論文の内容の要旨

Photoemission studies of new electron-doped cuprate high-temperature superconductors

(新規電子ドープ型銅酸化物高温超伝導体の光電子分光による研究)

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Since their discovery, the electronic structure of cuprate high-temperature superconductors has been intensively studied both experimentally and theoretically. Starting from the antiefrromagnetic (AF) Mott insulator, doping holes or electrons suppresses the AF order and induces the superconductivity. Since both hole- and electron-doped cuprates possess CuO_2 planes as a stage for the superconductivity, similarities and differences in their electronic structure should provide a clue for the mechanism of the high-temperature superconductivity. Unfortunately, however, most of studies have been concentrated on the hole-doped cuprates because of their rich materials variety and higher superconducting (SC) transition temperatures. The recent discovery of superconductivity without chemical electron doping (i.e., without Ce substitution for rare-earth atoms) in thin films [1] and powdered samples [2] have attracted much attention to electron-doped cuprates. Removal of excess oxygen through efficient annealing can suppress the antiferromagnetism and induce superconductivity even in the parent compounds. Inspired by the breakthrough on thin films and powdered samples, new annealing method, which is called protect-annealing method, has also been developed for bulk single crystals, leading to the emergence of superconductivity down to heavily underdoped region [3]. In the present thesis, I have studied electronic structure of those “new" electron-doped cuprate superconductors by means of photoemission spectroscopy.

In chapter 3, thin films of the SC parent compound Pr_2CuO_4 have been synthesized and studied by angle-resolved photoemission spectroscopy (ARPES). In order to perform ARPES measurements, which is highly surface sensitive, we first synthesized the SC Pr_2CuO_4 by growing it under highly reducing condition, instead of annealing it after the growth *ex-situ*, to avoid the surface contamination. Then, we carried out ARPES measurements and observed clear Fermi surfaces, whose area suggests electron concentration is much larger than half filling. Chapter 4 was devoted to relatively bulk-sensitive hard X-ray photoemission and soft X-ray absorption spectroscopy on the SC parent compound Nd_2CuO_4 and related materials. We have observed a chemical-potential shift between insulating and SC Nd_2CuO_4, which again suggests that SC parent compound is not at half-filling, but is doped with electrons, probably due to oxygen deficiency.

In chapter 5, we have performed a systematic ARPES study on protect-annealed underdoped $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ single crystals with varying Ce concentration and annealing condition to reveal the difference between the effect of Ce doping and annealing on the electronic structure. Efficient annealing was found not only to dope the system with electrons, but also to remove a gap at the Fermi level and decrease the magnitude of AF band splitting. We have concluded that as-grown sample contains disorder which produces the Coulomb gap and increase AF correlation, and the disorder is removed by annealing.

In chapter 6, the nature of the AF band splitting, which is called AF pseudogap in electron-doped cuprates, has been studied by ARPES. We have revealed that the AF pseudogap shows non-trivial momentum dependence, and concluded from comparison with a variational Monte-Carlo calculation [4] that it is due to the effect of strong electron correlation beyond the simple AF band splitting.

In chapter7, we have studied the SC gap of protect-annealed $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ single crystals. Although AF correlation was strongly suppressed by protect annealing, the SC gap was found to have *d*-wave symmetry, which may be mediated by AF spin fluctuations.

We have thus studied the electronic structure of the “new" electron-doped cuprate superconductors focusing on the effect of annealing on the carrier concentration, AF correlation, and superconductivity. The present study will not only advance our understanding of the electron-doped cuprate superconductors but also promote reconsideration of the electronic structure and paring mechanism of the hole-doped cuprate superconductors.

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