**AFRL-AFOSR-VA-TR-2021-0077**

# Enhancing Superconductivity at Atomically Precise Interfaces

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The grant FA9550-15-1-0474, “Enhancing Superconductivity at Atomically Precise Interfaces”, facilitated the synthesis and investigation of a variety of novel interfacial superconducting materials and candidate superconducting systems, including FeSe / SrTiO3, highly strained RuO2, the cuprate analogue Sr2-xKxIrO4, enhanced surface superconductivity at the surface of Ba(Fe0.95Co0.05)2As2, epitaxially strained interfaces of the parent cuprate superconductor La2CuO4. This grant resulted in a total of 9 publications, including 4 in Nature Communications, 1 in Physical Review X, 1 in Physical Review Letters (in press), 1 in Physical Review Materials, 1 in Applied Physics Letters, and 1 in Physical Review B; the complete list of publications is at the end of this document.

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# Final Report Document for FA9550-15-1-0474

*Enhancing Superconductivity at Atomically Precise Interfaces*

## Narrative

The grant FA9550-15-1-0474, *"Enhancing Superconductivity at Atomically Precise Interfaces"*, facilitated the synthesis and investigation of a variety of novel interfacial superconducting materials and candidate superconducting systems, including FeSe / $SrTiO_3$, highly strained $RuO_2$, the cuprate analogue $Sr_{2-x}K_xIrO_4$, enhanced surface superconductivity at the surface of $Ba(Fe_{0.95}Co_{0.05})_2As_2$, epitaxially strained interfaces of the parent cuprate superconductor $La_2CuO_4$. This grant resulted in a total of 9 publications, including 4 in *Nature Communications*, 1 in *Physical Review X*, 1 in *Physical Review Letters* (in press), 1 in *Physical Review Materials*, 1 in *Applied Physics Letters*, and 1 in *Physical Review B*; the complete list of publications is at the end of this document.

A major thrust of our AFOSR-supported research efforts has been investigating the enhanced interfacial superconductivity in monolayer FeSe / $SrTiO_3$, where the superconducting $T_c$ is known to be enhanced from 8 K in bulk to over 30 K in a monolayer film on $SrTiO_3$. Interestingly, single-atom-thick layers of FeSe synthesized on $SrTiO_3$ have been found to exhibit spectroscopic signatures of superconductivity at much higher temperatures than bulk FeSe. A better understanding of the nature and origin of this enhanced superconducting state holds potential for opening up a new frontier for high-temperature superconductivity through engineering atomic interfaces. To achieve this, we employed, for the first time, a combination of angle-resolved

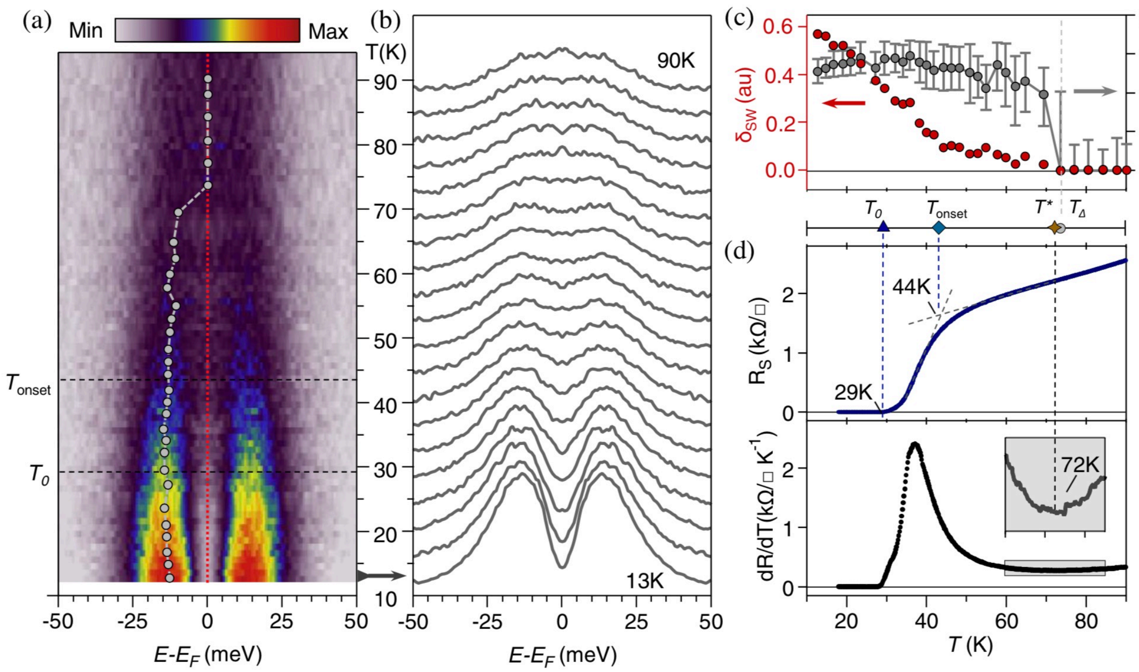


**Figure 1.** Comparison of temperature-dependent gap closing behavior and corresponding resistive superconducting transition. (a) Symmetrized EDCs taken at kF from over 100 individual spectra collected between 12 and 94 K. The color scale indicates the EDC intensity, with increasing temperature along the vertical axis. The gray circles track the quasiparticle peak position as a function of the temperature. (b) Selection of symmetrized EDCs from the data in (a). The temperature (vertical) axis is matched to that of (a). (c) Extracted energy gap Δ (right axis) as a function of the temperature from the data in (a). Δ is defined as half of the separation between the EDC peak positions indicated in (a). The red symbols (left axis) track the suppression spectral weight δSW at EF [dotted line in (a)] relative to 90 K. (d) Sheet resistance (blue line, top) and dR=dT (black line, bottom) as a function of the temperature measured in situ for the same sample presented in (a) and (b).

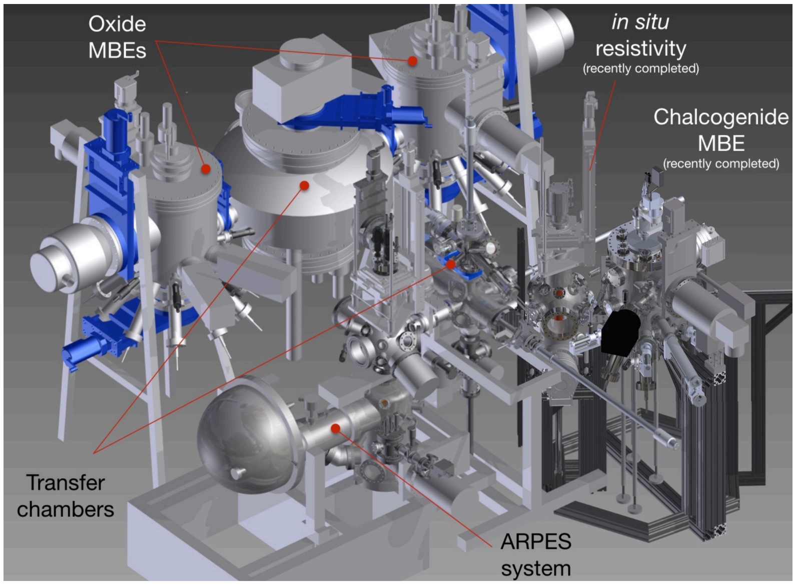


**Figure 2.** Combined *in situ* MBE, ARPES, and 4-point transport system developed from AFOSR supported used for experiments in Refs. 1, 2, and 4.

photoemission spectroscopy and *in situ* resistivity measurements to simultaneously probe both the electronic states and superconducting behavior of pristine monolayer FeSe / $SrTiO_3$, as reported in B.D. Faeth *et al., Physical Review X*, 2021[1]. While spectroscopic measurements indicate the initial formation of a superconducting gap at temperatures as high as 70 K, a true zero-resistance state is not achieved until below 30 K. We show that this discrepancy is due to an unprecedentedly large "pseudogap regime"—a suppression in the density of states extending above the superconducting critical temperature—not previously observed in iron-based superconductors, but arising here from the intrinsic 2D nature of the system, as shown in Figure 1. Our AFOSR-supported work not only clarifies many of the mysteries and apparent inconsistencies surrounding monolayer FeSe / $SrTiO_3$ but also provides insights into the important role of reduced dimensionality in driving the unique behavior of interfacial high-temperature superconductors. This work required the development of a first-of-its-kind combined MBE synthesis system, coupled to an ARPES system, as well as a chamber for performing *in situ* 4-point probe resistivity measurements in UHV (shown in Figure 2), developed with the support of this AFOSR grant, due to the fragility of the FeSe monolayer (which disintegrates upon exposure to air / moisture).

In addition to clarifying the nature of the superconductivity in monolayer FeSe / $SrTiO_3$, we have also been able to quantify the strength of the interfacial electron-phonon coupling between the interfacial $SrTiO_3$ phonons and the FeSe monolayer (B.D. Faeth et al., Physical Review Letters, 2021[2]). Angle-resolved photoemission spectroscopy (ARPES) has played a key role in elucidating the nature of many-body interactions in a multitude of quantum materials, including cuprates, manganites, titanates, ruthenates, and iridates, to name a few. More recently, the discovery of polaronic quasiparticles in quantum materials with low carrier densities by ARPES, through the observation of so-called "replica bands", has been of great interest. Nowhere has this been more evident than in monolayer FeSe / $SrTiO_3$, where the discovery of replica bands has spurred theoretical work suggesting that the coupling to interfacial $SrTiO_3$ phonons could account for the large enhancement of the superconducting $T_c$ in that system. On the other hand, recent work by Li and Sawatzky (*Phys. Rev. Lett.* **120**, 237001) called into question this interpretation, suggesting that the replica bands in FeSe / $SrTiO_3$ could also arise from extrinsic, photoelectron "final state" loss effects. This possibility is particularly concerning, since such effects could be generalized to many other systems, since the situations where polaronic quasiparticles should be observed (i.e. low carrier densities) would also be where such extrinsic loss effects would be most prevalent. This controversy remains unresolved and presents a true challenge to ARPES' role as the flagship probe of many-body interactions in quantum materials. In this work, also primarily supported by AFOSR, we were able to conclusively resolve this controversy by performing highly detailed ARPES studies of FeSe / $SrTiO_3$ where we vary the incident photon energy over a wide range, thereby directly testing and convincingly rule out the extrinsic photoelectron loss scenario, demonstrating that the presumed interfacial electron-phonon coupling is indeed intrinsic. Moreover, our quantitative studies allow us, for the first time, to directly and confidently extract the interfacial electron-phonon coupling constant, λ=0.19 +/ 0.02, as shown in Figure 3. Comparing this result to theory suggests that interfacial electron-phonon coupling should contribute to an enhancement of the superconducting $T_c$ in monolayer FeSe / $SrTiO_3$, although cannot account for the entire observed effect. This also suggests that the observation of polaronic quasiparticles by ARPES in the broader range of quantum materials is most likely intrinsic, and introduces a new methodology for 1) determining whether such replica bands are indeed intrinsic, and 2) if so, reliably and quantitatively extracting an intrinsic electron-phonon coupling constant λ.

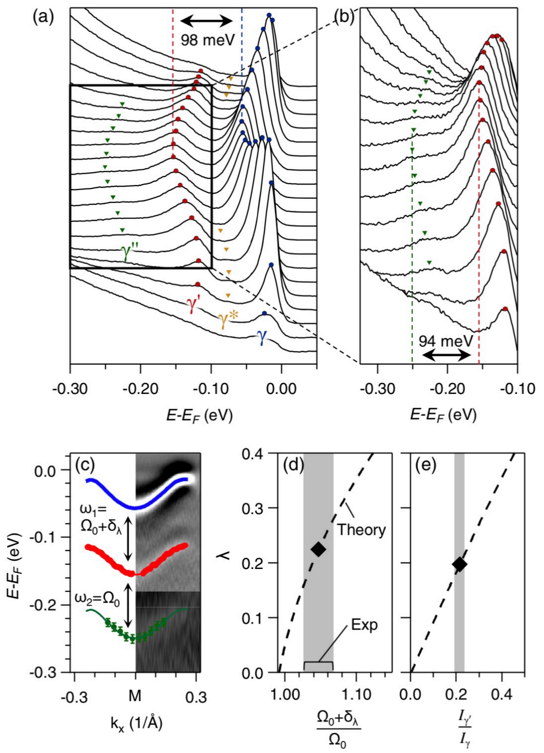


**Figure 3.** Observation of second-order replica bands in single-layer FeSe/SrTiO3. (a),(b) EDCs across the spectra at M shown F3:2 as a waterfall plot. Blue, red, yellow, and green markers track the main band (γ), 98 meV replica (γ'), and 60 meV replica (γ*), and 190 meV second order replica (γ''), respectively. (c) Band positions based on fits to the EDC peak positions. (d),(e) Determination of the electron-phonon coupling constant λ basedon the γ0 blueshift (d) and replica band intensity (e). Theoretical behavior based on work by Li, Devereaux, and Lee. Grey regions indicate the experimental uncertainty.

In addition to monolayer FeSe / $SrTiO_3$, our AFOSR-supported work also produced the **first-ever example of the transmutation of a normal metal into a superconductor through the application of strain** (J.P. Ruf *et al., Nature Communications* 2021[3]). Specifically, we demonstrated that superconductivity can be stabilized by imposing a huge biaxial strain upon $RuO_2$ using epitaxy. This approach of strain engineering, which exploits epitaxy, is static, disorder-free, allows for the use of sophisticated experimental probes, and enables integration with other materials in novel artificial interfaces and device structures. Until this work, strain had been used to modify properties of known superconductors—but never to transform a previously non-superconducting material into a superconductor. Through a synergistic combination of characterization techniques—including electrical transport, x-ray diffraction, scanning transmission electron microscopy, *in situ* angle-resolved photoemission spectroscopy, and density functional theory, as shown in Figure 4—we were also able to reveal the mechanism behind this strain-stabilized superconductivity: the large, anisotropic strains redistribute the electronic carriers amongst the different *4d* orbitals, enhancing the density of states near the Fermi level. This first example demonstrates how strain engineering of superconductivity can likely be broadly applied to transmute other non-superconducting materials into superconductors, for instance, other compounds with orbital degeneracies.

In addition to enhancement of superconductivity by interfacial engineering (FeSe / $SrTiO_3$) and strain ($RuO_2$), we have also used our in situ resistivity system supported through AFOSR funding to investigate enhanced superconductivity at the surface of cleaved bulk crystals. Utilizing *in situ* transport measurements, we showed that the superconducting critical temperature on the cleaved surface of single crystal $Ba(Fe_{0.95}Co_{0.05})_2As_2$ is enhanced by at least 4K above that over that of the bulk (C.T. Parzyck et al, *Applied Physics Letters*, 2020[4]). While samples measured in air show a single, sharp superconducting transition, those cleaved in ultra-high vacuum (UHV) exhibit a double resistive transition, with the higher temperature step appearing at 21K, as shown in Figure 5. This secondary transition is only observed on samples cleaved in UHV and vanishes as soon as the samples are exposed to air; furthermore, the secondary transition can be controllably suppressed by the deposition of sub-monolayer quantities of potassium atoms from an evaporative source. The observed sensitivity of this transition to both vacuum conditions and evaporated dopants emphasizes the localization of this effect to the top few layers of the crystal, however, determination of the precise structure, thickness, and doping of the effected region remains a challenge. These measurements underscore the care that must be taken when comparing surface and bulk sensitive probes of the superconducting state, as subtle structural changes or an altered chemical environment induced by the cleaving process can influence the low energy physics in unexpected ways.

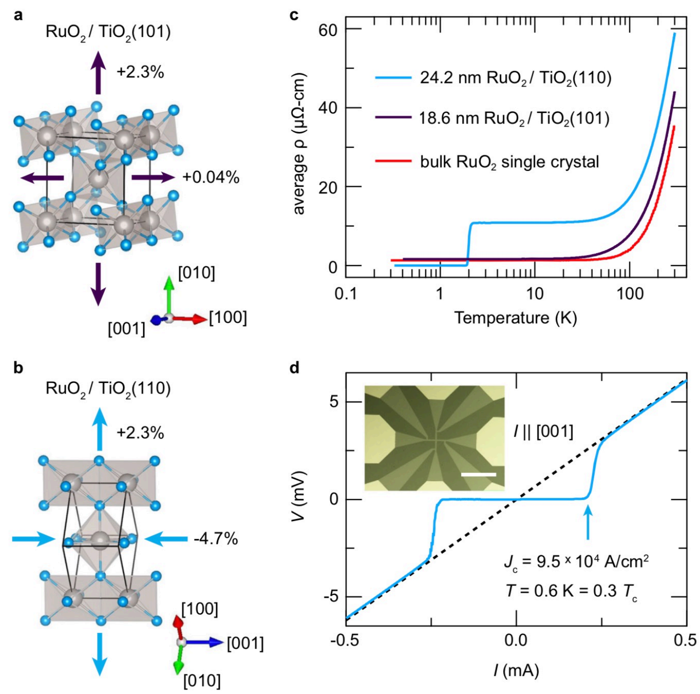


**Figure 4**. Electrical transport behavior of bulk $RuO_2$ single crystals and epitaxially strained $RuO_2$ thin films. (a), (b) Schematic diagrams of the crystal structures and in-plane lattice mismatches with $TiO_2$ substrates of $RuO_2$ thin films synthesized in (101)- and (110)-orientations. Gray and blue spheres represent Ru and O atoms, respectively. c Average resistivity versus temperature curves for 24.2 nm thick $RuO_2$ (110) and 18.6 nm thick $RuO_2$ (101) films, compared to results for bulk RuO2 single crystals. (d) V(I) curve measured at 0.6 K on a 10 μm-wide resistivity bridge lithographically patterned on the $RuO_2$(110) sample from (c) (as shown in the inset: scale bar = 200 μm), which has the direction of current flow parallel to $[001]_{rutile}$.

We have also used AFOSR funding to explore the possibility of superconductivity in the family of iridates, which is known to be a close analogue to the superconducting cuprates. Although we were not able to directly able to observe superconductivity in this system, we were able to modify the surface structure of these materials through potassium adsorption to cleanly introduce hole dopants for the first time (J.N. Nelson, *Nature Communications* 2020[5]). Layered iridates such as $Sr_2IrO_4$ have been the subject of recent intense interest due to the interplay between Coulomb

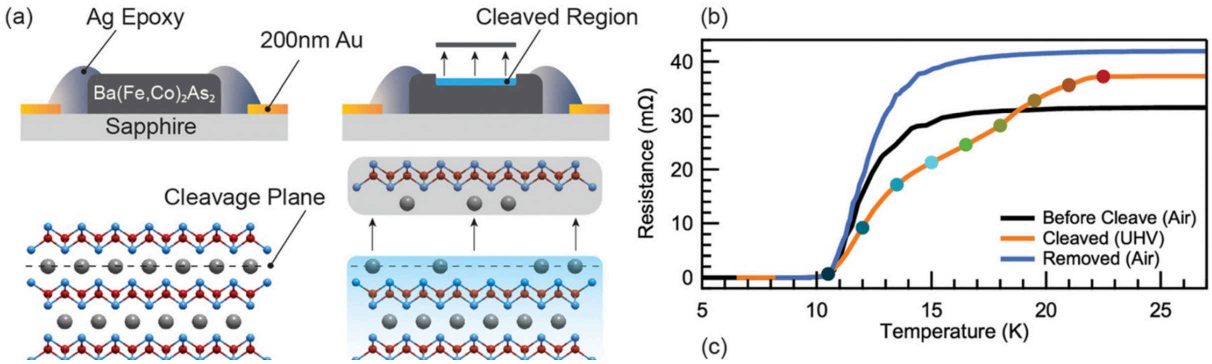


**Figure 5.** (a) Schematic of measurement. A four point corner contact geometry is used to eliminate wiring and contact resistances from the measurement. However, the cleaved surface (teal) is unavoidably measured in parallel, and in series, with the uncleaved regions of the sample. (b) Four point resistance of sample before cleaving, after cleaving, and after exposure of cleaved sample to air. A measurement current of 50 µA was used; at this value, no noticeable change in the bulk R(T) curve was observed with changing applied current.

interactions and large spin-orbit interactions, and their remarkable similarities to the parent high-$T_c$ cuprate superconductors. In particular, their evolution upon electron and hole doping has been a focus of activity, yet hole-doped iridates remain largely enigmatic, due to difficulties in effectively introducing mobile, hole-like carriers. In our AFOSR-supported work, we achieved the first ever investigation of intrinsically hole-doped $Sr_{2-x}K_xIrO_4$, which reveals that the Mott gap collapses upon hole doping, as shown in Figure 6. This remarkable discovery points towards a universal underlying electronic structure for both electron- and hole-doped iridates, in clear contrast to the cuprates which show a strong asymmetry between electron and hole doping. Furthermore, our findings also stand in contrast to earlier works on $Sr_2Ir_{1-x}Rh_xO_4$, suggesting that these earlier studies were strongly influenced by the extremely large disorder potential introduced by Rh substitution on the Ir site. This work was enabled through a synergistic combination of reactive oxide molecular beam epitaxy, substitutional diffusion of K for Sr to achieve hole doping, and *in situ* angle-resolved photoemission spectroscopy (ARPES). In particular, our novel substitutional diffusion approach allowed us to circumvent the extremely high vapor pressure of K-based compounds, thereby enabling the doping of holes into the $IrO_2$ planes in a clean manner to reveal the intrinsic behavior of the layered iridates upon hole doping for the first time.

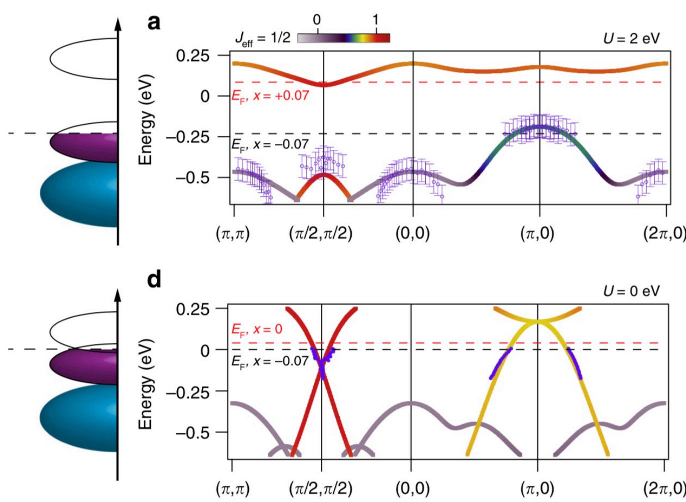


**Figure 6.** Tight-binding model compared with extracted band dispersions. a Tight-binding model of the band structure with an additional mean-field Coulomb repulsion term $U = 2$ eV illustrating the behaviour of undoped $Sr_2IrO_4$ with extracted experimental dispersions of undoped $Sr_2IrO_4$ shown (purple circles), together with a schematic density of state. Dashed black line indicates the chemical potential with x = 0.07 hole doping in a rigid band shift scenario similar to Rh-doped $Sr_2IrO_4$, dashed red line indicates chemical potential with x = 0.07 electron doping. d Tight-binding model with U = 0 eV, where the Mott gap has collapsed with extracted experimental dispersions of $Sr_{1.93}K_{0.07}IrO_4$ together with a schematic density of states.

In addition to these works, our AFOSR grant also provided support for investigations of strain-engineered cuprates[6], and the investigation of related ruthenates[7] and iridates[8,9] which are known to be adjacent to known and proposed unconventional superconductors ($Sr_2RuO_4$, and $Sr_2IrO_4$).

## Papers Published

1. B.D. Faeth, S.L. Yang, J.K. Kawasaki, J.N. Nelson, P. Mishra, C.T. Parzyck, C. Li, D.G. Schlom, and K.M. Shen. Incoherent Cooper Pairing and Pseudogap Behavior in Single-Layer FeSe/$SrTiO_3$. *Physical Review X* **11**, 021054 (2021). *DOI : 10.1103/PhysRevX.11.021054*

2. B.D. Faeth, S. Xie, S.L. Yang, J.K. Kawasaki, J.N. Nelson, S. Zhang, C.T. Parzyck, P. Mishra, C. Li, C. Jozwiak, A. Bostwick, E. Rotenberg, D.G. Schlom, and K.M. Shen. Interfacial Electron-Phonon Coupling Constants Extracted from Intrinsic Replica Bands in Monolayer FeSe/$SrTiO_3$. *Physical Review Letters* **127**, 016803 (2021). *DOI : 10.1103/PhysRevLett.127.016803*

3. J.P. Ruf, H. Paik, N.J. Schreiber, H.P. Nair, L. Miao, J.K. Kawasaki, J.N. Nelson, B.D. Faeth, Y. Lee, B.H. Goodge, B. Pamuk, C.J. Fennie, L.F. Kourkoutis, D.G. Schlom, and K.M. Shen. Strain-stabilized superconductivity. *Nature Communications* **12**, 59 (2021). *DOI : 10.1038/s41467-020-20252-7*

4. C.T. Parzyck, B.D. Faeth, G.N. Tam, G.R. Stewart, and K.M. Shen. Enhanced surface superconductivity in $Ba(Fe_{0.95}Co_{0.05})_2As_2$. *Applied Physics Letters* **116**, 062601 (2020). *DOI : 10.1063/1.5133647*

5. J.N. Nelson, C.T. Parzyck, B.D. Faeth, J.K. Kawasaki, D.G. Schlom, and K.M. Shen. Mott gap collapse in lightly hole-doped $Sr_{2-x}K_xIrO_4$. *Nature Communications* **11**, 2597 (2020). *DOI : 10.1038/s41467-020-16425-z*

6. O. Ivashko, M. Horio, W. Wan, N.B. Christensen, D.E. McNally, E. Paris, Y. Tseng, N.E. Shaik, H.M. Rønnow, H.I. Wei, C. Adamo, C. Lichtensteiger, M. Gibert, M.R. Beasley, K.M. Shen, J.M. Tomczak, T. Schmitt, and J. Chang. Strain-engineering Mott-insulating $La_2CuO_4$. *Nature Communications* **10**, 786 (2019). *DOI : 10.1038/s41467-019-08664-6*

7. L. Miao, N.J. Schreiber, H.P. Nair, B.H. Goodge, S. Jiang, J.P. Ruf, Y. Lee, M. Fu, B. Tsang, Y. Li, C. Zeledon, J. Shan, K.F. Mak, L.F. Kourkoutis, D.G. Schlom, and K.M. Shen. Strain relaxation induced transverse resistivity anomalies in $SrRuO_3$ thin films. *Physical Review B* **102**, 064406 (2020). *DOI : 10.1103/PhysRevB.102.064406*

8. L. Miao, Y. Lee, A.B. Mei, M.J. Lawler, and K.M. Shen. Two-dimensional magnetic monopole gas in an oxide heterostructure. *Nature Communications* **11**, 1341 (2020). *DOI : 10.1038/s41467-020-15213-z*

9. J.N. Nelson, J.P. Ruf, Y. Lee, C. Zeledon, J.K. Kawasaki, S. Moser, C. Jozwiak, E. Rotenberg, A. Bostwick, D.G. Schlom, K.M. Shen, and L. Moreschini. Dirac nodal lines protected against spin-orbit interaction in $IrO_2$. *Physical Review Materials* **3**, 064205 (2019). *DOI : 10.1103/PhysRevMaterials.3.064205*

## Invited Talks & Seminars

1. Electronic Materials & Applications 2021 (online) 01/2021
2. Los Alamos National Laboratory, Los Alamos NM 02/2020
3. 47th Conference on Physics and Chemistry of Surfaces and Interfaces (Boulder) 01/2020
4. University of Florida Physics Colloquium, Gainsville FL 10/2018
5. Moore Foundation EPiQS Symposium, Monterey CA 10/2018
6. Columbia University, Condensed Matter Seminar, New York, NY 9/2018
7. Low Energy Electrodynamics in Solids 2018, Portonovo Italy 6/2018
8. MIT Chez Pierre Condensed Matter Seminar, Cambridge MA 5/2018
9. Rutgers Laboratory for Surface Modification / IAMDN Seminar, Rutgers, NJ 2/2018
10. Physics Colloquium, Temple University, Philadelphia PA 11/2017
11. Condensed Matter Seminar, University of Michigan, Ann Arbor, MI 10/2017
12. International Workshop on Oxide Electronics 24, Chicago, IL 09/2017
13. ARPES & Topology, PARADIM Summer School, Johns Hopkins Univ. 07/2017
14. APS March Meeting Invited Speaker, New Orleans LA 3/2017
15. Brookhaven National Laboratory Seminar, Brookhaven NY 12/2016
16. Synchrotron Workshop for Thin Film Characterization & Growth, CHESS-U 6/2016
17. Condensed Matter Seminar, University of Illinois at Urbana Champaign 3/2016
18. Physics Colloquium, University of Washington, Seattle, WA 11/2015
19. MEMS Seminar, Yale University, New Haven, CT 9/2015

## Awards & Patents

- Prof. Shen appointed Director of the Laboratory of Atomic and Solid State Physics (LASSP) at Cornell (2021)
- Prof. Shen was named as the James A. Weeks Professor of Physical Sciences (endowed chair) at Cornell (2019)
- Prof. Shen named Stephen H. Weiss Presidential Fellow (highest teaching award at Cornell) (2019)
- Prof. Shen promoted to Full Professor of Physics at Cornell (2017)
- Jocienne Nelson (GRA supported by grant) named Director's Postdoctoral Fellow at NREL (2021)

## Personnel Supported

- Dr. Shuolong Yang (as a postdoctoral scholar). Worked on MBE growth and ARPES measurements for FeSe / $SrTiO_3$. Now an Assistant Professor in the School of Molecular Engineering at the University of Chicago.
- Dr. Jason Kawasaki (as a postdoctoral scholar). Worked on MBE synthesis and ARPES studies of potential superconducting iridates. Now an Assistant Professor in Materials Science & Engineering at the University of Wisconsin.
- Jocienne Nelson (as GRA; awarded Ph.D. in 2020). Worked on MBE synthesis and ARPES studies of potential superconducting iridates. Now a Director's Postdoctoral Fellow at the National Renewable Energy Laboratory (NREL).
- Brendan Faeth (as GRA; awarded Ph.D. in 2020). Worked on MBE growth and ARPES measurements for FeSe / $SrTiO_3$.Now a staff scientist at the Platform for the Accelerated

Realization, Analysis, and Discovery of Interface Materials (PARADIM), an NSF Materials Innovation Platform.

- Jacob Ruf (as GRA; awarded Ph.D. in 2019). Worked on ARPES and transport measurements of new superconductor $RuO_2$, and performed calculations on iridate and ruthenate materials. Now a postdoctoral scholar at the Max Planck Institute for the Chemical Physics of Solids, Dresden, Germany.

**Collaborations Enabled**

- Prof. Gregory Stewart, Department of Physics, University of Florida. Prof. Stewart synthesized the bulk crystals of $Ba(Fe_{0.95}Co_{0.05})_2As_2$ where we discovered enhanced surface superconductivity (C.T. Parzyck *et al., Applied Physics Letters* **116**, 062601).
- Prof. Johan Chang, University of Zurich. Prof. Chang performed resonant inelastic x-ray scattering measurements on samples of thin film superconductors synthesized through this grant (*Nature Comm.* **10**, 786).
- Prof. Malcolm Beasley, Stanford University. A collaboration with Prof. Beasley (also funded by AFOSR) enabled the experiments performed by Prof. Chang mentioned above (*Nature Comm.* **10**, 786).
- Dr. Eli Rotenberg, Advanced Light Source, Lawrence Berkeley National Laboratory. Two of the projects were conducted in collaboration with Dr. Rotenberg's team & beamline at the Advanced Light Source synchrotron at LBNL. (*Phys. Rev. Lett.* **127**, 016803; *Phys. Rev. Matr.* **3**, 064205)
- Prof. Lena Kourkoutis, Applied & Engineering Physics at Cornell. We collaborated with Prof. Kourkoutis on performing transmission electron microscopy (TEM) measurements of the thin film samples synthesized in this proposal (*Nature Comm.* **12**, 59; *Physical Review B* **102**, 064406).
- Prof. Darrell Schlom, Materials Science & Engineering at Cornell. The majority of experiments here involved a combination of molecular beam epitaxy and *in situ* ARPES. This is a long-standing collaboration between the PI and Prof. Schlom that has been enabled through AFOSR support.

**References**

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# Final Report Document for FA9550-15-1-0474

*Enhancing Superconductivity at Atomically Precise Interfaces*

The grant FA9550-15-1-0474, *"Enhancing Superconductivity at Atomically Precise Interfaces"*, facilitated the synthesis and investigation of a variety of novel interfacial superconducting materials and candidate superconducting systems, including FeSe / $SrTiO_3$, highly strained $RuO_2$, the cuprate analogue $Sr_{2-x}K_xIrO_4$, enhanced surface superconductivity at the surface of $Ba(Fe_{0.95}Co_{0.05})_2As_2$, epitaxially strained interfaces of the parent cuprate superconductor $La_2CuO_4$. This grant resulted in a total of 9 publications, including 4 in *Nature Communications*, 1 in *Physical Review X*, 1 in *Physical Review Letters* (in press), 1 in *Physical Review Materials*, 1 in *Applied Physics Letters*, and 1 in *Physical Review B*; the complete list of publications is at the end of this document.

A major thrust of our AFOSR-supported research efforts has been investigating the enhanced interfacial superconductivity in monolayer FeSe / $SrTiO_3$, where the superconducting $T_c$ is known to be enhanced from 8 K in bulk to over 30 K in a monolayer film on $SrTiO_3$. Interestingly, single-atom-thick layers of FeSe synthesized on $SrTiO_3$ have been found to exhibit spectroscopic signatures of superconductivity at much higher temperatures than bulk FeSe. A better understanding of the nature and origin of this enhanced superconducting state holds potential for opening up a new frontier for high-temperature superconductivity through engineering atomic interfaces. To achieve this, we employed, for the first time, a combination of angle-resolved

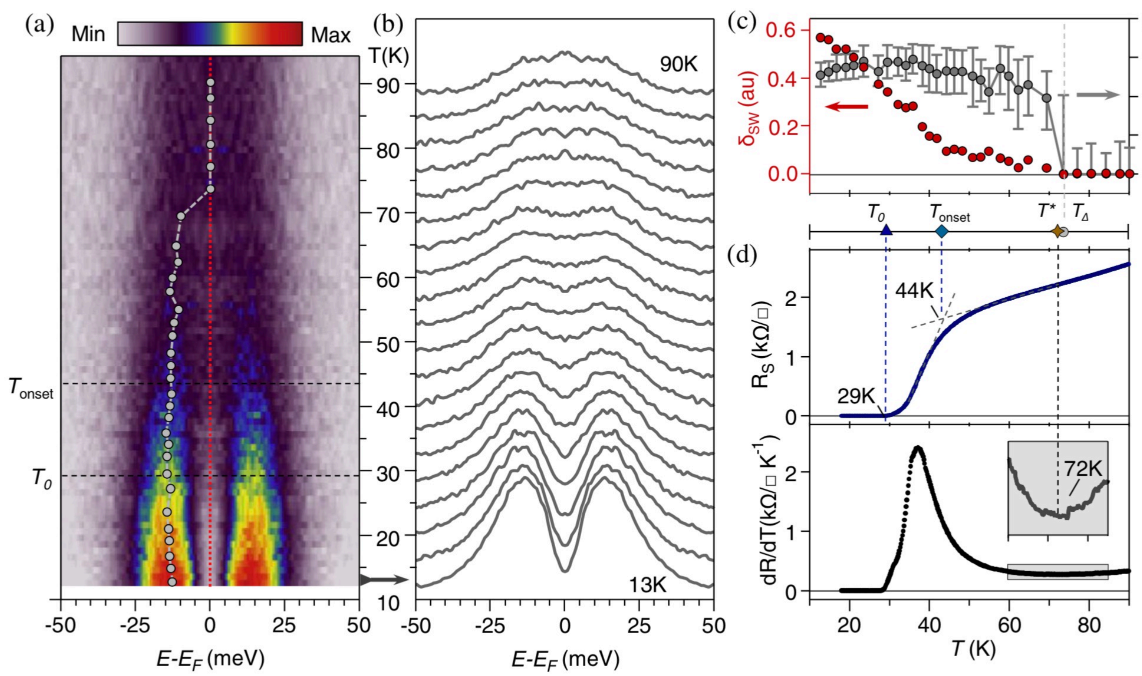


**Figure 1.** Comparison of temperature-dependent gap closing behavior and corresponding resistive superconducting transition. (a) Symmetrized EDCs taken at kF from over 100 individual spectra collected between 12 and 94 K. The color scale indicates the EDC intensity, with increasing temperature along the vertical axis. The gray circles track the quasiparticle peak position as a function of the temperature. (b) Selection of symmetrized EDCs from the data in (a). The temperature (vertical) axis is matched to that of (a). (c) Extracted energy gap Δ (right axis) as a function of the temperature from the data in (a). Δ is defined as half of the separation between the EDC peak positions indicated in (a). The red symbols (left axis) track the suppression spectral weight δSW at EF [dotted line in (a)] relative to 90 K. (d) Sheet resistance (blue line, top) and dR=dT (black line, bottom) as a function of the temperature measured in situ for the same sample presented in (a) and (b).

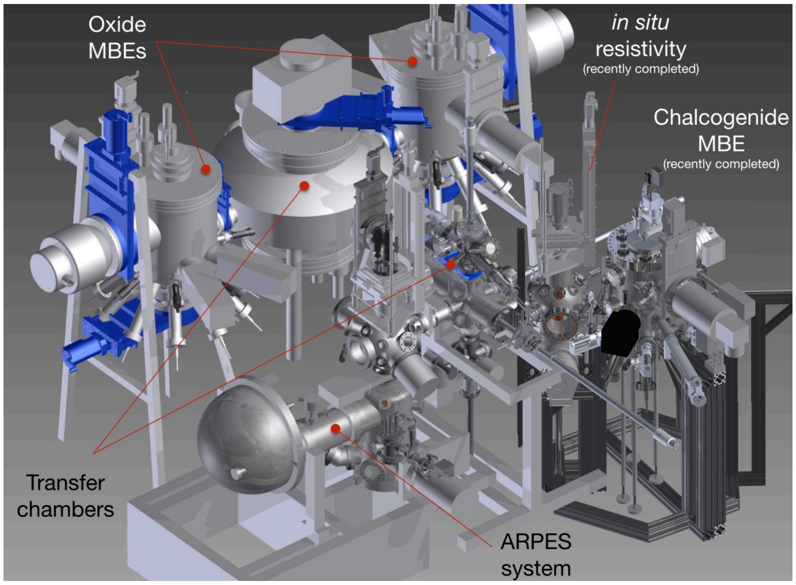


**Figure 2.** Combined *in situ* MBE, ARPES, and 4-point transport system developed from AFOSR supported used for experiments in Refs. 1, 2, and 4.

photoemission spectroscopy and *in situ* resistivity measurements to simultaneously probe both the electronic states and superconducting behavior of pristine monolayer FeSe / $SrTiO_3$, as reported in B.D. Faeth *et al., Physical Review X*, 2021[1]. While spectroscopic measurements indicate the initial formation of a superconducting gap at temperatures as high as 70 K, a true zero-resistance state is not achieved until below 30 K. We show that this discrepancy is due to an unprecedentedly large "pseudogap regime"—a suppression in the density of states extending above the superconducting critical temperature—not previously observed in iron-based superconductors, but arising here from the intrinsic 2D nature of the system, as shown in Figure 1. Our AFOSR-supported work not only clarifies many of the mysteries and apparent inconsistencies surrounding monolayer FeSe / $SrTiO_3$ but also provides insights into the important role of reduced dimensionality in driving the unique behavior of interfacial high-temperature superconductors. This work required the development of a first-of-its-kind combined MBE synthesis system, coupled to an ARPES system, as well as a chamber for performing *in situ* 4-point probe resistivity measurements in UHV (shown in Figure 2), developed with the support of this AFOSR grant, due to the fragility of the FeSe monolayer (which disintegrates upon exposure to air / moisture).

In addition to clarifying the nature of the superconductivity in monolayer FeSe / $SrTiO_3$, we have also been able to quantify the strength of the interfacial electron-phonon coupling between the interfacial $SrTiO_3$ phonons and the FeSe monolayer (B.D. Faeth et al., Physical Review Letters, 2021[2]). Angle-resolved photoemission spectroscopy (ARPES) has played a key role in elucidating the nature of many-body interactions in a multitude of quantum materials, including cuprates, manganites, titanates, ruthenates, and iridates, to name a few. More recently, the discovery of polaronic quasiparticles in quantum materials with low carrier densities by ARPES, through the observation of so-called "replica bands", has been of great interest. Nowhere has this been more evident than in monolayer FeSe / $SrTiO_3$, where the discovery of replica bands has spurred theoretical work suggesting that the coupling to interfacial $SrTiO_3$ phonons could account for the large enhancement of the superconducting $T_c$ in that system. On the other hand, recent work by Li and Sawatzky (*Phys. Rev. Lett.* **120**, 237001) called into question this interpretation, suggesting that the replica bands in FeSe / $SrTiO_3$ could also arise from extrinsic, photoelectron "final state" loss effects. This possibility is particularly concerning, since such effects could be generalized to many other systems, since the situations where polaronic quasiparticles should be observed (i.e. low carrier densities) would also be where such extrinsic loss effects would be most prevalent. This controversy remains unresolved and presents a true challenge to ARPES' role as the flagship

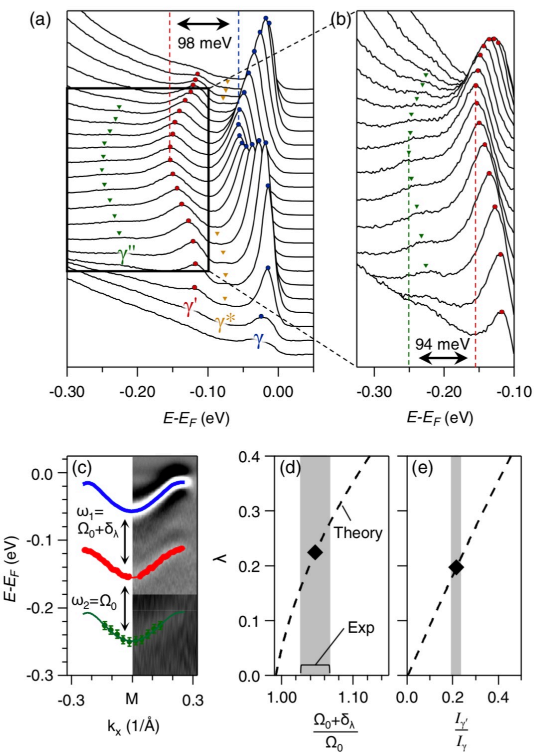


**Figure 3.** Observation of second-order replica bands in single-layer FeSe/SrTiO3. (a),(b) EDCs across the spectra at M shown F3:2 as a waterfall plot. Blue, red, yellow, and green markers track the main band (γ), 98 meV replica (γ'), and 60 meV replica (γ*), and 190 meV second order replica (γ''), respectively. (c) Band positions based on fits to the EDC peak positions. (d),(e) Determination of the electron-phonon coupling constant λ basedon the γ0 blueshift (d) and replica band intensity (e). Theoretical behavior based on work by Li, Devereaux, and Lee. Grey regions indicate the experimental uncertainty.

probe of many-body interactions in quantum materials. In this work, also primarily supported by AFOSR, we were able to conclusively resolve this controversy by performing highly detailed ARPES studies of FeSe / $SrTiO_3$ where we vary the incident photon energy over a wide range, thereby directly testing and convincingly rule out the extrinsic photoelectron loss scenario, demonstrating that the presumed interfacial electron-phonon coupling is indeed intrinsic. Moreover, our quantitative studies allow us, for the first time, to directly and confidently extract the interfacial electron-phonon coupling constant, λ=0.19 +/ 0.02, as shown in Figure 3. Comparing this result to theory suggests that interfacial electron-phonon coupling should contribute to an enhancement of the superconducting $T_c$ in monolayer FeSe / $SrTiO_3$, although cannot account for the entire observed effect. This also suggests that the observation of polaronic quasiparticles by ARPES in the broader range of quantum materials is most likely intrinsic, and introduces a new methodology for 1) determining whether such replica bands are indeed intrinsic, and 2) if so, reliably and quantitatively extracting an intrinsic electron-phonon coupling constant λ.

In addition to monolayer FeSe / $SrTiO_3$, our AFOSR-supported work also produced the **first-ever example of the transmutation of a normal metal into a superconductor through the application of strain** (J.P. Ruf *et al., Nature Communications* 2021[3]). Specifically, we demonstrated that superconductivity can be stabilized by imposing a huge biaxial strain upon $RuO_2$ using epitaxy. This approach of strain engineering, which exploits epitaxy, is static, disorder-free, allows for the use of sophisticated experimental probes, and enables integration with other materials in novel artificial interfaces and device structures. Until this work, strain had been used to modify properties of known superconductors—but never to transform a previously non-superconducting material into a superconductor. Through a synergistic combination of characterization techniques—including electrical transport, x-ray diffraction, scanning transmission electron microscopy, *in situ* angle-resolved photoemission spectroscopy, and density functional theory, as shown in Figure 4—we were also able to reveal the mechanism behind this strain-stabilized superconductivity: the large, anisotropic strains redistribute the electronic carriers amongst the different *4d* orbitals, enhancing the density of states near the Fermi level. This first example demonstrates how strain engineering of superconductivity can likely be broadly applied to transmute other non-superconducting materials into superconductors, for instance, other compounds with orbital degeneracies.

In addition to enhancement of superconductivity by interfacial engineering (FeSe / $SrTiO_3$) and strain ($RuO_2$), we have also used our in situ resistivity system supported through AFOSR funding to investigate enhanced superconductivity at the surface of cleaved bulk crystals. Utilizing *in situ* transport measurements, we showed that the superconducting critical temperature on the cleaved surface of single crystal $Ba(Fe_{0.95}Co_{0.05})_2As_2$ is enhanced by at least 4K above that over that of the bulk (C.T. Parzyck et al, *Applied Physics Letters*, 2020[4]). While samples measured in air show a single, sharp superconducting transition, those cleaved in ultra-high vacuum (UHV) exhibit a double resistive transition, with the higher temperature step appearing at 21K, as shown in Figure 5. This secondary transition is only observed on samples cleaved in UHV and vanishes as soon as the samples are exposed to air; furthermore, the secondary transition can be controllably suppressed by the deposition of sub-monolayer quantities of potassium atoms from an evaporative source. The observed sensitivity of this transition to both vacuum conditions and evaporated dopants emphasizes the localization of this effect to the top few layers of the crystal, however, determination of the precise structure, thickness, and doping of the effected region remains a challenge. These measurements underscore the care that must be taken when comparing surface and bulk sensitive probes of the superconducting state, as subtle structural changes or an altered chemical environment induced by the cleaving process can influence the low energy physics in unexpected ways.

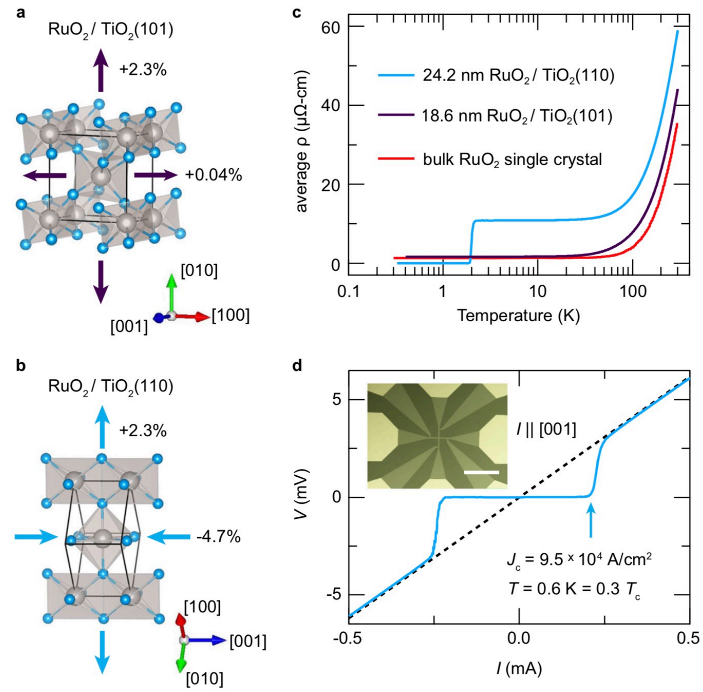


**Figure 4**. Electrical transport behavior of bulk $RuO_2$ single crystals and epitaxially strained $RuO_2$ thin films. (a), (b) Schematic diagrams of the crystal structures and in-plane lattice mismatches with $TiO_2$ substrates of $RuO_2$ thin films synthesized in (101)- and (110)-orientations. Gray and blue spheres represent Ru and O atoms, respectively. c Average resistivity versus temperature curves for 24.2 nm thick $RuO_2$ (110) and 18.6 nm thick $RuO_2$ (101) films, compared to results for bulk RuO2 single crystals. (d) V(I) curve measured at 0.6 K on a 10 μm-wide resistivity bridge lithographically patterned on the $RuO_2$(110) sample from (c) (as shown in the inset: scale bar = 200 μm), which has the direction of current flow parallel to $[001]_{rutile}$.

We have also used AFOSR funding to explore the possibility of superconductivity in the family of iridates, which is known to be a close analogue to the superconducting cuprates. Although we were not able to directly able to observe superconductivity in this system, we were able to modify the surface structure of these materials through potassium adsorption to cleanly introduce hole dopants for the first time (J.N. Nelson, *Nature Communications* 2020[5]). Layered iridates such as $Sr_2IrO_4$ have been the subject of recent intense interest due to the interplay between Coulomb

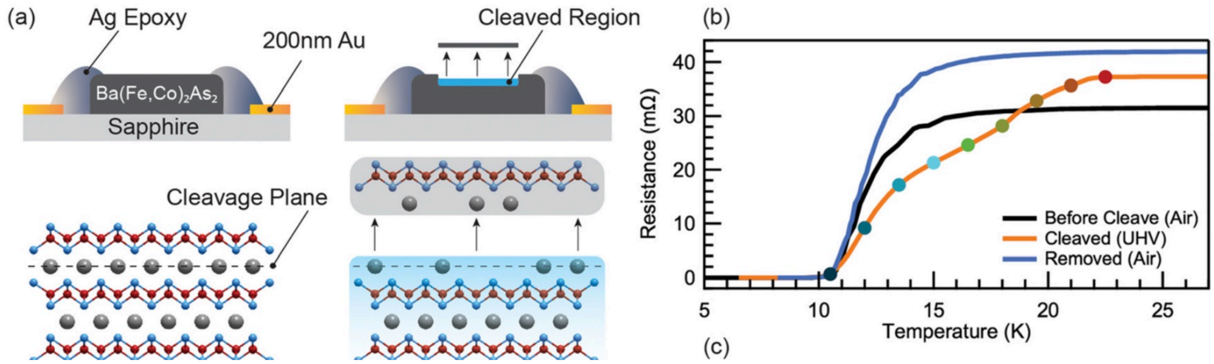


**Figure 5.** (a) Schematic of measurement. A four point corner contact geometry is used to eliminate wiring and contact resistances from the measurement. However, the cleaved surface (teal) is unavoidably measured in parallel, and in series, with the uncleaved regions of the sample. (b) Four point resistance of sample before cleaving, after cleaving, and after exposure of cleaved sample to air. A measurement current of 50 μA was used; at this value, no noticeable change in the bulk R(T) curve was observed with changing applied current.

interactions and large spin-orbit interactions, and their remarkable similarities to the parent high-$T_c$ cuprate superconductors. In particular, their evolution upon electron and hole doping has been a focus of activity, yet hole-doped iridates remain largely enigmatic, due to difficulties in effectively introducing mobile, hole-like carriers. In our AFOSR-supported work, we achieved the first ever investigation of intrinsically hole-doped $Sr_{2-x}K_xIrO_4$, which reveals that the Mott gap collapses upon hole doping, as shown in Figure 6. This remarkable discovery points towards a universal underlying electronic structure for both electron- and hole-doped iridates, in clear contrast to the cuprates which show a strong asymmetry between electron and hole doping. Furthermore, our findings also stand in contrast to earlier works on $Sr_2Ir_{1-x}Rh_xO_4$, suggesting that these earlier studies were strongly influenced by the extremely large disorder potential introduced by Rh substitution on the Ir site. This work was enabled through a synergistic combination of reactive oxide molecular beam epitaxy, substitutional diffusion of K for Sr to achieve hole doping, and *in situ* angle-resolved photoemission spectroscopy (ARPES). In particular, our novel substitutional diffusion approach allowed us to circumvent the extremely high vapor pressure of K-based compounds, thereby enabling the doping of holes into the $IrO_2$ planes in a clean manner to reveal the intrinsic behavior of the layered iridates upon hole doping for the first time.

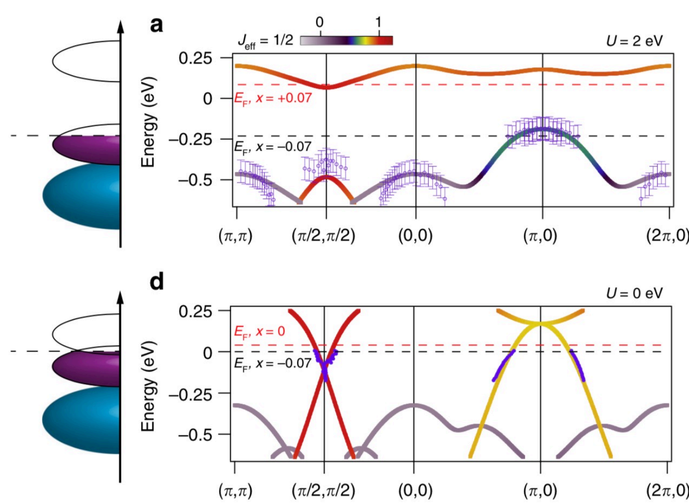


**Figure 6.** Tight-binding model compared with extracted band dispersions. a Tight-binding model of the band structure with an additional mean-field Coulomb repulsion term $U = 2$ eV illustrating the behaviour of undoped $Sr_2IrO_4$ with extracted experimental dispersions of undoped $Sr_2IrO_4$ shown (purple circles), together with a schematic density of state. Dashed black line indicates the chemical potential with x = 0.07 hole doping in a rigid band shift scenario similar to Rh-doped $Sr_2IrO_4$, dashed red line indicates chemical potential with x = 0.07 electron doping. d Tight-binding model with U = 0 eV, where the Mott gap has collapsed with extracted experimental dispersions of $Sr_{1.93}K_{0.07}IrO_4$ together with a schematic density of states.

In addition to these works, our AFOSR grant also provided support for investigations of strain-engineered cuprates[6], and the investigation of related ruthenates[7] and iridates[8,9] which are known to be adjacent to known and proposed unconventional superconductors ($Sr_2RuO_4$, and $Sr_2IrO_4$).

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