

International Journal of Modern Physics B
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DIPOLAR CLUSTERS AND FERROELECTRICITY IN HIGH T_c SUPERCONDUCTORS *

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We show that doping of hole charge carriers induces formation of resonance plaquettes (RP) having electric dipolar moments and fluctuating stripes in cuprates. A single RP is created by many-body interactions between the dopant ion or a charge fluctuation outside and holes inside the CuO plane. In such a process Coulomb interacting holes in the CuO plane are self-organised into 4-particles resonance valence bond plaquettes bound with dopants or polarons located in the spacer layer between CuO planes. Such RPs have ordered and disordered phases. They are ordered into charge-density waves (CDW) or stripes only at certain conditions. The lowest energy of the ordered phase corresponds to a local anti-ferroelectric ordering. The RPs mobility is very low at low temperatures and they are bound into dipole-dipole pairs. Electromagnetic radiation interacts strongly with RPs electric dipoles and when the sample is subjected to it the mobility changes significantly. This leads to a fractal growth of dipolar RP clusters. The existence of electric dipoles and CDW reveal a series of new phenomena such as ferroelectricity, strong light and microwave absorption and the field induced superconductivity.

Keywords: Charge density wave; anti-ferroelectricity; Jahn-Teller effect, pseudogap and high-temperature superconductivity, two-dimensional Luttinger liquid

A guided migration of doped oxygen atoms in $\text{La}_2\text{CuO}_{4+y}$ with nano-scale synchrotron radiation scanning X-ray diffraction in the temperature range $180 \text{ K} < T < 330 \text{ K}$ found in Refs^{1,2} created a huge puzzle on its origin. Randomly distributed Oxygen dopants the LaO plane order into clusters after of illumination. The higher superconducting transition temperature arises with their better order. These fundamental discoveries ^{1,2} pose the questions: **Why the radiation increases the mobility of oxygen ions?, Why they are ordered? and Why**

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the superconductivity arises at higher temperature with this order? The inhomogeneity of cuprate superconductors coupled with dopant atoms is well documented also in other materials and in different experiments like using scanning tunneling microscope^{3,4,5,6}, photoemission spectra (ARPES)⁷ suggesting that the oxygen dopant-induced states are mixed with Cu atoms and measurements of dielectric constant etc.⁸ So, In Sr doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO)^{9,10} a peculiar temperature dependence of the Hall coefficient, R_H , has been observed and analyzed within a two-band model. It was argued that the effective hole density can be written as the sum of two components $n_{\text{eff}}(x, T) = x + n_1 e^{-\Delta(x)/2k_B T}$. **The analysis suggested that at small doping**, $0.01 < x < 0.08$, and below the room temperature each dopant atom creates one hole. At higher temperatures the hole density increases rapidly and for each x that temperature behavior of the density was well fitted with an activation law. The true nature of this two-band behaviour and the activation energy $\Delta(x)$ was left as an open question¹⁰. At low doping the coefficient n_1 fitted to the experimental data is independent of x and larger than 1 hole/Cu. In Ref. [9] the value $n_1 = 2.8$ and in Ref. [10] the value $n_1 \approx 4$ was found. **At higher doping** $0.08 < x < 0.21$ and below the room temperature the hole density increases as a function of doping faster than the number of dopant atoms and, more strangely, for a given x when the temperature increases from 0K to 50K the carrier density decreases. This suggests that the charge density can fluctuate between the two bands. Therefore, LSCO is not behaving as a simple, single-band, but rather a two-band correlated non-Fermi liquid^{11,12}.

Debate between two competing orders in the pseudogap region focuses mainly in the interpretation of ARPES measurements on the nature of gap functions and Fermi arcs.^{13,14,15,16,17} Very recent experiments found evidences of sharp phase transitions at temperatures between the superconducting critical temperature T_c and the pseudogap temperature at T^* .^{18,19} At zero temperature inside the superconducting dome there are two phase transitions²⁰. Also the temperature dependence of resistivity changes from quadratic to linear behavior inside the pseudogap region with increasing doping and temperature.^{21,22}

Using the microscopic approach²³ we show that here bound states appear because dopant atoms e. g. Sr^{2+} are replacing the La^{3+} , and therewith inducing extra negative charges into spacer layers. At low doping these negative charges are able to bind holes. The key ingredient in binding holes into dopant atom is the near degeneracy of the d-state bands with $x^2 - y^2$ and z^2 symmetry in the CuO plane. The Jahn-Teller distortions in cuprates, such as La_2CuO_4 , elongate the oxygen octahedron surrounding the central Cu ion and split the degeneracy of the associated e_g orbitals of the Cu d^9 -state. This happens in the highest partially occupied $x^2 - y^2$ -orbital, which together with the doubly occupied O p_x, p_y -orbitals form a strong covalent bonding. Their straight hybridization gives rise to the bonding, non-bonding and half-filled anti-bonding bands and predicts a good metal, in sharp contrast with experiments finding a large charge gap. The failure of the band theory indicates a strong Coulomb interaction (e.g. on site Hubbard U), which may exceed well the

bandwidth of the tight-binding, anti-bonding band.

The Hubbard U is much larger than the energy separation between the Cu $x^2 - y^2$ and O p -orbitals-the charge transfer gap $\Delta_{CT} \sim 1 - 2 \text{ eV}$, which is much larger than the hybridisation integral, $t_{dp} \sim 0.350 \text{ meV}$ ^{24,25,26}. Therefore single electrons are localized on Cu sites on the Cu $x^2 - y^2$ orbitals forming the Cu²⁺ states. Their spins are anti-ferromagnetically aligned (via the super-exchange interaction that involves virtual hopping to the neighbouring O p - orbitals) to create the anti-ferromagnetic Mott insulator²⁷. The formal valence state Cu³⁺, which should arise with doping would already have large negative $\Delta_{CT} < 0$ and therefore should be rather represented by Zhang-Rice singlet, i.e. as Cu³⁺ \rightarrow Cu²⁺ L , (see, the Ref.²⁸ for a detail). There the doped holes would go not so much to the d-shells but rather to the oxygens, creating oxygen holes (though the quantum numbers of the respective states would be the same as those of Cu³⁺). In these Zhang-Rice singlets the hole is distributed between the Cu³⁺ and four neighbouring oxygens. Cuprates, like La₂CuO₄, are layered ionic crystals. The (CuO₂)²⁻ layer is negatively charged and two spacer layers (La₂O₂)²⁺ are positively charged. Oxygen atoms form an octahedral cell around Cu²⁺ and the apex oxygen atoms containing two extra electrons filling the p-shell are in the LaO- layer. In the parent anti-ferromagnetic insulator compound the degeneracy of cubic e_g states is removed by the Jahn-Teller effect, which elongates the oxygens octahedron. Copper, on the other hand, is a transition metal and it can easily give out one electron and transfer into Cu³⁺ \rightarrow Cu²⁺ L sharing the electron with octahedron oxygens and forming Zhang-Rice singlet.

Dopant atoms settle in the LaO spacer layer substituting La atoms like in the case of Sr doping or intercalated like oxygen atoms. Oxygen atoms are small in size and thus mobile. They easily fill their p-shell with two electrons and become ionized. When this happens the negative impurity charge pushes the negatively charged apex oxygen down to CuO plane. This restores the e_g symmetry and helps to remove one electron from neighbouring Cu-ions to form Zhang-Rice singlet (the anti-Jahn-Teller effect).^a At large enough doping holes created ("Zhang-Rice singlet") band in the CuO plane. Many complexes containing specific transition-metal central ions with special valency show this effect.²⁹ Every new hole appearing during hole-doping in the parent compound leads to strong frustration of the original antiferromagnetic state. This leads to rapid suppression of antiferromagnetism in La_{2-x}Sr_xCuO₄ even by small hole concentration. Four holes bound by dopant atoms due to correlations³⁰ form a resonance plaquette(RP). It is similar to the resonance valence bonds described by Anderson²⁷. These RPs together with dopant atoms or polarons induce electrical dipolar moments.

The interaction between dipolar RPs is short-ranged and varies as a function of separation distance with the $1/r^3$ tail. Because of their low mobility, CDW nucleation or RPs condensation starts at different parts of the sample and with dop-

^aNote that with this anti-Jahn-Teller effect associated with the squeezing of the oxygen octahedra, the hole state has a two fold degeneracy that is in addition of the conventional Kramers degeneracy.

ing lead to patches of different directional order with a fractal structure. There are strings or stripes like those which arise due to electron-phonon interaction^{31,32,33}. Any isolated charge associated with an impurity or a charge fluctuation in LaO spacer is inducing the anti-Jahn-Teller shift of the apex O ion^{23,30} and therewith creates RP in CuO plane. To describe these RPs we developed the many-body variational theory where four holes are trapped by the impurity,^{23,34,35,36} and derived a proper energetic description of RP states which reproduce experimental pseudogap results^{9,10}. Here we assume that the hole band is two-fold degenerate. The RPs behave as quasi-classical objects moving along in a nearly flat band and form a two-dimensional Luttinger liquid described in the Ref.³⁷ or orbital Non-Fermi liquid¹² or glass³⁸. The RP fluctuations play a huge role in the scattering of the remaining mobile holes and are a source of Planckian dissipations, which has the shortest possible relaxation time named as the Planck time³⁹.

An irradiation create excitons of intermediate radius around RP. Such an exciton may create a pair of lattice defects⁴⁰ such as the negatively charged oxygen interstitials, i-O, and the positively charged vacancy, V+. Such excitonic mechanism of the defect production has been observed experimentally^{41,42}. When the vacancy, V+ will approach to another i-O, they annihilate. The creation of such virtual pairs increases significantly the mobility of the i-O's and stripy local lattice distortions, noted as Q3 are created^{43,44}. The probability to such excitons with X-ray illumination very fast vanishes with the doping. This explains why the Q3 clusters are arising only in the very underdoped cuprates.

The density of dipole moments associated with RPs increases with doping and vanishes at the pseudogap temperature. The binding energy of holes into these dipolar clusters defines the pseudogap, which we identify also as the activation energy of the two fluid model used by Gorkov and Teitelbaum.^{9,10,45} Dipole moments have a strong interaction with electromagnetic radiation and subjected to such radiation dipoles become mobile. Due to the dipole-dipole attraction existing for some dipole orientations and repulsion for other orientations they may form clusters. This finding explains the recent observation of the self-organization of mobile oxygen dopant ions in LCO by Bianconi et al.^{1,2}. Under irradiation oxygen ions resting in the LaO layer as well as dipoles get excited and are forced to move towards the energetically most favourable positions. **Ferroelectricity in $\text{La}_2\text{CuO}_{4+y}$** was reported at exceptionally low oxygen doping.⁴⁶ To explain this the magneto-electric coupling was used⁴⁷. The ferroelectricity may arise due to electric dipoles. We think that **the dipole formation is the source of the ferroelectricity** seen in recent experiments⁴⁶ and of the peculiar behaviour of the dielectric constant⁸. The RPs described may also play a very important role in the mechanism of high temperature superconductivity. Their presence in the vicinity of the hole band edge may lead to shape resonances as described recently by Bianconi⁴⁸, that can be an origin of the Cooper pairing in cuprates. Our results suggest that pseudogap formation and high temperature superconductivity are interaction driven and therefore these materials belong to a new class of holographic superconductors⁴⁹.

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