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Synthesis and Spectroscopy of Novel Superconducting Oxides and Heterostructures

Kyle Shen
CORNELL UNIVERSITY

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Final Report

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Final Report Document for FA9550-12-1-0335

PECASE : Synthesis and Spectroscopy of Novel Superconducting Oxides & Heterostructures

The grant FA9550-12-1-0335, “PECASE : Synthesis and Spectroscopy of Novel Superconducting Oxides & Heterostructures”, was facilitated the synthesis and investigation of a variety of novel superconducting oxides (La_2CuO_4 , $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$, Sr_2RuO_4), as well as other superconductors with topological surface states ($[\text{Tl}_4](\text{Tl}_{1-x}\text{Sn}_x)\text{Te}_3$), and other oxides that are possible hosts for unconventional superconductivity ($\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$ and various iridates). This grant resulted in a total of 9 publications, including 4 in *Physical Review Letters*, 1 in *Nano Letters*, and 2 in *Physical Review B*; the complete list of publications is at the end of this document.

The main thrust of our efforts have been in epitaxial thin films of complex oxides which either are known to host high-temperature superconductivity (e.g. cuprates such as La_2CuO_4 , H.I. Wei *et al.* and $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$, L. Maritato *et al.*), or on odd-parity superconductors that may play an important role in topological quantum computation applications (e.g. Sr_2RuO_4 , B. Burganov *et al.*), or are new families of materials, such as iridates, that have been proposed to be possible new high-temperature superconductors due to their close similarities to the high- T_c cuprates (e.g. SrIrO_3 , R. Tang *et al.*, $\text{Sr}_3\text{Ir}_2\text{O}_7$, P.D.C. King *et al.*, Y.F. Nie *et al.*, $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$).

One of the primary systems that we investigated were epitaxially stabilized cuprates which could be synthesized as single crystals in any manner other than by thin film growth. In the cuprates, carrier doping of the Mott insulating parent state is necessary to realize superconductivity as well as a number of other exotic states involving charge or spin density waves. Cation substitution is the primary method for doping carriers into these compounds, and is the only known method for electron doping in these materials. The work by H.I. Wei *et al.*, published in *Physical Review Letters*, reported electron doping without cation substitution in epitaxially stabilized thin films of La_2CuO_4 grown via molecular-beam epitaxy in the so-called T' structure. We used angle-resolved photoemission spectroscopy to directly measure their electronic structure and conclusively determine that these compounds are electron doped with a carrier concentration of 0.09 ± 0.02 e- per Cu. We proposed that intrinsic defects, most likely oxygen vacancies, are the sources of doped electrons in these materials. Our results suggest a new approach to electron doping in the cuprates.

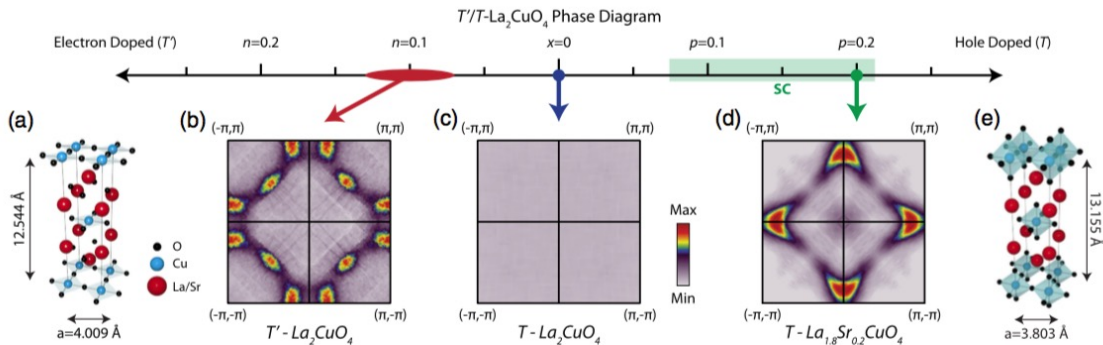
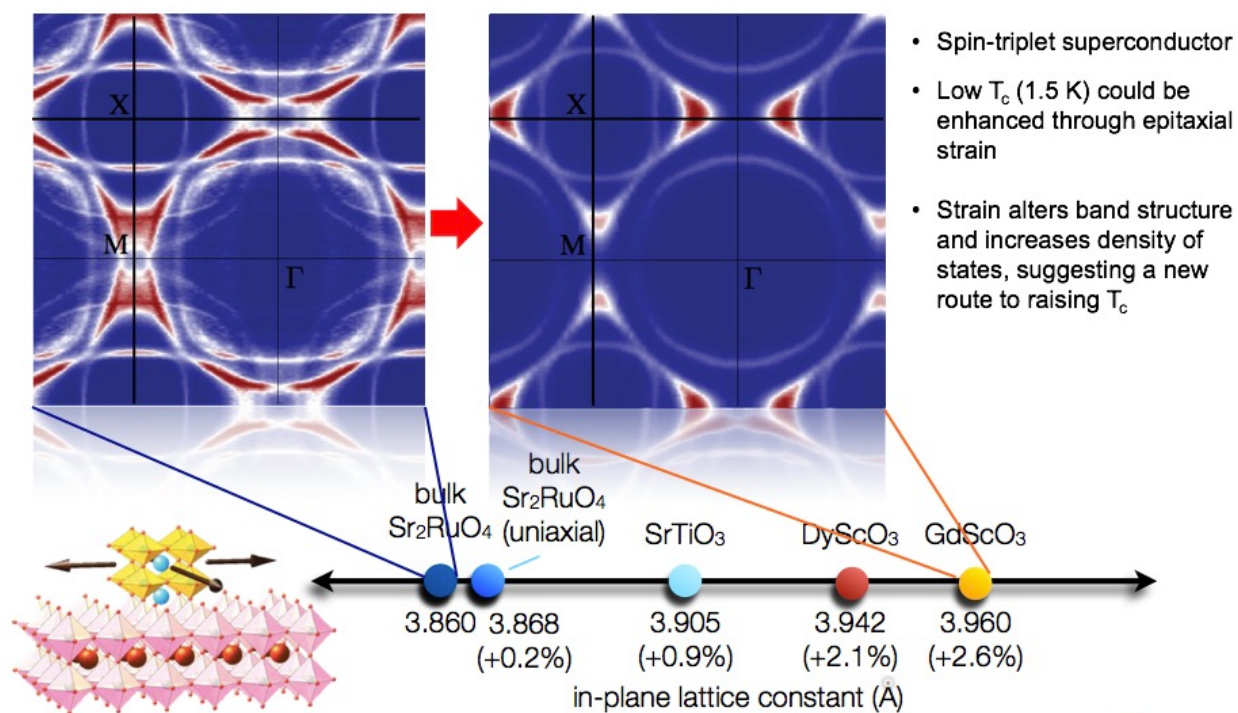
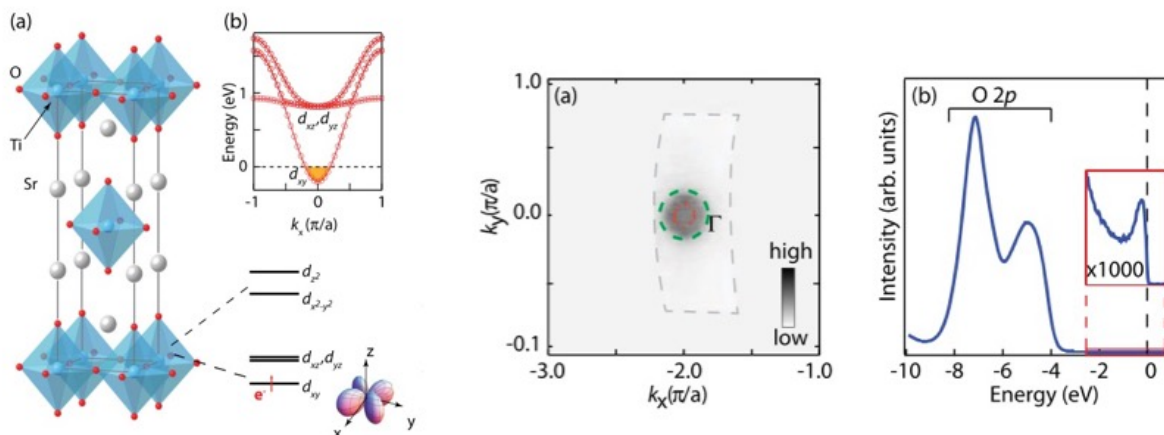


FIG. 1. Structure of (a) T' - La_2CuO_4 and (e) T - La_2CuO_4 . (b)–(d) Fermi surface maps of (b) as-grown T' - La_2CuO_4 , (c) undoped T - La_2CuO_4 , and (d) T - $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ ($T_c = 27$ K). All maps show integrated spectral weight within $E_F \pm 25$ meV, with (b) and (d) measured at 30 and (c) at 180 K.

Another notable highlight included the use of strain engineering to demonstrate how the Fermi surface topology and quantum many-body interactions can be manipulated via epitaxial strain in the spin-triplet superconductor Sr_2RuO_4 and its isoelectronic counterpart Ba_2RuO_4 using oxide molecular beam epitaxy, *in situ* angle-resolved photoemission spectroscopy, and transport measurements, by B. Burganov *et al.*, and published in *Physical Review Letters*. Near the topological transition of the γ Fermi surface sheet as shown in Figure 2, we observed clear signatures of critical fluctuations, while the quasiparticle mass enhancement is found to increase rapidly and monotonically with increasing Ru-O bond distance. Our work demonstrated the possibilities for using epitaxial strain as a disorder-free means of manipulating emergent properties, many-body interactions, and potentially the superconductivity in correlated materials.



Finally, a third highlight of the research was investigating $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$, by Y.F. Nie *et al.*, published in *Physical Review Letters*, which was interesting from the standpoint of its possible relationship to its isostructural cuprate counterparts, such as $\text{La}_{2-x}\text{CuO}_4$. In particular, this material was of interest due to the fact that if sufficient La was doped into the system, it could be thought of as a d^1 (single electron in the $3d$ shell) counterpart to the d^9 cuprates (single hole in the $3d$ shell). We reported the formation and observation of an electron liquid in $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$, the quasi-two-dimensional counterpart of SrTiO_3 , shown in Figure 3, through reactive molecular-beam epitaxy and *in situ* angle-resolved photoemission spectroscopy. The lowest lying states were found to be comprised of Ti $3d_{xy}$ orbitals, and exhibited unusually broad features characterized by quantized energy levels and a reduced Luttinger volume. Using model calculations, we explained these characteristics through an interplay of disorder and electron-phonon coupling acting cooperatively at similar energy scales, which provides a possible mechanism for explaining the low free carrier concentrations observed at various oxide heterostructures.



- La doping of $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$ forms a metallic, two-dimensional electron liquid
- Strong interplay between electrons & the lattice is observed in this material
- If sufficiently La doped, could be a d^1 analogue of superconducting cuprates

Physical Review Letters (2015)

List of Publications

- H.I. Wei, C. Adamo, E.A. Nowadnick, E.B. Lochocki, S. Chatterjee, J.P. Ruf, M.R. Beasley, D.G. Schlom, and K.M. Shen. Electron Doping of the Parent Cuprate La_2CuO_4 without Cation Substitution. *Physical Review Letters* **117**, 147002 (2016).
- J.K. Kawasaki, M. Uchida, H. Paik, D.G. Schlom, and K.M. Shen. Evolution of electronic correlations across the rutile, perovskite, and Ruddelsden-Popper iridates with octahedral connectivity. *Physical Review B* **94**, 121104 (2016).
- B. Burganov, C. Adamo, A. Mulder, M. Uchida, P.D.C. King, J.W. Harter, D.E. Shai, A.S. Gibbs, A.P. Mackenzie, R. Uecker, M. Bruetzsch, M.R. Beasley, C.J. Fennie, D.G. Schlom, and K.M. Shen. Strain Control of Fermiology and Many-Body Interactions in Two-Dimensional Ruthenates. *Physical Review Letters* **116**, 197003 (2016).
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- Y.F. Nie, D. Di Sante, S. Chatterjee, P.D.C. King, M. Uchida, S. Ciuchi, D.G. Schlom, and K.M. Shen. Formation and Observation of a Quasi-Two-Dimensional d_{xy} Electron Liquid in Epitaxially Stabilized $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$ Thin Films. *Physical Review Letters* **115**, 096405 (2015).

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- K.E. Arpino, D.C. Wallace, Y.F. Nie, T. Birol, P.D.C. King, S. Chatterjee, M. Uchida, S.M. Koohpayeh, J.J. Wen, K. Page, C.J. Fennie, K.M. Shen, and T.M. McQueen. Evidence for Topologically Protected Surface States and a Superconducting Phase in $[\text{Ti}_4](\text{Ti}_{1-x}\text{Sn}_x)\text{Te}_3$ Using Photoemission, Specific Heat, and Magnetization Measurements, and Density Functional Theory. *Physical Review Letters* **112**, 1479 (2014).
- P.D.C. King, T. Takayama, A. Tamai, E. Rozbicki, S.M. Walker, M. Shi, L. Patthey, R.G. Moore, D. Lu, K.M. Shen, H. Takagi, and F. Baumberger. Spectroscopic indications of polaronic behavior of the strong spin-orbit insulator $\text{Sr}_3\text{Ir}_2\text{O}_7$. *Physical Review B* **87**, 241106 (2013).
- L. Maritato, A. Galdi, P. Orgiani, J.W. Harter, J. Schubert, K.M. Shen, and D.G. Schlom. Layer-by-layer shuttered molecular-beam epitaxial growth of superconducting $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films. *Journal of Applied Physics* **113**, 053911 (2013).

Layer-by-layer shuttered molecular-beam epitaxial growth of superconducting $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films

L. Maritato,^{1,2,a)} A. Galdi,¹ P. Orgiani,¹ J. W. Harter,³ J. Schubert,⁴ K. M. Shen,^{3,5} and D. G. Schlom^{2,5}

¹Dipartimento di Ingegneria dell'Informazione, Ingegneria Elettrica e Matematica Applicata-DIEM, University of Salerno and CNR-SPIN, 84084 Fisciano (SA), Italy

²Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

³Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA

⁴Forschungszentrum Julich, Institute of Bio- and Nano-systems IBN, D-52425 Julich, Germany and Forschungszentrum Julich, JARA Fundamentals of Future Information Technology, D-52425 Julich, Germany

⁵Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA

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Superconducting $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films have been grown on GdScO_3 substrates by reflection high-energy electron diffraction calibrated layer-by-layer molecular-beam epitaxy. X-ray diffraction analysis has confirmed the infinite layer structure after an *in situ* vacuum annealing step. *In situ* photoemission spectroscopy indicates that the vacuum annealing step employed immediately after film growth to achieve superconducting films results in oxygen loss from the films. The superconducting critical temperature depends on the La content x , with the highest value obtained for $x \sim 0.10$. Resistivity as a function of temperature $\rho(T)$ curves of optimally doped samples show a T^2 temperature dependence characteristic of a scattering process where electron-electron interactions dominate. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4790150>]

I. INTRODUCTION

The ACuO_2 infinite-layer (IL) compounds, where CuO_2 sheets with four-fold Cu atoms coordinated by O are separated by Ca and/or Sr cations (A), have the simplest structure of all known superconducting cuprates.^{1,2} In spite of this structural simplicity, bulk synthesis of superconducting ILs presents many difficulties (particularly for SrCuO_2), requiring the use of high-pressure techniques.^{3,4} Partial substitution of large rare-earth (RE) 3+ ions (La, Pr, Nd, Sm, Gd) for Sr^{2+} produces *n*-type superconducting compounds with a maximum critical temperature T_c around 43 K.^{5,6} IL materials, along with the $\text{RE}_{2-x}\text{Ce}_x\text{CuO}_4$ compounds (maximum T_c around 30 K (Refs. 7 and 8)), are the two most investigated materials showing electron-doped high temperature superconductivity.⁹ Several groups have grown doped IL thin films by various deposition techniques^{10–17} (molecular-beam epitaxy (MBE), laser ablation, sputtering) to study their superconducting properties. To obtain good superconducting IL films, the use of suitable substrates is critical.^{10,11} The biaxial strain induced by the substrate plays an important role in determining the Cu-O coordination number, e.g., the presence or absence of apical oxygen. In particular, while compressive in-plane epitaxial strain (as in the case of SrTiO_3 substrates) generally gives IL films with inferior superconducting performances,^{13–15} in-plane tensile strain (KTaO_3 and DyScO_3 substrates) produces IL superconducting films with critical temperatures close to the bulk value and with low metallic resistivities.^{10–12,17}

Reflection high-energy electron diffraction (RHEED) assisted layer-by-layer MBE, with its ability to control growth at the level of single atomic planes, is an excellent technique for fabricating IL layered systems. Very good superconducting IL thin films have been produced by co-deposition MBE,^{10,11} while (probably due to the use of SrTiO_3 substrates) IL samples with inferior superconducting properties have been obtained by RHEED-assisted layer-by-layer MBE.¹² Here we report the growth of IL epitaxial $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films on GdScO_3 (110) substrates with superconducting critical temperatures as high as 35 K by using shuttered MBE. In addition to measuring the transport properties of the samples, they have been investigated by *in situ* photoemission spectroscopy. The ability to fabricate *n*-type superconducting IL films with this layer-by-layer technique provides a way to study interface effects in heterostructures based on this class of materials.

II. SAMPLE PREPARATION

$\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ films were grown in a Veeco GEN10 dual-chamber oxide MBE system using a shuttered layer-by-layer deposition process performed in purified O_3 at a background pressure of 1×10^{-6} Torr. The films were deposited on GdScO_3 (110) substrates which have a distorted perovskite structure with a pseudo-cubic lattice constant of 0.3968 nm.¹⁸ During growth, the substrate temperature T_s , as measured by a thermocouple and pyrometer, was in the range 500–550 °C. Immediately following film growth, the samples were vacuum annealed *in situ* (typically around 10^{-8} Torr) at temperatures typically a few degrees higher than T_s for 30 min and then cooled to room temperature in vacuum. This annealing step

^{a)}Author to whom correspondence should be addressed. Electronic mail: lmaritato@unisa.it.

Evolution of electronic correlations across the rutile, perovskite, and Ruddlesden-Popper iridates with octahedral connectivity

Jason K. Kawasaki,^{1,2,3,*} Masaki Uchida,⁴ Hanjong Paik,² Darrell G. Schlom,^{2,3} and Kyle M. Shen^{1,3,†}

¹Laboratory for Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, USA

²Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

³Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York 14853, USA

⁴Department of Applied Physics, University of Tokyo, Tokyo, Japan

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The confluence of electron correlations and spin-orbit interactions is critical to realizing quantum phases in 5d transition metal oxides. Here, we investigate how the strength of the effective electron correlations evolve across a series of d^5 iridates comprised of IrO_6 octahedra, ranging from the layered correlated insulator Sr_2IrO_4 , to the three-dimensional perovskite semimetal SrIrO_3 , to metallic rutile IrO_2 in which the octahedra are arranged in a mixed edge and corner sharing network. Through a combination of reactive oxide molecular-beam epitaxy, *in situ* angle-resolved photoemission spectroscopy, core level photoemission, and density functional theory, we show how the effective electron correlations weaken as a function of increasing connectivity of the IrO_6 network and p - d hybridization. Our results demonstrate how structure and connectivity can be used to control the strength of correlations in the iridates.

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Electron-electron correlations play an essential role in renormalizing the ground state of many transition metal oxides. While this renormalization was once thought to be weak in the late transition metals due to the extended spatial extent of 5d orbitals, it is now well appreciated that spin-orbit coupling can enhance the effects of correlations, particularly in the case of iridium oxides. A prime example is that of Sr_2IrO_4 , for which band theory predicts a metallic ground state, but the combination of spin-orbit coupling and correlations give rise to an antiferromagnetic $J_{\text{eff}} = 1/2$ insulator [1]. This combination of spin-orbit coupling and correlations has proven key to the physics of proposed states in the iridates, including superconductivity [2–5], the Kitaev model [6], the Weyl semimetal [7–9], and other topological states [10,11].

The majority of these exotic states have been typically proposed for iridates in the perovskite AIrO_3 [10–13], layered Ruddlesden-Popper $\text{A}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ [1,14–16], and pyrochlore $\text{A}_2\text{Ir}_2\text{O}_7$ [9,17] structures, where A is an alkaline earth metal. These different crystal structures share as a common building block IrO_6 octahedra where the Ir^{4+} is in a $5d^5$ configuration. For example, SrIrO_3 is a material in which the octahedra form a three-dimensional corner sharing network and is proposed to be a topological crystalline insulator with line nodes protected by crystal symmetry [10,11]. Sr_2IrO_4 is composed of a two-dimensional octahedral network and is proposed to be a $J_{\text{eff}} = 1/2$ superconductor upon electron doping [2–5]. Another material which shares the same IrO_6 ($5d^5$) building block is the rutile polymorph of IrO_2 . In the perovskite, Ruddlesden-Popper, and pyrochlore structures, the IrO_6 octahedra are connected in exclusively corner-sharing networks, whereas in the rutile structure, the octahedra exhibit a higher degree of connectivity and are instead tiled with a mixture of both corner and edge sharing neighbors [Fig. 1(a)].

IrO_2 exhibits a number of properties that make it fundamentally interesting and technologically relevant, particularly for spintronic applications. These include novel magnetotransport properties, with a large spin Hall angle which clearly highlights the importance of spin-orbit coupling [18], as well as a Hall effect whose carrier sign can be switched by changing the orientation of the external magnetic field [19]. In addition, IrO_2 is a very promising catalyst for the oxygen evolution reaction [20,21]. Given its similar *local* structure, one might expect IrO_2 to share many of the same properties as the other iridates. On the other hand, it is known that subtle structure distortions, such as octahedral tilts, can dramatically alter the properties of complex oxides in general [22], and perovskite iridates in particular [13]. Therefore, the precise role of electron correlations in determining the properties across iridates with different connectivity remains an open question.

In this Rapid Communication, we investigate how the strength of the effective correlations across the iridates varies with the connectivity of the IrO_6 octahedra using a combination of reactive oxide molecular-beam epitaxy (MBE) synthesis, *in situ* angle-resolved photoemission spectroscopy (ARPES), core level spectroscopy, and density functional theory. In surprising contrast to Sr_2IrO_4 and SrIrO_3 , we find that electron-electron correlations are unusually weak in IrO_2 , surprising for a transition metal oxide. We discover that the combination of increasing the octahedral connectivity, the metal-oxygen covalency, and the metal-metal interactions reduce the effective correlation strength when going from the antiferromagnetic Mott insulator Sr_2IrO_4 to Fermi liquid IrO_2 , which does not exhibit any appreciable mass enhancement. Thin films of (001) SrIrO_3 , Sr_2IrO_4 , and (110) IrO_2 were grown by MBE on $(\text{LaAlO}_3)_{0.29}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.71}$ (LSAT) (001) substrates (SrIrO_3 , Sr_2IrO_4) and TiO_2 (110) substrates (IrO_2). The films were grown under a background partial pressure of 10^{-6} torr of distilled ozone at a substrate temperature of 900 °C for Sr_2IrO_4 , 650 °C for SrIrO_3 , and 350 °C for IrO_2 . Additional details about the growth and characterization of SrIrO_3 and Sr_2IrO_4 can be found in Ref. [13]. X-ray diffraction (XRD,

*Current address: Department of Materials Science and Engineering, University of Wisconsin, Madison WI 53706.

†kmshen@cornell.edu

Strain Control of Fermiology and Many-Body Interactions in Two-Dimensional Ruthenates

B. Burganov,¹ C. Adamo,^{2,3} A. Mulder,⁴ M. Uchida,¹ P. D. C. King,^{1,5,6} J. W. Harter,¹ D. E. Shai,¹
A. S. Gibbs,⁷ A. P. Mackenzie,^{5,8} R. Uecker,⁹ M. Bruetzmann,⁹ M. R. Beasley,³ C. J. Fennie,⁴
D. G. Schlom,^{2,6} and K. M. Shen^{1,6,*}

¹Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA

²Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

³Department of Applied Physics, Stanford University, Stanford, California 94305, USA

⁴School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, USA

⁵School of Physics and Astronomy, University of St Andrews, St Andrews, Fife KY16 9SS, United Kingdom

⁶Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA

⁷Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany

⁸Max Planck Institute for Chemical Physics of Solids, D-01187 Dresden, Germany

⁹Leibniz Institute for Crystal Growth, D-12489 Berlin, Germany

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Here we demonstrate how the Fermi surface topology and quantum many-body interactions can be manipulated via epitaxial strain in the spin-triplet superconductor Sr_2RuO_4 and its isoelectronic counterpart Ba_2RuO_4 using oxide molecular beam epitaxy, *in situ* angle-resolved photoemission spectroscopy, and transport measurements. Near the topological transition of the γ Fermi surface sheet, we observe clear signatures of critical fluctuations, while the quasiparticle mass enhancement is found to increase rapidly and monotonically with increasing Ru-O bond distance. Our work demonstrates the possibilities for using epitaxial strain as a disorder-free means of manipulating emergent properties, many-body interactions, and potentially the superconductivity in correlated materials.

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Pressure plays a key role in modifying the properties of materials with strong electronic correlations, for instance, enhancing the transition temperature of the cuprate superconductors or driving quantum phase transitions in heavy fermion systems. Unfortunately, leading techniques for investigating the electronic structure, such as angle-resolved photoemission spectroscopy (ARPES) and STM, are incompatible with typical high pressure or strain apparatus. The epitaxial growth of thin films on deliberately lattice mismatched substrates provides a clean and accessible analogue to external pressure and has been used to dramatically alter the electronic phases of many complex oxides [1–4]. In the family of ruthenium oxides, the strong structure-property relationship leads to a wide variety of ground states including unconventional superconductivity [5], metamagnetism and electronic liquid crystalline states [6–8], ferromagnetism, antiferromagnetism and spin-glass behavior [9–11], without changing the formal oxidation state of the Ru ion. Among them, Sr_2RuO_4 is an ideal candidate to explore the effects of biaxial strain and chemical pressure, since the extreme sensitivity of its superconducting ground state to disorder [12] precludes enhancement of T_c through chemical substitution. The possibly chiral nature of the superconducting state has given rise to proposals utilizing Sr_2RuO_4 as a platform for realizing Majorana fermions, exotic Josephson junctions,

and non-Abelian topological quantum computation [13,14]. Hydrostatic pressure was shown to suppress both the T_c [15] and quasiparticle enhancements [16], but recent experiments applying a uniaxial strain of 0.2% demonstrated a strong nonlinear enhancement of T_c [17]. Obtaining uniaxial strains of greater than 0.5% is a challenge in rather brittle metal oxides, but biaxial strains of 2%–3% are readily achievable in epitaxial thin films grown on deliberately lattice mismatched substrates. Here we demonstrate epitaxial strain engineering as a disorder-free means to dramatically manipulate the electronic structure of Sr_2RuO_4 and its sister compound, Ba_2RuO_4 , through a combination of reactive oxide molecular beam epitaxy (MBE) growth and *in situ* ARPES. We are able to observe a topological transition in the γ Fermi surface (FS) sheet (i.e., a Lifshitz transition) through the selection of appropriate substrates. In addition, we observe signatures of quantum criticality in both ARPES and electrical transport near the Lifshitz transition, as well as a surprisingly large enhancement of the quantum many-body interactions with increasing in-plane lattice constant.

Thin films of Sr_2RuO_4 and Ba_2RuO_4 were synthesized by reactive oxide MBE and the in-plane lattice constant (i.e., the Ru-O-Ru bond distance) can be increased from 3.87 to 3.97 Å ($\Delta a/a = 2.6\%$) through the selection of appropriate substrates. Sr_2RuO_4 films were found to relax

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Oxygen evolution reaction electrocatalysis on
SrIrO₃ grown using molecular beam epitaxy†Runbang Tang,^{‡a} Yuefeng Nie,^{‡ab} Jason K. Kawasaki,^{‡bc} Ding-Yuan Kuo,^a
Guido Petretto,^d Geoffroy Hautier,^d Gian-Marco Rignanese,^d Kyle M. Shen,^{bc}
Darrell G. Schlom^{ac} and Jin Suntivich^{*ac}

Electrochemical generation of oxygen via the oxygen evolution reaction (OER) is a key enabling step for many air-breathing electrochemical energy storage devices. IrO₂ (Ir⁴⁺: 5d⁵) ranks among the most active known OER catalysts. However, it is unclear how the environment of the Ir⁴⁺ oxygen-coordination octahedra affects the OER electrocatalysis. Herein, we present the OER kinetics on a single-crystal, epitaxial SrIrO₃(100)_p perovskite oxide synthesized using molecular-beam epitaxy on a DyScO₃(110) substrate. We find that by switching the host structure of the Ir⁴⁺ oxygen-coordination octahedra from corner- and edge-sharing rutile (IrO₂) to purely corner-sharing perovskite (SrIrO₃), the OER activity increases by more than an order of magnitude. We explain our finding with the correlated, semimetal electronic structure of SrIrO₃; our density functional theory calculations reveal that the adsorption energetics on SrIrO₃ depends sensitively on the electron–electron interaction, whereas for IrO₂, it depends rather weakly. This finding suggests the importance of correlations on the OER and the design of future transition metal oxide electrocatalysts.

The kinetics of the oxygen evolution reaction (OER, in alkaline: 4OH[−] → O₂ + 2H₂O + 4e[−]) is central to the efficiency of many air-breathing electrochemical energy storage systems, including solar- and electricity-driven electrolysis^{1–3} and rechargeable metal–air batteries.^{4–6} In an effort to find superior materials as OER catalysts to decrease the activation overpotential, Trasatti has surveyed the OER kinetics over a large number of transition

metal oxides⁷ and identified IrO₂ and RuO₂ as the most active binary OER electrocatalysts. Decades later, using *ab initio* calculations, Nørskov and Rossmeisl have suggested that the high OER activities of these precious-metal oxides are due to the stable formations of the intermediates during the OER.^{8–10} Using the scaling relation, they also established the surface oxygen binding as a descriptor to the OER activity. Inspired by this finding, intensive efforts have been spent on identifying strategies for controlling the surface oxygen interactions by using, for example, transition metal substitutions,^{11–13} structural engineering,^{14,15} and support interactions.^{16–18} Although these efforts have led to successful developments of new OER electrocatalysts, the studies have largely focused on poly-disperse-oxide materials. The reliance on the polydisperse materials complicates the process of connecting the surface structure with the electrochemical mechanism as there can be different terminations, structural defects, or even multiple phases present within the same catalytic material.^{19,20}

In the past few decades, advances in deposition technologies and substrate availabilities have enabled the growth of single-crystal transition metal oxide films with high structural perfection. These advances have driven recent work in elucidating the electrochemistry on single-crystal transition metal oxides and allowed for a very precise determination of the electrokinetics.²⁰ Still, very few well-defined, single-crystal 5d transition metal oxides surfaces, notably IrO₂, have been studied as OER catalysts.^{20,21} Herein, we report the OER kinetics on a well-defined, single-crystal 5d perovskite-oxide SrIrO₃ catalyst that was synthesized using molecular-beam epitaxy (MBE). We find that the OER activity of the SrIrO₃ is more than an order of magnitude higher than IrO₂, despite both SrIrO₃ and IrO₂ sharing the same active Ir⁴⁺O₆ octahedral unit. Our density function theory (DFT) calculations assuming a previously reported OER pathway^{8–10} suggest the OOH* formation as the most energy-intensive intermediate on SrIrO₃ during the OER. We further find that the calculated energetics depends on the Hubbard *U*, which reflects the correlated nature of SrIrO₃. Although this correlation renders the process of assigning the

^aDepartment of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA. E-mail: jsuntivich@cornell.edu^bLaboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA^cKavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York 14853, USA^dInstitute of Condensed Matter and Nanosciences (IMCN), Université Catholique de Louvain, Louvain-la-Neuve 1348, Belgium

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‡ Equal contributions.

Formation and Observation of a Quasi-Two-Dimensional d_{xy} Electron Liquid in Epitaxially Stabilized $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$ Thin Films

Y. F. Nie,^{1,2,3} D. Di Sante,^{4,5} S. Chatterjee,² P. D. C. King,^{2,6} M. Uchida,² S. Ciuchi,^{4,7}
D. G. Schlom,^{3,6} and K. M. Shen^{2,6,*}

¹National Laboratory of Solid State Microstructures and College of Engineering and Applied Sciences,
Nanjing University, Nanjing 210093, People's Republic of China

²Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA

³Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

⁴Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, Coppito, L'Aquila I-67100, Italy

⁵CNR-SPIN, Via Vetoio, L'Aquila I-67100, Italy

⁶Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA

⁷CNR-ISC, Via dei Taurini, Rome I-00185, Italy

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We report the formation and observation of an electron liquid in $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$, the quasi-two-dimensional counterpart of SrTiO_3 , through reactive molecular-beam epitaxy and *in situ* angle-resolved photoemission spectroscopy. The lowest lying states are found to be comprised of Ti $3d_{xy}$ orbitals, analogous to the $\text{LaAlO}_3/\text{SrTiO}_3$ interface and exhibit unusually broad features characterized by quantized energy levels and a reduced Luttinger volume. Using model calculations, we explain these characteristics through an interplay of disorder and electron-phonon coupling acting cooperatively at similar energy scales, which provides a possible mechanism for explaining the low free carrier concentrations observed at various oxide heterostructures such as the $\text{LaAlO}_3/\text{SrTiO}_3$ interface.

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Strontium titanate (SrTiO_3) is a key building block in oxide electronics, particularly for the formation of two-dimensional electron liquids (2DELs) at SrTiO_3 interfaces and surfaces. For instance, the interface between $\text{LaAlO}_3/\text{SrTiO}_3$ [1], exhibits exotic properties such as superconductivity and ferromagnetism. There have also been reports of high temperature superconductivity at the monolayer $\text{FeSe}/\text{SrTiO}_3$ interface. At the $\text{LaAlO}_3/\text{SrTiO}_3$ interface or SrTiO_3 surface, the degeneracy of the t_{2g} orbitals is lifted [2–4], and the d_{xy} states play an important role in the observed ferromagnetism [5] and the superconducting phase diagram [6,7]. An alternate strategy to break the t_{2g} degeneracy and realize a 2DEL is to interrupt the three-dimensional network of corner-sharing TiO_6 octahedra with a double SrO layer, resulting in Sr_2TiO_4 , the quasi-two-dimensional $n = 1$ end member of the Ruddlesden-Popper (RP) series $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$, of which SrTiO_3 is the other three-dimensional, $n = \infty$ end member. Sr_2TiO_4 could also provide a natural platform for exploring exotic superconductivity, ferroelectricity, and magnetism in the titanates. Bulk single crystals of Sr_2TiO_4 have never been synthesized [8], hindering the utility and understanding of this compound, and its electronic structure remains unexplored to date.

In this Letter, we report the synthesis and investigation of the electronic structure of lanthanum doped $\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$ by a combination of oxide and *in situ* angle-resolved photoemission spectroscopy (ARPES).

We observe a single d_{xy} band resulting in a circular Fermi surface near the Fermi energy, in addition to a number of unexpected features. The measured Luttinger volume is approximately a factor of 4 smaller than expected, and the spectra exhibit a series of energy levels with $\Delta = 93$ meV separation, reminiscent of the phonon replicas recently reported in monolayer FeSe on SrTiO_3 [9]. We employ model calculations which cooperatively treat the effects of disorder and electron-phonon (*e-ph*) coupling to successfully explain these apparent discrepancies.

Epitaxial La-doped Sr_2TiO_4 films with a thickness of 20 formula units were grown on (001) LSAT $[(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{1/2}\text{Ta}_{1/2}\text{O}_3)_{0.7}]$ substrates by MBE at 850°C in 10^{-7} torr of O_2 using a shuttered growth technique [10]. *In situ* ARPES measurements were taken at 20 K at an energy resolution of $\Delta E = 12$ meV with a VG Scienta R4000 electron analyzer and He-I α photons ($h\nu = 21.218$ eV). Details of the sample growth, DFT calculations, and the theoretical model are provided in the Supplemental Material [11], which includes Refs. [12–15].

Because of the layered crystal structure and an increase in the titanium apical oxygen distance over the in-plane oxygens (2.1%), the degeneracy in Ti t_{2g} orbitals is removed [Fig. 1(b)]. Similar to the high- T_c cuprates and many other layered compounds, the very weak interlayer hopping leads to quasi-two-dimensional electronic states in Sr_2TiO_4 . Upon electron doping (La substitution for Sr), the

Polycrystalline Graphene with Single Crystalline Electronic Structure

Lola Brown,[†] Edward B. Lochocki,[‡] José Avila,[§] Cheol-Joo Kim,[†] Yui Ogawa,^{†,||} Robin W. Havener,[⊥] Dong-Ki Kim,[†] Eric J. Monkman,[‡] Daniel E. Shai,[‡] Haofei I. Wei,[‡] Mark P. Levendorf,[†] María Asensio,[§] Kyle M. Shen,^{*,‡,#} and Jiwoong Park^{*,†,#}

[†]Department of Chemistry and Chemical Biology, [‡]Department of Physics, Laboratory of Atomic and Solid State Physics, [⊥]School of Applied and Engineering Physics, and [#]Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York 14853, United States

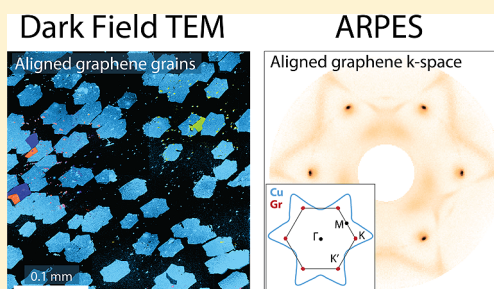
[§]Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin-BP 48, 91192 Gif sur Yvette Cedex, France

^{||}Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

S Supporting Information

ABSTRACT: We report the scalable growth of aligned graphene and hexagonal boron nitride on commercial copper foils, where each film originates from multiple nucleations yet exhibits a single orientation. Thorough characterization of our graphene reveals uniform crystallographic and electronic structures on length scales ranging from nanometers to tens of centimeters. As we demonstrate with artificial twisted graphene bilayers, these inexpensive and versatile films are ideal building blocks for large-scale layered heterostructures with angle-tunable optoelectronic properties.

KEYWORDS: Graphene, hexagonal boron nitride, dark-field transmission electron microscopy, angle-resolved photoemission spectroscopy, artificial twisted bilayer



Chemical vapor deposition (CVD) on copper (Cu) has recently emerged as a powerful growth technique for realizing large scale graphene and hexagonal boron nitride (*h*-BN) films in an inexpensive and simple way, enabling their production up to meter scale.^{1,2} However, these films do not exhibit crystalline alignment over distances critical to the large scale production of spatially uniform vertical heterostructures. For example, CVD grown graphene films are usually comprised of small, randomly rotated grains,^{3,4} and even though some recipes can create graphene grains nearly one centimeter in size,^{5,6} neighboring grains rarely maintain a common orientation. Previous studies have shown that controlling the graphene crystallinity requires ordered substrates with strong templating interactions during growth. For instance, graphene deposited on the symmetry-matched surface lattices of certain single crystal metals, including ruthenium (0001), iridium (111), rhodium (111), and Cu (111), can follow the substrate's rotational orientation under specific growth conditions;⁶ a recent example is the growth of a graphene film aligned over 1 mm on a sputtered Cu (111) film.⁸ Another recent paper has demonstrated aligned graphene growth on 5 cm germanium (110) wafers.⁹ Graphene, although generally not a single layer, can also be grown epitaxially on silicon carbide (SiC) substrates. These aligned growth methods, however, all suffer from complicated and expensive substrate preparation^{8,9} or transfer procedures.¹⁰

In this report, we present a growth method for graphene and *h*-BN that combines the scalability and ease of transfer inherent

to Cu foil based CVD with the lattice uniformity achieved on ordered templating substrates. Our method relies on two key factors: (1) Cu foil recrystallization and (2) growth parameters optimized for reduced reactivity (see Figure 1a). First, we produce long-range crystallinity in the Cu foil (Nilaco corporation, #CU-113213, 99.9% purity) by annealing it for up to 12 hours at a temperature of 1030 °C, which is close to its melting point, in an Ar/H₂ environment (see Supporting Information, Supplementary Figures 4 and 5). This procedure generates a single Cu(111) domain with a spatially uniform in-plane orientation over the entire foil, which we have verified up to 16 cm using bulk sensitive Laue X-ray diffraction (XRD) (Figure 1a, insets) and surface-sensitive spatially resolved backscatter electron diffraction (BSED) (Figure 3a). Second, graphene or *h*-BN is grown using carefully chosen growth parameters that reduce the nucleation density,⁶ suppress bilayer growth,^{11,12} and, most importantly, favor angular correlation between graphene or *h*-BN grains and the underlying Cu(111) surface^{13,14} (see Methods in the Supporting Information for more details about foil preparation and growth). The final results are continuous graphene and *h*-BN films (Figures 1c, middle and 1d, bottom); however, we often intentionally limit the growth time to produce a partial coverage that facilitates characterization of individual grains.

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Evidence for Topologically Protected Surface States and a Superconducting Phase in $[\text{Ti}_4](\text{Ti}_{1-x}\text{Sn}_x)\text{Te}_3$ Using Photoemission, Specific Heat, and Magnetization Measurements, and Density Functional Theory

K. E. Arpino,^{1,2} D. C. Wallace,^{1,2} Y. F. Nie,^{3,4} T. Birol,⁵ P. D. C. King,^{3,6} S. Chatterjee,³ M. Uchida,³ S. M. Koohpayeh,² J.-J. Wen,² K. Page,⁷ C. J. Fennie,⁵ K. M. Shen,^{3,6} and T. M. McQueen^{1,2,*}

¹Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, USA

²Institute for Quantum Matter, Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218, USA

³Department of Physics, Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, USA

⁴Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

⁵School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, USA

⁶Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York 14853, USA

⁷Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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We report the discovery of surface states in the perovskite superconductor $[\text{Ti}_4]\text{TiTe}_3$ (Ti_5Te_3) and its nonsuperconducting tin-doped derivative $[\text{Ti}_4](\text{Ti}_{0.4}\text{Sn}_{0.6})\text{Te}_3$ as observed by angle-resolved photoemission spectroscopy. Density functional theory calculations predict that the surface states are protected by a Z_2 topology of the bulk band structure. Specific heat and magnetization measurements show that Ti_5Te_3 has a superconducting volume fraction in excess of 95%. Thus Ti_5Te_3 is an ideal material in which to study the interplay of bulk band topology and superconductivity.

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Charge carriers in Dirac-like bands have a linear energy-momentum relationship described by the Dirac equation; they offer the unique opportunity to investigate the intersection of special relativity and quantum mechanics. However, materials exhibiting Dirac-like states are relatively rare, the most notable examples being graphene [1], Z_2 topological insulators [2], and topological crystalline insulators [3]. Materials which combine nontrivial band topologies with superconductivity have the ability to test the predictions of new states of matter and open the field for new technologies such as quantum computing [4–7], but producing such materials has been a challenge [8–10].

In this Letter, we report the discovery of Dirac-like surface states in $[\text{Ti}_4](\text{Ti}_{1-x}\text{Sn}_x)\text{Te}_3$, as observed by angle-resolved photoemission spectroscopy (ARPES). Density functional theory (DFT) predicts these surface states to be Z_2 topologically protected due to a spin-orbit-driven band parity inversion at the Z time reversal invariant momentum point of the first Brillouin zone. Specific heat and magnetization measurements show that Ti_5Te_3 exhibits fully gapped, bulk superconductivity below $T_c = 2.40(1)$ K with a 96% volume fraction.

The $[\text{Ti}_4]M\text{Te}_3$ ($M = \text{Ti}, \text{Sn}, \text{Pb}, \text{Bi}, \text{Sb}, \text{La}, \text{Nd},$ and Mo [11–14]) compounds have a tetragonal perovskite structure (ABO_3), shown in Fig. 1(a) [15]. The cavities of a three-dimensional network of corner-sharing $M\text{Te}_6$ octahedra are occupied by interconnected Ti_4 tetrahedra. There are several ways in which the $[\text{Ti}_4]M\text{Te}_3$ structure can produce topologically protected surface states. First, the mirror planes which protect surface states in rock salt topological

crystalline insulators such as SnTe are also present in the basic perovskite structure of this family; the appropriate band inversions at points protected by mirror symmetry similarly may yield a topological crystalline insulator state in body-centered tetragonal symmetry. Second, the body-centered tetragonal crystal class of $[\text{Ti}_4]M\text{Te}_3$ structure has four sets of time-reversal invariant points: one Γ , four N , two X , and one Z . If spin-orbit coupling produces an odd number of band parity inversions, e.g., a single inversion at either the Γ or Z point, but not both, strong Z_2 topologically protected surface states would result [18].

To check these possibilities, first principles (DFT) calculations were performed with full-potential linear augmented wave formalism as implemented in WIEN2K [19]. Exchange-correlation energies are calculated with Perdew-Burke-Erzenhof functional [20]. An $8 \times 8 \times 8$ unshifted k -point grid is used in the Brillouin zone of the primitive body-centered tetragonal cell. Results reported were double checked by repeating calculations in projector augmented wave formalism, as implemented in VASP, and no disagreements were found [21]. The $I4/mcm$ cell used for the calculations was determined by Rietveld refinements to neutron powder diffraction data collected on Ti_5Te_3 at $T = 295, 100,$ and 15 K on the NPDF instrument at the Los Alamos Neutron Science Center, which show no evidence of a structural transition down to $T = 15$ K. These data are consistent with the structural data obtained from synchrotron x-ray diffraction at higher temperatures. Our DFT calculations for Ti_5Te_3 , shown in Figs. 1(c) and 1(d), show spin-orbit coupling



Spectroscopic indications of polaronic behavior of the strong spin-orbit insulator $\text{Sr}_3\text{Ir}_2\text{O}_7$

P. D. C. King,^{1,2,3,*} T. Takayama,⁴ A. Tamai,^{1,5} E. Rozbicki,¹ S. McKeown Walker,^{1,5} M. Shi,⁶ L. Patthey,^{6,7} R. G. Moore,⁸ D. Lu,⁹ K. M. Shen,^{2,3} H. Takagi,^{4,10} and F. Baumberger^{1,5,6,†}

¹*SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife KY16 9SS, United Kingdom*

²*Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA*

³*Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA*

⁴*Department of Physics, University of Tokyo, Hongo, Tokyo 113-0033*

⁵*Département de Physique de la Matière Condensée, Université de Genève, 24 Quai Ernest-Ansermet, 1211 Genève 4, Switzerland*

⁶*Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

⁷*SwissFEL, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

⁸*Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA*

⁹*Stanford Synchrotron Radiation Lightsources, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA*

¹⁰*Magnetic Materials Laboratory, RIKEN Advanced Science Institute, Wako, Saitama 351-0198, Japan*

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We investigate the bilayer Ruddlesden-Popper iridate $\text{Sr}_3\text{Ir}_2\text{O}_7$ by temperature-dependent angle-resolved photoemission. At low temperatures, we find a fully gapped correlated insulator, characterized by a small charge gap and narrow bandwidths. The low-energy spectral features show a pronounced temperature-dependent broadening and non-quasiparticle-like Gaussian line shapes. Together, these spectral features provide experimental evidence for a polaronic ground state. We observe similar behavior for the single-layer cousin Sr_2IrO_4 , indicating that strong electron-boson coupling dominates the low-energy excitations of this exotic family of $5d$ compounds.

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The strong spin-orbit interaction in the $5d$ shell is predicted to stabilize a variety of exotic ground states in iridium-based transition-metal oxides, including Mott insulators,^{1–3} Weyl semimetals,⁴ correlated topological insulators,^{5–8} and spin-triplet superconductors.⁹ Moreover, iridates were recently proposed as an analog of the cuprates, and as such, a potential platform for engineering high-temperature superconductivity.¹⁰ This initially appears surprising given the weak influence of electron correlations expected for spatially extended $5d$ orbitals. Nonetheless, Sr_2IrO_4 and $\text{Sr}_3\text{Ir}_2\text{O}_7$, which both host partially filled $5d$ shells, are found to be insulating.^{11,12} For Sr_2IrO_4 , this was recently attributed^{1,2} to a reconstruction of the underlying electronic structure by a cooperative interplay of structural distortions and, crucially, the strong spin-orbit coupling, leaving a half-filled $J_{\text{eff}} = 1/2$ band that is sufficiently narrow that even moderate correlation strengths can drive a Mott transition. This $J_{\text{eff}} = 1/2$ space can be mapped onto a pseudospin-1/2 Hubbard model, providing the analogy to the cuprates.¹⁰ Microscopically, however, the similarity of the insulating ground states in these parent compounds remains an open question. The orbital configuration is $5d^5$ in $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ as compared to $3d^9$ in the cuprates. Spin-orbit interactions play an important role in the former,^{1,2,13–20} while the behavior of the latter is dominated by strong electron correlations. Even the range of validity of the strong spin-orbit $J_{\text{eff}} = 1/2$ Mott picture for the iridates, on which links to the cuprates have been based, remains an open question.^{21–25} As such, detailed studies of the low-energy electronic excitations of iridates are required to elucidate the nature of the complex many-body ground states of these compounds.

Indeed, kinetic, Coulomb, crystal-field, and spin-orbit energy scales are all of similar magnitude in the iridates, potentially leading to the close proximity of sev-

eral competing ground states. For example, optical conductivity measurements revealed a metal-insulator transition (MIT) upon increasing dimensionality through the layered Ruddlesden-Popper series $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$,³ with the conducting three-dimensional end member predicted to be an exotic semimetal.²⁶ The $n = 2$ compound, which crystallizes in an orthorhombic structure [space group $Bbca$ (Ref. 12)], is composed of Ir-O bilayers separated by Sr-O blocking layers. As for the single-layer compound Sr_2IrO_4 , the IrO_6 octahedra are slightly elongated along the c axis, and exhibit a large (staggered) in-plane rotation ($\sim 11^\circ$ in $\text{Sr}_3\text{Ir}_2\text{O}_7$). The bilayer structure is expected to result in an intermediate dimensionality and physical properties close to the border line between the insulating single-layer compound Sr_2IrO_4 and the (semi)metallic three-dimensional end member SrIrO_3 ,³ promising new insights into the nature of the MIT and the unconventional insulating ground states of iridates.

Here, we study its low-energy electronic structure by angle-resolved photoemission (ARPES). We find a small charge gap to a weakly dispersive band, reminiscent of a $J_{\text{eff}} = 1/2$ lower Hubbard band, although with other nearby dispersive bands that complicate this picture. The lowest-energy excitations show a non-quasiparticle-like Gaussian line shape and a strong temperature dependence of the line width. These spectral properties are notably similar to manganites²⁸ and lightly doped cuprates²⁷ and provide experimental evidence for a polaronic ground state in layered $5d$ iridates.

ARPES measurements were performed at the Surface and Interface Spectroscopy (SIS) beamline of the Swiss Light Source and beamline V-4 of the Stanford Synchrotron Radiation Lightsources, and using a laboratory He-lamp system. Measurements were made using photon energies between 16 and 120 eV and both Scienta R4000 and SPECS Phoibos

Electron Doping of the Parent Cuprate La_2CuO_4 without Cation Substitution

Haofei I. Wei,¹ Carolina Adamo,² Elizabeth A. Nowadnick,³ Edward B. Lochocki,¹ Shouvik Chatterjee,¹
Jacob P. Ruf,¹ Malcolm R. Beasley,² Darrell G. Schlom,^{4,5} and Kyle M. Shen^{1,5,*}

¹Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, USA

²Department of Applied Physics, Stanford University, Palo Alto, California 94306, USA

³School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, USA

⁴Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA

⁵Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA

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In the cuprates, carrier doping of the Mott insulating parent state is necessary to realize superconductivity as well as a number of other exotic states involving charge or spin density waves. Cation substitution is the primary method for doping carriers into these compounds, and is the only known method for electron doping in these materials. Here, we report electron doping *without* cation substitution in epitaxially stabilized thin films of La_2CuO_4 grown via molecular-beam epitaxy. We use angle-resolved photoemission spectroscopy to directly measure their electronic structure and conclusively determine that these compounds are electron doped with a carrier concentration of $0.09 \pm 0.02 e^-/\text{Cu}$. We propose that intrinsic defects, most likely oxygen vacancies, are the sources of doped electrons in these materials. Our results suggest a new approach to electron doping in the cuprates, one which could lead to a more detailed experimental understanding of their properties.

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In quantum many-body systems, exotic phenomena are typically realized through carrier doping. One example is in the cuprates, where high- T_c superconductivity arises via doping of a Mott insulating parent state [1]. Carrier doping in the cuprates, as in many other strongly correlated systems, is typically achieved through cation substitution, e.g. divalent Sr^{2+} cations for trivalent La^{3+} cations in p -type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [2] or tetravalent Ce^{4+} cations for trivalent cations in n -type $\text{R}_{2-x}\text{Ce}_x\text{CuO}_4$ ($R = \text{La}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}$) [3–5]. Cation substitution doping, however, introduces disorder at the dopant site which can reduce T_c [6,7] and prevent the use of disorder-sensitive techniques such as measurements of magnetic quantum oscillations in studying these compounds. In hole-doped cuprates, this limitation can be overcome by doping through control of oxygen stoichiometry rather than cation substitution, which can result in less disordered samples that allow the use of quantum oscillations to study compounds such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [8,9], $\text{YBa}_2\text{Cu}_4\text{O}_8$ [10,11], $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [12], and $\text{HgBa}_2\text{CuO}_{4+\delta}$ [13] to achieve a deeper understanding of the cuprate phase diagram. In the electron-doped cuprates, however, cation substitution remains the only reported pathway to carrier doping.

The necessity of doping in achieving superconductivity and the validity of the doped Mott insulator paradigm in the n -type cuprates has recently been called into question by work on epitaxial thin films of nominally undoped R_2CuO_4 ($R = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) synthesized in the so-called T' phase [14–16]. The authors have observed metallic and even superconducting behavior in the absence of cation doping, a scenario which may be consistent with dynamical

mean field theory (DMFT) studies showing that the parent T' compounds may be better described as weakly correlated Slater insulators rather than strongly correlated charge transfer insulators [17,18].

Here, we report electron doping without cation substitution in epitaxially stabilized thin films of La_2CuO_4 grown by reactive oxide molecular-beam epitaxy (MBE). We employ angle-resolved photoemission spectroscopy (ARPES) to measure the electronic structure and directly determine the carrier concentration of these thin films, confirming their electron doped nature. We also demonstrate that the carrier concentration can be controlled by compensating electron carriers with doped holes by substituting Sr^{2+} for La^{3+} , driving the system back into a Mott insulating state. We propose that intrinsic defects, most likely oxygen vacancies, are sources of the as-grown electron carriers. This work rules out the possibility of intrinsic metallic behavior in seemingly undoped thin films due to the collapse of the Mott gap in the T' structure.

Bulk La_2CuO_4 typically crystallizes in a body-centered tetragonal structure, also called the T phase, shown in Fig. 1(e). In this structure, the Cu atoms are sixfold coordinated with oxygen atoms—four in-plane and two in the out-of-plane apical positions. This T -phase compound is the parent of p -type cuprates such as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ [1] and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [2]. Via epitaxy, it is also possible to stabilize another polymorph of La_2CuO_4 in which the Cu atoms are only fourfold coordinated with in-plane oxygens, without any apical oxygens [15,19]. This structure, shown in Fig. 1(a), is also called the T' phase and

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Abstract

The grant FA9550-12-1-0335, "PECASE : Synthesis and Spectroscopy of Novel Superconducting Oxides & Heterostructures", was facilitated the synthesis and investigation of a variety of novel superconducting oxides (La_2CuO_4 , $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$, Sr_2RuO_4), as well as other superconductors with topological surface states ($[\text{Ti}_4](\text{Ti}_{1-x}\text{Sn}_x)\text{Te}_3$), and other oxides that are possible hosts for unconventional superconductivity ($\text{Sr}_{2-x}\text{La}_x\text{TiO}_4$ and various iridates). This grant resulted in a total of 9 publications, including 4 in Physical Review Letters, 1 in Nano Letters, and 2 in Physical Review B; the complete list of publications is at the end of this document.

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