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BCS-type superconductivity due to correlations in high-T_c materials

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Abstract. We describe high-T_c superconductors as spin-$\frac{1}{2}$ doped Mott insulators. We hypothesise that the doped Mott insulator is not a Fermi liquid. We show that this leads to important consequences as far as superconductivity is concerned. In particular, we find s-wave superconductivity which behaves as the usual BCS superconductivity.

1. Introduction

Since the discovery by Bednorz and Müller of high-T_c superconductors, a number of theoretical ideas have been put forward (Rice 1987). Among them, Anderson (1987) has suggested that correlations between electrons are important and has proposed the resonant valence bond model. We have proposed (Cyrot 1987a, b, c, Cyrot *et al* 1988) in a series of papers a somewhat different model although starting from the same hypothesis of strong correlations.

Indeed there exists strong arguments in favour of this hypothesis. Let us first recall that the properties of these types of perovskite had already been discussed before the discovery of Bednorz and Müller in using the hypothesis of strong correlations (Lyon-Caen and Cyrot 1973, Khomskii and Kugel 1975). We have used these ideas to predict antiferromagnetic behaviour for pure La_2CuO_4 (Cyrot 1987a, b, c) contrary to the belief at that time on this material. The low values of the magnetic moment, sometimes taken as an indication of small value for correlations, are well explained when taking into account the quantum fluctuations which are important for spin-$\frac{1}{2}$ (Takahashi 1987). Two-dimensional fluctuations above T_N have been observed (Shirane *et al* 1987) and explained by the spin-$\frac{1}{2}$ Heisenberg antiferromagnet (Chakravarty *et al* 1988). All these facts lead us to believe that the antiferromagnetic state is a spin-$\frac{1}{2}$ Heisenberg antiferromagnet and not a Slater antiferromagnet because of nesting of the Fermi surface. The same situation occurs in the compound $YBa_2Cu_3O_6$ which is insulating antiferromagnetic (Tranquada *et al* 1988, Rossat-Mignod *et al* 1988).

As soon as these materials are doped, giving a few per cent of holes in the CuO_2 plane, the antiferromagnetism is destroyed. As the number of carriers is always small, they cannot screen completely the Coulomb interaction on the copper site. Thus the copper electrons can move but are always subject to a strong on-site repulsion.

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Two types of theory have been developed in this limit: the resonant valence band theory and a theory which we call 'superexchange superconductivity'. The first theory developed by Anderson and co-workers supposes that the ground state is a resonant valence band ground state where the excitations are holons which pairs to lead to superconductivity. The second theory proposed by Baskaran *et al* (1987) and Cyrot (1987a, b, c) uses directly the superexchange interaction to make Cooper pairs.

In this paper, we wish to develop some aspects of the second approach and to show that we end up with a superconductor which has nearly all the properties of the usual BCS superconductor.

2. The model

Our basic starting Hamiltonian describes carriers in a nearly filled Hubbard lower sub-band which are coupled by a superexchange interaction through the oxygen atoms. Thus,

$$H = \sum_{i,j} t_{ij}(1 - n_{i-\sigma})C^{+}_{i\sigma}C_{j\sigma}(1 - n_{j-\sigma}) + \sum_{ij} JS_i \cdot S_j \tag{1}$$

where i and j are first-nearest-neighbour sites and t_{ij} is an effective hopping integral between the copper sites in the CuO_2 plane.

Not only is J related to t_{ij} and the Coulomb correlation U but, as the superexchange is via the oxygen anion, J is also related to the difference between the d and p atomic levels of copper and oxygen. The way that the kinetic energy is treated leads to very different results. This kinetic energy is usually treated by a Gutzwiller (1963) approximation (Brinkman and Rice 1970), i.e. one introduces a mass enhancement $1/\delta$, where δ is the number of holes in the sub-band. Thus we are led to the total Hamiltonian

$$H = -\sum_{ij\sigma} \delta t C^{+}_{i\sigma}C_{j\sigma} + \sum_{ij} JS_i \cdot S_j. \tag{2}$$

This Gutzwiller approximation used by most workers replaces a local constraint by a global one and is equivalent to the mean-field approximation in the slave boson approach. If we consider the kinetic energy term as that of a half-filled band with a reduced band width δw, it is well known that it leads to serious drawbacks. The most important is that there are four states per site leading to an entropy $R \ln 4$ instead of $R \ln 2$ as the double occupancy is impossible as long as the temperature is smaller than U. This serious drawback has also been recognised as the origin of the breakdown in the calculation of the susceptibility. We think that the problem lies in the fact that the large density of states due to the reduced band width mainly arises from spin fluctuations. We have to distinguish clearly between the total density of states for all excitations and the density of states of current carriers (Mott 1974). In trying to construct a superconducting state, we have to consider only the last factor. The numbers of carriers is in the large-U limit given by $1 - n$. Owing to correlations, we do not know how to write the quasi-particle states at the Fermi level. To overcome this difficulty and to take into account the fact that the number of available states in the lower Hubbard sub-band is only one per site, we use statistics with only one state per $\boldsymbol{k}$-vector with spin up or down.

The volume of the Fermi surface is thus doubled and the Luttinger theorem is violated in the Mott state. Our approach is closely related to a phenomenological one developed recently by Spalek and Wojcik (1988). These workers assume that the double occupancy

in a Mott insulator is forbidden not only in real space but also in reciprocal space. Thus, if the $k\sigma$ state is occupied, the $k - \sigma$ state does not exist. (The doubly occupied configurations are projected out from the physical space.)

This result has a very important effect on the possible superconductivity. In a Fermi liquid state, one obtains a d-wave superconductivity which presents the absence of a gap in some directions in k-space. Properties of this superconductivity are different from those of BCS superconductivity. In the case where one assumes a non-Fermi liquid behaviour, one obtains a s-wave superconductivity which has all the properties of a BCS superconductivity.

3. Effect of doping on the critical temperature

In previous papers, we have shown that superconductivity can be obtained by performing a BCS linearisation of the term $S_i^+ S_j^- + S_i^- S_j^+$. Such a linearisation permits us to diagonalise the effective Hamiltonian with a Bogoliubov transformation. The quasi-particle energy is

$$E_k = (\xi_k^2 + J^2\gamma_k^2\Delta^2)^{1/2} \qquad \text{with } \Delta^* = \langle C_{i\uparrow}^+ C_{j\downarrow}^+ \rangle. \tag{3}$$

ξ_k measures the energy from the chemical potential μ of the superconducting phase, $\xi_k = \varepsilon_k - \mu$ and

$$\gamma_k = \begin{cases} \cos(k_x a) + \cos(k_y a) \\ \cos(k_x a) - \cos(k_y a) \end{cases} \qquad \text{for} \begin{cases} \text{s-wave superconductivity} \\ \text{d-wave superconductivity.} \end{cases} \tag{4}$$

The gap and chemical potential are given by the two self-consistent equations

$$\frac{2}{J} = \frac{1}{N}\sum_k \gamma_k^2 \frac{\tanh(\beta E_k/2)}{E_k} \tag{5}$$

$$2(1-\delta) = \frac{1}{N}\sum_k \left[1 - \frac{\xi_k}{E_k}\tanh\left(\beta\frac{E_k}{2}\right)\right]. \tag{6}$$

In order to find the critical temperature for s or d symmetry, one must solve equations (5) and (6) with $\Delta = 0$. Thus one gets

$$\delta - 1/2 = \tfrac{1}{2}\int N(\varepsilon)\tanh\left(\frac{\beta(\varepsilon-\mu)}{2}\right)\mathrm{d}\varepsilon \tag{7}$$

$$\frac{2}{J} = \int \tilde{N}(\varepsilon)\tanh\left(\frac{\beta(\varepsilon-\mu)}{2}\right)\frac{\mathrm{d}\varepsilon}{\varepsilon-\mu}. \tag{8}$$

Equation (7) gives the chemical potential μ as a function of the filling of the band $n = 1 - \delta$, for a normal metal. Here $N(\varepsilon)$ is the square lattice density of states (as represented in figure 1) for a hopping integral $t\delta$.

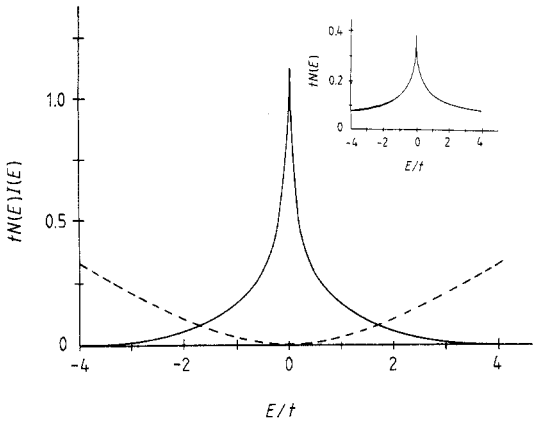

Figure 1. The effective density $N(E)$ of states as a function of energy for s(———) and d(———) symmetry. The inset shows the square lattice density $N(E)$ of states.

Equation (8) is analogous to the BCS equation for T_c. However, in the present theory the integration is taken over the whole band and not for $|\varepsilon - \mu|$ less than the Debye energy. Furthermore the density of states is replaced here by an effective density $\tilde{N}(\varepsilon)$ (figure 1):

$$\tilde{N}(\varepsilon) = N(\varepsilon)I(\varepsilon) = \sum_k \gamma_k^2 \delta(\varepsilon - \varepsilon_k). \tag{9}$$

The properties of our model, and in particular the critical temperature, can be analysed in a simple way if $N(\varepsilon)$ and $\tilde{N}(\varepsilon)$ are nearly constant for $|\varepsilon - \mu|$ less than a few kT_c. This approximation is valid except for very small δ ($\delta \leqslant 0.05$ for our two choices of parameters: $t/J = 10$ and 2.5). This is because the bandwidth is $8t\delta \simeq 1$–0.1 eV, much greater than $kT_c \leqslant 10^{-2}$ eV ($\simeq$120 K). Thus $N(\varepsilon)$ and $\tilde{N}(\varepsilon)$ can vary appreciably in a region of a few kT_c around μ, only if the chemical potential is very close to the band edge where $N(\varepsilon)$ and $\tilde{N}(\varepsilon)$ are discontinuous. This corresponds to a very small number δ of holes for which the ground state is an antiferromagnetic Néel state.

Now we split the integral in (8) into two parts: $|\varepsilon - \mu| < \hbar\omega_c$ (domain d) and $|\varepsilon - \mu| > \hbar\omega_c$ (domain D), where $\hbar\omega_c$ is chosen to be of the order of a few kT_c ($\hbar\omega_c \geqslant 2kT_c$). Thus, for $|\varepsilon - \mu| < \hbar\omega_c$, we have $\tilde{N}(\varepsilon) = \tilde{N}(\mu)$ and, for $|\varepsilon - \mu| > \hbar\omega_c$, we have

$$\tanh[\beta(\varepsilon - \mu)/2] \simeq \pm 1. \tag{10}$$

Equation (8) is then written

$$\int_d \tanh\left(\frac{\beta(\varepsilon - \mu)}{2}\right) \frac{d\varepsilon}{\varepsilon - \mu} = \frac{2}{J\tilde{N}(\mu)} - \int_D \frac{\tilde{N}(\varepsilon)\, d\varepsilon}{\tilde{N}(\mu)|\varepsilon - \mu|} \tag{11}$$

which is analogous to the BCS equation for the critical temperature with $2/VN(\mu)$ replaced by the right-hand side of equation (11) and the Debye frequency replaced by ω_c.

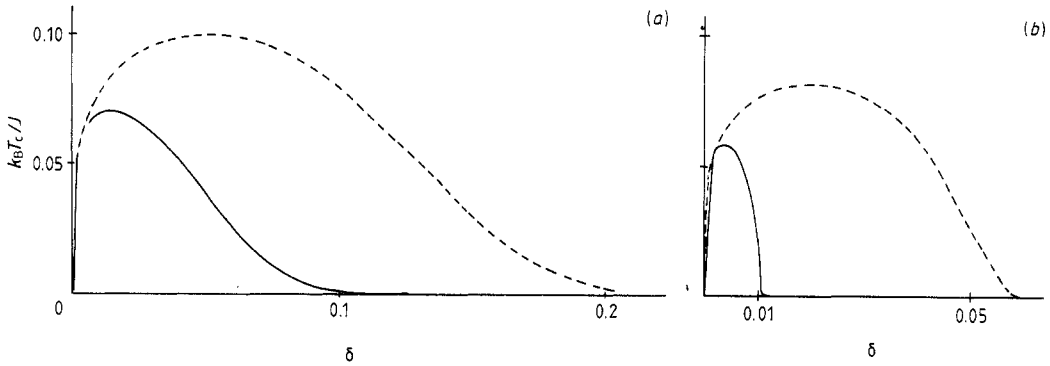

Figure 2. The critical temperature for the square lattice as a function of doping for (*a*) s symmetry and (*b*) d symmetry for two values of the parameter t/J: $t/J = 2.5$ (– – –); $t/J = 10$ (———).

We can use the BCS solution which is valid as long as $\tanh(\beta\hbar\omega_c/2) \simeq 1$ since this condition is fulfilled for $\delta \geqslant 0.05$. So the critical temperature is

$$kT_c = 1.14W(\mu)\exp[-1/J\tilde{N}(\mu)] \tag{12}$$

where

$$W(\mu) = \hbar\omega_c \exp\left(\frac{1}{2}\int_D \frac{\tilde{N}(\varepsilon)\,d\varepsilon}{\tilde{N}(\mu)|\varepsilon - \mu|}\right). \tag{13}$$

The expression for $W(\mu)$ which replaces the Debye frequency is complicated but it is proportional to the hopping integral t for a given δ and does not depend on the chosen $\hbar\omega_c$.

In our model, the band contains only one electron and the range of interest for doping corresponds to a chemical potential μ between $\mu/t\delta \simeq 2$ and $\mu/t\delta = 4$ (band edge). Thus we see from figure 1 that $\tilde{N}(\mu)$ is larger for s-type than for d-type superconductivity. As a consequence, we predict an s-type superconductivity in contrast with many researchers who predict a d symmetry. We note that, in their theory, the band is nearly half filled (it contains two electrons) and $\tilde{N}(\mu)$ is indeed larger for d-type than for s-type symmetry.

We have made a complete numerical study of the critical temperature for s and d symmetry which confirms the above prediction. The result is shown in figure 2 for two values of the parameter t/J, but from the work of Mila *et al* (1988) it seems that the best choice is $t/J \simeq 2.5$. We note, however, that the superconductivity is favoured when t/J decreases.

We have also studied the case of the linear chain where only s symmetry occurs. Similar behaviour is found for the critical temperature as a function of doping (figure 3).

In conclusion, our model predicts only an s-type superconductivity whose critical temperature has an appropriate order of magnitude. The critical temperature tends to zero for small doping.

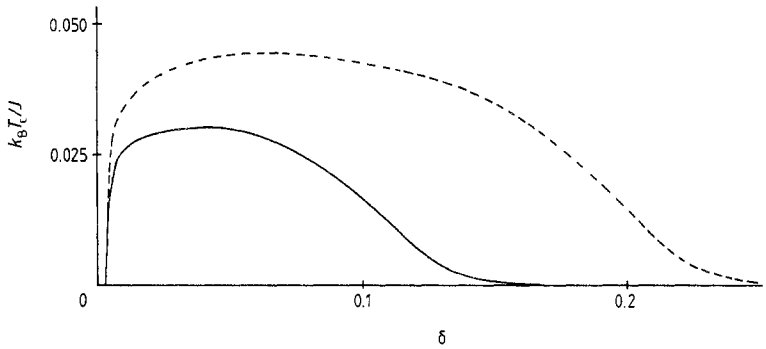

Figure 3. As figure 2 but for a linear chain.

4. BCS-like properties

We now consider doping with $\delta \geqslant 0.05$ such that $N(\varepsilon)$ and $\tilde{N}(\varepsilon)$ are almost constant for $|\varepsilon - \mu|$ less than a few kT_c. In this range of doping, the order parameter has s symmetry and in fact many other properties are BCS-like.

4.1. Excitation spectrum

The first point is that $\gamma_k = \cos(k_x a) + \cos(k_y a) = \varepsilon_k / t\delta$ is also almost constant for $|\varepsilon - \mu|$ less than a few kT_c. Thus the excitation energies are

$$E = \sqrt{[(\varepsilon - \mu)^2 + \gamma^2 J^2 \Delta^2]} \tag{14}$$

where $\gamma = \gamma_k(\mu)$. This is exactly the spectrum of a BCS-like superconductor with a gap $\gamma J\Delta$.

4.2. Temperature dependence of the gap

Within our approximation the chemical potential μ is independent of the temperature and equal to its value for a normal metal at $T = 0$ (equation (6)). The integral in equation (5) can again be split into two parts: $|\varepsilon - \mu| < \hbar\omega_c$ and $|\varepsilon - \mu| > \hbar\omega_c$ where $\hbar\omega_c$ is a few kT_c. This leads to the gap equation

$$\int_d \frac{\tanh(\beta E/2)}{E} \, d\varepsilon = \frac{2}{J\tilde{N}(\mu)} - \int_D \frac{\tilde{N}(\varepsilon)}{\tilde{N}(\mu)} \frac{d\varepsilon}{|\varepsilon - \mu|} \tag{15}$$

where E is given by (14). Again this equation is identical with the BCS equation with $2/VN(\mu)$ replaced here by the right-hand side (which is also temperature independent).

This implies that the gap $\gamma J\Delta$ has exactly the same temperature dependence in our theory as in the BCS theory:

$$\gamma J\Delta(T)/kT_c = f(T/T_c). \tag{16}$$

In particular, at zero temperature, $\gamma J\Delta = 1.76\, kT_c$.

4.3. Other properties

In conclusion, we see that for $\delta \geqslant 0.05$ the properties of the superconductor have three important features of the BCS model:

(i) excitation spectrum (equation (14));
(ii) temperature dependence of the gap (equation (16));
(iii) constant density of states in the region of the gap.

It follows that thermodynamic properties such as the specific heat have BCS behaviour. This is also true for other properties such as ultrasonic attenuation and nuclear relaxation.

We end with a comment on these BCS results. Like the BCS theory, our theory is a mean-field theory which completely neglects fluctuations. It has been pointed out by many researchers (see, e.g., Deutscher *et al* 1988) that in these new materials the Ginsburg criterion for complete neglect of fluctuations is not fulfilled. The ratio kT_c/E_F is not 10^{-4} as in ordinary superconductors. In our model, this ratio is of the order of 10^{-1}. Thus fluctuations must play a role near T_c and reduce the critical temperature compared with its mean-field value. This can have serious consequences, for instance an increase in the ratio $2\gamma J\Delta/kT_c$ compared with the BCS value, without invoking any strong coupling effect (Vaks *et al* 1967).

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