\alpha_k = 1 - \gamma\varepsilon|v|.$$

Then, to second order in ϵ, equation (20) is replaced by:

$$\langle \underset{\sim}{K}|V|\underset{\sim}{K}\rangle \cong \frac{2\gamma\varepsilon}{|v|}\langle \underset{\sim}{k}|V|\underset{\sim}{k}\rangle \tag{22}$$

while equation (21) is unchanged.

As ε varies linearly with overdoping $(z - z_0)$ at the Fermi level, the *gap equation* (17) *acquires besides its real* $d_{x^2-y^2}$ *gap* $\Delta^r_{\underset{\sim}{K}}$, *an imaginary component* $\mathrm{i}\Delta^i_{\underset{\sim}{K}}$, *increasing linearly with overdoping* and with (s or d_{xy}) symmetry due to the node of $\langle K|V|K\rangle$ along AB:

$$\Delta_{\underset{\sim}{K}} \cong \Delta^r_{\underset{\sim}{K}} + \mathrm{i}\Delta^i_{\underset{\sim}{K}}. \tag{23}$$

The strong Van Hove anomaly at the corners of the square, Figure 2 contributes little to the imaginary part because γ goes to zero at A. In the pseudogap, both high densities of states involved in the real and imaginary parts of the gap are reduced from the values deduced from the densities of states such as (11). Also, with increasing overdoping, these densities decrease, leading to a general attenuation of $\Delta_{\underset{\sim}{K}}$ and of T_c.

Finally for *underdoped samples*, one can assume the Fermi wave functions in the pseudogap (Fig. 3) to be built mostly with localised Bloch functions of complex wave vectors. Taking for instance

$$\begin{aligned} k_x a + kya &= \pi + \mathrm{i}\lambda \\ k_x - k_y &= 0 \end{aligned} \tag{24}$$

we find, using again wave functions of the long range AF,

$$E_{\underset{\sim}{K}} \cong E_d + t\sqrt{2}(1 + \mathrm{ch}\frac{\lambda}{2})\frac{1}{2} - \left[|v|^2 - \frac{t^2 \mathrm{sh}^2\frac{\gamma}{2}}{(1+\mathrm{ch}\frac{\lambda}{2})^2}\right]^{1/2}$$

that λ vanishes at the gap edge and varies linearly again with underdoping $(z_0 - z)$. Thus $E_{\underset{\sim}{K}} - E_{\underset{\sim}{k}}$ only varies to second order in λ. To the same approximation that leads to (23), we find then a pure $d_{x^2-y^2}$ superconductive gap, with equation (21) unchanged. Here, the densities of states involved in (17) decrease faster with (under)doping, leading again to a decrease of gap and T_c with increasing $z_0 - z$.

These predictions are in general qualitative agreement with experiments on the variation with doping of T_c and with the symmetry of the superconductive gap [12]. The imaginary part of the gap observed for overdoped (holes) samples increases linearly with doping and seems to be of d_{xy} symmetry. The fact that the imaginary part of the gap develops progressively means in particular that the real and imaginary parts of the gap have their physical origin in the same general type of coupling [28]. Finally, if our interpretation is correct, the couplings discussed here *are* expressions of the phonon coupling $\langle \underset{\sim}{k}'|V|\underset{\sim}{k}\rangle$ when the AF order is taken into account. If it is responsible for superconductivity, this could explain the modest but real isotope effect observed in T_c [7].

The same type of analysis should apply to *electron-doped* compounds if, as we believe, short range AF order develops beyond the observed long range AF one. Here, it would be the AB peak of the pseudogap, Figure 3, which would be involved and it is easy to show that the same conclusions apply to the *symmetry of the superconductive gap* and to the *maximum of* T_c for the crossing by the Fermi level of the (AB) peak of the pseudogap at $z = z'_0$. As magnetic moments are expected to decrease slowly with electron-doping, the pseudogap should be here less marked in width and in the height of its peaks. Thus $T_c(z)$ is expected to have *a maximum value* $T_c(z'_0)$ *smaller than for hole-doped compounds*, as is indeed the case (Fig. 1). A superconductive gap with $d_{x^2-y^2}$ symmetry has also been observed in underdoped electron compounds [29]. But more systematic studies are obviously in order in this range, to test in particular an imaginary (s or d_{xy}) character of the gap increasing linearly with overdoping.

6 Conclusions

We present an approximate description of superconductivity in cuprates which we feel has some original aspects. We stress that, if covalency is notable in the CuO_2 planes, as the symmetry between electron- and hole-doping suggests, holes are present in very sizeable amounts in O $2p$ as well as Cu $3d$ orbitals, for electron-doped as well as hole-doped compounds. In a situation somewhat similar to that of transitional metals, electron correlations should play a secondary role, and not be able to localise holes into a

Vervey-Mott insulator. Using a simplified model where the Coulomb intraatomic energy U is neglected but for magnetic properties where its effects are treated in Hartree-Fock perturbation, we describe the electronic structures of long range commensurate AF. We point out that, for large enough doping this should be replaced by some sort of short range AF, with a characteristic pseudogap. We think that this is observed in hole- doped compounds such as YBCO with commensurate AF, where the peak in T_c occurs when the Fermi level crosses the lower energy peak of this pseudogap. This explains the large value of observed T_c, but also the symmetry of the superconductive gap ($d_{x^2-y^2}$ for underdoped, $d_{x^2-y^2}+$ is or id_{xy} for overdoped samples, where the imaginary part varies proportional to the overdoping). In this approach, the symmetry of the gap is related to the special symmetry of the wave functions in and near the pseudogap; it is coherent with an isotropic attractive phonon mediated interaction, while an interaction mediated by AF fluctuations would not lead to any appreciable gap. T_c should show a small isotope effect, in qualitative agreement with experiment.

It is expected that the same scheme should apply to electron-doped compounds, where O $2p$ shells should also have holes in appreciable amounts; superconductivity should develop in a range of short range AF, with its features characteristic of a pseudogap. The superconductive gap should again have a basic $d_{x^2-y^2}$ symmetry, with an imaginary (s or d_{xy}) character increasing proportional to overdoping. Here too, the optimum T_c should take place when the (here AB) peak of the pseudogap crosses the Fermi level, and T_c should show a small isotope effect.

If these qualitative predictions are all confirmed, the theoretical picture should be completed. More quantitative estimates of Δ and of the magnetic moments could give a more precise estimate of U. Electron correlations could then be explicitly included [1], and the coupling between CuO_2 planes should be included [7] to actually estimate T_c. From that point of view, it is rather surprising that the recent experiments on doping of apparently a single CuO_2 plane by electric voltage could give a large and well defined drop of resistivity at T_c, contrary to Kosterlitz and Thouless's predictions.

Two major difficulties for quantitative estimates relate to the short range AF order. First, what is exactly its self consistent fine scale structure and the corresponding variations of the density of states in the pseudogap for the AF commensurate with the lattice considered here [13]? Is it static or slowly fluctuating in time at low temperatures? What is the current description of superconductivity in LSCO? Finally, from the point of view developed here, it is difficult anyway to analyse in detail the electronic structure in the normal state above T_c. It is true that, in hole-underdoped samples, the peak B of the pseudogap is expected to be related to a feature somewhat broadened by magnetic disorder but very flat in energy in the reciprocal space: this seems to be observed in the excitation of holes [26,31]. A less marked feature is expected in overdoped hole samples, corresponding to electron excitations to the same peak of the pseudogap and a (fainter) anomaly is expected in the scheme along the line $T_{p'}$, Figure 3. Similar observations should be possible in the electron-doped samples. The analogy with long range AF certainly suggests electronic Hall conduction for hole-overdoping and hole-Hall conduction for electron- overdoping, in agreement with observations [10]. But the switch in sign of the Hall conduction when going from over to underdoping remains to be explained in detail. Also the exact form of the Fermi surface and its broadening by magnetic disorder remain to be worked out, especially for underdoped samples.

It can be noted also that a long range AF is often observed near to a superconductive one [32]. For our specific mechanism to work, a fringe of short range AF should be observed next to the long range one, in the doping or pressure conditions where superconductivity is observed.

We can compare *in fine* our approach with other somewhat similar ones, also using a delocalised electron picture for the cuprates.

– Our approach, leading to a dominant superconductive d gap, is in practice very near to Pines' approach [21], although the detail of the local densities associated with the pseudogap should be introduced into his computations. Also, as we start from a phonon coupling, we could account for a (small) isotope effect. Finally the small imaginary component predicted for overdoping is not present in his picture.

– Our own previous approaches [7,9] assumed short range AF in the underdoped range only, leading then, in the overdoped range, to a phonon coupling and superconductivity with an s gap due to the Van Hove anomaly pictured in punctuated line, Figure 3. This should have been dominant on the d coupling by AF fluctuations, leading to a first order transition of the gap near optimal doping in YBCO [29]. This is not observed, and the presence of AF short range order in the overdoped range observed by neutrons [7] as well as by NMR techniques in pure and doped samples of YBCO [33] contradicts our initial assumption.

– The band structure of delocalised Cu $3d$ and O $2p$ electrons renormalised for large repulsions U [28] contains two Van Hove anomalies when Δ is large and a (smaller) transfer integral is added between second neighbours Cu. This reproduces a density of states analogous to that of the pseudogap g', Figure 3 and the changes with electron- or hole-doping of the Hall conductivity and of the thermal variation of the electrical resistivity can be satisfactorily explained in that way [4]. Besides the apparent symmetry between hole- and electron-dopings, this model can explain the Fermi surfaces as measured by ARPES [3].

However such success with experiments can only result from a very fine tuning of the value taken for t' and for the unrenormalised value of Δ/t (very near to the Brinkman and Rice critical value 4). Such special values of the parameters could be considered as somewhat artificial and the band approximation used in these conditions of very strong scattering by U can be questioned for the corresponding very narrow bands.

Finally, all of the approaches referred to above neglect the short range AF which is at the basis of our analysis.

It is true that, in the tJ model, a term of this sort could be introduced by considering the (small) effect of J. In our own model, with U of the order of t, it is the AF that strongly contracts the energy scale of the band structure near the AF gap (by replacing Eq. (1) by Eq. (6)). Also, in the short range AF case, the notions of reciprocal space, of band structure and Fermi surface need to be redefined, especially in the underdoped range, where our model explains the low temperature increase of resistivity by the partial localisation of the electron states in the pseudogap.

In conclusion, there are definite similarities in a number of delocalised schemes proposed more or less recently and it is only the general fit of predicted properties with observations that can allow one to choose between them. We are aware that our own model, being so far very qualitative, fulfils with difficulty this condition.

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