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Crystal Growth and Neutron Scattering Study of Spin Correlations of the T′-Structured $Pr_{2-x}Ca_xCuO_4$

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Abstract. We studied Ca-doping effect on spin correlations in T'-structured cuprate oxide RE_2CuO_4 (RE: rear earth) with growing a sizable single crystal of $Pr_{2-x}Ca_xCuO_4$ (x=0.05 and 0.10) 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_2CuO_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_2CuO_4, which is quite different from the drastic doping evolution of magnetism in T-RE_2CuO_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_2CuO_4 (R: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_2CuO_4 having distorted K_2NiF_4-type (T) crystal structure, long-ranged antiferromagnetic (AFM) order is destroyed by a small amount of hole-doping, while that in Nd_2CuO_4-type (T') structured RE_2CuO_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_2CuO_4 showed that Néel temperature (T_N) is much lower than that in T-La_2CuO_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_2CuO_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 $Y_{1-z}La_z(Ba_{1-x}La_x)_2Cu_3O_y$ [4]. Recently, the abrupt drop of T_N in the film of T'-$La_{2-x}Ce_xCuO_{4-\delta}$ similar to the sharp phase boundary of three- dimensional magnetic order in T-$La_{2-x}Sr_xCuO_4$ [5] and even the appearance of superconductivity in the T'-$La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ [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 $Pr_{2-x}Ca_xCuO_4$.

2. Experimental Details and Results

2.1. Sample preparation

For the study of electron-hole symmetry of magnetism, we selected T'-RE_2CuO_4 (RE: rear 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'-$(Pr,Nd)_{2-x}(Ca,Sr)_xCuO_4$ 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 $Pr_{2-x}Ca_xCuO_4$ and $Eu_{2-x}Ca_xCuO_4$ by a standard solid-state reaction. The appropriate ratio of dried Pr_6O_{11}, Eu_2O_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-

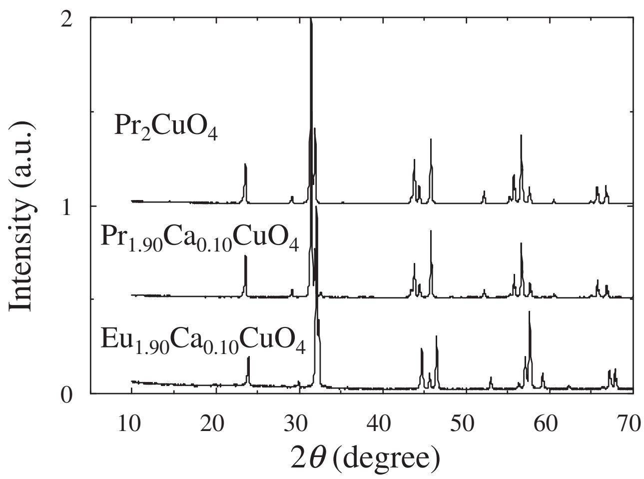

Figure 1. X-ray powder diffraction pattern of T'-structured Pr_2CuO_4, $Pr_{1.90}Ca_{0.10}CuO_4$ and $Eu_{1.90}Ca_{0.10}CuO_4$.

solvent floating-zone method to grow the single crystal of $Pr_{2-x}Ca_xCuO_4$ with $x = 0.05$ and 0.10. The growth condition is almost the same as that for $La_{2-x}Sr_xCuO_4$ [8]. The single crystal of Pr_2CuO_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 ∼100 mm and diameter of ∼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_2CuO_4. For the clear visualization, the result for $Pr_{1.90}Ca_{0.10}CuO_4$ and Pr_2CuO_4 is shifted along the vertical direction. Similar to the result of Pr_2CuO_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 (θ_M) of crystal was checked by neutron scattering. We confirmed that the width of Bragg peak is the resolution limited value, corresponding to θ_M less than 0.2° in angle unit. From these results, we conclude that a high-quality single crystal of hole-dope T'-$Pr_{2-x}Ca_xCuO_4$ 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 ∼0.07 (oxygen loss) for conditions (i) and (ii), respectively. The magnetic susceptibility (χ) was measured for all as-prepared and annealed samples by a SQUID magnetometer. Figure 2 shows

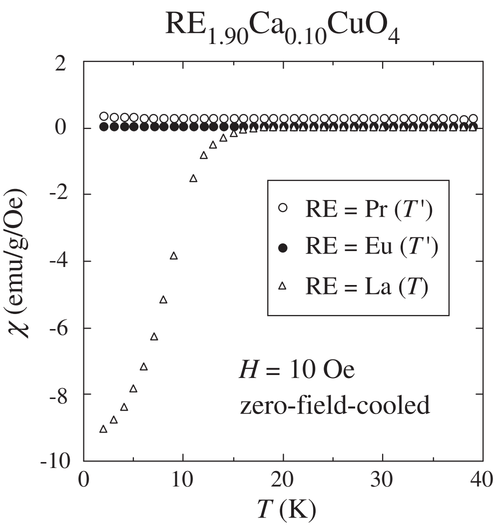

Figure 2. Magnetic susceptibility of T'-$Pr_{1.90}Ca_{0.10}CuO_4$ and T'-$Eu_{1.90}Ca_{0.10}CuO_4$ measured at 10 Oe after zero-field-cooling process. No evidence of superconducting transition was detected in these samples. For the comparison, our result for superconducting T-$La_{1.90}Ca_{0.10}CuO_4$ is shown.

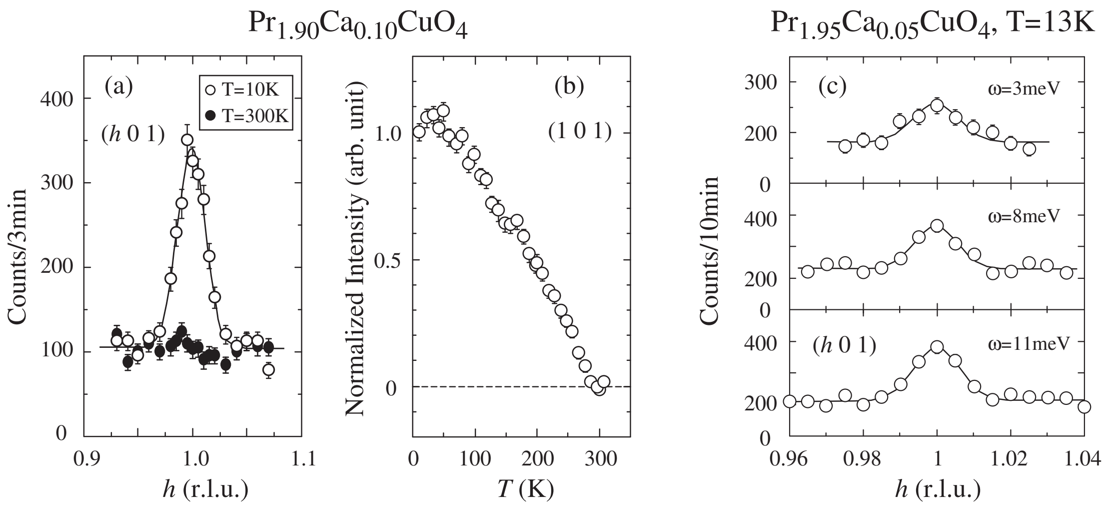

Figure 3. (a) Magnetic peak profile measured at 10K and 300K in the as-grown T'-$Pr_{1.90}Ca_{0.10}CuO_4$. (b) Temperature dependence of normalized peak-intensity at (1 0 1). (c) Inelastic neutron scattering spectra for annealed $Pr_{1.95}Ca_{0.05}CuO_4$ measured at 13 K and at 3, 8 and 11 meV.

the temperature dependence of χ 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'-$R_{1.90}Ca_{0.10}CuO_4$, while χ for the T-$La_{1.90}Ca_{0.10}CuO_4$ shows a shielding signal below ∼15 K. Qualitatively the same result was obtained for both oxygen-annealed and argon-annealed T'-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 AKANE (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'-$RE_{2-x}Ce_xCuO_4$ /citeKeimer92. In this notation, (1 0 l) 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 ∼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_2CuO_4. In the electron-doped T'-$RE_{2-x}Ce_xCuO_4$, 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'-$RE_{2-x}Ce_xCuO_4$ [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'-$RE_{2-x}Ce_xCuO_4$.

One possible explanation for the persistence of long-ranged magnetic order is that the mobile carrier is not effectively doped by Ca-substitution. In $YBa_2CuO_{7-\delta}$ (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_2CuO_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_2CuO_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 $Pr_{2-x}Ca_xCuO_4$ combined with that for $La_{2-x}Sr_xCuO_4$ and electron-doped $Pr_{2-x}Ce_xCuO_4$ 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 $Pr_{2-x}Ca_xCuO_4$ 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_2CuO_4. These results are quite different from the drastic doping evolution of superconductivity and magnetism in T-$La_{2-x}Sr_xCuO_4$, indicating a contrasting Ca doping effect on the physical properties in T' and T systems.

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