Imaging doped holes in a cuprate superconductor

Superconductivity is induced by carrier doping in layered cuprates. The superconducting transition temperature T_c commonly shows a dome-shaped doping dependence and reaches the maximum at the optimal carrier doping x_{op} (see Fig. 1); below x_{op} (underdoped region) and beyond x_{op} (overdoped region) the physical properties are quite different. Despite comprehensive studies on the doping dependence of magnetism as well as lattice dynamics, the microscopic explanation for such contrasting behavior is still an unresolved issue related to the mechanism of high-temperature superconductivity. Information on the orbital character of doped carriers and its doping evolution is indispensable for solving this problem.

In hole-doped cuprates, it is established that holes predominantly enter the oxygen 2*p* orbitals in the underdoped (UD) region, but the robustness of such orbital characters in the overdoped (OD) region has not been fully understood. Distinct doping dependences of neutron scattering [1,2], and X-ray and optical spectroscopies [3,4] suggest a change in the oxygen 2*p* orbital character in the OD region. In order to detect a change in the orbital character, we must consider the spectral differences between different doping levels; this requires high-quality data for extracting weak wave function effects. Moreover, it is essential to measure a physical quantity that is connected to wave functions, such as the electron momentum density (EMD). Compton scattering is one of the most promising techniques for investigating the doped holes because it allows direct access to the EMD.

The advantages of Compton scattering over other spectroscopies are that we do not need a nearly defect-free single crystal or clean surface or ultrahigh vacuum or low temperature. Since the matrix element involved in the scattering process is much simpler, the conversion from Compton X-ray line shapes to EMDs is straightforward. For example, using Compton scattering, we can measure the EMD of a disordered compound at any temperature, even under an electric or magnetic field. Synchrotron-based X-ray Compton scattering has established itself as a viable technique for investigating orbital characters and Fermi surfaces of bulk systems in wide classes of materials.

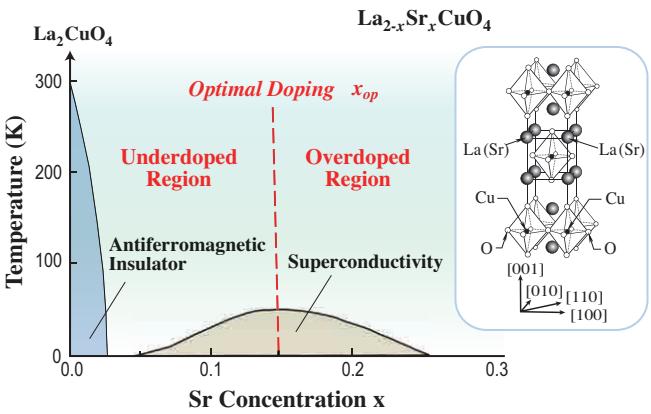

Fig. 1. Phase diagram and crystal structure of $La_{2-x}Sr_xCuO_4$. [5]

In this study [5], we obtained two-dimensional electron momentum densities (2D-EMDs), which represent one-dimensional integrals along the [001] direction of three-dimensional EMDs, for single crystalline samples of $La_{2-x}Sr_xCuO_4$ (LSCO) with four different hole concentrations, x=0.0, 0.08, 0.15, and 0.30 at room temperature. The experiment was carried out at beamline **BL08W**, using 115 keV X-rays. The 2D-EMDs were reconstructed by the direct Fourier method from each set of ten Compton profiles measured equally spaced between the [100] and [110] directions. Because of the strong two-dimensionality of LSCO, the directional character of the electronic ground state is preserved in the 2D-EMDs. To clarify the evolving nature of doped holes, we examined the differences in 2D-EMD between two samples with different doping levels. This subtraction provides information on changes in orbital occupation numbers associated with doped holes.

Our experimental data clearly show the difference between the UD and OD regions. This is demonstrated in Fig. 2, where the difference 2D-EMD between the x_{op} (x=0.15) and heavily OD (x=0.30) samples displays a markedly different feature from that in the UD region between the nondoped (x=0.0) and x_{op} (x=0.15) samples. Although some parts are still puzzling and subject to future research, we observed two distinct images with different symmetry properties: one (A-type) shows the peaks along the [100] axes and the other (B-type) has peaks along the diagonal directions (see Fig. 3). The evolution of these features with hole doping is evidence that a change or crossover behavior in the doped-hole character take place near the optimal doping x_{op}.

In layered cuprates, the angular dependence of wave functions is primarily set by the *d* orbitals of Cu, which hybridize with properly symmetrized combinations of *p* orbitals on nearest-neighbor oxygen atoms (see Fig. 4). The EMD, which is the squared modulus of the momentum-space wave function, of its orbital electron has the same directional symmetry as the corresponding charge density since the momentum-space wave function is connected to

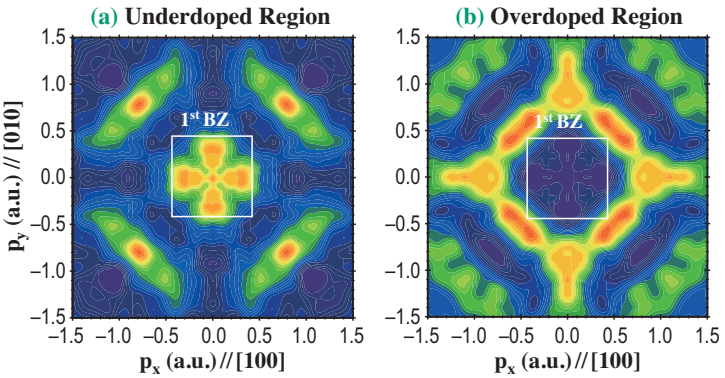

Fig. 2. Experimental difference 2D-EMDs in $La_{2-x}Sr_xCuO_4$ between two hole doping concentrations. **(a)** Underdoped: nondoped (x=0.0) minus optimal doped (x=0.15), **(b)** Overdoped: optical doped (x=0.15) minus heavily overdoped (x=0.30). The white square represents the first Brillouin zone. a.u.: atomic units.

the real-space wave function through the Fourier transformation. Our experimental data, which reveal two directionally different images, suggest a two-orbital model that incorporates both the e_g states, namely, the $x^2 - y^2$ and z^2 hybridized states. The A-type feature is associated with predominantly Cu $3d_{x^2-y^2}$ states, coupled with the molecular orbital state $P_{ZR} = P_{1x}$-P_{2y}-P_{3x}+P_{4y} to form the so-called Zhang-Rice singlet, where numbers 1 to 4 label the four O atoms and subscripts x and y denote the direction of the O $2p$ orbital in the plaquette of four O atoms surrounding a Cu atom in the CuO_2 plane. The B-type feature is assigned to the Cu $3d_{z^2}$ state hybridized with the molecular orbital $P_0 = P_{1x}$-P_{2y}-P_{3x}+P_{4y}. By varying the relative Cu character of the molecular states, the model properly describes the experimental data, i.e., the weight shift from low momenta (within 1st BZ) to high momenta (in higher BZs) as it moves from UD to OD. This indicates that, although holes in the UD region primarily populate the O $2p_{x/y}$ orbitals, the character of doped holes in the OD region is very different in that these holes mostly enter Cu e_g orbitals.

The present result demonstrates that holes in the Cu e_g orbital are newly induced in the OD region. The coexistence of two types of holes either in the O $2p_{x/y}$ or Cu e_g orbital may cause electronic phase separation, as the Cu-holes locally destroy the superconductivity and degrade the incommensurate antiferromagnetic correlation in the OD region [2]. Therefore, it is important to increase the robustness of O $2p_{x/y}$ holes to achieve higher T_c.

Finally, we show the use of Compton scattering for direct, bulk-sensitive imaging of the orbital character of dopants in the ground state of complex materials. This information is inaccessible by other highly resolved spectroscopies.

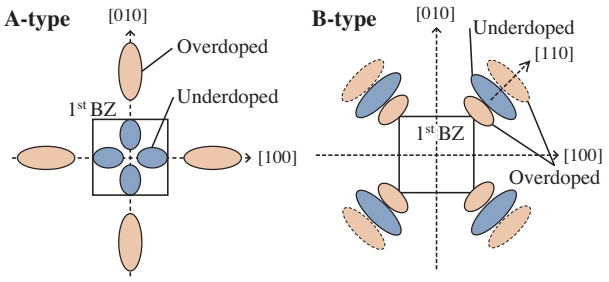

Fig. 3. Two features with different symmetry properties observed in Fig. 2.

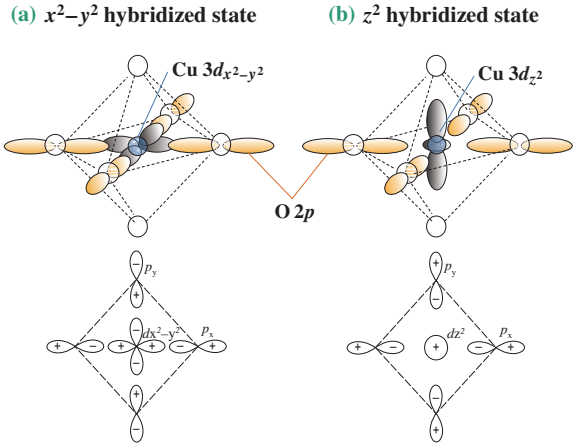

Fig. 4. Two hybridized states: **(a)** x^2–y^2 state and **(b)** z^2 state. (Top) Orbital configurations in CuO_6 octahedron. (Bottom) Wave function phase relationship on CuO_2 plane.

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