Pseudogap of metallic layered nickelate $R_{2-x}\text{Sr}_x\text{NiO}_4$ ($R = \text{Nd, Eu}$) crystals measured using angle-resolved photoemission spectroscopy

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We have investigated charge dynamics and electronic structures for single crystals of metallic layered nickelates, $R_{2-x}\text{Sr}_x\text{NiO}_4$ (RSNO, $R$ being rare earth element) with $K_2\text{NiF}_4$ type structure. This system undergoes an insulator-metal transition with vertical-stripe charge ordering at $x \sim 0.8$, as contrasted to the normal metallic behavior even in the metallic region at $x = 1.0$ and it evolves into the Drude peak at $x = 1.3$. This doping evolution is similar to the previous results for La$_{2-x}\text{Sr}_x\text{CuO}_4$ thin films. These transport and optical properties indicate that an anomalous metallic state is realized at $x \sim 1.1$ as contrasted to the normal metallic behavior above $x \sim 1.3$. Here we report angle-resolved photoemission spectroscopy (ARPES) experiments for the metallic layered nickelate Eu$_{0.9}\text{Sr}_{1.1}\text{NiO}_4$ (ESNO), which is located close to the insulator-metal boundary shown by a gray arrow in Fig. 1(c).

Single crystals of RSNO ($R = \text{Nd, Eu}$) were grown with the floating-zone method in a high-pressure oxygen atmosphere ($p_{O_2} = 10-60$ atm). The crystals obtained have a typical dimension of $2 \times 2 \times 0.5$ mm$^3$ for $x = 1.1$. In RSNO systems, the electronic phase diagram was reported to be least affected by variation of $R$.
species, which is also confirmed up to a higher \( x \) region in the present study as shown in Figs. 1(a) and (b). We chose \( R = \text{Eu} \) (ESNO) for ARPES experiments because of its better sample quality and cleavage property. Laser-ARPES measurements with an excitation energy \( h\nu = 6.994 \) eV and an instrumental energy resolution of 3 meV were carried out at ISSP, University of Tokyo using a VG-Scienta R4000 electron analyzer. Unless otherwise noted, the measurements were performed with circular polarized light to observe all the orbital components. The samples were cleaved and measured at 7 K and the pressure was below \( 2 \times 10^{-11} \) Torr throughout the measurement. We confirmed that the sample degradation was negligible during the measurement. The local-density approximation (LDA) calculation for the electronic structure of ESNO was performed with the LMTO and NMTO methods. In order to avoid the LDA for the 4\( f \) electrons in Eu\(^{3+}\), they were treated as frozen core. This makes it inconvenient to use the virtual-crystal approximation for Eu\(_{0.9}\)Sr\(_{1.1}\)NiO\(_4\), which was therefore substituted by Eu(Rb\(_{0.1}\)Sr\(_{0.9}\))NiO\(_4\) with the virtual Rb\(_{0.1}\)Sr\(_{0.9}\)-atom, the one with 0.1 proton less than Sr.

In the upper half of Fig. 2(a), we show the Fermi surface for ESNO as revealed by ARPES. Only one sheet of the Fermi surface is discerned, which is a large hole-like one centered at the M point. To determine its orbital character, we measured the polarization-dependent ARPES in the experimental configurations shown in Fig. 2(f). The results (Figs. 2(b)-(e)) clearly show that the band dispersion along the momentum cut A (B) appears only in \( p\) (\( s \)) configuration. From the matrix element argument, the corresponding wave function should be characterized by odd parity with respect to the mirror planes a (110) and b (110) shown in Fig. 2(f). This indicates that the large hole sheet has \( x^2 - y^2 \) character at the point where it crosses the \( \Gamma - M \) line and suggests that the low-energy physics of ESNO is dominated by the antibonding \( p_{d\sigma} \) \( O_{\alpha \sigma} - Ni_{\alpha \sigma} - O_{\beta \sigma} \) orbital, like that of the high-\( T \_c \) cuprates. This is not trivial, because one expects not only \( x^2 - y^2 \) but also \( 3z^2 - r^2 \) character when the \( e_g \) shell is 1/4 rather than 3/4 filled. However, hybridization between \( x^2 - y^2 \) orbital and any axial orbital such as \( 3z^2 - r^2 \) is forbidden along the \( \Gamma - M \) line. As a consequence, at a \( \Gamma - M \) line crossing, the Fermi surface must have either \( x^2 - y^2 \) or \( 3z^2 - r^2 \) character. But there can be several crossings, and this is in fact what happens in the lower half of Fig. 2(a), where we show the cross sections with the \( k_z = 0 \) and \( k_z = \pi/c \).
The black/yellow coloring (dark/light contrast) gives the planes of the Fermi surface of ESNO calculated in LDA. The characteristic energy scale is 0.3-0.6 eV in the cuprates and a gap-like feature appears at $E_F$. We can clearly see this nodal-antinodal dichotomy in the energy distribution curves (EDCs) shown in Figs. 3(f)-(h). While the sharp quasiparticle peak is found close to the nodal points, the spectral weight around $E_F$ becomes largely suppressed upon moving away from the nodal region. This feature demonstrates a marked resemblance to the high-energy pseudogap with the same momentum-space symmetry as the $d$-wave superconducting gap $\Delta_{1}$ and $\Delta_{2}$. It is universally observed for underdoped cuprates and believed to be an intrinsic feature of the high-$T_c$ superconductors.

As shown in Fig. 3(a), the band shows a symmetric dispersion around the $\Gamma$ point up to 0.6 eV along the $\Gamma$-M nodal direction. Hereafter, we use the term ‘nodal’ also for the present result on the nickelates, to stress the clear resemblance of the pseudogap phenomena common to these materials, as will be shown later. One can clearly see a kink-like structure around 0.25 eV, which is very similar to the so-called giant kink observed in cuprates [18, 20]. The characteristic energy scale is 0.3-0.6 eV in the cuprates and a number of origins have been suggested, including the effects of coupling to some bosons, strong electron correlation [18], and photoemission matrix elements [19]. Recently, broad but similar features have been observed around 0.2 eV also in other correlated oxides such as LaNiO$_3$ [21] and SrVO$_3$ [22]. Therefore, this high-energy anomaly seems to be a momentum-resolved ubiquitous feature observed in Mott transition systems, and the convincing theory must explain this ubiquity and the difference of their energy scales. As shown in Fig. 3(c), on the other hand, ESNO does not clearly show any kink structure at $\sim$ 70 meV, which has been universally observed among the various layered cuprates [23–25] and discussed in the light of the electron coupling to a bosonic mode (phonon [25] or spin excitation $\Delta_{1}$) as a possible glue for the Cooper pair. The absence of the low-energy kink in non-superconducting ESNO conversely suggests its possible key role for the emergence of high-$T_c$ superconductivity unique in the layered cuprates.

Hereafter, we focus on the near-$E_F$ electronic structure along off-nodal directions. Figures 3(d) and (e) show the ARPES image plots along the momentum cuts B and C, as sketched in Fig. 3(b). On approaching the ($\pi$, 0) region, the clear quasiparticle dispersion gets suppressed and a gap-like feature appears at $E_F$. We can clearly see this nodal-antinodal dichotomy in the energy distribution curves (EDCs) shown in Figs. 3(f)-(h). While the sharp quasiparticle peak is found close to the nodal points, the spectral weight around $E_F$ becomes largely suppressed upon moving away from the nodal region. This feature demonstrates a marked resemblance to the high-energy pseudogap with the same momentum-space symmetry as the $d$-wave superconducting gap $\Delta_{1}$ and $\Delta_{2}$. It is universally observed for underdoped cuprates and believed to be an intrinsic feature of the high-$T_c$ superconductors.

In Fig. 4(a), we show the momentum-dependent pseudogap dependence of the pseudogap in Eu$_{0.9}$Sr$_{1.1}$NiO$_4$. The pseudogap size $|\Delta|$ is estimated from the peak position of the symmetrized EDC spectra shown in (b). The open circles labeled with alphabets (A to H) denote the $k_{F}$ positions. The gray arrows indicate the wave vector of the expected charge correlation in this system. (b) A sharp nodal quasiparticle peak is transformed into a broad pseudogap feature over $\sim$ 0.1 eV while approaching the ($\pi$, 0) region.
dogap energy along the expected Fermi surface, which is estimated by the peak position of the symmetrized EDC spectra at $k_F$ as shown in Fig. 4(b). This behavior is strikingly similar to the Fermi-arc phenomena in the cuprates [27]. On approaching the ($\pi$, 0) region, the sharp quasiparticle peak is suppressed and converted into a broad gapped feature over $\sim 0.1$ eV. Twice the value of its energy scale ($\sim 0.2$ eV) is well in accord with that of the pseudogap observed in the optical conductivity spectra (Fig. 1(b)). Its consistency indicates that the pseudogap in optical spectroscopy reflects the structure around ($\pi$, 0). This Fermi-arc like behavior also reflects the transport properties. In case no pseudogap is considered on the Fermi surface, we can estimate the Hall coefficient to be $R_{H\text{ARPES}} = 4 \pm 1 \times 10^{-4} \text{cm}^3/\text{C}$ from the area of the Fermi surface. It approximately corresponds in Ca$_{2-x}$Na$_x$Cu$_2$O$_2$Cl$_2$ [30]. Considering the comparable size of the high-energy pseudogap, it is unlikely that its origin is related to the spin correlation. In the layered nickelates, the checkerboard type charge ordering persists above $x = 0.5$ with introducing the excess holes to $d_{x^2-y^2}$ orbital states, and its melting plays a key role in driving the insulator-metal transition around $x \sim 1$ [2, 5]. Therefore, the high-energy checkerboard type charge correlation should give rise to the momentum-dependent pseudogap, which may particularly affect the ($\pi$, 0) and equivalent regions connected with its wave vector $q = (\pi/a, \pi/a)$. Also in the layered cuprates, various charge ordering or correlation patterns have been reported so far. The vertical-stripe type charge ordering is observed by scanning tunneling microscopy in Ca$_{2-x}$Na$_x$Cu$_2$O$_2$Cl$_2$ [30]. In both cases, a strong dichotomy of the quasiparticle peak at nodal and antinodal regions is observed by ARPES [31]. Here it is worth noting that similar dichotomy is observed in a ferromagnetic bilayer manganite with local charge-ordering correlations [32]. All these results may suggest the possibility that the Fermi surface dichotomy with the high-energy pseudogap commonly arises from the real-space charge correlation.

Our ARPES experiments thus show that the metallic states in layered nickelates and cuprates share the basic electronic structures such as the $d_{x^2-y^2}$ orbital-derived single Fermi surface with similar shape and Fermi-arc dichotomy with the high-energy pseudogap at the antinodal region. The high-energy pseudogap may be commonly interpreted as the manifestation of the real-space charge correlation. On the other hand, the clear difference appears in low-energy ($< 100$ meV) features, as represented by the lack of the low-energy kink and small pseudogaps. Therefore, finding the origin of these similarities and differences may contribute to further understanding of the microscopic mechanism behind the high-$T_c$ superconductivity.

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