Supplemental Material for
Localized Charge Excitations of La$_{2-x}$Sr$_x$NiO$_{4+\delta}$
Revealed by Oxygen $K$-edge Resonant Inelastic X-ray Scattering

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BY MULTI GAUSSIAN FITTINGS OF THE O K-EDGE RIXS SPECTRA

The lineshapes of the charge excitations observed in the RIXS spectra of LSNO are best adjusted using a model with five gaussian functions (Fig. S 1). The energy calibration and resolution function were obtained from measurements of a gold plate immediately before the measurement. Since the peaks observed in LSNO largely overlap, the elastic line was fixed at zero energy with energy resolution of 140 meV. The peak position of Low-E charge excitation for $n_h = 0.10$ is estimated from the peak position of the spectral weight after subtraction of the other components.
Fig. S1. (Color online) The details of multi Gaussian in O K-edge RIXS spectra for LSNO. (a) $h$ dependence for $n_h = 0.10$ along the $[h, 0]$ direction. (b) $h$ dependence for $n_h = 0.33$ along the $[h, 0]$ direction. (c) $h$ dependence for $n_h = 0.33$ along the $[h, h]$ direction. (d) Temperature dependence for $n_h = 0.33$ at $q = (0.07, 0.07)$. (e) $h$ dependence for $n_h = 0.33$ along the $[h, h]$ direction at 200 K and 350 K. Gray lines are the spectral weight of Low-E charge excitation after subtraction of the elastic peak, low-energy tail, High-E charge excitation, the 2.0 eV charge excitation, and high-energy tail.
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Strontium-doped lanthanum nickelates La$_{2-x}$Sr$_x$NiO$_{4+y}$ (LSNO) and cuprates La$_{2-x}$Sr$_x$CuO$_4$ show remarkably different conductivity as insulating and superconductivity in the similar electronic structure and physical properties, and it is important to clarify the nature of hole doping. We performed resonant inelastic X-ray scattering (RIXS) study of LSNO at oxygen K-edge in order to investigate the charge excitations of doped holes. It newly found that the observed charge excitations are strongly localized from the little energy-dispersion in the O K-edge RIXS spectra. This localized character is associated with the absence of the superconductivity and could be an origin of wider hole density of charge-stripe ordered phase in nickelates than that in cuprates. Furthermore, for finite momentum, conspicuous energy position changes with temperature were observed at a charge-ordering transition temperature. In addition with the previous spectroscopic techniques, the possible origin of the localized charge excitations are also discussed.

Effects of carrier doping into insulating transition-metal oxides are a central issue in strongly correlated electron systems. Parent insulators are categorized into the following two Mott insulators or charge-transfer insulators [1, 2]. In the former, the on-site Coulomb repulsion ($U$) of the $d$ electrons is smaller than the energy of charge transfer ($\Delta$) from the oxygen $2p$ to the transition-metal $d$ levels ($U < \Delta$), while, in the latter, $\Delta < U$ which is the case for the layered perovskite lanthanum cuprate La$_2$CuO$_4$ as well as its isostructural nickelate La$_2$NiO$_{4+\delta}$ (LNO) [3–5]. These parent materials have weak inter-layer coupling of two-dimensional Heisenberg antiferromagnets with $S = 1$ (Ni$^{2+}$:d$^8$) for LNO or $S = 1/2$ (Cu$^{2+}$:d$^9$) for LCO local spins, which shows three-dimensional antiferromagnetic behavior at 330 K and 270 K respectively [6, 7]. When holes are doped into LNO and LCO by the Sr$^{2+}$ ion substitution for the La$^{3+}$ ions, La$_{2-x}$Sr$_x$NiO$_{4+\delta}$ (LSNO) and La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), they predominantly occupy the oxygen $2p$ orbitals, revealed by oxygen K-edge X-ray absorption spectroscopy (XAS) [8–11].

As an extension of XAS, resonant inelastic X-ray scattering (RIXS) allows to discuss the element- and bulk-sensitive charge and spin excitations for finite momentum [12, 13]. In particular, O K-edge (1s-2p) RIXS is able to provide experimentally and theoretically information such as Zhang-Rice singlet, crystal field, and charge transfer excitations by electron correlation, complementary to K-edge RIXS of 3$d$ transition metal [18–27]. In the case of LSCO, O K-edge RIXS successfully probed charge dynamics originating from doped hole states which revealed the charge excitations with energy-momentum dispersions on the order of the transfer energy ($\sim$0.4 eV) [26]. On the other hand, in the case of LSNO, Ni K-edge (1$s$-4$p$) RIXS studies have observed the energy-momentum dependent charge excitation at 1.5 eV due to the doped holes [14, 15], whereas the low-energy charge excitation less than 1.0 eV observed by optical measurements [4, 16, 17] was not observed due to the strong elastic peak intensity. O K-edge RIXS is expected to give the energy-momentum dispersion of the low-energy charge excitation and help us to understand the effects of hole doping in charge-transfer insulators.

With the discovery of superconductivity in an infinite-layer nickelate Nd$_{0.8}$Sr$_0.2$NiO$_2$ single-crystal thin film [28], it is important to clarify the reason why LSNO does not exhibit superconductivity from the direct observation of hole doping. LSNO behaves as an insulator up to $x \sim 0.8$ [29], while LSCO becomes superconducting at $x \sim 0.05$ [30], suggesting the different properties of doped hole states between the two systems. The charge-spin stripe ordering derived from Ni$^{2+}$ and Ni$^{3+}$ sites in the NiO$_2$ plane observed by electron, X-ray and neutron diffraction techniques around 0.22 $\lesssim n_h \lesssim 0.50$ ($n_h = x + 28$) [31–35]. Ordering transition temperatures, $T_{CO}$ and $T_{SO}$, show maximum ($T_{CO} = 240$ K, $T_{SO} = 180$ K) when $n_h = 0.33$ [36]. Angle-resolved photoemission spectroscopy (ARPES) for metallic layered nickelate ($n_h > 1.0$) indicates that the Ni $d_{z^2-r^2}$ and $d_{3z^2-r^2}$ multi-band feature with varying orbital character works against the emergence of the superconductivity [37, 38]. However, since LSNO with charge-spin stripe ordering behaves as an insulator and is not suitable for ARPES, the energy-momentum dispersion of the charge dynamics as well as the spin dynamics is required to clarify the relationship among the charge ordering, and superconductivity.

In this paper, we performed O K-edge RIXS measurements of LSNO to investigate charge excitations of doped holes in momentum space. It revealed that the observed charge excitations are consistent with those in the optical conductivity and strongly localized from the energy-
momentum dispersionless $O$-edge RIXS spectra. Localized charge excitations are related to the absence of superconductivity and the wider hole density of charge-stripe ordered phase in the nickelates than that in the cuprates. Furthermore, for finite momentum, the energy position changes are observed at $T_{CO}$. We discussed the possible origin of the localized charge excitations.

The $O$ $K$-edge XAS and RIXS experiments were performed by using the HORNET spectrometer at BL07LSU of SPring-8 [39, 40]. The X-ray spectra of single crystals of LSNO with $(x, \delta, n_{h}) = (0.00, 0.05, 0.10), (0.33, 0.00, 0.33)$, prepared by the traveling solvent floating zone method, were measured at 30–350 K. The $O$ $K$-edge XAS was measured in the partial fluorescence yield (PFY) mode by using a silicon drift detector. The RIXS spectra were taken with energy resolution of $\sim 140$ meV, determined by the measurement of an elastic peak of a gold plate. The crystals were cleaved along the crystalline $ab$-plane ($NiO_{2}$ plane) in the air before the measurement. As shown in Fig. 1(a), the vertical-polarized X-rays ($E$) with respect to the scattering plane, defined as incident and scattered X-ray vectors, were irradiated on the $ab$-plane ($E//ab$). The scattering angle $(\varphi)$ was fixed to $135^\circ$ and the crystalline $c$-axis was kept parallel to the scattering plane. The momentum transfer $(q = k_{in} - k_{out})$ was tuned by changing the sample angles $\omega$ and $\phi$, where $\omega$ controls the magnitude of the projected momentum $(q_{//})$ in $ab$-plane and the azimuthal angle $\phi$ determines the scattering plane. In our measurements, the $[0, 0]$ and $[b, h]$ directions were reached by fixing $\phi$ at $0^\circ$ and $45^\circ$ respectively and the sign of $q_{//}$ was positive when $\omega$ was rotated clockwise from the specific angle corresponding to $q_{//} = 0$. The value of $q_{//}$ were calculated from the degree of $\omega$, $|k_{in}|$, and the tetragonal lattice parameters of $a = b = 3.82$Å [41, 42], and expressed with the unit of $2\pi/a$. All the RIXS spectra were normalized by the total integrated RIXS intensity after subtracting the constant background.

Figure 1(b) shows the $O$ $K$-edge XAS spectra with $E//ab$ for LSNO with $n_{h} = 0.10$ and 0.33. The spectra were normalized at 536 eV corresponding to $0.3s\ 2p_{x,y}$ main peak [43]. Since dipole selection rules indicate that only $1s\ 2p_{x,y}$ transition are allowed for $E//ab$, the Ni $3d_{x^{2}-y^{2}}$ final state at 532.5 eV and the pre-edge peaks, labeled as A and B, at 528.7 eV and 529.8 eV were observed. From ligand field theory on a NiO$_{6}$ cluster, the peaks A and B were assigned as the high-spin ($S = 1$) and the low-spin ($S = 0$) states of Ni$^{2+}$ ions, respectively [11]. We confirmed the number of $n_{h}$ from the spectral intensity $\mu(n_{h})$ integrated from 525 to 530.9 eV, and obtained the value of $\mu(0.1)/\mu(0.33) = 0.74$, which is consistent with the previous work [11].

In order to investigate the excitations of doped holes, we performed O $K$-edge RIXS at the incident photon energy ($h\nu_{in}$) in pre-edge peaks from 528.4 eV to 529.8 eV. Figure 1(c) shows the $h\nu_{in}$ dependence of O $K$-edge RIXS spectra of LSNO with $n_{h} = 0.10$ and 0.33 at finite $q_{//}$ as a function of the energy loss ($h\nu_{in} - h\nu_{out}$). The high-energy peak above 3 eV is assigned as a fluorescence due to the continuous shift to higher energy sides. On the other hand, excitations at 0.6 eV, 1.2 eV, and 2.0 eV corresponding to the energy scale below the charge transfer gap ($\sim 4.0$ eV) for LNO [5] are assigned as the Raman components due to the absence of the energy shift with $h\nu_{in}$. These excitations are consistent with those of optical conductivity for LSNO [4, 16, 17]. In addition, the observed charge excitations are in good agreement with the numerically exact-diagonalization based on the Hubbard model for two-dimensional doped nickelate [44]. Their Hamiltonian take into account electron hopping ($t \sim 0.3$ eV), on-site Coulomb interaction, and Hund’s-rule coupling ($J \sim 1.4$ eV) between electrons in $e_{g}$ orbitals under octahedral symmetry, whereas crystal field splitting between $e_{g}$ orbitals, O $2p$ orbitals, and electron-phonon interaction are neglected. It has been revealed that charge excitations at 0.6 eV, 1.2 eV, and 2.0 eV reflect the motion of carriers which keeps the $S = 1$ configuration and changes doubly occupied sites from $S = 1$ to $S = 0$ configurations respectively. Therefore, we demonstrate that O $K$-edge RIXS detects the charge excitations originating from doped holes within LSNO.

From O $K$-edge RIXS spectra at $h\nu_{in} = 528.7$ eV in Fig. 1(b), the intensity of the charge excitation at 0.6
eV clearly evolves with increasing \( n_h \), whereas the intensity change of the charge excitation at 1.2 eV is small. Next, let us discuss the \( q_{//} \) and \( n_h \) dependence of the charge excitations, especially at 0.6 eV and 1.2 eV (hereafter Low-E and High-E charge excitations), of LSNO at 30 K. In Figs. 2(a)-(c), at \( T = 30 \) K, O K-edge RIXS spectra for LSNO with \( n_h = 0.10, 0.33 \) along [\( h,0 \)] and [\( h,h \)] directions show little change with \( q_{//} \), suggesting that the observed charge excitations have the energy-momentum dispersionless. To investigate the behavior of these dispersions, we fitted the spectra by using multiple Gaussian. We considered not only the Low- and High-E charge excitations, but also the elastic peak, the low-energy tail in the elastic peak at 0.2 eV, the 2.0 eV charge excitation, and high-energy tail. The low-energy tail is due to phonon and magnetic components reported by the Raman scattering and Ni L\(_2\)-edge (2p-3d) RIXS [45–47]. Figure 2(d) shows that multiple Gaussians can reproduce the experimental spectra. Note that the peak position of Low-E charge excitation for \( n_h = 0.10 \) is estimated from the peak position of the spectral weight after subtraction of the others. We found that the Low-E charge excitation in \( n_h = 0.33 \) is shifted to higher energy loss side by ~0.1 eV than \( n_h = 0.10 \), consistent with the hole doping dependence of the optical conductivity [4]. This energy shift was also observed at other \( q_{//} \), as shown in Figs. 2(e) and (f) (the fitting results for O K-edge RIXS spectra are summarized in supplemental materials [48]). On the other hand, the peak position of Low- and High-E charge excitations for each \( n_h \) are independent of \( q_{//} \). Therefore, we consider that the charge excitations of LSNO have localized characters.

The energy-momentum dispersionless charge excitations of doped holes for LSNO with \( n_h = 0.33 \) are quite different nature from those for LSCO [26]. This localized charge excitations could lead to wider hole density of these charge-stripe ordered phases in nickelates than those in cuprates [50] and is related to the reason why LSNO does not show superconductivity. In the following, we argued possible explanations for the localized charge excitations of LSNO with \( n_h = 0.33 \). One is that the doped holes form polarons originating from electron-phonon coupling. A previous optical studies have been suggested that the electron-phonon coupling is larger of LSNO than that of LSCO [51]. Indeed, the four-band model taking Ni 3d\(_{x^2−y^2}, 3d_{3z^2−r^2}\) and O 2p\(_{x,y}\) orbitals into account predicts that the polaron becomes stable if \( \Delta \ll U \) [52], and X-ray photoemission (XPS) proposes that the polaron can exist stably in LSNO because of \( \Delta \ll U \) for LSNO [5] and \( \Delta \ll U \) for LSCO [53]. This different coupling strength corresponds to the size of polarons, which is smaller for LSNO than that for LSCO. Our O K-edge RIXS results implies that the localized charge excitations reflects the presence of small polaron of LSNO. The other possible origin is the magnitude of the spin in parent materials. A lot of optical conductivity, XAS, and ARPES studies suggests that the doped hole enters into O 2p\(_x\) orbital hybridized with d\(_{x^2−y^2}\) orbital [4, 11, 16, 17, 37, 38, 43]. In addition, XPS shows that the spin of the doped hole nearest to the Fermi level is found to be antiparallel to the Ni\(^{2+}\) spins [5]. The hopping of the d\(_{x^2−y^2}\)-symmetry hole to the neighboring site is energetically unfavorable because of the antiferromagnetic coupling with the Ni spin. Furthermore, the quantum spin fluctuation of the antiferromagnetic states in LNO (\( S = 1 \)) is much weaker than in LCO (\( S = 1/2 \)), and it would lead to lower mobility to the doped holes within LSNO. The hole localization due to spin-polaron...
FIG. 3. (Color online) T dependence of O K-edge RIXS spectra for LSNO with \( n_h = 0.33 \). (a) The spectral changing at \( q_{//} = (0.07, 0.07) \). The peak plots of charge excitations obtained by the multiple Gaussian and \( 2\Delta_C \) cited Ref. [16] are also shown in (b). (c) \( q_{//} = (h, h) \) dependence of O K-edge RIXS spectra at each temperatures, and the peak positions of charge excitations obtained by multiple Gaussian fittings are shown in (d). The horizontal dashed lines denote the energy positions of charge excitations. The error bar of the peak energy is within the size of the markers.

In summary, we performed O K-edge RIXS measurements for LSNO with \( n_h = 0.10 \) and 0.33 and successfully observed the charge excitations of doped holes. The charge excitations are independent of the momentum transfer, reflecting the localized character. This nature is different from that for LSCO, showing that the localized charge excitations are associated with the absence of the superconductivity and the formation of the polaron and the spin fluctuation in LSNO. We demonstrate that O K-edge RIXS is an effective method to observe the charge excitations originating from doped holes within charge transfer insulators and expect the observation of delocalized charge excitations of an infinite-layer nickelate superconductor from momentum-resolved measurements.

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