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Novel In-Gap Spin State in Zn-Doped $La_{1.85}Sr_{0.15}CuO_4$

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Low-energy spin excitations of $La_{1.85}Sr_{0.15}Cu_{1-y}Zn_yO_4$ were studied by neutron scattering. In $y = 0.004$, the incommensurate magnetic peaks show a well-defined "spin gap" below T_c. The magnetic signals at $\omega = 3$ meV decrease below $T_c = 27$ K for $y = 0.008$, also suggesting the gap opening. At lower temperatures, however, the signal increases again, implying a novel *in-gap* spin state. In $y = 0.017$, the spin gap vanishes and elastic magnetic peaks appear. These results clarify that doped Zn impurities induce the novel in-gap state, which becomes larger and more static with increasing Zn.

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It is widely accepted that the antiferromagnetism on a hole-doped CuO_2 plane in lamellar copper oxides is relevant to the high-T_c superconductivity. Therefore, a complete description of the interplay between the spin correlations and the dynamics of doped holes is indispensable to clarify the high-T_c mechanism.

The momentum and energy structure of antiferromagnetic (AF) spin correlations on the CuO_2 plane in $La_{2-x}Sr_xCuO_4$ (LSCO), which is a prototypical high-T_c superconductor, have been extensively studied by neutron scattering [1]. The spin excitations of the superconducting LSCO exhibit a quartet of peaks at the incommensurate wave vectors $Q_\delta = (\frac{1}{2} \pm \delta\ \frac{1}{2}\ 0), (\frac{1}{2}\ \frac{1}{2} \pm \delta\ 0)$ in the high temperature tetragonal (HTT) notation [2], and there exists a linear relation between δ and T_c in the underdoped region ($x \leq 0.15$) [3]. Neutron scattering studies have also revealed a well-defined gap on spin excitation spectra, often called "spin gap," in LSCO [4–6] and $YBa_2Cu_3O_{7-\delta}$ (YBCO) [7,8] around the optimally doped concentrations. Although the interrelations between the superconducting gap in the electronic state and the spin gap are not completely understood, the results of the neutron scattering studies indicate a strong relevance of the q, ω-dependent spin excitations to the superconductivity and have contributed to the development of theoretical frameworks such as the *stripe* model [9] and the *fermiology* [10]. However, the microscopic nature of spin correlations and their contributions to the high-T_c pairing mechanism still remain open questions.

A small amount of doped Zn^{2+} ions, substituting for Cu^{2+} ions, strongly suppresses the superconductivity [11]. In addition, NMR studies [12,13] have revealed that a Zn impurity induces staggered magnetic moments on Cu sites around the impurity, indicating that Zn doping strengthens AF spin correlations on the CuO_2 plane. Neutron scattering studies have also revealed a drastic change in the low-energy spin dynamics: In Zn-free $La_{1.86}Sr_{0.14}CuO_4$, a gaplike nature has been confirmed below $T_c = 33$ K [14], while the low-energy spin excitations survive even below $T_c = 19$ K in $La_{1.86}Sr_{0.14}Cu_{0.988}Zn_{0.012}O_4$ [15]. Furthermore, the spin correlations become static while the incommensurate wave vector stays at Q_δ [16]. Some recent theories concluded that the local antiferromagnetism is induced around nonmagnetic impurities, where the superconductivity is locally suppressed [17,18]. These facts indicate the importance of microscopic coexistence and competition between the superconductivity and the AF order.

A comprehensive neutron scattering study of the AF spin correlations in Zn-doped $La_{1.85}Sr_{0.15}CuO_4$ single crystals was performed to elucidate how the spin-gap state is broken and how the AF correlations are induced by Zn doping. To obtain quantitative information about the Zn-doping dependence of spin excitation spectra, it is essential to control the Zn-doping rate accurately. Furthermore, large and spatially homogeneous crystals are required because of the weak magnetic signals. We have overcome such difficulties by combining an improved traveling-solvent-floating-zone (TSFZ) method [19] and a quantitative analysis of Zn impurities using the inductively coupled plasma (ICP) method. The structural properties (size, shape, mosaicness, etc.) were also unified for all the samples so that the spin excitation spectra can be quantitatively compared among different samples.

Single crystals were grown by the TSFZ method. The studied samples ($\sim 1\ \mathrm{cm}^3$) were cut from the single crystal rods and properly annealed to eliminate oxygen deficiencies. The concentrations of Zn, Sr, and Cu ions were precisely determined at several different points of each sample by a state-of-the-art ICP system (Shimadzu ICPS-7500), showing that Sr and Zn ions are doped homogeneously into the crystals. The obtained concentrations are listed in Table I. T_c was determined from the shielding signal as a function of temperature using a SQUID magnetometer, which is in good agreement with those of previous studies [11] for all the samples (see Table I). The structural phase transition temperature T_{d1} from the HTT to low-temperature orthorhombic phases was determined by neutron diffraction. Note that T_{d1} is

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TABLE I. Sr and Zn concentrations determined by ICP analysis and T_c measured by SQUID. $R_{\text{Zn-Zn}}$ denotes the mean distance between nearest-neighbor Zn atoms.

Sample	Sr x	Zn y	T_c	$R_{\text{Zn-Zn}}$
$y = 0$	0.143(3)	$\cdots$	37 ± 1 K	$\cdots$
$y = 0.004$	0.146(4)	0.004(1)	33 ± 1 K	60 ± 7 Å
$y = 0.008$	0.147(4)	0.008(1)	28 ± 1 K	42 ± 3 Å
$y = 0.017$	0.147(4)	0.017(1)	16 ± 2 K	29 ± 1 Å

quite sensitive to the Sr concentration. The obtained values are identical for all the samples ($\simeq$ 185 K) and consistent with that of Zn-free LSCO at $x = 0.15$ [4]. The results indicate that the Sr concentration is exactly $x = 0.15$ and that the Zn impurities do not affect the averaged crystal structure.

Neutron scattering experiments were performed on the Tohoku University triple axis spectrometer (TOPAN) installed at JRR-3M in Japan Atomic Energy Research Institute. The initial and final neutron energies were tuned by the pyrolytic graphite (PG) monochromator and fixed at 13.5 meV by the PG analyzer. A one-inch-thick PG filter was inserted in the scattered beam to eliminate higher-order contaminations. An additional PG filter was put in the incident beam for studying the elastic peaks. We mounted all the crystals in the ($hk0$) zone and defined the reciprocal lattice unit (rlu) in the HTT notation. To normalize the data, we have utilized the acoustic phonons measured under the fixed condition because phonon intensity is considered proportional to the effective volume of a sample.

Figures 1(a) and 1(b) show q-scan profiles at $\omega = 3$ meV for $y = 0.004$ and $y = 0.008$, taken at 10–12 K (open circles) and just above T_c (closed circles). The scan trajectory is depicted in the inset of Fig. 1(b). Above T_c, the spin excitations have peaks at Q_δ with $\delta \sim 0.12$ for both the samples. At 12 K, which is well below T_c, the signal vanishes for $y = 0.004$, implying the opening of the spin gap, while the intensity still remains at Q_δ for $y = 0.008$. Energy spectra of the q-integrated dynamical spin susceptibility $\chi''(\omega)$ around 10 K are plotted in Figs. 2(a)–2(c) for $y = 0.004$, 0.008, and 0.017. The open diamonds and the solid lines in the figures denote $\chi''(\omega)$ for $y = 0$. All the data are corrected with the thermal population factor and normalized by the acoustic phonon. It is remarkable that $\chi''(\omega)$ for all the samples have a maximum and almost identical intensity around $\omega = 8$ meV while $\chi''(\omega)$ below 8 meV develops with increasing doped Zn. These systematic changes cannot be explained by either a simple broadening of the gap structure or a simple reduction of the gap energy in a homogeneous superconducting state because both cases should be associated with the variation of $\chi''(\omega)$ near the gap energy. For example, in the case of the gap broadening, the spectral weight just below the gap energy should increase while the weight above the gap energy decreases. Therefore, these energy spectra indicate that

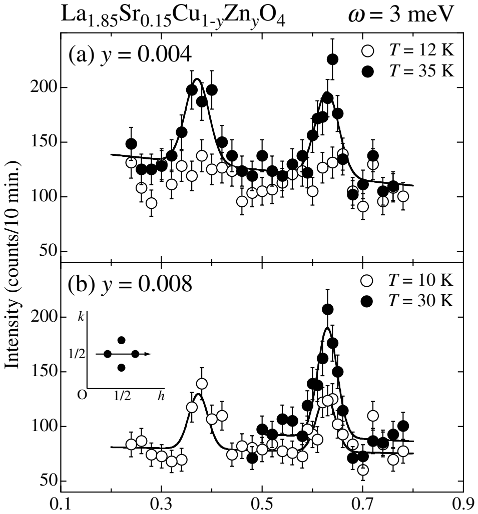

FIG. 1. q profiles along the h direction through (π, π) at the transfer energy $\omega = 3$ meV for (a) $y = 0.004$ and (b) $y = 0.008$ below (open circles) and above (solid circles) T_c.

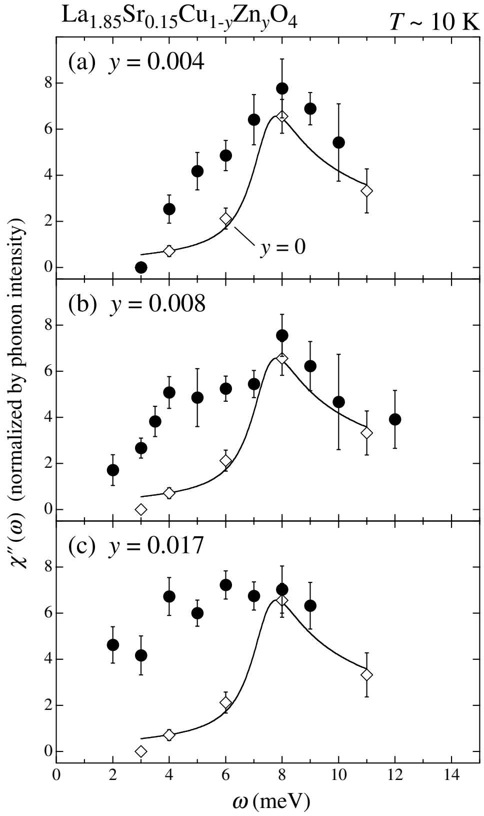

FIG. 2. Energy dependence of the q-integrated $\chi''(\omega)$ for (a) $y = 0.004$, (b) $y = 0.008$, and (c) $y = 0.017$ around 10 K. Open diamonds in all the figures denote the data for $y = 0$, which are fitted with a phenomenological dynamical spin susceptibility (solid lines) introduced in Ref. [6].

Zn doping induces an *additional* spin excitation in the spin gap below $\omega \sim 8$ meV and that, with further Zn doping, the novel spin excitation is enhanced and shifts to lower energies, i.e., becomes more static.

The additional spin excitations are also seen in the temperature dependence of the $\chi''(\omega)$ at $\omega = 3$ meV [χ'' (3 meV)]. The results are summarized in Figs. 3(a)–3(c), showing a systematic variation of the spin excitations as a function of Zn doping. In $y = 0.004$, χ'' (3 meV) starts decreasing below T_c and goes to zero around 10 K, corresponding to the evolution of spin-gap state. The χ'' (3 meV) of $y = 0.008$ exhibits an interesting temperature dependence: As temperature is reduced, the χ'' (3 meV) once decreases around T_c, which suggests the gap opening, but then increases *again* below ~20 K. The low-temperature upturn indicates that the additional spin excitations develop with decreasing temperature. As shown in Fig. 3(c), χ'' (3 meV) for $y = 0.017$ is almost temperature independent around T_c, which is qualitatively consistent with the result of $La_{1.86}Sr_{0.14}Cu_{0.988}Zn_{0.012}O_4$ [15], and suggests a complete vanishing of the spin-gap state.

Elastic scattering experiments were performed for $y = 0.008$ and $y = 0.017$ to investigate static spin correlations. In $y = 0.008$, no signal was detected down to $T = 1.5$ K while, in $y = 0.017$, sharp elastic peaks were observed below ~20 K at the same incommensurate wave vector Q_δ as observed in the inelastic scattering measurements. Figure 4 shows temperature dependence of the elastic peak intensity for $y = 0.017$. The inset shows the q profile at 1.5 K with the 40 K data subtracted as background. An in-plane spin correlation length is estimated at ~80 Å, which was obtained from the intrinsic linewidth of the $y = 0.017$ peak profile. The results for $y = 0.008$ and $y = 0.017$ suggest that the novel spin state in $y = 0.008$ is purely dynamical and becomes more static with increasing Zn doping.

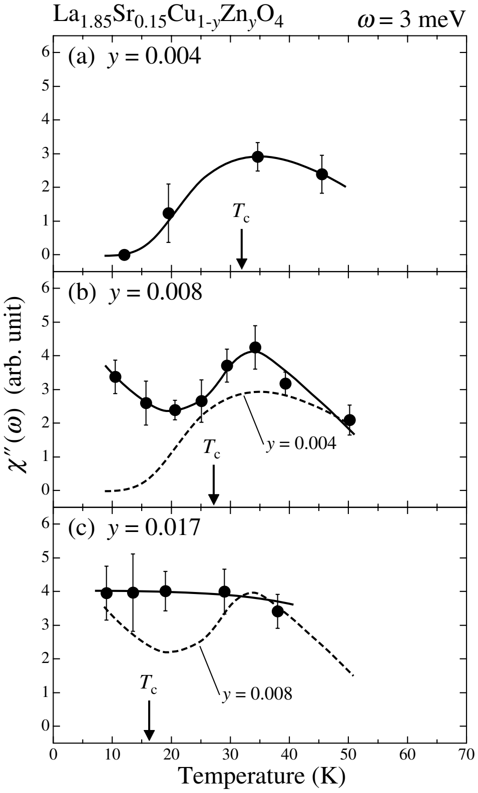

FIG. 3. Temperature dependence of the q-integrated χ'' (3 meV) for (a) $y = 0.004$, (b) $y = 0.008$, and (c) $y = 0.017$. Solid lines in all the figures are guides to the eye.

The present study has shown that the reduction of T_c and the development of AF correlations are continuously tunable by doping Zn impurities, where the superconductivity and AF ground state competitively coexist. Energy dependence of $\chi''(\omega)$ shows that Zn doping enhances a low-energy spin excitation while no significant variation occurs around the $\omega = 8$ meV region, where the gap starts opening in Zn-free LSCO. Furthermore, the temperature dependence of χ'' (3 meV) for $y = 0.008$ indicates that, with decreasing temperature, the induced spin excitations are followed by an opening of the spin gap. These two facts imply that a Zn doping yields a novel in-gap spin state, which becomes robust with increasing Zn doping and with decreasing temperature as well. In the YBCO system, Zn doping also induces a low-energy spin excitation which coexists with a gaplike feature, suggesting two kinds of Cu sites; one around Zn ions and the other almost Zn independent [20]. This result is consistent with that of NMR studies [12,13], showing that the local moments are induced at the Cu sites around Zn ions. Thus, we speculate that the induced local magnetic moments around a doped Zn ion start dynamically correlating with those around other Zn ions for $y = 0.004$, and result in a spatial coherence among the induced moments, which gives rise to the novel in-gap spin state at particular q positions. This spatial coherence becomes more static with the reduction of $R_{\text{Zn-Zn}}$ and temperature. In muon spin relaxation (μSR) studies, Nachumi *et al.* [21]

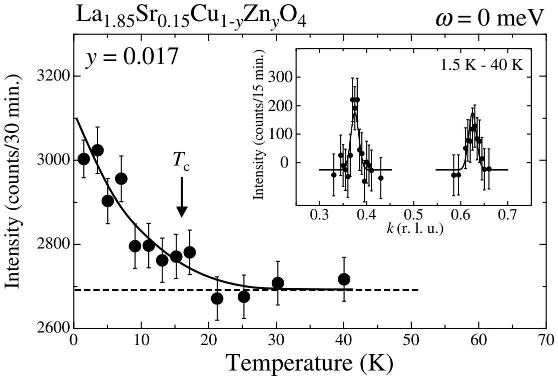

FIG. 4. Temperature dependence of the incommensurate elastic peak intensity of $x = 0.017$. The solid line is a guide to the eye. The inset shows the difference profile at 1.5 and 40 K.

proposed a "swiss cheese" model in which charge carriers in an area of $\pi\xi_{ab}^2$ ($\xi_{ab} \sim 18$ Å) around Zn impurities are excluded from the superconductivity. These results support a picture that the superconductivity is *locally* destroyed by the induced moments around Zn impurities but still survives. This might give a possible explanation for the microscopic coexistence of the superconductivity and the antiferromagnetism, as an inhomogeneous mixture of these two ground states [17,18].

Static spin correlations characterized by the incommensurate elastic magnetic peaks are observed in $y = 0.014$ [22] and 0.017, where the $R_{\text{Zn-Zn}}$ values are 32 and 29 Å, respectively. The in-plane spin correlation lengths for $y = 0.014$ and 0.017 exceed 80 Å which is much longer than those of $R_{\text{Zn-Zn}}$ and ξ_{ab} in the μSR study [21]. These facts show that the static correlations originate *not* from the independent local magnetisms around Zn impurities *but* from the long-range AF coherence among the induced moments around different Zn ions. In addition, the elastic magnetic peaks for $y = 0.014$ and $y = 0.017$ have the same incommensurate wave vector Q_δ as that of the in-gap spin excitations in $y = 0.008$. Thus, we conclude that the in-gap state continuously connects to an AF ground state with increasing Zn impurities, i.e., with decreasing $R_{\text{Zn-Zn}}$. We note that these results are in contrast to the case of LSCO at $x = 0.12$, where 3% of Zn doping not only completely suppresses the superconductivity but also disturbs the long-range AF order [23]. However, recent μSR studies for LSCO at $x = 0.115$, which has static spin correlations, showed that with increasing Zn, the spin correlations are primarily enhanced but destroyed by further Zn doping [24]. In the present case, Zn-free LSCO ($x = 0.15$) shows the spin-gap state, indicating that there is no long-range order as a ground state. Therefore further Zn doping is required for stabilizing a long-range order than that required for $x \sim 0.12$.

A recent neutron scattering study under a magnetic field has shown that the field-induced spin excitations on $La_{1.837}Sr_{0.163}CuO_4$ originate from the network among vortex cores in which the spin correlations are antiferromagnetic [25]. These results are relevant to our results and imply that the superconductivity can competitively coexist with an AF ground state which is introduced by the local impurities or vortices.

The present study has revealed that Zn doping gives rise to an additional spin state, which we call the in-gap state, at the same Q_δ positions of the incommensurate magnetic peaks. We interpret that these excitations originate from a spatial coherence among local AF regions near doped Zn ions. However, the microscopic mechanism for the emergence of the in-gap state still remains to be clarified. There are two possible scenarios: one is a spin-density-wave-like excitation from the staggered AF moments near doped Zn, and the other is a *local* renormalization of superconducting state near Zn-induced AF regions. More systematic study by further Zn doping and at different Sr concentrations is required to elucidate how these novel spin excitations essentially arise.

In conclusion, we found that a novel in-gap spin state is induced in $La_{1.85}Sr_{0.15}CuO_4$ by doping Zn, which develops with increasing Zn and decreasing temperature. A systematic variation from the spin-gap state to the static spin correlations via the in-gap spin state indicates a competitive coexistence of the superconducting and AF regions in the form of their inhomogeneous mixture. The present study shows the importance of the underlying AF ground state which locally substitutes for the superconducting state by small perturbations.

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