Unusual pseudogap-like features observed in iron oxypnictide superconductors

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We have performed a temperature-dependent angle-integrated laser photoemission study of iron oxypnictide superconductors LaFeAsO:F and LaFePO:F exhibiting critical transition temperatures ($T_c$)'s of 26 and 5 K, respectively. We find that high-$T_c$ LaFeAsO:F exhibits a temperature-dependent pseudogap-like feature extending over $\sim$0.1 eV about the Fermi level at 250 K, whereas such a feature is absent in low-$T_c$ LaFePO:F. We also find $\sim$20-meV pseudogap-like features and signatures of superconducting gaps both in LaFeAsO:F and LaFePO:F. We discuss the possible origins of the unusual pseudogap-like features through comparison with the high-$T_c$ cuprates.

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Realization of room-temperature superconductivity is one of the ultimate goals in the field of materials science. In order to achieve a high critical-transition temperature ($T_c$), one needs to elucidate how materials can overcome $T_c \sim 40$ K, a so-called BCS limit predicted from a theory of phonon-mediated superconductivity [1]. The highest $T_c$ reported to date is $\sim 160$ K in the cuprates [2, 3], and their high-$T_c$ mechanism is believed to be linked to mysterious pseudogaps observed in the abnormal metallic phase at $T > T_c$ [4]. Recently, transition-metal oxypnictides composed of alternate stacking of Ln$_2$O$_3$ layers and $T_2$P$_n$$_2$ layers (Ln: lanthanide; T: Fe or Ni; Pn: P or As) were identified as new high-$T_c$ materials [5, 6, 7, 8] that exceed the BCS limit up to 55 K [9, 10, 11, 12]. The mechanism of the high-$T_c$'s has been the subject of strong debate: it is unclear whether the mechanism is a parallel case to the high-$T_c$ cuprates or a completely new case.

Photoemission spectroscopy (PES) is a powerful tool to investigate the electronic structures of materials. Angle-integrated PES studies on FeAs-based superconductors have revealed pseudogaps with energies ranging from 15 to 40 meV at $T \lesssim 100$ K [13, 14, 15, 16, 17]. However, subsequent angle-resolved PES studies on iron oxypnictides [18, 19] showed that the Fermi surfaces in the normal state were fully preserved, contrasted to the doping-dependent pseudogaps of the cuprates that cause the Fermi-surface sectors to vanish [20]. Herein, we present a comparative electronic-structure study of optimally-F-doped LaFeAsO:F (As26) [3] and LaFePO:F (P05) [5] exhibiting $T_c$'s of 26 and 5 K, respectively. Through investigating the $T$ dependence of the angle-integrated spectra recorded by a laser PES system [21], we find that even the low-$T_c$ P05 exhibits a pseudogap feature similar to those of the high-$T_c$ FeAs system [13, 14, 15, 16, 17]. We also find a large $T$-dependent pseudogap feature specific to high-$T_c$ As26 manifesting at high $T$'s. Our study shows that pseudogaps do exist in the iron oxypnictides, but they are qualitatively different from the doping-dependent pseudogaps of the cuprates.

Polycrystalline As26 and P05 were fabricated as described elsewhere [5, 6, 22]. The F contents substituting for O in As26 and in P05 were estimated to be 11 and 6 %, respectively. Laser PES measurements with an excitation energy of $h\nu = 6.994$ eV were performed at ISSP, University of Tokyo [21]. The base pressure of the spectrometer was $<2 \times 10^{-11}$ Torr throughout the measurements. The Fermi level ($E_F$) was carefully calibrated within an accuracy of $\pm 0.01$ meV by recording Fermi cutoffs of Ag or Au in electrical contact with the sample and the analyzer. The spectra were recorded in an angle-integrated mode and typical energy resolutions during As26, P05 and Au measurements were 3, 3, and 1 meV, respectively.

We adopted “soft scraping” for the sample surface preparation, as we could obtain signatures of superconducting gaps in the spectra (described later) through this method. First, we polished the sample and made the surface convex. Then, the sample was introduced into the PES spectrometer and was softly scraped once with a diamond file at 150 K. Since the diamond file had a point contact with the convex surface of the sample, soft scraping resulted in a couple of lines of scratches on the surface. With the aid of a large-magnification CCD camera allowing us to view the laser spot position on the surface (spot diameter was $\lesssim 300$ μm) [21], we searched along the scratch for the highest photoemission count rate. After
the measurements, we checked the surface by an optical microscope and found a plate-like area of \(~200 \times 50 \ \mu m^2\) [image inset in Fig. (1) at the exact position where we had recorded the spectra. We note that the spectra recorded on fractured surfaces mostly showed \(T\) dependence of a Fermi-Dirac function even below \(T_c\), an unusual situation for a superconductor. We speculate that fracturing mostly resulted in exposure of metallic grain boundaries in the present sample.

The main panels of Fig. (1) (a) and (b) show laser PES spectra of As26 and P05, respectively, recorded during a \(T\) cycling. The sequence of the \(T\) cycling is indicated by arrows. The inset shows the spectra in a wide energy range. (b) Spectral DOS weights of As26 (left panel) and P05 (right panel) at several energies, derived from the data shown in Fig. 2 (circles) and in Fig. 3 (a) (crosses). The dotted lines are guide to the eye. The inset shows the depression rate of the spectral DOS weights with decreasing \(T\) from 70 to 30 K.

FIG. 1: Temperature dependence of the laser PES spectra of As26 (a), P05 (b) and Au (c). The spectra were normalized to the intensity at 40 meV below \(E_F\). The upper-right insets in (a) and (b) show enlarged plots near \(E_F\). The lower-left insets in (a) and (b) show wide-range spectra recorded at \(T \leq 100\) K and normalized to the intensity at -40 meV. The spectral DOSs of As26, P05 and Au derived from the spectra shown in the main panels of (a-c) are shown in (d-f), respectively. The inset in (c) shows a plate-like area of As26 (indicated by arrows) on which we recorded the spectra.

FIG. 2: Superconducting-gap feature of As26. (a) Near-\(E_F\) spectra of As26 recorded during a \(T\) cycling. The sequence of the \(T\) cycling is indicated by arrows. The inset shows the spectra in a wide energy range. (b) Spectral DOS weights of As26 (left panel) and P05 (right panel) at several energies, derived from the data shown in Fig. 2 (circles) and in Fig. 3 (a) (crosses). The dotted lines are guide to the eye. The inset shows the depression rate of the spectral DOS weights with decreasing \(T\) from 70 to 30 K.
Comparing the spectral DOSs of As26 and P05 at 5 \(\leq T \leq 20\) K shown in Fig. 1(d) and (e), respectively, one notices that the spectral weight at \(\sim 5\) meV about \(E_F\) of As26 is more depressed than that of P05. The rapid depression of the spectral DOS weight of As26 below \(T_c\) was reproducibly observed in a \(T\)-cycling measurement conducted separately [Fig. 2(a)], and we identify it to the opening of a superconducting gap. The line shapes of the spectral DOSs of As26 at \(T = 5\) and 10 K are almost identical [Fig. 1(d)], indicating that the superconducting gap is mostly opened at \(T = 10\) K, reasonable for a \(T_c = 26\) K sample. The signature of the superconducting gap of As26 is further highlighted in Fig. 2(b): the spectral DOS weights of both As26 and P05 in the normal state are \(T\)-linear due to the \(\sim 20\) meV pseudogap, but those of As26 for \(E - E_F \gtrsim 5\) meV exhibit rapid depressions below \(T_c = 26\) K. The spectra of P05 in the superconducting state were recorded by another laser PES spectrometer designed for low-\(T\) measurements as shown in Fig. 3(a) [25]. The spectral DOS of P05 at 2 K shown in Fig. 3(b) steepens towards \(E_F\) at \(E - E_F \gtrsim 1\) meV, attributable to the superconducting gap of P05 [please compare it with the \(T\)-independent spectral DOS of Au shown in Fig. 1(f) serving as a control of the laser-PES setup]. The signature of the superconducting gap occurring at \(\sim 1\) meV about \(E_F\) is reasonably smaller than that of As26 concerning the \(T_c\). However, the spectra recorded in the superconducting states of As26 and P05 fail to exhibit superconducting peaks and are not fully gapped. The finite intensity at \(E_F\) in the superconducting state may be caused by a non-superconducting volume [26], and therefore, this issue remains to be clarified in future.

Although the pseudogap features of high-\(T_c\) As26 and low-\(T_c\) P05 were nearly identical at \(T \leq 70\) K, prominent difference between the two emerges at high \(T\)’s. Figure 4(a) and (b) show spectra of As26 and P05, respectively, recorded in a wide-\(T\) range, and Fig. 4(c) and (d) show spectral DOSs of As26 and P05, respectively. There is a large pseudogap feature in the spectral DOS of As26 that becomes as large as \(\sim 0.1\) eV at 250 K but that shrinks with decreasing \(T\). On the other hand, the pseudogap feature of P05 is confined within \(\pm \sim 20\) meV about \(E_F\) at \(T \leq 150\) K. We also performed He I PES measurements and confirmed that the large \(T\)-dependent pseudogap was present in As26 but not in P05, even though the spot diameter of the He lamp was as large as \(\sim 5\) mm [27]. On et al. also observed a large \(T\)-dependent pseudogap feature in SmFeAsO:Fe, although they could not exclude extrinsic polycrystalline effects for this feature [28]. Since the signature of the superconducting gap in As26 [Fig. 2] serves as a credit that the spectra are reflecting the bulk electronic structure, we believe that the large \(T\)-dependent pseudogap is an intrinsic feature of As26.

FIG. 4: Laser PES spectra of As26 (a) and P05 (b) recorded in a wide-\(T\) range, and the spectral DOSs of As26 (c) and P05 (d) derived from the spectra shown in (a) and (b), respectively. The spectra were normalized to the intensity at \(E - E_F = -180\) meV, well beyond the energy region affected by the pseudogaps and the Fermi-Dirac broadenings.

Since the depression rates of the spectral-DOS weights with decreasing \(T\) from 70 to 30 K in As26 and P05 are nearly identical [inset in Fig. 2(b)], we consider that the \(\sim 20\)-meV pseudogap feature observed in As26 and P05 at \(T \leq 70\) K have a common origin. The \(\sim 20\)-meV pseudogap is presumably unrelated to magnetism concerning the diversity of magnetic susceptibilities between As26 and P05 (the former shows a small paramagnetic behavior whereas the latter shows Curie-Weiss-like paramagnetism [5]). Since \(\sim 20\) meV coincides with the energy scale of local Fe-As lattice vibrations which are softened compared to what is expected from local-density approximation calculations [28, 29], the \(\sim 20\)-meV pseudogaps could be attributed to electronic excitations coupled to such vibronic modes. In fact, Chainani et al. [30] attributed the \(\sim 70\)-meV pseudogap of a phonon-mediated superconductor, \(\text{Ba}_1-x\text{K}_x\text{BiO}_3\) [30], to strong electron-phonon coupling, since \(\sim 70\) meV is the energy of a breathing phonon mode. Even though isotropic electron-
phonon couplings have been predicted to be weak in the iron oxypnictides [31], strong anisotropic couplings still have a chance to exist [32]. It is also interesting to note that Hashimoto et al. [33] recently introduced a ∼70-meV pseudogap that occurs in the angle-integrated PES spectra of hole-doped La$_2$CuO$_4$ in the entire hole concentrations [33]. This new ∼70-meV pseudogap superimposed on the doping-dependent pseudogap of the cuprates [33] may share a common point to the ∼20-meV pseudogaps presented herein, since both are independent of $T_c$ or of doping. Hashimoto et al. proposed that the ∼70-meV pseudogap could be linked to $T$ dependence of ∼70-meV kinks ubiquitously observed in the nodal quasiparticle dispersions in the cuprates [34]. In fact, an angle-resolved PES study on (Sr,Ba)$_{1-x}$(K,Na)$_x$Fe$_2$As$_2$ reported dispersion kinks at 15-50 meV below $E_F$ [35], corroborating with the energy scale of the ∼20-meV pseudogap.

On the other hand, the large $T$-dependent pseudogap of high-$T_c$ As$_{26}$, which is considered to be superimposed on the ∼20-meV pseudogap, cannot be attributed to precursors of the superconducting gap, since the energy scale of ∼0.1 eV at 250 K is exceedingly larger than the superconducting gap size of ∼5 meV. One scenario for the large $T$-dependent pseudogap of As$_{26}$ is that the electronic excitations are coupled to spin fluctuations in the normal state of As$_{26}$, since the magnetic correlations of the antiferromagnetic parent compound [36,37] may persist in the F-doped superconductor. However, it is difficult to understand the $T$ dependence of the pseudogap in the spin-fluctuation scenario unless we invoke a situation such as the coupled-mode energy of the spin fluctuation becomes large at high $T$’s. Alternatively, we recall that similar $T$-dependent pseudogaps have been observed in Kondo insulators [38,39] and in thermoelectric skutterudites showing little signatures of electron correlations [40]. Although the origin of the $T$-dependent pseudogaps in these materials is also unclear [38,39,40], the common place is that they are narrow-gap [38,39] or semimetallic [40] materials having low carrier concentrations. Therefore, the $T$-dependent pseudogap of As$_{26}$ may be a fingerprint that As$_{26}$ is also a low-carrier density semimetal [27], consistent with a picture given in ref. [24].

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