7 Local-to-Bulk Electronic Correlation Project

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

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7-1 Background of research

High-transition-temperature superconductivity in cuprate oxide emerges when the appropriate number of charge carriers is introduced in a Mott insulator. Since the superconducting phase exists in the vicinity of antiferromagnetically ordered phase[1] [see Fig. 1(a)], the common role of AF spin fluctuation in the mechanism of superconductivity is widely accepted. Furthermore, high-T_c cuprate superconductors commonly contain CuO_2 planes in their crystal structure, and therefore the intrinsic physical properties of the CuO_2 plane have been intensively discussed. At the same time, much attention has been paid to the structural parameters and/or the local environment around the CuO_2 plane, which causes the individual character in actual materials. For example, in hole-doped $La_{2-x}(Sr,Ba)_xCuO_4$, a corrugation of the CuO_2 plane with a particular pattern in the low-temperature-tetragonal phase stabilizes the spin and charge stripe orders, which competes with the superconductivity[2, 3]. Furthermore, the distance between the apical oxygen and the CuO_2 plane can affect the orbital hybridization between $3d_{x^2-y^2}$ and $3d_{3r^2-z^2}$, and thereby, the height of apical oxygen is an important factor for the reconstruction of the Fermi surface[4].

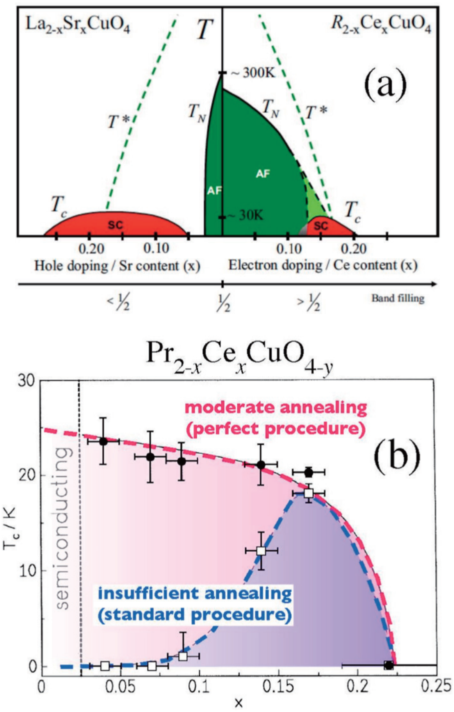


Fig. 1: (a) Widely accepted phase diagram for R_2CuO_4. In the electron-doped side (right half), the superconducting phase appears with the suppression of antiferromagnetically ordered phase upon doping at the carrier density of ~0.15/Cu. (b) Superconducting transition temperature in $Pr_{2-x}Ce_xCuO_{4-y}$ after the moderate annealing (closed circles) and standard annealing (open squares) procedures. Figures are taken from Refs. 1 and 8.

The R_2CuO_{4-y} (R: Pr, Nd, Eu, …) with Nd_2CuO_4-type (abbreviated as *T'*) structure is recognized as an antiferromagnetic (AF) Mott insulator as is the case for the K_2NiF_4-type (abbreviated as *T*) La_2CuO_4[5]. The stoichiometric *T'*-structure is characterized by the absence of apical oxygen above and below Cu sites, which is in stark contrast to the *T*-structured system where the Cu ion is surrounded by six oxygen ions forming an octahedron. Surprisingly, Naito's group experimentally showed the appearance of superconductivity in a thin film of "undoped" *T'*-R_2CuO_{4-y}[6]. If this is the case for bulk sample, the mother compound of so-called "electron-doped" superconductors is not a Mott insulator. Subsequently, a mean field calculation of electronic structure pointed out that the *T'*-system can have metallic character, while the *T*-system is a Mott insulator[7]. Therefore, determination of the ground state in *T'*-R_2CuO_{4-y} is now an important issue in the research of high-T_c

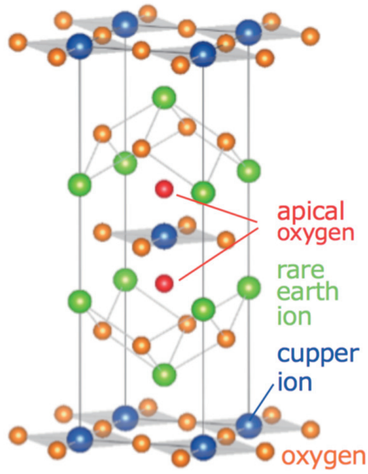


Fig. 2: Crystal structure of *T*'-$R_2CuO_{4+\delta}$ (*R*: rare earth). The *T*'-structure contains flat CuO_2 planes with the Cu in the four-coplanar coordination. Apical oxygen existing in the as-prepared sample is believed to suppress the superconductivity and be removed by annealing.

superconductivity to understand the inherent nature of the undoped CuO_2 plane and to study a variety of superconducting mechanisms. This is also important for reinvestigating the electron-hole symmetry of physical properties in doped Mott insulators while taking the individual crystal structure into account.

7-2 Previously proposed crystal structure

In actual compounds, the as-prepared sample of the *T*'-system is an antiferromagnetic insulator in a wide Ce-doping range and an adequate oxygen reduction procedure is required for the emergence of superconductivity. Brinkmann *et al.* reported the importance of the annealing procedure and extension of the superconducting phase toward zero-doping by moderate annealing[8] [Fig. 1(b)]. This result is probably consistent with the appearance of undoped superconductivity reported by Naito.

The crystal structural of oxygenized and reduced $Nd_{2-x}Ce_xCuO_4$ was examined soon after the discovery of superconductivity in *T*'-structured compounds[9]. Consistent differences between the two samples were difficult to find at that time. In the mid 1990s, Schultz *et al.* refined the crystal structure with the assumption of the existence of apical oxygen. They reported the smaller occupancy rate of the apical oxygen site in the reduced sample[10]. This result was referred to in connection with the role of annealing in the emergence of superconductivity for a long time. In 2007, based on the fact that the finite secondary phase (R_2O_3) appears after the annealing, Kang *et al.* proposed a defect-repair model[11]. In this model, defects of Cu in the as-prepared sample can be removed through the reconstruction of CuO_2 planes and interstitial expelling of the excess atoms as R_2O_3. However, some samples do not show evidence of the secondary phase after annealing, while the as-prepared non-superconducting sample turns into superconductor after annealing. Therefore, the common effect of annealing on the structural change and its role in the superconducting mechanism are still under debate.

7-3 Need for complementary use of quantum beam

To clarify the linkage between the structural change induced by a slight reduction of oxygen and the metal-insulator transition, precise measurements utilizing advanced quantum-beam techniques are indispensable. Furthermore, in contrast to extensive studies on hole-doped systems, there have been few systematic measurements of the effects of annealing and Ce-doping on physical properties and crystal structure, due

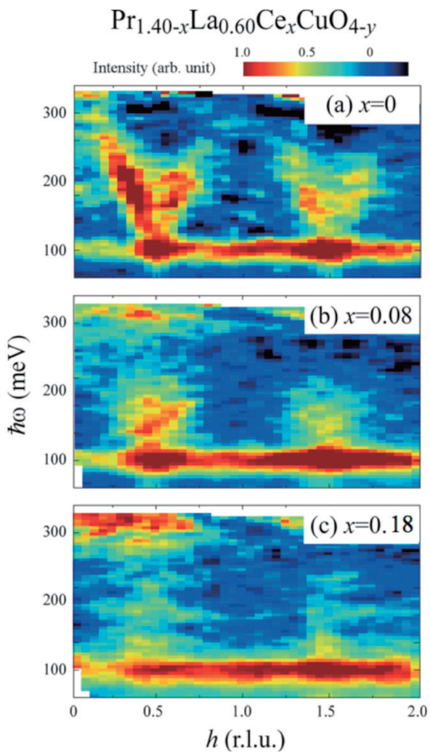


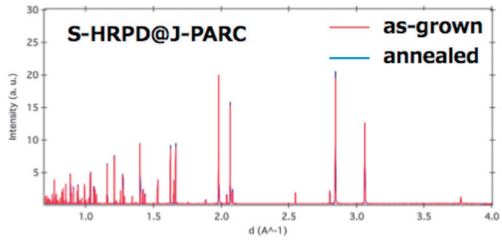
Fig. 3: Spin excitation spectrum in the as-prepared *T*'-$Pr_{1.4-x}La_{0.6}Ce_xCuO_4$ with (a) x = 0, (b) 0.08 and (c) 0.18. Electron-doping effect on the spin excitation was clarified by neutron scattering measurement.

to the lack of availability of large single crystals of superconducting *T*'-cuprate. Therefore, the magnetic correlations and electronic state should be investigated by spectroscopic probes. In addition to overcoming difficulties in crystal growth and the emergence of superconductivity, the development of instrumental techniques has enabled us to carry out accurate measurements on relatively small crystals. (See Fig. 3 as a reference of high-energy spin excitation obtained by inelastic neutron scattering measurement. Also, see Ref. 12.) Therefore, it is time to study *T*'-$R_2CuO_{4+\delta}$ by a combination of excellent material synthesis and advanced quantum-beam techniques. In this project, we aim to clarify the inherent nature of *T*'-structured cuprate oxide and related materials by complementary use of a quantum beam.

7-4 Reinvestigation of crystal structure

The value of removing oxygen evaluated from the weight loss after annealing was reported to be only ~2–3%, and the distinct changes in the structural parameters regarding oxygen ions are not fully determined yet. Therefore, we tried to detect differences in the structure of as-prepared and annealed samples by neutron powder diffraction measurement at Super-HRPD in MLF/J-PARC.

Figure 4 shows the diffraction pattern of as-prepared and annealed Pr_2CuO_4, which is recognized as the parent compound of electron-doped high-T_c superconductor. The experiment was done as a general-use program at MLF/J-PARC before starting this project. The reduced oxygen content estimated from the weight loss of the sample was ~0.04. To extract information on the occupancy of oxygen at the apical and in-plane sites, we carried out Rietveld analysis. Although the R-factor is less than 2%, meaning that the structural parameters are accurately defined, the preliminary analysis showed a negligible difference in the structural parameters in two samples. Since it is difficult to evaluate clear differences at present, we simulated the atomic-selective diffraction patterns while varying the occupancy of apical oxygen and in-plane oxygen. However, such a simple model causes distinct changes in the Bragg peaks and the result is inconsistent with no clear difference in the diffraction pattern of two samples. This result suggests that the structural change is much more complex than the picture



	a(Å)	c(Å)	z	O	χ^2	Re(%)
as-grown	3.960	12.2379	0.24123	0.011283	1.7952	4.9721
annealed	3.964	12.2412	0.02093	0.006644	1.5909	5.2302

Fig. 4: Neutron diffraction pattern of as-prepared and annealed Pr_2CuO_4. The evaluated parameters are summarized in the table.

proposed by earlier studies. In this project, we should investigate the local structure and/or carry out more precise measurement on single crystal.

7-5 Kick-off meeting

To share the aims of the project and exchange information on the current status of individual research led by the project members, we held the kick-off meeting on March 10th, 2016 at CMRC/KEK, Tsukuba.

The meeting started with greetings by Prof. Kadono (CMRC/KEK), followed by an introduction of the project by Prof. Fujita (Tohoku Univ.). In the scientific session, Prof. Tohyama (Tokyo Univ. of Science) reviewed the electronic state of *T*' cuprate oxides and pointed out the remaining issues from a theoretical viewpoint. Recent results of structural studies done with precise single-crystal X-ray diffraction were reported by Prof. Kimura (Tohoku Univ.), and the significant effect of annealing on the rare earth positions was mentioned. Profs. Adachi (Sophia Univ.) and Kadono (CMRC/KEK) discussed the possible scenario of undoped superconductivity from the results of systematic μSR measurements. An NMR study on the effect of annealing on the local magnetism was reported by Prof. Mukuta (Osaka Univ.), and the feasibility of X-ray spectroscopy for studying the electronic state of cuprate oxide was proposed by Prof. Ishii (SPring-8/JAEA). Participants from CMRC and MLF also presented advanced quantum-beam techniques and possible contributions to the project. About 30 people, including students and young researchers, attended the meeting.

We reconfirmed the importance of structural changes induced by annealing for a full

Fig. 5: Pictures of kick-off meeting on March 10th at CMRC/KEK.

understanding of the superconducting mechanism and genuine ground state in *T*' cuprate oxides. This kick-off meeting provided an important opportunity to exchange ideas on recent and long-standing researches regarding *T*' cuprate and discuss different types of spectroscopy measurements on particular research issues.

7-6 Future perspective

The electron-doped superconductor was first discovered by Tokura's group and subsequently the possibility of undoped superconductivity in the same system was reported by Naito's group. After the discovery, the superconductivity of the *T*'-system was studied from the viewpoint of a doped Mott insulator, in connection with the electron-hole symmetry of physical properties. The study of undoped superconductivity will provide a new route for research of strongly correlated electron systems. At present, the difference in the ground state of R_2CuO_4 is considered to be the result of different local structure, that is, a perfect CuO plane without random potential from chemical disorder has a metallic nature, while the existence of disorder stabilizes the insulating state. This means that the *T*'-system provides a unique opportunity to study the connection between the superconductivity in a doped Mott insulator and undoped superconductivity. To shed more light on superconductivity in the *T*'-system, we will systematically investigate the effects of both annealing and Ce-doping on the physical properties, especially magnetic correlations, by neutron scattering and μSR measurements.

Acknowledgement

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