

# SSRL 50 Years – VUV and Soft X-ray Materials Science

April 20, 2023

Zhi-xun Shen

Stanford Institute for Materials and Energy Sciences

Stanford University and SLAC National Accelerator Laboratory

Stanford  
University



U.S. DEPARTMENT OF  
**ENERGY**

Acknowledgement – Piero Pianetta, Ingolf Lindau, Donghui Lu, and Makoto Hashimoto

# Outline



- Pioneering days
- Case Study – Angle-resolved photoemission from quantum materials
- Building an ecosystem – bridging other activities at SLAC and Stanford
- Some reflections



# Historical Context—Motivation

- State of the art high energy physics storage ring, SPEAR, began operation at SLAC in 1972
- Would be used to study uncharted territory in particle physics and ultimately discovered quarks and lepton
- Could this source of high intensity x-rays be used to do something novel for materials/chemistry/biology?
- Demonstration experiment showing that an x-ray beam could be extracted from SPEAR and some useful science could be performed



# Pioneering Days

DATE: 18 June 1968

TO : Prof. W. Panofsky ✓  
Dr. E. Garwin

FROM : Prof. W. E. Spicer

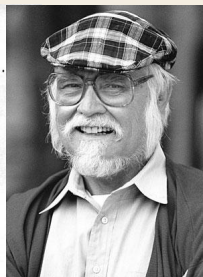
SUBJECT: Use of Cyclotron Radiation from Storage Ring for Solid State Studies

My purpose in writing this is to ascertain whether or not there might be any long-term interest in using the cyclotron radiation from the SLAC storage ring for solid state studies. The possibility of using the radiation is beginning to open up new fields for solid state physics and chemistry. If SLAC does obtain a new storage ring, it would seem a pity not to explore any long-range possibilities for the use of the cyclotron radiation for solid state studies. I would be glad to discuss this with you if there appears to be any interest on the part of SLAC.

I thought it worthwhile to mention this to you at this time since we will have a visit from Dr. Stig Hagstrom, who has been very active in the Swedish work on ESCA (electron spectroscopy for chemistry analysis) in which X-rays are used to photo-inject electrons whose energy spectra are subsequently measured. (Professor Kai Seigbahn, who is perhaps the senior member of the group which has developed this technique, will give an Interdisciplinary Colloquium on this subject on August 8.) Doctor Hagstrom has pointed out the great advantages in this as well as other work which could be made through the use of cyclotron radiation. Since he will be interested in a one or two year visiting position in this country within the next few years, you might be interested in meeting him if SLAC has any long-range interests in using the cyclotron radiation for solid state studies. Doctor Hagstrom will be visiting in this vicinity July 2-8, and I will be glad to set up a meeting with him if this would be of interest to you.

WES:bjmc  
Attachment

*W. Spicer*



Spicer's 1968 letter to Panofsky

ROUGH DRAFT 3-13-72

PROPOSAL  
TO  
SLAC LAB-OPERATIONS COMMITTEE  
TO CONDUCT  
PRELIMINARY EXPERIMENTS ON THE SPEAR  
BY THE SYNCHROTRON RADIATION PORT

for the period  
~~April 1~~, 1972 - December 31, 1972  
*July 1*

S. Doniach  
W. Spicer  
A. Bienenstock  
G. Brogren (visiting scientist)  
Wm. Marshall Jr.  
Mark Rosenberg

Proposal led by Doniach,  
Spicer and Bienenstock (1972)



Doniach  
Bienenstock  
Winick



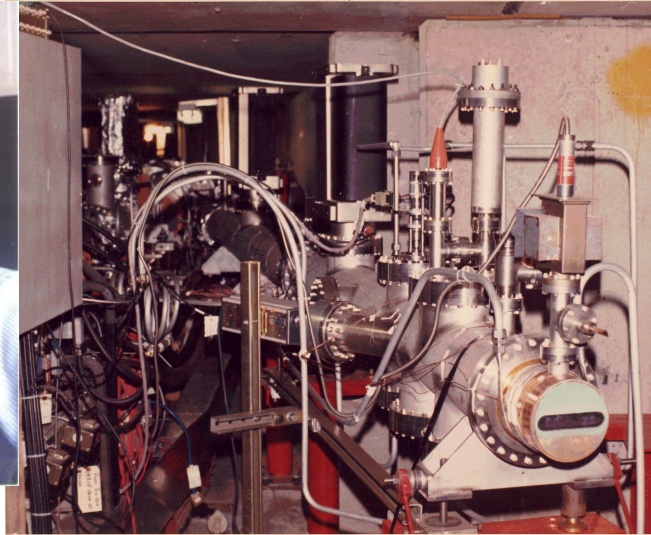
Spicer and Lindau



# Pioneering Days - Seeing the Light, 1973



Ingolf and Piero

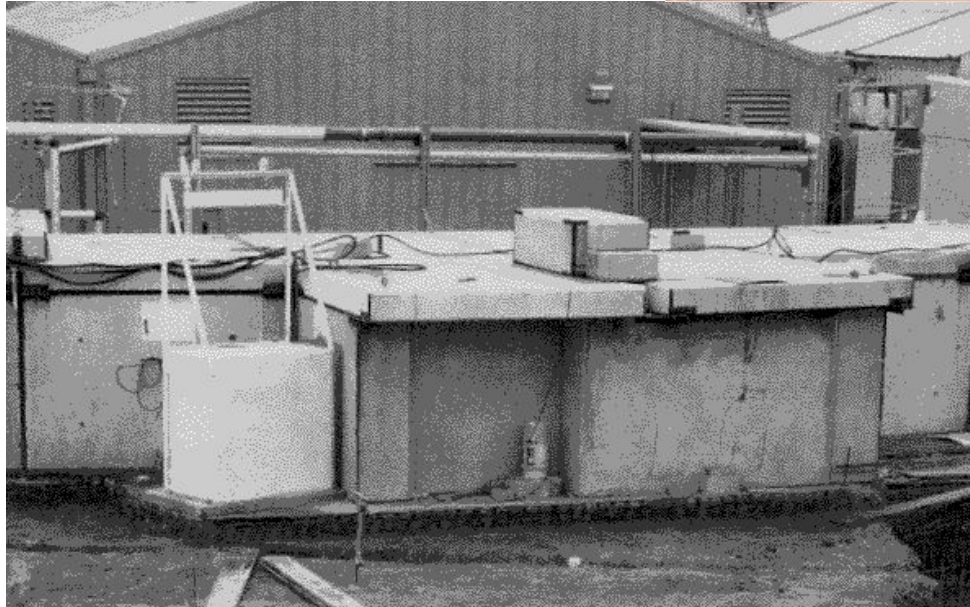


7/6/73



7-6-73

TV-camera on Be-fil  
(control room)



First attempt to get out sync. light;

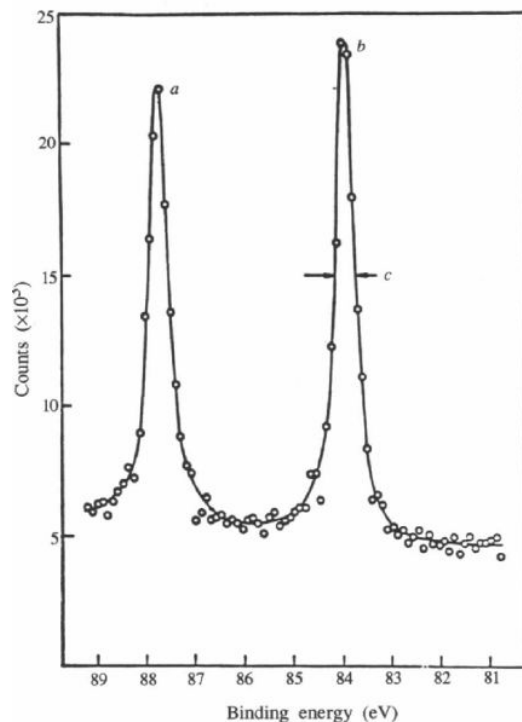
10.42 a.m. open vertical mask  $\begin{cases} 1.5 \text{ GeV} \\ 22.5 \text{ mA} \end{cases}$

Light on the Be-fil (first noticeable at  
5.45 V on the  
vertical mask position)

The picture shows the vertical mask completely  
open, and the sync. light is there - right  
in the middle of the Be-fil

# First Public Reports, 1974

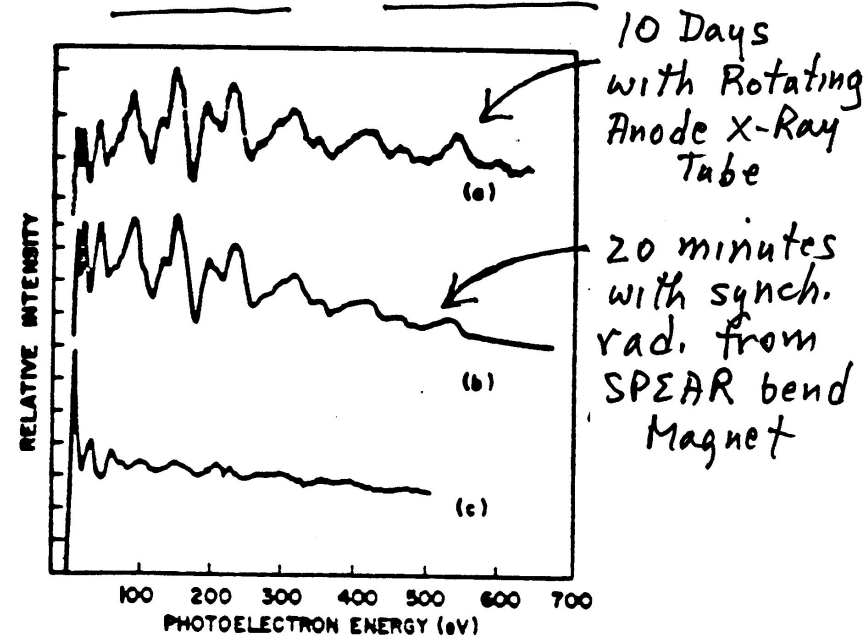
Photoemission from Au 4f



"X-ray Photoemission with Use of Synchrotron Radiation," I. Lindau, P. Pianetta, S. Doniach and W. E. Spicer, SSRP, Stanford University, Proc. IV International Conf. on Vac. Ultraviolet Rad. Phys., Hamburg, July 22-26, 1974, p. 805. (Invited Paper)

Lindau, Pianetta, Doniach, Spicer, Nature 250, 214 (1974)

1974 EXAFS



"EXAFS Measurements at SPEAR," P. Eisenberger, Bell Laboratories, B. Kincaid, S. Hunter, Stanford University, D. Sayers, E. A. Stern, University of Washington, and F. Lytle of Boeing Aerospace Co., Proc. IV International Conf. on Ultraviolet Rad. Phys., Hamburg, July 22-26, 1974, p. 806.

Eisenberger, Kincaid, Hunter, Sayers, Stern, and Lytle (1974)



# “Those were such happy times – and not so long ago”

## Some VUV and Soft X-ray Experimenters

Dave



Ingolf



Joe

Ingolf

Shozo

Zahid

Chuck

Piero





## Determination of the Oxygen Binding Site on GaAs(110) Using Soft-X-Ray-Photoemission Spectroscopy\*

P. Pianetta, I. Lindau, C. Garner, and W. E. Spicer  
*Stanford Electronics Laboratories and Stanford Synchrotron Radiation Project,  
Stanford University, Stanford, California 94305*  
(Received 25 August 1975)

The first steps in the oxidation of GaAs(110) are examined through shifts in the As and Ga 3d levels as a function of oxygen exposure. We observe a large chemical shift in the As 3d levels (about 4 eV) while the Ga 3d levels were shifted by less than 1 eV. This gives direct evidence for oxygen bonding to arsenic at the GaAs(110) surface, and illustrates the change in chemical character which can take place in atoms at the surfaces of compounds.

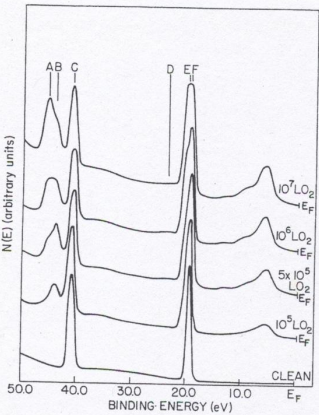


FIG. 1. Photoemission spectra of clean and oxidized GaAs(110) for 100-eV photon energy.

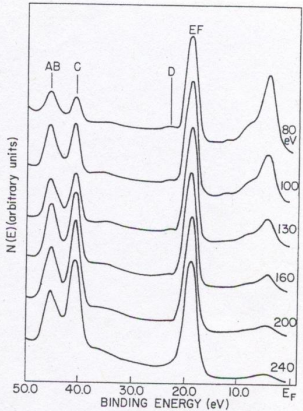


FIG. 2. Photoemission spectra of heavily oxidized ( $10^7$  L) GaAs(110) as a function of photon energy.

## Angle-resolved photoemission from valence bands of Cu and Au single crystals using 32–200-eV synchrotron radiation\*

J. Stöhr, G. Apai, P. S. Wehner, F. R. McFeely, R. S. Williams, and D. A. Shirley  
*Materials and Molecular Research Division, Lawrence Berkeley Laboratory  
and Department of Chemistry, University of California, Berkeley, California 94720*  
(Received 14 June 1976)

The directional anisotropy in photoemission from valence bands of Cu and Au single crystals has been studied in the photon energy ranges  $32 \leq h\nu \leq 200$  eV, and  $32 \leq h\nu \leq 130$  eV, respectively. Angle-resolved photoemission energy distributions were obtained for electrons emitted in the [001] and [111] directions. Dramatic differences were found between the two directions and strong variations with energy were obtained over the entire energy range. The results are discussed in terms of final-state band-structure effects and/or strong inelastic damping in the final state. For Cu, spectra taken at  $h\nu = 90$  eV along the same symmetry directions at high ( $90^\circ$ ) and low ( $35^\circ$ ) take-off angles from the surface show a pronounced narrowing of the *d* band at low take-off angles. This is attributed to a preferential sampling of the local density of states at the surface by using an appropriate photon energy and take-off angle. The energy dependence of the Au 5*d* intensity has been measured and is found to decrease by a factor of  $\sim 50$  over the investigated photon energy range 40–190 eV.

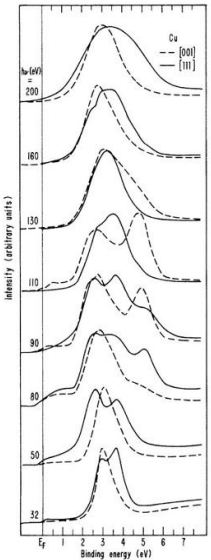


FIG. 4. Comparison of photoemission spectra taken along the Cu [001] and [111] directions (dashed and solid lines, respectively) for various photon energies. The experimental geometry was the same as for Fig. 3.

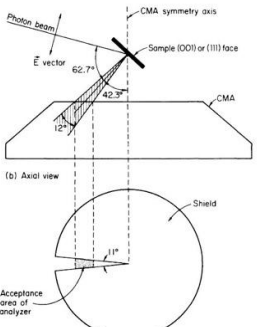


FIG. 1. Experimental geometry for angle resolved photoemission studies of Cu and Au single crystals. A cylindrical-mirror analyzer (CMA) is modified by means of a slit aperture (shield) to allow angle resolved measurements. The effective angular resolution is  $\pm 6^\circ$  in the horizontal and  $\sim 4^\circ$  in the vertical plane.

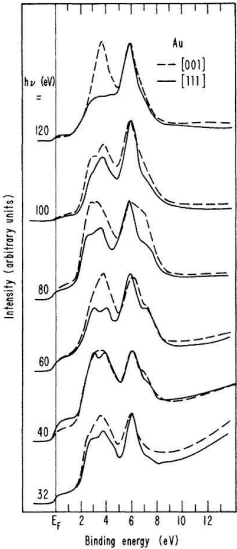
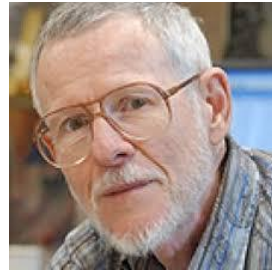
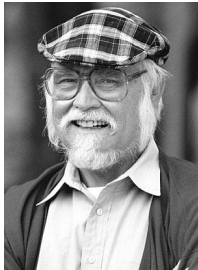


FIG. 8. Comparison of photoemission energy distributions along the [001] and [111] direction of Au (dashed and solid lines) in the range  $32 \leq h\nu \leq 120$  eV. The spectra were taken from Fig. 7.



# Photoemission Study of Correlated Materials



Jim Allen

## Anderson Hamiltonian description of the experimental electronic structure and magnetic interactions of copper oxide superconductors

Zhi-xun Shen

*Stanford Electronics Laboratory, Stanford University, Stanford, California 94305  
and Department of Applied Physics, Stanford University, Stanford, California 94305*

J. W. Allen\*

*Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304*

J. J. Yeh

*Stanford Electronics Laboratory, Stanford University, Stanford, California 94305*

J.-S. Kang\*

*Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304  
and Department of Physics and Institute for Pure and Applied Physical Sciences,  
University of California at San Diego, La Jolla, California 92093*

W. Ellis

*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

W. Spicer and I. Lindau

*Stanford Electronics Laboratory, Stanford University, Stanford, California 94305*

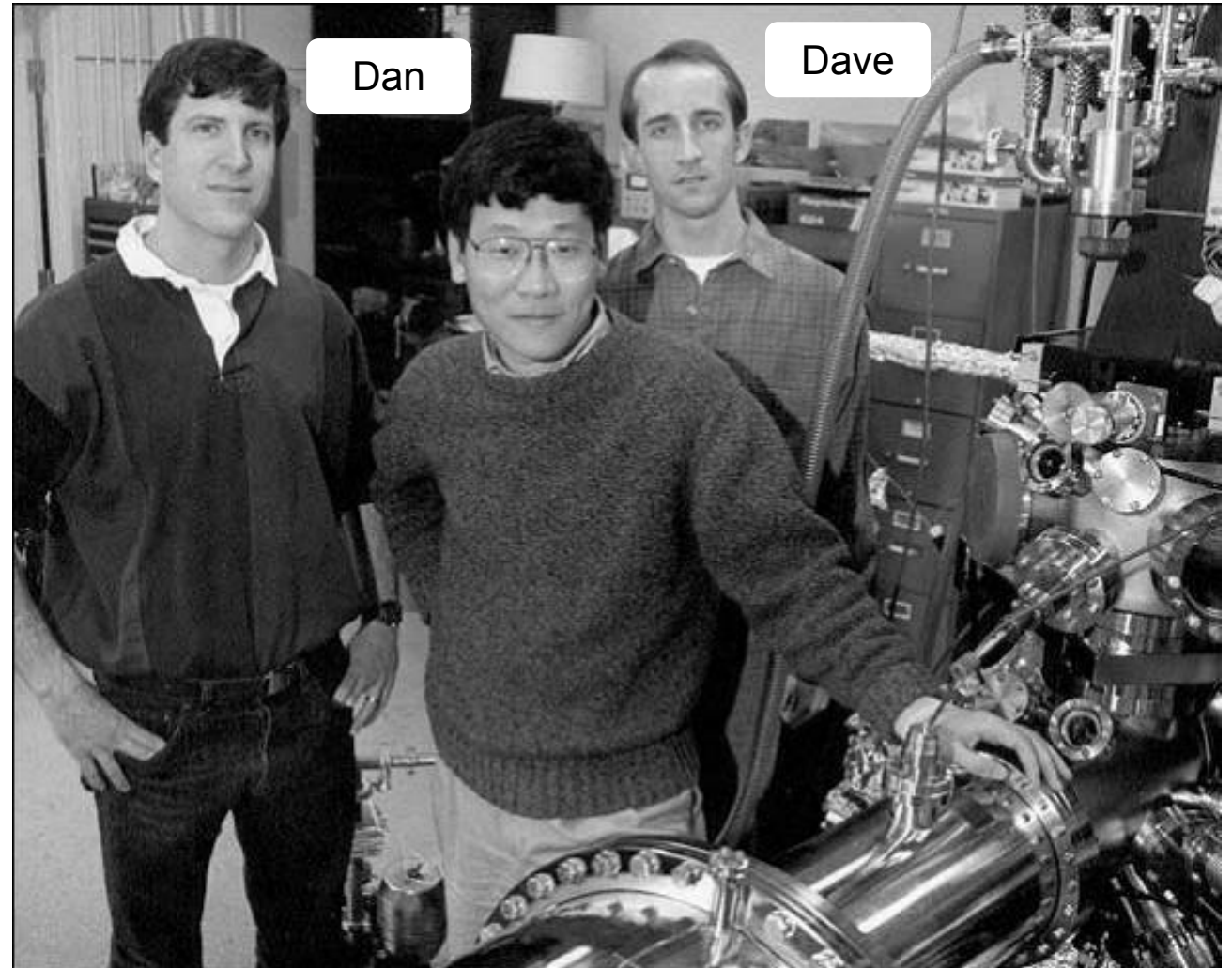
M. B. Maple, Y. D. Dalichaouch, and M. S. Torikachvili

*Department of Physics and Institute for Pure and Applied Physical Sciences, University of California at San Diego,  
La Jolla, California 92093*

J. Z. Sun and T. H. Geballe

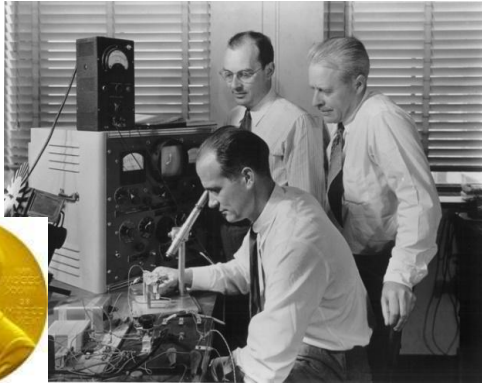
*Department of Applied Physics, Stanford University, Stanford, California 94305*

(Received 20 July 1987)

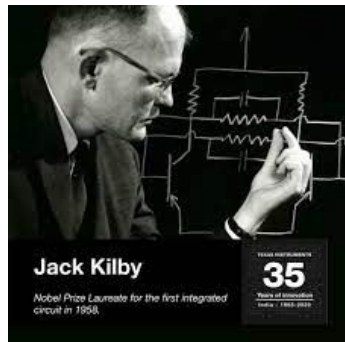


# Scientific foundation for next generation quantum materials

SLAC



Invention of transistor (1957 Nobel Prize)



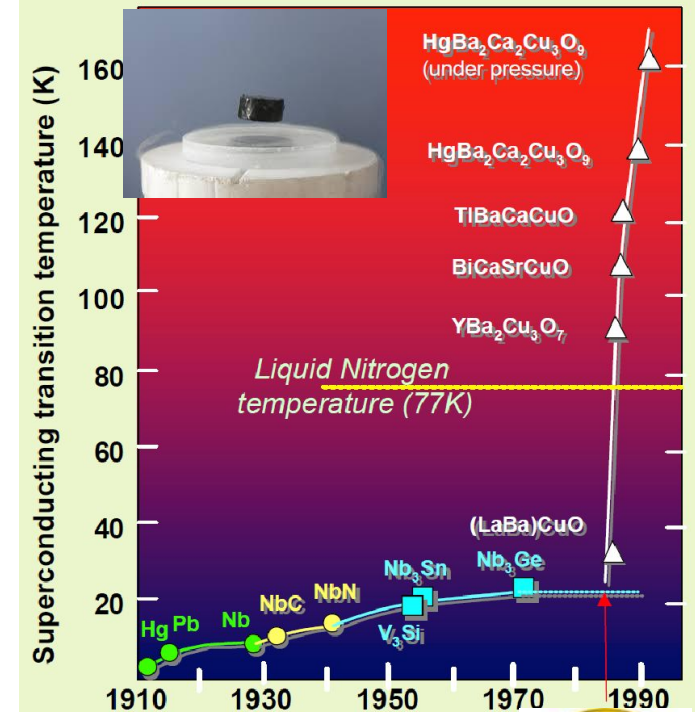
Invention of Integrated circuit (2000 Nobel Prize)

First generation quantum theory played a vital role in the development of “1<sup>st</sup> generation of quantum technologies” like semiconductors.

Adequate quantum theory is yet to be developed for other classes of quantum materials, for example cuprate high temperature superconductors.

Precision measurement of key quantum parameters is imperative to the development of “next generation quantum theory” – in the search for the next “magic material”

## Superconductivity in alloys and oxides



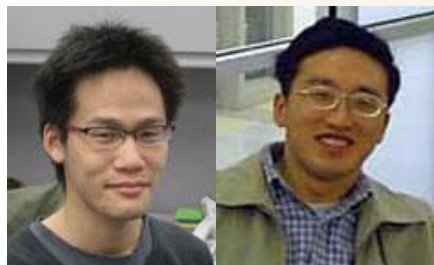
Bednorz  
Muller  
1987





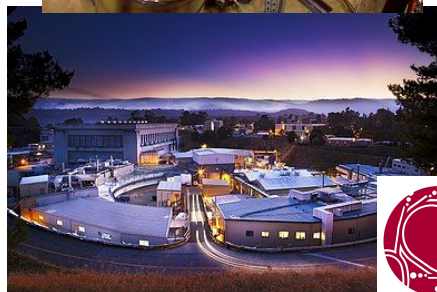
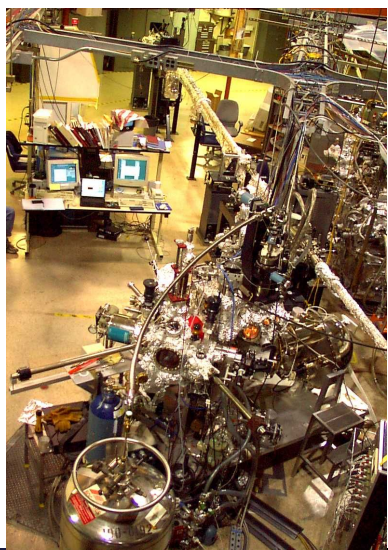
# Modern Angle-Resolved Photoemission Spectroscopy (ARPES)

SLAC

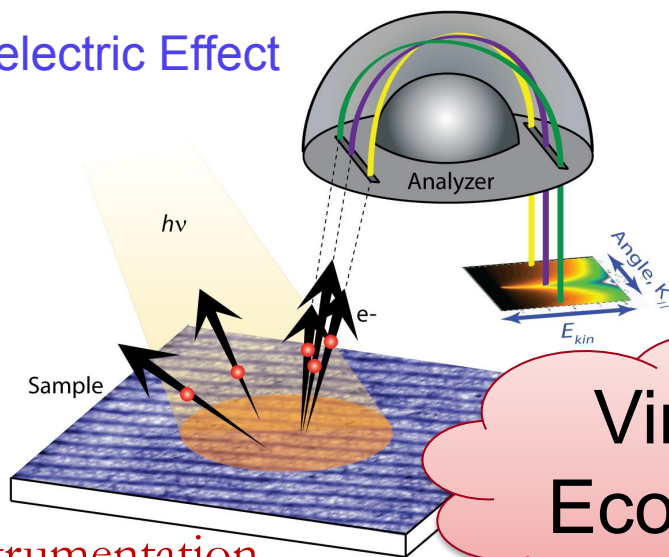


Makoto

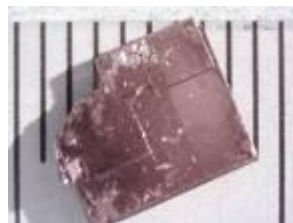
Donghui



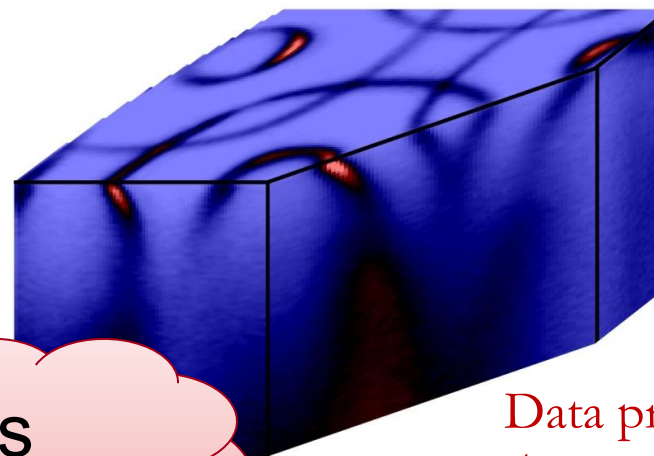
Photoelectric Effect



Instrumentation

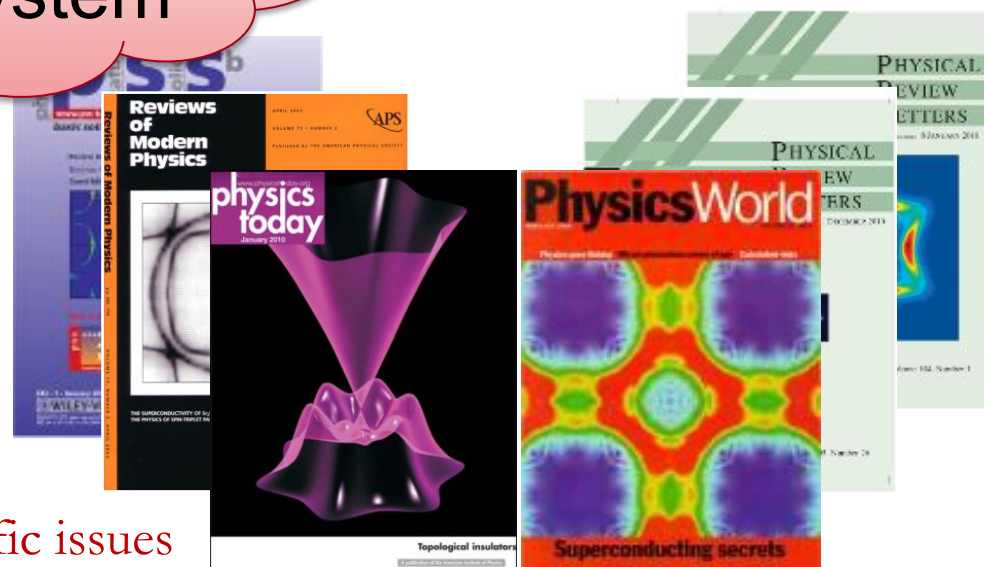


Materials/Samples environment



Data processing  
/Simulation

Scientific issues

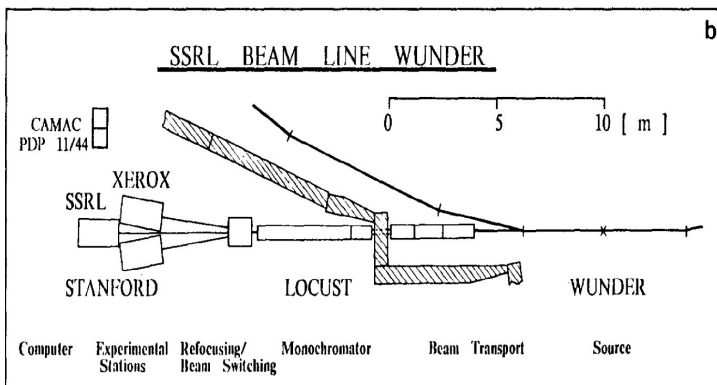


# Evolution of ARPES Program at SSRL

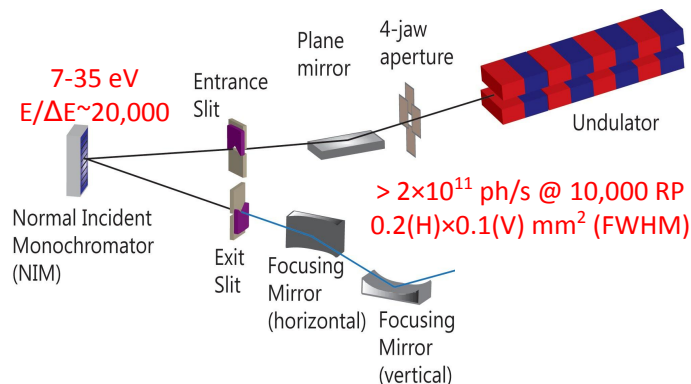
BL-5 produces ~ 30% of synchrotron related ARPES papers in high impact journals  
– Science, Nature journals, PRL, PRX, PNAS (1990-2022)



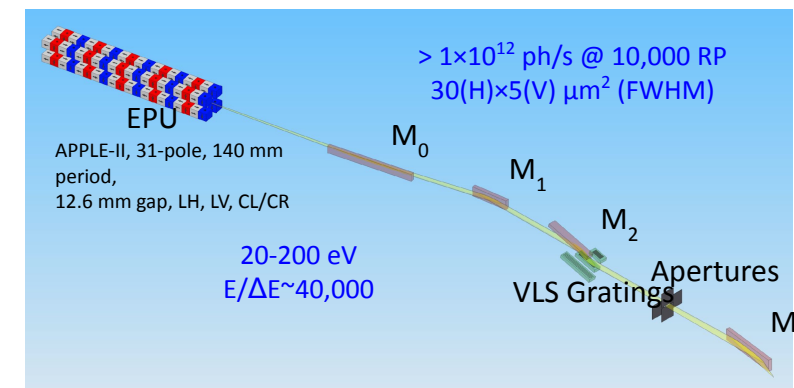
## BL 5-3 (Before 1999)



## BL5-4 (2000 – )



## BL5-2 (2017 – )

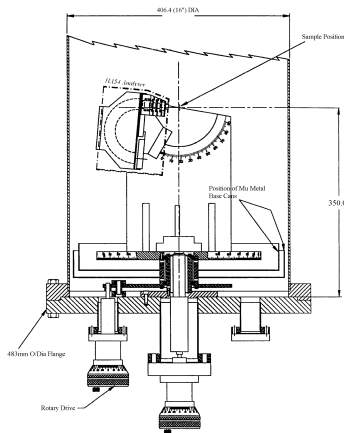


## Multi-channel detector (1991)

2000

2017

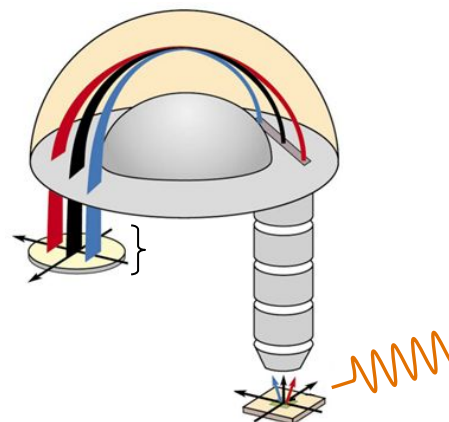
### BL5-3 VSW HA50



### BL5-4 GU Program

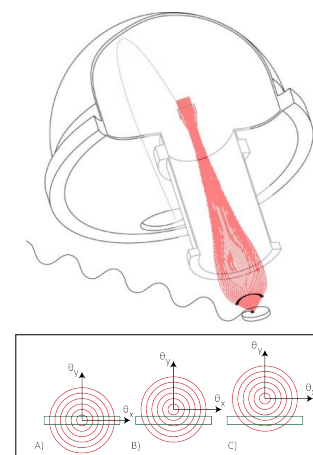
	$\Delta E$ (meV)	$\Delta \theta$	$\Theta$
< 2000	20-40	2°	2°
now	2-5	0.3°	30°

### BL5-4 Scientia R4000



### BL5-2 GU Program

### BL5-2 Scientia DA30-L

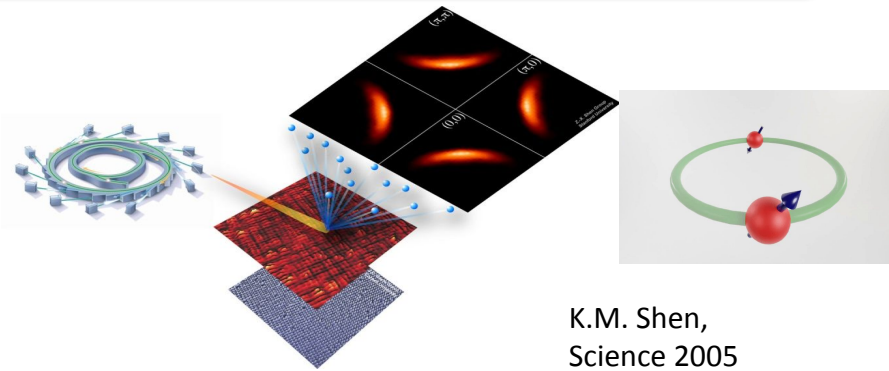




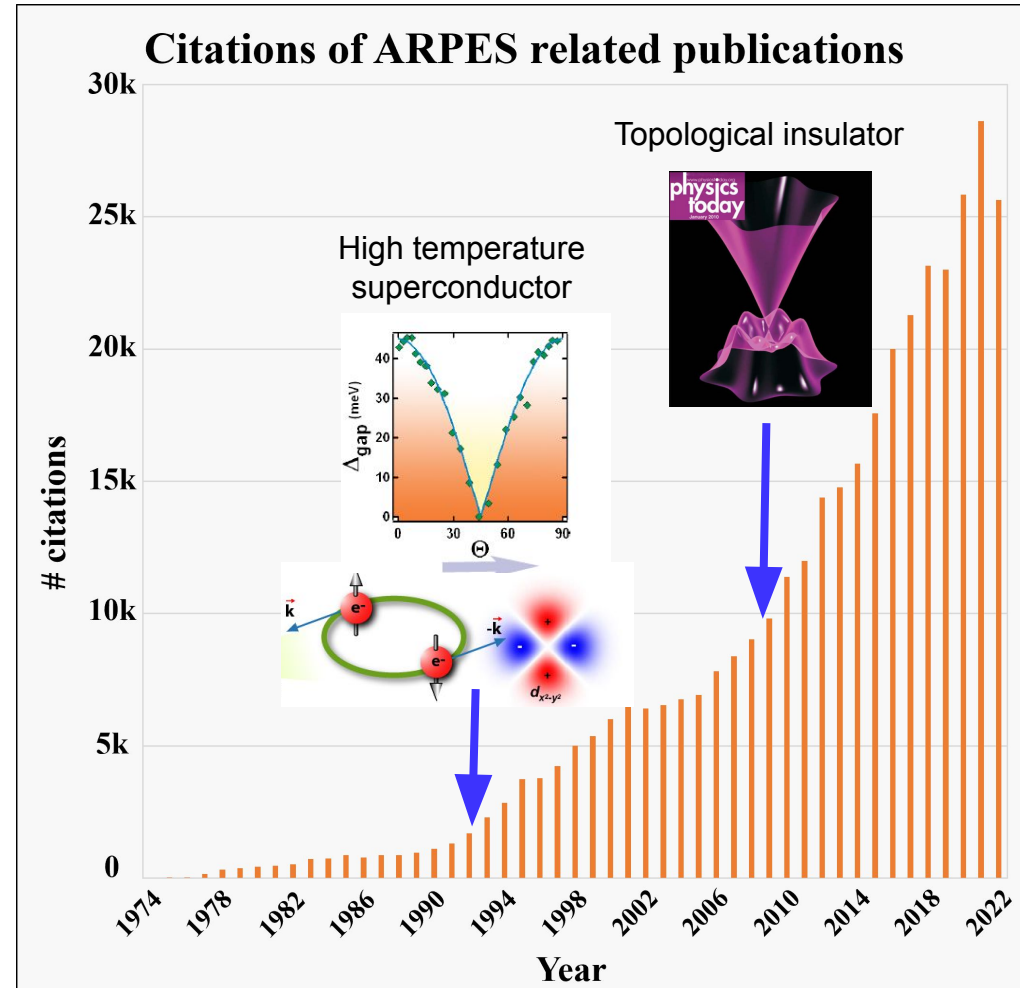
# Probing important quantum numbers of electrons

## Angle-resolved photoemission spectroscopy (ARPES)

Synchrotron based photoemission records energy and momentum of electrons



- Dessau et al., Phys. Rev. Lett. **66**, 2160 (1991)  
Z.X. Shen, et al, Phys. Rev. Lett. **70**, 1553 (1993)  
B.O. Wells et al., Phys. Rev. Lett **74**, 964 (1995)  
Z.X. Shen et al., Science **267**, 343 (1995)  
A.G. Loeser et al., Science, **273**, 325 (1996)  
A. Lanzara et al., Nature, **412**, 510 (2001)  
N.P. Armitage et al., Phys. Rev. Lett. **87**, 147003 (2001)  
K. Tanaka et al. Science, **314**, 1910 (2006)  
D. Hsieh et al., Nature **452**, 970 (2008)  
Y. L. Chen et al., Science **325**, 178 (2009)  
Y. He et al., Science, **362**, (2018)  
S.D. Chen et al., Science, **366**, 6469 (2019)  
Z.Y. Chen et al., Science, **373**, 1235 (2021)  
S.D. Chen et al., Nature, **601**, 562 (2022)

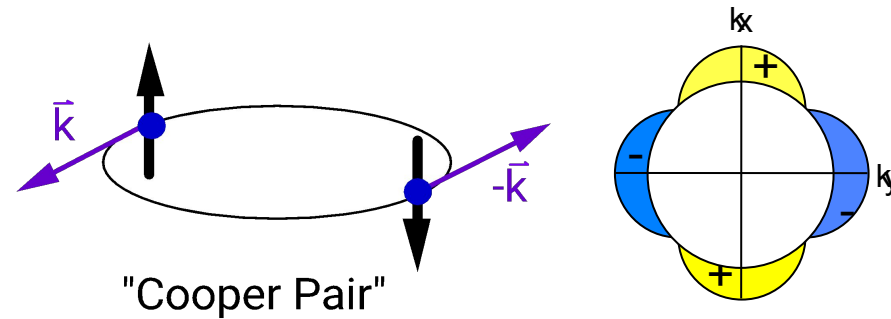
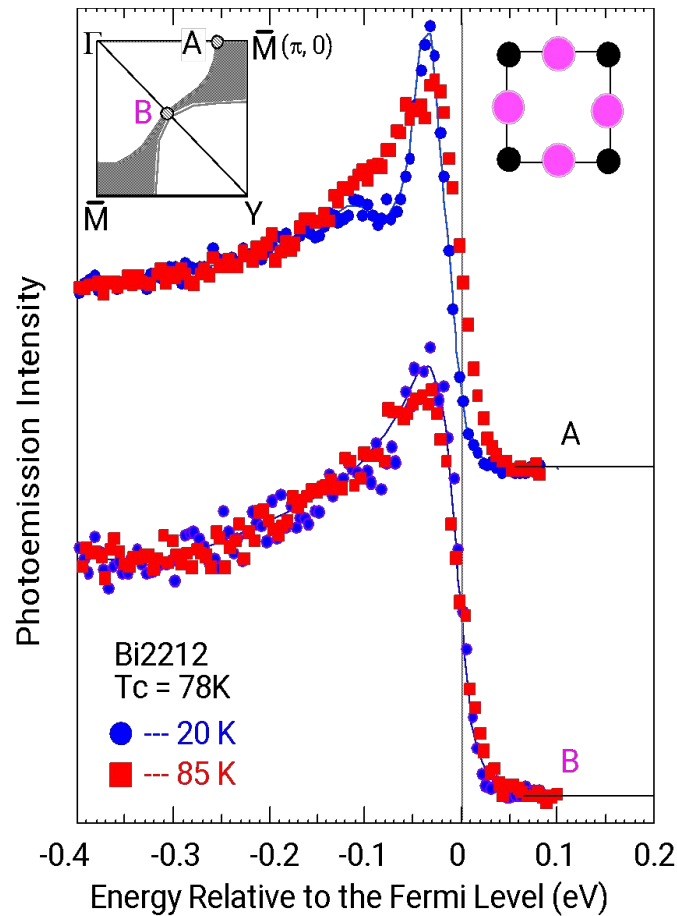


# ARPES : Then and Now

30 years ago

SLAC

*1993 : Detection of an anisotropic d-wave gap*



One EDC with 30 meV &  $\pm 1^\circ$  resolution :

**3 hours per spectrum**

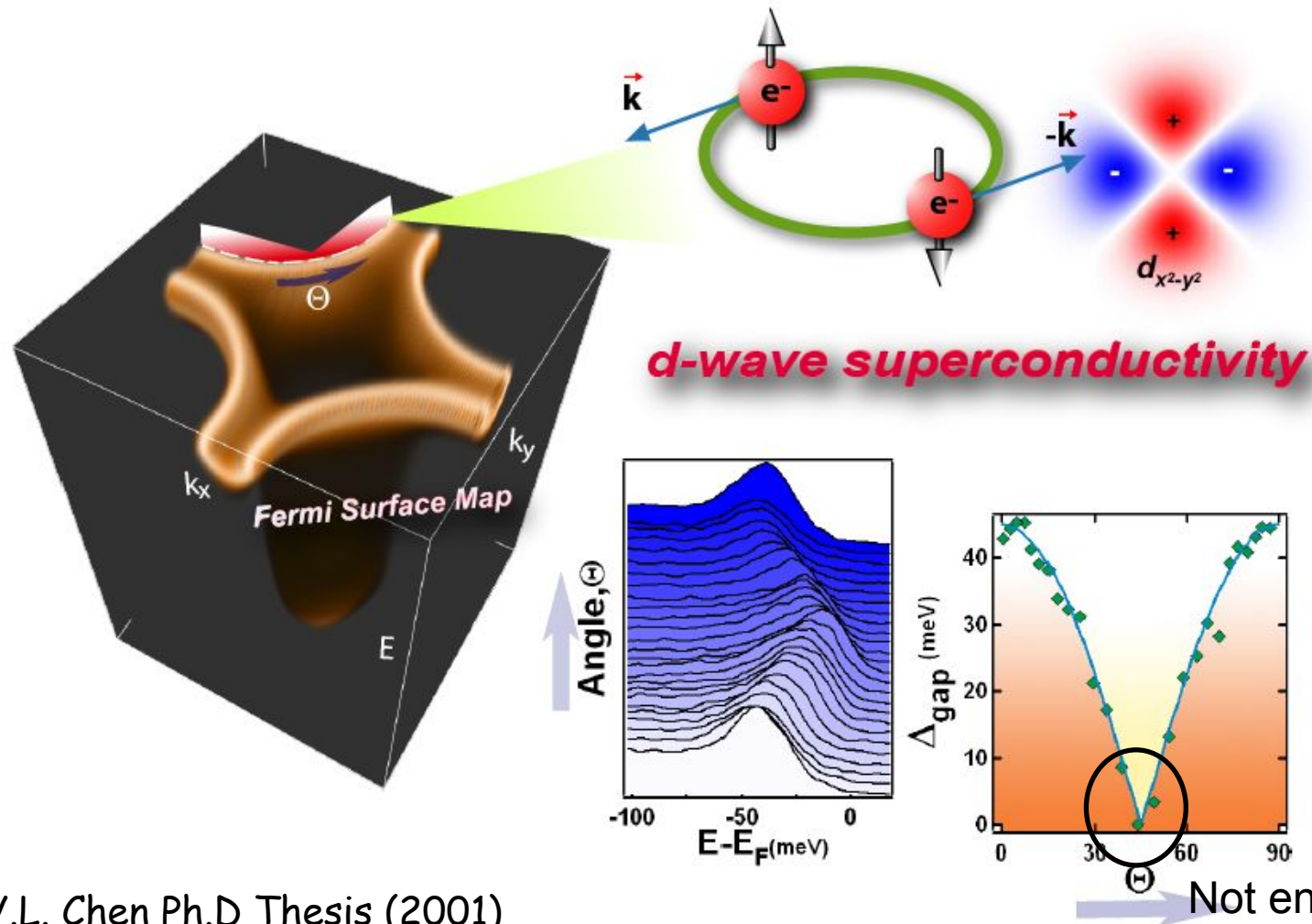
Shen, Dessau, Wells, *et al.*, PRL **70**, 1553 (1993)



# D-wave Superconductivity

20 years ago

SLAC



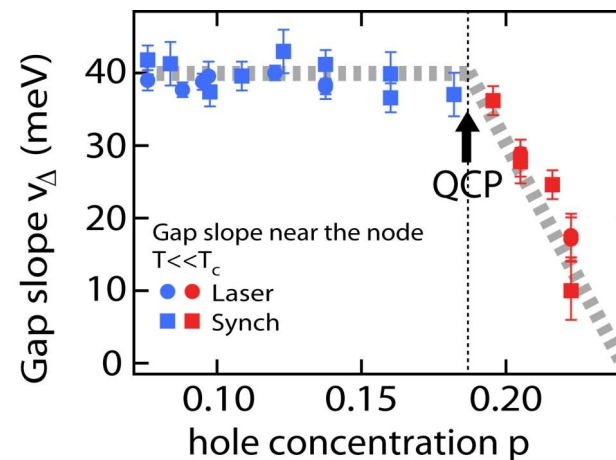
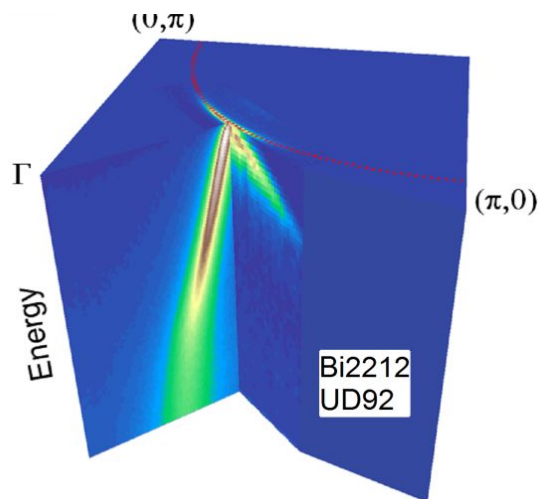
P. Bogdanov, Y.L. Chen Ph.D Thesis (2001)

M. Hashimoto et al., Nature Physics 6, 414-418 (2010)

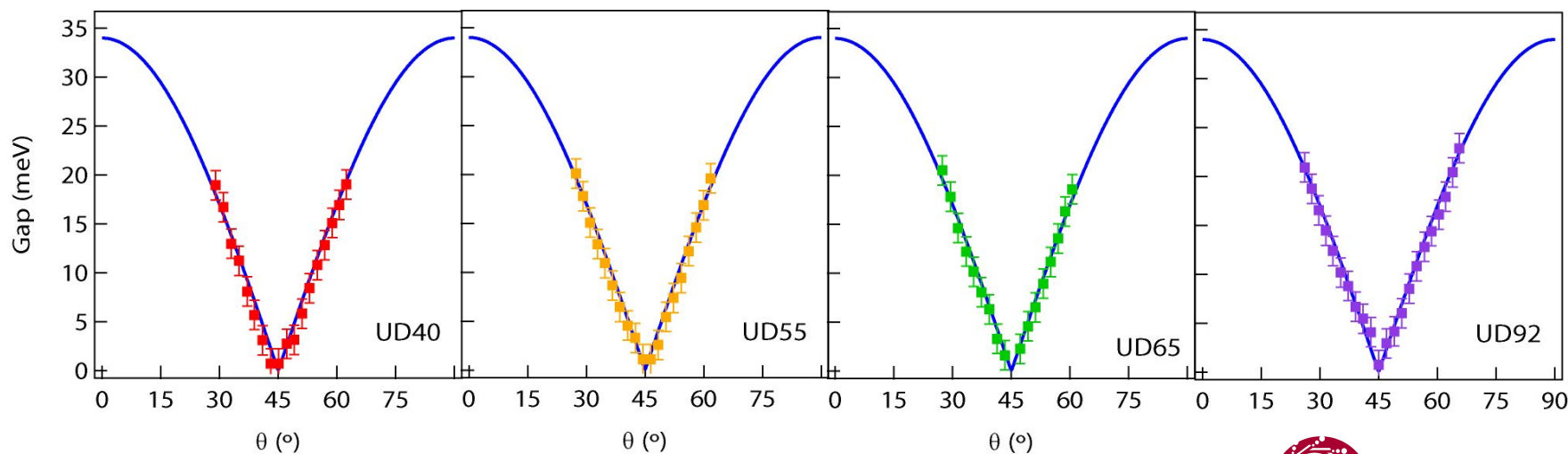
# Precision Measurement of the d-Wave Node

10 years ago

SLAC



Inna





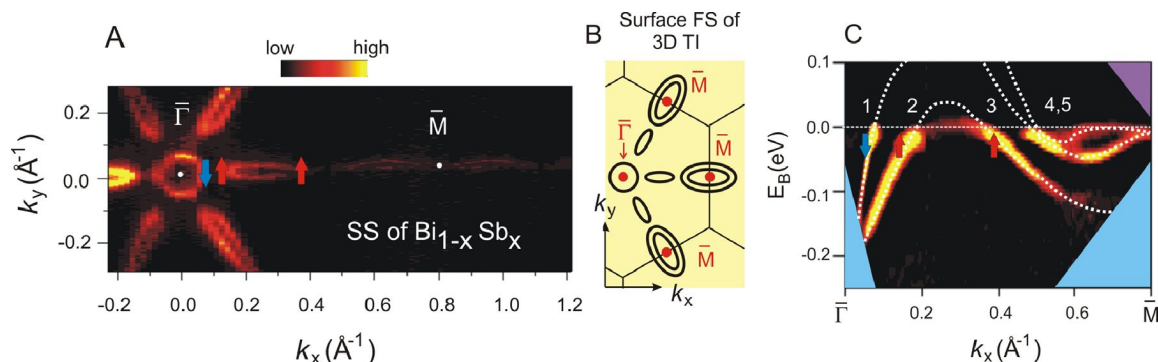
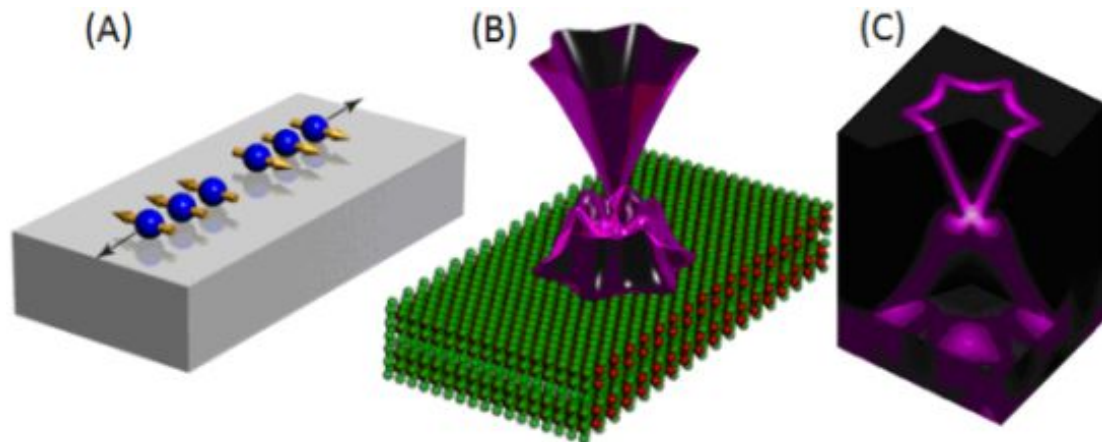
# Topological states of quantum matter

SLAC

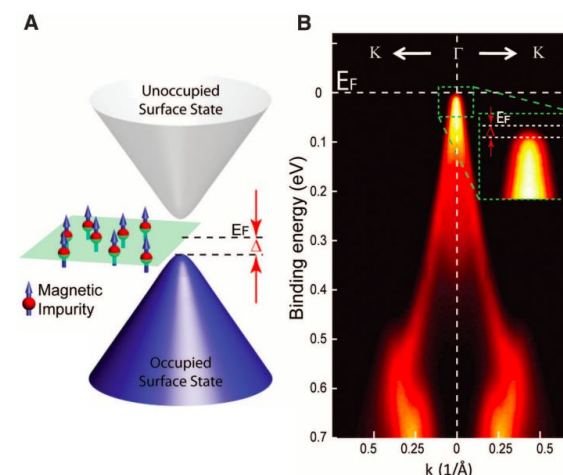
Discovery of 3D topological insulators using synchrotron lightsources – role of wavefunctions

ALS  
ADVANCED  
LIGHT SOURCE

SSRL



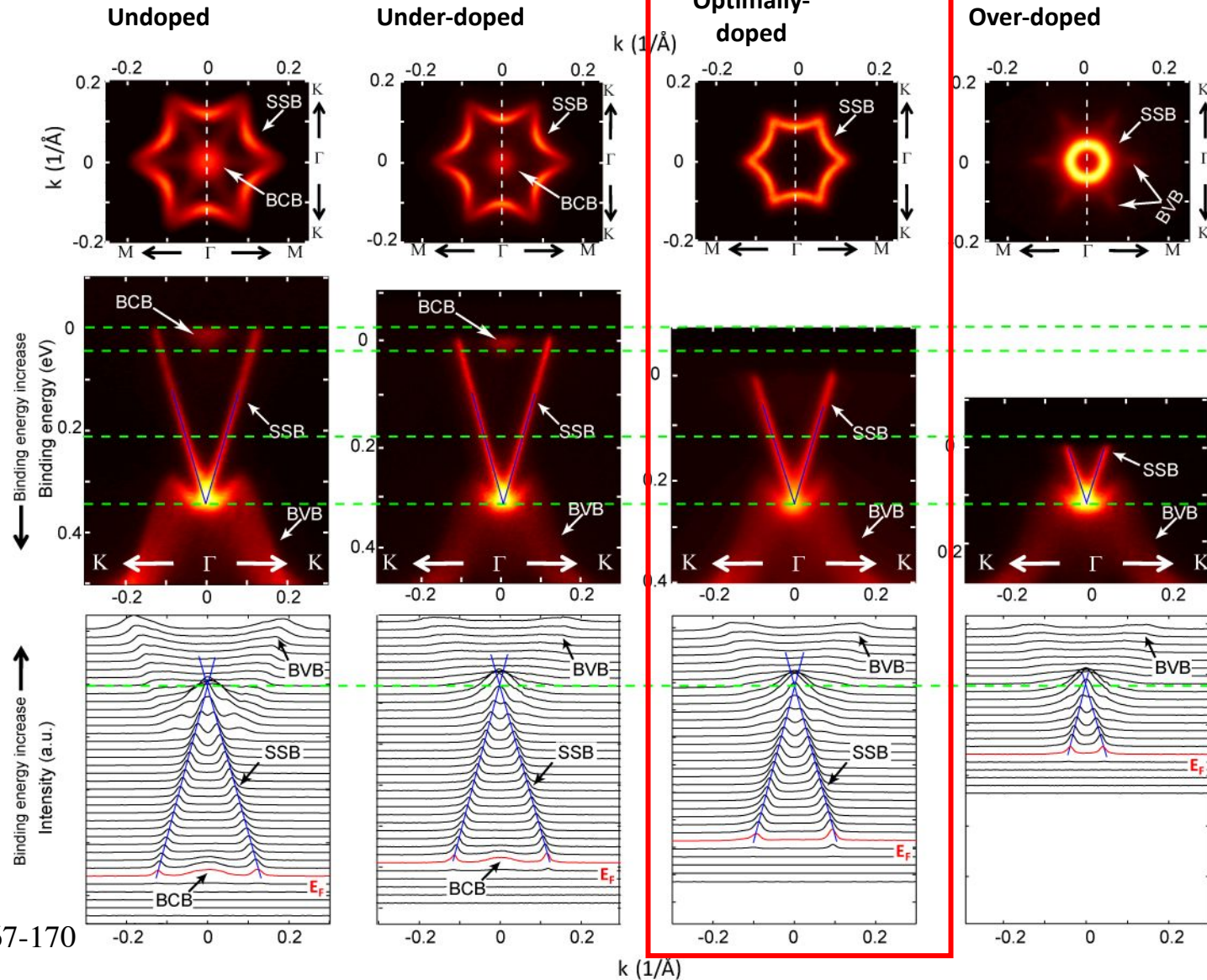
D. Hsieh *et al.*, *Nature* **452**, 970 (2008)  
Y. L. Chen *et al.*, *Science* **325**, 178 (2009)  
Y. L. Chen *et al.*, *Science* **329**, 659 (2010)



Synchrotron-ARPES reveals key features of topological insulators in momentum space:

- Bulk band gap with band inversion
- Odd number of robust Dirac cones on the surface
- Massive Dirac surface states by time-reversal symmetry breaking

# “Hydrogen Atom” of topological insulator - Bi<sub>2</sub>Te<sub>3</sub>



Y. L. Chen *et al.*,  
*Science* **325**, 178  
(2009)

Sample  
Fisher group



Yulin

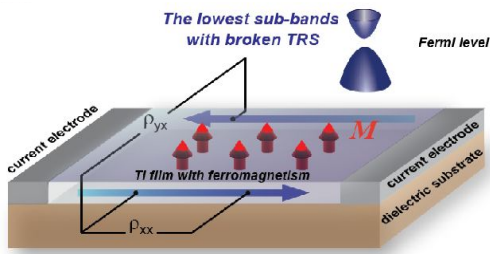
SIMES

$E_F$  (undoped)  
BCB bottom

BVB top

Dirac point position

## Quantum Anomalous Hall



Cr<sub>0.15</sub>(Bi<sub>0.1</sub>Sb<sub>0.9</sub>)<sub>1.85</sub>Te<sub>3</sub>

Chang *et al.* 2013, *Science* **340**, 167-170





# University Groups trained by the ARPES program at SSRL



Dan Dessau  
UC Boulder



Barry Wells  
U Connecticut



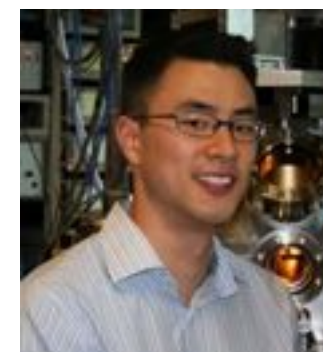
Peter Armitage  
Johns Hopkins



Zahid Hasan  
Princeton



Alessandra Lanzara  
UC Berkeley



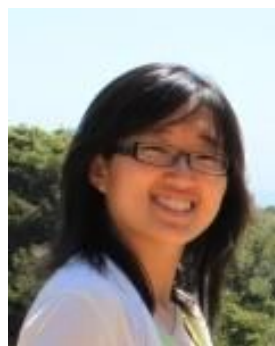
Kyle Shen  
Cornell



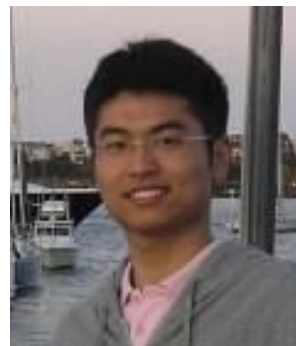
Tanja Cuk  
UC Boulder



Inna Vishik  
UC Davis



Ming Yi  
Rice



Shuolong Yang  
U of Chicago



Heike Pfau  
Penn State



Yu He  
Yale

**SSRL played a vital role incubating several Joint SLAC-Stanford interdisciplinary Research Institutes and Centers:**

- Photon Ultrafast Laser Science and Engineering (PULSE):

<https://ultrafast.stanford.edu/>



- Stanford Institute for Materials and Energy Sciences (SIMES):

<http://simes.stanford.edu/>



- SUNCAT: <http://suncat.slac.stanford.edu/>



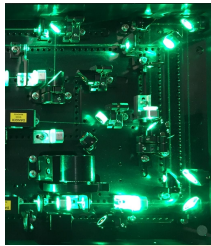


# Building an Ecosystem

Synergetic activities using advanced instrumentation, synthesis/control and simulation

SLAC

Towards complete experiments to advance quantum materials –  
energy, momentum, spin, time, space ...



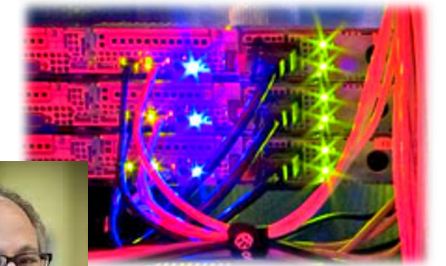
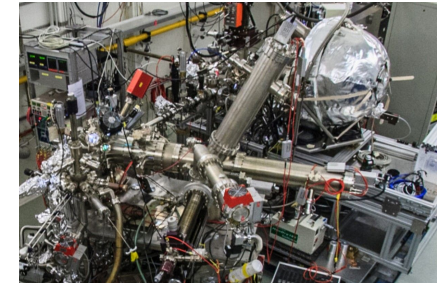
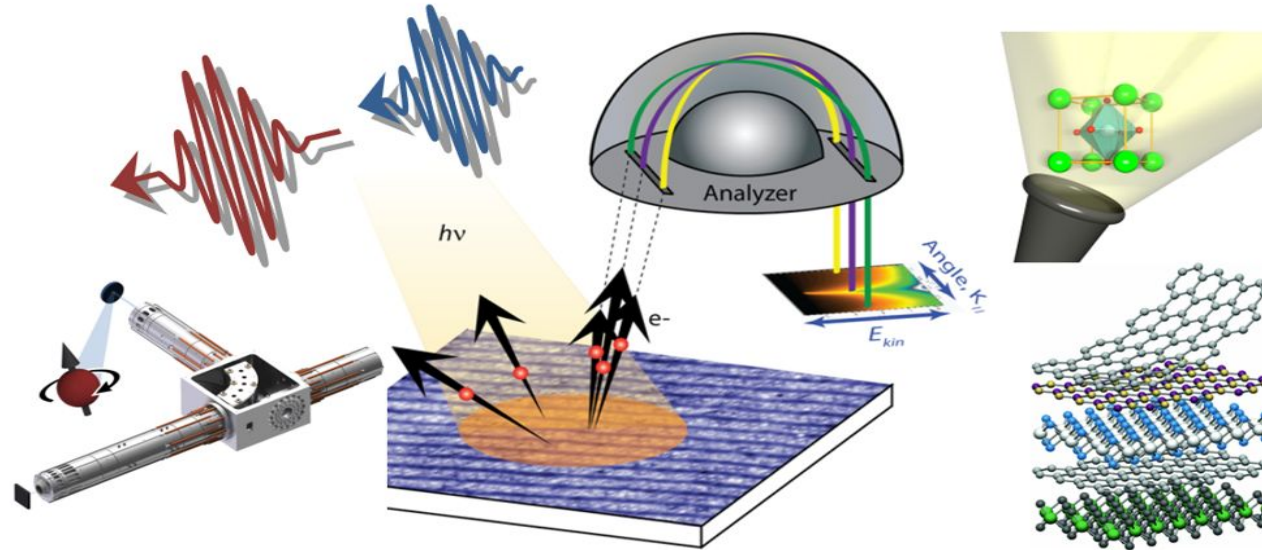
Lab based  
tools



Jonathan



Patrick



Tom



SIMES

LCLS



SSRL



SLAC





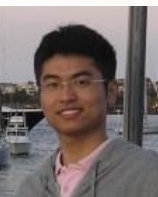


# Bridge to LCLS and LCLS-II

## How do electrons and atoms behave on their natural length and time scales?



Ultra-bright & ultra-fast x-ray laser for recording movies of electrons and atoms in motion



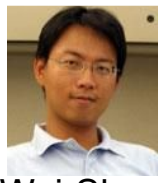
Shuolong



Jonathan



Patrick



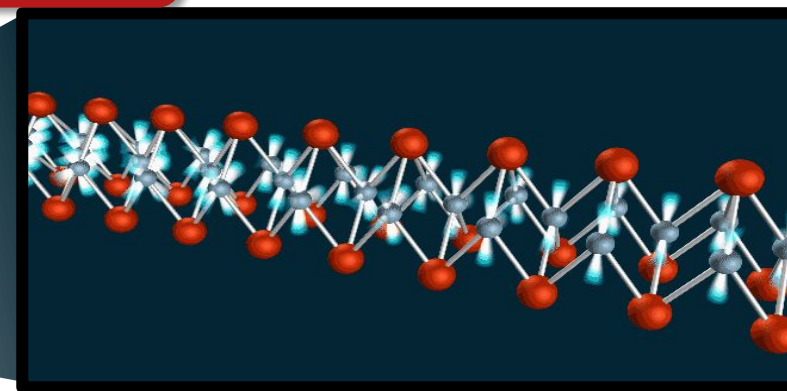
Wei-Sheng



Diling

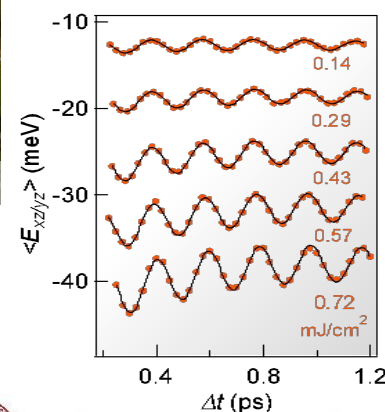


Linac Coherent Light Source (LCLS)  
SLAC National Accelerator Lab

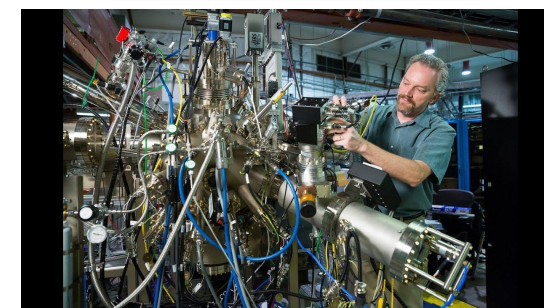
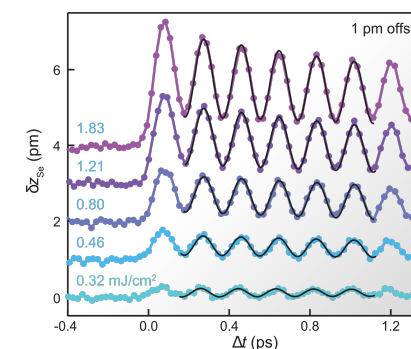


- Thin Films grown at SSRL were important for this experiment
- “THz lock-in” using LCLS achieved precision not possible any other way
- Harmonious cooperation of electrons and atoms enhances properties

Electrons



Atoms



Rob Moore

F. Schmitt et al., Science 321, 1649 (2008)  
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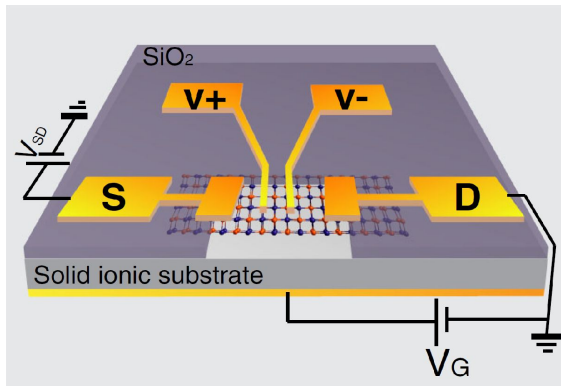




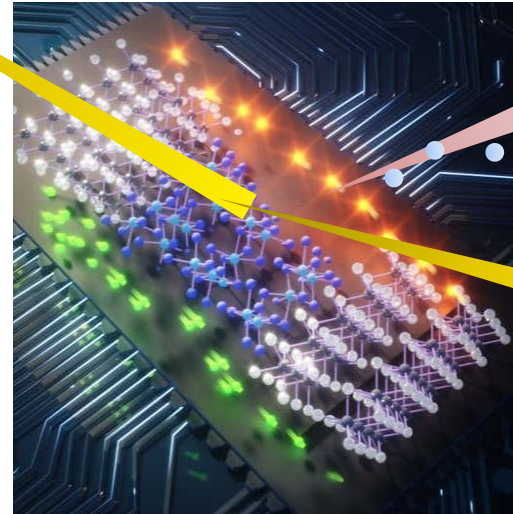
# Expanding Soft X-ray Capability at SSRL

## Complementary light sources

- micro(nano)-focused beam
- Soft x-ray for ARPES (heterostructure)
- Lasers for ultra-high-resolution, spin-resolved, and time-resolved ARPES



## QIS materials & device



## in-situ device fabrication & versatile sample environment

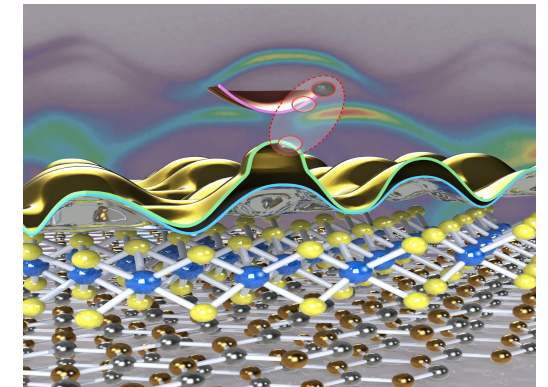
- *in-situ* clean environment (inert gas, UHV) for sample exfoliation/device fabrication
- micro(nano)-precision sample manipulator



Donghui Makoto Jun-Sik

## Multimodal characterization tools

- ARPES (+ *multi-channel spin detector*)
- Momentum microscope (PEEM)
- STM, AFM
- RSXS/RIXS with advanced detector
- X-ray Raman spectroscopy



# Historical Context — Reflection

- State of the art high energy physics storage ring, SPEAR, began operation at SLAC in 1972
- Would be used to study uncharted territory in particle physics and ultimately discovered quarks and lepton
- Could this source of high intensity x-rays be used to do something novel for materials/chemistry/biology?
- Demonstration experiment showing that an x-ray beam could be extracted from SPEAR and some useful science could be performed





# Historical Context — Reflection

- Could this source of high intensity x-rays be used to do something novel for materials/chemistry/biology?
- What we have learnt?
- Open to new ideas – also partnership SLAC/Stanford
- Build a transformative tool in a science rich environment (1973-1975 – “November Revolution” and beyond ... )
- Invest in young people ... creating a pipeline of young talent





# SSRL 50 Years – the Future is Bright

April 20, 2023

Zhi-xun Shen

Stanford Institute for Materials and Energy Sciences

Stanford University and SLAC National Accelerator Laboratory

Stanford  
University



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**ENERGY**

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