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Temperature-dependent pseudogap in the oxypnictides $LaFeAsO_{1-x}F_x$ and $LaFePO_{1-x}F_x$ seen via angle-integrated photoemission

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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 pseudogaplike 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 pseudogaplike features and signatures of superconducting gaps in both LaFeAsO:F and LaFePO:F. We discuss the possible origins of the unusual pseudogaplike 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_2O_2 layers and T_2Pn_2 layers (Ln: lanthanide; T: Fe or Ni; Pn: P or As) were identified as new high-T_c materials[5–8] that exceed the BCS limit up to 55 K.[9–12] 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 for investigating the electronic structures of materials. Angle-integrated PES studies on FeAs-based superconductors have revealed pseudogap features with energies ranging from 15 to 40 meV at $T \lesssim 100$ K.[13–17] However, subsequent angle-resolved PES studies on iron oxypnictides[18,19] showed that the Fermi surfaces in the normal state were fully preserved, in contrast 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) (Ref. 5) and LaFePO:F (P05) (Ref. 6) 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.[13–17] 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 charge-coupled device (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 using an optical microscope and found a platelike area of $\sim 200 \times 50$ μm^2 (image

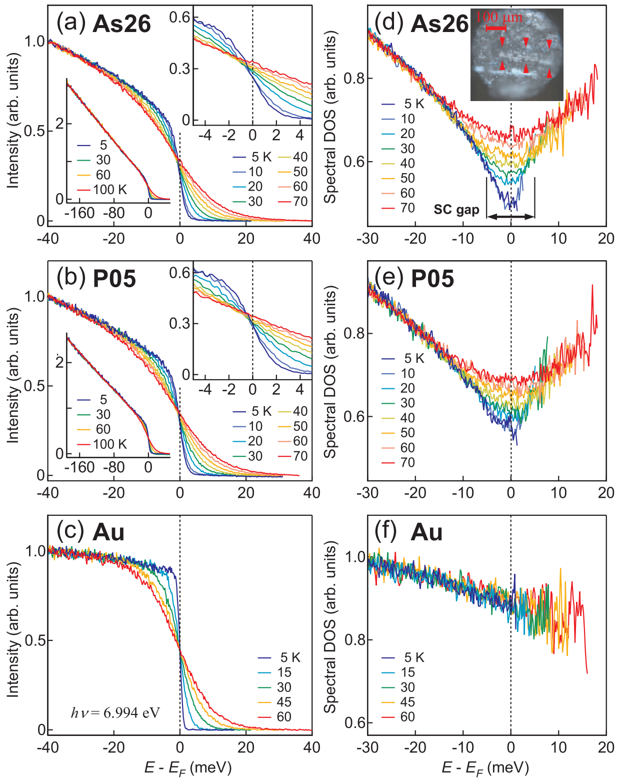

FIG. 1. (Color) Temperature dependence of the laser-PES spectra of (a) As26, (b) P05, and (c) Au. The spectra were normalized to the intensity at 40 meV below E_F. The upper-right insets of (a) and (b) show enlarged plots near E_F. The lower-left insets of (a) and (b) show wide-range spectra recorded at $T \leq 100$ K and normalized to the intensity at −40 meV. The spectral densities of states (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 of (c) shows a platelike area of As26 (indicated by arrows) on which we recorded the spectra.

inset of 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.

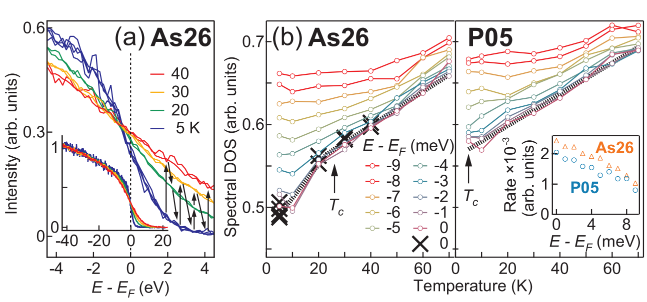

FIG. 2. (Color) Superconducting-gap feature of As26. (a) Near-E_F spectra of As26 recorded during a T cycling. The sequence of the T cycling is indicated by arrows. The inset shows the spectra in a wide energy range. (b) Spectral DOS weights of As26 (left panel) and P05 (right panel) at several energies, derived from the data shown in (a) (crosses) and in Figs. 1(d) and 1(e) (circles). The dotted lines are guides for the eyes. The inset shows the depression rate of the spectral DOS weights with decreasing T from 70 to 30 K.

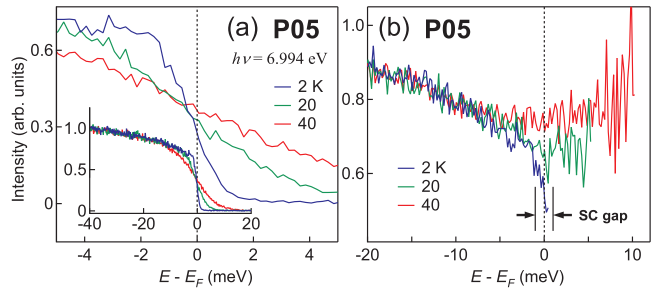

FIG. 3. (Color) Superconducting-gap feature of P05. (a) Laser-PES spectra recorded on fractured P05. The inset shows wide-energy-range spectra normalized to the intensity at 40 meV below E_F. (b) Spectral DOS of P05 showing signatures of the superconducting gap and the pseudogap.

The main panels of Figs. 1(a) and 1(b) show laser-PES spectra of As26 and P05, respectively, recorded at $T \leq 70$ K. Here, the spectra were normalized to the intensity at 40 meV below E_F since the spectra showed little change at $E-E_F < -40$ meV at $T \leq 100$ K as shown in the lower-left insets of Figs. 1(a) and 1(b). The spectra of both As26 and P05 show almost linear slopes toward E_F, consistent with the calculations based on local-density approximation.[23,24] In the magnified plots of the near-E_F spectra of As26 and P05 shown in the upper-right insets of Figs. 1(a) and 1(b), respectively, one can see that the intensity at E_F gradually becomes weak with decreasing T. The intensity variation at E_F is observed already at between 70 and 60 K, considerably higher than the T_c. This is in strong contrast to the T dependence of a "normal" metal as demonstrated by that of Au in Fig. 1(c). Clearly, all the spectra of Au intersect at a single point at E_F

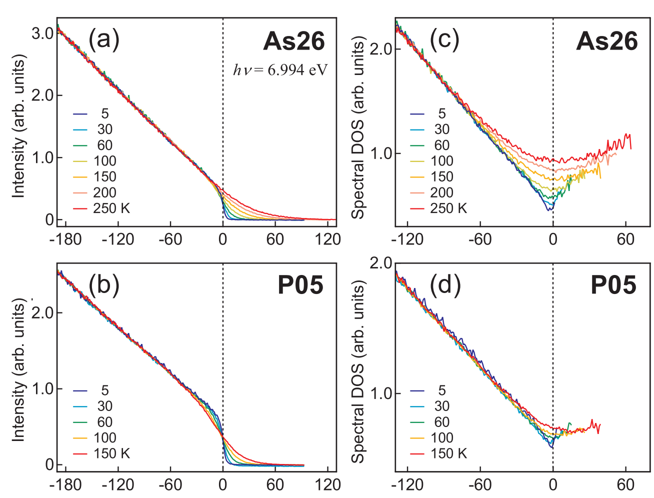

FIG. 4. (Color) Laser-PES spectra of (a) As26 and (b) P05 recorded in a wide-T range, and the spectral DOSs of (c) As26 and (d) P05 derived from the spectra shown in (a) and (b), respectively. The spectra were normalized to the intensity at $E-E_F = -180$ meV, well beyond the energy region affected by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

since their T dependence obeys that of a Fermi-Dirac distribution function which takes a T-independent value of 1/2 at E_F. Thus, the metallic phase above the superconducting phase of As26 and P05 is pseudogapped, i.e., the near-E_F spectral weight is mysteriously depressed with decreasing T even in the absence of an apparent order parameter.

In order to investigate the energy scale of the pseudogaps at $T \leq 70$ K, we have divided the laser-PES spectra of As26 and P05 by the Fermi-Dirac distribution function convoluted with a Gaussian corresponding to the instrumental resolution. Through this procedure, one can isolate the T dependence of spectral DOS from that of the Fermi-Dirac distribution function. The spectral DOSs of As26 and P05 thus obtained are shown in Figs. 1(d) and 1(e), respectively. One can see that the spectral DOS of As26 is depressed with decreasing T below 70 K in the energy range of $\pm\sim 20$ meV, and we identify it to the 15–40 meV pseudogaps reported in the angle-integrated PES studies on the FeAs system.[13–17] Surprisingly, a T dependence similar to the ~20-meV pseudogap of As26 is present even in the spectral DOS of low-T_c P05 [Fig. 1(e)]. This indicates that the ~20-meV pseudogaps at $T \lesssim 100$ K are commonly observed in the iron oxypnictides and are irrelevant to T_c. The anomalous pseudogap features of As26 and P05 are in clear contrast to the T-independent spectral DOS of Au shown in Fig. 1(f) representing a normal metal.

Comparing the spectral DOSs of As26 and P05 at $5 \leq T \leq 20$ K shown in Figs. 1(d) and 1(e), respectively, one notices that the spectral weight at ~5 meV at 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 be 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 ~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 toward 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 ~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 nonsuperconducting volume.[26] Therefore, this issue remains to be clarified in the future.

Although the pseudogap features of high-T_c As26 and low-T_c P05 were nearly identical at $T \leq 70$ K, a prominent difference between the two emerges at high T's. Figures 4(a) and 4(b) show spectra of As26 and P05, respectively, recorded in a wide-T range, and Figs. 4(c) and 4(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 ~0.1 eV at 250 K but shrinks with decreasing T. On the other hand, the pseudogap feature of P05 is confined within $\sim\pm 20$ meV at 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 ~5 mm.[27] Ou *et al.*[15] also observed a large T-dependent pseudogap feature in SmFeAsO:F, although they could not exclude extrinsic polycrystalline effects for this feature. 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.

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 of Fig. 2(b)], we consider that the ~20-meV pseudogap features observed in As26 and P05 at $T \leq 70$ K have a common origin. The ~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,[6] whereas the latter shows Curie-Weiss-like paramagnetism.[5]) Since ~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 ~20-meV pseudogaps could be attributed to electronic excitations coupled to such vibronic modes. In fact, Chainani *et al.*[30] attributed the ~70-meV pseudogap of a phonon-mediated superconductor, $Ba_{1-x}K_xBiO_3$,[30] to strong electron-phonon coupling since ~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 an ~70-meV pseudogap that occurs in the angle-integrated PES spectra of hole-doped La_2CuO_4 in the entire range of hole concentrations.[33] This new ~70-meV pseudogap superimposed on the doping-dependent pseudogap of the cuprates[33] may share a common point with the ~20-meV pseudogaps presented herein since both are independent of T_c or of doping. Hashimoto *et al.*[33] 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 $(Sr,Ba)_{1-x}(K,Na)_xFe_2As_2$ 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 As26, 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 As26 is that the electronic excitations are coupled to spin fluctuations in the normal state of As26 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 that 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,[38–40] 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 As26 may be a fingerprint that As26 is also a low-carrier-density semimetal,[27] consistent with a picture given in Ref. 24.

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