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ABSTRACT

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Oxide superconductors are described in terms of macroscopic wave functions  $\psi$  and  $\phi$  corresponding, respectively, to electron pairs of the superconducting and insulating states. In terms of the total free energy of the system, including the effect of interaction, we discuss the electrodynamic responses of the oxide superconductors in relation with the experiments to date.

A PHENOMENOLOGICAL APPROACH TO HIGH  $T_c$  OXIDE SUPERCONDUCTORS †

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The discovery of high  $T_c$  oxide superconductors,<sup>1,2</sup> has not only signalled a new era for technology, but it has also posed great challenges regarding the question as to how the oxides have such high  $T_c$  superconductivity. During the past few months many interesting aspects of the materials have been reported based on thermodynamics and spectroscopic measurements raising several controversies. As it stands today, these oxides belong to a new class of superconductors.

In general, most oxides are insulators or semiconductors at low temperature. Only a handful of them are poor metals. Particularly for materials like Ba-La-Cu-O, and related compounds, it has been known that the basic material lanthanum cuprate is an antiferromagnetic insulator. On doping with an alkali earth, the system undergoes an insulator-metal transition, and soon after the superconductivity appears. There have been some more recent studies on the same materials having stoichiometric composition exhibiting superconductivity<sup>3</sup> of high  $T_c$ . From structural considerations it has been known that these materials are made up of perovkite layers of corner-sharing  $\text{CuO}_6$  octahedra, interlinked with corner-sharing square planar  $\text{CuO}_4$ . Whether it is a doped, or a stoichiometric material,  $\text{CuO}_4$  units form a square lattice. At present the most considered opinion is that when a divalent alkali earth cation is substituted for the trivalent lanthanum (or yttrium), the  $\text{Cu}^{2+}$  ion tends to go to  $\text{Cu}^{3+}$ . The occurrence of  $\text{Cu}^{3+}$  also depends on the oxygen vacancy. On the whole copper remains in a mixed valent state, which is a requirement for the Cu-O plane to be metallic and this condition is essential for superconductivity.

Quite a few attempts have been made to understand how these materials possess superconductivity. Some workers believe<sup>4</sup> that the oxides are

conventional phonon-mediated strongly-coupled BCS superconductors; but, apparently, the Debye phonon frequency has an upper bound which will fail to give the observed  $T_c$  in these materials within the conventional BCS picture. Another related mechanism<sup>5</sup> which has been suggested for the oxides, is due to bipolarons - bound pairs of electrons with a cloud of phonons. This picture, though attractive, fails to produce high  $T_c$  for strong enough coupling, because the scale of energy is still due to phonons. More recently Anderson has generalized the Pauling's theory of resonant valence bond (RVB) relevant to the oxide materials<sup>6</sup>. In this picture the valence electrons are Heitler-London bonded singlet antiferromagnetic pairs. It satisfies Hubbard's half-full band condition, so that the virgin lanthanum cuprate is an insulator having all localized valence bond pairs as in a Neel state. Doping with the alkali earths the pairs become mobile as in a liquid. Correlations amongst the pairs establish an order that is considered as the origin of superconductivity. Anderson's proposal is based on the experimental facts on the oxides and it is considered to have the potential of giving very high  $T_c$ , since the energy scale is no longer due to phonons, but rather it is due to inter-electronic exchange. A complete test of the RVB theory is yet to be carried out for all the superconducting properties of the oxides.

In this paper, by following the spirit of Anderson's work, we attempt to develop a phenomenological macroscopic approach to understand some of the electro-dynamical aspects of the oxide superconductors. Based on the fact that the nature of the materials is inhomogeneous, with several experimentally observed anomalies in, for instance, resistivity and phonon spectrum, we start with a hypothesis that in the normal state (just above  $T_c$ ) there exists quasilocalized domains of valence-bond pairs,

which are characterized by a complex order parameter  $\phi$ . These domains are weakly linked and, therefore, the resistivity of the sample is very high. The onset of superconductivity ( as the resistivity begins to drop ) is taken care of by another complex order parameter  $\psi$ , which refers to an extended type of electron paired states. These two order parameters are assumed to be suitably coupled through a temperature-dependent factor. The strength of the coupling is further assumed to depend on the paired densities in both phases.

Assuming that the order parameters are spatially inhomogeneous close to  $T_c$ , we can write the free energy  $F$  of the system, in the presence of a magnetic field  $\vec{H}$ , as composed of functionals of the order parameters:

$$F = F[\psi] + F[\phi] + F_I[\psi, \phi], \quad (1)$$

where  $F[\psi]$  and  $F[\phi]$  are free energy densities<sup>7</sup> of the order parameters  $\psi$  and  $\phi$  respectively.  $F_I$  denotes the free energy functional, corresponding to the coupling of the two order parameters  $\psi$  and  $\phi$ . We note here that analysis of free energies involving multiple phases have been done in the past in the context of the coexistence of superconductivity and magnetism<sup>8</sup>. Likewise, we attempt here a new description which will be valid in the vicinity of a transition involving a quasilocalized RVB and superconducting ( itinerant ) state:

$$F[\psi] = \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} |(-i\hbar\vec{\nabla} - \frac{e^*}{c}\vec{A})\psi|^2 + \frac{H^2}{8\pi}, \quad (2)$$

Here,  $e^* = 2e$ , and  $m^*$  denotes the effective mass of the itinerant pair, where  $\vec{A}$  is the vector potential corresponding to the magnetic field  $\vec{H}$ ;  $\alpha$  and  $\beta$  are the well-known Ginzburg-Landau ( GL ) parameters<sup>8</sup>. A similar expansion exists for  $F[\phi]$ . As we have said before, both order parameters are coupled through the vector potential  $\vec{A}$  and in order to keep it in a gauge invariant form, in a simple fashion, we choose

$$F_I[\psi\phi] = \gamma |(-i\hbar\vec{\nabla} - \frac{e^*}{c}\vec{A})\psi\phi|^2, \quad (3)$$

where  $\gamma$  is the coupling strength in appropriate units, incorporating the effective mass. The free energy  $\mathcal{F}$  is given by,

$$\mathcal{F} = \int d\vec{r} F(\vec{r}). \quad (4)$$

We minimize  $\mathcal{F}$  with respect to  $\psi$  and obtain the equation:

$$\beta |\psi|^2 \psi + (\alpha + 2\gamma|\phi|^2)\psi + \left(\frac{1}{2m^*} + 2\gamma|\phi|^2\right)(-i\hbar\vec{\nabla} - \frac{e^*}{c}\vec{A})^2\psi = 0, \quad (5)$$

where  $\Gamma$  is given by,

$$\Gamma = \phi^* (-i\hbar\vec{\nabla} - \frac{e^*}{c}\vec{A})^2 \phi = \text{const.} \quad (6)$$

A similar equation follows by varying  $\mathcal{F}$  with respect to  $\phi$ .

Finally, we minimize  $\mathcal{F}$  with respect to  $\vec{A}$ . By considering the mass of the localized pairs to be heavier relative to those of the itinerant

pairs, we omitted the contribution from the  $F[\phi]$  to obtain the current density as

$$\vec{j} = \frac{e^* \hbar}{2im^*} (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) + \frac{e^* \hbar \delta}{i} [(\psi \phi)^* \vec{\nabla} (\psi \phi) - (\psi \phi) \vec{\nabla} (\psi \phi)^*] - |\psi|^2 \left[ \frac{e^{*2}}{m^* c} + \frac{2e^* \delta}{c} |\phi|^2 \right] \vec{A}. \quad (7)$$

In deriving Eqns. (5-7) we have used the corresponding boundary conditions. By setting  $|\psi|^2 = |\psi_0|^2 \tau$ , and by assuming  $\phi$  as spatially weakly inhomogeneous, to first order in  $\vec{H}$ , eqn. (7) can be cast in the form:

$$\vec{\nabla}^2 \vec{H} = \frac{1}{\lambda_N^2} \vec{H} \quad (8)$$

where,

$$\lambda_N^{-2} = |\psi_0|^2 \left[ \frac{16\pi e^2}{m^* c^2} + \frac{32\pi e^2 \delta}{c^2} |\phi|^2 \right] \quad (9)$$

In other words,  $\lambda_N$  denotes the new penetration length.

For a very weak field, and by setting  $f = \psi / \psi_0$ , eqn. (5) becomes,

$$\xi_N^2(\tau) \nabla^2 f + (1 + \frac{2\delta}{\alpha} \tau) f - f^3 = 0, \quad (10)$$

where,

$$\xi_N^2(\tau) = -\frac{\hbar^2}{\alpha} \left( \frac{1}{2m^*} + 2\delta |\phi|^2 \right). \quad (11)$$

$\xi_N$  is the new coherence length, which is temperature dependent through  $\alpha$  and  $\delta$ . For a negative coupling strength  $\delta$ , we find from eqns. (9) and (10) that,

$$\xi_N < \xi_{GL} \quad \text{and} \quad \lambda_N > \lambda_{GL}$$

For  $K_N = \lambda_N / \xi_N$ , we have  $K_N > K_{GL}$ , where  $\xi_{GL}$ ,  $\lambda_{GL}$  and  $K_{GL}$  denote the corresponding values of the parameters in the GL theory.

We calculate the total flux density  $\Phi$  as given by,

$$\Phi_N = \int \vec{A} \cdot d\vec{l} \equiv \int \vec{H} \cdot d\vec{S} \quad (12)$$

$$= \left[ n_1 + n_2 \left( \frac{1}{2m^* |\phi|^2 \delta} + 1 \right)^{-1} \right] \Phi_0 \equiv l \Phi_0, \quad (13)$$

where,

$$\Phi_0 = ch/2e \approx 2 \times 10^{-7} \text{ gauss cm}^2$$

is the flux quantum in the GL theory, and  $n_1$ ,  $n_2$ , and  $l$  are integers or zero. This condition fixes the relationship of  $\delta$  and  $|\phi|^2$ . Now,

by using  $\xi_N$ ,  $\lambda_N$  and  $\Phi_0$  as given above, we find that,

$$H_{c_1}^N \approx \frac{1}{2K_N} l n K_N < H_{c_1}^{GL} \quad (14)$$

and

$$H_{c_2}^N = \frac{1}{2\pi \xi_N^2} \Phi_0 > H_{c_2}^{GL}. \quad (15)$$

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In summary, we have developed a phenomenological approach to understand mainly the electro-dynamical properties of the high  $T_c$  oxide superconductors. Due to the structural inhomogeneity it is likely that anti-ferromagnetic fluctuations help to develop superconducting grains randomly in otherwise domains of Mott-Hubbard insulators having localized pairs. By assuming a coupling between these two domains through an internal field we have obtained the following features:

- (i) Large penetration depth,
- (ii) Small superconducting coherence length, implying narrow cores in the vortex structures,
- (iii) High  $H_{c2}$ ,
- (iv) Low  $H_{c1}$ , and
- (v) A small pinning force.

All of these features observed in the recent experiments<sup>9, 10</sup> are reconciled with the predictions of our theory. We further argue that the high  $T_c$  is a consequence of strong correlations in the order parameters, which can be realized from our calculated small coherence lengths (the latter being inversely proportional to the  $T_c$ ). The Meissner state is reduced since the  $H_{c1}$  is lower. In this state all the pairs in the sample go to the extended states by forming a glassy superconductor which we may call an insulator-metal transition of the second kind.

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