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ORIGINAL PAPER

Shape Resonances in Superconducting Gaps and Complexity in Superstripes

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Abstract The emerging scenario of superstripes for high temperature superconductors is presented. The complexity of the electronic structure of doped cuprates results from two electronic components and nanoscale phase separation. In this lattice, charge and magnetic complexity the unconventional high temperature superconductivity emerges in a broken symmetry. Shape resonances in superconducting gaps are discussed.

Keywords Shape resonances · Fano resonance · Superstripes · Lattice complexity · Layered superconducting materials

1 Introduction

There is growing consensus that disorder is emerging as an intrinsic essential feature to design a high-temperature superconductors (HTS) after 25 years of experimental research since the 1986 discovery. Nearly all HTS perovskite families were discovered in the first six years of material science research for new perovskite superconductors. In 1993 it was noticed that all known HTS share the same material lattice architecture: a superlattice of metallic atomic layers intercalated by spacer layers [1, 2] as shown in Fig. 1. The critical temperature (T_c) was raised from 35 K in doped La_2CuO_{4+y} to the maximum critical temperature known so far, 139 K in $Hg_{0.2}Tl_{0.8}Ba_2Ca_2Cu_3O_{12+y}$, by changing the oxide spacer layers (12 in Fig. 1) intercalated between the superconducting atomic CuO_2 layers (11 in Fig. 1). These results have shown the key role of the oxide spacer layers (12) for the control of the critical temperature. The intrinsic disorder is due to the dopants inserted in the spacer layers and lattice distortions of the CuO_2 plane due to the lattice misfit inducing one-dimensional striped pattern.

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2 The Holes in the CuO_2 Plane

The spacer layers' host dopants (oxygen interstitials or atomic substitutions) that control the density of holes in the oxygen $2p_{x,y}$ orbital in the CuO_2 plane are called ligand holes $\underline{L}$. A new set of states $3d^9\underline{L}$ [3, 4] forms an impurity band in the Mott-like charge transfer gap between the $3d^9$ and $3d^{10}\underline{L}$ in many-body states of undoped CuO_2. These states at the Fermi level form a metallic phase above the critical density at the insulator-to-metal transition. Evidence on the local electronic structure in doped perovskites has been obtained by the application of X-ray Absorption Spectroscopy (XAS) developed with the use of synchrotron radiation sources, that has provided unique information on the local electronic configurations and the local spatial structure extracted from strong peaks in the X-ray Absorption Near Edge Structure (XANES) and the weak features in the Extended X-ray Absorption Fine Structure (EXAFS).

The XANES features are due to final excited states in the continuum where the photoelectron wavelength is of the order of interatomic distance and its lifetime is very short so that its mean free path is less than a nanometer. This powerful tool probes the unoccupied local electronic states [5] and the coordination geometry [6] of transition metal ions in solutions molecules [7, 8], surface layers [9–11] and disordered layered materials [12].

The investigation of cuprate perovskites using Cu L_3 XANES has provided evidence for the structure and symmetry of the unoccupied hole states in $YBa_2Cu_3O_{7-y}$ by

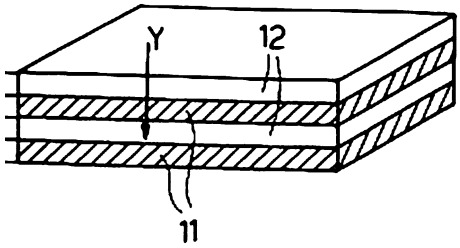

Fig. 1 The generic heterostructure at atomic limit showing high temperature superconductivity. The figure shows the superlattice of superconducting atomic layers (11) intercalated by the spacer layers (12) (from Ref. [1])

varying y. An extra spectral density appears in doped superconducting perovskites in the $2p-\varepsilon d$ transitions in the range between 932 and 935.5 eV which appears only above the insulator–metal transition at $y = 0.3$. This new peak is due to transitions from the initial states induced by doping $3d^9\underline{L}$ to the $\underline{2p}3d^{10}\underline{L}$ final state, where $\underline{L}$ denotes the hole in the ligand orbital.

The first evidence of multi-band superconductivity in cuprates has been found by XANES in $YBa_2Cu_3O_{7-y}$ for $y > 0.66$ where the planar Cu $3d^9\underline{L}$ states in the CuO_2 plane coexist with the vertical Cu $3d^9\underline{L}$ states in the CuO_2 chains [13, 14]. These experiments have provided not only evidence for multi-band superconductivity but also for the spatial segregation of two sets of electronic states in two different portions in La_2CuO_4 [15] and Bi2212 [16, 17], and the coexistence of distorted and undistorted domains [18]. The distorted domains have been associated with the electronic structure characterized by partial gaps in selected points of the k-space $(0, \pi)(\pi, 0)$ at the origin of the so-called pseudogap matter. Therefore the pseudogap has been associated with the spatial organization of a second electronic component near the localization limit: polarons or bipolarons [18–20]. Similar results have been found in other unconventional superconductors like $BaPb_{1-x}Bi_xO_{3-\delta}$ [21].

The coexistence of small polarons and free carriers in cuprates has been confirmed by Müller et al. [22] in $La_{2-x}Sr_xCuO_4$ derived from susceptibility measurements.

Mitsen and Ivanenko have proposed a model where a pair of $3d^9\underline{L}$ states is located in two adjacent cations forming a two-atom negative-U center. Owing to virtual transitions of electron pairs to these NUCs, states $(\overline{k}\uparrow, -\overline{k}\downarrow)$ in the vicinity of the FS are pairwise coupled, which leads to superconducting pairing in the system [23–25]. In fact, the localized charges are a source for local closing of cation–anion gap favoring the realization of an unusual electron–electron interaction paring mechanism. This model, based on the coexistence of localized pairs and free carriers, has been recently extended by Ivanenko and Mitsen to discussion of the superconductive pairing mechanism in pnictides [26].

The self-organization of localized states giving charge density waves and spin density waves has been object of active discussion for many years. The proximity to a metal–insulator transition has been proposed to explain some of the properties of high-temperature superconductivity in layered perovskite structures by Kopaev and Rusinov [27]. In these quasi two-dimensional compounds there is coexistence of the Fermi contour situated in extended flat-band of electron dispersion and spatial stripe hole self-organization that partly promote antiferromagnetic ordering. The relative motion of a pair with large momentum may result in a rise of both quasi-stationary states, which explains a pseudogap in the quasi-particle spectrum and a condensate of pairs corresponding to the superconducting state. In this landscape it has been proposed that the repulsion-induced hyperbolic pairing allows one to explain some fundamental features of high-T_c cuprates [28, 29]. A phase where d-wave superconductivity coexists with charge-density waves (CDWs) implies different symmetries of the order parameters. The CDW influence on superconducting energy gap $\Delta(T)$ is such that it deviates substantially from the canonical $dx^2 - y^2$ form and implies deviations from the standard ratio $2\Delta/T_c$ [30].

3 Controlling the Critical Temperature via Shape Resonances

The material-dependent variables controlling the electronic structure of transition metal oxides by lattice strain are now of high interest for quantum materials by design. The control of self-organization of atomic defects under compressive strain, or of atomic interstitials under tensile strain is the core of active research for new functional materials by design. The tolerance factor in three-dimensional manganite perovskites is well established [31]. In multilayered cuprates made of CuO_2 layers intercalated by spacer layers the material-dependent variable is the misfit strain between different layers and deformation of the CuO_2 lattice due to misfit strain measured by XANES and EXAFS [32–34]. The misfit strain induced self-organization of the localized electronic states has been identified by the formation of striped lattice domains as shown in Fig. 2. The lattice of localized states pattern has been associated with a type of generalized polaronic Wigner crystal [35–37] that coexists with free particles [38]. The experimental evidence that the self-organization of lattice distortions and dopants produces subbands due to quantum size effect and that the chemical potential is tuned near the Lifshitz critical point for a vanishing Fermi surface has been the driving force for the 1993 proposal of the mechanism to amplify the superconducting critical temperature via the shape resonance in the superconducting gaps [39, 40]. The clear experimental realization of

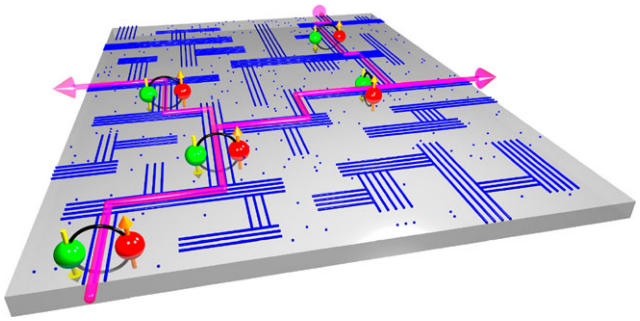

Fig. 2 The pattern of striped patches in the superconducting CuO_2 planes (layers 11 in Fig. 1) due to self-organization of oxygen interstitials in the spacer layers and of striped lattice deformation due to the misfit strain

the T_c amplification tuning the chemical potential near the Lifshitz point for a vanishing Fermi surface has been provided first by magnesium diborides [41, 42] and later by iron-based superconductors [43–45].

The process of gap amplification via shape resonance is related with the quantum theory of configuration interactions between closed and open channels known also as Fano resonances or Feshbach resonances [46]. The effect was discovered to explain the lineshape of absorption spectra above the ionization limit in atomic spectra due to two electron excitations. The first case investigated by Ugo Fano in 1935 was the two-electron photoexcitation in helium $He(1s^2) + h\nu \rightarrow He(1s^0 2s^1 np^1)$ where the mixing between quasi-bound stationary state with continuum states $He(1s^0 2s^1 np^1) \leftrightarrow He(1s^1) + \varepsilon p$, where εp is a free photoelectron, occurs [46]. Fano obtained the formula for the spectral lineshape of the scattering cross section:

$$F(\varepsilon) = a\frac{(q+\varepsilon)^2}{\varepsilon^2+1} + b$$

Using a phenomenological parameter q and a reduced energy ε defined by $2(E - E_0)/\Gamma$, where E_0 is the resonant energy and Γ is the width of the autoionized state, this equation predicts a maximum and a minimum in the Fano lineshape as shown in Fig. 3. The Fano formula is a superposition of the Lorentzian lineshape of the discrete level $\frac{q^2-1}{\varepsilon^2+1}$ with a flat continuous background and a mixing term $q\frac{2\varepsilon}{\varepsilon^2+1}$. This theory describes well the experimental atomic photoabsorption cross section for the excitations of two electrons above the continuum threshold and was later used to explain the experimental cross section for the capture of a free neutron into the nucleus around the energy of the nuclear shape resonance. The deviation of the cross section from the Lorentzian is measured by the Fano lineshape parameter q that can be easily extracted form experimental data. For a very large value of q the lineshape approaches a Lorentzian because of the lack of quantum interference between the states in the continuum and the quasi-bound

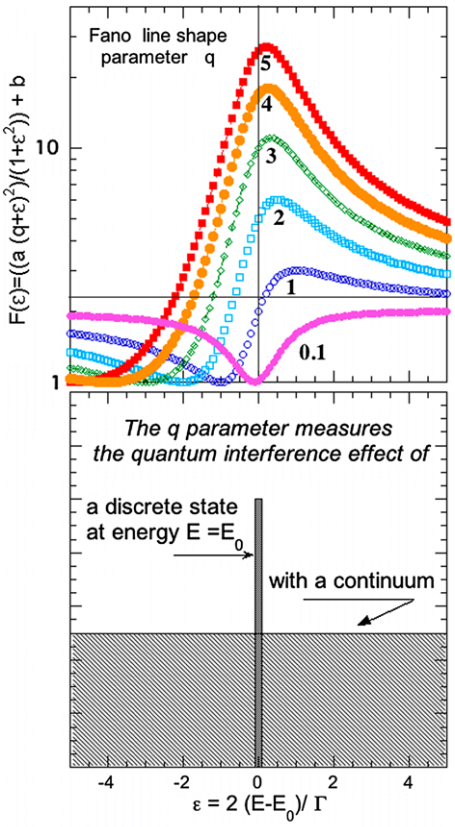

Fig. 3 The evolution of the Fano lineshape for the shape resonance as a function of the strength of the interference term proportional to $1/q$, where q is the parameter of the Fano formula

states. By decreasing the value of q a minimum develops at energies lower than the energy of the quasi-bound state at E_0 and the maximum moves well above the quasi-bound state. In the extreme case of strong interference, proportional to $1/q$, the minimum of the cross section moves close to the quasi-bound state energy E_0 and becomes very large while the maximum moves far away from E_0 and its intensity vanishes. The result is that for very high interference the shape resonance gives essentially an anti-resonance driven by the negative interference effects.

There is no such resonance in classical physics between the localized mode and the free wave. On the contrary, the quantum world shows the shape resonance between a free wave and a localized mode. The difference between the energy of the free wave and the energy of the local mode is the tuning parameter.

The asymmetric Fano lineshape with both the anti-resonant suppression and the resonant enhancement of the wave transmission is found also in the theory proposed by Anderson to describe localized magnetic states in metals called the Fano–Anderson Hamiltonian in solid-state

physics:

$$H = \varepsilon_c b^+ b + \sum_k \left[\varepsilon_k c_k^+ c_k + A_k\left(c_k^+ b + b^+ c_k\right)\right]$$

This Hamiltonian is often used to describe heavy fermion systems and Kondo insulators and is called "Anderson impurity model." Following Mahan it is called the "Anderson or the Fano model depending on whether the speaker is a solid state or atomic physicist". The first term describes a localized state at fixed energy ε_c and operators b^+ and b. This state is usually called impurity. The second term describes a continuous set of states with energy ε_κ and k wave-vector and operators c^+ and c that have a finite bandwidth given by the tight-binding models of solids or by a free-electron model. The third term describes the mixing between these two kinds of states describing the process where the continuum particle hops onto the impurity $(b^+ c_k)$ or particle hops off the impurity into the continuum $(c_k^+ b)$ that describe the scattering resonance for the particle at the Fermi level. The particles can be bosons or fermions; in this last case they preserve the spin orientation jumping from the bound state to the continuum and vice versa.

A case of configuration interaction between many-body functions is the case of multi-gap superconductivity [47–52] arising from the mixing between a Bardeen–Cooper–Schriffer (BCS) condensate in a first band i with a Bose-like condensate in a different band j with a finite width. The interference term, called the "interband pairing" transfers a pair of spin-up and spin-down particles from the first i to the second j condensate and vice versa. The extension of the BCS theory to overlapping bands is given by

$$\begin{aligned} H = {} & \sum_k \varepsilon_{kc} c_k^* c_k + \sum_k \varepsilon_{kb} b_k^* b_k - \sum_{k,k'} V_{cc} c_{k\uparrow}^* c_{-k\downarrow}^* c_{-k'\uparrow} c_{k'\downarrow} \\ & - \sum_{k,k'} V_{bb} b_{k\uparrow}^* b_{-k\downarrow}^* b_{-k'\uparrow} b_{k'\downarrow} \\ & - \Bigg(\sum_{k,k'} J_{cb}\left(k,k'\right) c_{k\uparrow}^* c_{-k\downarrow}^* b_{-k'\uparrow} b_{k'\downarrow} \\ & + \sum_{k,k'} J_{bc}\left(k,k'\right) b_{k\uparrow}^* b_{-k\downarrow}^* c_{-k'\uparrow} c_{k'\downarrow} \Bigg) \end{aligned}$$

The first two terms give the kinetic energy ε_{kb} and ε_{kc} of the two bands and c, c^*, b and b^* are the corresponding annihilation and creators operators. The third and fourth terms V_{cc}, V_{bb}, are the weak electron–electron attraction forming the cooper pairs and giving the BCS condensates in each band. The summations extend only over different $\vec{k}$ values in the two bands corresponding to energies with a distance $\pm\hbar\omega$ of the Fermi surface. The fifth and sixth terms are the mixing terms due to mixing of the two condensates with the transfer of a pair from the b to c band and vice versa.

Here each macroscopic condensate is characterized by an order parameter, the superconducting gap, that can be measured and the interband term acts as the link between the wave-functions of the two or more condensates giving a single critical temperature. J. Kondo in 1963 proposed that the last mixing terms $\sum_{k,k'} J(k,k')(b_{k\uparrow}^* b_{-k\downarrow}^* c_{-k'\downarrow} c_{k'\uparrow} + \text{c.c.})$, where the exchange integral $J(k,k')$ may be repulsive or attractive, is responsible for the increase of the transition temperature in complex multi-Fermi surfaces giving multi-gap superconductors also in the case where pairs are formed only in one of the two bands. In the extreme case of a first bosonic set of states (hard core bosons "b") and itinerant electrons "c" the Hamiltonian is given by

$$\begin{aligned} H = {} & \sum_k (\varepsilon_{ck} - \mu) c_k^* c_k + 2 \sum_i (E_b - \mu) b_i^* b_i - \sum_{i,j} V_{ij} b_i^* b_j \\ & + \left(\sum_{k,q} J_q(k) c_{k\uparrow}^* c_{-k\downarrow}^* b_q + \text{h.c.} \right) \end{aligned}$$

where c^* and b^* are the creation operators of electrons in the Fermi surface and bosonic pairs, respectively. In this model of a narrow set of bosonic states degenerate with the Fermi level of the free particles a strong mixing depletes the quasi-particle spectral function of the free particles and induces a pseudogap in the large Fermi surface that does not favor the gap amplification. This pseudogap effect corresponds to the negative interference effect in the Fano-lineshape.

Let us now consider the case of a finite bandwidth of the second band.

The shape resonance gives an amplification of the critical temperature that occurs in the case of a finite bandwidth of the second set of states j. The BCS equation for the critical temperature is a non-trivial function of the superconducting gaps $\Delta_n(k)$ located at different point of the momentum space

$$\Delta_n(k) = -\frac{1}{N} \sum_{n',k'} V_{n,n'}\left(k,k'\right) \frac{tgh[(\xi_{n'}(k'))/2T_c]}{2\xi_{n'}(k')} \Delta_{n'}\left(k'\right)$$

where the energy $\xi_n(k) = \varepsilon_n(k) - \mu$ and μ is the chemical potential. The charge density ρ and the chemical potential in the superconducting phase are related by

$$\rho = \frac{1}{S} \sum_n^{N_b} \sum_{k_x,k_y} \left(1 - \frac{\varepsilon_n(k_x,k_y) - \mu}{\sqrt{(\varepsilon_n(k_x,k_y) - \mu)^2 + \Delta_{n,k_y}^2}} \right)$$

The interesting fact is that the BCS equation contains the renormalization of the interaction due to opening of the superconducting gaps in all subbands.

Near the Lifshitz transition the ground-state BCS wave function corresponds to an ensemble of overlapping Cooper pairs at weak coupling (BCS regime) and evolves to molec-

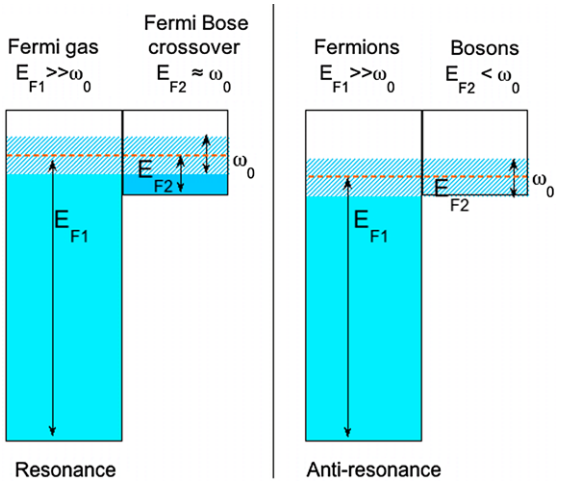

Fig. 4 The shape resonance in the superconducting gaps gives a maximum T_c amplification where the Fermi level is in the first large Fermi surface, or high Fermi energy E_F is tuned around the bottom E_{2L} of the second band. *Left side*: The shape resonance in the superconducting gaps is tuned via the Lifshitz energy parameter $E_F - E_{2L}/\omega_0 \approx 1$ where ω_0 is the pairing interaction. *Right side*: The shape resonance gives the suppression of the critical temperature or anti-resonance like in the Fano resonance where the Lifshitz energy parameter $E_F - E_{2L}/\omega_0 \approx 0$

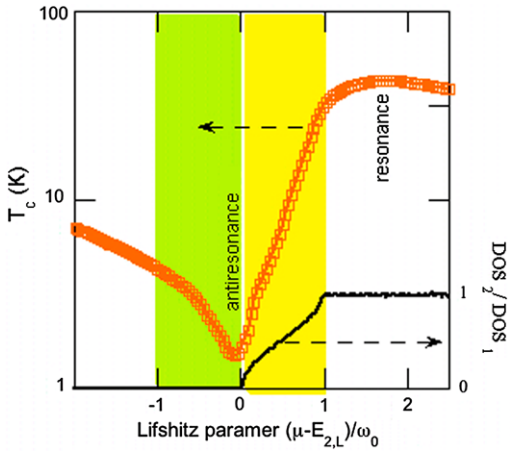

Fig. 5 The variation of the critical temperature T_c as a function of the shift of the chemical potential around the bottom of a second band showing the Fano anti-resonance suppression of the critical temperature where the Fermi energy is tuned at the bottom of the second band for the zero Lifshitz energy parameter. The maximum temperature is reached at the maximum of the shape resonance above the 3D→2D topological phase transition in the second band for the value of the Lifshitz energy parameter around 1

ular (non-overlapping) pairs with bosonic character as the chemical potential approaches the band edge (BEC regime). The crucial point is that the BCS equation for the superconducting gap has to be coupled to the equation that fixes the fermion density: with increasing coupling (or decreasing density), the chemical potential results strongly renormalized with respect to the Fermi energy E_F of the non-interacting system.

The shape resonances in the superconducting gaps in these multi-gap superconductors occurs where the chemical potential is tuned near the vanishing of one Fermi surface or the bottom of a second band, as shown in Fig. 4. We have recently investigated the shape resonances in superconducing gaps in a superlattice of quantum wells [53, 54]. While approaching the bottom of the second superlattice subband the DOS shows a standard jump as in Fig. 5. The variation of the critical temperature with the Lifshitz energy parameter, measuring the distance from Lifshitz critical point, shows a strong deviation from the variation of the density of states. We observe the anti-resonant suppression of the critical temperature at the Lifshitz point as in the Fano anti-resonant regime in Fig. 3 where the Lifshitz energy parameter is zero. The amplification of the critical temperature T_c as a function of the shift of the chemical potential reaches the maximum driven by the shape resonance above the 3D → 2D topological phase transition in the second band where the value of the Lifshitz energy parameter is around 1.5.

4 Complexity

For many years most scientists assumed a homogeneous distribution of dopants but recently a new microscopy, scanning micro X-ray diffraction, has been used to investigate the oxygen interstitial self-organization [55]. The variation of the critical temperature as a function of the internal structural organization of oxygen interstitials that could be changed via simple heat treatments has been clarified. The oxygen interstitial while has a tendency to order forming stripes, never forms a fully ordered crystals but a complex pattern of ordered striped bubbles separated by a disordered phase as shown in Fig. 2. The higher superconductivity was obtained when the microstructure was most 'connected,' meaning that it is possible to trace a path with the same nanostructure over a large distance. Crystals with stronger fractal patterns show superconducting at higher temperatures than those with weaker fractal patterns. Probably this superfluid phase is not as is described in the current generally accepted physics for a homogeneous disordered granular superconductor. It looks like the complex world of statistical distributions with "no scale" (the same social networks as "Facebook," "Twitter," etc.) show high-temperature superconductivity. Moreover, we have shown that we can manipulate regions of high-temperature superconductivity illuminating with X-rays [55] which causes a small scale rearrangement of the oxygen atoms in the material [56, 57]. This ability to rearrange the phase separation and nanoscale structure of a superconductor opens new design perspectives for superconducting circuits as shown in Fig. 6. In conclusion, we have shown that the material complexity is an essential feature of a high-T_c superconductivity.

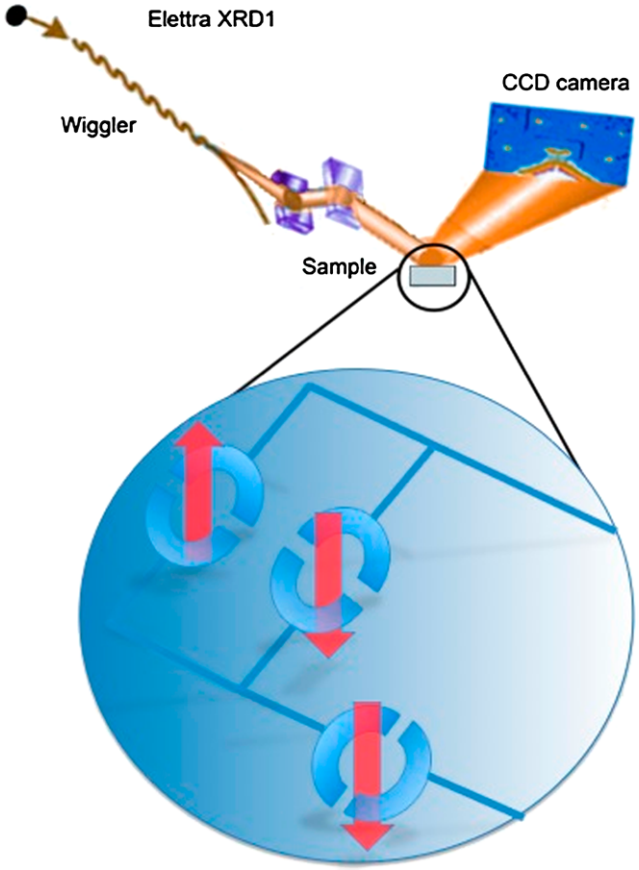

Fig. 6 The X-ray illumination of the La_2CuO_{4+y} is used to see the self-organization, to manipulate the ordering of oxygen interstitials and to write intricate superconducting circuits in complex perovskites

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