4 Local-to-Bulk Electronic Correlation Project

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

Project Leader: Masaki Fujita

4-1 Background of research

Evidence showing the importance of the crystal structure on the physical properties of high-T_c cuprates has increased recently. The mother compound of electron-doped Nd_2CuO_4-type superconductor (abbreviated as T') is recognized as an antiferromagnetic (AF) Mott insulator, as is the case for hole-doped La_2CuO_4 with K_2NiF_4-type (abbreviated as T) structure (See Fig. 1(a)). However, the appearance of superconductivity in thin films and powder samples of "undoped" T'-R_2CuO_{4-y} synthesized at low temperature was reported recently [1, 2]. These experimental results suggest that the mother compound of a so-called "electron-doped" superconductor is not a Mott insulator, and a new superconducting mechanism in cuprate oxides should be studied. Subsequently, a mean field calculation of the electronic structure reported that the T'-system can have metallic character, while T-system is a Mott insulator [3]. Furthermore, first principal calculations by Weber et al. show that the ground state of a non-doped T' material is a Slater insulator in which the insulating behavior is governed by long-range magnetic order [4]. Therefore, determination of a genuine ground state in T'-R_2CuO_{4-y} is currently an important issue in the research on high-T_c superconductivity.

The as-prepared bulk sample of a T'-system is an antiferromagnetic insulator for a wide range of Ce doping concentration. Reduction annealing is required to suppress AF order and to bring about superconductivity. Brinkmann and co-workers reported expansion of the superconducting phase toward zero-doping by moderate annealing [5], which would be consistent with the emergence of undoped superconductivity. Therefore, the role of annealing is key understanding the inherent nature of undoped flat CuO_2 planes as well as the mechanism that causes superconductivity in the T'-phase.

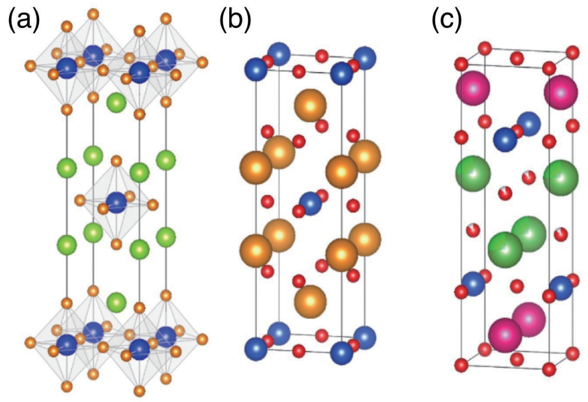

Fig. 1: Crystal structure of $R_2CuO_{4+\delta}$. (R: rare earth) with (a) T-, (b) T'-, and (c) T*-structure. T'-structure has flat CuO_2 plane with the four-coplanar coordination for Cu ions. The excess oxygens are considered to exist at the apical site in the as-prepared sample, and the superconductivity appears by removeing the excess oxygens by the annealing.

The stoichiometric T'-structure is characterized by the absence of apical oxygen above and below Cu sites, which is contrast to the T-structured La_2CuO_4 where the Cu ion is surrounded by 6 oxygen ions. There are a couple of models describing the structural change induced by annealing. Schultz and co-workers first refined the crystal structure by assuming the existence of apical oxygen. They reported a relatively small occupancy rate of apical oxygen in the reduced sample, suggesting the realization of the ideal T'-phase by removing apical oxygens [6]. This result was referred in connection with the role of

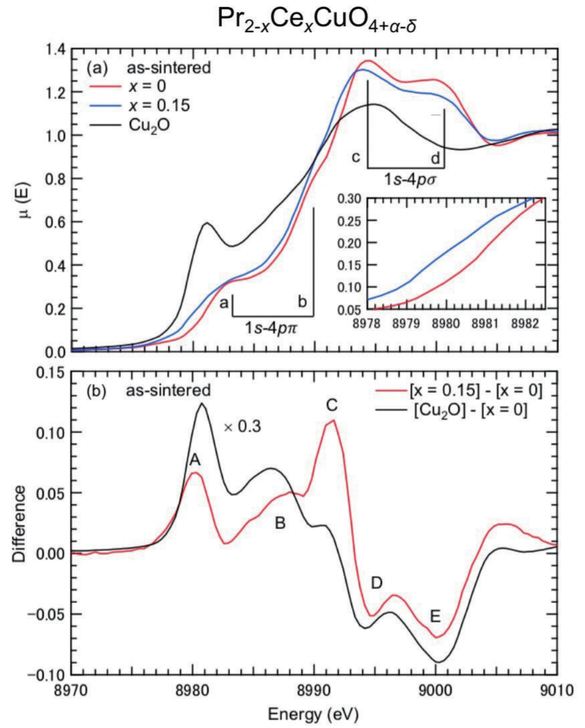

Fig. 2: (a) Spectra for as-sintered (AS) $Pr_{2-x}Ce_xCuO_4$ with x = 0 and x = 0.15 compared with the spectrum for Cu_2O. (b) Subtracted spectrum for AS $Pr_{2-x}Ce_xCuO_4$ with x = 0 and x = 0.15 compared with the subtracted near-edge spectrum for Cu_2O and AS Pr_2CuO_4. Figures are taken from Ref. 9.

annealing for the emergence of superconductivity for some time. In 2007, Kang and co-workers proposed a defect-repair model based on a fact that the finite secondary phase (R_2O_3) appears after the annealing [7]. In this model, Cu defects in the as-prepared sample can be removed by reconstruction of the CuO_2 planes by interstitially expelling the excess atoms as R_2O_3. However, some samples did not show evidence of a secondary phase after annealing, while the as-grown sample was not superconducting. Therefore, the common role of annealing on the structural change and in the superconducting mechanism is still under debate. Since the value of oxygen removal is small (~2, 3%) [8], evaluating clear differences in the structural parameters regarding oxygen ions between the as-sintered and annealed samples is difficult. State-of-the-art instruments with a complementary use of quantum beams are required to determine the structural parameters and gain a full understanding of the superconducting mechanism.

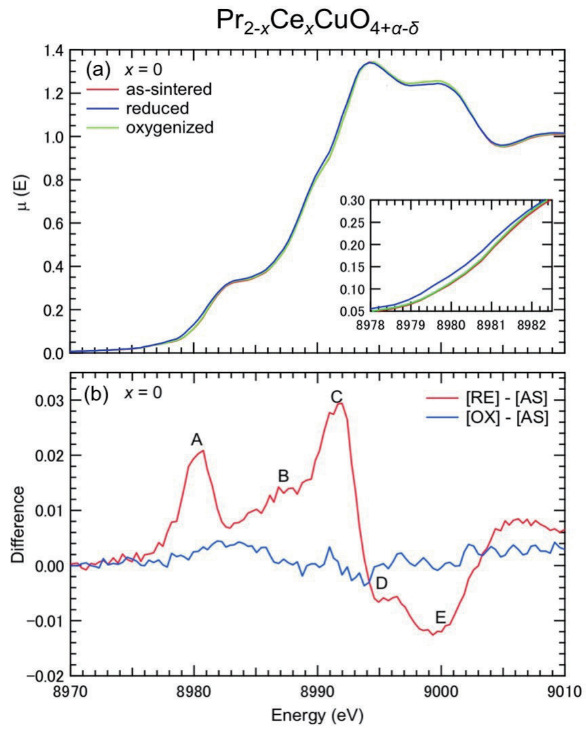

Fig. 3: (a) Spectra for as-sintered (AS), reduced (RE), and oxygenized (OX) Pr_2CuO_4. (b) Subtracted spectrum for AS and RE Pr_2CuO_4 (red line) compared with the subtracted spectra for AS and OX Pr_2CuO_4 (blue line). Figures are taken from Ref. 9.

4-2 Annealing effect on electronic state

To investigate the reduction annealing effects on the electronic states around the copper sites, we performed Cu *K*-edge X-ray absorption measurements on $Pr_{2-x}Ce_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$. [9]. Figure 2(a) shows near-edge spectra for the as-sintered (AS) $Pr_{2-x}Ce_xCuO_4$ with x = 0 and x = 0.15. Absorption spectra for Cu_2O are also plotted as a reference of Cu^+ configuration. The spectra clearly change due to Ce doping. In Fig. 2(b), the difference spectrum between the AS PCCO with x = 0 and x = 0.15 (denoted as [AS PCCO with x = 0.15] – [AS PCCO with x = 0]) is shown together with that between Cu_2O and AS PCCO with x = 0 (denoted as [Cu_2O] – [AS PCCO with x = 0]). The peak at ~8981 eV corresponds to the 1s-4pπ transition for Cu^+, and the similarity in the structure of [AS PCCO with x = 0.15] – [AS PCCO with x = 0] and [Cu_2O] – [AS PCCO with x = 0] demonstrates the production of Cu^+ by Ce-substitution. This result is consistent with the spin dilution model that assumes electron doping on copper sites by Ce-substitution. Figure 3(a) shows the absorption spectra for the as-sintered (red line) and

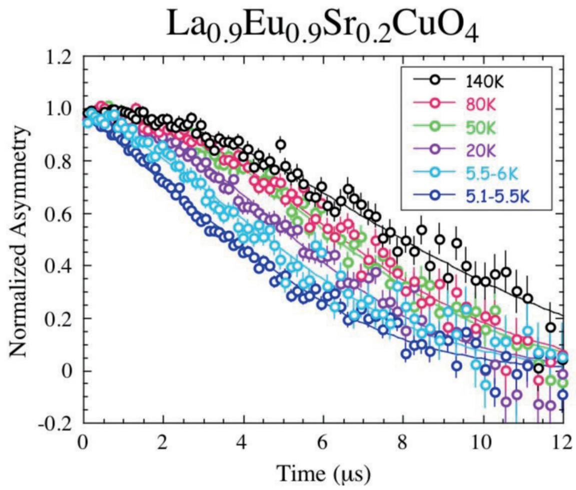

Fig. 4: Zero-field μSR time dependence for non-SC T^*-$La_{0.9}Eu_{0.9}Sr_{0.2}CuO_4$. The data are normalized after subtraction of the constant background signal. Figure was taken from Ref. 11.

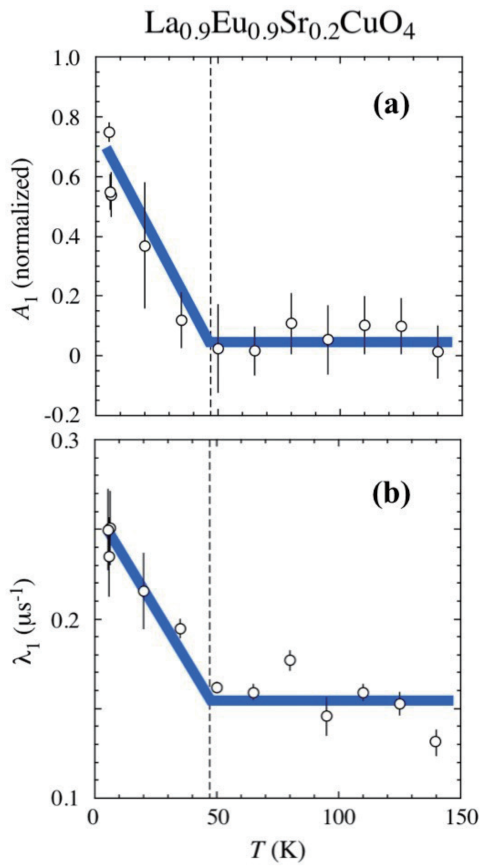

Fig. 5: (a) Temperature dependence of (a) the initial asymmetry and (b) depolarization rate during exponential relaxation in T^*-$La_{0.9}Eu_{0.9}Sr_{0.2}CuO_4$. Dashed lines represent the onset temperature at which the exponential component starts to appear upon cooling. Figures are taken from Ref. 11.

annealed (blue line) samples, and Fig. 3(b) indicates the subtracted spectra between the data for the annealed sample and that for the as-sintered sample. Importantly, the spectra changed due to annealing in a similar manner as the case of Ce substitution. The subtracted spectrum shows a similar structure as [AS PCCO with x = 0.15] – [AS PCCO with x = 0], indicating an electron density increase at the copper sites due to annealing. This reduction annealing effect on the near-edge spectra is reverted by the additional oxidation annealing.

4-3 Annealing effect on spin correlations

A systematic study with further reference systems is important to clarify the structural effect on the physical properties. The T^*-structured compound, which is an isomer of 214 compounds, has an intermediate crystal structure between the T'- and T-structure. In the T^*-structured compound, half of the T-phase and half of the T'-phase alternatively stack along the c-direction in the unit cell (see Fig. 1(c)). It is known that the T^*-compound of $Nd_{2-x-y}Ce_xSr_yCuO_4$ (T_c(max) ~32 K) exhibits superconductivity with hole-doping [10]. For the emergence of superconductivity in the T^*-phase, oxygen annealing is required to repair the oxygen site defect on the CuO_2 plane, which is the opposite method for removing apical oxygen by reduction annealing for the case of the electron doped T'-structured compound [5]. Therefore, the T^*-compound is a suitable system to study the universality of hole-doping, as well as the effect of annealing on magnetism. However, to the best of our knowledge, there is no report on magnetism in the T^*-compound, possibly due to difficulties in the preparation of a high quality sample. In this project, we newly synthesized T^*-structured $La_{1-x/2}Eu_{1-x/2}Sr_xCuO_4$ with $0.12 \le x \le 0.22$, and we performed muon spin relaxation (μSR) measurements for the as-prepared and non-superconducting $La_{0.9}Eu_{0.9}Sr_{0.2}CuO_4$ sample at the D1 beamline in J-PARC/MLF [11]. The advantage of the $La_{1-x/2}Eu_{1-x/2}Sr_xCuO_4$ system is that there is no rare earth magnetic moment. Therefore, the intrinsic signal from Cu spins can be easily observed from μSR measurements.

Figure 4 shows the zero-field μSR time spectra for the as-sintered LESCO with x = 0.20. A Gaussian-type time spectra was observed at temperatures above ~20 K. Upon cooling, the muon spin relaxation changes gradually, and an

Fig. 6: A group photo of workshop held at the Institute for Materials Research, Tohoku University.

exponential-type decay component appears at low temperature. Therefore, the spin correlation develops upon cooling. From qualitative analysis of the spectra, we found that the exponential-type relaxation component develops below ~50 K. Figs. 5(a) and (b) show the initial asymmetry and depolarization rate for exponential relaxation. However, no evidence of oscillatory behavior was detected, even at 5 K, indicating the absence of long-range magnetic order. These results are different from the appearance of long-range magnetic order with a higher Néel temperature in the as-sintered and non-SC *T*'-structured compound. Thus, magnetism in the as-sintered compound is somehow different between the *T** and *T*' compounds, although both show superconductivity after annealing. Differences in the local crystal structure between the two systems would be the origin of magnetism in each material.

4-4 Project workshop

To share the status of progress in individual research groups and exchange recent results, we held a two-day workshop from January 31 at IMR Tohoku University. More than twenty scientists and a couple of students attended the workshop, and they intensely discussed the genuine ground state and electronic correlation in the *T*'-structured compound. The future prospect of both neutron and muon investigations were also discussed during the evening session. The workshop program is shown below.

January 31, 2018
Opening (T. Adachi, Sophia Uni.)

Afternoon session 1 (Chair: Y. Koike, Tohoku Univ.)
■ Cu, La-NMR for T'-cuprate oxide (H. Izawa, Chiba Univ.)
■ Structural variation in electron doped high-T_c superconductor PLCCO induced by annealing (H. Kimura, Tohoku Univ.)
■ Effect of annealing on successive evolution of spin correlation in an electron doped high-T_c superconductor (K. M. Suzuki, Tohoku Univ.)
■ Effect of annealing on the Cu K-edge x-ray-absorption near-edge structure in an electron doped high-T_c superconductor (S. Asano, Tohoku Univ.)
■ Field-induced magnetism in the lightly-doped region of multi-layered cuprate

Afternoon session 2 (Chair: M. Ogata, Univ. of Tokyo)
■ Spin susceptibility in the magnetic phase (K. Kuboki, Kobe Univ.)
■ Composite excitation spectrum and Bethe hypothesis of quantum many-body systems (H. Matsueda, NIT, Sendai College)
■ Bethe hypothesis and composite excitation for Lieb-Liniger model

Night session (Chair: R. Kadono, KEK)
■ Future perspective of neutron science (M. Fujita, Tohoku Univ.)
■ Future perspective of muon science (T. Ada-

chi, Sophia Uni.)
■ Free discussion

1 Feb. 2018
Morning session (Chair: H. Yamase, NIMS)
■ Impurity-induced Mott transition (H. Yokoyama, Tohoku Univ.)
■ Effect of quasi-periodic modulation in the one dimensional topological superconducting model (T. Sugimoto, Tokyo Univ. of Science)
■ High energy spin fluctuations in $LaFePO_{1-y}$ (M. Ishikado, CROSS)
■ Renormalization of the magnetic excitation band in $Ba_{0.75}K_{0.25}Fe_2As_2$ by the electron correlation effect (N. Murai, J-PARC)

Afternoon session (Chair: M. Mori, JAEA)
■ t-t'-J model of magnetic excitation and charge stripe (T. Tohyama, Tokyo Univ. of Science)
■ Charge and spin excitations in copper oxide superconductors (K. Ishii, QST)
■ Duality in charge excitation spectra in copper oxide high temperature superconductors (H. Yamase, NIMS)
■ Observation of magnetic order in the multiferroic compound RMn_2O_5 (Y. Ishii, Tohoku Univ.)

Closing (M. Fujita, Tohoku Univ.)

The workshop has received a favorable response, and those in attendance requested that a workshop be held in the following year.

References

[1] M. Naito, S Karimoto, and A. Tsukada: Supercond. Sci. Technol. **15** (2002) 1663.
[2] T. Takamatsu, M. Kato, T. Noji, Y. Koike, Applied Physics Express, **5** (2012) 073101.
[3] H. Das and T. Saha-Dasgupta, Phys. Rev. B **79** (2009) 134522.
[4] C. Weber, K. Haule, and G. Kotilar: Nature Phys. **6** (2010) 574.
[5] M. Brinkmann, T. Rex, H. Bach, and K. Westerholt: Phys. Rev. Lett. **74** (1995) 4927.
[6] P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, J. L. Peng, and R. L. Greene: Phys. Rev. B 49 (1994) 15322, A. J. Schultz, J. D. Jorgensen, J. L. Peng, and R. L. Greene: Phys. Rev. B **53** (1996) 5157.
[7] H. J. Kang, P. Dai, B. J. Campbell, P. J. Chupas, S. Rosenkranz, P. L. Lee, Q. Huang, S. Li, S. Komiya, and Y. Ando: Nature Materials **6** (2007) 224.
[8] K. Kurahashi, H. Matsushita, M. Fujita, K. Yamada,J. Phys. Soc. Jpn. **71** (2002) 910.
[9] J. Akimitsu, S. Suzuki, M. Watanabe, and H. Sawa, Jpn. J. Appl. Phys. **27** (1988) L1859.
[10] S Asano, K M Suzuki, D Matsumura, K Ishii, T Ina, and M. Fujita, J. Phys.: Conf. Ser. **969** (2018) 012051.
[11] M. Fujita, K. M. Suzuki, S. Asano, A. Koda, H. Okabe, and R. Kadono, JPS Conf. Proc. **21** (2018) 011026.