Enhanced Charge Gap in the Bilayer Manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ near $x = 0.4$

Myung Whun Kim,[1,*] H. J. Lee,[1,†] B. J. Yang,[2] K. H. Kim,[2] Y. Moritomo,[3] Jaejun Yu,[2] and T. W. Noh[1,‡]

[1]*ReCOE & FPRD, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea*
[2]*CSCMR & FPRD, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea*
[3]*Department of Physics, University of Tsukuba, Tsukuba 305-8573, Japan*

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We have investigated the optical conductivity spectra of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.3 \leq x \leq 0.5$) systematically and found that for x near 0.4 the charge gap shows enhancement of up to ~0.3 eV just above the long-range magnetic ordering temperature. From comparison of this charge gap with other experimental results, we conclude that the peculiar x dependence of the charge gap cannot be understood in terms of the charge and lattice correlations only. We suggest that the unusual enhancement originates from the cooperative coupling between the short-range charge or lattice correlations and the quasi-one-dimensional energy band near the Fermi level.

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Strong charge correlation is one of the generic features of many doped Mott insulators. There are numerous examples, often signaled by anomalies in physical properties. The famous $x = 1/8$ anomaly and stripe correlation in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ [1], the static charge-spin stripes and enhanced optical gap near $x = 1/3$ of $La_{2-x}Sr_xNiO_4$ [2,3], and the *CE*-type charge or orbital order with a large optical gap near $x = 1/2$ of $La_{1-x}Ca_xMnO_3$ [4] are all well-known examples of unusually stable charge correlation at a specific doping concentration. Although the origin of the charge correlation is fascinating in its own right, the influence of the charge correlation on the physical properties of those materials remains a more challenging question.

$La_{2-2x}Sr_{1+2x}Mn_2O_7$ (LSMO) exhibits intriguing short-range charge or lattice correlations near or above the long-range magnetic ordering temperature [5,6]. Since the earliest studies in this field, the origin of the strong localization tendency of doped holes has been a subject of continued interest and debate [7]. While the system is thought to be a ferromagnetic (FM) metal at low temperatures, a recent angle-resolved photoemission (ARPES) experiment reported that a minimal Fermi surface of $x = 0.4$ is formed only along the nodal direction, while most of the Fermi surface is gapped, reminiscent of the Fermi surface of high-T_C superconductors [8]. While strong charge-lattice coupling has been hypothesized to be the cause of this localization, it is not clear how such a bosonic coupling causes a correlated metallic system to turn into a strongly localized state at the microscopic level.

In this Letter, we report experimental findings concerning the localized state in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ from systematic doping (x)-dependent studies of the charge gap in optical conductivity spectra. The charge gap of LSMO with $0.3 \leq x \leq 0.5$ is largest near $x = 0.4$ in the paramagnetic insulating state just above the long-range FM ordering temperature T_C. We compare the temperature dependence of the charge gap with the x-ray or neutron scattering peak intensity to investigate the role of the short-range charge or lattice correlations in forming the localized state. The similar temperature dependences of the charge gap and scattering intensities suggest strongly that the charge gap is due to short-range charge or lattice correlations. However, we also found that the enhancement of the charge gap cannot be simply understood only in terms of the charge or lattice correlations. Based on a comparison of the optical conductivity, x-ray or neutron scattering, and ARPES data, we suggest a possible mechanism for the unusual x dependence of the charge gap enhancement: a cooperative interplay between the charge or lattice correlations and the momentum space topology of the energy band.

Single crystals of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.3 \leq x \leq 0.5$) were grown using the floating-zone method. The samples were characterized using resistivity and magnetization measurements [9]. Cleaved ab planes were prepared for measurement of the optical reflectivity. Temperature-dependent reflectivity spectra $R(\omega)$, where ω is the photon energy, were measured at temperatures of 15 to 290 K and over a wide ω range of 0.01 to 30 eV. The NIM-Beam line at the Pohang Accelerator Laboratory was used for the high-energy (5–30 eV) measurements. We used the Kramers-Kronig transformation to obtain the optical conductivity spectra $\sigma(\omega)$ from $R(\omega)$. Details of the optical experiments are described elsewhere [10].

The charge gap is a quantitative measure of the carrier localization in perovskite manganites [4,11]. A good example is the x dependence of the charge gap in $La_{1-x}Ca_xMnO_3$ (LCMO) [4]. In LCMO, the onset temperature for the short-range charge ordering and the charge gap both increase steeply as x decreases from 0.8 to 0.5. This shows that the stability of the carrier localization due to the charge or lattice correlations is reflected in the magnitude of the charge gap.

The relationship between the charge gap and the degree of carrier localization also appears to be valid in the ground state of LSMO. Figure 1(a) shows $\sigma(\omega)$ at 15 K. The spiky features are optical phonons. $\sigma(\omega)$ is depleted below

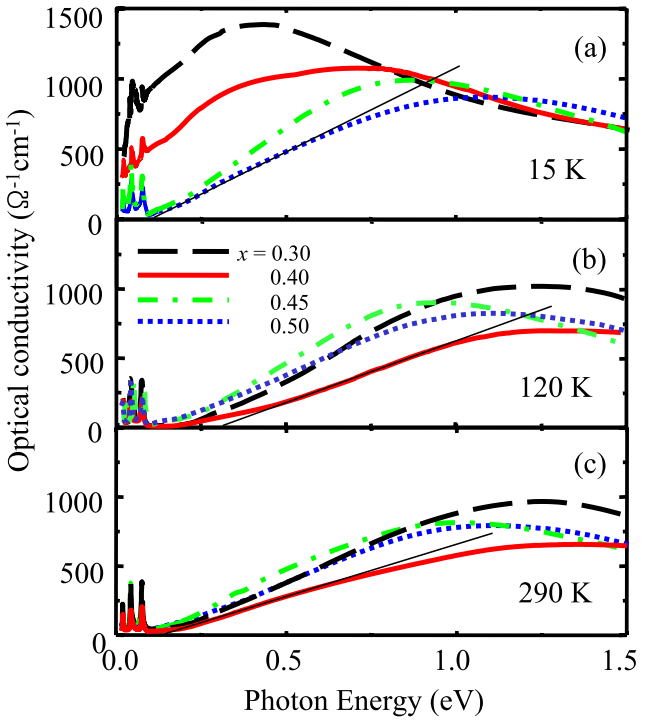

FIG. 1 (color online). $\sigma(\omega)$ of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.3 \leq x \leq 0.5$) at (a) 15, (b) 120, and (c) 290 K. The thin solid lines represent the extrapolation used to estimate the charge gap.

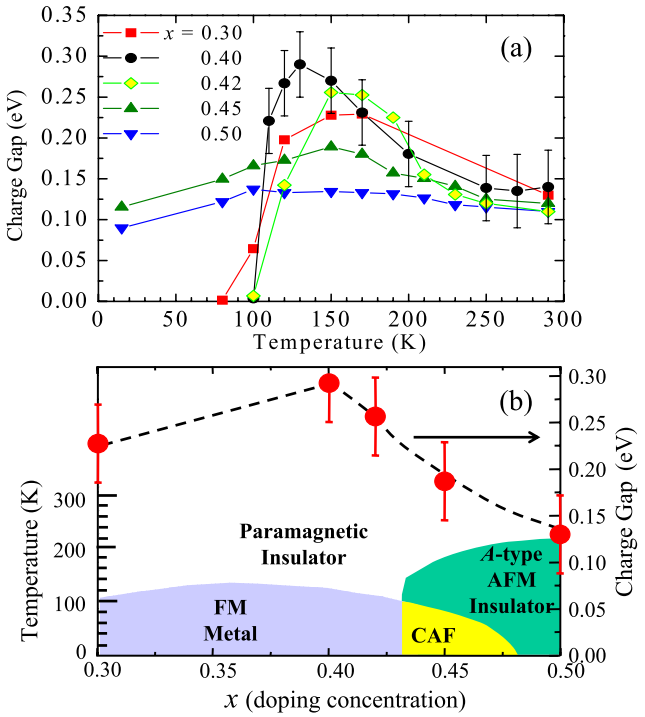

FIG. 2 (color online). (a) The temperature-dependent charge gap obtained from $\sigma(\omega)$. The error bars for the other compounds are similar in size to those for $x = 0.40$. (b) The x dependence of the charge gap obtained at just above T_C or T_N is superimposed on the schematic phase diagram. The dashed line is a guide to the eye.

1.0 eV, forming a finite charge gap at $x = 0.50$, in which charge ordering was observed [12] (for the definition of the charge gap, see [13]). As x deviates from 0.50, the charge gap shrinks, and vanishes eventually for $0.30 \leq x \lesssim 0.42$, over which range FM metallic states are formed so that the effective charge or lattice correlation is minimal or negligible [14].

Nevertheless, the proportionality between the charge gap and carrier localization might not be valid at high temperature. $\sigma(\omega)$ at 120 K reveal an intriguing finding. As shown in Fig. 1(b), $\sigma(\omega)$ for $x = 0.4$ below 1 eV is clearly more depleted than that for $x = 0.5$ (i.e., the charge gap for $x = 0.40$ is larger than that for $x = 0.50$). At this temperature, $x = 0.40$ is in the paramagnetic insulating state, whereas $x = 0.50$ is in the charge-ordered insulating state. This is unexpected, since the norm in perovskite manganite is that the charge gap of the paramagnetic insulating state is usually smaller than that of the charge-ordered insulating state [4]. Such enhancement of the charge gap for $x = 0.40$ seems to exist up to 290 K, as shown in Fig. 1(c).

As shown in Fig. 2(a), we have investigated the temperature dependence of the charge gap for all the samples to understand the unexpected x dependence of $\sigma(\omega)$ at 120 K. To our surprise, the largest charge gap in LSMO emerges from the paramagnetic insulating state near $x = 0.40$, for which the ground state is FM metallic. The temperature dependence of the charge gap of $x = 0.40$ above T_C is reminiscent of the similar behavior in perovskite manganites showing charge-ordered ground states [4,11], for which the charge gap shows a significant increase as the temperature decreases. Conversely, the temperature dependence of the charge gap of $x = 0.50$ shows no significant increase near the charge-ordering temperature T_{CO} ($\sim$220 K), except for the slight enhancement around 150 K and slight decrease below 100 K. Figure 2(a) shows that the charge gap just above the FM metallic state is much more enhanced than that of the charge-ordered insulating state in LSMO, implying that the mechanism of the charge gap enhancement in LSMO may differ from that in perovskite manganites.

Figure 2(b) shows that the x dependence of the charge gap at just above T_C or T_N is peaked around $x = 0.40$. Such a dependence on x reminds us of the similar behavior of the charge gap in LCMO, in which the charge gap is largest near $x = 0.50$. In LCMO, the enhancement of the charge gap has been attributed to strong CE-type charge-ordering fluctuations resulting from proximity to the bicritical point [4]. In LSMO, however, the enhancement of the charge gap near $x = 0.40$ cannot easily be understood in the same way. As inferred from the phase diagram in Fig. 2(b), the possible bicritical point should be rather close to $x = 0.45$; however, the charge gap for $x = 0.45$ is much smaller than that of $x = 0.40$. The enhancement of the charge gap near $x = 0.40$ should be attributed to a new mechanism beyond the charge-ordering fluctuations near a bicritical point.

However, it should be noted that charge or lattice correlations still play an important role in the charge gap formation in LSMO. Figure 3 shows that the temperature dependence of the charge gap is very similar to that of the x-ray or neutron scattering satellite peak intensity. The satellite peak arises from polaron correlations [5] or from the stripelike short-range charge ordering [6]. The analogous temperature dependences of the charge gap and of the satellite peak intensity suggest that the charge gap is intimately related to the short-range charge or lattice correlations in LSMO despite the aforementioned discrepancies with the perovskite manganites.

Although the charge or lattice correlations play an important role in the charge gap formation, they may not be sufficient to explain the anomalous x dependence. According to transport measurements, T_{CO} decreases drastically as x decreases from 0.7 and the signature of the long-range charge ordering disappears when $x \lesssim 0.45$, implying that the charge or lattice correlations become weaker as x becomes smaller [15]. Consistent with the transport data, x-ray scattering data show that the correlation length of the Jahn-Teller–type short-range lattice ordering in $x = 0.475$ is much shorter than that in $x = 0.5$ [12]. In contrast, for $0.4 \leq x \leq 0.5$ the charge gap systematically increases as x becomes smaller, as shown in Fig. 2(b). These results show that the enhancement of the charge gap near $x = 0.4$ cannot be easily explained only in terms of the strength of charge or lattice correlations and suggest that additional mechanisms are present.

The intimate relationship between the charge gap and the stability of charge or lattice correlations reminds us of the conventional charge density wave (CDW) scenario. According to the scenario, when the CDW is formed the size of the gap is proportional to the lattice displacement. The intensity of the superlattice peak arising from the charge density/lattice modulation is proportional to the square of the lattice displacement [16]. Therefore, a linear relationship between the gap and the square root of the satellite peak intensity is expected, as is reflected in Figs. 3(a)–3(d). Furthermore, recent ARPES experiments have demonstrated that LSMO with $x = 0.40$ has a quasi-one-dimensional band structure near the Fermi level, a prerequisite for CDW formation [8,17], which also prompted us to resort to the CDW model to explain the gap enhancement.

Despite the similarities, the conventional CDW model cannot easily explain the following observations: (i) the scale of the charge gap (~0.3 eV) is too large for a CDW gap alone, (ii) the gap edge is seen over a wide energy range and is not as sharp as expected from the conventional model, (iii) the length scale of the charge or lattice correlations is only a few nanometers [6,18], and (iv) the x-ray or neutron scattering intensity is suppressed when the Fermi surface becomes distinct as the temperature decreases. These are in contrast to the prediction of the conventional model.

Interestingly, the degree of carrier itinerancy seems to be related to the enhancement of the charge gap. The effect of Nd-ion substitution on the behavior of the charge gap supports this idea. We measured the temperature dependence of the charge gap of $(La_{1-z}Nd_z)_{1.4}Sr_{1.6}Mn_2O_7$ ($z = 0$, 0.1, and 0.2), as shown in Fig. 4(a). The Nd-ion substitution causes bandwidth narrowing, so that the ground state changes from the metallic to the insulating state as the Nd-ion concentration increases [19]. However, the maximum value of the charge gap decreases from ~0.22 to ~0.1 eV as the Nd-ion concentration increases, implying that stronger localization emerges from a more metallic ground state.

We suggest a novel cooperative interplay between localization due to the charge or lattice correlations and delocalization due to the planar itinerant motion of the carriers

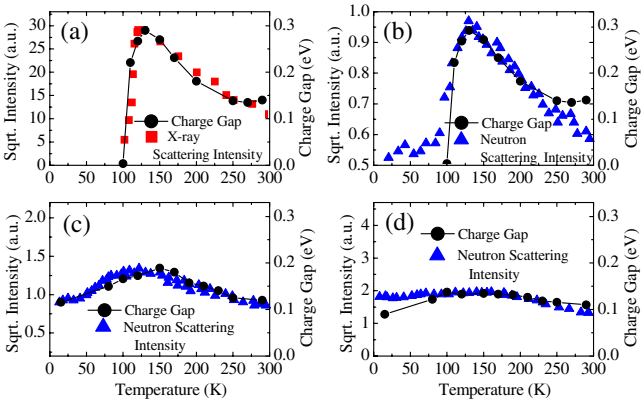

FIG. 3 (color online). Comparison between the temperature dependences of the charge gap (circles) and that of the square root intensity of the satellite peak measured (a) using x-ray scattering technique (diamonds) for $x = 0.40$ and (b) using neutron scattering (diamonds) for $x = 0.40$, (c) for $x = 0.45$, and (d) for $x = 0.50$ (here, we used the $x = 0.48$ data for the satellite peak intensity). The x-ray and neutron scattering data were reproduced from Refs. [5,6].

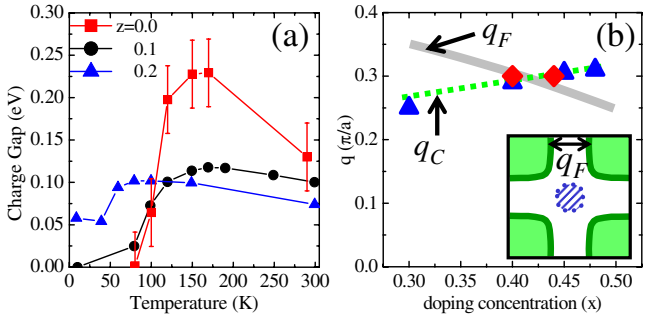

FIG. 4 (color online). (a) The temperature dependence of the charge gap in $(La_{1-z}Nd_z)_{1.4}Sr_{1.6}Mn_2O_7$ ($z = 0$, 0.1, and 0.2). The error bars for the other compounds are similar in size to those for $z = 0$. (b) The solid triangles and solid diamonds represent q_C obtained from Refs. [5,6]. The solid line corresponds to the calculated doping dependence of q_F. The dashed line is a visual guide to q_C. The inset shows the calculated Fermi surface of $x = 0.40$ and the definition of q_F.

as a possible explanation for the anomalous x dependence of the charge gap. While the charge or lattice correlations become weaker as x decreases from 0.50, the itinerancy seems to become more significant [i.e., the low-energy ($\lesssim 0.1$ eV) spectral weight becomes greater and the charge gap feature at low temperatures becomes weaker, according to Fig. 1(a) and the ARPES data [20]]. Near $x = 0.40$, above T_C, the short-range or dynamic FM spin correlations remain [21,22], so the carrier itinerancy is partially preserved and a quasi-one-dimensional Fermi surface forms, which can coexist with the short-range modulation of charge density and lattice. As Chuang *et al.* also discussed [17], such a modulation could be stabilized more by the quasi-one-dimensional Fermi surface via the Fermi surface nesting if the original Fermi surface is matched with the shifted one by the reciprocal lattice vector of the short-range charge or lattice correlations.

However, it is still not clear why the gap enhancement peaks around the specific doping of $x = 0.4$. A possible explanation is that $x = 0.4$ is close to the special point where the cooperative coupling effect becomes largest. The findings presented in Fig. 4(b) support this idea. We investigated the doping dependence of the theoretical electronic band structure near the Fermi level [23] and the doping dependence of the experimentally available values for the short-range charge or lattice correlation reciprocal lattice vector q_C [5,6]. We found that the calculated energy band has a quasi-one-dimensional momentum dependence, as shown in the inset of Fig. 4(b), which fits the ARPES data well [8,17,20]. Interestingly, the size of the calculated Fermi surface nesting vector (q_F) decreases, whereas q_C increases slowly or remains constant as x increases. As a consequence, near $x = 0.4$, the curves for q_F and q_C cross. This is a possible explanation for why such cooperative coupling can be enhanced and why the charge gap peaks near $x = 0.4$. This observation implies the existence of a novel polaronic quasiparticle state in which the dynamics is strongly coupled with the spin-ordering and the Fermi-surface topology, forming a pseudogap feature up to high temperatures. This scenario presents a challenge to our knowledge of the charge or lattice correlated states in two-dimensional doped Mott insulators and justifies further theoretical and experimental studies.

In conclusion, we found enhancement of the charge gap just above the long-range ferromagnetic ordering temperature near $x = 0.4$ in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.3 \leq x \leq 0.5$). We suggest a possible mechanism for the enhancement that involves a novel cooperative interplay between the short-range charge or lattice correlations and a nested energy band near the Fermi level. Our experimental findings and the physics described may be generally applicable to other layered transition metal oxides in explaining the anomalous doping-dependent enhancement of the charge gap.

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*Current address: Department of Physics, Chonbuk National University, Jeonju 561-756, Korea.
†Current address: Department of Physics, University of California at Berkeley, Berkeley, CA 94720, USA.
‡Corresponding author.
Electronic address: twnoh@snu.ac.kr

[1] J. M. Tranquada *et al.*, Nature (London) **375**, 561 (1995).
[2] T. Katsufuji *et al.*, Phys. Rev. B **60**, R5097 (1999).
[3] H. Yoshizawa *et al.*, Phys. Rev. B **61**, R854 (2000).
[4] K. H. Kim *et al.*, Phys. Rev. Lett. **88**, 167204 (2002).
[5] L. Vasiliu-Doloc *et al.*, Phys. Rev. Lett. **83**, 4393 (1999).
[6] M. Kubota *et al.*, J. Phys. Soc. Jpn. **69**, 1986 (2000).
[7] P. Littlewood and Š. Kos, Nature (London) **438**, 435 (2005).
[8] N. Mannella *et al.*, Nature (London) **438**, 474 (2005).
[9] Y. Moritomo *et al.*, Nature (London) **380**, 141 (1996).
[10] H. J. Lee *et al.*, Phys. Rev. B **62**, 11 320 (2000).
[11] H. L. Liu, S. L. Cooper, and S.-W. Cheong, Phys. Rev. Lett. **81**, 4684 (1998).
[12] S. B. Wilkins *et al.*, Phys. Rev. B **67**, 205110 (2003).
[13] The charge gap is defined as the onset energy of the steeply rising part of $\sigma(\omega)$ and is determined from the linear extrapolation shown as the thin solid lines in Fig. 1. This is a reasonable method for estimating the size of the polaronic gap feature in doped manganites; it was employed in previous works (Refs. [4,11]).
[14] We found a report of a similar $\sigma(\omega)$ measurement for $x = 0.3$ [see H. M. Rønnow *et al.*, Nature (London) **440**, 1025 (2006)]. In their study, the sharp peak in $\sigma(\omega)$ exists below $\sim$0.07 eV at 10 K. However, we observed only a slight decrease in $\sigma(\omega)$ with decreasing ω, which gives a dc conductivity of $\sim 500\ \Omega^{-1}\,\mathrm{cm}^{-1}$. The reason for the difference in $\sigma(\omega)$ is not clear at present; however, in the insulating state above $\sim$120 K, our $\sigma(\omega)$ is similar to that of Rønnow *et al.*, despite the difference at 10 K.
[15] J. Dho *et al.*, J. Phys. Condens. Matter **13**, 3655 (2001).
[16] G. Grüner, *Density Waves in Solids* (Addison-Wesley, Reading, MA, 1994), and references therein.
[17] Y.-D. Chuang *et al.*, Science **292**, 1509 (2001).
[18] B. J. Campbell *et al.*, Phys. Rev. B **65**, 014427 (2001).
[19] Y. Moritomo and M. Itoh, Phys. Rev. B **59**, 8789 (1999).
[20] Z. Sun *et al.*, Phys. Rev. Lett. **97**, 056401 (2006).
[21] D. N. Argyriou *et al.*, Phys. Rev. B **55**, R11 965 (1997).
[22] T. G. Perring *et al.*, Phys. Rev. Lett. **78**, 3197 (1997).
[23] In our calculation, we assumed that the local Mn spins are ferromagnetically aligned in a MnO_2 plane. For compounds of $La_{2-2x}Sr_{2+2x}Mn_2O_7$ with $0.3 \leq x \leq 0.5$, the spins within a single MnO_2 layer are always ferromagnetically aligned below T_C or T_N, regardless of the overall long-range ordering pattern.