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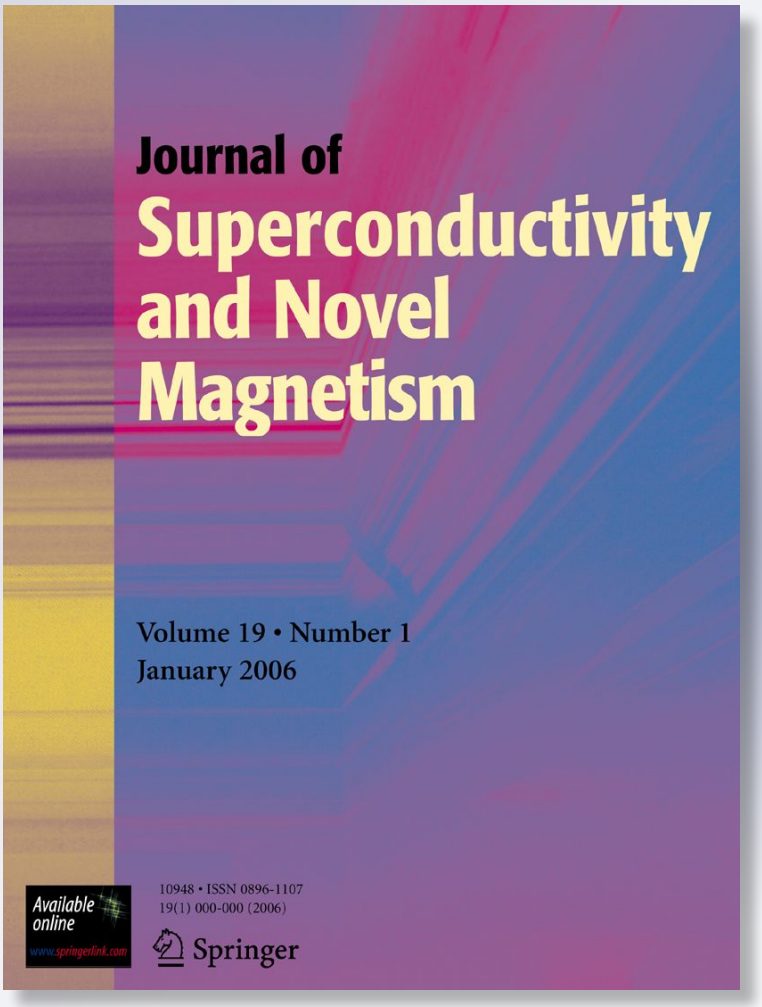

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ORIGINAL PAPER

Striped Organization of Hole Excitations and Oxygen Interstitials in Cuprates as a Route to Room-Temperature Superconductivity

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Abstract There is increasing evidence that the adequate approach to the puzzle of high-temperature superconductivity in cuprates has to bear in mind the local lowering of crystal symmetry. According to the author's model, the bound states of dopant ions and hole orbitals in lightly doped cuprates can be treated as pseudoatoms. Their alignment leads to formation of extended quantum protectorates—bosonic stripes (BS) characterized by a set of discrete widths. The simulations of electronic properties performed for $La_2CuO_{4+\delta}$, $YBa_2Cu_3O_{6+\delta}$, and $HgBa_2Ca_2Cu_3O_{8+\delta}$ in the framework of this scenario are consistent with experimental data. It is argued that the concept of BS hierarchy may help not only to clarify the heart of unconventional physics of cuprates but also to answer the crucial questions about perspectives to raise the superconducting critical temperature above 300 K.

Keywords Superconducting cuprates · Charge segregation · Hole-rich stripes · Collectivized orbitals · Pairing

1 Introduction

After 25 years of unprecedented efforts to understand the mysterious physics of superconducting cuprates, a fairly large number of fundamental questions still remain disputable. An important part of them relate to the underlying interactions that can be responsible for nanoscale segregation. The inherent propensity of copper based oxides to the spatially inhomogeneous distribution of charge carriers [1–6] is found to be more pronounced below the so-called optimal doping $\bar{n}_{po} = 0.16$ that maximizes the change of superconducting critical temperature T_c versus $\bar{n}_p$. In the class of cuprates with hole conduction considered here, $\bar{n}_p$ denotes the mean hole density in the overlapping $2p$-shells normalized to one cell of oxygen sublattice of CuO_2 layers.

As follows from experimental findings, the holes in CuO_2 layers tend to be arranged into quasi-one-dimensional ensembles—*stripes* [7–18]. Under similar confinement of charge degrees of freedom (interpreted within the framework of string formalism as convolution of one axis belonging to the coordinate sector of phase space), one can expect a lowering of kinetic energy due to formation of hole local pairs [19] with their subsequent dynamical ordering within the hole-rich stripes. The most heatproof of them are believed to be persisting up to the upper threshold $T^*(\bar{n}_p)$ of pseudogap fadeaway [9] in the generic T–$\bar{n}_p$ diagram.

Another array of key questions deal with the problem devoted to revealing the microscopic origin of pseudogap regime (PGR) that extends over $T^*(\bar{n}_p) \sim 10^3$ K at low values of $\bar{n}_p < 1/36$. Along with direct observations of a partial suppression of spectral weight in electronic spectra at low binding energies $E_B < 0.15$ eV, the pseudogap fingerprints were found to display in temperature dependences of transport and magnetic properties an onset of departure from their high temperature behavior [20–22]. The emergence of PGR signatures well above $T_c(\bar{n}_p)$ border clearly indicates a radical difference between pairing mechanisms in the cuprates and in conventional superconductors with strongly overlapping Cooper pairs [23, 24]. Despite huge progress in experimental techniques, the genesis of pseudogap remains a subject of long-standing debates: whether the PGR is an extraordinary state with hidden short-range

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order that competes with superconducting correlations or a precursor to percolation superconductivity arising within the domelike segment limited by the $T_c(\bar{n}_p)$ border. Against this questionable background, there is increasing argumentation in support to the idea of preformed hole pairs which can emerge well above the $T_c(\bar{n}_p)$ limit [25–27].

2 Formation of Bosonic Stripes in PGR

In light of the string model [28–31], the formation of hole pairs in one of the most explored $YBa_2Cu_3O_{6+\delta}$ compound can be imagined as follows. When the index δ does not exceed 0.1, the vast majority of hole excitations have been localized. At this stage, the hole kinetics and their binding energy $E'_{B\eta}$ are mainly determined by the rank η of given quantized hole orbitals (rhombons) [30], generated by dopant ions within oxygen sublattice of CuO_2 layers. The bound states of oxygen interstitials with the nearest single or paired holes (composite bosons) from adjacent oxygen $2p$-shells of CuO_2 layers can be treated as pseudoatoms which tend to be aligned into chains when δ is raised above 0.1. The strong overlapping of the rhombons during this process accompanied by local breaking of $C4$ symmetry results in an appearance of collectivized zigzag orbitals along the chains.

According to [28–31], the dynamical ordering the hole pairs on such orbitals is associated with pseudogap opening. In this case, the coherent state of these paired holes can be described in terms of quasi-one-dimensional quantum protectorates—nanosized bosonic stripes (BS). The hierarchy of BS is determined by their discrete width $w_\eta = \eta a$, where η is the rank of primary rhombons and a is the averaged distance between neighboring cations in CuO_2 layers. At $\delta \approx 0.5$, the contingent of BS has to be characterized by a rather wide distribution in w_η.

Since the thermal stability of BS is reduced with increasing their rank at $\delta > 0.2$, one can expect the formation of frustrated network consisting of superconducting nanochannels with different local critical temperatures $T^*_{c\eta}(\delta) = C^*_\eta D^*_\eta \hbar\bar{\omega}_0/[2k_B(2\eta^2+\eta)]$ [30]. Here, the parameter C^*_η takes into account the compatibility of given BS with the potential extra-relief created by dopant ions [28, 30], while the dome-shaped dependence D^*_η can be approximated by the formula $D^*_\eta = 1 - (1 - \delta/\delta_\eta)^2$, k_B is the Boltzmann constant. The averaged eigenvalue of zero modes $\hbar\bar{\omega}_0 \approx E^*_{B\sigma} = \hbar\bar{\omega}_0 = \hbar^2/2m_e\check{r}_0^2 \approx 2.06$ eV for extended coherent states (strings) along O–O bonds is defined in the first approximation by the mean interval $\check{r}_0 \approx 0.27$ nm between O nuclei in CuO_2 layers; m_e is the electron rest mass. It is worth noting that the apical values $T^*_{c\eta}(\delta) \approx$ 1200, 570, 330, 220, and 155 K ($C^*_\eta = D^*_\eta = 1$) in the five-level diagram [29] limiting the persistence threshold of BS with the rank η from 2 to 6 were obtained without application of adjustable parameters. The proliferation of sixth-rank BS at $\delta = 0.96$ gives rise to percolation superconductivity with $T^*_{c\eta}(\delta) = 92$ K ($C^*_\eta = 0.6$). The highest value $T^*_{c\eta}(\delta) \approx 1200$ K for PGR in the generic T–$\bar{n}_p$ diagram for $YBa_2Cu_3O_{6+\delta}$ is achieved at $\delta_\eta \approx 0.22$ provided that the space between the second-rank BS is filled with fermion-like rhombons [31]. The predictive ability of the string model was verified experimentally at temperatures up to 1300 K [28, 29].

3 Peculiarities of BS in Oxygen-Doped Cuprates

As was argued in [31], the formation of BS and their fermionic surroundings can be identified with the peak and hump in cuprate electronic spectra [32–34]. The bosonic states are located at the binding energies $E''_{B\eta} = \hbar\bar{\omega}_0/8\eta$, while the fermionic hole excitations are distributed around $E'_{B\eta} = 4E''_{B\eta}$ [35]. The value of $E''_{B\eta}$ defines the modulus of complex gap $|\Delta_{s\eta}|$ for the hole superconducting order in BS with given rank η. The simulated spectral characteristics of $YBa_2Cu_3O_{6+\delta}$ including the superconducting gap anisotropy at $\delta \approx 1$ are turned out in good agreement with measured values [35–37].

Taking into account that the concept of pseudoatoms can be applied to other superconducting cuprates (first of all to oxygen-doped), it is of interest to make an attempt to clarify the question about significant difference in superconducting parameters displayed, for example, by optimally doped compounds: $La_2CuO_{4+\delta}$, $YBa_2Cu_3O_{6+\delta}$, and $HgBa_2Ca_2Cu_3O_{8+\delta}$.

As follows from an analysis, the most favorable conditions for stabilization of the sixth-rank BS can be realized in $HgBa_2Ca_2Cu_3O_{8+\delta}$ due to alignment of dopants in HgO_δ layers at $\delta = 1/6$. Under applying the fairly high hydrostatic pressure one can expect the increasing probability of mutual organization of hole excitations and oxygen interstitials into striped structure composed mainly of BS with $w_\eta = 6a$. A fragment of the CuO_2 layer illustrating the similar striped structurization of hole pairs is sketched in Fig. 1. Here, the solid and open circles denote Cu and O ions, respectively, while the half-filled circles mark the axial projections of interstitials in O5 sites [38] from the adjacent HgO_δ layer with $\delta = 1/6$. The most likely trajectories of hopping holes in CuO_2 layer are depicted by arrows. If a $HgBa_2Ca_2Cu_3O_{8+\delta}$ sample contains a sufficiently large concentration of such fragments, the onset of percolation superconductivity may achieve the theoretically possible maximum $T^*_{c\eta}(\delta) = 155$ K limited by the thermal stability of sixth-rank BS. Indeed, the record high temperature $T_{co} \approx 153$ K corresponding the onset of superconducting transition was reported for Hg-1223 samples under $P = 150$ kbar [39].

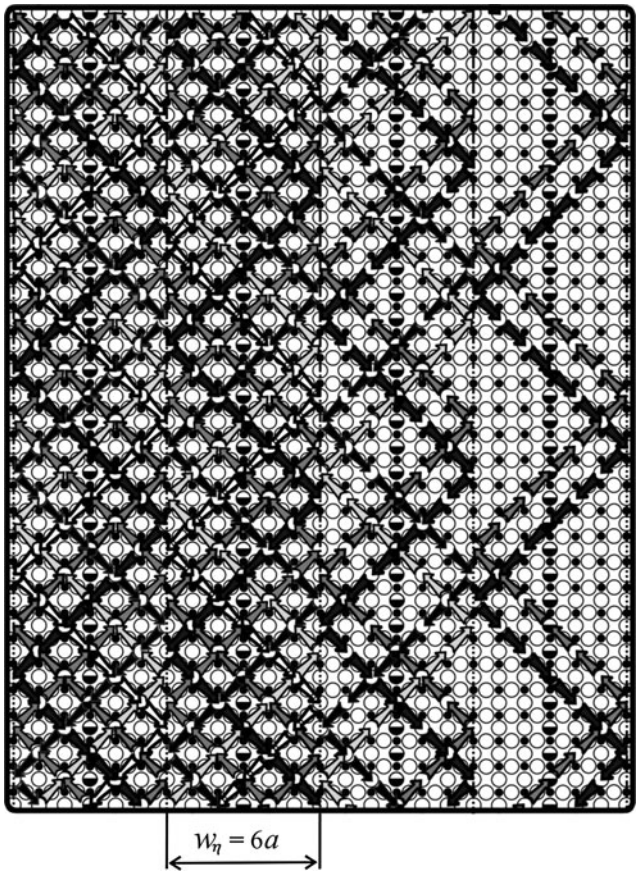

Fig. 1 The most probable trajectories (depicted by *arrows*) of hopping hole pairs in a CuO_2 fragment of $HgBa_2Ca_2Cu_3O_{8+\delta}$. The right half–plane contains only a part of these trajectories. The mutual organization of hole excitations and oxygen dopants in the adjacent HgO_δ spacer with $\delta = 1/6$ results in formation of sixth-rank BS ($w_\eta = \eta a = 6a$) characterized by thermal stability $T^*_{c\eta}(\delta) = 155$ K. The positions of O and Cu ions in the CuO_2 layer are denoted by *open* and *solid circles*, respectively. The axial projections of oxygen interstitials from the nearest HgO_δ layer are marked by *half-filled circles*

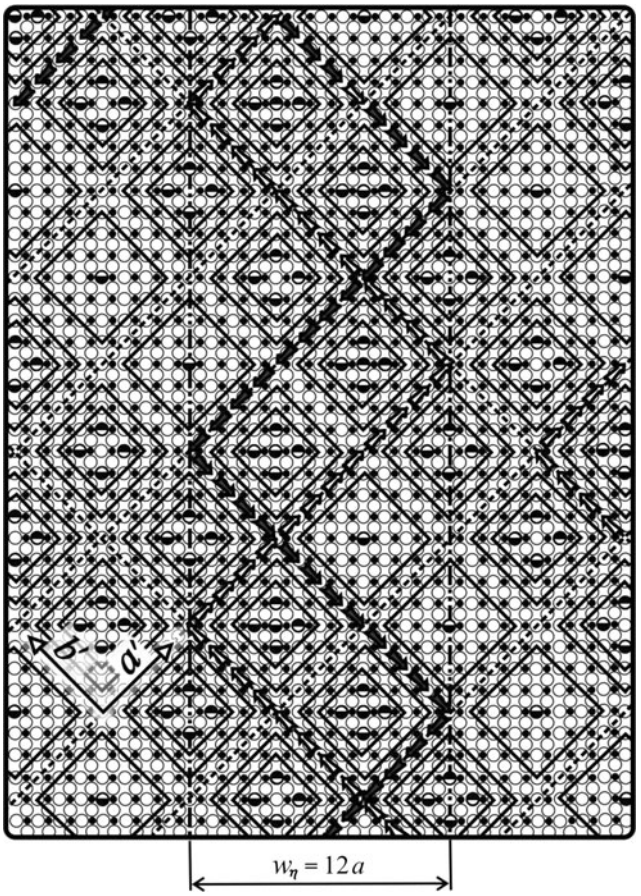

Fig. 2 Sketch of simulated hole trajectories and appropriate distribution of oxygen interstitials in a fragment of $La_2CuO_{4+\delta}$ with $\delta \approx 1/8$. The localized hole orbitals in the CuO_2 layer are denoted by *solid lines* (*rhombs*), while the zigzagging trajectories belonging to twelfth-rank BS with $T^*_{c\eta}(\delta) = 40$ K are depicted by *arrows*. Projections of oxygen interstitials from the adjacent $La_2O_{2+\delta}$ layers placed above and below the given fragment of CuO_2 are marked by symbols ◓ and ◒, respectively. The *dashed lines* denote the $12a' \times 4b'$ superstructural cells

Much more complicated pattern in distribution of oxygen dopants takes place in $La_2CuO_{4+\delta}$ compounds with $\delta \approx 1/8$. In this case, the percolation superconductivity with the theoretically highest temperature has to be realized due to availability of CuO_2 fragments containing twelfth-rank BS with $T^*_{c\eta}(\delta) = 40$ K. Just at that temperature, the significant fraction of $La_2CuO_{4+\delta}$ single-crystal samples with optimal δ from 0.1 to 0.12 demonstrates a transition into superconducting state [40].

The trajectories of hole pairs involved into twelfth-rank BS with $w_\eta = 12a$ belonging to one of the modeled fragment of CuO_2 layer (potentially suitable for superconductivity) are shown by arrows in Fig. 2.

In this sketch, the symbols ◓ and ◒ mark the projections of oxygen interstitials from the adjacent $La_2O_{2+\delta}$ spacer layers placed above and below the given fragment of CuO_2. The distribution of these dopants is associated with the emergence of the dominant $12a' \times 4b'$ superstructural cell (dashed lines in Fig. 2). Here the parameters a' and b' of the fundamental cell are given in orthorhombic notation corresponding *Fmmm* space group with axes directed along O–O bonds. Note, that the presence of $12a' \times 4b'$ supercell is in agreement with the main satellite peaks for the superconducting Q2 phase characterized by $T_c = 40$ K [40]. After quenching the sample from $T = 370$ K, this phase disappears, but it can be artificially patterned (e.g., as filaments in desired circuits) by means of X-ray or electron beams [41].

4 Prospects for Increasing T_c above 300 K

Besides numerous experimental data interpreted by their authors as indications of filamentary superconductivity at $T \approx 155$ and 220 K [42, 43], there are intriguing observations of anomalies in cuprate electronic properties at 330 and 570 K [21, 44] corresponding to the thermostability

$T^*_{c\eta}(\delta)$ of BS with the ranks $\eta \leq 4$. For example, the examination of the in-plane resistivity $\rho_{\parallel}(T)$ of underdoped $YBa_2Cu_3O_{6+\delta}$ crystals revealed that their temperature dependences of $\rho_{\parallel}(T)$ demonstrate an S-shape bend under heating the samples $\delta = 0.3$–0.4 above 330 K [21]. In addition, the sample with $\delta = 0.3$ displays a maximum in the thermopower $S(T)$ near the same temperature. As δ is increased, the maximum in $S(T)$ first moves to 220 K, and then jumps to ≈150 K [21].

It is also of interest to pay attention to the mysterious properties of monoxide $CuO_{1-\delta}$ whose magnetic susceptibility $\chi(T)$ demonstrates a broad maximum at $T \approx 600$ K in addition to the "sagging" of $\chi(T)$ below 220 K [45]. The broad maxima at $T \approx 220$ and 330 have been also registered in its thermopower $S(T)$ [46]. It has been argued that both the "sagging" of $\chi(T)$ below 220 K and the electrical instabilities with sharp resistivity drops (more than 11 orders of magnitude) at the same temperature [47] can be attributed to the formation of percolation network consisting of superconducting filaments. It is reasonable to note that this simple cupric oxide is often considered as a progenitor of superconducting cuprates bearing in mind that the monoxide CuO is characterized by a propensity to the formation of quasi one-dimensional (zigzagged) charge stripes [48].

The inference about a superconducting origin of observed anomalies in $CuO_{1-\delta}$ was supported in the study of CuO single crystals with copper films deposited on their natural faces. From measurements of the I–V characteristics in the accessible temperature range ($T \leq 550$ K), it was established that the linear extrapolation of the critical current $I_c(T)$ to the temperature axis yields the maximum $T_{ci} \approx 1200$ K [49].

5 Conclusion

In summary, the string model first developed to simulate the doping-depended evolution in electronic properties of $YBa_2Cu_3O_{6+\delta}$ is demonstrated to be extendable for $HgBa_2Ca_2Cu_3O_{8+\delta}$ and $La_2CuO_{4+\delta}$. The performed simulations of their superconducting parameters are in good agreement with experimental data. This agreement yields a rather convincing reason to think that the key role in unconventional physics of cuprates has to be assigned to the processes of hole ordering into bosonic stripes, the most narrow of which may survive up to 1200 K. From this point of view, the extraordinary properties of underdoped cuprates in the pseudogap regime have to be caused by formation of frustrated network consisting of superconducting nanochannels composed of BS with an extremely wide distribution of local critical temperatures up to $T^*_{c\eta} \approx 1200$ K. There are solid grounds to hope that the proposed consideration may help in purposeful searching of a route to construct materials that would be able to superconduct above room temperature. In the early stages, this purpose could require applying the nanotechnology facilities.

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