4 Local-to-Bulk Electronic Correlation Project

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

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4-1 Background of research

After the discovery of electron-doped superconductivity in $R_{2-x}Ce_xCuO_{4-y}$ (R: Pr, Nd, Eu, …) with Nd_2CuO_4-type (abbreviated as *T*') structure [1], the electron-hole symmetry of physical properties was intensively discussed in connection with the universal mechanism of high-transition-temperature superconductivity [2]. The mother compound of electron-doped superconductor 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. However, Naito's and Koike's groups recently reported the appearance of superconductivity in thin films and low-temperature synthesized powder samples of "undoped" *T*'-R_2CuO_{4-y}, respectively [3, 4]. These experimental results suggest that the mother compound of so-called "electron-doped" superconductor is not a Mott insulator, and so a new approach to the superconducting mechanism in cuprate oxides should be studied. Subsequently, a mean field calculation of electronic structure reported that the *T*'-system can have metallic character, whereas the *T*-system is a Mott insulator [5]. Therefore, the determination of genuine ground state in *T*'-R_2CuO_{4-y} is now an important issue in the research of high-T_c superconductivity.

In real compounds, as-prepared samples of the *T*'-system are antiferromagnetic insulators over a wide Ce-doping range. The reduction annealing procedure is required to suppress AF order and the emergence of superconductivity. It was reported that the superconducting phase can expand toward zero-doping by moderate annealing [6], which is consistent with the emergence of undoped superconductivity after adequate annealing. Therefore, the role of annealing is a key to understanding the inherent nature of the undoped CuO_2 plane as well as the mechanism of superconductivity in the *T*'-structured cuprate.

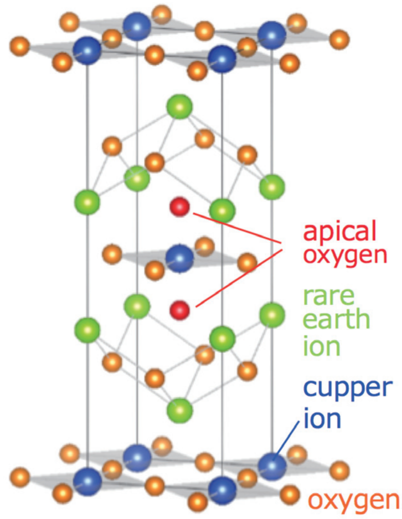

Fig. 1: Crystal structure of *T*'-$R_2CuO_{4+\delta}$. (*R*: rare earth) *T*'-structure contains a flat CuO_2 plane with the Cu in the four-coplanar coordination. Apical oxygen existing in the as-prepared sample is believed to suppress the superconductivity and be removed by annealing.

The stoichiometric *T*'-structure is characterized by the absence of apical oxygen above and below Cu sites, which is in contrast to the *T*-structured La_2CuO_4 where the Cu ion is surrounded by six oxygen ions. There are two models for 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 sites in reduced samples, suggesting that ideal *T*'-strucured compound could be realized by removing apical oxygens [7]. This result was referred to in connection with the role of

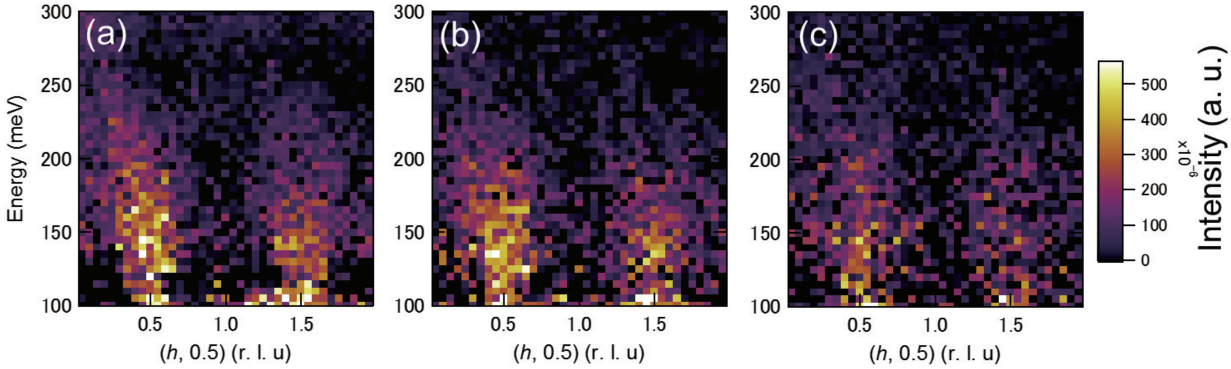

Fig. 2: Magnetic excitation spectra in annealed $Pr_{1.4}La_{0.6}CuO_4$ measured at (a) 6 K, (b) 300 K and (c) 470 K.

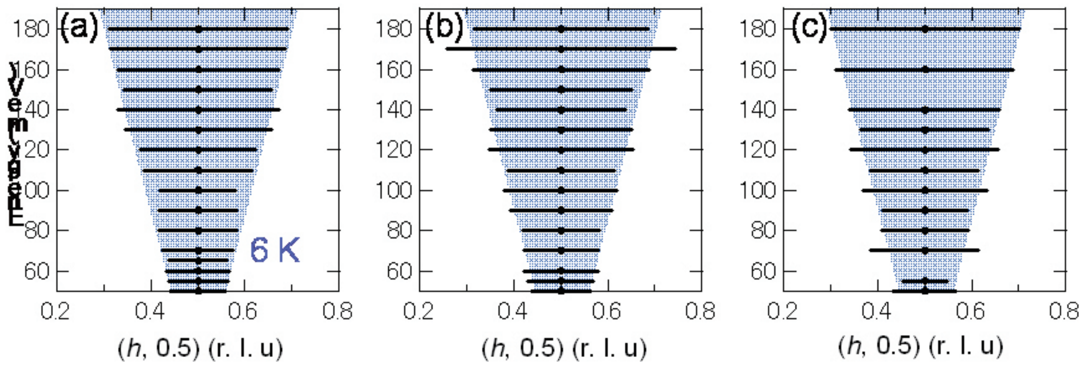

Fig. 3: The spectral shape of magnetic excitations evaluated by the analysis for (a) 6 K, (b) 300 K and (c) 470 K. Horizontal bars indicate the peak width in HWHM.

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 annealing, Kang and co-workers proposed a defect-repair model [8]. In this model, a defect of Cu in the as-prepared sample can be removed through a reconstruction of CuO_2 planes with 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-grown sample is a non-superconductor. Therefore, the common role of annealing in the structural change and in the superconducting mechanism is still under debate. Since the value of oxygen removal (~2, 3%) is small [9], it is difficult to identify clear differences in the structural parameters regarding oxygen ions between the as-sintered and annealed samples. In order to determine structural parameters and fully understand the superconducting mechanism, state-of-the-art instruments and the complementary use of quantum beams are required.

4-2 Thermal evolution of magnetic excitation

The genuine ground state of *T*'-structured cuprate oxide has attracted much attention as a new mechanism of superconductivity. In order to shed more light on this issue, we studied the thermal evolution of the spin excitation spectrum in annealed $Pr_{1.4}La_{0.6}CuO_4$ by inelastic neutron scattering measurement at HRC in J-PARC/MLF.

Figure 1 shows the excitation spectrum measured at 6 K, 300 K and 470 K. By using a large number of crystals, we succeeded in observing the excitation spectrum in a wide energy and momentum space above and below the Néel temperature T_N (~180 K). At the base temperature, dispersive excitation up to ~300 meV was observed. The dispersion relation was found to be consistent with that for La_2CuO_4 and as-grown $Pr_{1.4}La_{0.6}CuO_4$, and can be well reproduced by a simple spin-wave model with the nearest exchange coupling of ~140 meV. Even at the high temperature of 470 K, which is higher than $2T_N$, the magnetic signal remains around the zone center. Then, we fitted the energy-sliced spectrum by a single Gaussian function to evaluate the temperature dependence of spectral shape and dynamical spin susceptibility. Figure 3 shows the spectral shape at three temperatures obtained by the analysis. The peak width along the momentum direction (full-width at half-maximum) enlarges with increasing energy transfer, reflecting the outward dispersion of spin

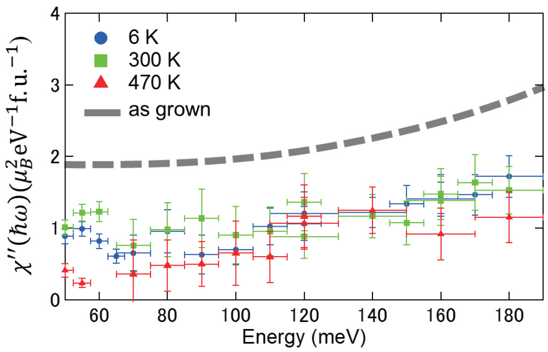

Fig. 4: Energy dependence of dynamical spin susceptibility $\chi''(\omega)$ in the annealed $Pr_{1.4}La_{0.6}CuO_4$ for 6 K, 300 K and 470 K. The dashed line corresponds to $\chi''(\omega)$ for the as-grown $Pr_{1.4}La_{0.6}CuO_4$.

wave excitation as seen in La_2CuO_4 [10]. The shapes at 300 K and 470 K are almost the same as that at 6 K. Therefore, the spectral shape is robust against the temperature even above T_N. Similarly, as seen in Fig. 4, the dynamical spin susceptibility shows negligible temperature dependence in a wide energy range below 180 meV. From these results, we conclude that the magnetic ground state is the same as that of La_2CuO_4, which is known to be a Mott insulator, in origin. The spin dynamics in the present system originate from the corrective motion of localized spins with a strong super-exchange coupling. Due to the large coupling constant (~1500 K), the thermal effect of the spin correlation could be negligible and does not affect the excitation spectrum in the measured temperature range below 470 K.

4-3 Annealing effect on spin correlations

To clarify the effects of reduction annealing on the static spin correlation, we performed muon spin rotation measurements on as-sintered and annealed Eu_2CuO_4 at the D1 beamline in J-PARC/MLF.

Figure 5(a) shows time spectra of zero-field μSR at representative temperatures for as-sintered (i.e. non-annealed) Eu_2CuO_4. At ~270 K the depolarization develops sharply, and a small fraction of an oscillation component is observed in the temperature range between 150 K and 250 K. Upon cooling, the oscillation once disappears at 150 K, and with further cooling another oscillation with the full magnetic volume fraction develops below 120 K. Figure 5(b) shows the temperature dependences of the local magnetic field at the muon site estimated from the frequencies of the

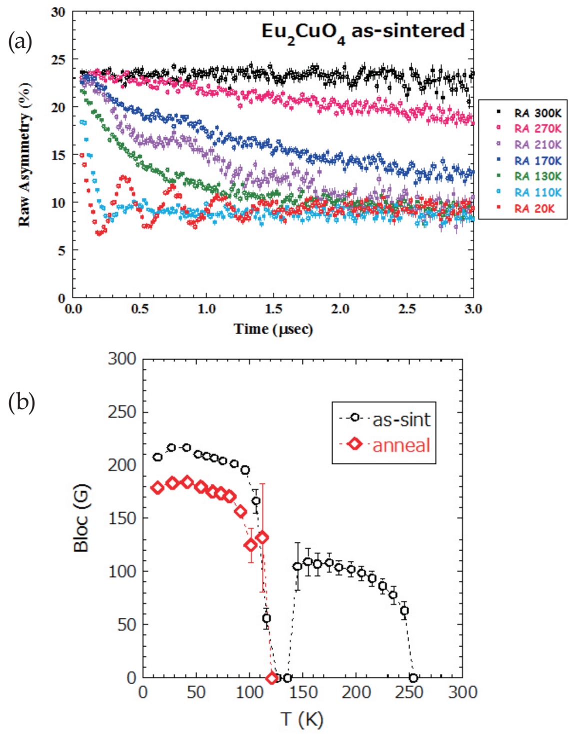

Fig. 5: (a) Zero-field μSR spectra of as-sintered Eu_2CuO_4 measured at the D1 beamline in J-PARC/MLF. (b) Temperature dependences of the local magnetic fields estimated from the frequency of the oscillation in the spectra for as-sintered and annealed Eu_2CuO_4.

oscillation. It is clearly seen that two magnetic phases develop at high and low temperatures. For the annealed Eu_2CuO_4, basically similar behavior has been observed, but clear evidence of oscillation in the high-temperature magnetic phase was not detected. The development of depolarization starts at 260 K for the annealed sample, which is slightly lower than that of the as-sintered sample. The oscillation component in the high-temperature phase of the as-sintered sample is possibly induced by a chemical defect, namely the quasi-static short-range magnetic order appears in the vicinity of defects. Thus, the existence of oscillation only in the as-sintered sample suggests the removal of defects by annealing. However, since the long-range magnetic order in two samples takes place at a similar temperature and since the magnetic moment at low temperature is comparable, the effect of chemical defects on the stability of long-range magnetic order is quite weak.

The existence of two magnetic phases is an unexpected result as it has been reported that the Néel temperature in the parent compounds of T'-structure RE_2CuO_4 is about 250–270 K. The present results suggest that the Cu spins are still

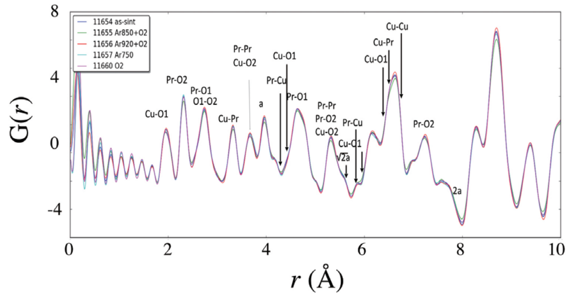

Fig. 6: Atomic pair distribution function measurement by neutron total scattering at NOVA on as-prepared and annealed Pr_2CuO_4.

fluctuating below 250 K with the two-dimensional magnetic correlation in the plane and finally form a three-dimensional order below ~120 K.

4-4 Local structure

We tried to detect differences in the local structure of as-sintered and annealed samples with different Ce concentrations by neutron total scattering measurement at NOVA in J-PARC/MLF.

Figure 6 shows the atomic pair distribution function obtained for as-prepared and annealed Pr_2CuO_4 measured at room temperature. The samples were prepared under different annealing conditions to control the oxygen content. The reduced oxygen content was estimated from the weight loss of the sample and the value was in the range of 0–0.04. As seen in the figure, the preliminary analysis showed a negligible difference in the pair distribution function in all samples. This means that the local structure as well as the bulk structure are not influenced markedly by annealing. For further investigation, we plan to take measurements at low temperature.

4-5 Project meeting

To share the state of progress in individual research groups and exchange information on recent results, we held a meeting on March 24th, 2017 at KEK/CMRC, Tokai campus.

The meeting started with the opening address and introduction of projects by Prof. Fujita (Tohoku Univ.). In the scientific session, he then discussed the possible ground state of the mother compound from the thermal evolution of magnetic excitations in both as-grown and annealed $Pr_{1.4}La_{0.6}CuO_4$.

Prof. Kimura (Tohoku Univ.) presented the results of a structural study done with precise single crystal X-ray diffraction measurement on Pr_2CuO_4

Fig. 7: Pictures of CMRC meeting held on March 25th at KEK/CMRC, Tokai Campus.

and Nd_2CuO_4. Comparing the detailed structure of annealed Pr_2CuO_4 prepared under different annealing conditions with that for as-grown Pr_2CuO_4, he explained that the change in the structural parameters could be induced by a relaxation of local stress through annealing. It was also reported that a significant annealing effect can be seen on the rare earth positions for Pr_2CuO_4, but not for Nd_2CuO_4.

The possible scenario of undoped superconductivity was introduced by Prof. Adachi (Sophia Univ.), who presented the recent development of sample preparation and the results of systematic μSR measurements.

The superconducting properties and possible non-doped superconductivity in thin films of an infinite-layer system were introduced by I. Ikeda (NTT/BRL). Oxygen vacancies would be the reason for the suppression of superconductivity in this system, in contrast to the discussion of excess oxygen for superconductivity in the *T*'-system.

Next, the phonon anomaly in Mn-doped $SrTiO_3$, which has attracted attention as a thermoelectric material, was reported by Prof. Kajimoto from the viewpoint of bulk phenomena induced by variation of local structure. Finally, a theoretical study on the coexistence of magnetic order and superconductivity in the hole-doped system was presented by Prof. Yamase.

Acknowledgements

In this project, two new collaborations have been started, and a project meeting with members provided the opportunity for exchange of information. We thank KEK/CMRC staff for their support with holding the meetings.

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