ABSTRACT

A general formalism of quantised charge transfer polarisation waves has been developed. The nature of possible superconductive pairing between oxygen holes is discussed. Unlike optical phonons these polarisation fields will give rise to dielectric bipolarons or bipolaron bubbles. In the weak coupling limit a new class of superconductivity is to be expected.

INTRODUCTION

The relevance of charge transfer excitation to superconductivity was first pointed out by Varma (1) et al. The idea of such a local short range interaction has since been extended to a variety of charge transfer excitations (2) in the high Tc oxides. This paper has its inspiration in the idea of polarisation waves that goes back to Hopfield (3) and revived recently by Aschcroft (4) with respect to the high Tc oxides. The basic notion of long range dipole-dipole interaction giving rise to a collective and quantised charge transfer wave is the key ingredient. Some of the detailed calculations are presented elsewhere (5).

A - POLARISATION WAVE FORMALISM

We want to make essential points clear. In the Hartree-Fock approximation, the state of an Unit Cell of CuO2 square is a Slater determinant of the occupied lowest energy orbital states. Consider an excitation α corresponding to moving one electron from a ground state to an excited state orbital costing an energy α. Figure 1 gives the relevant energy levels (6); figure 1a shows the charge transfer insulator gap energy Eg for zero-doping, while the arrows in figure 1b indicate the charge transfer excitation energy ωg to the Fermi level on p-type doping (1 signifying a ligand hole or 2p5 configuration).
Figure 1a. Energy band--undoped material
Figure 1b. Energy band--doped material
We define by $b_\alpha^+$ the operator to describe this excitation, which can be written in terms of the operator $a_n$ of the electronic state

$$b_\alpha^+ = a_m^+ a_n$$  \quad (1)

We approximate Hamiltonian of a single cell by

$$H = E_g + \sum_\alpha \omega_\alpha b_\alpha^+ b_\alpha$$  \quad (2)

$E_g$: ground state energy.

Define a dipole matrix element

$$\mu (\alpha) = \int d^3 r \, \phi_m^* (r) \times \phi_n (r)$$  \quad (3)

Where the two orbitals $\phi_n$ and $\phi_m$ differ by one unit of angular momentum. Introduce the polarisation operator in the vector direction $\vec{x}$ for the unit cell by

$$P_x = e \sum_\alpha \mu_x (\alpha) \, (b_\alpha + b_\alpha^+)$$ \quad (4)

This operator has the units of polarisation, which is charge times length - analogous to the displacement operator for a harmonic oscillator, which has the unit of length $\sim \left( \frac{\hbar}{2m} \right)^{1/2}$. We use the symbol $G_{xy} (i \omega)$ to denote the retarded correlation function of the $P$ operator with itself by

$$G_{xy}^0 (i \omega) = - \int_0 \beta e^{i \omega \tau} \langle T_\tau \, P_x (\tau) \, P_y (0) \rangle \, d \tau$$  \quad (5)

It is easily evaluated for the non interacting Hamiltonian (2).

$$G_{xy}^0 (i \omega) = \sum_\alpha \frac{2 e^2 \mu_x \mu_y \omega_\alpha}{(i \omega)^2 - \omega_\alpha^2}$$  \quad (6)

The quantity $- G^0 (i \omega)$ is actually the polarisability $\alpha^0 (i \omega)$ of the unit cell.
\[ \alpha (i \omega) = 2 e^2 \sum_{\alpha} \frac{\mu^2 (\alpha) \omega_{\alpha}}{\omega_{\alpha} - (i \omega)} \]  

(7)

So far our discussion has been confined to the properties of a single unit cell \( \text{CuO}_2 \). However when one excites dipoles in a cell \( i \), it has long-range dipole-dipole interaction with dipoles of the cell \( j \), given by

\[ H' = \vec{\mathbf{X}}_i \cdot \phi (R_i - R_j) \cdot \vec{\mathbf{X}}_j \]  

(8)

Where:

\[ \phi_{xy} (R) = \frac{\delta_{xy}}{R^3} - \frac{3 R_x R_y}{R^3} \]  

(8a)

Defining a Fourier transform

\[ T_{xy} (k) = \frac{\Omega_0}{4 \pi} \sum_{R} \phi_{xy} (R) \exp i R \cdot k \]  

(8b)

We get the resultant Hamiltonian in the \( k \)-space as

\[ H = E_g + \sum_{\alpha, k} \omega_{\alpha} b'^{*}_{\alpha, k} b_{\alpha, k} + \frac{1}{2} \sum_{k, \alpha \beta} V_{\alpha \beta} (k) \left[ b_{\alpha, k} + b'^{*}_{\alpha, -k} \right] \left[ b_{\beta, -k} + b'^{*}_{\beta, k} \right] \]  

(9)

where:

\[ V_{\alpha \beta} (k) = \frac{4 \pi e^2}{\Omega_0} \sum_{xy} \mu_x (\alpha) T_{xy} (k) \mu_y (\beta) \]  

(9b)

Thus the Dyson equation for the correlation function is the matrix equation

\[ G_{xy} (k, i \omega) = G^0_{xy} (k, i \omega) + \frac{4 \pi}{\Omega_0} \sum_{xy} G^0_{x'y'} (k, i \omega) T_{x'y'} (k) G_{y'y'} (k, i \omega) \]  

(10)

Solution of this equation will give us the collective excitation wave, that we have called charge transfer polarisation waves. In a cubic symmetry, it is solved to give

\[ G_{xy} = \frac{\alpha}{1 - \frac{4 \pi \rho}{3 \Omega_0}} \left[ \delta_{\mu \nu} - \frac{4 \pi \rho}{\Omega_0} \frac{k_x k_y}{(1 + \frac{8 \pi \rho}{3 \Omega_0}) k^2} \right] \]  

(11)
The quantity $G_{xy}$ is the static polarisability of the solid, just as $G_{xy}^0$ is the static polarisability of the unit cell. This gives us the dielectric function at long wave-length which has the Lorentz-Lorentz form

$$
\varepsilon(\omega) = \frac{1 + \frac{8\pi}{3\Omega_0} \alpha(k,\omega)}{1 - \frac{4\pi}{3\Omega_0} \alpha(k,\omega)}
$$

(12)

The pole and zero of the dielectric function gives us the transverse and longitudinal charge transfer polarisation waves respectively.

$$
\omega_t^2 = \omega_g^2 - \frac{1}{3} \Omega_p^2
$$

$$
\omega_l^2 = \omega_g^2 + \frac{2}{3} \Omega_p^2
$$

(13)

B - THE GAP EQUATION

Interaction between two carriers due to the longitudinal charge transfer waves is given by

$$
V(q,\omega) = \frac{4 \pi e^2}{q^2 \varepsilon(q,\omega)}
$$

(14)

Where $\varepsilon(q,\omega)$ is the dielectric constant as shown in fig (2), for a finite value of $\omega_t$. 

![Fig. (2) - Long wave length dielectric constant $\varepsilon(\omega)$](image-url)
We see immediately that excitations up to $\omega = \omega_t$ has repulsive interactions between two carriers and is attractive between $\omega_t$ and $\omega_b$. A B.C.S. like gap nonetheless appears at the Fermi Surface. The gap equation is given by

$$\Delta (\xi) = - \int_0^\infty \frac{K (\xi, \xi')}{\sqrt{\Delta^2 (\xi') + \xi'^2}} \tanh \left[ \frac{\sqrt{\Delta^2 (\xi') + \xi'^2}}{2 k T} \right] d\xi'$$

(15)

We can mimic the repulsive interaction at frequencies $0 < \omega < \omega_t$ and an attractive interaction between $\omega_t < \omega < \omega_b$, by two piecewise constant Kernels

$$k(\xi, \xi') = \begin{cases} \lambda_1 & 0 < \xi, \xi' < \omega_1 \\ -\lambda_2 & \omega_1 < \xi, \xi' < \omega_2 \end{cases}$$

(16)

We also assume two energy gaps

$$\Delta (\xi) = \begin{cases} \Delta_1 & 0 < \xi < \omega_1 \\ \Delta_2 & \omega_1 < \xi < \omega_2 \end{cases}$$

(17)

The gap equation is easily solved to give these two gaps $\Delta_1$ and $\Delta_2$.

We have

$$kT_c = 1.14 \omega_b \exp \left( - \frac{\lambda}{\lambda} \right)$$

(17a)

where

$$\frac{\lambda}{\lambda} = \frac{\lambda_2 g - 1}{D}$$

With $g = \ln \frac{\omega_2}{\omega_1}$

and $D = \lambda_1 - \lambda_2^2 g$

For $\frac{\omega_2}{\omega_1} = 6, \lambda_1 = 0.5, \frac{\lambda_2}{\lambda_1} = 0.76$ and $h \omega_1 = 0.5 \text{ eV}$, we obtain a $T_c \sim 300^\circ \text{k}$.

The same formalism will apply for optical phonons. Using $\hbar \omega_1 = 0.1 \text{ eV}$, $\frac{\omega_2}{\omega_1} = 2.25$ (corresponding to $\frac{\omega_2}{\omega_1} = 5$), $\lambda_1 = 0.3, \lambda_2 = 0.7$ gives a $\lambda = 0.6$ and a zero temperature gap $\Delta_1 = 36 \text{ m eV}$. We thus see that a dipole lattice or a Lorentz lattice in general can give rise to a B.C.S. kind of pairing and an energy gap at the Fermi surface, in spite of a net repulsive interaction in the small frequency range, and the most general solution admits at least more than one energy gap ($\Delta_2 > \Delta_1$).
The interaction of the carriers with the longitudinal polarisation field gives rise to polarons (Feynmann (7)). Will it give rise to bipolarons? The literature is quite scarce on the subject. While the answer is quite affirmative with the acoustic bipolarons, it seems to be less so with its optical counterpart. Early (8) calculations seemed to indicate that for a favorable range of the dielectric constant ratios \( \frac{\varepsilon_0}{\varepsilon_{\infty}} \sim 10 - 20 \) we may be able to have a dielectric bipolaron. More recent path (9) integral calculations put this ratio even higher. What is certain (10) is that if the carrier behaves like a localized classical charge (i.e., its interaction with polarisation field is recoil less), the phonon-mediated interaction will at best reduce the coulomb repulsion between the two charges form \( \frac{e^2}{\varepsilon_{\infty} \ell} \) to \( \frac{e^2}{\varepsilon_0 \ell} \) but does not lead to any attraction. We can see from figure 1b, that as the p-type doping is increased, there is an increasing component of low energy excitation \( \omega_0 \) (\( \omega_0 \) going down with \( \varepsilon_F \)) such that we expect \( \omega_0 \rightarrow 0 \), at some critical doping value \( x_c \), given by equation (13). With the longitudinal frequency \( \omega_l \rightarrow \sqrt{\frac{2}{3}} \Omega_p \) and because of the collapse of the Lorentz lattice, we can have the whole frequency range up to \( \omega_l \) where the dielectric constant is negative. This low frequency attraction will give \textit{instantaneous local interaction} between carriers, giving rise to (fig. 4b) \textit{dielectric bipolarons} or \textit{bipolaron bubble} (if its energy is embedded in the continuum of 1-particle states).

We can model the effective Hamiltonian by

\[
H_{\text{eff}} = \sum \epsilon_k C^+_k C_k - V \sum C^+_{k\sigma} C^+_{k'\sigma'} C_{k'\sigma'} C_{k\sigma} \quad (18)
\]

This Hamiltonian is strikingly different from the B.C.S Hamiltonian in not having the \( \omega \)-cut off and its general behavior pattern has been indicated (11). In the usual weak-coupling approximation and when the dielectric bipolaron interaction energy \( V \ll \varepsilon_F \), the superconductivity gap equation has been solved (5) to give

\[
\Delta = 8 \varepsilon_F \exp \left( -\frac{\varepsilon_F}{\varepsilon_c} \right) \quad (19)
\]

Where \( \varepsilon_c \) is an energy cut-off.

It is necessary to recall the essential ingredients leading to the equation (18) signifying an instantaneous attractive interaction \( V \) between two carriers.

We can define two key dimensionless parameters in the pairing scenarios.

- The dimensionless coupling constant
  \[
  \lambda = \frac{V}{\varepsilon_F} \quad (20a)
  \]

- Antiadiabaticity parameter
  \[
  \gamma = \frac{\hbar \omega}{\varepsilon_F} \quad (20b)
  \]
Signifying ratio of boson frequency to the Fermi energy.

There are several interesting differences of the electronic properties in the normal state between the adiabatic ($\gamma \ll 1$) and the antiadiabatic ($\gamma \gg 1$) regime. These differences are shown schematically in figure (3a) and (3b), as well as in fig. (4a) and (4b).

(a) The effective mass ratio $\frac{m^*}{m}$ is exponentially large (Holstein factor) around $\gamma = 1$ ($\lambda < 1$) but is completely unrenormalised in the antiadiabatic limit ($\lambda$) (fig. 3a).

(b) The electron life time $\tau$ at the Fermi surface is quite different in the two regimes. In the adiabatic regime $\frac{1}{\tau} << kT \sim T^2_{EF}$, which gives the usual metallic conductivity. In the antiadiabatic regime $\frac{1}{\tau} >> kT$ (fig. 3b) and is conjectured to be $\sim T$, if it behaves as a marginal Fermi liquid.

(c) In the adiabatic regime, the usual electron-phonon interaction (fig. 4a) gives the retarded non local attraction between electron-pairs. In the antiadiabatic regime the attraction is expected to be instantaneous and local (fig. 4b), forming a real-space electron-pair or a dielectric bipolaron bubble. The resulting normal and superconducting properties are bound to be different from the classical B.C.S. behavior.

In the B.C.S. behavior
\[ \frac{kT_c}{E_F} = \gamma \exp \frac{-1}{\lambda} \] (21a)

In the other limit, $\gamma \gg 1$
\[ \frac{kT_c}{E_F} = \exp \frac{-1}{\lambda} \] (21b)

In summary, we can say that presence of high frequency bosons ($\hbar \omega > E_F$) will lead to quasiparticles which are dielectric polarons with properties in the normal and superconducting states quite different from usual metals.
Fig. 3a - Effective mass of carriers as function of $\lambda = \frac{\hbar \omega}{E_F}$ or antiadiabaticity.

Fig. 3b - A carrier life time $\tau$ as function of temperature
Fig. (4a) - Electron-electron interaction in the adiabatic regime

Fig. (4b) - Electron-electron interaction in the antiadiabatic regime
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