Subband Structure of a Two-Dimensional Electron Gas Formed at the Polar Surface of the Strong Spin-Orbit Perovskite KTaO$_3$

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Abstract

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Today’s electronic devices largely rely on the tunability of narrow conducting channels in semiconductor hosts. Creating such two-dimensional electron gases (2DEGs) in oxides, which in bulk form generally show much larger and more diverse responses to external stimuli, holds the potential for devices with functionalities well beyond what we have experienced to date [1,2]. The prototypical oxide 2DEG is formed when SrTiO₃ is interfaced to the polar surface of another perovskite oxide [3]. This system indeed shows novel properties [4,5], such as an unusual coexistence of ferromagnetism and superconductivity [5,6]. Several combinations of ABO₃/SrTiO₃ heterostructures have been investigated to date, incorporating both Mott [7] and band insulators [3,8] as the overlayer. However, the 2DEGs formed were always found to reside in SrTiO₃. There is great current interest in inducing 2DEGs in more exotic parent materials [9]. The recent discovery that oxygen vacancies mediate the formation of a 2DEG at the bare surface of SrTiO₃ [10,11] may provide a route to achieve this.

Of particular interest are 5d transition-metal oxides (TMOs). Their large spin-orbit interactions are thought to drive the formation of a host of unconventional ground states such as J = 1/2 Mott insulators [12,13], correlated topological insulators [14–16], and spin-triplet superconductors [17]. Moreover, 5d TMOs offer the potential to incorporate the spintronic functionality sought in emerging schemes of semiconductor electronics [18–20] into all-oxide devices. They could therefore provide a novel and potentially very rich host for the engineering of artificial 2D electron systems. Understanding the interplay of strong spin-orbit coupling, quantum confinement, and electronic correlations within such a 2DEG is an essential step towards realizing their potential for practical applications. To date, however, this has been hampered by the difficulty of generating 2DEGs localized in 5d oxides via interface engineering.

Here, we show that such a 2DEG can be created at the (100) surface of the 5d perovskite KTaO₃. We utilize angle-resolved photoemission (ARPES) to provide the first direct measurement of the subband structure of a 5d oxide 2DEG. Our model calculations are in agreement with ARPES measurements of both SrTiO₃ and KTaO₃ 2DEGs, strongly constraining theoretical pictures of such systems. In particular, we find a delicate interplay of multiorbital physics, quantum confinement, and spin-orbit interactions, driving orbital ordering within the 2DEG. Surprisingly, however, the 2DEG does not exhibit the large Rashba spin splitting which might naturally be expected.

Single-crystal undoped KTaO₃ (commercial samples from Crystal Base, Japan) and lightly electron-doped KₓBa₁₋ₓTaO₃ (flux-grown samples, x < 0.001) were measured. The Ba doping yields a small residual bulk conductivity (n ∼ 1 × 10¹⁹ cm⁻³ from Hall effect measurements) which eliminates charging effects in ARPES but does not otherwise affect the conclusions of this Letter. ARPES...
measurements ($T = 20 \text{ K}$, $h\nu = 45–85 \text{ eV}$) were performed using Scienta R4000 hemispherical analyzers at beam line 10.0.1 of the Advanced Light Source and the SIS beam line of the Swiss Light Source, with an energy resolution between 8 and 35 meV and an angular resolution of 0.3°. Multiple samples were cleaved along the (100) surface at the measurement temperature in a pressure better than $3 \times 10^{-11}$ mbar. Preliminary in situ transport measurements performed at beam line 3.2a of the Synchrotron Light Research Institute (SLRI), Thailand, support the conclusions drawn from our ARPES work.

Our surface-sensitive ARPES measurements (Fig. 1) reveal a complex electronic structure with at least 4 dispersive electronlike bands which cross the chemical potential [Figs. 1(a) and 1(b)]. This directly indicates that the surface of this material has become strongly conducting, in contrast to its bulk. We note that these measurements were performed at a photon energy chosen to probe electronic states near to the Brillouin zone boundary along $k_z$, where no bulk bands are expected in the vicinity of the Fermi level. Moreover, the same states are observed for both lightly bulk-doped and insulating undoped KTaO$_3$ samples (not shown). These states have equal Fermi wave vectors and occupied bandwidth (within our experimental resolution), even though the bulk carrier density should vary by at least 5 orders of magnitude between the samples. This conclusively rules out bulk states as the source of the measured bands. Photon-energy-dependent measurements (not shown) further reveal that the observed states have no dispersion along $k_z$. They are therefore two-dimensional electronic states confined near the surface, unlike the three-dimensional bulk states.

After cleaving the sample, and upon exposure to intense UV light, the Fermi wave vectors of the states increase [Fig. 2(a)] and then saturate to give the electronic structure shown in Fig. 1. At the same time, the O 2$p$ valence bands shift to higher binding energy [Fig. 2(b)], indicating a downward bending of the valence and conduction bands relative to the Fermi level in the vicinity of the surface. This causes a buildup of charge near the surface [21]. In conventional semiconductors, these electrons do not occupy the original bulk electronic states: the electrostatic band bending potential, together with the potential step at the surface itself, forms a quantum well. This causes the conduction bands to reconstruct into ladders of partially filled two-dimensional subbands [22]. The two-dimensional metallic states that we measure here by ARPES are the first direct observation of such quantum-confined states in a 5$d$ TMO. The formation of the 2DEG is accompanied by the emergence of an in-gap defect peak [Fig. 2(b)], indicative of oxygen vacancies at the surface. This suggests that the density of the 2DEG in KTaO$_3$ may be tuned by controlling the positive surface charge resulting from a UV-stimulated desorption of oxygen, as recently found for a surface 2DEG created in SrTiO$_3$ [10].

However, unlike in SrTiO$_3$, the 2DEG in KTaO$_3$ exists right from the initial stages of our measurement [Fig. 2(a)]. This is most likely due to the polar nature of KTaO$_3$(100). In order to avoid the large energy cost associated with a

![FIG. 1 (color online). (a),(b) ARPES measurements of the Γ-X dispersion of surface 2DEG states in KTaO$_3$, measured using $p$- and s-polarized 55 eV synchrotron light around the $\Gamma_{11}$ and $\Gamma_{10}$ points, respectively. A schematic representation of the measured band structure is shown in the insets. (c),(d) Equivalent measurements of the Fermi surface.]
polar catastrophe, KTaO₃ likely cleaves, leaving approximately half a (KO)⁻ layer on the (TaO₂)⁺ surface. This structural arrangement may lower the formation energy for oxygen vacancies compared to SrTiO₃(100), allowing much more rapid initial formation of the 2DEG. Alternately, if the surface TaO₂ plane is terminated by less than half a KO layer, the 2DEG could exist directly following the sample cleave in order to screen the intrinsic positive charge associated with the polar surface. Instead of the creation of oxygen vacancies, the increase in 2DEG density with irradiation dose could also be associated with the desorption of (KO)⁻ from the surface. This would drive the system back towards an ideal polar surface. Intriguingly, from a comparison of model calculations (discussed below) to the ARPES measurements, we estimate the saturated density of the 2DEG to be \( N = 2 \times 10^{11} \text{ cm}^{-2} \), which is slightly lower than, but approaching, the 0.5e⁻ per unit cell \( (3.3 \times 10^{14} \text{ cm}^{-2}) \) which would be expected from a simple polar catastrophe argument [23] for a stoichiometric TaO₂ surface. Thus, while an interface between a polar and nonpolar surface does not always appear necessary to create an oxide 2DEG [10,11], these measurements suggest that it may help mediate its formation, either via intrinsic electronic reconstruction [23] or by promoting the formation of extrinsic defects. We note that (1 x 1) low-energy electron diffraction patterns were observed both before and after UV irradiation [see the inset to Fig. 2(a)], indicating that changes of the 2DEG are not driven by surface reconstruction of the cleaved KTaO₃ crystals.

The two highest binding energy bands of the resulting 2DEG [bands 1 and 2, Fig. 1(a)] have a light effective mass of \( m^* \sim 2 \sim 3m_e \). Together, the light and heavy mass bands contribute both concentric circular [Fig. 1(d)] as well as elliptical [Fig. 1(d)] electron pockets to the Fermi surface, suggesting that the electronic structure observed here is derived from multiple orbitals of different symmetries. Indeed, the bulk conduction bands of KTaO₃, as in SrTiO₃, are formed from three \( t_{2g} \) orbitals [27]. In the simplest picture, these form three \( d_{xy} \), \( d_{xz} \), and \( d_{zx} \)-derived interpenetrating ellipsoids, giving rise to one heavy and two light bands along the \( (100) \) directions [Fig. 3(a)]. However, spin-orbit coupling in KTaO₃ leads to a strong orbital hybridization. As shown in Fig. 3(b), this lifts the \( \Gamma \)-point degeneracy by splitting off a light band above a pair of light and heavy bands by a large energy gap of \( \Delta_{so} \sim 400 \text{ meV} \). The electronic bands we observe, however, have quite different characteristics (Fig. 1), with at least two light bands located at higher binding energies than the first heavy state.

In the following, we show that this can be attributed to a modification of the orbital occupancy due to quantum confinement. We start by discussing the simpler case of a

![FIG. 3 (color online). Local-density approximation (LDA) calculations of the bulk electronic structure and orbital character of KTaO₃ (a) excluding and (b) including spin-orbit coupling. (c) Comparison of measured dispersions to model tight-binding calculations of a surface 2DEG in SrTiO₃. (d) Equivalent calculations for a KTaO₃ 2DEG, including the strong spin-orbit coupling. The colored lines give a schematic decomposition of its orbital makeup. (e) Comparison of the KTaO₃ calculations to the experimental data from Figs. 1(a) and 1(b).](image-url)
SrTiO$_3$ surface 2DEG [Fig. 3(c)], where the spin-orbit split-off energy is small and can be neglected to first approximation [28]. We model the electronic structure using a tight-binding supercell with band bending included via additional on-site potential terms, similar to the method introduced by Stengel [30]. This model is solved self-consistently with Poisson’s equation, incorporating an electric-field-dependent dielectric constant [31], to yield the electronic structure shown in Fig. 3(c).

Starting at the highest binding energies, a ladder of multiple $d_{x^2-y^2}$-derived subbands is predicted. These are in good agreement with the multiple light states observed by ARPES [Fig. 3(c)]. This orbital assignment is consistent with their circular Fermi surfaces [10] and with the ladder of isotropic states recently observed in quantum oscillation measurements of $\delta$-doped SrTiO$_3$ quantum wells [32,33]. Because of the small interlayer hopping between $d_{xy}$ orbitals along the confinement direction, or equivalently their heavy effective mass along $k_z$, the most deeply bound of these subbands have wave functions which are dominantly localized on successive atomic planes below the surface, explaining why they can be clearly observed in ARPES [34].

On the other hand, the $d_{xz}$ and $d_{yz}$ orbitals have a significantly larger overlap along $k_z$, leading to a much lighter effective mass along this direction. The binding energy of the heavy and light pairs of $d_{xz/yz}$-derived subbands is correspondingly reduced [11], lifting the orbital degeneracy of the bulk band structure [35]. This effect can be seen in our measurements, where a heavy band, whose binding energy and dispersion are in good agreement with the calculated $d_{xz}$-derived subband, can just be resolved in the normalized spectrum shown in Fig. 3(c). Their reduced confinement energy results in subbands with envelope wave functions which are much more extended along $k$, than for the lower $d_{xy}$ bands, explaining the very weak spectral weight of the heavy bands in our measurements. The quantitative agreement of these calculations with the ARPES data confirms that the 2DEG in SrTiO$_3$ is generated by a near-surface band bending. This strongly supports first-principles calculations for the LaAlO$_3$/SrTiO$_3$ interface system that similarly find multiple coexisting confined and extended states within the 2DEG [36] and constrains theoretical models of orbital ordering and degeneracy in these systems.

Our calculations can be readily adapted to KTaO$_3$, as shown in Fig. 3(d) [37]. These can be qualitatively understood starting from the same orbital makeup as in SrTiO$_3$, but with some important additional features. (1) The lighter of the original $d_{xz/yz}$-derived states is shifted above the Fermi level by the large spin-orbit split-off energy, $\Delta_{so}$. This lifts the $\Gamma$-point degeneracy of $d_{xz/yz}$ states that is present for SrTiO$_3$. (2) Small hybridization gaps open up between the different subbands. (3) The orbital character of the lighter bands becomes strongly mixed. These characteristics are fully consistent with the measured band structure shown in Fig. 3(e), although some of the more subtle features of the calculations cannot easily be resolved experimentally.

The calculations also predict a small spin splitting of the 2DEG states around the hybridization gaps [Figs. 3(d) and 3(e)]. This can be attributed to the Rashba effect, which lifts spin degeneracy in the presence of a structural inversion asymmetry [39]. The symmetry breaking is provided here by the asymmetric potential well which confines the 2DEG. However, despite the strong spin-orbit interactions, the calculated spin splitting $\Delta k_{f}$ is only $\sim 0.01$ Å$^{-1}$ at the Fermi level. This is almost an order of magnitude smaller than recently observed for the seemingly similar system of a 2DEG in the heavy Bi-containing topological insulator Bi$_2$Se$_3$ [40], despite the much larger near-surface potential gradient confining the KTaO$_3$ 2DEG. We note, however, that a small Rashba splitting of 0.01 Å$^{-1}$ is consistent with spin precession lengths extracted from weak antilocalization measurements of a KTaO$_3$ field-effect transistor [41]. This is also consistent with our experimental data, where any Rashba splitting is too small to be resolved, placing a direct, model-independent, upper bound of $\sim 0.02$ Å$^{-1}$ for spin splitting at the Fermi level.

We attribute the small magnitude of the spin splitting to the particular electronic states involved: the degenerate $t_{2g}$ manifold of states at $\Gamma$ is split into an effective $J = 3/2$ doublet at the conduction band edge and a $J = 1/2$ split-off band [Fig. 3(b)] [12]. This is analogous to the valence, rather than conduction, bands of typical III–V semiconductors such as GaAs. In such systems, the $k$ linear term in the Rashba spin splitting of a 2D hole gas is forbidden due to symmetry, leaving the leading-order term as $k^3$ [42]. In the low-$k$ regime applicable here, this yields a very small Rashba splitting, even with the strong spin-orbit coupling and large potential gradient within the 2DEG.

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[24] This mass is in good agreement with very recent density-functional theory calculations for a KTaO3 interface-based 2DEG; see V. R. Cooper, arXiv:1201.3871.
[28] A recent calculation [29] suggests that orbital hybridization due to spin-orbit interactions may also play an important role for transport properties of SrTiO3-based 2DEGs. However, due to its small size, such features are not possible to resolve in the present experiment.
[34] As the potential becomes shallower, the wave functions of the highest dxy states within this ladder become much more delocalized along kz, making it difficult to resolve these predicted states in the ARPES measurements.
[37] To describe the electric field dependence of the dielectric constant, the experimental data of Ref. [38] were fit with the model described in Ref. [31]. Slightly better agreement with the ARPES data was obtained by reducing the effective critical field from 1.9 × 106 V m−1 to 1.1 × 106 V m−1, but this does not alter the generic subband structure or any other conclusions of this Letter.