4 Local-to-Bulk Electronic Correlation Project

– Emerging phenomena induced by deformation of local structure in strongly correlated electron system –

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4-1 Background and purpose of project

Evidence showing the importance of crystal structure on the physical properties of the high-Tc cuprates has increased recently. The mother compound of electron-doped superconductors with Nd$_2$CuO$_4$-type (abbreviated as $T'$) structure is recognized as an antiferromagnetic (AF) Mott insulator, as is the case for hole-doped La$_2$CuO$_4$ with K$_2$NiF$_4$-type (abbreviated as $T$) structure. However, the appearance of superconductivity in thin films and low-temperature synthesized powder samples of “undoped” $T'$-$R_2$CuO$_{4-y}$, was recently reported [1, 2]. These experimental results suggest that the mother compound of so-called “electron-doped” superconductors is not a Mott insulator. Subsequently, a mean field calculation of the electronic structure reported that the $T'$-type cuprates could have a metallic character, while the $T$-system could be a Mott insulator [3]. Furthermore, the first principal calculation by Weber et al. showed that the ground state of non-doped $T'$ materials is a Slater insulator in which the insulating behavior is governed by the magnetic long-range order [4]. Therefore, the determination of the genuine ground state in $T'$-$R_2$CuO$_{4-y}$ is now an important issue in the research of high-$T_s$ superconductivity.

The as-prepared bulk sample of $T'$-type cuprate was found to be an antiferromagnetic insulator in a wide Ce-doping range. Reduction annealing procedure is required for the suppression of the AF order and the emergence of superconductivity. Brinkmann and co-workers reported the expansion of the superconducting phase toward the zero-doping through a moderate annealing process [5], which would be consistent with the emergence of undoped superconductivity. Therefore, the role of annealing is key to understanding the inherent nature of undoped $T'$-type cuprate with flat CuO$_2$ planes and clarify the mechanism of “undoped” superconductivity.

The stoichiometric $T'$-structure is characterized by the absence of apical oxygen above and below Cu sites (See Fig. 1(a)), which is contrast to the $T$-structured La$_2$CuO$_4$ where the Cu ion is surrounded by 6 oxygen ions. There are a couple models for the structural change induced by annealing. Schulzt and co-workers first refined the crystal structure with the assumption of the existence of apical oxygen. They reported the relatively small occupancy rate of the apical oxygen site in the reduced sample, suggesting the realization.
of an ideal $T$-phase by removing apical oxygens [6]. This result was long recognized to be correlated with the role of annealing in the emergence of superconductivity. In 2007, because the finite secondary phase ($R_2O_3$) appears after the annealing process, Kang and co-workers proposed a defect-repair model [7]. In this model, Cu defects in the as-prepared sample could be removed through a reconstruction of CuO$_2$ planes by interstitially expelling the excess atoms as $R_2O_3$. However, some samples did not show an evidence of secondary phase after annealing, while the as-grown sample was non-superconductor. Therefore, the common role of annealing on the structural change and in the superconducting mechanism is still under debate. Because the value of removal oxygen (-2, 3%) is small [8], the evaluation of clear differences in the structural parameters regarding oxygen ions between the as-sintered (AS) and annealed samples is difficult. For the determination of the structural parameters and the full understanding of the superconducting mechanism, state-of-the-art instruments with a complementary use of quantum beams are required.

4-2 Annealing effect on electronic state in $T$-type cuprate [9]

![Fig. 2: (a) Difference spectra between as-sintered (AS) Pr$_{2-x}$Ce$_x$CuO$_4$ with various x values and AS Pr$_2$CuO$_4$. (b) Difference spectra between reduction annealed Pr$_2$CuO$_4$ and AS Pr$_2$CuO$_4$. Annealing was done at 900°C (yellow) and 940°C (blue).]

Ce-substitution and reduction annealing effects on the electronic states at the copper sites was studied by Cu K-edge x-ray absorption fine structure measurements. Figure 2(a) shows the difference spectra between the AS Pr$_2$CuO$_4$ and AS Pr$_{2-x}$Ce$_x$CuO$_4$ with several x values. Similar difference spectra between reduction annealed (RN) and AS Pr$_2$CuO$_4$ are shown in Fig. 2(b). Interestingly, the spectra were transformed by the Ce-substitution and the reduction annealing in a similar manner. Considering the electron-doping by Ce-substitution, this similarity indicates an increase of electron number at the copper sites by the annealing process. We note that the peak at ~8981 eV corresponds to 1s-4p$\pi$ Cu$^+$ transition, supporting the production of Cu$^+$ by both through Ce-substitution and by annealing. However, qualitative analysis of the spectra clarified that the electron number increases linearly with x in the AS PCCO; however, as seen in Fig. 3, this increase in electron number by the annealing process is not exactly equal to 2$\delta$ (amount of oxygen loss by the annealing), which can be expected from a charge neutrality of the sample. A larger electron number than 2$\delta$ suggests a production of holes in the sample. Therefore, two types of carrier would exist in the heavily annealed samples. These two types of carrier in $T$-type cuprates have been previously suggested to result from the Hall coefficient and Hall resistivity measurements on thin films [13, 14]. However, in the pres-
ent systematic study, we first showed that holes could more easily appear in the heavily Ce-doped sample with smaller $\delta$ values. Such a variation is possible owing to a transformation of band structure in the heavy electron dope region.

4-3 Magnetic and superconducting properties in $T^*$-type cuprate [11,12]

There is another isomer of the 214 system, that is, $T^*$-type copper oxide having CuO$_5$ pyramid coordination. The crystal structure of the $T^*$-214 system is composed of the $T$-type and the $T^*$-type structures with alternative stacking along the c-direction. (See Fig. 1(b).) Akimitsu and co-workers first reported the appearance of superconductivity in $T^*$-type Nd$_{2-y}$Ce$_y$Sr$_y$CuO$_4$. [10] Subsequently, several superconducting $T^*$-structured cuprates were synthesized. For the emergence of superconductivity in $T^*$-type cuprates, oxidation annealing under high pressures is necessary. It was reported that oxygen defects at the apical oxygen site existing in the AS compound can be repaired owing to oxidation annealing, resulting into the appearance of superconductivity. The repair of oxygen defects acts inversely proportional to the removal of excess oxygen for the case of the $T^*$-type cuprate [6]. Therefore, $T^*$-type cuprate could be a suitable reference for a study of the relationship among the local crystal structure, magnetism, and superconductivity, as well as that between Cu coordination and the physical properties. However, less is known about the physical properties of $T^*$-type cuprate, because of the difficulties in controlling the crystal growth and in obtaining SC samples by high pressure heat treatment. In this project, we synthesized $T^*$-structured La$_{1-x/2}$Eu$_{1-x/2}$Sr$_x$CuO$_4$ with $0.12 \leq x \leq 0.28$, and performed muon spin relaxation (µSR), magnetic susceptibility, and electric resistivity measurements of both AS and oxidation annealed samples to clarify the magnetic and superconducting properties. We confirmed that all annealed samples undergo superconducting transition at low temperature, while AS ones do not show evidence of superconductivity.

Figures 4(a) and 4(b) show the zero-field µSR time spectra for AS and annealed LESCO with $x = 0.14$. A Gaussian-type time spectrum remains in the oxygen annealed samples down to ~4 K, indicating the absence of a static magnetic order, whereas the time spectrum in the AS compound transformed into an exponential-type one upon cooling. Therefore, magnetic correlations evolve at low temperature in the non-superconducting samples. These results further indicate that the oxygen annealing process weakens the magnetic correlations and superconductivity competitively emerges with the disappearance of static magnetism. In Fig. 5, onset temperature for the appearance of superconductivity ($T_c$) in oxygen annealed samples and that of the fast depolarization component in the µSR time spectra ($T_m$) of AS sam-

![Fig. 5](image_url)
samples are summarized. $T_c$ decreases monotonically with Sr doping, while $T_m$ is almost constant in a wide Sr concentration range. Thus, the magnetic phase in the AS $T'$-type LESCO is robust against hole concentration.

4-4 Project workshop

To encourage students and young researchers in the research field of superconductivity and quantum beams, we held a two-day workshop during March 5th and 6th at IMR Tohoku University. This workshop was organized by PhD student Shun Asano, from the project leader's group. The scope of this workshop was not limited to superconductivity and quantum beams; therefore, several bright new faces from related fields were invited to the workshop. The speakers introduced their own research and shared interesting results with the participants. They intensively discussed the future prospects of research in superconductivity including new materials and quantum beam science. The workshop received high marks from the participants. The program of the workshop is shown below.

Workshop for young researchers
“New developments in quantum beam research and study of superconductors and its related materials”

May 5th, 2019
Opening (S. Asano, Tohoku Univ.)

Afternoon session 1 (Chair: K. Ishii, QST.)
$\cdot T'$-structured cuprate and related materials 1-
  ■ Cu spin fluctuations and electric state in electron-dope cuprate (T. Adachi, Sophia Univ.)
  ■ Electric state in $T'$-La$_{1.8}$Eu$_{0.2}$CuO$_4$ studied by µSR (T. Kawamata, Tohoku Univ.)
  ■ Structural change due to oxygen reduction annealing in electron doped superconductor (M. Mitarashi, Tohoku Univ.)
  ■ Superconductivity in MBE thin film of infinite layer cuprate (A. Ikeda, NTT.)

Afternoon session 2 (Chair: T. Yamamoto, Tohoku Univ.)
-Advanced quantum beam measurements-
  ■ Magnetic skyrmion study with neutron and synchrotron radiation x-ray T. Nakajima (RIKEN)
  ■ Photo-induced dynamics in ferromagnets observed by X-ray free electron laser K. Yamamoto (Univ. of Tokyo)
  ■ Observation of local magnetic structure by neutron total scattering T. Honda (KEK)

May 6th, 2019
Morning session (Chair: T. Adachi, Sophia Univ.)
$\cdot T'$-structured cuprate and related materials 2-
  ■ Observation of electronic excitation by resonant inelastic x-ray scattering (K. Ishida, QST)

Fig. 6: A group photo of workshop held at the Institute for Materials Research, Tohoku University.
■ Polarized hard X-ray photoelectron spectroscopy of the electron-doped copper oxide high-temperature superconductor Nd$_{2-x}$Ce$_x$CuO$_4$ (K. Yamagami, Univ. of Tokyo)
■ Annealing effect on the electronic state of T'-cuprate studied by X-ray absorption fine structure analysis (S. Asano, Tohoku Univ.)
■ Density wave and energy gap of Bi-based cuprate superconductors (T. Kurosawa, Hokkaido Univ.)
■ Superconducting state of multilayer copper oxide elucidated by angle-resolved photoelectron spectroscopy (S. Kunisada, Univ. of Tokyo)

Afternoon session (Chair: T. Honda, KEK)
- Future prospects of quantum beam measurements -
■ Structure of bilayer graphene intercalating superconductors by total reflection high-speed positron diffraction (A. Takayama, Waseda University)
■ Fast analysis of surface X-ray diffraction data using Bayesian inference (M. Anada Osaka Univ.)
■ Controlling superconductivity and BCS-BEC crossover studied by ion gate method (Y. Nakagawa, Univ. of Tokyo)
■ Study of spin-1/2 distorted square lattice magnetism T. Yamamoto, Tohoku Univ.)

■ Summary 1, T. Nakajima (RIKEN)
■ Summary 2, R. Kadono (KEK)

References