

Supplementary Information for “Orientation-dependent electronic structure in interfacial superconductors $\text{LaAlO}_3/\text{KTaO}_3$ ”

Xiaoyang Chen¹, Tianlun Yu¹, Yuan Liu², Yanqiu Sun², Minyinan Lei¹, Nan Guo¹, Yu Fan¹, Xingtian Sun¹, Meng Zhang², Fatima Alarab³, Vladimir N. Strocov³, Yilin Wang⁴, Tao Zhou¹, Xinyi Liu¹, Fanjin Lu¹, Weitao Liu¹, Yanwu Xie^{*2}, Rui Peng^{†1,5}, Haichao Xu^{‡1,5}, and Donglai Feng^{§6,7}

¹Advanced Materials Laboratory, State Key Laboratory of Surface Physics, and Department of Physics, Fudan University, Shanghai 200438, China

²School of Physics, Zhejiang University, Hangzhou, 310027, China

³Swiss Light Source, Paul Scherrer Institute, Villigen, CH-5232, Switzerland

⁴School of Future Technology and Department of Physics, University of Science and Technology of China, Hefei, 230026, China

⁵Shanghai Research Center for Quantum Sciences, Shanghai 201315, China

⁶National Synchrotron Radiation Laboratory and School of Nuclear Science and Technology, New Cornerstone Science Laboratory, University of Science and Technology of China, Hefei, 230026, China

⁷School of Emerging Technology and Department of Physics, University of Science and Technology of China, Hefei, 230026, China

August 6, 2024

*Corresponding author: ywxie@zju.edu.cn

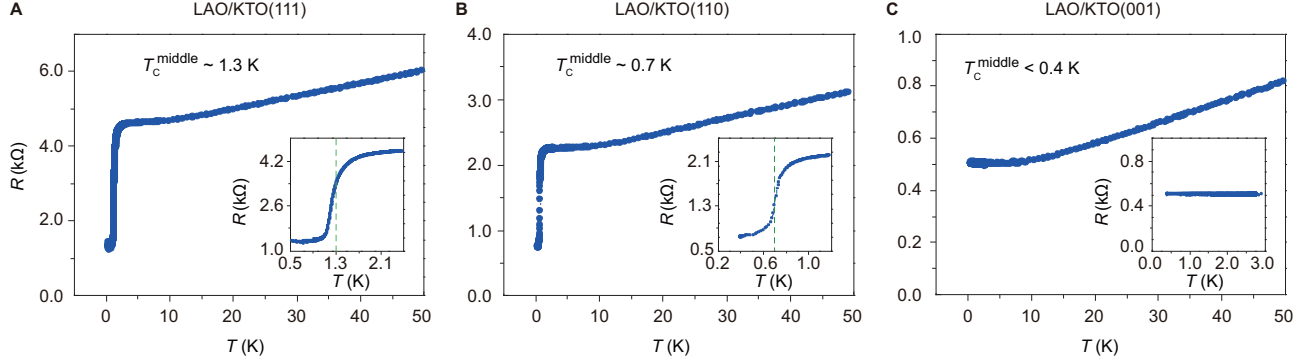
†Corresponding author: pengrui@fudan.edu.cn

‡Corresponding author: xuhaichao@fudan.edu.cn

§Corresponding author: dlfeng@ustc.edu.cn

Supplementary Note 1. Orientation-dependent superconductivity of 3 nm-LAO/KTO.

Supplementary Fig. 1 shows the superconducting transitions with $T_c^{\text{middle}} = 1.3$ K and 0.7 K in 3 nm-LAO/KTO(111) and 3 nm-LAO/KTO(110), respectively, while the superconductivity is absent down to 0.4 K in 3 nm-LAO/KTO(001). The orientation-dependent superconductivity with $T_c(111) > T_c(110) > T_c(001)$ is verified both in 3 nm-LAO/KTO (Supplementary Fig. 1) and 1.5 nm- AlO_x /1 nm-LAO/KTO (Fig. 1b in the main text).



Supplementary Fig. 1: Orientation-dependent superconductivity of 3 nm-LAO/KTO. (A-C) Temperature-dependent resistance of 3 nm-LAO/KTO(111), 3 nm-LAO/KTO(110), and 3 nm-LAO/KTO(001), respectively. Note that the measurements were conducted in a two-terminal configuration, and the residual resistance in the superconducting state of the LAO/KTO(110) and LAO/KTO(111) interfaces arise from the contact resistance.

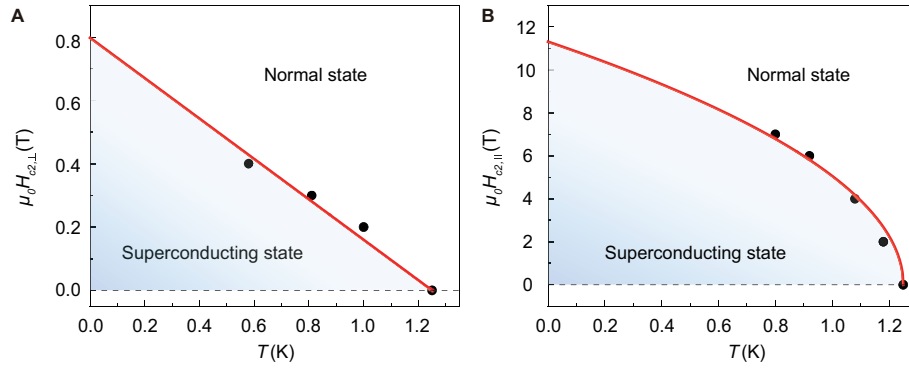
Supplementary Note 2. Estimation of the superconducting coherence length and superconducting layer thickness in LAO/KTO(111).

One can estimate the superconducting coherence length (ξ) and superconducting layer thickness (d_{SC}) based on the Ginzburg-Landau theory [1]:

$$\mu_0 H_{c2,\perp} = \frac{\phi_0}{2\pi\xi_{||}^2(0)} \left(1 - \frac{T}{T_c}\right)$$

$$\mu_0 H_{c2,\parallel} = \frac{\sqrt{3}\phi_0}{\pi\xi_{||}(0)d_{SC}} \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}}$$

where ϕ_0 is the flux quantum. From the measured temperature dependence of the out-of-plane upper critical field $H_{c2,\perp}$ and the in-plane upper critical field $H_{c2,\parallel}$ (Supplementary Fig. 2), we extract the zero-temperature Ginzburg-Landau coherence length $\xi_{||}(0)$ and the corresponding superconducting layer thickness d_{SC} , which are 20.3 nm and 5.0 nm, respectively. The strong anisotropy of the upper critical field, together with the smaller superconducting layer thickness compared with the in-plane coherence length ($d_{SC} < \xi_{||}$), indicate the two-dimensional superconductivity at the LAO/KTO(111) interface.

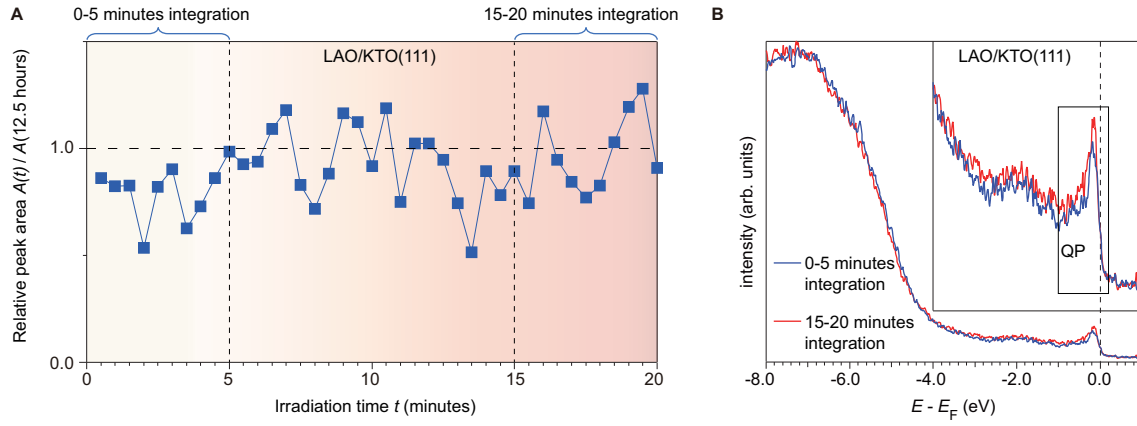


Supplementary Fig. 2: Upper critical field of the LAO/KTO(111) interfacial superconductivity. (A) Temperature dependence of the perpendicular upper critical field $H_{c2,\perp}$. Data were measured when the magnetic field was perpendicular to the (111) interface. (B) Temperature dependence of the parallel upper critical field $H_{c2,\parallel}$. Data were measured when the magnetic field was parallel to the (111) interface. All the data are fitted by the Ginzburg-Landau theory (red curves).

Supplementary Note 3. Negligible irradiation dependence of the interfacial states during SX-ARPES measurements.

It is reported that the synchrotron irradiation would create oxygen vacancies on the surface of insulating KTO substrates to form mobile electron gas [2, 3, 4]. To distinguish the intrinsic interfacial metallic states and the irradiation-induced metallic states, we performed SX-ARPES measurements on the LAO/KTO(111) interface at varied irradiation times. As shown in Supplementary Fig. 3A, the metallic states have always been presented since the beginning of the measurements, in contrast to the irradiation-induced metallic states which should gradually emerge during irradiation [2, 3, 4]. After 20 minutes of irradiation, the lineshape of the photoemission spectra shows little variation (Supplementary Fig. 3B). Quantitatively, the density of states at the Fermi energy measured at different irradiation times remains similar for the first 20 minutes and after 12.5 hours of irradiation (Supplementary Fig. 3A). These results indicate that the observed metallic states mainly come from the intrinsic interfacial states, rather than from synchrotron irradiation. The interfacial states of LAO/KTO(110) and (001) show similar results during irradiation, which were not shown here. The LAO overlayer may have protected the interface and reduced the effect of creating oxygen vacancies at KTO by irradiation.

The oxygen-vacancy states at around -2 eV binding energy were likely generated during the LAO deposition process, hence intrinsic to the interfacial electronic structures. The sample fabrication process involves low oxygen pressures (1×10^{-5} mbar) and high temperatures ($\sim 680^\circ\text{C}$) by PLD, which leads to the generation of oxygen vacancies in both the films and the substrates [5]. As the oxygen vacancies should be created above 450°C [2], the creation of oxygen vacancies during the 250°C in-situ annealing process before SX-ARPES measurements should be negligible.

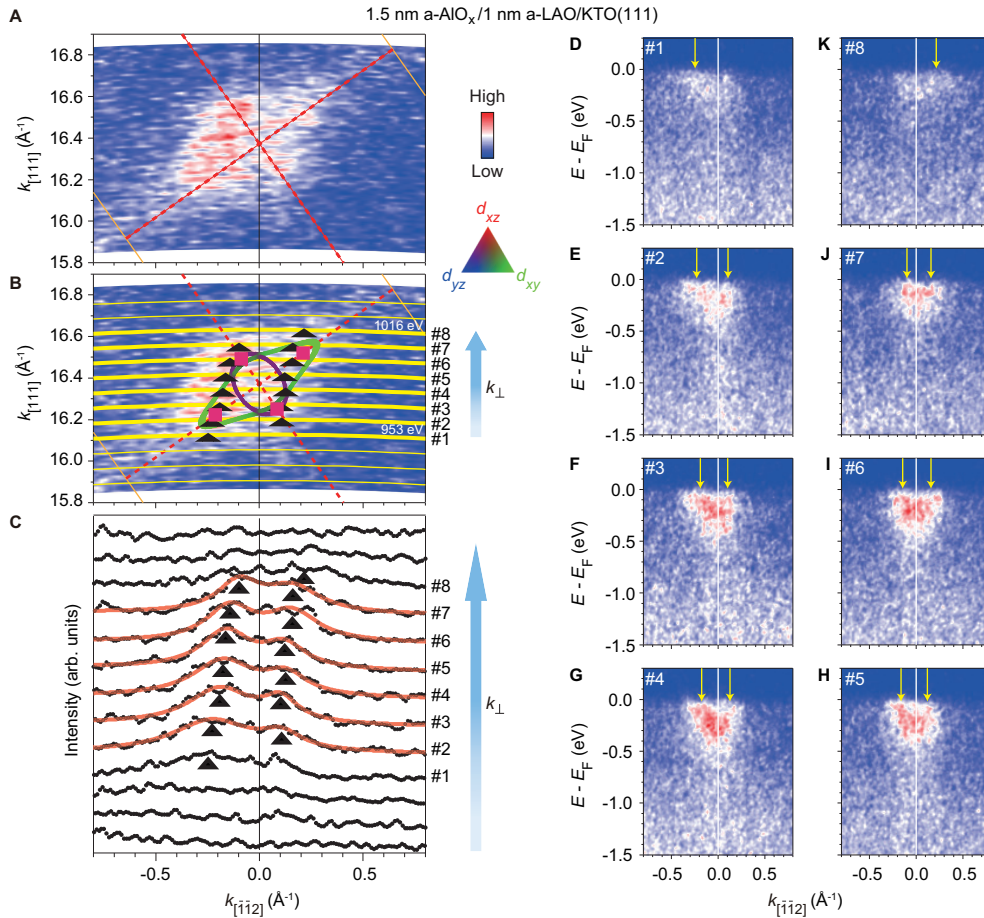


Supplementary Fig. 3: Irradiation time dependence of the LAO/KTO(111) interfacial states. (A) Irradiation time dependence of the relative peak area $A(t)/A(12.5 \text{ hours})$. (B) Energy distribution curves (EDCs) with momentum-integration over $[-0.3 \text{ \AA}^{-1}, 0.3 \text{ \AA}^{-1}]$. The two EDCs are measured during the irradiation time of 0~5 minutes (blue) and 15~20 minutes (red). The inset shows the zoomed-in view of EDCs near E_F . The black box illustrates the region of integration to get the peak area in (A).

Supplementary Note 4. Quasi-three-dimensional nature of the interfacial states in LAO/KTO.

4.1. LAO/KTO(111).

For 1.5 nm- AlO_x /1 nm-LAO/KTO(111), Supplementary Fig. 4C shows that the peak positions of the MDCs integrated at E_F vary along $k_\perp$. Together with the k_F s determined based on the major/minor axis of the elongated Fermi surfaces (red marker in Supplementary Fig. 4B, see details in Supplementary Figs. 6C-E), they consistently form a closed Fermi surface contour (Supplementary Fig. 4B). Moreover, the Fermi velocity (v_F) on both sides of the in-plane momentum center (i.e., $k_{\bar{1}\bar{1}2} = 0$) evolves with the photon energy. Specifically, below the Γ point, the v_F on the left side is smaller than the v_F on the right side (Supplementary Figs. 4D-F). At the Γ point, the v_F is equal on both sides (Supplementary Figs. 4G-H). Above the Γ point, the v_F on the left side is larger than the v_F on the right side (Supplementary Figs. 4I-K). The evolution of v_F with photon energy is dramatically different from intensity variations that arise from the matrix element effect and further demonstrates that the elongated Fermi surface is a genuine characteristic of the quasi-three-dimensionality.



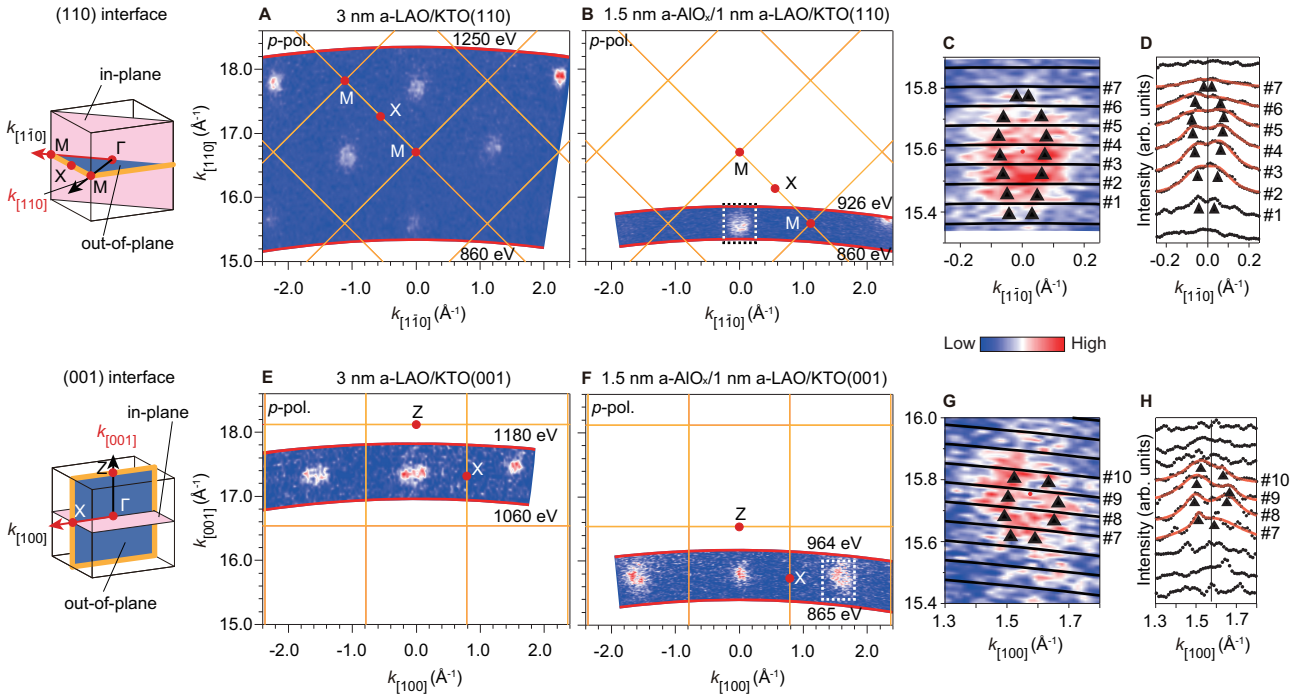
Supplementary Fig. 4: Out-of-plane Fermi surface of the LAO/KTO(111) interfacial states. (A-B) Out-of-plane Fermi surface map of LAO/KTO(111) integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ in $k_{\perp 111} - k_{\perp 112}$ plane using p -polarized photons from 921 eV to 1044 eV. The peak positions of the MDCs in (C) are marked by black triangles, and the k_F s determined by fitting MDCs along the major/minor axis of the elongated Fermi surface are marked by red squares. (C) MDCs integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ of spectra taken at different photon energies. Each selected MDC is fitted by two Lorentzian peaks and a linear background. (D-K) Photoemission spectra measured at the $k_\perp$ positions below the Γ point (D-F), near the Γ point (G-H) and above the Γ point (I-K). The fitted peak positions of the MDCs in (C) are specified by arrows in each panel.

4.2. LAO/KTO(110) and LAO/KTO(001).

The interfacial states of LAO/KTO(110) and LAO/KTO(001) disperse strongly along $k_{\perp}$ direction, similar to those of LAO/KTO(111).

Specifically, in contrast to the mere intensity variation along $k_{\perp}$ direction of the two-dimensional electron gas [2, 3], in the spectra of LAO/KTO(110) and (001) that are measured at different photon energies, the peak positions of the MDCs at E_F vary along $k_{\perp}$ direction, forming the closed Fermi surface contour (Supplementary Figs. 5C-D, G-H).

The depth of the electron gas is estimated as 5 ~ 7 nm, as will be discussed in Section 5 of Supplementary information, which deviates from both purely two-dimensional and purely three-dimensional, and that's why we call it "quasi-three-dimensional" in the main text. Concerning this wide confined region, our results of the varied k_{FS} along $k_{\perp}$ can be understood by the "extended quantum well" scenario [6, 7, 8]: a wide confined region introduces quantum well states consecutively, leading to more bulk-like features in ARPES spectra, as reflected in the out-of-plane intensity distribution around the virtual bulk Fermi surface and the formation of bands along $k_{\perp}$. Our results are consistent with the simulations in the work of S. Moser *et al.* [6], where the 5 nm depth of the electron gas would give three-dimensional electronic structures and strong dispersion along $k_{\perp}$. It would be surprising if the electronic structure remains two-dimensional in such a thickness, while the observed dominant three-dimensional character is as expected. All these results indicate that the interfacial states are located at the crystalline KTO side and are quasi-three-dimensional.



Supplementary Fig. 5: Out-of-plane Fermi surfaces of the LAO/KTO(110) and LAO/KTO(001) interfacial states. (A-B) Out-of-plane Fermi surface map integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ in $k_{[110]} - k_{[110]}$ plane (the blue Γ -M-X plane in the upper-left inset) measured on 3 nm-LAO/KTO(110) and 1.5 nm- AlO_x /1 nm-LAO/KTO(110), respectively. (C) Zoomed-in view of the photoemission intensity map inside the dashed box in (B). The cuts #1 ~ #6 are marked by black curves and the peak positions of the MDCs in (D) are marked by black triangles. (D) MDCs integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ along cuts #1 ~ #6, which are fitted by two Lorentzian peaks and a linear background. The peak positions of the MDCs at E_F are marked by black triangles. (E-F) Out-of-plane Fermi surface map integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ in $k_{[100]} - k_{[001]}$ plane (the blue Γ -X-Z plane in the lower-left inset) measured on 3 nm-LAO/KTO(001) and 1.5 nm- AlO_x /1 nm-LAO/KTO(001), respectively. (G) Zoomed-in view of the photoemission intensity map inside the dashed box in (F). The cuts #7 ~ #10 are marked by black curves and the peak positions of the MDCs in (H) are marked by black triangles. (H) MDCs integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ along cuts #7 ~ #10, which are fitted by two Lorentzian peaks and a linear background. The peak positions of the MDCs at E_F are marked by black triangles. The photon energy ranges, photon polarizations, and specific sample types are noted.

Supplementary Note 5. Luttinger volume and three-dimensional carrier density analysis.

According to the Luttinger theorem [9], the carrier density per volume (n_{3D}) can be estimated by the Luttinger volume (V_{FS}), which is the volume enclosed by the Fermi surface (FS) in k space:

$$n_{3D} = \frac{V_{FS}}{4\pi^3} \quad (1)$$

The FS of the electron-doped bulk KTO states is contributed by three Ta t_{2g} orbitals: d_{xy} , d_{xz} and d_{yz} (see details in Section 7 of Supplementary information). Before considering the effect of spin-orbital coupling (SOC) and inter-orbital hybridization, the three orbitals would form three identical ellipsoid-like FS sheets, respectively. SOC hybridizes the three orbitals and lifts one band above E_F . The resulting FS is contributed by only two bands with hybridized t_{2g} orbitals, forming a double-layered FS. To account for the band lift above E_F , we subtracted one sphere as an approximation, and the remaining volume V_{FS} could be estimated as:

$$V_{FS} = 3 \times \frac{4}{3}\pi k_a k_b^2 - \frac{4}{3}\pi k_b^3 \quad (2)$$

where the k_a and k_b are Fermi momenta (k_{FS}) along the ellipsoid major axis and the ellipsoid minor axis, respectively.

In LAO/KTO(111), the FS lobes are elongated along the major axis of the ellipsoid in the out-of-plane photoemission map ($k_{[\bar{1}\bar{1}2]} - k_{[111]}$) (Supplementary Fig. 6C), from which the high symmetric cuts along #1 ($k_{[110]}$) and #2 ($k_{[001]}$) are extracted. Along cut #2, the MDCs near E_F give $k_a = 0.26 \text{ \AA}^{-1}$ (Supplementary Fig. 6E). Along cut #1, the two Fermi momenta are not distinguishable in ARPES spectra. We take the MDC peak position as the mean value of the two Fermi momenta ($k_p = 0.15 \text{ \AA}^{-1}$) (Supplementary Fig. 6D), and obtained $k_b = 0.12 \text{ \AA}^{-1}$ based on the geometry of ellipsoid. n_{3D} is calculated by equations (1) and (2), which gives $n_{3D,(111)} = 3.2 \times 10^{20} \text{ cm}^{-3}$.

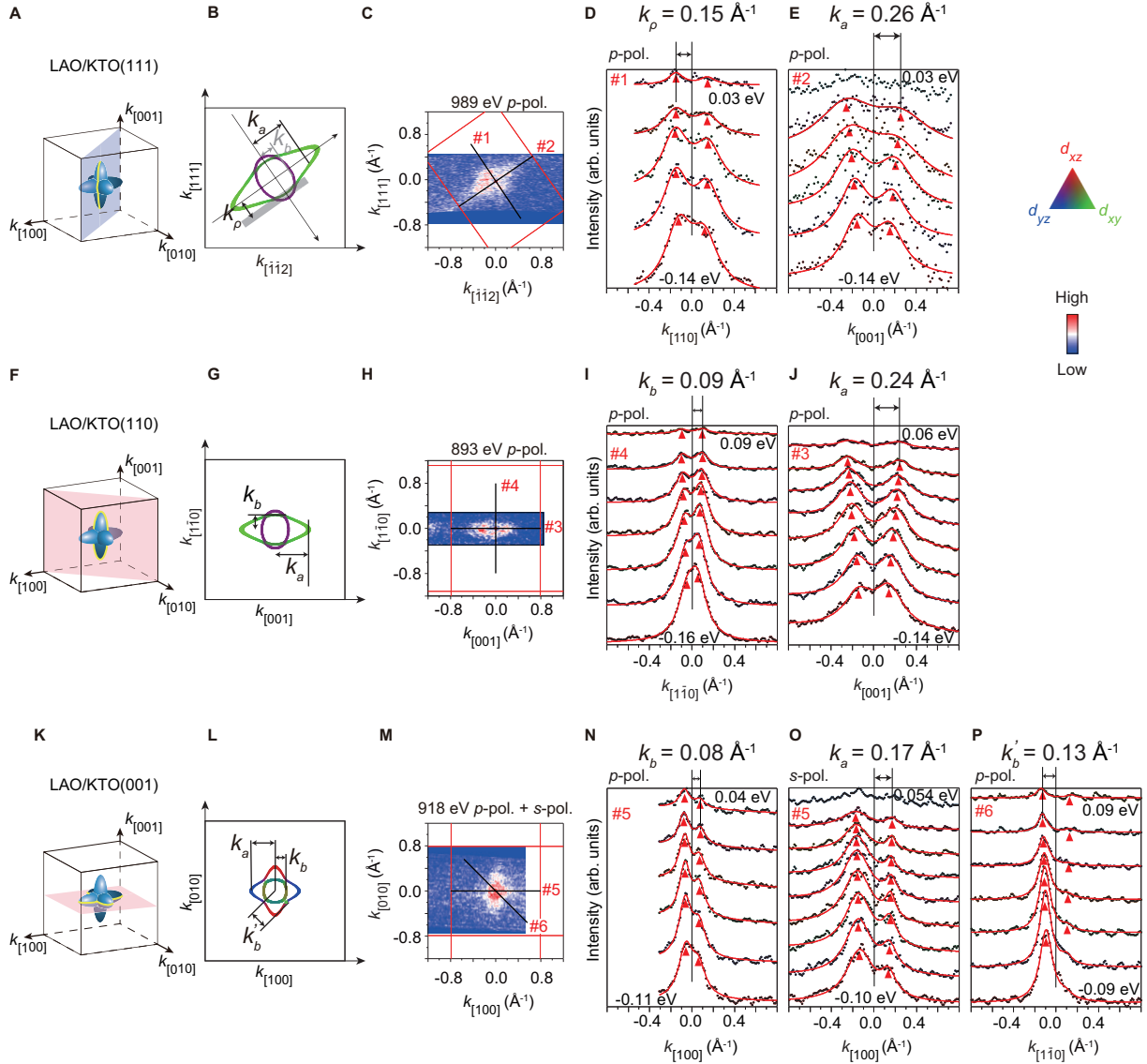
In LAO/KTO(110), the in-plane photoemission map ($k_{[1\bar{1}0]} - k_{[001]}$) gives the elongated Fermi surface along the major axis of the ellipsoid (Supplementary Fig. 6H). Along cut #3, the MDCs near E_F give $k_a = 0.24 \text{ \AA}^{-1}$ (Supplementary Fig. 6J). Along cut #4, spectra measured by p -polarized photons should be dominated by the inner band with d_{xy} orbital character, whose MDCs near E_F give $k_b = 0.09 \text{ \AA}^{-1}$ (Supplementary Fig. 6I). n_{3D} is calculated by equations (1) and (2), which gives $n_{3D,(110)} = 1.7 \times 10^{20} \text{ cm}^{-3}$.

In LAO/KTO(001), the elongated Fermi surface along the major axis of the ellipsoid could be observed in the in-plane photoemission map ($k_{[100]} - k_{[010]}$) (Supplementary Fig. 6M). Along cut #5, spectra measured by p -polarized photons only shows the inner band with d_{xz} orbital character, whose MDCs near E_F give $k_b = 0.08 \text{ \AA}^{-1}$ (Supplementary Fig. 6N). The spectra measured by s -polarized photons shows the outer band with dominant d_{yz} orbital character, whose MDCs near E_F give $k_a = 0.17 \text{ \AA}^{-1}$ (Supplementary Fig. 6O). Along cut #6, the spectra measured by p -polarization photons show only d_{xy} orbital, which exhibits a downward shift in binding energy, resulting in a larger k_F (see details in Section 6 of Supplementary information). The MDCs near E_F give its minor axis $k'_b = 0.13 \text{ \AA}^{-1}$ (Supplementary Fig. 6P). We assume the ellipticity does not change during the expansion, so the major axis can be estimated as $k'_a = k'_b(k_a/k_b) = 0.28 \text{ \AA}^{-1}$. $V_{FS,(001)}$ is calculated by:

$$V_{FS,(001)} = 2 \times \frac{4}{3}\pi k_a k_b^2 + \frac{4}{3}\pi k'_a k_b'^2 - \frac{4}{3}\pi k_b^2 k_b', \quad (3)$$

where the ellipsoid of d_{xy} is calculated separately to account for its expansion. Using Equations (1) and (3), we further get $n_{3D,(001)} = 2.0 \times 10^{20} \text{ cm}^{-3}$.

Supplementary Table 1 summarizes the fitting results of the Fermi momenta (k_{FS}), three-dimensional carrier densities (n_{3D} , calculated by Luttinger volume), two-dimensional carrier densities (n_{2D} , calculated by Hall resistivity) and the estimated lower limit of the electron gas thickness of LAO/KTO ($d_{e,min} = n_{2D}/n_{3D}$).



Supplementary Fig. 6: Luttinger volume analysis of the LAO/KTO interfacial states. (A) Sketch of the bulk cubic BZ and the ellipsoid-like FS of the electron-doped bulk KTO. The (110) plane is colored in blue. (B) FS of the electron-doped bulk KTO in the (110) plane. (C) Out-of-plane photoemission intensity map integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ in (110) plane ($k_{[1\bar{1}2]}-k_{[111]}$ plane) of the LAO/KTO(111) interfacial states. (D-E) MDCs near E_F along cuts #1 and #2 in (C), respectively. (F) Sketch of the bulk cubic BZ and the ellipsoid-like FS of the electron-doped bulk KTO. The (110) plane is colored in pink. (G) FS of the electron-doped bulk KTO in the (110) plane. (H) In-plane photoemission intensity map integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ in (110) plane ($k_{[001]}-k_{[1\bar{1}0]}$ plane) of the LAO/KTO(110) interfacial states. (I-J) MDCs near E_F along cuts #4 and #3 in (H), respectively. (K) Sketch of the bulk cubic BZ and the ellipsoid-like FS of the electron-doped bulk KTO. The (001) plane is colored in pink. (L) FS of the electron-doped bulk KTO in the (001) plane. (M) In-plane photoemission intensity map integrated over $[E_F - 150 \text{ meV}, E_F + 150 \text{ meV}]$ in (001) plane ($k_{[100]}-k_{[010]}$ plane) of the LAO/KTO(001) interfacial states. (N-P) MDCs near E_F along cuts #5 (p-pol.), #5 (s-pol.) and #6 (p-pol.) in (M), respectively. All MDCs are fitted by the Lorentzian peaks and linear background.

Supplementary Table 1: Summary of the Fermi momenta, carrier densities and the estimation on the thickness of the interfacial states.

Samples	Orbitals	k_a ($\text{\AA}^{-1}$)	k_b ($\text{\AA}^{-1}$)	n_{3D} (cm^{-3})	n_{2D} (cm^{-2})	$d_{e,min}$ (nm)
LAO/KTO(111)	d_{xy}, d_{xz}, d_{yz}	0.26	0.12	3.2×10^{20}	2.16×10^{14}	6.8
LAO/KTO(110)	d_{xy}, d_{xz}, d_{yz}	0.24	0.09	1.7×10^{20}	1.04×10^{14}	6.0
LAO/KTO(001)	d_{xz}, d_{yz}	0.17	0.08	2.0×10^{20}	1.12×10^{14}	5.5
	d_{xy}	0.28	0.13			

Supplementary Note 6. Comparison of LAO/KTO interfacial states with the KTO bulk states under a chemical potential shift.

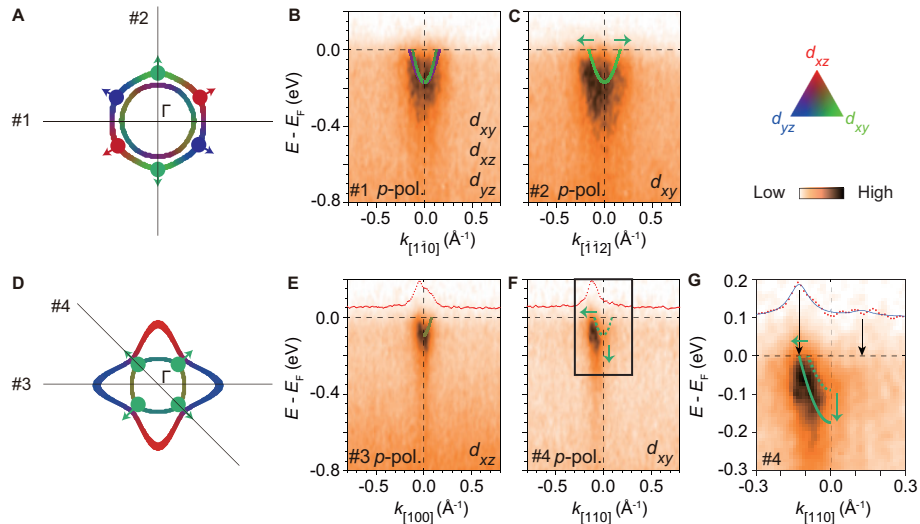
With the widely-confined region of 5~7 nm for the interfacial states of LAO/KTO, the electronic structures roughly agree with the density functional theory (DFT) calculations considering spin-orbital coupling on bulk KTO upon a chemical potential shift (Figs. 2d, 2h-2i, 3a-3b and 3f-3k in the main text). Here we discuss the fine differences in the electronic structure.

For LAO/KTO(111), upon a suitable chemical potential shift $\Delta\mu_{(111)}$ to account for the electron doping, the DFT-calculated Fermi surfaces (FS) consist of two hexagonal contours in the (111) plane (Supplementary Fig. 7A). In the experimental data, while the k_F along cut #1 agrees with the DFT-calculations under the chemical potential shift $\Delta\mu_{(111)}$ (Supplementary Fig. 7B, and see details of the k_F determination along the equivalent direction $k_{[110]}$ in Supplementary Fig. 6D), the experimental spectra along cut #2 show a larger k_F than the calculation (Supplementary Fig. 7C). Therefore, the experimental Fermi surface is slightly more anisotropic in the (111) plane than the calculations on bulk KTO.

For LAO/KTO(001), upon a suitable chemical potential shift $\Delta\mu_{(001)}$, while the experimental k_F along cut #3 agree well with DFT calculations (Supplementary Fig. 7E), the experimental k_F along cut #4 is larger than that of the DFT calculations (Supplementary Figs. 7F-G), suggesting a slight expansion of d_{xy} pocket (Supplementary Fig. 7D).

Similar differences between the experimental band structures and the calculations on the bulk materials were reported in the KTO(111) and KTO(001) surface two-dimensional electron gas (2DEG) [2, 3], which are attributed to the electron confinement effect [3, 4], but with a much-pronounced magnitude than that observed here. The finite but weaker confinement effect in LAO/KTO than that in surface 2DEG systems suggests that the interfacial states here are quasi-three-dimensional rather than pure two-dimensional or pure three-dimensional, consistent with the over 5 ~ 7 nm thickness of the interfacial states.

It's worth noting that although the finite interfacial confinement will modify the bulk band structure, it will not enlarge the occupied bandwidth. Even with 1 nm confinement, the in-plane effective mass of the lowest-lying d_{xy} component in the KTO(001) surface 2DEG shows negligible change [3], and the in-plane effective mass along $[1\bar{1}0]$ in the KTO(111) surface 2DEG remains almost unchanged [2]. Our analysis on determining the bandwidth of the bare band and simulating EPC is based on the data along $[1\bar{1}0]$ direction (Fig. 4a in the main text), where the modification of the in-plane effective mass is negligible with over 5 nm confinement. Therefore, the analysis along $[1\bar{1}0]$ direction considering a rigid shift of the DFT-calculated bulk band gives a reliable bandwidth of the bare band, which represents the upper limit of the



Supplementary Fig. 7: Comparison between the LAO/KTO interfacial states and the calculated KTO bulk states under a chemical potential shift. (A) DFT-calculated bulk KTO Fermi surface (FS) in the (111) plane, with a chemical potential shift accounting for the electron doping. The arrows schematically indicate that the outer FS contour of the LAO/KTO(111) interfacial state is slightly more anisotropic than the calculated one. (B-C) Photoemission intensity of the LAO/KTO(111) interfacial states along cuts #1 and #2 in (A), respectively. The green arrows in (C) schematically show the slight increase of k_F along this direction in LAO/KTO(111). (D) DFT-calculated bulk KTO FS in the (001) plane with a chemical potential shift accounting for the electron doping. The arrows schematically show that the k_F of the lowest-lying d_{xy} components at the inner FS contour expands for the LAO/KTO(001) interfacial states. (E-F) Photoemission intensity of LAO/KTO(001) interfacial states along cuts #3 and #4 in (D), respectively. The green arrows in (F) and (G) schematically show the directions along which the lowest-lying d_{xy} band shifts in binding energy (from the dashed line to the solid line in (G)) upon finite confinement, inducing the expansion of the k_F . (G) Zoomed-in view of the black box region in (F). The photoemission spectra weight is mainly contributed by the d_{xy} orbital along this direction.

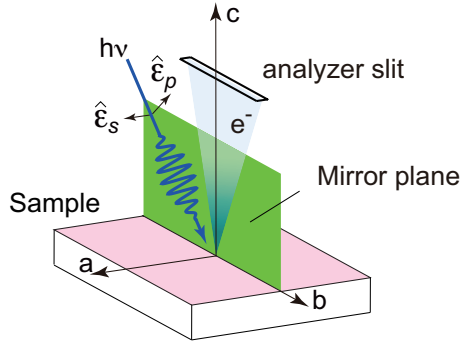
bandwidth before considering EPC.

Supplementary Note 7. Orbital characters of the LAO/KTO interfacial states are determined by the polarization-dependent ARPES measurements.

Supplementary Fig. 8 shows the experimental geometry of our SX-ARPES measurements. The mirror plane (bc -plane, colored in green in Supplementary Fig. 8) is defined by the analyzer slit and the surface normal. The photoemission intensity matrix element is written as:

$$|M_{f,i}^k|^2 \propto |\langle \phi_f^k | \hat{\epsilon} \cdot \mathbf{r} | \phi_i^k \rangle|^2 \quad (4)$$

where ϕ_f^k and ϕ_i^k are wave functions of the final and initial states, respectively, and $\hat{\epsilon}$ is the unit vector of the synchrotron radiation electric field. The spatial symmetry of $(\hat{\epsilon} \cdot \mathbf{r})$ with respect to the mirror plane is even (odd) for $p(s)$ -polarized photons. Since ϕ_f^k can be approximated as a plane wave which always has even spatial symmetry with respect to the mirror plane [10, 11], equation (1) indicates that only even (odd) initial states with respect to the mirror plane are visible by using $p(s)$ -polarized photons. Besides, in such experimental geometry, s -polarized photons will cause strong suppression of photoemission intensity along the mirror plane compared with p -polarized photons even if their photon beam intensity are the same [12], resulting in all the spectra measured by s -polarized photons are weaker than those measured by p -polarized photons.



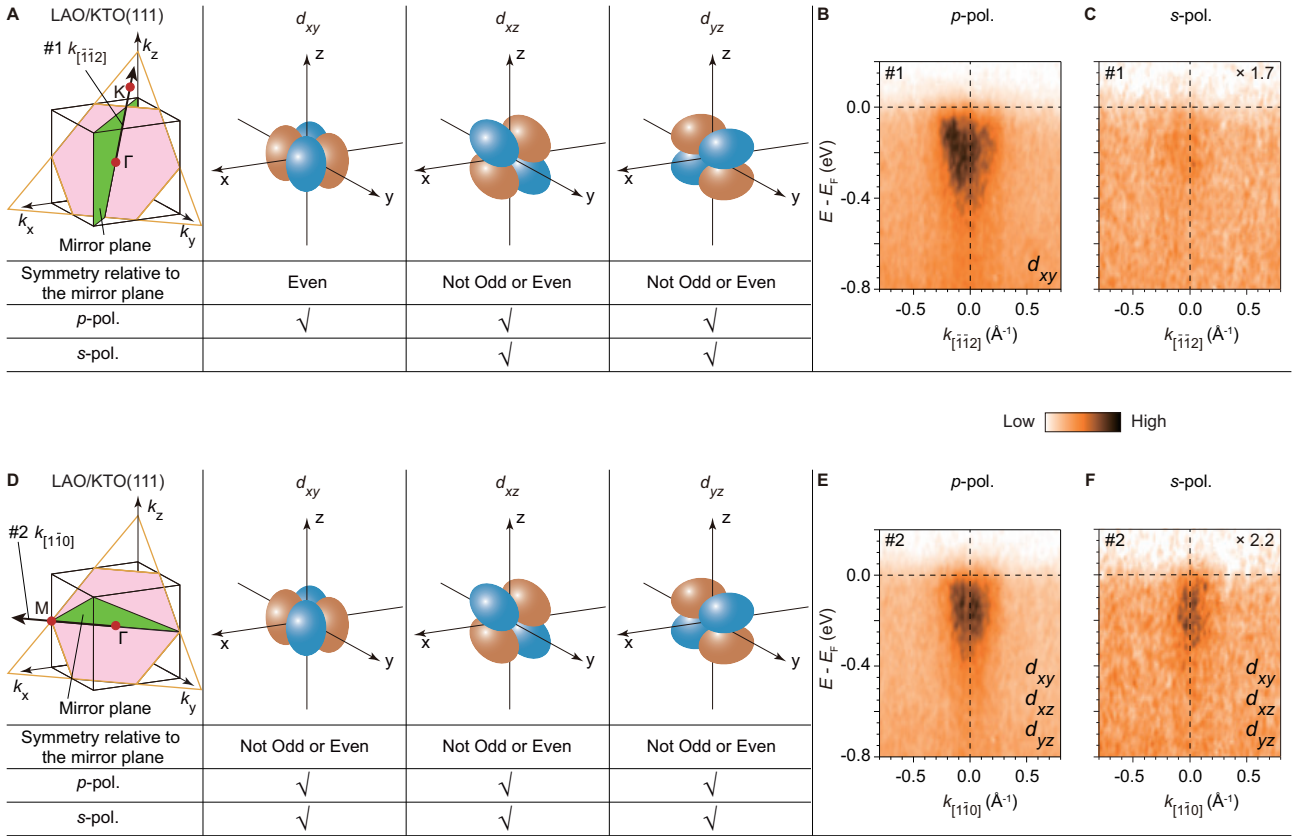
Supplementary Fig. 8: Experimental geometry of the polarization-dependent SX-ARPES measurements. The sample surface defines the ab plane (pink). The synchrotron radiation, analyzer slit and the sample surface normal lie in the mirror plane (green). The unit vector of the synchrotron radiation electric field $\hat{\epsilon}$ is normal to the mirror plane for s -polarized photons, while it is parallel to the mirror plane for p -polarized photons.

Next, we will discuss the orbital characters of the LAO/KTO(111), LAO/KTO(110) and LAO/KTO(001) interfacial states through polarization-dependent ARPES analysis.

7.1. LAO/KTO(111).

The measurement geometry along $k_{[\bar{1}\bar{1}2]}$ (Γ -K) of LAO/KTO(111) and the corresponding photoemission spectra are shown in Supplementary Figs. 9A-C. According to the spatial symmetry of three t_{2g} orbitals with respect to the mirror plane ($\bar{1}\bar{1}0$) (colored in green in Supplementary Fig. 9A), orbitals d_{xy} , d_{xz} and d_{yz} should be visible in the ARPES spectra measured by p -polarized photons, while d_{xz} and d_{yz} should be visible in the spectra measured by s -polarized photons (Supplementary Fig. 9A). However, almost no spectral weight could be seen in s -polarization (Supplementary Fig. 9C), which may be a result of photoemission intensity suppression by s -polarized photons [12] or the possible absence of d_{xz} and d_{yz} orbitals along this high symmetry direction. Therefore, the orbital compositions of LAO/KTO(111) along $k_{[\bar{1}\bar{1}2]}$ (Γ -K) should mainly be contributed by d_{xy} orbitals, while d_{xz} and d_{yz} are possibly absent and may dominate the other two Γ -K directions based on the symmetry of the (111) orientation.

The measurement geometry along $k_{[\bar{1}\bar{1}0]}$ (Γ -M) of LAO/KTO(111) and the corresponding photoemission spectra are shown in Supplementary Figs. 9D-F. All three t_{2g} orbitals are neither even nor odd with respect to the mirror plane ($\bar{1}\bar{1}2$) (colored in green in Supplementary Fig. 9D), indicating that all three orbitals d_{xy} , d_{xz} and d_{yz} should be visible in both p - and s -polarizations (Supplementary Fig. 9D). The finite photoemission intensity of both polarizations (Supplementary Figs. 9E-F) indicate the presence of d_{xy} , d_{xz} or d_{yz} . Considering that three t_{2g} orbitals are equivalent with respect to the [111] direction, the orbital compositions of the low-lying interfacial electronic state in LAO/KTO(111) should be contributed by all three t_{2g} orbitals: d_{xy} , d_{xz} and d_{yz} , with similar electron occupations.

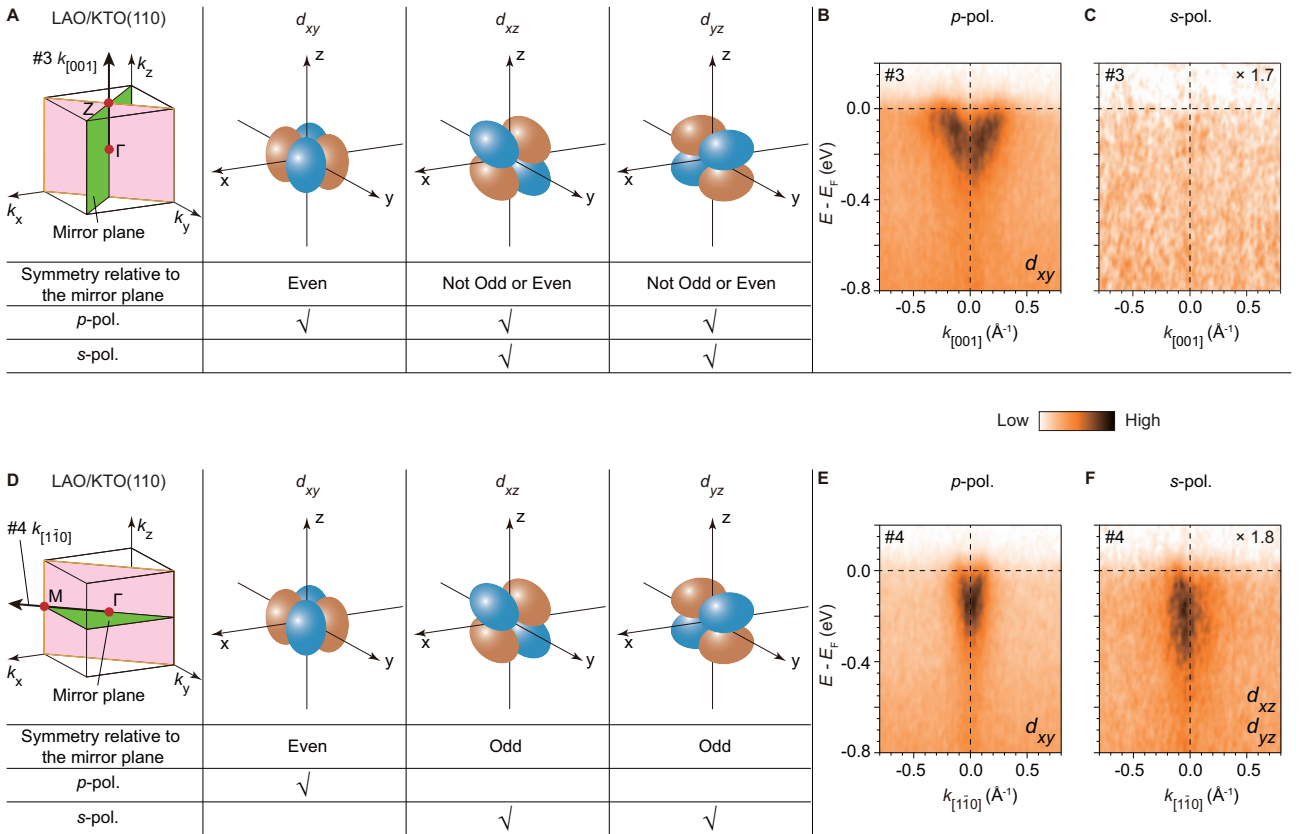


Supplementary Fig. 9: Polarization dependence of Ta t_{2g} orbitals and orbital compositions of the LAO/KTO(111) interfacial states. (A)(D) SX-ARPES experimental geometry along $k_{[\bar{1}\bar{1}2]}$ (Γ -K) and $k_{[\bar{1}\bar{1}0]}$ (Γ -M). The mirror plane (colored in green) is ($\bar{1}\bar{1}0$) plane and ($\bar{1}\bar{1}2$) in (A) and (D), respectively. Because KTO is a simple cubic crystal, the index of the mirror plane is identical both in reciprocal space ($k_x k_y k_z$) and real space (xyz). Each t_{2g} orbital is categorized as 'even' or 'odd' with respect to the mirror plane. If it is visible by p - or s -polarized photons, a '✓' mark is specified. The colors differentiate the signs of the petal-shaped t_{2g} wave functions. (B-C) Photoemission intensities along $k_{[\bar{1}\bar{1}2]}$ (Γ -K) measured by p - and s -polarized photons, respectively. (E-F) Photoemission intensities along $k_{[\bar{1}\bar{1}0]}$ (Γ -M) measured by p - and s -polarized photons, respectively. The orbitals that are visible in the spectra measured by specific polarized photons are listed on the right of each panel. To show dispersions clearly, a factor is multiplied for all spectra measured by s -polarized photons.

7.2. LAO/KTO(110).

The measurement geometry along $k_{[001]}$ (Γ -Z) of LAO/KTO(110) and the corresponding photoemission spectra are shown in Supplementary Figs. 10A-C. According to the spatial symmetries of three t_{2g} orbitals with respect to the mirror plane ($1\bar{1}0$) (colored in green in Supplementary Fig. 10A), d_{xy} , d_{xz} and d_{yz} should be visible in the spectra measured by p -polarized photons, while d_{xz} and d_{yz} should be visible in the spectra measured by s -polarized photons (Supplementary Fig. 10A). However, almost no spectra weight could be seen in the spectra measured by s -polarized photons (Supplementary Fig. 10C), which may be a result of photoemission intensity suppression by s -polarized photons [12] or the possible absence of d_{xz} and d_{yz} orbitals along this high symmetry direction. Therefore, the orbital compositions of LAO/KTO(110) along $k_{[001]}$ (Γ -Z) should mainly be contributed by d_{xy} orbitals, while d_{xz} and d_{yz} are possibly absent along this specific direction.

The measurements geometry along $k_{[1\bar{1}0]}$ (Γ -M) of LAO/KTO(110) and the corresponding photoemission spectra are shown in Supplementary Figs. 10D-F. According to the spatial symmetries of three t_{2g} orbitals with respect to the mirror plane (001) (colored in green in Supplementary Fig. 10D), d_{xy} should be visible in the spectra measured by p -polarized photons, while d_{xz} and d_{yz} should be visible in the spectra measured by s -polarized photons (Supplementary Fig. 10D). The finite photoemission intensities in p -polarization suggest the presence of d_{xy} orbital (Supplementary Fig. 10E), while the finite photoemission intensities in s -polarization suggest the presence of either d_{xz} or d_{yz} orbital (Supplementary Fig. 10F). Considering that the d_{xz} or d_{yz} orbitals are equivalent with respect to the $[110]$ direction, the orbital compositions of the low-lying interfacial electronic state in LAO/KTO(110) should be contributed by all three t_{2g} orbitals: d_{xy} , d_{xz} and d_{yz} .

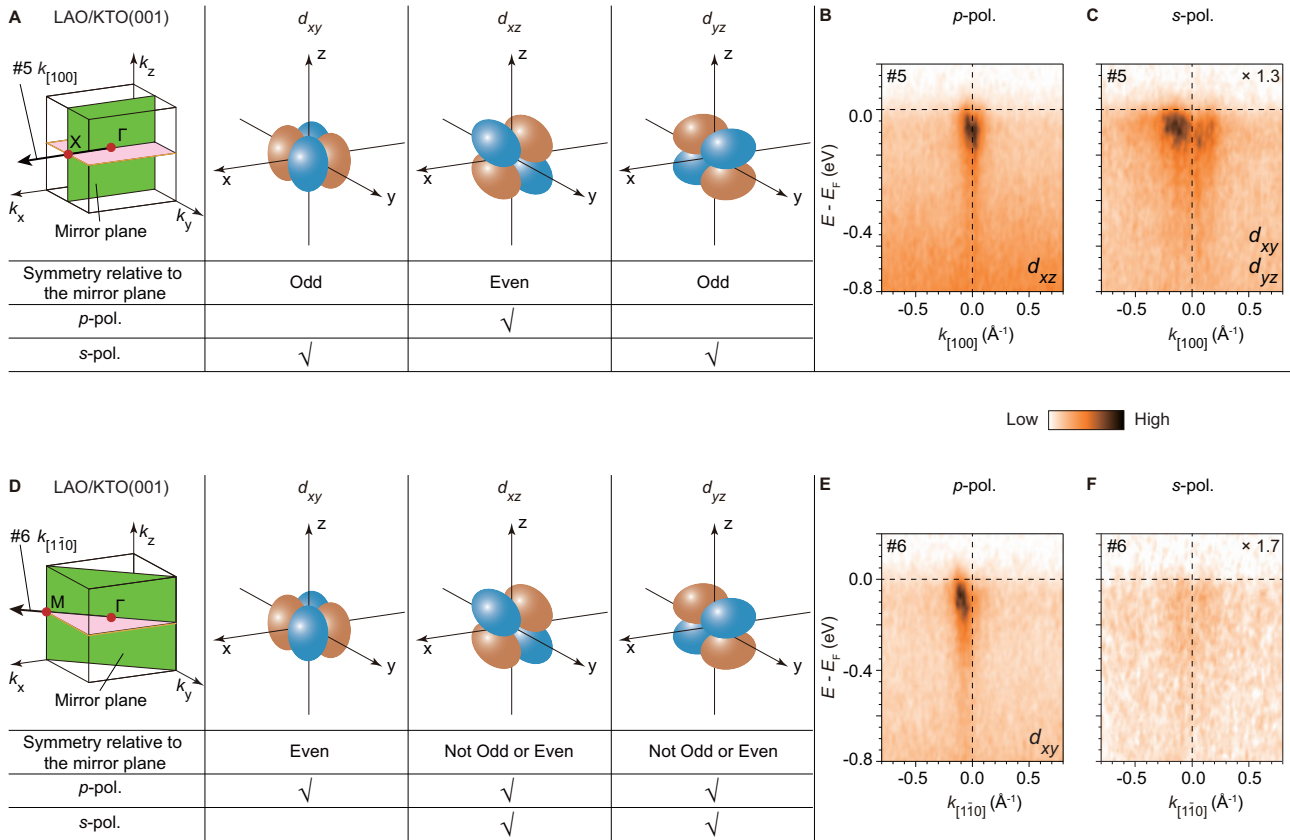


Supplementary Fig. 10: Polarization dependence of Ta t_{2g} orbitals and orbital compositions of the LAO/KTO(110) interfacial states. (A)(D) SX-ARPES experiment geometry along $k_{[001]}$ (Γ -Z) and $k_{[1\bar{1}0]}$ (Γ -M). The mirror plane is ($1\bar{1}0$) plane and (001) in (A) and (D), respectively. Because KTO is a simple cubic crystal, the index of the mirror plane is identical both in reciprocal space ($k_x k_y k_z$) and real space (xyz). Each t_{2g} orbital is categorized as ‘even’ or ‘odd’ with respect to the mirror plane. If it is visible in p - or s -polarized photons, a ‘✓’ mark is specified. The colors differentiate the signs of the petal-shaped t_{2g} wave functions. (B-C) Photoemission intensities along $k_{[001]}$ (Γ -Z) measured by p - and s -polarized photons, respectively. (E-F) Photoemission intensities along $k_{[1\bar{1}0]}$ (Γ -M) measured by p - and s -polarized photons, respectively. The orbitals that are visible in the spectra measured by specific polarized photons are listed on the right of each panel. To show dispersions clearly, a factor is multiplied for all spectra measured by s -polarized photons.

7.3. LAO/KTO(001).

The measurement geometry along $k_{[100]}$ (Γ -X) of LAO/KTO(001) and the corresponding photoemission spectra are shown in Supplementary Figs. 11A-C. According to the spacial symmetries of three t_{2g} orbitals with respect to the mirror plane (010) (colored in green in Supplementary Fig. 11A), d_{xz} should be visible in the spectra measured by p -polarized photons, while d_{xy} and d_{yz} should be visible in the spectra measured by s -polarized photons (Supplementary Fig. 11A). The finite photoemission intensity in p -polarization indicates the presence of d_{xz} orbital (Supplementary Fig. 11B), while the finite photoemission intensity in s -polarization indicates the presence of either d_{xy} or d_{yz} orbitals (Supplementary Fig. 11C).

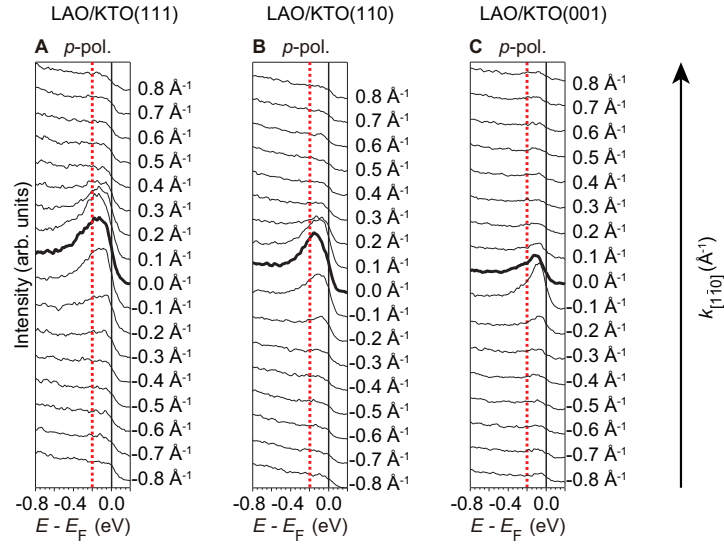
The measurement geometry along $k_{[1\bar{1}0]}$ (Γ -M) of LAO/KTO(001) and the corresponding photoemission spectra are shown in Supplementary Figs. 11D-F. According to the spatial symmetry of the three t_{2g} orbitals with respect to the mirror plane (110) (colored in green in Supplementary Fig. 11D), d_{xy} , d_{xz} and d_{yz} should be visible in the spectra measured by p -polarized photons, while d_{xz} and d_{yz} should be visible in the spectra measured by s -polarized photons (Supplementary Fig. 11D). However, almost no spectra weight could be seen in the spectra measured by s -polarized photons [12] or possible absence of d_{xz} and d_{yz} orbitals along this high symmetry direction. The finite photoemission intensity in p -polarization indicates the presence of d_{xy} orbital (Supplementary Fig. 11E). Combining the analysis along $k_{[100]}$ (Γ -X), the orbital compositions of the low-lying interfacial electronic state in LAO/KTO(001) should be contributed by all three t_{2g} orbitals: d_{xy} , d_{xz} and d_{yz} .



Supplementary Fig. 11: Polarization dependence of Ta t_{2g} orbitals and orbital compositions of the LAO/KTO(001) interfacial states. (A)(D) SX-ARPES experiment geometry along $k_{[100]}$ (Γ -X) and $k_{[1\bar{1}0]}$ (Γ -M). The mirror plane is (010) plane and (110) in (A) and (D), respectively. Because KTO is a simple cubic crystal, the index of the mirror plane is the same both in reciprocal space ($k_x k_y k_z$) and real space (xyz). Each t_{2g} orbital is categorized as ‘even’ or ‘odd’ with respect to the mirror plane. If it is visible in p - or s -polarized photons, a ‘✓’ is specified. The colors differentiate the signs of the petal-shaped t_{2g} wave functions. (B-C) Photoemission intensities along $k_{[100]}$ (Γ -X) measured by p - and s -polarized photons, respectively. (E-F) Photoemission intensities along $k_{[1\bar{1}0]}$ (Γ -M) measured by p - and s -polarized photons, respectively. The orbitals that are visible in the spectra measured by specific polarized photons are listed on the right of each panel. To show dispersions clearly, a factor is multiplied for all spectra measured by s -polarized photons.

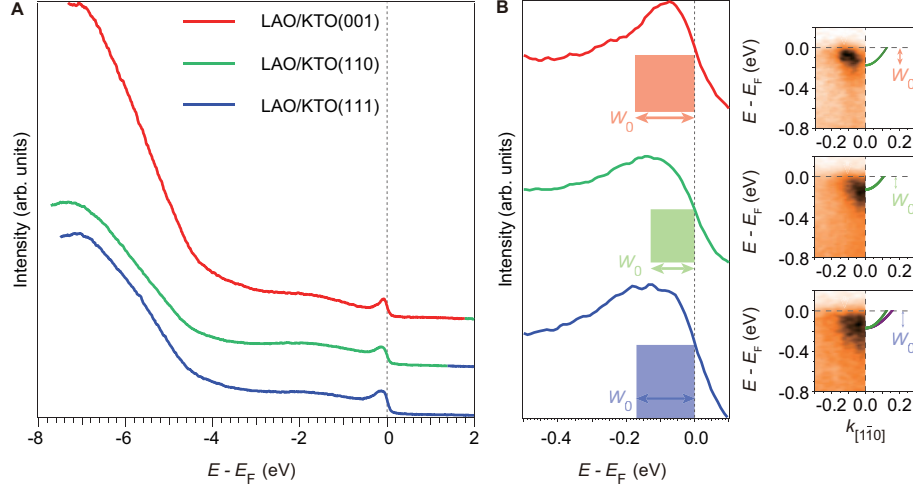
Supplementary Note 8. The upper limit of the occupied bandwidth from the EDCs of LAO/KTO and excluding different occupied bandwidth as the origin of the different EDC linewidth.

In the main text, the occupied bandwidth before considering EPC (the bare bandwidth W_0) was obtained by aligning the k_{FS} of the calculated bulk band and the experimental values. Here we show the EDCs around the Γ point of the photoemission data along $[1\bar{1}0]$ for LAOKTO(111), (110) and (001). The peaks of EDCs suggest that the band bottoms are located at binding energies less than 0.2 eV for all three samples (red dashed line in Supplementary Fig. 12), supporting the analysis by aligning the k_{FS} with the DFT-calculated band, and attributing the extra spectra weight as the polaronic tail. Expanding the occupied bandwidth to explain the spectra weight tail can be excluded.



Supplementary Fig. 12: The upper limit of the occupied bandwidth. EDCs of the photoemission spectra of (A) LAO/KTO(111), (B) LAO/KTO(110) and (C) LAO/KTO(001) along $[1\bar{1}0]$. The corresponding polarizations used in the measurements are noted in each panel. All these results show that the band bottom for three samples should be at binding energy less than 0.2 eV (red dashed line).

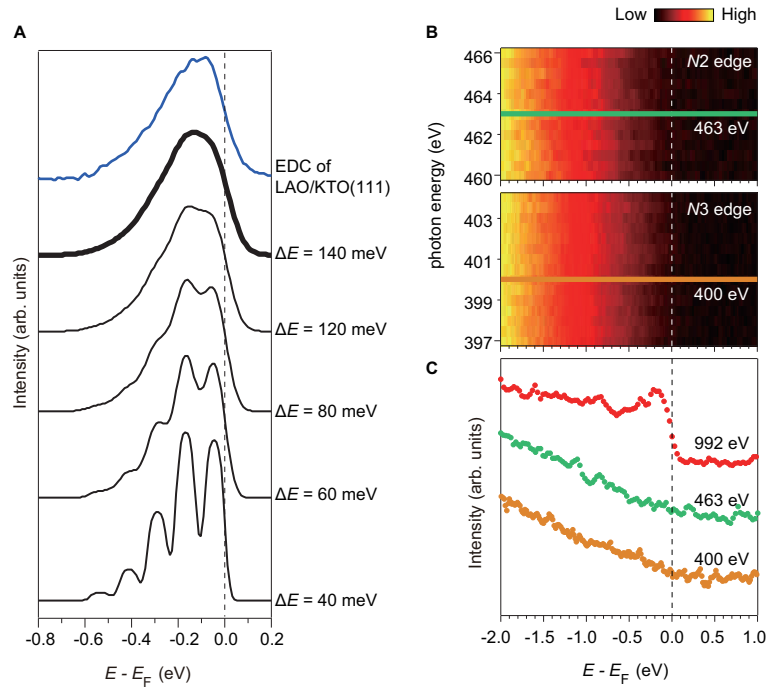
Supplementary Fig. 13 displays the large energy scale valence band of LAO/KTO(111), (110) and (001) and their zoomed-in view near the E_F . The occupied bandwidth (W_0 in Supplementary Fig. 13B) determined by aligning experimental k_F and DFT calculations are slightly different among the three samples. However, the different occupied bandwidths cannot explain the different EDC linewidth (Supplementary Fig. 13B). In our Franck-Condon fittings (Figs. 4h-j in the main text, see details in Section 13 of Supplementary Information), we have also taken into account the different occupied bandwidths.



Supplementary Fig. 13: Excluding different occupied bandwidth as the origin of the different EDC linewidth. (A) The momentum-integrated EDCs of LAO/KTO(111), (110) and (001). The integrated region is $[-0.3, 0.3] \text{ \AA}^{-1}$. (B) Zoomed-in view near the E_F of the momentum-integrated EDCs. W_0 is the bare occupied bandwidth obtained by aligning experimental k_F with the DFT calculations, as shown on the right side of panel B

Supplementary Note 9. Origin of the observation of tail-like spectral weight without peak-dip-hump structure.

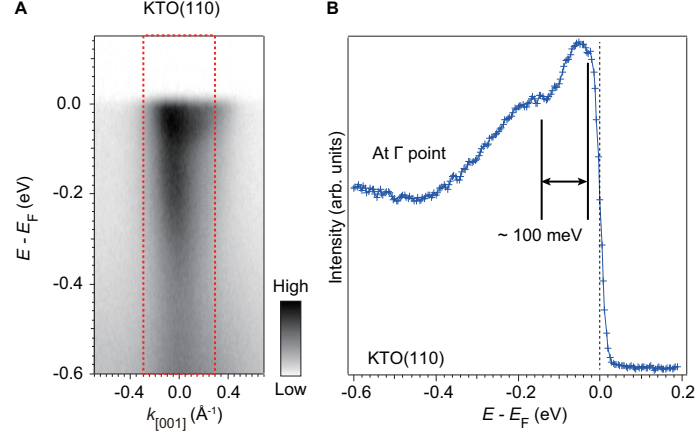
Peak-dip-hump (PDH) structure typically appears in APRES spectra in the presence of the electron-phonon coupling (EPC) when the energy resolution is sufficient, as shown by previous ARPES studies on LAO/STO using SX-ARPES near the Ti *L*-edge (~ 460 eV) with an energy resolution of approximately $40 \sim 50$ meV [13]. However, insufficient energy resolution would smear out the PDH structure, resulting in a broad peak with tail-like spectral weight (see the simulations with a fixed coupling strength and varied energy resolution in Supplementary Fig. 14A). Due to the thick overlayer of $2.5 \sim 3$ nm in LAO/KTO, the detection of the buried interface requires a large probing depth of the high-energy photons. We have conducted measurements at photon energies lower than 800 eV, including the Ta *N*-edge resonance, but were unable to observe the metallic electronic states at the interface (Supplementary Figs. 14B-C). Only with high energy photons of ~ 1000 eV that significantly enhance the detection depth, can the interfacial metallic states be resolved. With the high energy photons of ~ 1000 eV used, 140 meV is the optimized energy resolution based on the current experimental setup. Such energy resolution would give a tail-like spectral weight without the peak-dip-hump structure (Supplementary Fig. 14A), as observed in our experiments. After ruling out other possibilities, such as the inelastic scattered electrons (non-dispersive), the electron correlation (reducing the bandwidth), the interfacial confinement (see details in Section 6 of Supplementary information), the large occupied bandwidth and different occupied bandwidth (see details in Section 8 of Supplementary information), we conclude that although the PDH structure cannot be resolved under the current resolution, the EPC remains the only reasonable explanation for the observed spectra.



Supplementary Fig. 14: (A) Simulations with a fixed electron-phonon coupling constant λ of 0.85 and varied energy resolutions ΔE of 40, 60, 80, 120 and 140 meV, respectively. The insufficient energy resolution (ΔE) smears out the peak-dip-hump structure in the EDC of LAO/KTO(111). (B) Angle-integrated photoemission spectra measured at varied photon energies across the Ta *N*2- and *N*3-edge. (C) Angle-integrated energy distribution curves (EDCs) taken at photon energies of 400 eV, 463 eV and 992 eV, respectively.

To complement the limitation of SX-ARPES measurements on KTO interfacial states, we conducted additional experiments on KTO(110) surface 2DEG using vacuum-ultraviolet-ARPES (VUV-ARPES), which shows peak-dip-hump structure and serves as a complement to our work on the LAO/KTO interface.

The advantage is that KTO surface states can be measured by VUV-ARPES with much better resolution. KTO(110) shows the peak-dip-hump (PDH) lineshape with the hump located at around 100 meV, close to the energy of the LO4-derived Fuchs-Kliwer surface phonon mode (Supplementary Fig. 15). In a previous ARPES study on the KTO(111) surface 2DEG [14], a prominent PDH structure is also observed. These results emphasize the importance of EPC in the KTO-related system.



Supplementary Fig. 15: Peak-dip-hump lineshape of KTO(110) surface 2DEG. (A) ARPES spectra of KTO(110) surface 2DEG. The spectra are measured using 63 eV photons at 11 K and the total energy resolution is ~ 30 meV. (B) EDC integrated over $[-0.3, 0.3] \text{ \AA}^{-1}$ around the Γ point of KTO(110) surface 2DEG, the integrated region is indicated as a dashed red box in panel A. A peak-dip-hump structure is resolved with an energy separation of ~ 100 meV.

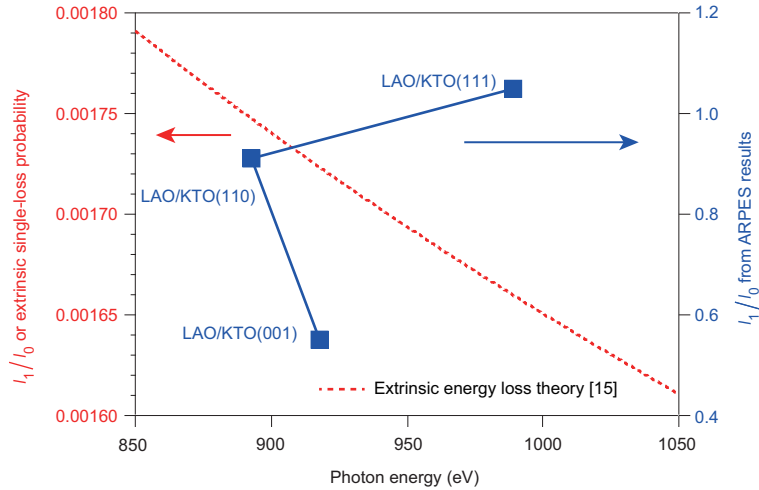
Supplementary Note 10. Extrinsic energy loss of the emitted photoelectrons is not the major contribution of the observed polaronic tails in LAO/KTO.

The extrinsic contribution of the intensity ratio between the first replica band and the main band (I_1/I_0), or the extrinsic single-loss probability (P) is written as [15]:

$$P(\Omega, \theta, E_K) = \frac{2}{a_0 \Omega} \frac{\hbar}{\sqrt{2mE_K}} \frac{1}{\cos\theta} \text{Im} \left(\frac{-1}{\epsilon(\Omega) + 1} \right)$$

where Ω is the energy loss, a_0 is the Bohr radius, m , E_K and θ are photoelectron's mass, kinetic energy and emission angle with respect to the surface norm, respectively, $\epsilon(\Omega)$ is the dielectric function. In the spectra for EPC strength analysis (Figs. 4b-4d in the main text), θ is close to zero. Considering a fixed extrinsic energy loss that corresponds to a specific phonon mode, the only variable to affect P is E_K .

In our studies, high-energy soft X-ray photons are used, and the kinetic energy is 10 ~ 50 times larger than the 22 ~ 100 eV vacuum ultra-violet ARPRS [16]. Because P is inversely proportional to $\sqrt{E_K}$, the intensity ratio I_1/I_0 should be in the order of 1×10^{-3} (red dashed line in Supplementary Fig. 16), which could not explain the observed large intensity ratio in our experiments (see details in Section 13 of Supplementary information). Moreover, the photoemission spectra of the three interfaces were taken at different photon energies that correspond to the bulk Γ points of LAO/KTO(111), LAO/KTO(110) and LAO/KTO(001), which are 989 eV ($\Gamma_{6,6,6}$) for the (111) sample, 893 eV ($\Gamma_{7,7,0}$) for the (110) sample, and 918 eV ($\Gamma_{0,0,10}$) for the (001) sample. If the coupling were primarily contributed by the extrinsic part, one would expect $I_1/I_0(110) > I_1/I_0(001) > I_1/I_0(111)$ (red dashed curve in Supplementary Fig. 16). However, such an expected trend is different from the observed EPC variation, that is $I_1/I_0(111) > I_1/I_0(110) > I_1/I_0(001)$ (blue curve in Supplementary Fig. 16). Therefore, Extrinsic energy loss of the emitted photoelectrons is not the major contribution of the observed polaronic tails in LAO/KTO.

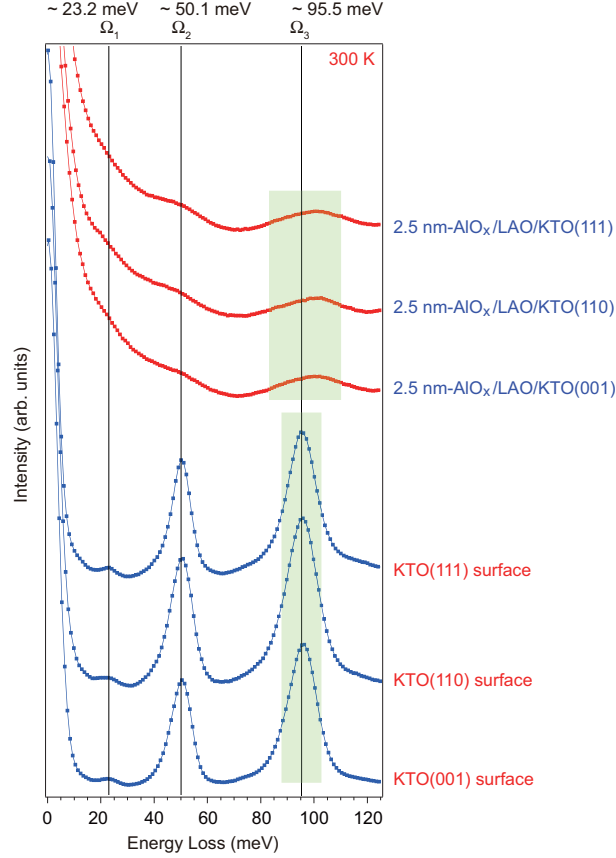


Supplementary Fig. 16: Excluding extrinsic energy loss of the emitted photoelectrons as the major origin of the polaronic tail. Extrinsic single-loss probabilities at zero emission angle in photon energy range from 850 eV to 1050 eV (red dashed curve) are calculated based on the extrinsic energy loss theory [15]. The extrinsic single-loss probability represents the extrinsic coupling contribution of the intensity ratio between the 1st replica band and the main band (I_1/I_0). The experimental values of I_1/I_0 based on the Franck-Condon fittings using 95 meV phonons (blue squares) do not show the same trend with the extrinsic single-loss probability and they are far larger than the extrinsic contribution, which excludes the extrinsic coupling as the main contribution of the polaronic tail in LAO/KTO.

Supplementary Note 11. Fuchs-Kliwer phonon modes at KTO surfaces and LAO/KTO interfaces with different orientations.

High-resolution electron energy loss spectroscopy (HR-EELS) measurements were performed to characterize the phonon modes at the KTO surfaces and the LAO/KTO interfaces (Supplementary Fig. 17). At the KTO surfaces, three phonon modes with energies $\Omega_1 \sim 23.2$ meV, $\Omega_2 \sim 50.1$ meV and $\Omega_3 \sim 95.5$ meV are observed. Ω_2 and Ω_3 are slightly lower in energy than the corresponding bulk longitudinal optical (LO) modes ($\Omega_{LO3} = 52$ meV and $\Omega_{LO4} = 103$ meV) [17, 18, 19, 20], indicating that they are LO-derived surface Fuchs-Kliwer modes [21, 22].

At the LAO/KTO interfaces, the Drude tail-like metallic backgrounds indicate the conducting interface. There are two phonon modes with similar energy as the Ω_2 and Ω_3 Fuchs-Kliwer modes at KTO surfaces, yet with weaker intensity and broader lineshape in LAO/KTO, which can be understood considering the surface sensitivity of HR-EELS and the 2.5 nm overlayer in LAO/KTO.



Supplementary Fig. 17: Fuchs-Kliwer phonon modes at the KTO surfaces and LAO/KTO interfaces. High-resolution electron energy loss spectra of the KTO surfaces and LAO/KTO interfaces. All the spectra were measured at room temperature. Three Fuchs-Kliwer phonon modes are specified and the width of Ω_3 peaks is schematically indicated by the green rectangles.

Supplementary Note 12. Background subtraction to remove the spectral weight from the inelastically scattered electrons.

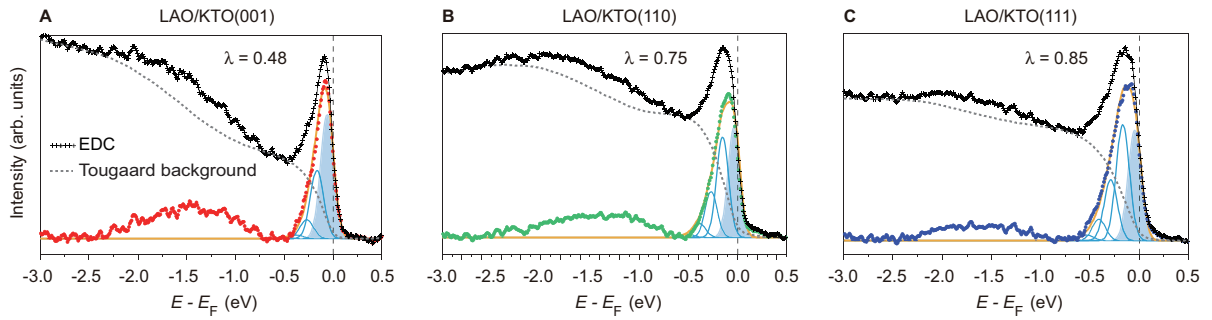
As the metallic interface is buried below 2.5 ~ 3 nm overlayers, inelastic electron scattering would induce a background with the reduced kinetic energy of the scattered photoelectrons. Besides, oxygen-vacancy-induced intensities at the binding energy $E - E_F = -0.5 \sim -3$ eV [4] were observed in the momentum-integrated EDCs of LAO/KTO, while the localized oxygen-vacancy-induced states could extend near E_F and may affect the semi-quantitative analysis. Here we show two kinds of background subtraction to get the spectral weight from the dispersive band and its replicas.

12.1. Tougaard background.

Empirically, the spectral weight of the inelastically scattered electrons can be described as the Tougaard background [23, 24, 25]. Following the method used in the work of C. Liu et al. [25], the intensity of the Tougaard background $T(\varepsilon)$ can be calculated by a Gaussian-type energy loss cross-section function for a certain EDC $I(\varepsilon)$:

$$T(\varepsilon) = A \int_{\varepsilon}^{\infty} e^{-\frac{4 \ln 2 (\varepsilon' - \varepsilon)^2}{w^2}} I(\varepsilon') d\varepsilon'$$

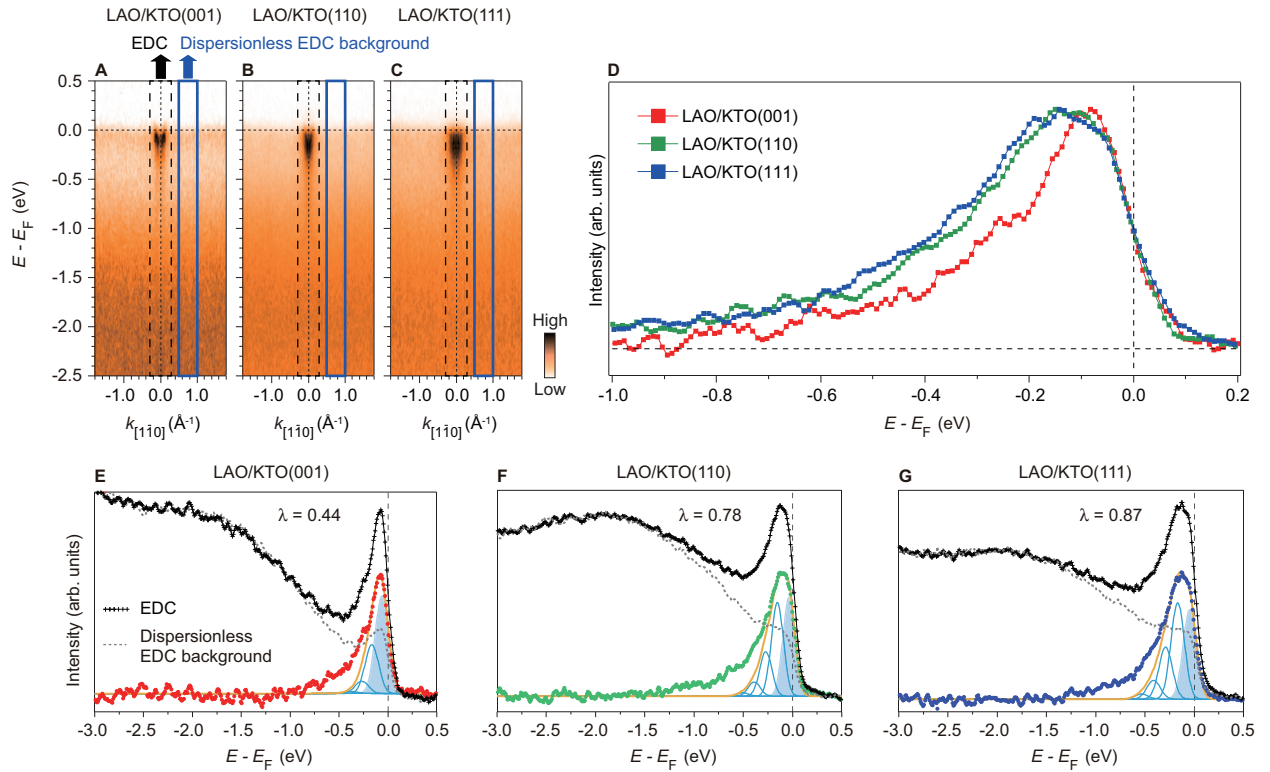
where $\varepsilon = E - E_F$ is electron binding energy. w is the full width at half maximum (FWHM) of the Gaussian-type energy loss cross-section function. A is a normalization factor. The parameters are adjusted to give zero intensity at the inflection points of the EDCs after the background is removed. The calculated Tougaard background for the momentum-integrated EDC of LAO/KTO is shown in Supplementary Fig. 18. The Franck-Condon fittings on the near- E_F peaks are shown and the details of fittings are described in Section 13 of the Supplementary information.



Supplementary Fig. 18: Removing the Tougaard background. (A-C) Original momentum-integrated EDCs (black), Tougaard backgrounds (gray dashed curves), and EDCs after removing the Tougaard background of LAO/KTO(001), LAO/KTO(110) and LAO/KTO(111), respectively. The corresponding Franck-Condon fittings and the retrieved dimension-less EPC constant λ are attached (see details in Section 13 of Supplementary Information).

12.2. Dispersionless EDC background.

At large momenta away from the Γ point (the blue boxes in Supplementary Figs. 19A-C), the dispersive band vanishes whereas the dispersionless spectra weight appears with finite spectral weight near Fermi energy (grey dashed lines in Supplementary Figs. 19E-G). It can arise from the tail of the oxygen-vacancy-induced states extending to the Fermi level, or from photoelectrons that are quasielastically scattered yet the momenta are varied. After removing the dispersionless EDC background (Supplementary Fig. 19D), LAO/KTO(111) still has the broadest peak and the most prominent spectral tail (blue), followed by LAO/KTO(110) (green), and LAO/KTO(001) (red) the least. When compared to removing a Tougaard background, removing a dispersionless EDC background keeps a longer spectral weight tail which could not be well-fitted by the Franck-Condon model since the intensity of the high-order replicas decreases quickly. Therefore, there still remains a large portion of the inelastically scattered photoelectrons after removing a dispersionless EDC background. However, a consistent trend in the strength of EPC across three interfaces is observed regardless of the background used, i.e. $\lambda(111) > \lambda(110) > \lambda(001)$ (Supplementary Fig. 19E-G). In fact, this result is guaranteed by the different polaronic tails in the spectra without any background subtraction (Figs. 4b-4d in the main text).



Supplementary Fig. 19: Removing the dispersionless EDC background. (A-C) Photoemission spectra without removing any background of LAO/KTO(001), (110) and (111), respectively. The momentum-integrated EDC and the dispersionless EDC background are integrated over the momentum range indicated by the dashed black box and the blue box, respectively. (D) The momentum-integrated EDCs after removing the dispersionless EDC background. (E-G) The momentum-integrated EDCs (black curves), dispersionless EDC background (gray dashed curves), and EDCs after removing the dispersionless EDC background of LAO/KTO(001), LAO/KTO(110) and LAO/KTO(111), respectively. The corresponding Franck-Condon fittings and the retrieved dimension-less EPC constant λ are attached.

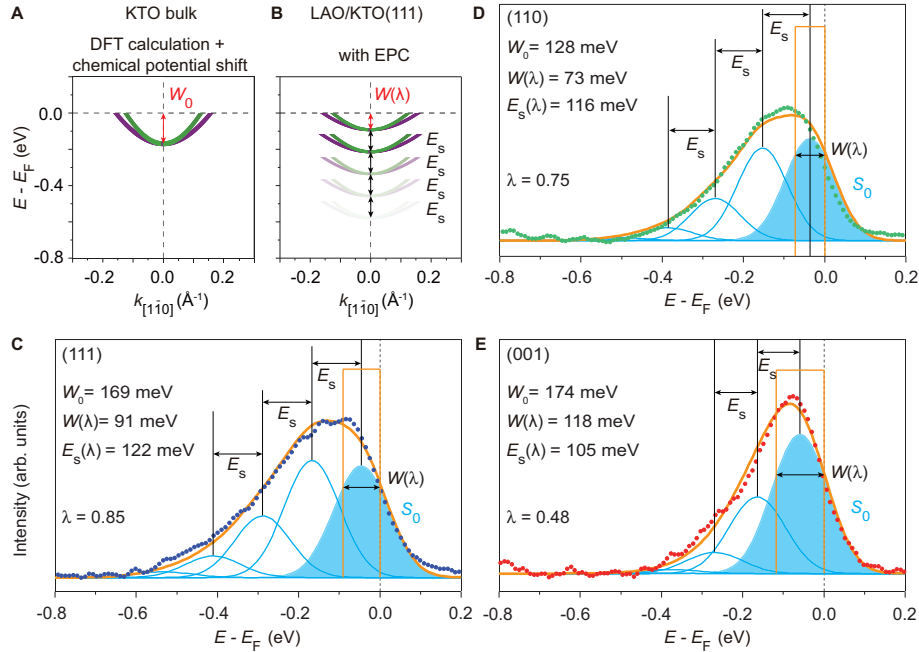
Supplementary Note 13. Details on electron-phonon coupling fittings.

In this section, we present the fitting details on the electron-phonon coupling (EPC) for the momentum-integrated EDC after subtracting the Tougaard background (Fig. 4h-4j in the main text), including the fitting parameters, error bar description, and fittings with Ω_2 phonons. We also present the fitting details for the EDC at k_F after subtracting the Tougaard background (Fig. 4k-4m in the main text).

After removing the Tougaard background of the inelastically-scattered electrons, we fit the momentum-integrated EDCs as a function of binding energy ($\varepsilon = E - E_F$) and the dimension-less EPC constant (λ) according to the Franck-Condon model, in which the relative intensity among different replica bands should follow Poisson distribution [26, 28, 27]:

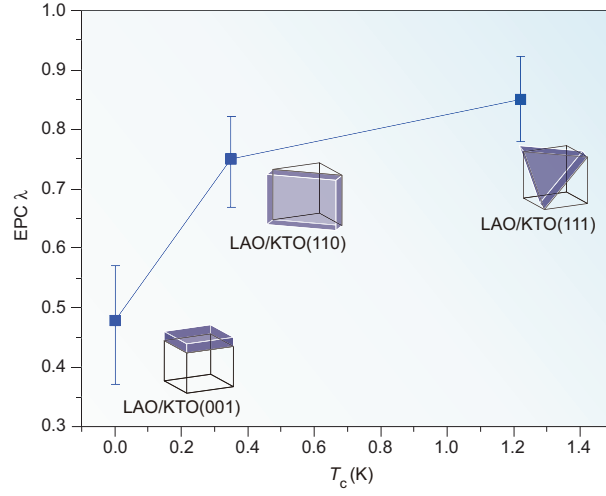
$$I(\varepsilon, \lambda) = \sum_{l=0}^n \frac{[\alpha(\lambda)]^l}{l!} S_l(\varepsilon, \lambda) \quad (5)$$

where $\alpha(\lambda)$ is a parameter determined by EPC [30]. $S_0(\varepsilon, \lambda)$ is a resolution-convolved rectangular function simulating the density of states (DOS) of the main band whose bandwidth is renormalized by EPC with $W(\lambda) = W_0/(1 + \lambda)$ [29] (Supplementary Fig. 20B), where W_0 is obtained by aligning the k_F of the experimental value and the DFT-calculation (Supplementary Fig. 20A). The DOS of a parabolic band integrated along one momentum cut should be $\propto E^{1/2}$, while under the small electron filling and the practical energy/momentum broadening, the specific peak shape of DOS has a minor effect on the fitting results of EPC λ and the approximation by a rectangular function works well. The two edges of $S_0(\varepsilon, \lambda)$, separating in energy by $W(\lambda)$, are located at the Fermi energy and the band bottom, respectively, which represent the two energy cutoffs of the main band in the momentum-integrated EDC. $S_l(\varepsilon, \lambda)$ represents the DOS of the l -th replica ($l = 1, 2, 3, \dots$), which follows the lineshape of $S_0(\varepsilon, \lambda)$ but has an energy shift of $l \cdot E_S(\lambda)$ (Supplementary Fig. 20B). The energy separation $E_S(\lambda)$ is slightly larger than the phonon energy due to the renormalization induced by EPC [30]. The renormalization of $E_S(\lambda)$ and $\alpha(\lambda)$ are based on the the quantum Monte Carlo simulations [30].



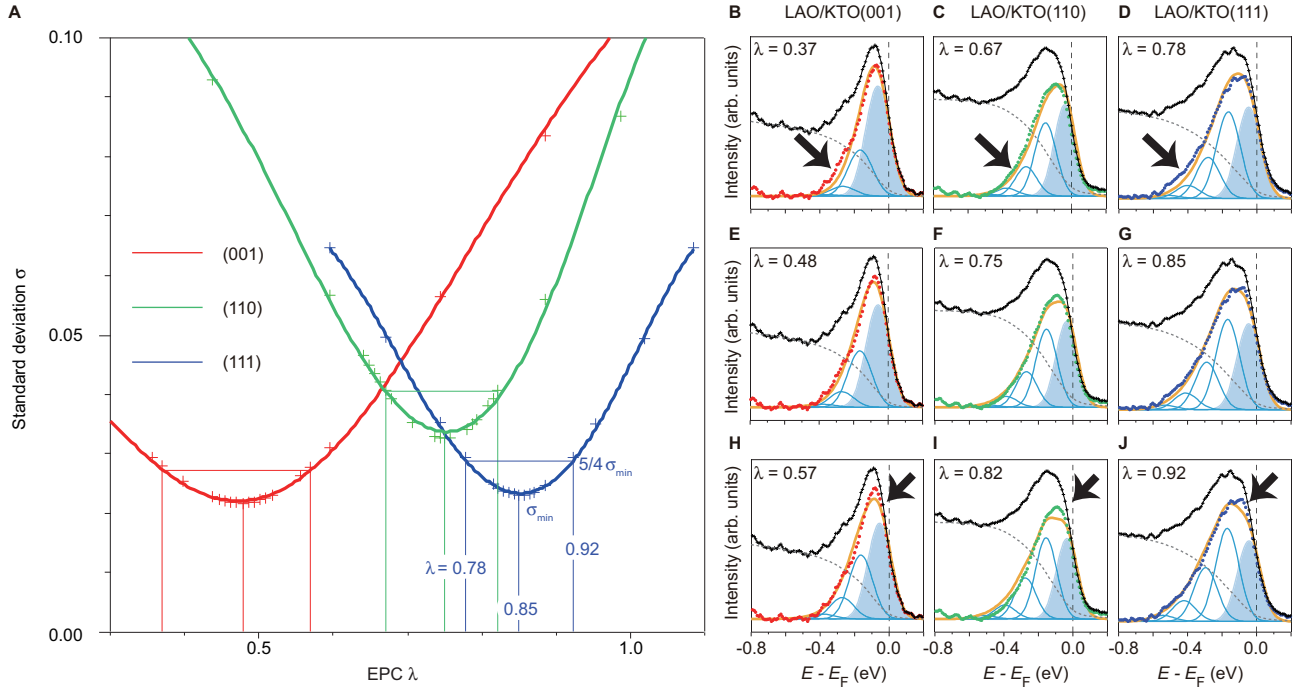
Supplementary Fig. 20: Details on the semi-quantitative Franck-Condon fittings for momentum-integrated EDCs using Ω_3 (~95 meV) phonons. (A) The calculated bulk KTO band along $[1\bar{1}0]$ with a chemical potential shift to fit the experimental determined three-dimensional carrier density (see details in Section 5 of Supplementary information). The bandwidth without considering EPC is noted as W_0 . (B) Schematic sketch of the renormalized main band and replicas of LAO/KTO(111) by EPC. The bandwidth W_0 in (A) is renormalized to $W(\lambda) = W_0/(1 + \lambda)$ by EPC [29]. The relative intensities of the main band and replicas $\alpha(\lambda)$, as well as the energy separation $E_S(\lambda)$ are based on the simulations in [30]. The transparency of replicas reflects the relative intensity as the fitting results in (C). (C-E) Franck-Condon fittings for EDCs integrated over $[-0.3, 0.3] \text{ \AA}^{-1}$ of LAO/KTO(111), LAO/KTO(110) and LAO/KTO(001) respectively. Each EDC was fitted by a renormalized main band (blue shade) and a series of replicas (blue curves), which are simulated by the resolution-convolved rectangular functions. Their intensities follow the Poisson distribution of $[\alpha(\lambda)]^l/l!$, where α is a constant for a fixed λ . $W(\lambda)$, $E_S(\lambda)$ and $\alpha(\lambda)$ are all dependent on dimensionless coupling constant λ in the fittings.

As shown in Supplementary Fig. 21, the dimension-less EPC constant (λ) with $\lambda(111) > \lambda(110) > \lambda(001)$ coincides with that of the superconductivity with $T_c(111) > T_c(110) > T_c(001)$ from both the qualitative comparison (Figs. 4b-4d in the main text, Supplementary Fig. 19D) and the semi-quantitative fittings (Supplementary Figs. 18A-C, Supplementary Figs. 19E-G). Our observation provides a straightforward explanation for the orientation-dependent superconductivity at the LAO/KTO interfaces.



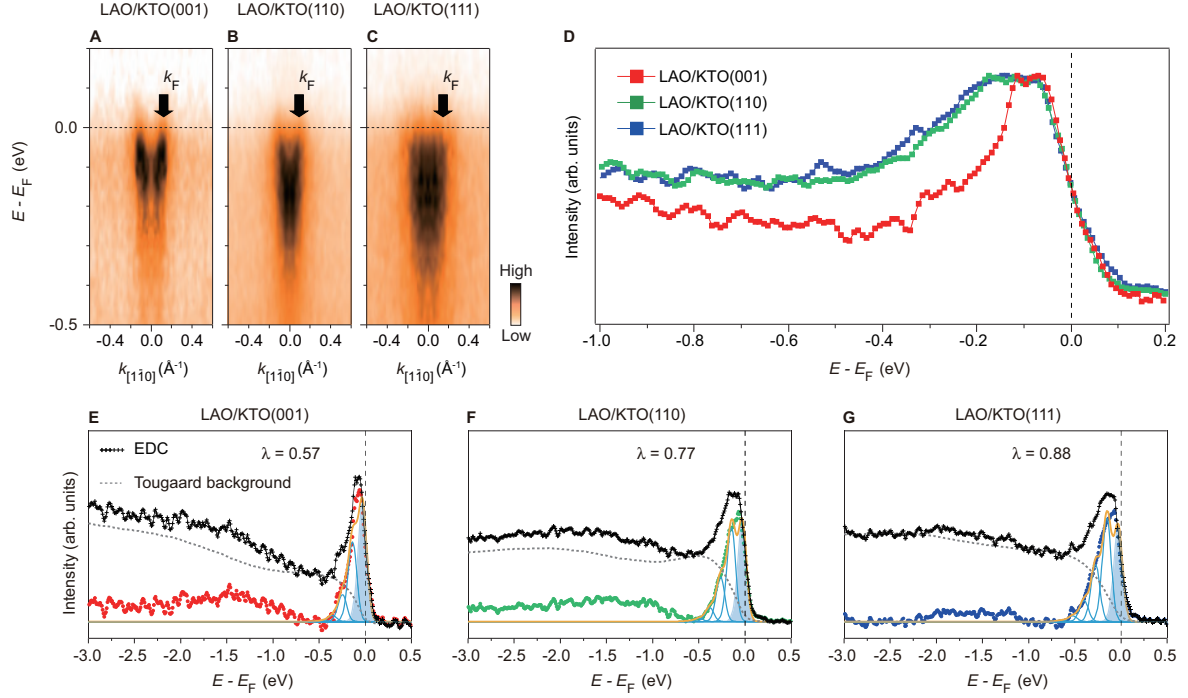
Supplementary Fig. 21: Orientation-dependent dimension-less EPC constant λ and superconducting critical temperature T_c . Dimension-less EPC constant λ plotted as a function of superconducting T_c . The error bars are determined by analyzing the standard deviation (σ) of the fittings (see details in Supplementary Fig. 22).

The fitted λ s in Supplementary Figs. 18-21 correspond to the minimum standard deviation ($\sigma_{\min}$) of the fitted curves, and the error bars in Supplementary Fig. 21 correspond to fittings within 125% of the $\sigma_{\min}$, i.e. $\sigma < \frac{5}{4}\sigma_{\min}$ (Supplementary Fig. 22A). This criterion ensures that the deviation between the fitted curve and the experimental EDC is acceptable when the value of λ falls within the boundaries of the error bar. (Supplementary Figs. 22B-D and Supplementary Figs. 22H-J).



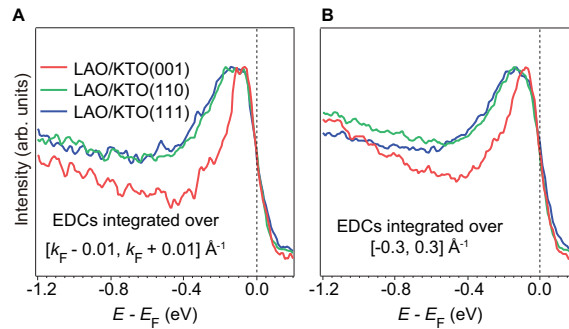
Supplementary Fig. 22: The descriptions of the error bar and the Franck-Condon fittings at the boundaries of the error bar. (A) The standard deviation σ of the Franck-Condon fittings with respect to the dimensionless EPC constant λ . The values of λ that corresponds to the $\sigma_{\min}$ and the error bar boundaries are specified for LAO/KTO(001), (110) and (111). (B-J) The Franck-Condon fittings using ~ 95 meV phonons with λ corresponding to the $\sigma_{\min}$ and the error bar boundaries. The deviations between the experimental EDC and the fitted curve using λ at the error bar boundaries are indicated by arrows in (B-D) and (H-J).

Here we discuss the analysis of the EDCs at k_F . Supplementary Fig. 23D shows the EDCs at k_F s and the EDC linewidth also follows $111 > 110 > 001$. We fit the EDCs with a series of Gaussian peaks considering Fermi-Dirac distribution and energy resolution. The peak intensities follow the Poisson distribution as described in equation (5). As shown in Supplementary Fig. 23E-G. The fitted EPC constant λ also follows $\lambda(111) > \lambda(110) > \lambda(001)$.



Supplementary Fig. 23: Semi-quantitative Franck-Condon fittings for EDCs at k_F using Ω_3 (~ 95 meV) phonons. (A-C) ARPES spectra measured along $k_{[1\bar{1}0]}$ direction of LAO/KTO(001), (110) and (111), respectively. (D) EDCs of LAO/KTO(001), (110) and (111) at the corresponding k_F indicated in (a). (E-G) Franck-Condon fitting results of EDCs in panel D. The Tougaard backgrounds are used in these fittings. The main band and replicas are represented by a series of Gaussian peaks whose FWHM are set as the energy resolution in ARPES measurements. The Fermi-Dirac distribution and energy resolution broadening are considered.

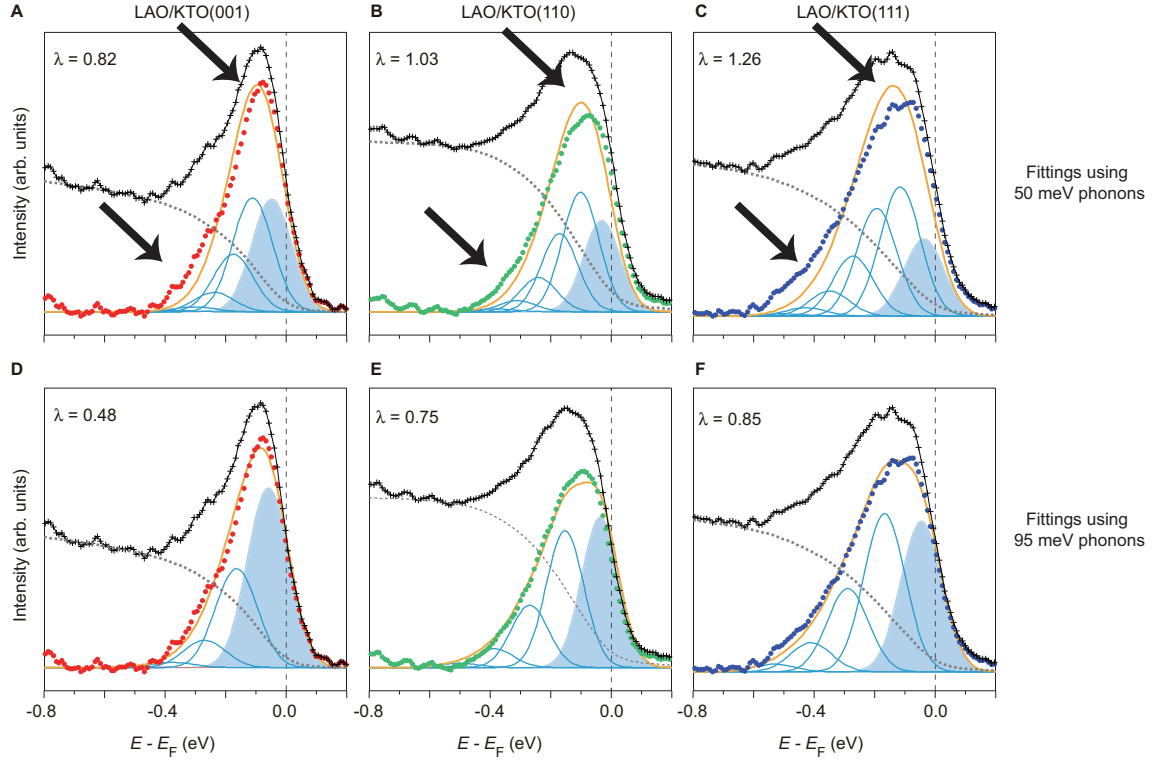
Due to the high photon energy used, the in-plane momentum resolution of $\Delta k_{\perp} \sim 0.02 \text{ \AA}^{-1}$ is poor as compared to the small values of k_F in the order of $0.1 \text{ \AA}^{-1}$. The distinctions between EDCs at k_F s and those integrated over the electron pocket region are not significant (Supplementary Fig. 24). Therefore, the integrated EDCs are retained in our manuscript to improve the signal-to-noise ratio.



Supplementary Fig. 24: Comparison between EDCs at k_F and momentum-integrated EDCs. (A) EDCs of LAO/KTO(001), (110) and (111) at the corresponding k_F . (B) EDCs of LAO/KTO(001), (110) and (111) integrated over $[-0.3, 0.3] \text{ \AA}^{-1}$.

We also fit the spectra considering the coupling between electrons and Ω_2 phonons of 50 meV. As shown in Supplementary Figs. 25A-C, the fittings using Ω_2 phonons cannot give out good results, and the deviation between the experimental data and the fitted curves is more dramatic than the fittings using Ω_3 phonons of 95 meV (Supplementary Figs. 25D-F). Therefore, it is not likely that the long tails are fully induced by the coupling between electrons and Ω_2 phonons. Consistently, according to previous calculation results on SrTiO₃, the ~ 99 meV optical phonons couple with electrons more strongly than the ~ 58 meV phonons because the ~ 99 meV optical phonons are the most polar modes with a larger electric dipole field [31, 32]. KTO has the same phonon spectra as STO which should show the same coupling behaviors [19].

In real situations, multiple phonons should contribute to the polaronic spectra, and partial coupling with Ω_2 is possible. We emphasized that we aim to get a semi-quantitative trend of the EPC strength across three LAO/KTO interfaces using a minimal set of fitting parameters rather than extracting a precise value of the dimensionless EPC constant. Consequently, fittings that consider only Ω_3 phonons while neglecting the weaker EPC with Ω_2 are shown in the main text for simplicity and rigidity.



Supplementary Fig. 25: Semi-quantitative Franck-Condon fittings for momentum-integrated EDCs using Ω_2 (~ 50 meV) phonons. EDCs integrated over $[-0.3, 0.3] \text{ \AA}^{-1}$ of the photoemission spectra in Figs. 4b-4d in the main text. After subtracting Tougaard backgrounds (grey dashed curve), the EDCs are fitted by the Franck-Condon model using Ω_2 phonons (~ 50 meV) in (A-C) and using Ω_3 phonons (~ 95 meV) in (D-F). These fitted λ s correspond to the minimum standard deviation of the fitted curve. The fittings using 50 meV phonons are not as good as those using 95 meV phonons. The arrows in (A-C) indicate the obvious deviations between the fitted curves and the experimental data.

References

- [1] Y. Kozuka, M. Kim, C. Bell, B. G. Kim, Y. Hikita, H. Y. Hwang, Two-dimensional normal-state quantum oscillations in a superconducting heterostructure. *Nature* **462**, 487-490 (2009).
- [2] F. Y. Bruno, S. McKeown Walker, S. Riccò, A. la Torre, Z. Wang, A. Tamai, T. K. Kim, M. Hoesch, M. S. Bahramy, F. Baumberger, Band structure and spin-orbital texture of the (111)-KTaO₃ 2D electron gas. *Adv. Electron. Mater.* **5**, 1800860 (2019).
- [3] A. F. Santander-Syro, C. Bareille, F. Fortuna, O. Copie, M. Gabay, F. Bertran, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, N. Reyren, M. Bibes, A. Barthélémy, P. Lecoeur, J. Guevara, M. J. Rozenberg, Orbital symmetry reconstruction and strong mass renormalization in the two-dimensional electron gas at the surface of KTaO₃. *Phys. Rev. B* **86**, 121107 (2012).
- [4] P. D. King, R. H. He, T. Eknapakul, P. Buaphet, S. K. Mo, Y. Kaneko, S. Harashima, Y. Hikita, M. S. Bahramy, C. Bell, Z. Hussain, Y. Tokura, Z. X. Shen, H. Y. Hwang, F. Baumberger, W. Meevasana, Subband structure of a two-dimensional electron gas formed at the polar surface of the strong spin-orbit perovskite KTaO₃. *Phys. Rev. Lett.* **108**, 117602 (2012).
- [5] Y. Sun, Y. Liu, S. Hong, Z. Chen, M. Zhang, Y. Xie, Critical Thickness in Superconducting LaAlO₃/KTaO₃(111) Heterostructures. *Physical Review Letters* **127**, 086804 (2021).
- [6] S. Moser, V. Jovic, R. Koch, L. Moeschini, J. S. Oh, C. Jozwiak, A. Bostwick, E. Rotenberg, How to extract the surface potential profile from the ARPES signature of a 2DEG. *Journal of Electron Spectroscopy and Related Phenomena* **225**, 16-22 (2018).
- [7] V. N. Strocov, Photoemission response of 2D electron states. *Journal of Electron Spectroscopy and Related Phenomena* **229**, 100-107 (2018).
- [8] V. N. Strocov, F. Lechermann, A. Chikina, F. Alarab, L. L. Lev, V. A. Rogalev, T. Schmitt, M. A. Husanu, Dimensionality of mobile electrons at x-ray-irradiated LaAlO₃/SrTiO₃ interfaces. *Electronic Structure* **4**, 015003 (2022).
- [9] J. M. Luttinger, Fermi surface and some simple equilibrium properties of a system of interacting Fermions. *Phys. Rev.* **119**, 1153-1163 (1960).
- [10] Y. Zhang, L. X. Yang, F. Chen, B. Zhou, X. F. Wang, X. H. Chen, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, J. P. Hu, B. P. Xie, D. L. Feng, Out-of-plane momentum and symmetry-dependent energy gap of the pnictide Ba_{0.6}K_{0.4}Fe₂As₂ superconductor revealed by angle-resolved photoemission spectroscopy. *Phys. Rev. Lett.* **105**, 117003 (2010).
- [11] H. C. Xu, M. Xu, R. Peng, Y. Zhang, Q. Q. Ge, F. Qin, M. Xia, J. J. Ying, X. H. Chen, X. L. Yu, L. J. Zou, M. Arita, K. Shimada, M. Taniguchi, D. H. Lu, B. P. Xie, D. L. Feng, Electronic structure of the BaTi₂As₂O parent compound of the titanium-based oxypnictide superconductor. *Phys. Rev. B* **89**, 155108 (2014).
- [12] S. Moser, An experimentalist's guide to the matrix element in angle-resolved photoemission. *Journal of Electron Spectroscopy and Related Phenomena* **214**, 29-52 (2017).
- [13] C. Cancellieri, A. S. Mishchenko, U. Aschauer, A. Filippetti, C. Faber, O. S. Barisic, V. A. Rogalev, T. Schmitt, N. Nagaosa, V. N. Strocov, Polaronic metal state at the LaAlO₃/SrTiO₃ interface. *Nat. Commun.* **7**, 10386 (2016).
- [14] C. Bareille, F. Fortuna, T. C. Rödel, F. Bertran, M. Gabay, O. Hijano Cubelos, A. Taleb-Ibrahimi, P. Le Fèvre, M. Bibes, A. Barthélémy, T. Maroutian, P. Lecoeur, M. J. Rozenberg, A. F. Santander-Syro, Two-dimensional electron gas with six-fold symmetry at the (111) surface of KTaO₃. *Scientific Reports* **4**, 3586 (2014).
- [15] F. Li, G. A. Sawatzky, Electron Phonon Coupling versus Photoelectron Energy Loss at the Origin of Replica Bands in Photoemission of FeSe on SrTiO₃. *Phys. Rev. Lett.* **120**, 237001 (2018).
- [16] B. D. Faeth, S. Xie, S. Yang, J. K. Kawasaki, J. N. Nelson, S. Zhang, C. Parzyck, P. Mishra, C. Li, C. Jozwiak, A. Bostwick, E. Rotenberg, D. G. Schlom, K. M. Shen, Interfacial Electron-Phonon Coupling Constants Extracted from Intrinsic Replica Bands in Monolayer FeSe/SrTiO₃. *Phys. Rev. Lett.* **127**, 016803 (2021).
- [17] H. Vogt, H. Uwe, Hyper-Raman scattering from the incipient ferroelectric KTaO₃. *Phys. Rev. B* **29**, 1030-1034 (1984).
- [18] H. Vogt, Hyper-Raman tensors of the zone-center optical phonons in SrTiO₃ and KTaO₃. *Phys. Rev. B* **38**, 5699-5708 (1988).

- [19] C. H. Perry, R. Currat, H. Buhay, R. M. Migoni, W. G. Stirling, J. D. Axe, Phonon dispersion and lattice dynamics of KTaO_3 from 4 to 1220 K. *Phys. Rev. B* **39**, 8666-8676 (1989).
- [20] S. Jandl, M. Banville, P. Dufour, S. Coulombe, L. A. Boatner, Infrared study of oxygen vacancies in KTaO_3 . *Phys. Rev. B* **43**, 7555-7560 (1991).
- [21] H. Ibach, Optical surface phonons in zinc oxide detected by slow-electron spectroscopy. *Phys. Rev. Lett.* **24**, 1416-1418 (1970).
- [22] H. Lourenço-Martins, M. Kociak, Vibrational surface electron-energy-loss spectroscopy probes confined surface-phonon modes. *Phys. Rev. X* **7**, 041059 (2017).
- [23] S. Tougaard, Quantitative analysis of the inelastic background in surface electron spectroscopy. *Surf. Interface Anal.* **11**, 453-472 (1988).
- [24] S. Tougaard, Practical guide to the use of backgrounds in quantitative XPS. *J. Vac. Sci. Technol. A* **39**, 011201 (2021).
- [25] C. Liu, R. P. Day, F. Li, R. L. Roemer, S. Zhdanovich, S. Gorovikov, T. M. Pedersen, J. Jiang, S. Lee, M. Schneider, D. Wong, P. Dosanjh, F. J. Walker, C. H. Ahn, G. Levy, A. Damascelli, G. A. Sawatzky, K. Zou, High-order replica bands in monolayer FeSe/SrTiO_3 revealed by polarization-dependent photoemission spectroscopy. *Nat. Commun.* **12**, 4573 (2021).
- [26] G. D. Mahan, Many-Particle Physics. (Plenum, New York, ed. 3, 2000), pp. 224-226.
- [27] Z. Wang, S. McKeown Walker, A. Tamai, Y. Wang, Z. Ristic, F. Y. Bruno, A. de la Torre, S. Ricco, N. C. Plumb, M. Shi, P. Hlawenka, J. Sanchez-Barriga, A. Varykhalov, T. K. Kim, M. Hoesch, P. D. King, W. Meevasana, U. Diebold, J. Mesot, B. Moritz, T. P. Devereaux, M. Radovic, F. Baumberger, Tailoring the nature and strength of electron-phonon interactions in the $\text{SrTiO}_3(001)$ 2D electron liquid. *Nat. Mater.* **15**, 835-839 (2016).
- [28] C. Chen, J. Avila, E. Frantzeskakis, A. Levy, M. C. Asensio, Observation of a two-dimensional liquid of Fröhlich polarons at the bare SrTiO_3 surface. *Nat. Commun.* **6**, 8585 (2015).
- [29] F. Marsiglio, Eliashberg theory: A short review. *Annals of Physics* **417**, 168102 (2020).
- [30] Z.-X. Li, T. P. Devereaux, D.-H. Lee, Electronic and phononic properties of a two-dimensional electron gas coupled to dipolar phonons via small-momentum-transfer scattering. *Phys. Rev. B* **100**, 241101(R) (2019).
- [31] D. M. Eagles, Polaron coupling constants in SrTiO_3 . *Journal of Physics and Chemistry of Solids* **26**, 672 (1965).
- [32] D. M. Eagles, Polar modes of lattice vibration and polaron coupling constants in rutile (TiO_2). *Journal of Physics and Chemistry of Solids* **25**, 1243-1251 (1964).