Pseudogap of Optimally Doped $La_{1.85}Sr_{0.15}CuO_4$ Observed by Ultrahigh-Resolution Photoemission Spectroscopy

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We have performed an ultrahigh-resolution ($\Delta E \sim 7$ meV) photoemission spectroscopy on $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K) at 16–250 K. We found a pseudogap at E_F with the size of 30–35 meV, which is gradually filled in by a transfer of states from the higher energy region with increasing temperature, but persists over 200 K. The gap energy is consistent with the characteristic temperatures of the magnetic susceptibility and the Hall coefficient. The temperature evolution is well scaled with that of the Hall coefficient. The pseudogap is not smoothly connected to the superconducting gap ($\Delta \sim 8$ meV) below T_c, suggesting a different origin from that in $Bi_2Sr_2CaCu_2O_8$.

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One of the current central issues in the high-temperature superconductor (HTSC) is the pseudogap observed by various experimental probes [1–6] at temperatures above the superconducting transition temperature (T_c). High-resolution angle-resolved photoemission spectroscopy (ARPES) has elucidated that the pseudogap is smoothly connected to the superconducting gap with the same $d_{x^2-y^2}$ symmetry, suggesting that the pseudogap is a precursor of the superconducting condensation [6]. PES has revealed many important properties of the pseudogap with $Bi_2Sr_2CaCu_2O_8$ (Bi2212) since a stable crystal surface for PES measurements is easily obtained by *in situ* cleaving in Bi2212. On the other hand, a variety of anomalous electronic and thermodynamic properties such as the magnetic susceptibility and the Hall coefficient in the normal states have been reported for $La_{2-x}Sr_xCuO_4$ (LSCO) [7,8]. LSCO has a simple crystal structure with a single CuO_2 plane, but the unstable crystal surface under vacuum as well as the relatively small superconducting gap has hindered the detailed PES study. Recently Ino *et al.* have performed a systematic high-resolution ($\Delta E \sim 22$ meV) PES study on LSCO with various doping and reported a "high-energy pseudogap" of 0.1–0.2 eV for the optimally to under doped samples [9]. However, it is not clear how the "high-energy pseudogap" is correlated to the "small-energy pseudogap" as observed in Bi2212 or further to the superconducting gap itself, because they have not measured the temperature dependence. In order to clarify whether the (high-energy and small-energy) pseudogap is a universal feature for all HTSC's and how they are correlated with each other, a temperature-dependent PES study with an energy resolution comparable to or better than the superconducting gap has been desired.

In this Letter, we report results of a temperature-dependent ultrahigh-resolution ($\Delta E \sim 7$ meV) PES on $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K). We observed an anomalous but systematic evolution of the density of states (DOS) near E_F as a function of temperature (16–250 K), which suggests opening of a pseudogap as well as a superconducting gap at E_F. We compare the present PES results with those of Bi2212 as well as with the reported anomalous normal-states properties to discuss the origin of the pseudogap.

Single crystals of $La_{1.85}Sr_{0.15}CuO_4$ were grown by the traveling-solvent floating-zone method and then annealed under oxygen flow at 900 °C for 50 h. The electron-probe microanalysis was employed to determine the composition. The SQUID measurement showed that the T_c (onset) is 38 K. Details of the preparation and characterization have been described elsewhere [10]. Ultrahigh-resolution PES measurements were performed using a SCIENTA SES-200 spectrometer with a high-flux discharge lamp and a toroidal grating monochromator. We set the total energy resolution at 7 meV to obtain a reasonable count rate near E_F. The base pressure of the spectrometer was 5×10^{-11} Torr. We tried both cleaving and scraping to prepare a clean surface of sample for PES measurement and found that the surface in either case underwent degradation very fast, in particular at high temperatures. To obtain reliable data, we repeated scraping every 30 min at several temperatures from 16 to 250 K and summed all the spectra measured at the same temperature. We confirmed that there were no spectral changes during this time interval and a 9-eV peak known as a fingerprint of a dirty surface did not appear [11]. Since the surface was scraped, the PES spectrum is angle integrated, reflecting the DOS modulated by the photoionization cross section. This was confirmed by the experimental fact that the PES spectrum shows no essential angular dependence. We have measured three sets of PES spectra with different samples and confirmed the results shown here being reproducible. The temperature of the sample was measured with a calibrated Pt resistor embedded just below the sample, and its accuracy has been estimated to be within 1 K. The Fermi level of the sample was referenced to a gold film

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evaporated onto the sample substrate, and its accuracy is estimated to be better than 0.5 meV.

Figure 1(a) shows the ultrahigh-resolution PES spectra near E_F of $La_{1.85}Sr_{0.15}CuO_4$ measured at several temperatures from 16 to 250 K, compared with those of gold as a reference (inset). The spectral intensity is normalized with the area under the curve from -100 to 200 meV binding energy. We find that the PES spectrum of gold shows a systematic temperature dependence, which is well fitted by the Fermi Dirac (FD) function with an almost flat DOS across E_F. It is remarked that all the PES spectra of gold intersect the same point at E_F irrespective of temperature. This is reasonable because the FD function always takes the same value (0.5) at E_F independently of temperature. In contrast, the temperature dependence of the PES spectrum of $La_{1.85}Sr_{0.15}CuO_4$ looks very anomalous. The PES spectrum does not intersect at E_F nor even at one point with the same binding energy; the intersecting point is gradually shifted toward the high binding energy with increasing temperature. We also find that the spectral intensity at E_F gradually increases with increasing temperature in sharp contrast to the case of gold. These differences in the PES spectrum as a function of temperature clearly indicate that the temperature-induced spectral change in $La_{1.85}Sr_{0.15}CuO_4$ is due not only to the FD function but also to a systematic evolution of the spectral weight in the vicinity of E_F. It is well known that LSCO undergoes a faster degradation under vacuum than Bi2212 and the degradation speed is enhanced at higher temperatures. In fact, we observed an aging effect at high temperatures; the spectral intensity near E_F started to decrease 2–3 hours after scraping, showing that the surface became insulating. In contrast, the PES spectra in Fig. 1(a), which were recorded within 30 min after scraping, show just an opposite behavior that the spectral intensity at E_F *increases* at higher temperature. We thus conclude that the spectral change as a function of temperature in Fig. 1(a) is intrinsic. One may correlate this temperature-induced spectral change to the opening of the superconducting gap, but it is noted that the T_c of the present sample is 38 K, much lower than 250 K, at which the spectral intensity at E_F still increases. Thus, the observed temperature-induced spectral change near E_F in Fig. 1(a) is anomalous, suggesting the existence of a relatively large pseudogap at E_F.

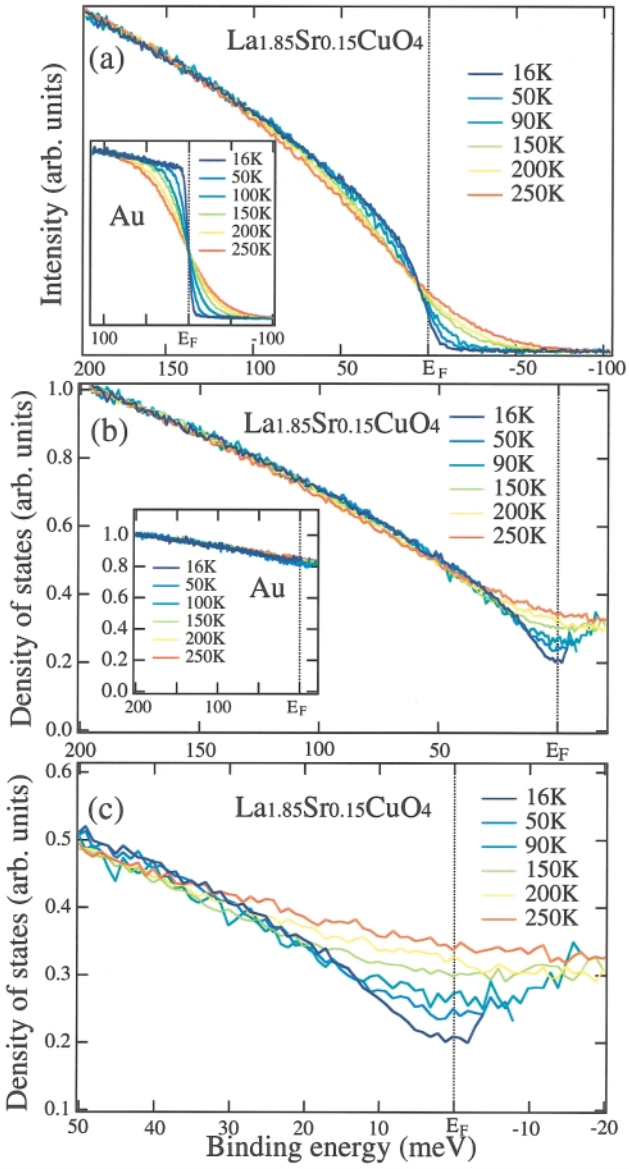

FIG. 1 (color). (a) Temperature dependence of ultrahigh-resolution angle-integrated PES spectra near E_F of $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K) compared with those of gold (inset). (b) Temperature dependence of the density of states of $La_{1.85}Sr_{0.15}CuO_4$ compared with that of gold (inset). (c) Same as (b) in an expanded energy scale.

In order to see more directly the change of DOS near E_F, we divided each PES spectrum by the FD function at each temperature, convoluted with a Gaussian with the instrumental resolution (7 meV). This procedure serves as a good approximation as long as we discuss the structure in the DOS larger than the energy resolution (7 meV), as demonstrated in the previous studies [12]. Figure 1(b) shows the results for $La_{1.85}Sr_{0.15}CuO_4$ compared with gold (inset). The intensity of the spectral DOS is normalized with the area under the curve from E_F to 200 meV binding energy since the spectra coincide with each other in the energy range over 200 meV. We find that the DOS of gold is almost flat with no anomaly at E_F and is temperature independent. In contrast, we find that the DOS near E_F of $La_{1.85}Sr_{0.15}CuO_4$ is remarkably suppressed up to about 30–35 meV binding energy at low temperatures, suggesting that a pseudogap opens [13]. The gap has a finite DOS at E_F and is gradually filled in with increasing temperature. We also find that the DOS around 50–150 meV slightly decreases with increasing temperature, which suggests that the DOS is transferred between the near-E_F (E_F–35 meV) region and the higher-binding energy (50–150 meV) region.

Figure 1(c) shows the same spectral DOS near E_F in an expanded energy scale. We clearly find the systematic

change of the spectral DOS near E_F as a function of temperature. At the lowest temperature (16 K), the DOS exhibits a relatively deep dip with the width of about 10 meV from E_F while the DOS's at higher temperatures have a smooth broad dip which starts around 30–35 meV binding energy. The deep dip in the DOS at 16 K may be related to the superconducting gap and is discussed later. Here we concentrate on the spectral change in the wider temperature range. Since the T_c of the sample is 38 K, the spectral change indicates that the DOS near E_F gradually increases with increasing temperature and does not saturate even at 200 K far above the T_c. The broad hump around 100 meV in the PES spectra at low temperatures [Fig. 1(b)] may correspond to the "high-energy pseudogap" reported by Ino *et al.* [9], who take the point of maximum curvature in the PES spectra as the gap size instead of measuring the temperature dependence. However, the present temperature-dependent ultrahigh-energy resolution PES measurement has directly observed the pseudogap itself, showing that the gap size is much smaller than that reported by Ino *et al.* It is noted that the pseudogap value (30–35 meV ~ 350–400 K) observed in the present study is comparable to the characteristic temperatures observed in the fundamental electronic and thermodynamic properties. The magnetic susceptibility of optimally doped LSCO shows a broad maximum around 400 K [7], and the Hall coefficient starts to increase around 500 K with decreasing temperature [8]. In addition, the observed systematic change of the DOS at E_F shows a good correspondence to the temperature dependence of the Hall coefficient [8]. The DOS at E_F at 250 K is approximately 1.5–2 times larger than that at 50 K, and the inverse of the Hall coefficient at 250 K is found to be also 1.5–2 times larger than that at 50 K [8]. Recently, Startseva *et al.* [14] have reported a pseudogap in $La_{2-x}Sr_xCuO_4$ ($x = 0.13, 0.14$) from their temperature-dependent infrared spectroscopy. The size ($2\Delta \sim 60$ meV), the temperature range (below T_c to 400 K), and the temperature invariance of the gap size show a remarkably good agreement with the present results.

Next we discuss the superconducting gap in $La_{1.85}Sr_{0.15}CuO_4$. As found in Fig. 1(c), the spectral DOS at the lowest temperature (16 K) shows a relatively steep decrease near E_F compared with the others at higher temperatures. This suggests that an additional gap with a smaller energy size opens at the low temperature below T_c. The inset of Fig. 2 shows the comparison of high-resolution PES spectra near E_F at 16 and 50 K. We find that the intersecting point of both curves is not on E_F but a few meV (~3 meV) away from E_F and a finite spectral DOS remains at E_F even at 16 K. This suggests that an anisotropic superconducting gap may open at low temperatures in $La_{1.85}Sr_{0.15}CuO_4$. In order to roughly estimate the size of superconducting gap as well as the order parameter, we tried to fit the 16-K spectrum using several model functions with s or d symmetry on an assumption of a linearly decreasing DOS to E_F. As

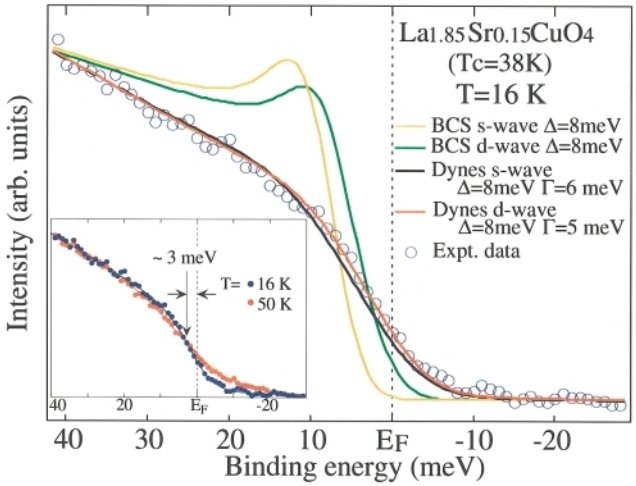

FIG. 2 (color). Ultrahigh-resolution angle-integrated PES spectrum near E_F of $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K) measured at 16 K (open circles), compared with the result of several numerical fittings. Inset shows comparisons of PES spectra at 16 K (superconducting state) and 50 K (normal state).

shown in Fig. 2, a simple BCS function with the FD function convoluted with the instrumental resolution does not reproduce the spectrum satisfactorily. This is mainly because the 16-K spectrum has a substantial DOS at E_F with no superconducting condensation peak below E_F. While the lack of a clear condensation peak in the PES spectrum is consistent with the tunneling experiment [15], the origin for the broadening of the spectrum is unclear at present. The lack of long-range structural order on a scraped surface and/or the random replacement of La with Sr atoms may shorten the lifetime of Cooper pairs. In order to obtain a better fitting, we used the Dynes function (broadened BCS function) [16] as employed in the analysis of tunneling spectra as well as in the previous angle-integrated PES study of Bi2212 [17]. A fairly good fitting has been obtained with $\Delta = 8 \pm 1$ meV and Γ (broadening parameter) $= 5 \pm 1$ meV as shown in Fig. 2, although it is difficult to determine the order parameter since the fittings with d or s symmetry gives little difference. The obtained value of $\Delta \sim 8$ meV corresponds to $2\Delta/k_BT_c \sim 5.2$, which is slightly smaller than those obtained from the Raman (~7.7 at $x = 0.17$) [18] and the specific heat experiment (~7.5 at $x = 0.16$) [19], but is comparable with that from the neutron scattering (~6) [20]. The present value of $2\Delta/k_BT_c \sim 5.2$ also agrees well with that from the PES experiment on Bi2212 (~5.5) [17]. It is noted here that the size of the superconducting gap (~8 meV) in $La_{1.85}Sr_{0.15}CuO_4$ is much smaller than that of the pseudogap (30–35 meV) and that both gaps do not seem to be smoothly connected to each other. This shows a sharp contrast to the case of Bi2212 where the "pseudogap" observed by ARPES is smoothly connected to the superconducting gap.

Next we discuss the relationship between the pseudogap and the superconducting gap in $La_{1.85}Sr_{0.15}CuO_4$ as well as the origin of the pseudogap. It is useful to summarize

the experimental results on the "pseudogap" in Bi2212 [3–6]: (1) The pseudogap is smoothly connected to the superconducting gap; (2) the temperature (T^*) at which the pseudogap is closed decreases with doping in contrast with the T_c; (3) the T^* at the optimal doping is slightly higher than T_c; (4) in the overdoping region both almost coincide with each other or the pseudogap disappears. From these results on Bi2212, it is expected that the pseudogap in optimally doped $La_{1.85}Sr_{0.15}CuO_4$ with the T_c of 38 K should be at most ~8 meV in the width (Δ) and disappear around 50 K. This expectation is not consistent with the experimental observation in Fig. 1, where we find that the pseudogap survives over 200 K and the size is much larger than that of the superconducting gap. We also find that the size of the pseudogap is almost independent of temperature and the temperature effect is just to fill in the gap. This shows a sharp contrast with the pseudogap in Bi2212 where the pseudogap is gradually narrowed and filled in with increasing temperature [4]. These comparisons lead to the conclusion that the pseudogap of $La_{1.85}Sr_{0.15}CuO_4$ observed in the present angle-integrated PES is different from the pseudogap of Bi2212 observed by ARPES. The pseudogap in Bi2212 has been regarded as a precursor of the superconducting condensation since it is smoothly connected to the superconducting gap. On the other hand, the pseudogap observed in $La_{1.85}Sr_{0.15}CuO_4$ may be produced through a different mechanism, probably due to the antiferromagnetic correlation. The temperature dependence of the pseudogap may reflect the evolution of the short-range antiferromagnetic ordering with temperature. The good agreement in the energy scale between the pseudogap and the characteristic temperatures in the fundamental electronic and thermodynamic properties supports this scenario. However, it is not clear from the present experimental result whether LSCO has a small pseudogap as observed in Bi2212. Further studies are necessary to address this problem as well as to elucidate the interrelation between the two different pseudogaps.

In conclusion, we have performed a temperature-dependent ultrahigh-resolution ($\Delta E \sim 7$ meV) PES on optimally doped $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K) and found a pseudogap at E_F and its temperature evolution. The pseudogap has a size of 30–35 meV and shows a gradual temperature evolution from low temperature to over 200 K. With increasing temperature the pseudogap is gradually filled in by a transfer of spectral weight (DOS) from the energy region of 50–150 meV binding energy, but does not change the size. The numerical simulation to the spectrum at the superconducting state has showed that the size of superconducting gap (Δ) is ~8 meV, indicating that the pseudogap is not smoothly connected to the superconducting gap in $La_{1.85}Sr_{0.15}CuO_4$. These results suggest that the pseudogap observed in $La_{1.85}Sr_{0.15}CuO_4$ is different from that of Bi2212 observed by ARPES. The energy scale (30–35 meV) shows a good correspondence to the characteristic temperatures of the fundamental electronic and thermodynamic properties. This suggests that the pseudogap observed in $La_{1.85}Sr_{0.15}CuO_4$ originates in the antiferromagnetic correlation and the observed temperature dependence is due to the evolution of the short-range antiferromagnetic ordering with temperature. It is thus inferred that there are at least two different pseudogaps in HTSC's: A large one is due to the antiferromagnetic correlation and dominates the electronic and thermodynamic properties in the normal state, while a small one is closely related to the superconducting pairing. The interrelation between the two pseudogaps as well as their relation to the superconducting mechanism is an open question for future studies.

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