Tailoring the nature and strength of electron-phonon interactions in the $SrTiO_3$(001) two-dimensional electron liquid

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Surfaces and interfaces offer new possibilities for tailoring the many-body interactions that dominate the electrical and thermal properties of transition metal oxides [1–3]. Here, we use the prototypical two-dimensional electron liquid (2DEL) at the $SrTiO_3$(001) surface [4–7] to reveal a remarkably complex evolution of electron-phonon coupling with the tunable carrier density of this system. At low density, where superconductivity is found in the analogous 2DEL at the $LaAlO_3/SrTiO_3$ interface [8–13], our angle-resolved photoemission data show replica bands separated by 100 meV from the main bands. This is a hallmark of a coherent polaronic liquid and implies long-range coupling to a single longitudinal optical phonon branch. In the overdoped regime the preferential coupling to this branch decreases and the 2DEL undergoes a crossover to a more conventional metallic state with weaker short-range electron-phonon interaction. These results place constraints on the theoretical description of superconductivity and allow for a unified understanding of the transport properties in $SrTiO_3$-based 2DELs.

Carrier concentration is a key parameter defining the ground state of correlated electron systems. At the $LaAlO_3/SrTiO_3$ interface, the 2DEL density can be tailored by field-effect gating. As the system is depleted of carriers, its ground state evolves from a high mobility 2DEL [4], into a two-dimensional superconductor [8–10] with pseudogap behaviour [11] and possible pairing above T_c [12]. An analogous 2DEL can be induced by doping the (001) surface of $SrTiO_3$. As for the interface, the surface 2DEL is confined by a band bending potential in $SrTiO_3$ and consists of an orbitally polarized ladder of quantum confined Ti t_{2g} electrons that are highly mobile in the surface plane [5–7, 14]. Thus far, the surface 2DEL has only been studied at carrier densities around $2\dot{1}0^{14}$ cm^{-2}, approximately a factor of five higher than typically observed at the $LaAlO_3/SrTiO_3$ interface [5–7]. In the following, we present ARPES data extending to lower carrier densities that are directly comparable to the $LaAlO_3/SrTiO_3$ interface. We achieve this by preparing $SrTiO_3$(001) wafers *in situ*, which results in well ordered clean surfaces that can be studied by ARPES over extended timescales as they are less susceptible to the UV induced formation of charged oxygen vacancies reported for cleaved $SrTiO_3$ [5, 7, 15, 16]. Details of the sample preparation are given in the methods section.

Fig. 1 **a** shows an energy-momentum intensity map for a 2DEL with a carrier density of

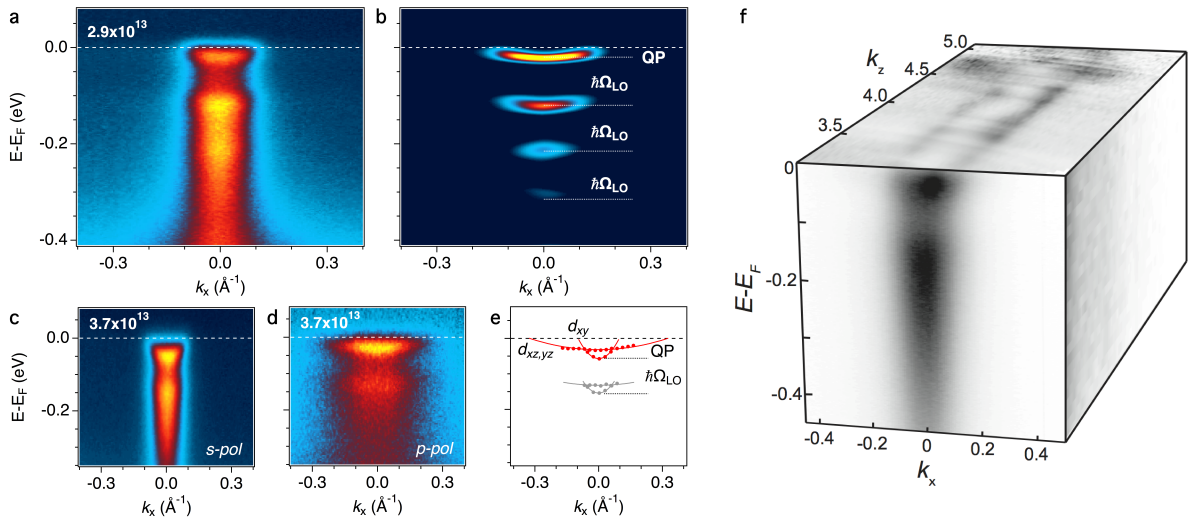

FIG. 1. **A two-dimensional liquid of large polarons in $SrTiO_3$.** **a,b** Energy-momentum intensity map and curvature plot for a 2DEL with $n_{2D} = 2.9 \cdot 10^{13}$ cm^{-2} taken at a photon energy of 44 eV with s-polarization. Note the dispersive replica bands at higher binding energy arising from strong coupling to the LO_4 phonon branch of $SrTiO_3$. **c,d** Data taken on a sample with $n_{2D} = 3.7 \cdot 10^{13}$ cm^{-2} using s and p polarized light with $h\nu = 85$ eV to selectively excite the light xy and heavy xz/yz orbitals. **e** Dispersion of the main and first replica bands extracted from the data in **c,d**. **f** Photon energy dependent measurements showing the lack of dispersion along k_z. All data were measured in the second Brillouin zone to avoid the minimum of the matrix elements at normal emission.

$n_{2D} \approx 2.9 \cdot 10^{13}$ cm^{-2} estimated from the Luttinger volume of the first light subband and the two equivalent heavy subbands (see Supplementary Information section 2). The most striking feature of this data are replica bands at higher binding energy following the dispersion of the primary quasiparticle (QP) bands. The replica bands are all separated by ≈ 100 meV and progressively loose intensity but can be visualized up to the third replica in the curvature plot shown in Fig. 1 **b**. From the equal energy spacing of the replica bands we can rule out that they represent distinct subbands arising from quantum confinement [5–7, 16]. We thus interpret the replicas as shake-off excitations involving a single non-dispersive bosonic mode coupling electrons of momentum $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$. From its energy of ≈ 100 meV, we can identify this mode as the highest frequency longitudinal optical phonon branch (LO_4) of $SrTiO_3$ [17]. A plasmon mode in the same energy range [17, 18] can be excluded from the

negligible density dependence of the mode frequency observed in Fig. 2. Our ARPES data show that the coupling to this mode largely preserves the dispersion in the replica bands and thus must be restricted to small values of **q**. This is a hallmark of Fröhlich polarons, quasiparticles formed by an excess electron dressed by a polarization cloud extending over several lattice sites that follows the charge as it propagates through the crystal [2, 19–22]. Such a large polaron state preserves band-like transport but has an increased effective mass m^*. From our ARPES data we can directly quantify this effect. Using a parabolic fit of the band dispersion in Fig. 1 **a** we find $m^*_{xy} \approx 1.4$ m$_e$. Using a bare band mass of $m_0 = 0.6$ m$_e$ [7, 15] this corresponds to a mass enhancement $m^*_{xy}/m_0 \approx 2.3$, indicative of an intermediate *e-p* coupling strength.

In Fig. 1 **c-f** we investigate a sample with slightly higher carrier density. Using *s* and *p* polarized light, respectively, we selectively excite electrons from the light *xy* band with ≈ 50 meV occupied bandwidth and a shallower heavy band derived from *xz/yz* orbitals. Both bands show a clear peak-dip-hump line shape with a dispersive replica band as summarized in Fig. 1 **e**. This implies that the entire orbitally polarized 2DEL including the heavy *xz/yz* states, which are believed to be important for superconductivity [9–11], is a polaronic liquid at low carrier densities. The lifting of the orbital degeneracy by approximately 20 meV can be attributed to quantum confinement in the band bending potential which increases the energy of out-of-plane orbitals [7, 23]. The reduced dimensionality arising from quantum confinement is visualized directly in Fig. 1 **f** where we show the absence of dispersion along the surface normal k_z, characteristic of two-dimensional electronic states.

We now turn our attention to the strength of *e-p* coupling. Its systematic evolution with carrier density in the $SrTiO_3$(001) 2DEL is shown in Fig. 2. Using *s*-polarized light, we resolve a single d_{xy} QP band at low density. Energy distribution curves extracted at k_F show a strongly reduced weight of the coherent QP and at least two phonon satellites each separated by ≈ 100 meV. Empirically, we find that the experimental spectra are well described by a Franck-Condon model using a single phonon mode of ≈ 100 meV. Highly restricted fits using the characteristic Poisson distribution $I_n/I_{QP} = a_c^{2n}/n!$ for the intensity ratio of the n-th phonon satellite and the QP peak in the Franck-Condon model are shown in Fig. 2 **g-l**. Details of the fits are described in Supplementary Information. From this analysis we infer a quasiparticle residue $Z \approx 0.2$ at the lowest density studied here. This is beyond the validity of the perturbation theory result for the Fröhlich model of $Z =$

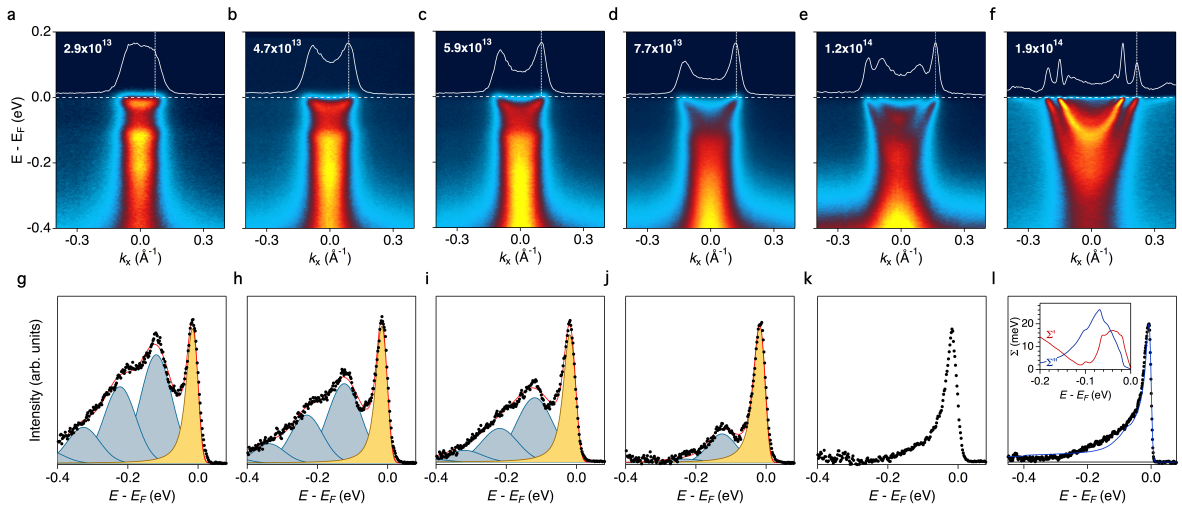

FIG. 2. **Evolution of the 2DEL spectral function with carrier concentration. a-f**, Raw energy-momentum intensity maps of 2DELs with increasing carrier concentration indicated in units of cm^{-2}. **g-l**, Energy distribution curves at the Fermi wave vector indicated by a dashed white line in the corresponding image plots. An exponential background describing the tail of the in-gap state at ≈ -1.1 eV has been subtracted from the raw EDCs (see Supplementary Information). In **g-j** we show fits to a Franck-Condon model with a single phonon mode. The coherent quasiparticle and incoherent phonon satellites are coloured in yellow and blue, respectively. **l** shows a calculation of the spectral function using the conventional Eliashberg *e-p* self-energy for the high-density limit found in Ref. [7] and reproduced in the inset.

$1 - \alpha/2$ [24, 25], where α is the dimensionless coupling constant, placing the $SrTiO_3$ 2DEL in a theoretically challenging regime of intermediate coupling. Moreover, the ratio of lattice energy to electron kinetic energy is neither small nor independent of doping, which excludes a Migdal-Eliashberg approach. We therefore estimate α from the experimentally determined quasiparticle residue Z using the results of diagrammatic quantum Monte Carlo simulations of the Fröhlich model reported in Ref. [25]. This gives $\alpha \approx 2.8$ at the lowest carrier density, comparable to $\alpha = 2 - 3$ reported for lightly doped bulk $SrTiO_3$ based on an analysis of optical conductivity data [26, 27].

As the carrier density increases, the Fermi wave vector increases monotonically, and new subbands become discernible. Concomitantly, the spectral weight of the phonon satellites weakens and for densities above $n_2 \approx 9 \cdot 10^{13}$ cm^{-2} they can no longer be resolved experimentally. At high density *e-p* coupling is not only weaker but also of fundamentally different

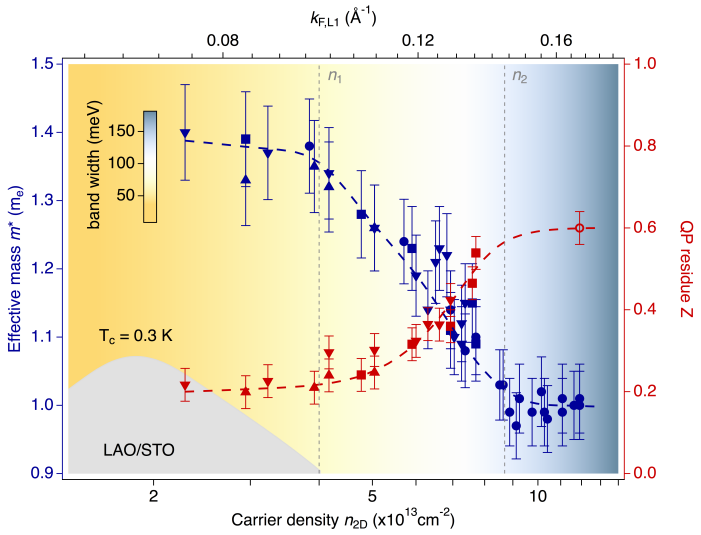

FIG. 3. **Effective mass and quasiparticle residue in the $SrTiO_3$ 2DEL.** Evolution of the effective mass m^* (blue symbols) and quasiparticle residue Z (red symbols) with carrier density. Different symbols indicate data taken on substrates annealed at different temperature. Closed red symbols are obtained from Franck-Condon fits, while the last value with open symbol in the adiabatic Migdal-Eliashberg regime has been calculated from $Z = m_0/m^*$. Error bars indicate the reproducibility of our results. An additional systematic error cannot be excluded. The background color encodes the bare band width of the first light subband calculated from the experimentally determined k_F shown in the top-axis, assuming a bare mass of $m_0 = 0.6$ m_e. Dashed lines are guides to the eye. The dome shaped superconducting phase observed at the $LaAlO_3/SrTiO_3$ interface is indicated in grey.

nature. This is illustrated in Fig. 2 **f,l**. In this regime, the quasiparticle dispersion shows a weak kink at an energy of ≈ 30 meV and no signs of replica bands can be discerned in the raw data or in curvature plots (see Supplementary Information, Fig. S4), providing direct evidence for a suppression of the long-range Fröhlich interaction. Instead, consistent with Ref. [7], we find that the spectral function and e-p self-energy of the high-density 2DEL can be described by Migdal-Eliashberg theory with $\lambda \approx 0.7$ and the same coupling to the entire phonon density of states.

In order to track the crossover from the polaronic state to short-range e-p coupling, we analyse the quasiparticle residue and effective mass of the dispersive bands close to the Fermi level as a function of 2D carrier concentration. The results are summarized in

Fig. 3 where we plot m^* obtained from fits to the QP dispersion and $Z(k_F)$ from fits to a Franck-Condon model as described above. Three distinct regimes can be identified. Below $n_1 \approx 4 \cdot 10^{13}$ cm^{-2} both quantities depend weakly on carrier density and appear to saturate around $m^* \approx 1.4$ m$_e$ and $Z(k_F) \approx 0.2$, respectively. At intermediate carrier concentrations of $n_{2D} = 4-9 \cdot 10^{13}$ cm^{-2}, the polaronic state persists, as is seen most directly from the spectra in Fig. 2 **h-j** showing a clear phonon satellite over this entire regime. However, approaching $n_2 \approx 9 \cdot 10^{13}$ cm^{-2}, where the phonon satellites are no longer resolved experimentally, the quasiparticle residue increases by more than a factor of two to $Z \approx 0.5$ and the effective coupling strength decreases to $\alpha \approx 1.3$. This is opposite to the trend expected for short-range *e-p* coupling [28] and thus strongly supports our identification of long-range interactions as described by the Fröhlich model. We note that the weak coupling to the LO_4 branch close to n_2 reported in Fig. 3 has recently been confirmed for the $LaAlO_3/SrTiO_3$ interface 2DEL in a soft x-ray ARPES study reporting $Z \approx 0.4$ for a sample with $n_{2D} \approx 8 \cdot 10^{13}$ cm^{-2}, in excellent agreement with our findings [29].

The effective mass decreases more slowly than the quasiparticle residue and saturates at $m^* \approx 1.0$ m$_e$ at high density. This slow decrease is characteristic of the Fröhlich model where $Z < m_0/m^*$. For weak to intermediate coupling, the effective mass of Fröhlich polarons can be approximated as $m^*/m_0 = 1/(1-\alpha/6)$ [19, 25]. As shown in Supplementary Information Fig. S6, this relation systematically underestimates the effective masses obtained directly from the quasiparticle dispersion but reproduces their trend as a function of density. We tentatively assign this behavior to the effect of electron-electron interactions, which is not fully included in the analysis of Z in the polaronic regime. Indeed, the factor between the two effective masses is approximately 1.3, which is consistent with the mass-enhancement due to electronic correlations estimated in Ref. [7]. For densities above n_2, described by Migdal-Eliashberg theory, $Z = m/m^*$ suggesting that the quasiparticle residue saturates around $Z = 0.6$ in the high-density 2DEL.

We attribute the breakdown of the polaronic state at high carrier density to improved electronic screening suppressing the long range Fröhlich interaction. In order to estimate the cross-over from dielectric screening in the polaronic regime to predominantly electronic screening, we compare the polaron radius $r_p = (\hbar/2m^*\Omega_{\mathrm{LO}_4})^{1/2}$ [19] with the electronic screening length. Using the experimentally determined parameters we find $r_p \approx$ 6 Å. Given the relatively large dielectric constant of doped $SrTiO_3$, electronic screening

is in the Thomas-Fermi regime and the screening length can be estimated from $r_{\mathrm{TF}} = (\epsilon\epsilon_0 E_F/2e^2 n_{3D})^{1/2}$ for a 3D electron liquid. Assuming a uniform charge distribution over a 2DEL thickness of 3 unit cells and a static dielectric constant $\epsilon_0 = 100$, which provides a good description of the band-bending potential in the doped surface region [7, 16], we estimate that $r_{\mathrm{TF}} = r_p$ for a density $n_{2D} \approx 5 \cdot 10^{13}$ cm^{-2}, slightly above n_1 where Z starts to increase progressively resulting in a reduced effective coupling constant α. At higher carrier densities, electronic screening will rapidly become more important as ϵ_0 decreases simultaneously with the increase in n. We note that the moderate electronic screening length r_{TF} justifies the above use of an expression for 3D electron liquids. This basic picture is consistent with the temperature dependence of the electron mobility in $SrTiO_3$ 2DELs [30] and further confirmed by our calculations of the spectral function reported in supplementary Fig. S5. Using exact diagonalization of a model Hamiltonian with constant coupling parameter, we find pronounced replica bands at low carrier density and a rapid suppression of the replicas as the carrier density is increased over the relevant range. These calculations thus reproduce the key experimental findings of our study and support the idea that increasing electronic screening drives the observed breakdown of the polaronic liquid at high carrier densities.

The above results demonstrate that *e-p* interaction in $SrTiO_3$ based 2DELs is remarkably complex and strongly dependent on carrier density. This provides insight into the superconducting pairing mechanism at the $LaAlO_3/SrTiO_3$ interface, which has so far eluded experimental investigation. As shown in Fig. 3, superconductivity in $LaAlO_3/SrTiO_3$ interface 2DELs [8–10, 31] occurs in the polaronic low-density regime and its suppression on the overdoped side coincides with a gradually decreasing coupling to the LO_4 branch. This supports the notion that superconductivity is phonon mediated [13, 32, 33] and suggests that the pairing potential is dominated by the exchange of high-frequency longitudinal phonons rather than soft modes. We note that our experimental spectral functions do not exclude the formation of large bipolarons, which have been discussed early on in the context of superconductivity in polar oxides [34, 35]. Superconducting susceptibilities calculated within our exact diagonalization scheme reported in supplementary information section 5 provide additional insight. Although limitations in the Hilbert space size prohibit a quantitative comparison with experiment, the calculations clearly show that the dominant pairing channel has *s*-wave symmetry. Moreover, the saturation of the superconducting suscepti-

bility with carrier density found in this model provides evidence for a competition between the opposite trends of density of states and effective *e-p* coupling underlying dome-shaped superconductivity in $SrTiO_3$ 2DELs. We note that coupling to the LO_4 branch of $SrTiO_3$ with comparable strength was also invoked to explain the anomalously high superconducting critical temperature of FeSe monolayers on $SrTiO_3$ substrates [2, 36].

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Methods The Nb-doped (0.5 wt%) and La-doped (0.075 wt%) $SrTiO_3$(001) surfaces were prepared by mild Ar^+ sputtering (600 eV, 2 μA, 5 min) followed by annealing in $2\cdot10^{-6}$ mbar oxygen for 0.5 h at temperatures varying from 700 to 1000°C as monitored by an infrared pyrometer. Consistent with measurements on *in situ* prepared and cleaved $SrTiO_3$, we find no spectral weight in the entire bulk band gap on freshly prepared surfaces (see Supplementary Information, Fig. 1) [5, 15, 16]. Quantum confined metallic states appear concomitant with a localized in-gap state at higher energy after exposure of the surface to synchrotron light [5, 15, 16]. We find that the rate at which the 2DEL carrier density increases under the synchrotron beam increases with the annealing temperature and exploit this to stabilize low-carrier densities over the extended exposure times required for detailed ARPES measurements. ARPES measurements were performed at the SIS beamline of the Swiss Light Source, the I05 beamline of Diamond Light Source and the 1^2 beamline of BESSY II at the Helmholtz-Zentrum Berlin. Data was acquired at $T \approx 20$ K with $h\nu = 30 - 100$ eV and

energy and angular resolutions of $10 - 25$ meV and $\approx 0.2°$, respectively.

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