Crystal Growth and Neutron Scattering Study of Spin Correlations of the T'-Structured Pr$_{2-x}$Ca$_x$CuO$_4$

Masaki Fujita
Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan

Kenji Tsutsumi, Tomohiro Miura
Department of Physics, Tohoku University, Sendai, Miyagi 980-8578, Japan

Sergey Danilkin
Bragg Institute, ANSTO, Locked Bag 2001, Kirrawee DC NSW 2232, Australia
E-mail: fujita@imr.tohoku.ac.jp

Abstract. We studied Ca-doping effect on spin correlations in T' -structured cuprate oxide RE$_2$CuO$_4$ (RE: rear earth) with growing a sizable single crystal of Pr$_{1.95}$Ca$_{0.05}$CuO$_4$ as well as synthesizing powder samples of Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ and Eu$_{1.90}$Ca$_{0.10}$CuO$_4$. In the all as-prepared and annealed samples, no evidence of shielding signal associated with superconductivity was observed by magnetic susceptibility measurement. Elastic neutron scattering measurements on the as-grown Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ clarified the existence of long-ranged magnetic order with commensurate spin correlation. The ordering temperature was determined to be 290K, which is comparable to Néel temperature in the parent compound of Pr$_2$CuO$_4$. The existence of commensurate low-energy spin excitation was also confirmed by inelastic neutron scattering measurements for the annealed Pr$_{1.95}$Ca$_{0.05}$CuO$_4$. These results strongly suggest a negligible Ca-doping effect on the physical properties in T'-RE$_2$CuO$_4$, which is quite different from the drastic doping evolution of magnetism in T'-RE$_2$CuO$_4$.

1. Introduction

High transition temperature (high-$T_c$) superconductivity in cuprate oxide emerges with doping of either types of carrier into an antiferromagnetically ordered Mott insulator. In the RE$_2$CuO$_4$ (RE: rear earth) system, which has a simple crystal structure, the electron-hole symmetry of magnetism has been intensively studied in connection with a common mechanism of superconductivity. In La$_2$CuO$_4$ having distorted K$_2$NiF$_4$-type (T) crystal structure, long-ranged antiferromagnetic (AFM) order is destroyed by a small amount of hole-doping, while that in Nd$_2$CuO$_4$-type (T') structured RE$_2$CuO$_4$ (RE=Pr, Nd, Pm, Sm, Gd) with no apical oxygen is quite robust against electron-doping [1]. In both systems, AFM spin fluctuations remain in the superconducting (SC) phase, indicating a common relation between the spin correlations and the superconductivity. However, a recent muon spin rotation/relaxation experiment on T'-La$_2$CuO$_4$ showed that Néel temperature ($T_N$) is much lower than that in T'-La$_2$CuO$_4$ [2], implying that the crystal structure is an important factor to determine the physical properties. Furthermore, in the electron-doped T'-system, the as-grown sample does not show superconductivity and an
adequate annealing procedure is required for the emergence of superconductivity, while the as-grown hole-doped \( T' \)-system undergoes the superconducting (SC) transition. Thus, the study of physical properties in a system with identical crystal structure is required to clarify the genuine electron-hole symmetry.

Tsukada et al. first achieved Ce-doping into thin film of \( T' \)-La\(_2\)CuO\(_4\), which is never succeeded for bulk sample, and reported the resistivity in samples with different Ce concentrations [3]. They claimed a breaking down of electron-hole symmetry at zero doping from the enhancement of insulating nature by Ce doping. Furthermore, Segawa et al. reported a different stacking pattern of AFM layers in hole and electron sides of \( Y_{1-x}La_x(Ba_{1-x}La_x)_2Cu_3O_y \) [4]. Recently, the abrupt drop of \( T_N \) in the film of \( T' \)-La\(_{2-x}\)Ce\(_x\)CuO\(_4\) similar to the sharp phase boundary of three-dimensional magnetic order in \( T' \)-La\(_{2-x}\)Sr\(_x\)CuO\(_4\) [5] and even the appearance of superconductivity in the \( T' \)-La\(_{1.8-x}\)Eu\(_{0.2}\)Sr\(_x\)CuO\(_4\) [6] have been reported. Although these results are attractive for the study of electron-hole symmetry in the identical crystal structure, no systematic study of spin fluctuation on these compounds has been done, due to the difficulties in the availability of large sample and/or in the sufficient carrier doping for both electron and hole sides.

In order to make progress on this issue, we have explored the adequate system of which sizable single crystal can be available. In this paper, we report the result of crystal growth of hole-doped \( T' \)-system and the first neutron scattering measurement of Pr\(_{2-x}\)Ca\(_x\)CuO\(_4\).

2. Experimental Details and Results

2.1. Sample preparation

For the study of electron-hole symmetry of magnetism, we selected \( T' \)-RE\(_2\)CuO\(_4\) (RE: rare earth) and attempted the hole-doping by substituting bivalent ion such as Ca\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\) for RE\(^{3+}\) ion. Although there are few reports which show the phase stability of \( T' \)-(Pr,Nd)\(_{2-x}\)(Ca,Sr)\(_x\)CuO\(_4\) for small \( x \) [7], no physical properties were so far obtained for single crystal. Therefore, we have made efforts to grow a sizable single crystal with the aim of performing the neutron scattering study of spin correlations. We first prepared the powder sample of Pr\(_{2-x}\)Ca\(_x\)CuO\(_4\) and Eu\(_{2-x}\)Ca\(_x\)CuO\(_4\) by a standard solid-state reaction. The appropriate ratio of dried Pr\(_6\)O\(_{11}\), Eu\(_2\)O\(_3\), CaCO\(_3\), and CuO powders were mixed and sintered at 900 °C for 12 hour with a couple of intermediate re-grindings. Then, we applied a traveling-

![Figure 1. X-ray powder diffraction pattern of \( T' \)-structured Pr\(_2\)CuO\(_4\), Pr\(_{1.90}\)Ca\(_{0.10}\)CuO\(_4\) and Eu\(_{1.90}\)Ca\(_{0.10}\)CuO\(_4\).](image-url)
solvent floating-zone method to grow the single crystal of Pr$_{2-x}$Ca$_x$CuO$_4$ with $x = 0.05$ and 0.10. The growth condition is almost the same as that for La$_{2-x}$Sr$_x$CuO$_4$ [8]. The single crystal of Pr$_2$CuO$_4$ and and pressed powder of CuO were used as the seed rod and the solvent, respectively. The grown crystalline rod is columnar in the shape with length of $\sim$100 mm and diameter of $\sim$6 mm.

2.2. Sample characterization

The actual concentrations of Pr, Ca and Cu in the single crystal were confirmed to be the same as nominal ones by inductively-coupled plasma. We checked the phase purity of samples by X-ray powder diffraction measurement. In Fig. 1, the diffraction pattern for powder sample of Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ and Eu$_{1.90}$Ca$_{0.10}$CuO$_4$ is shown together with Ca-free Pr$_2$CuO$_4$. For the clear visualization, the result for Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ and Pr$_2$CuO$_4$ is shifted along the vertical direction. Similar to the result of Pr$_2$CuO$_4$, all reflections in Ca-doped samples can be labeled in the I4/mmm symmetry, indicating that the single phased sample is successfully obtained. The evaluated in-plane (a) and out-plane (c) lattice constants are 3.949 Å and 12.20 Å for Pr$_{1.90}$Ca$_{0.10}$CuO$_4$, and 3.900 Å and 11.90 Å for Eu$_{1.90}$Ca$_{0.10}$CuO$_4$, respectively. The identical results were obtained for the powdered single crystal of Pr$_{1.90}$Ca$_{0.10}$CuO$_4$. The mosaic spread ($\theta_M$) of crystal was checked by neutron scattering. We confirmed that the width of Bragg peak is the resolution limited value, corresponding to $\theta_M$ less than 0.2° in angle unit. From these results, we conclude that a high-quality single crystal of hole-dope $T'$-Pr$_{2-x}$Ca$_x$CuO$_4$ was successfully obtained for the first time.

In order to examine whether the post-annealing affects superconductivity or induces superconductivity, single crystal of Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ was annealed under oxidizing and deoxidizing conditions; (i) annealing under oxygen gas flow at 900 °C for 24 hours and (ii) annealing under argon gas flow at 900 °C for 10 hours. The variation of oxygen contents in molar ratio, which was evaluated from the weight change by annealing, was $<0.01$ (oxygen gain) and $\sim0.07$ (oxygen loss) for conditions (i) and (ii), respectively. The magnetic susceptibility ($\chi$) was measured for all as-prepared and annealed samples by a SQUID magnetometer. Figure 2 shows

![Figure 2](image-url)

Figure 2. Magnetic susceptibility of $T'$-Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ and $T'$-Eu$_{1.90}$Ca$_{0.10}$CuO$_4$ measured at 10 Oe after zero-field-cooling process. No evidence of superconducting transition was detected in these samples. For the comparison, our result for superconducting $T$-La$_{1.90}$Ca$_{0.10}$CuO$_4$ is shown.
the temperature dependence of $\chi$ of the as-grown samples measured under the magnetic field of 10 Oe after zero-field cooling process. As seen in the figure, no evidence of superconductivity was observed in the $T'_1$-$Pr_{1.90}Ca_{0.10}CuO_4$, while $\chi$ for the $T$-$La_{1.90}Ca_{0.10}CuO_4$ shows a shielding signal below $\sim$15 K. Qualitatively the same result was obtained for both oxygen-annealed and argon-annealed $T'_1$-samples. Therefore, the emergence of superconductivity in the hole-doped system strongly depends on the crystal structure.

### 2.3. Neutron scattering measurement

Absence of superconductivity in the Ca substituted system implies the existence of competing magnetic order at low temperature. The nature of spin correlation, namely commensurate or incommensurate, is important to be clarified for understanding the relation between the magnetism and superconductivity. We, therefore, carried out neutron scattering, which is a momentum selective method, on the single crystal of $Pr_{2-x}Ca_xCuO_4$. The elastic and inelastic measurements were done with using triple-axis spectrometer ANAKE installed at the JRR-3 research reactor in Japan Atomic Energy Agency and TAIPAN at Bragg Institute in Australian Centre for Neutron Scattering, respectively. The incident (final) energy of neutron was fixed to be 19.6 meV (14.7 meV) at ANAKE (TAIPAN) and the sample was mounted so that [1 0 0] and [0 0 1] orthorhombic crystalline directions are in the horizontal scattering plane. Note that in this paper we use the orthorhombic notation following the previous works for $T'_1$-$RE_{2-x}Ce_xCuO_4$ [citeKeimer92]. In this notation, (1 0 1) corresponds to the magnetic Bragg positions in the pristine $Pr_2CuO_4$.

Figure 3(a) shows the profile of elastic neutron scattering from $Pr_{1.90}Ca_{0.10}CuO_4$ crystal. Scan was done along [1 0 0] direction through (1 0 1). At low temperature, clear magnetic Bragg peak with the resolution-limited width was observed, indicating the existence of long-ranged AFM order as observed in non-doped $Pr_2CuO_4$. The temperature dependence of normalized peak-intensity is plotted in Fig. 3(b). Upon cooling, the intensity starts to develop at $\sim$290 K, which is the same as $T_N$ in $Pr_2CuO_4$.

To see the dynamical spin correlations, we measured the magnetic excitations in the annealed
Pr$_{1.95}$Ca$_{0.05}$CuO$_4$ up to 11 meV. The observed spectra for 3, 8 and 11 meV are shown in Fig. 3(c). In the measured energy region, a single peak center at (1 0 1) was detected, meaning that commensurate correlation is robust against the energy transfer. These results strongly suggest that the bulk magnetism is not affected by Ca-doping at least for $x \leq 0.1$. The negligible Ca-doping effect on magnetism is quite contrastive to the quick drop of $T_N$ by hole-doping in the $T'$-structured system.

3. Discussion

Here, we discuss the origin of robust spin correlations against chemical doping and absence of superconductivity in the $T'$-RE$_2$CuO$_4$. In the electron-doped $T'$-RE$_{2-x}$Ce$_x$CuO$_4$, superconductivity emerges after the suppression of AFM order by reduction annealing. The removal of apical oxygen partially existing in the as-prepared sample is considered to be crucial for the appearance of superconductivity in $T'$-RE$_{2-x}$Ce$_x$CuO$_4$ [9]. In the present $T'$-system, both as-prepared and reduction annealed samples are non-superconductor. Thus, the existence of apical oxygen would not be the reason for emergence of commensurate spin correlations and absence of superconductivity. They would be intrinsic natures of $T'$-RE$_{2-x}$Ce$_x$CuO$_4$.

One possible explanation for the persistence of long-ranged magnetic order is that the mobile carrier is not effectively doped by Ca-substitution. In YBa$_2$CuO$_{7-\delta}$ (YBCO), Pr-substitution induces a remarkable suppression of superconductivity, and the hybridization of Pr 4f and O 2p orbitals is considered to be the origin of hole-localization [10]. Therefore, one may think that similar hole-trapping effect by Pr ions results into the robust AFM ordered phase. If only the Pr ion among the rear earth ions causes the hole-localization, we could expect the appearance of superconductivity in the other 4f ions-based $T'$-RE$_2$CuO$_4$ by Ca substitution. However, the present experimental fact showing that Eu$_{1.90}$Ca$_{0.10}$CuO$_4$ does not shows superconductivity is inconsistent with the above scenario. Thus, the orbital-hybridization is not the dominant factor for the persistence of AFM order against Ca(Sr)-doping. Another possible reason is that the hopping of holes within a CuO$_2$ plane is restricted due to the weak overlaps of Cu 3d and O 2p orbitals. The in-plane lattice constant in the present system is larger than that in $T$-RE$_2$CuO$_4$, resulting into the weaker overlaps of orbitals in $T'$-system. Since the mobility of holes is related with the reduction of $T_N$ [11], no increase of mobility leads the unchanged $T_N$. In this context, by applying chemical and/or physical pressures, the mobility of holes could be enhanced by the greater overlaps of orbitals. As a result, AFM order expected to degrade analogous to the case of $T$-LSCO.

We believe that further systematic studies of spin correlations for hole-doped Pr$_{2-x}$Ca$_x$CuO$_4$ combined with that for La$_{2-x}$Sr$_x$CuO$_4$ and electron-doped Pr$_{2-x}$Ce$_x$CuO$_4$ provides an important opportunity to clarify not only the common hole-doping effect on the spin correlations but also the genuine electron-hole symmetry of physical properties regardless of the crystal structure.

Summary

We obtained the single phase of $T'$-structured Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ and Eu$_{1.90}$Ca$_{0.10}$CuO$_4$ by a solid-state reaction and succeed in growing the single crystal of Pr$_{2-x}$Ca$_x$CuO$_4$ with $x=0.05$ and 0.10 for the first time. Magnetic susceptibility measurement clarified the absence of superconductivity in all as-grown and annealed samples. Elastic neutron scattering measurement showed the development of long-ranged AFM order in as-grown Pr$_{1.90}$Ca$_{0.10}$CuO$_4$ below ~290K. The inelastic magnetic signal was also confirmed at the commensurate (0.5, 0.5, 0) reciprocal position, as is the case for the parent Pr$_2$CuO$_4$. These results are quite different from the drastic doping evolution of superconductivity and magnetism in $T$-La$_{2-x}$Sr$_x$CuO$_4$, indicating a contrasting Ca doping effect on the physical properties in $T'$ and $T$ systems.
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