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# FLUCTUATIONS OF ORDER PARAMETERS IN THE HIGH $T_c$ SUPERCONDUCTORS *

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ABSTRACT

Recently we have proposed a phenomenological approach in terms of two coexisting macroscopic order parameters corresponding to the superconducting and insulating states and have discussed the electrodynamical responses of the superconducting ceramics. In this paper we discuss the fluctuations of the order parameters both in the static and in the dynamical situations in the mean field approach and obtain results for the electrical conductivity which possesses anomalies as in granular materials.

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Soon after Bednorz and Müller[1] reported the possibility of high temperature superconductivity in the Ba-La-Cu-O materials, several laboratories of the world produced a host of data on various aspects in the ceramic superconductors[2]. Observed anomalies in many physical properties indicate that the nature of superconductivity in the ceramics is, perhaps, unconventional and therefore, it has not been possible to reach a consensus for a microscopic mechanism in the theoretical understanding[3].

Reported transition temperatures are mostly but curiously around 40 °K and 90 °K depending on the materials and their preparations. There seems to be also reports on the superconducting onset temperature at about 240 °K[4] and at the room temperature[5]. However, it is very clear that the zero resistivity has been achieved much above the liquid nitrogen temperature in several ceramics. From the structural analysis it is known that the materials are at least biphasic[6] having a superconducting black phase and a nonsuperconducting green phase. Lately from the neutron diffraction studies it is known[7] that the superconducting phase is oxygen-deficient orthorhombic perovskites containing mixed valent copper ions coordinated with oxygen in the square planar lattice. Generally the plane is electrically conducting with occasional nonconducting islands due to inhomogeniety or structural disorder.

Recently Anderson[8] has proposed a novel mechanism relevant to the ceramic materials, which is known as the 'resonant valence bond' (RVB) theory. A series of papers[9] on the RVB theory have high-lighted the microscopic collective aspects of superconductivity and antiferromagnetism as have been experimentally observed. In this picture the valence electrons are Heitler-London-bonded singlet antiferromagnetic pairs. The virgin lanthanum cuprate is a Mott-Hubbard antiferromagnetic insulator having all localized valence bond pairs. The antiferromagnetic state remains till 220 °K [10]. The presence of the divalent alkalies (either by doping in place of a trivalent lanthanum or in a stoichiometric composition) makes the materials depart from the Hubbard half-full band condition. Now the pairs are mobile as in a fluid having no long range order. The superconductivity appears when these pairs are Bose-condensed at low temperature. The basic mechanism which is likely to play the main role in the insulating-superconducting transition is the short range inter-electronic interaction. On the whole the RVB theory seems to possess the required potential to give very high $T_c$, since the energy scale is no longer due to phonons, but it is rather due to interelectronic exchange interactions. However, a complete test of the RVB theory is yet to be carried out.

Very recently we have developed a phenomenological macroscopic theory[11] based on the experimental fact that the ceramic materials are inhomogeneous and possess structural disorder. Our picture relies on the RVB theory on a macroscopic length scale comparable to the coherence length $\xi_0$. It is a



two component generalized Ginzberg-Landau theory. We have started with the hypothesis that around the transition temperature there are two coexisting domains (overlapping) of pairs characterized by two complex order parameters $\Psi$ and $\Phi$. In the domains of $\Phi$, the electronic states are localized having very short mean free paths. Such states are RVB states with very low mobility. The domains of $\Psi$ contain extended type of pair states having long mean free paths. These two domains coexist and interact through a suitable coupling. The volumes of the domains depend on the morphology of the materials and on the temperature.

On using the Ginzberg-Landau type of analysis[12] we have shown that the ceramic oxides are extreme type II superconductors. These materials possess large penetration depth, short coherence length, high second critical field $H_{c2}$, low first critical field $H_{c1}$ and small pinning force. We have also found that the critical current is smaller compared to other low $T_c$ materials. These features are consistent with the recent experimental findings in ceramic superconductors.

In view of the above-mentioned success of our analysis we felt that it is interesting to consider the fluctuations of the order parameters in the temperature regime above the superconducting $T_c$. The effects of the fluctuations in the Ginzberg-Landau formalism as well as in the microscopic BCS theory have many interesting consequences[13]. For instance, it has been known[14] that small frequency and nonzero wave vector modes of the fluctuations contribute to the conductivity and the susceptibility above the $T_c$. At the superconducting

onset temperature the coherence length is less than 10 Å which is comparable to the inter-particle spacings ($\sim (\text{density})^{-1/3}$). therefore, the superconducting fluctuations are very important. In our present approach we consider the static and the dynamical fluctuations and their responses in a mean field approach. From the nature and the strength of the interaction we argue that the superconducting transition is to an insulating state as has been observed in most of the experiments[15].

We write the free energy of the system in the presence of a magnetic field $\bar{H}$, as composed of functional of the order parameters, $\Psi$ and $\Phi$ (as in ref. 11) :

$$\mathcal{F} = \int d\bar{r} \; \{F[\Psi] + F[\Phi] + F_I[\Psi,\Phi]\}, \quad (1)$$

where

$$F[\Psi] = \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 + \frac{1}{2m^*}\left|(-i\nabla - e^*\bar{A})\Psi\right|^2 + \frac{H^2}{8\pi} \quad (2a)$$

A similar expression is written for $F[\Phi]$.

Here $e^* = 2e$, $m^*$ and $\Gamma^*$ denote the effective masses of the itinerant and localized pair respectively. $\bar{A}$ is the vector potential corresponding to the magnetic field. $\alpha$, $\beta$ and $\tilde{\alpha}$, $\tilde{\beta}$ are the well-known Ginzberg-Landau parameters for the $\Psi$ and $\Phi$ fields respectively. $\gamma$ is the coupling factor between $\Psi$ and $\Phi$ . The last term of (1) is chosen in a simple fashion in a gauge invariant form to take into account the interactions of the localized and itinerant pairs as locally

$$F_I[\Psi,\Phi] = \gamma\left|[-i\nabla - e^*\bar{A}]\Psi\Phi\right|^2 \quad (2b)$$



We remind that the order parameter $\Phi$ vanishes at another transition temperature denoted by $\tilde{T}_c$ for the insulator-metal transition ($\tilde{T}_c > T_c$) .

By varying $\mathcal{F}$ with respect to $\Psi$ and $\Phi$ ,we obtain two generalized coupled Ginzberg-Landau equations and by varying $\mathcal{F}$ with respect to $\bar{A}$, we obtain the current density[11]. Now in order to consider the fluctuation conductivity above $T_c$, we retain the terms only to the order of $|\Psi|^2$ and it is in the absence of the external magnetic field.

We Fourier-transform the quantities with the normalization volume V, as given by

$$\mathcal{F} = \frac{1}{V}\sum_{\bar{k}}\left\{\left[\alpha_1 + \frac{1}{2\mu}k^2\right]\Psi^*_{\bar{k}}\Psi_{\bar{k}} + \left[\tilde{\alpha}_1 + \frac{1}{2\tilde{\mu}}k^2\right]\Phi^*_{\bar{k}}\Phi_{\bar{k}}\right. \quad (3)$$

where

$$\alpha_1 = \alpha + 2\gamma\Gamma$$

$$\frac{1}{2\mu} = \frac{1}{2m^*} + 2\gamma|\Phi|^2$$

$$\tilde{\alpha}_1 = \tilde{\alpha} + 2\gamma\tilde{\Gamma} + \tilde{\beta}|\Phi|^2$$

$$\frac{1}{2\tilde{\mu}} = \frac{1}{2M^*} + 2\gamma|\Psi|^2$$

and $\Gamma$ and $\tilde{\Gamma}$ are defined before.[11]

The current density $\bar{j}_{\bar{k}}$ is given by

$$\bar{j}_{\bar{k}} = \frac{1}{V}\sum_{\bar{k}'}\left[\frac{2e}{\mu_1}\bar{k}'\Psi^*_{\bar{k}'-\bar{k}/2}\Psi_{\bar{k}'+\frac{\bar{k}}{2}} + \frac{2e}{\tilde{\mu}_1}\bar{k}'\Phi^*_{\bar{k}'-\frac{\bar{k}}{2}}\Phi_{\bar{k}'+\bar{k}/2}\right] \quad (4)$$

where $$\frac{1}{\mu_1} = \frac{1}{m^*} + 2\gamma|\phi|^2$$

and $$\frac{1}{\tilde{\mu}_1} = \frac{1}{M^*} + 2\tilde{\gamma}|\psi|^2 .$$

We calculate the average using the free energy given by (3) for the mean square fluctuations of the order parameter, $\Psi$.

$$\langle|\psi_k|^2\rangle = \frac{T}{\mathcal{L}_1 + \frac{k^2}{2\mu}} . \tag{5}$$

It is seen that the condensate density ($\bar{k} = 0$) vanishes at a larger T with smaller slope, since $\mathcal{L}_1$ is larger than $\mathcal{L}$, besides the fluctuations are larger in comparision to those of the one component Ginzberg-Landau theory. We also calculated the current-current correlation $\langle \bar{j}_k , \bar{j}_{-k} \rangle$. Since the latter does not contain enough information on the static electrical conductivity as has been discussed by many authors[13,14], we consider below the frequency-dependent conductivity in our generalized two component Ginzberg-Landau formalism.

The time-dependent equations for the order parameters are written in the simple form as

$$\gamma \frac{\partial}{\partial t} \Psi(\bar{r},t) = -\frac{\delta \mathcal{F}}{\delta \Psi} \tag{6}$$

and

$$\tilde{\gamma} \frac{\partial}{\partial t} \Phi(\bar{r},t) = -\frac{\delta \mathcal{F}}{\delta \Phi} , \tag{7}$$

where $\gamma$ and $\tilde{\gamma}$ are hydrodynamical parameters[13]. On Fourier-transforming with respect to the space and time variables we obtain from (6)



$$(i\omega + \Delta_k)\Psi(k,\omega) = 0 \tag{8}$$

where $$\Delta_k = \frac{1}{\gamma}\left\{\alpha_1 + \frac{1}{2\mu}k^2\right\} ,$$

$$\gamma = \frac{\pi\alpha}{8T_c\varepsilon} \quad \text{and} \quad \varepsilon = \frac{T - T_c}{T_c} .$$

A similar equation will follow from (7), but it will be nonlinear in $\Phi$, since $|\Phi|^4$ term is contained in it. By using the above results we have calculated the fluctuation spectra, $\langle|\psi(\bar{k},\omega)|^2\rangle$, current-current fluctuations $\langle \bar{j}_k(\omega) , \bar{j}_{-k}(-\omega)\rangle$ and response functions as have been done in the one-component case by Schmidt[14].

In our analysis we separate the conductivity above $T_c$ as

$$\sigma = \sigma^f(\Psi) + \sigma(\Phi) . \tag{9}$$

$\sigma^f(\Psi)$ is the contribution to the conductivity due to fluctuations of $\Psi$. For $\omega \to 0$ we calculate $\sigma^f(\Psi)$ within the relaxation time approximation. Above but near $T_c$ in three dimension the conductivity falls as

$$\sigma^f(\Psi) \sim \frac{1}{\sqrt{T - T_c}} . \tag{10}$$

We have not obtained a closed form of $\sigma(\Phi)$, which is the contribution to the conductivity of the insulating domains. But we argue that since the $T_c$ of the materials are reasonably high, we expect this conductivity is of activated type[16].

$$\sigma(\Phi) \sim \exp(-\Delta E/T) . \tag{11}$$

As mentioned above we are now concerned about the temperature regime $T_c < T < \tilde{T}_c$. In our picture the resistivity (which is inverse of the diagonal $\sigma(\vec{k})$) will decrease with temperature. The $\Phi$ component will dominate the fall of resistivity near $T_c$. As soon as $T \to \tilde{T}_c$ the pair (localized) breaking takes place, the material will behave like a normal metal with the rise of resistivity as temperature increases. This prediction of our theory is consistent with the observed resistivity behaviour above the superconducting trasition[15]. This behaviour is reminiscent of the granular nature of the materials. The superconducting and the insulating domains vary as a function of temperature which would influence the conductivity. Recently Lee and Read[17] have argued that the superconductivity in the high $T_c$ oxides are non-BCS type, the pair breaking takes place at $T = T_c$. This analysis explains the resistivity rise in materials which are annealed in the oxygen atmosphere (see for example, Cava et al (18)). Yttrium compounds also exhibit this type of behavior. In these situations the $\tilde{T}_c$ is very close to $T_c$. As a result the fluctuation conductivity and the normal broken pair conductivity add up as considered in our picture. Then the resistivity rises linearly as T (metallic). An important empirical observation has been made recently by Sreedhar et al.[19] regarding the high transition temperature in two kinds of ceramics: La compounds and Y compounds. A quantity $\alpha$ defined as the nominal ratio of $Cu^{3+}$ and $Cu^{2+}$, seems to guide the $T_c$ by exhibiting a broad maximum. In fact it is possible to establish that the quantity



$\mathcal{L}$ is a function of the dopant concentration, x and the oxygen deficiency, y. Even in the stoichiometric compounds[20] and in the virgin $La_2Cu\,O_4$[21] a certain amount of oxygen deficiency only is responsible for high $T_c$ for a particular value of $\mathcal{L}$. A relief map of $\mathcal{L}(x,y,T)$ is desirable for a quantitative prediction of $T_c$. An intermediate value of $\mathcal{L}$ at which $T_c$ is maximum gives an idea about the microscopic inhomogeniety in the materials. For small value of $\mathcal{L}$ the system is insulating and for large value of $\mathcal{L}$ the system becomes metallic. Obviously in the intermediate range a coexistence of two phases are likely to occur. In our theory the effective mass of the pair is larger due to the interaction effects. Recent specific heat measurements[22] seem to support this point of view.

Summarizing we have considered the fluctuations of the order parameters above the transition temperature. The ceramic materials seem to have two transition temperatures. The superconductor-insulator transition takes place first at a lower temperature followed by the insulator-metal transition.

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