Scientific Opportunities with Soft X-Rays for Understanding Emergent Phenomena in Complex Materials

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Outline

- The big picture
- Science with Soft X-Rays (Dynamics)
  - Resonant Scattering

    Spin, Orbital and charge ordering (time evolution)
  - Resonant Inelastic Scattering
    - Collective low energy excitations
    - Mapping out the many body wave function
  - Angle-Resolved Photoemission (ARPES)
    - Nano-, Spin- and Time-Resolved ARPES
  - Real Time Surface Chemical Reactions (Energy applications)
- The instrumentation

Understanding complex phenomena require sharper and sharper tools

The Big Picture

Grand Challenges

Five Grand Challenges for Science and the Imagination for BES

- *How do we control materials and processes at the level of electrons ?*
- *How do we design and perfect synthesis of revolutionary new forms of matter with tailored properties ?*
- *How do remarkable properties of matter emerge from complex correlations of atomic and electronic constituents and how can we control these properties ?*
- *How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living systems ?*
- *How do we characterize and control matter away—especially very far away—from equilibrium ?*

Overall Challenge: *Making the Leap from Observation Science to Control Science*

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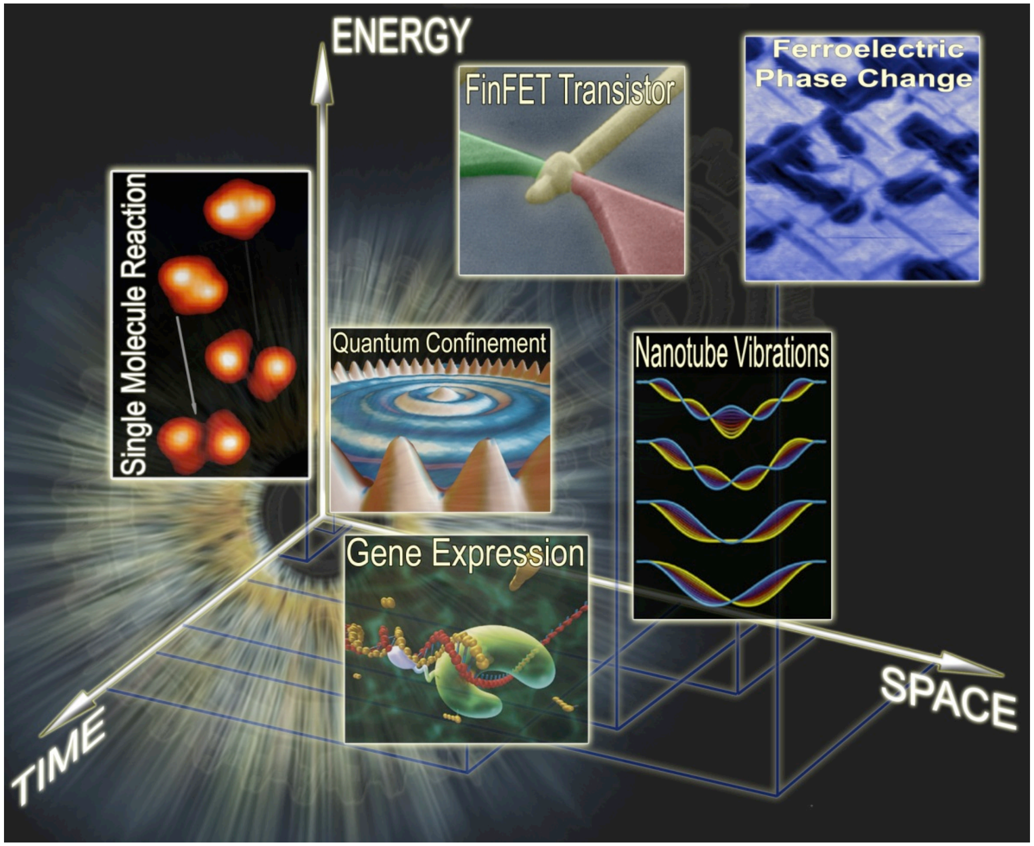
Designing materials to have the properties we want require the ability to see functionality at the relevant *time, length & energy scales.*

We will need *to develop & disseminate new tools* capable of viewing the inner workings of matter — at the level of electrons, atoms or molecules



Why X-Rays ?

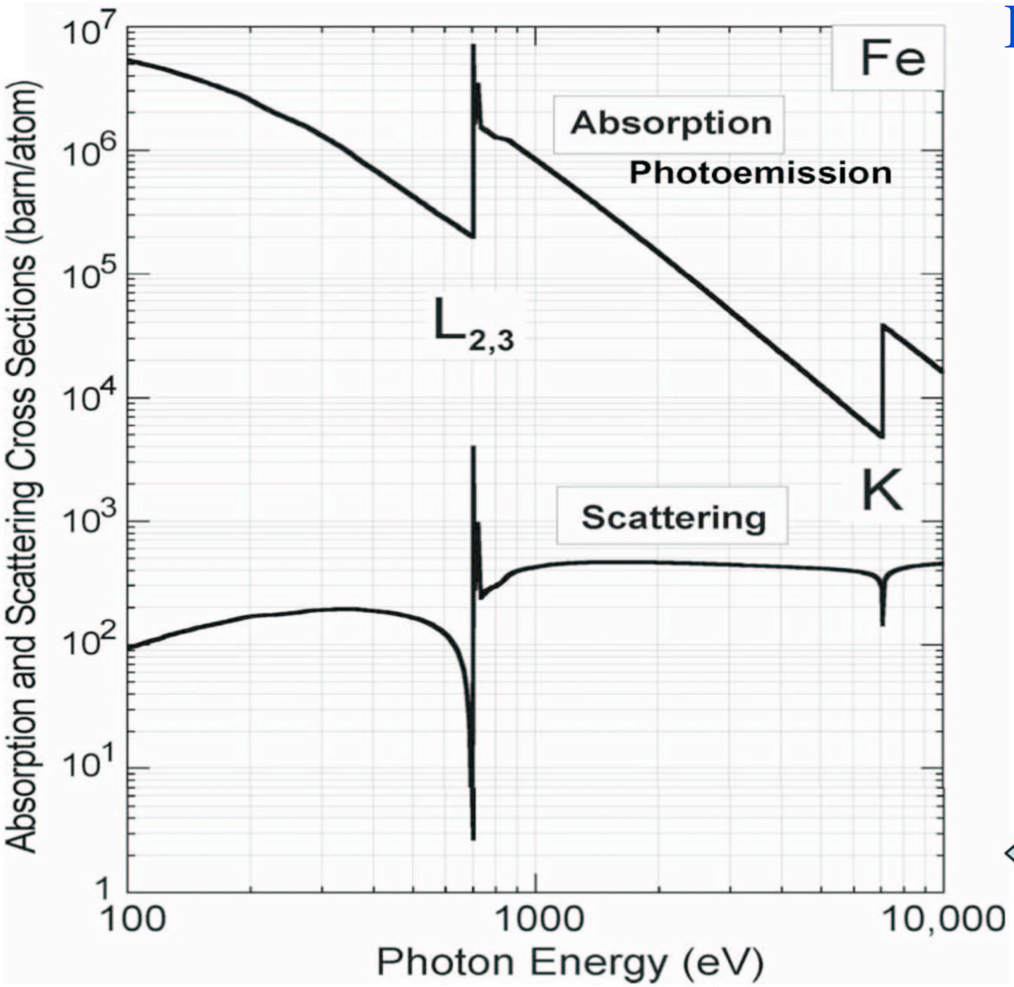
Not neutrons or electrons

Why X-Rays (& not neutrons or electrons) ?

Tunable x-rays offer variable interaction cross section

Optical

Electrons



neutrons

Courtesy: J Stohr

Emergent Phenomena

—

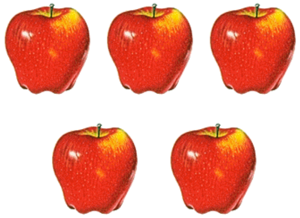
Strongly Correlated electron Systems

Highly Correlated Electron System

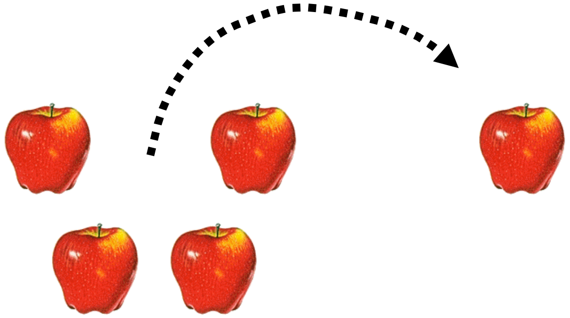
uncorrelated system

correlated system

ground state

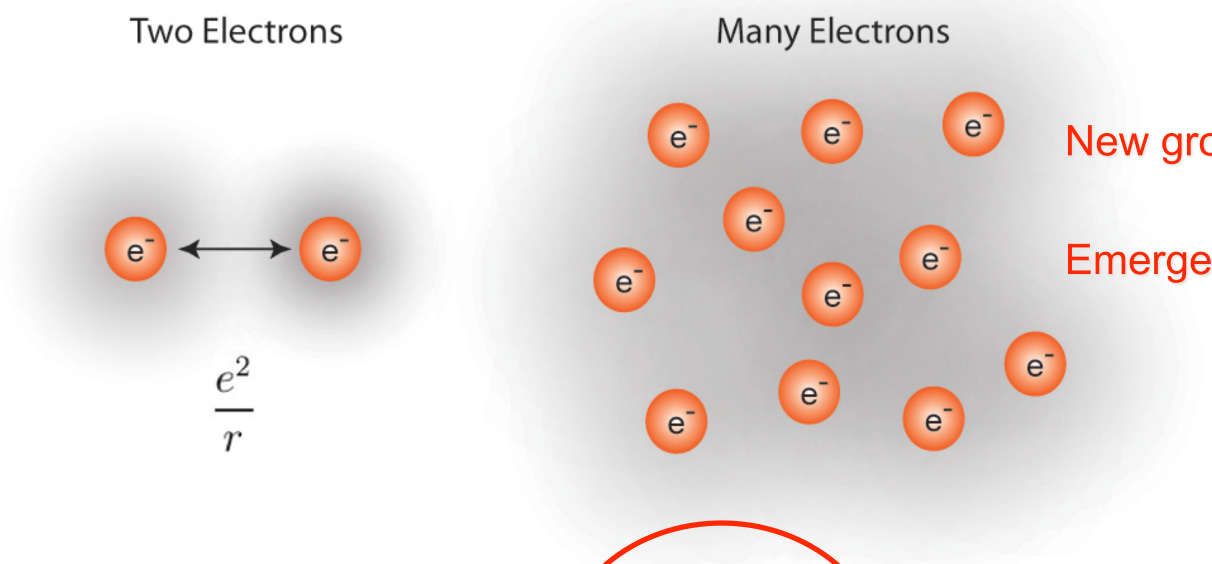


with external perturbation…



The responses are different due to correlation effect!

Strongly Correlated System



New ground states.

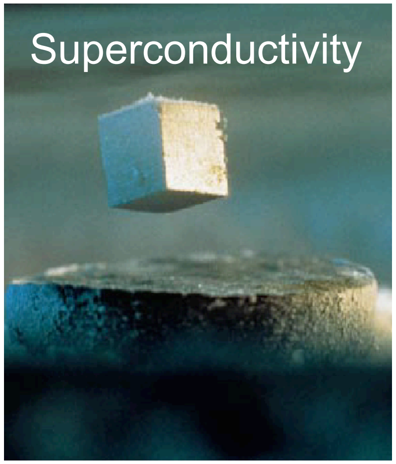
Emergent Phenomena!

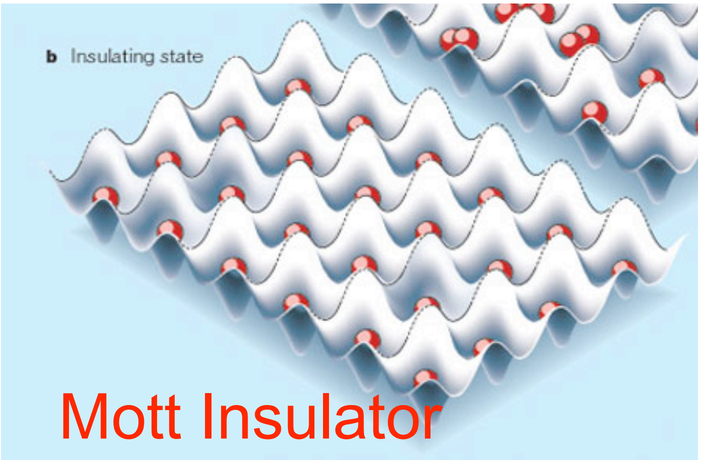
$$H = -\sum_{j=1}^{N} \frac{\hbar^2}{2m} \nabla_j^2 + \sum_{j<k}^{N} \frac{e^2}{|r_j - r_k|}$$

Correlations !

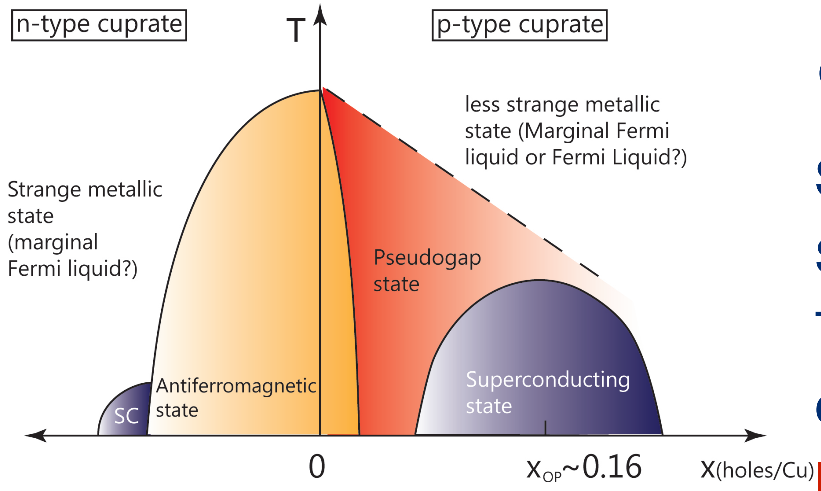
- **New ground states created due to the correlations among the many particles.**

Understand the Quantum Matter of Electrons.





High-Tc SC



Thermodynamic measurements:

Resistivity, Specific heat, Penetration depth…

Macroscopic information.

Spectroscopic measurements:

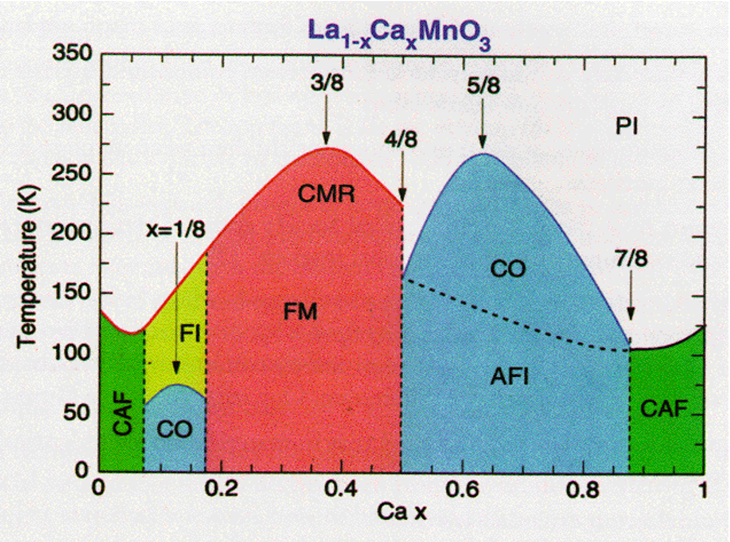
Single-particle spectrum -> Quasi particle

Two-particle correlation function -> collective excitations.

Microscopic information.

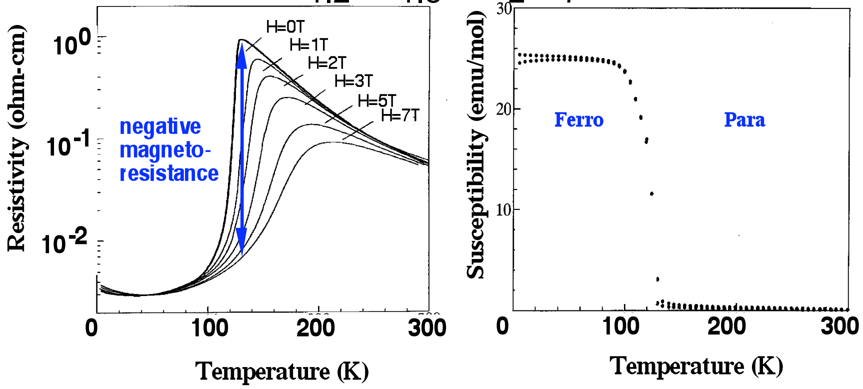
Colossal Magnetoresistance (CMR) Effect

Novel Electronic Phases



CO : Charge Order (Stripes)
FI : Ferromagnetic Insulator
AFI : Antiferro. Insulator
CAF : Canted AFM Insulator
CMR : Colossal MagnetoResis.

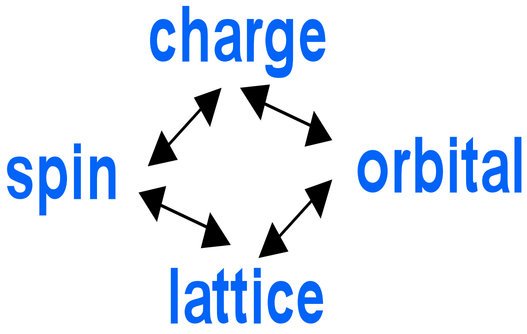
$La_{1.2}Sr_{1.8}Mn_2O_7$



- O Large drop of resistivity upon relatively small magnetic fields
- O Para → Ferromagnetism
- O Most dramatic on the insulating phase (short range orbital order)

Manganites Exhibit Interplay of Charge, Spin, lattice and Orbital degrees of freedom

Interacting **degrees of freedom (complex electron systems)**



Competition among many *Length, Energy* , *and Time* scales
Determine the physics of these systems

Resonant Soft X-ray Scattering:

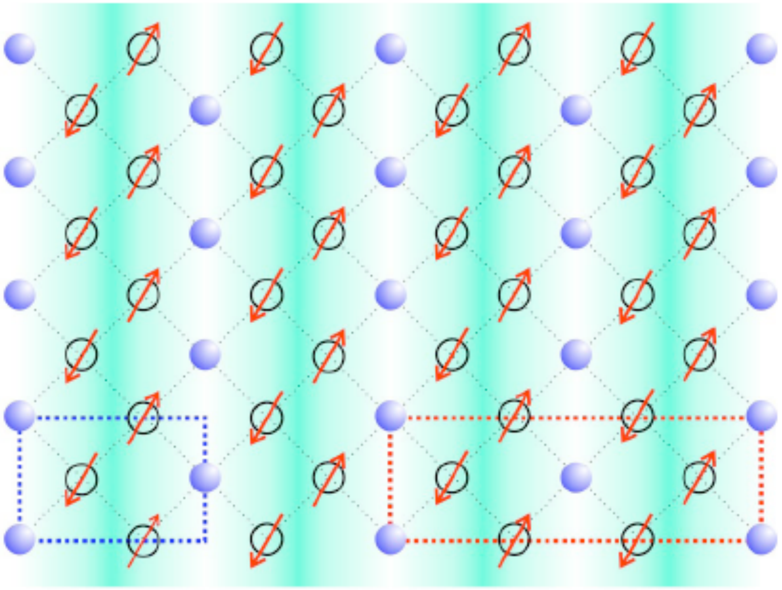
for Understanding Electronic Ordering in Correlated Electron Systems

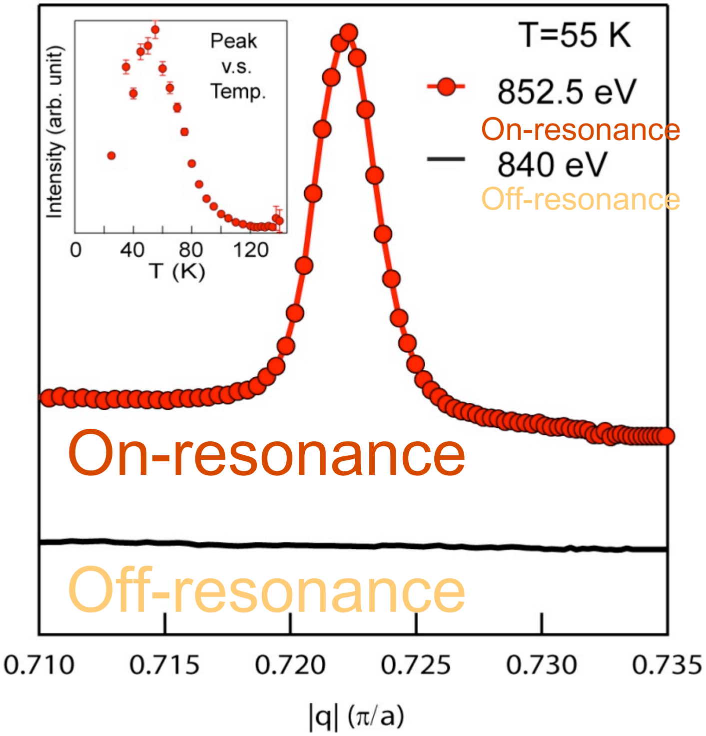
Resonant Soft X-Ray Scattering

Spin stripes – Nickelates

Example: 1

$La_{2-x}Sr_xNiO_4$ with x=0.25





At Spin Ordering : (1 - ε ,0,0)

Explore the nature of spin stripe phase at low temperature and around transition to elucidate the spin glass phase at this doping

W.S. Lee, Z.X. Shen, Stanford U.
Y.-D. Chuang, Z. Hussain, ALS
unpublished

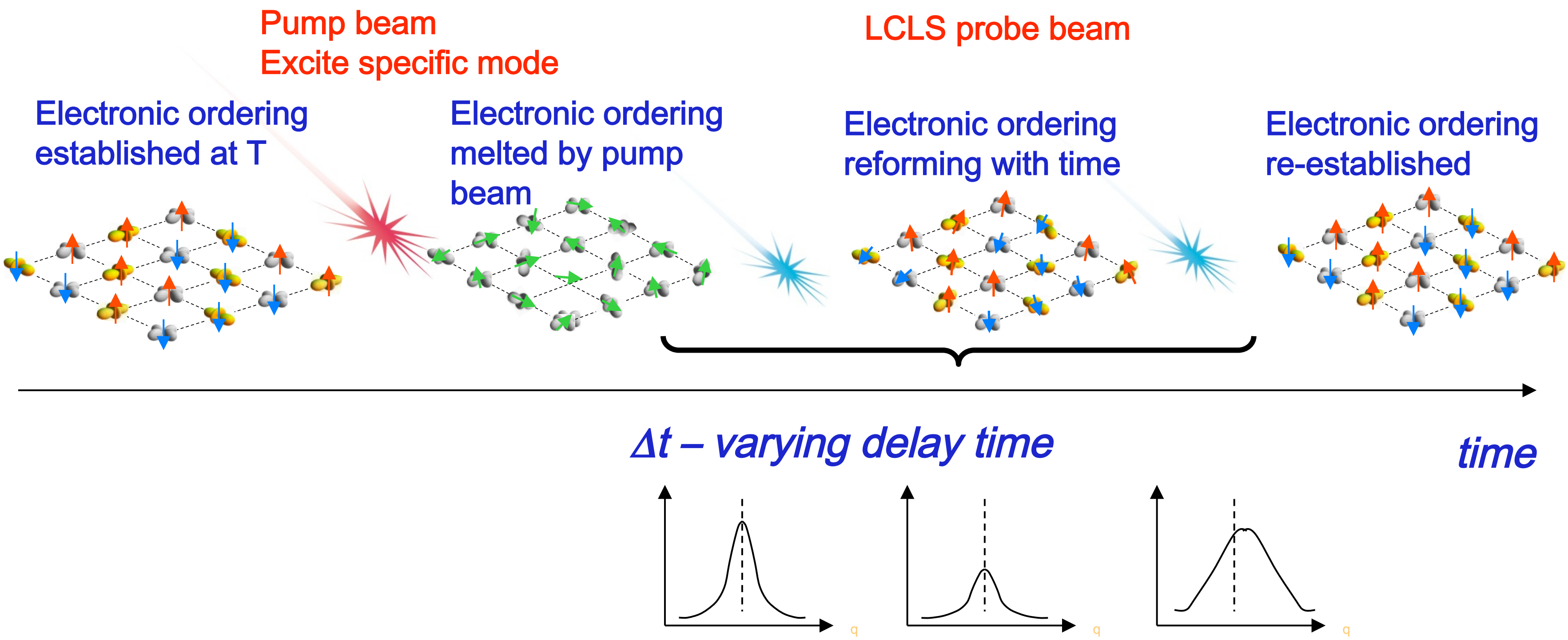
Time-Scale of Various Phenomena

- Ultra-fast time regime: ≤ 200fs (ΔE >10meV)
  - Electron Correlation Time ~ 100 attosec (a/V_{fermi})
  - Electron excitation/de-excitation (<fs)
  - Electron-Electron Scattering ~ 10 fs
  - Electronic vibrational period ~ 100 fs
  - Charge density wave/charge transfer
  - Magnetization Dynamics
- Time regime: ~ 200fs - 2ps (ΔE ~1-10 meV)
  - Phase transition (diamond ↔ graphite)
  - Electron-Phonon Interaction ~ 1 ps
- Time regime: > 1-100ps
  - Stripe fluctuation in High Temp Superconductor
  - Magnetic recording-present (~ 1ns 100ps)
  - Protein folding (ps-s)

Resonant Soft X-Ray Scattering Experiment @LCLS

Q: How electronic ordering states (orbital stripes, charge ordering state, spin stripes) form after perturbation?

A: pump-probe type experiments with fs probe pulse might be able to answer this question…



Pump beam
Excite specific mode

LCLS probe beam

Electronic ordering established at T

Electronic ordering melted by pump beam

Electronic ordering reforming with time

Electronic ordering re-established

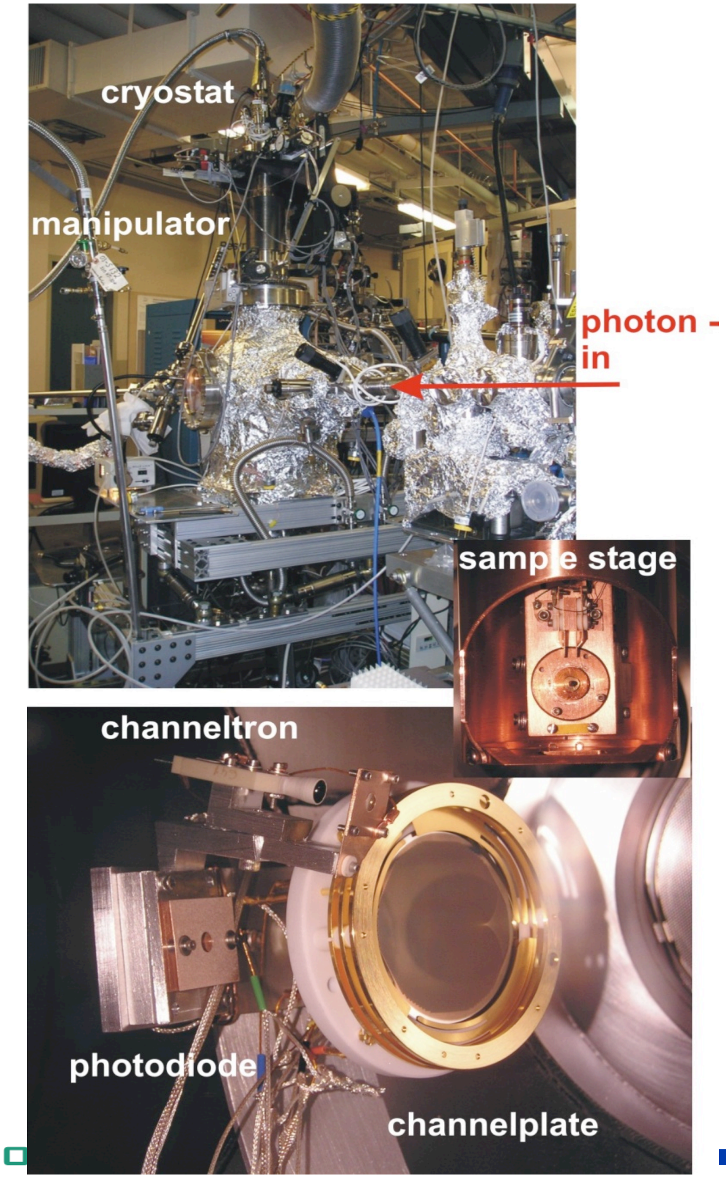
Δt – varying delay time

time

Studying the peak position (ordering vector), width (correlation length) and intensity (volume fraction), the dynamic aspect of the ordering can be revealed

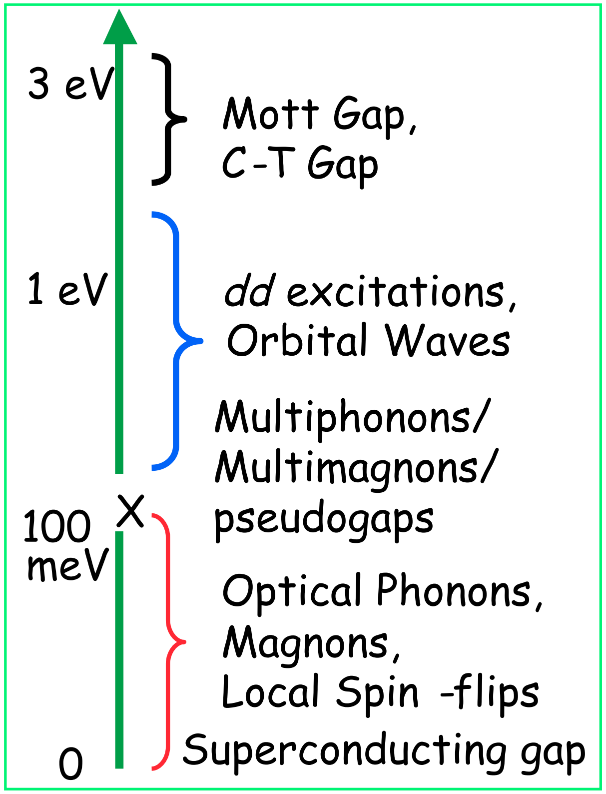
Resonant X-Ray Scattering Setup

- Current capability
  - Sample cryostat/manipulator has 3-translation (X,Y,Z) & 2-rotation degrees of freedom (θ,ϕ).
  - $15K < T < 400K$.
  - Total fluorescent yield (photodiode down to 0.1pA signal & channeltron with pulse counting rate >MHz) and total electron yield (sample-to-ground current).
  - Detectors move in both horizontal (360 degrees) & vertical (45 degrees) scattering planes.
  - All motions are motorized.
  - Plan to add the option of replacing resistive anode detector with in vacuum CCD.



- Simplest q-resolved scattering probe.
- Suitable for gaining more experience of using LCLS to do q-resolved scattering experiment.

Energy Scale of Important Excitations



3 eV

Mott Gap,
C-T Gap

1 eV

dd excitations,
Orbital Waves

Multiphonons/
Multimagnons/
pseudogaps

100 meV

X

Optical Phonons,
Magnons,
Local Spin -flips

0

Superconducting gap

- **Orbital fluctuations: ~ 100 meV - 1.5eV**
- **Multiphonons/magnons ~ 50-500 meV**
- **Pseudogap ~ 30-300 meV**
- **quasi e-h pairs ~ 1-250 meV**
- **Collective modes from competing order (QCP, Aslamazov-Larkin)~ 1-150 meV**
- **Optical Phonons: ~ 10 - 70 meV**
- **Single Magnons: ~ 10 meV - 40 meV**
- **Superconducting gap ~ 1 – 35meV**

Realizing Potential of Inelastic Scattering

What are techniques of choice?

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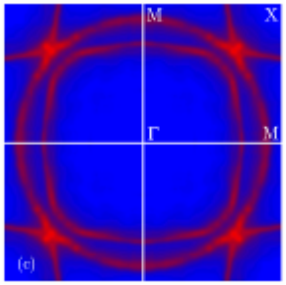
with both ***energy*** and ***momentum***

resolution

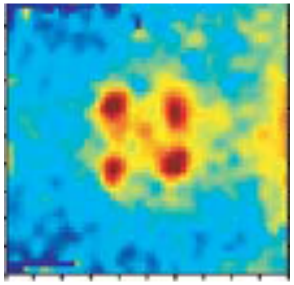
Fundamental Spectroscopies of Condensed Matter

Spectral functions (One-particle properties)
Correlation functions (two-particle properties)



1-particle response

- Angle resolved photoemission (ARPES) :
  Single-particle spectrum $A(k,\omega)$



2-particle responses

- Spin : Inelastic Neutron Scattering (INS) :
  (neutrons carry magnetic moment)
  Spin fluctuation spectrum $S(q,\omega)$
- Charge : Inelastic x-ray scattering (IXS) :
  Coupled excitation in the
  Charge Channel $N(q,\omega)$ or (q,t)

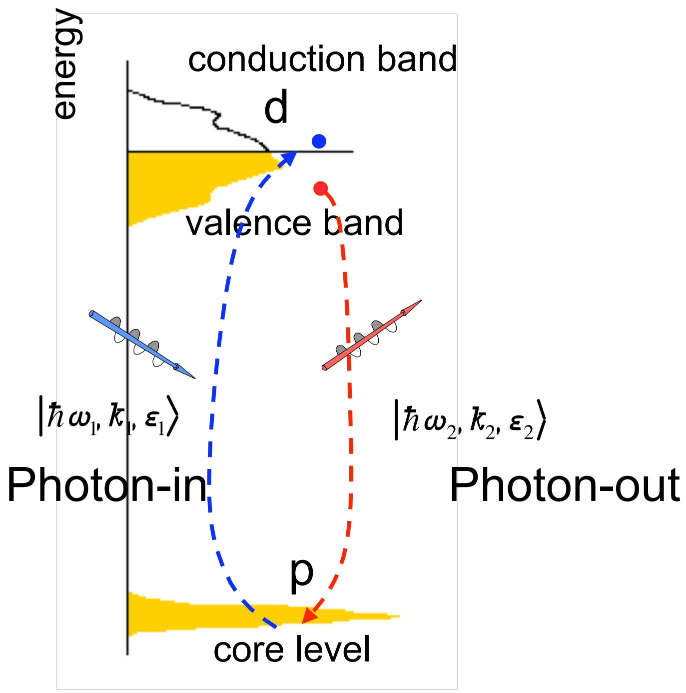
?

Ultrafast Measurements:

- separate correlated phenomena in the time domain

- direct observations of the underlying correlations as they develop

Resonant Inelastic soft X-ray Scattering (*Raman* Spectroscopy with finite q)



Energy loss: $\omega=\omega_2-\omega_1$

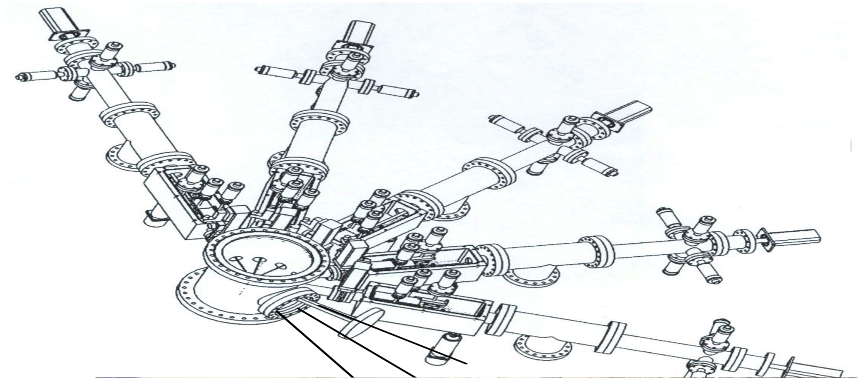
Momentum transfer: $q=k_2-k_1$

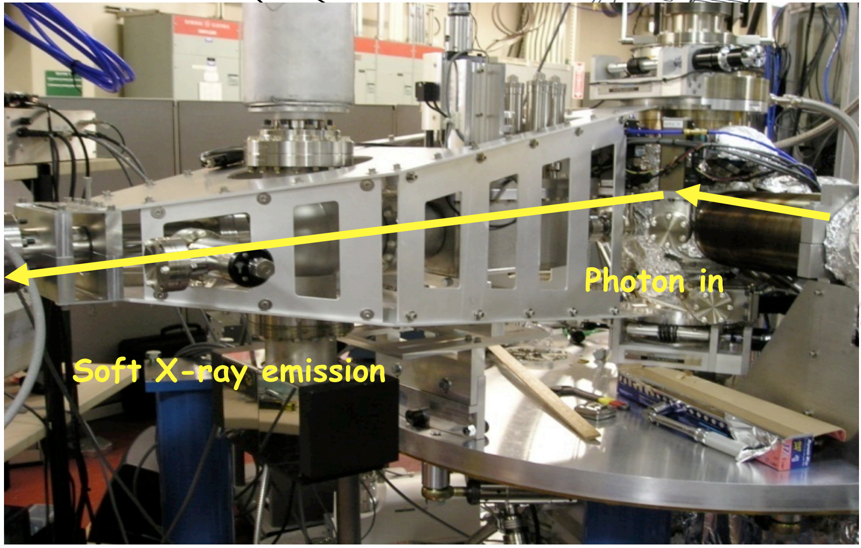
Resonance: $\omega_1 \sim \omega_{edge}$

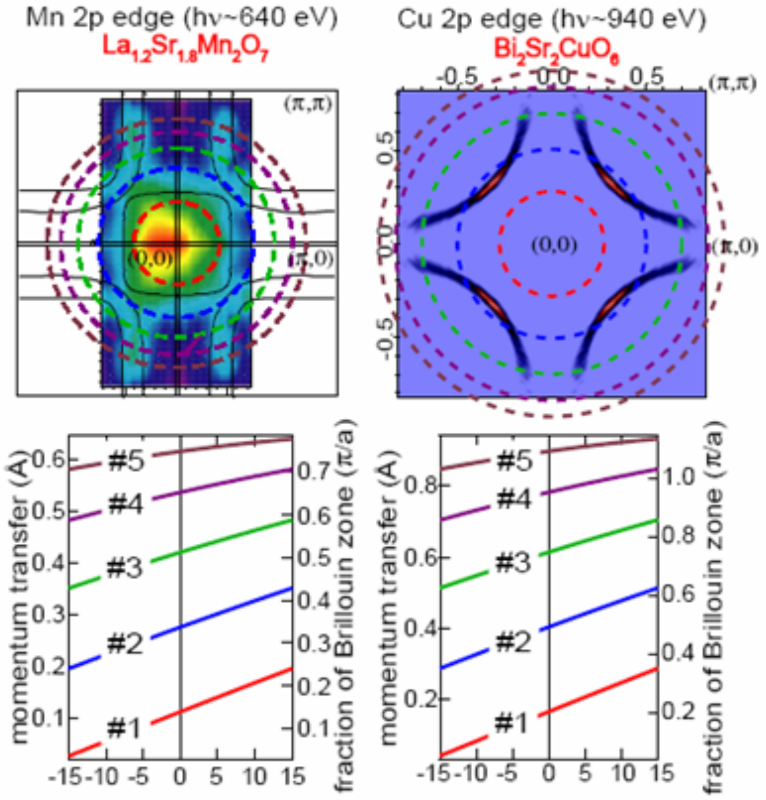
Why???

- ➢Can be applied in the presence of **magnetic/electric field**
- ➢**Bulk sensitive** probe for studying unoccupied electronic states
- ➢Optically forbidden **d-d** excitation
- ➢Finite **q** transfer allows one to study indirect Mott gap
- ➢Couples to **charge density** directly (Neutrons couples to spin).
- ➢Energy Resolution **not** limited by the **core hole lifetime**: achieve k_BT resolution

Momentum-Resolved Soft X-ray Inelastic Scattering





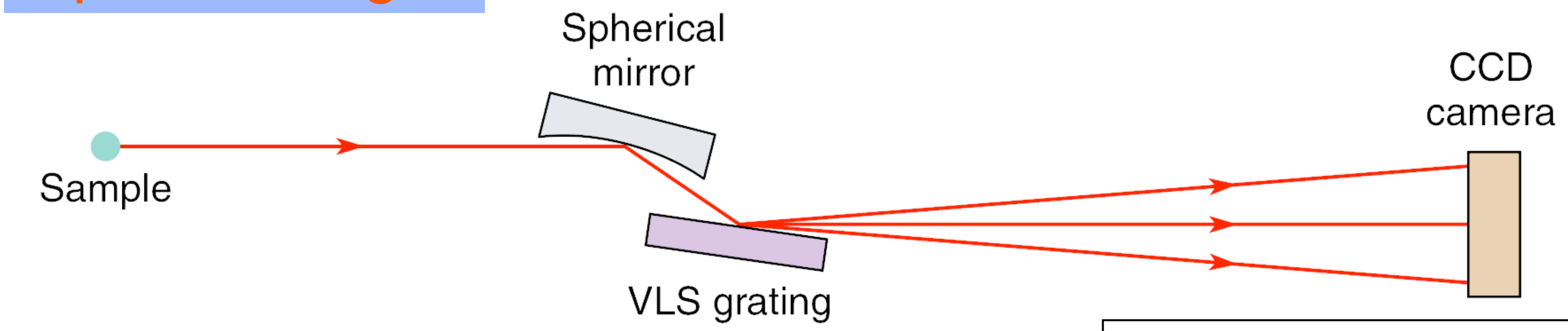


By combining the rotation of chamber and 5 mounting ports, one is able to perform momentum-resolved RIXS;

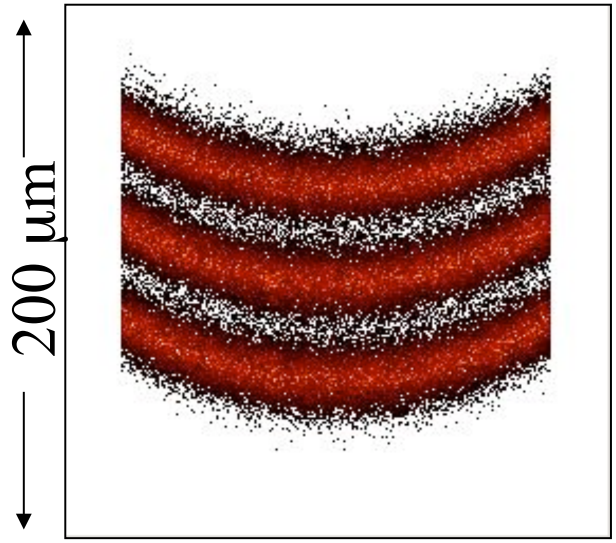
Need Resolving Power ~ 30,000-100,000 @ 1 keV QERLIN !!

meV Resolution VLS Spectrograph for MERLIN Beamline

Optical Design



Ray Traces



hν = 49 eV ± 5meV

- Calculated/measured Resolution
  3 meV (high efficiency)
- Overall length = 2 meters.
- Spectrograph for Merlin beamline

(completed and tested in 2007)

Possible experiments

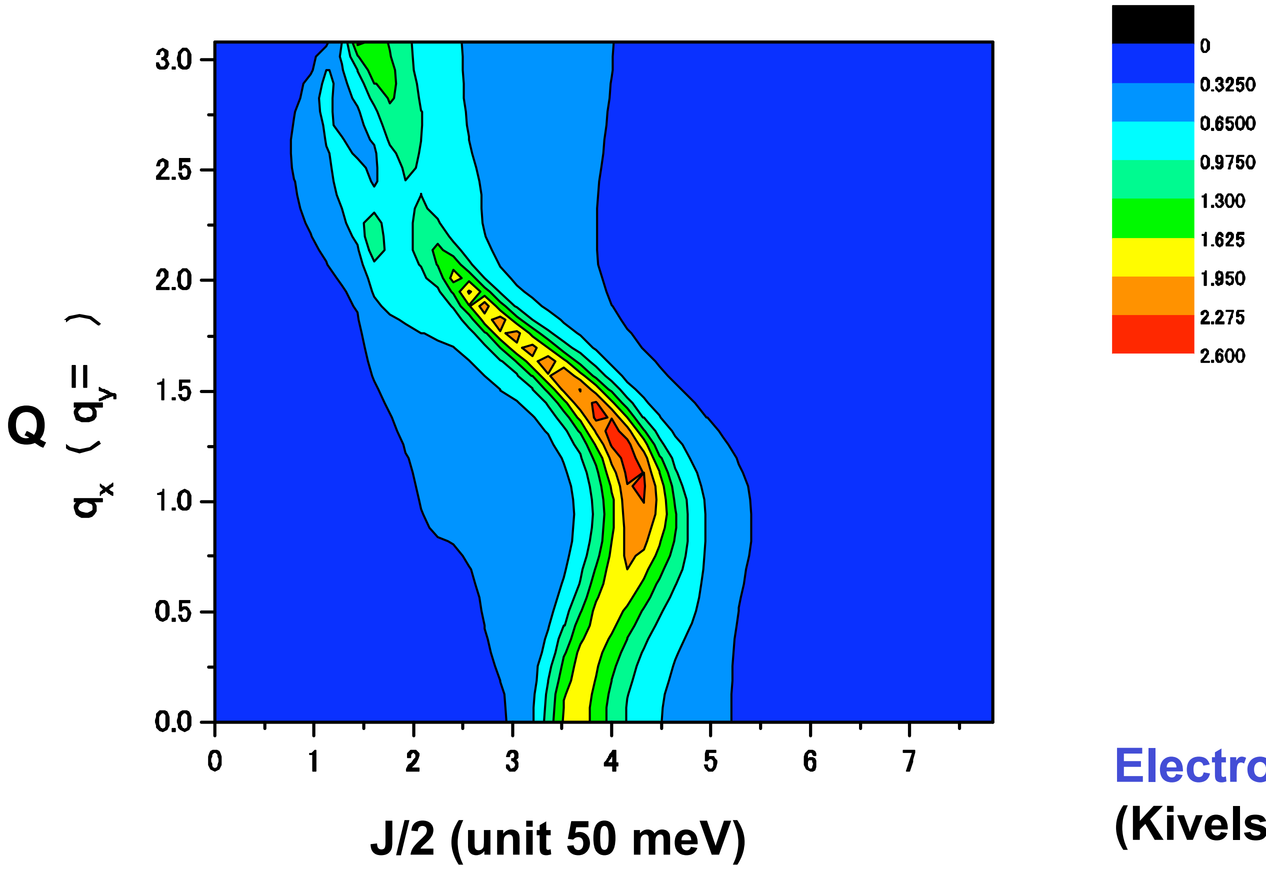
—

Collective Modes in

- *d*-wave Superconductors
- Manganites

Collective Charge modes in d-wave Superconductors

X-ray form factor for a novel collective charge mode predicted in gauge theories (RVB Gauge theory, P.A. Lee (2002))



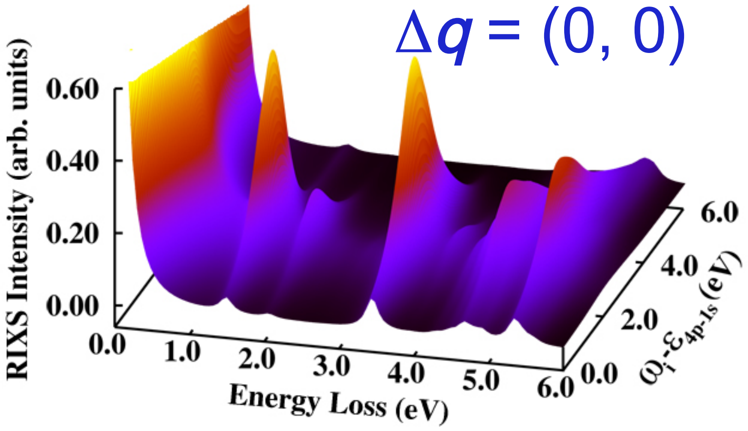
Electronic liquid crystal modes

(Kivelson, Emery)

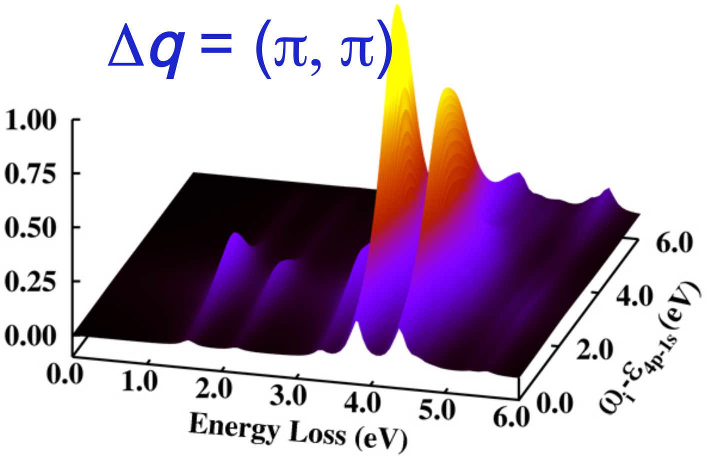
q-Dependent Energy Loss

Theory - T. P. Devereaux

Cu K edge RIXS



$\Delta q = (0, 0)$

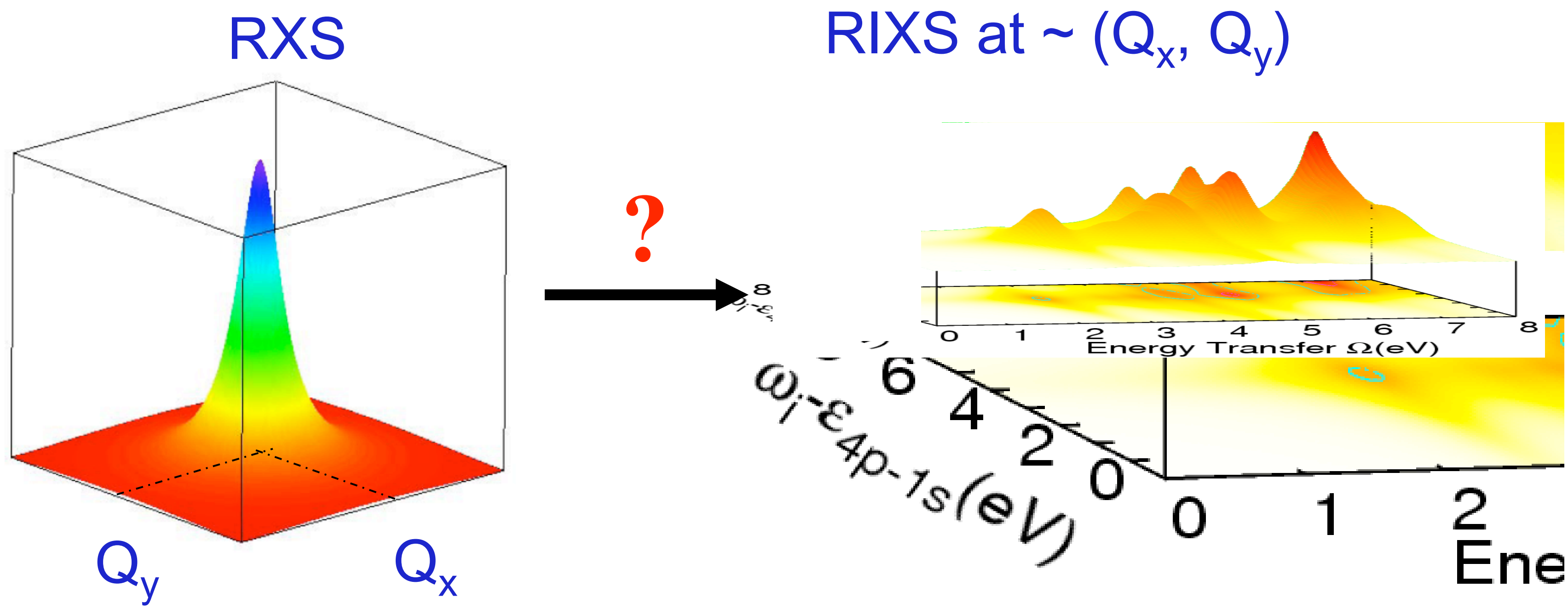


$\Delta q = (\pi, \pi)$

$$I(\omega_i,\Omega=\omega_i-\omega_f)\propto\sum_f\left|\sum_i\sum_{4p}\frac{\langle\psi_f|\sum_l p^\dagger_{4p}s_l\ e^{i\mathbf{q}_{\mathrm{out}}\cdot\mathbf{r}_\mathbf{l}}|\psi_{ci}\rangle\langle\psi_{ci}|\sum_j p_{4p}s^\dagger_j\ e^{i\mathbf{q}_{\mathrm{in}}\cdot\mathbf{r}_\mathbf{j}}|\psi_0\rangle}{E_{ci}+\epsilon_{4p-1s}-E_0-\hbar\omega_i-i\Gamma_1}\right|^2\times\delta\left(E_f-E_i-\hbar\Omega\right)$$

Both D*q* dependence and (q_{in} q_{out}) dependence can provide much information about the wave function projection onto the intermediate states.

Energy Loss Feature at the Q

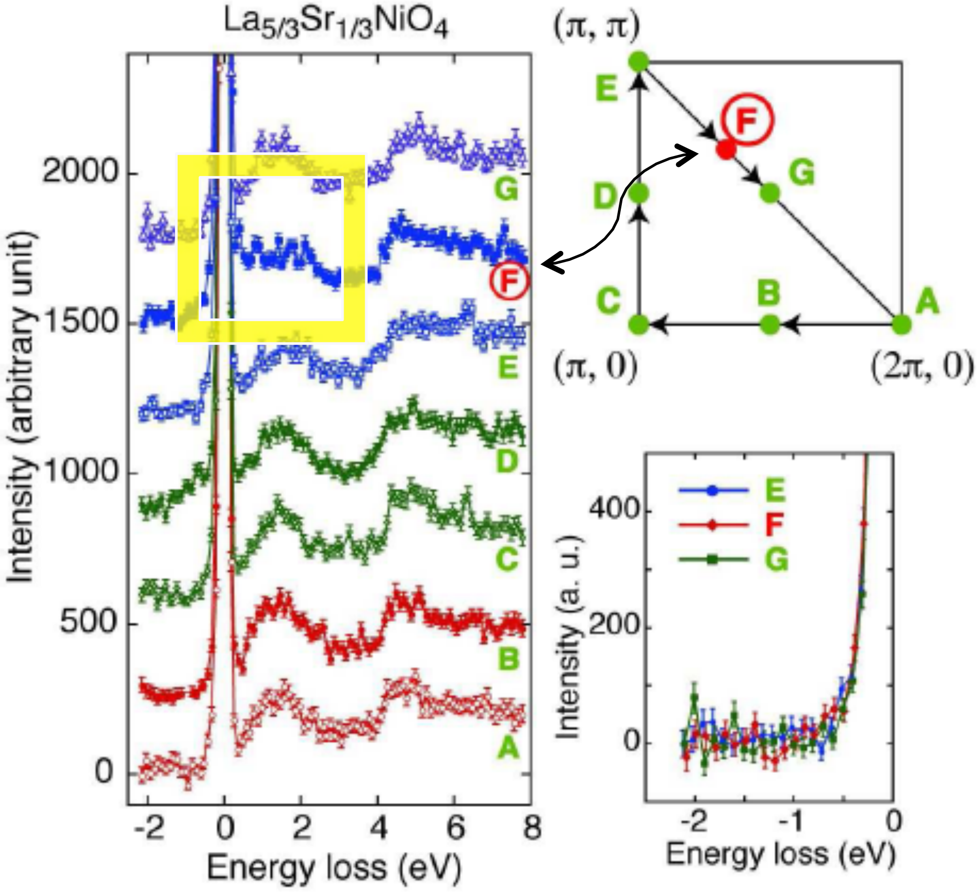


RXS

RIXS at ~ (Q_x, Q_y)

- Whether there is any energy loss features at ordering vector?
- Energy features at Q proximity to the charge ordering in the phase diagram?

RIXS of LSNiO



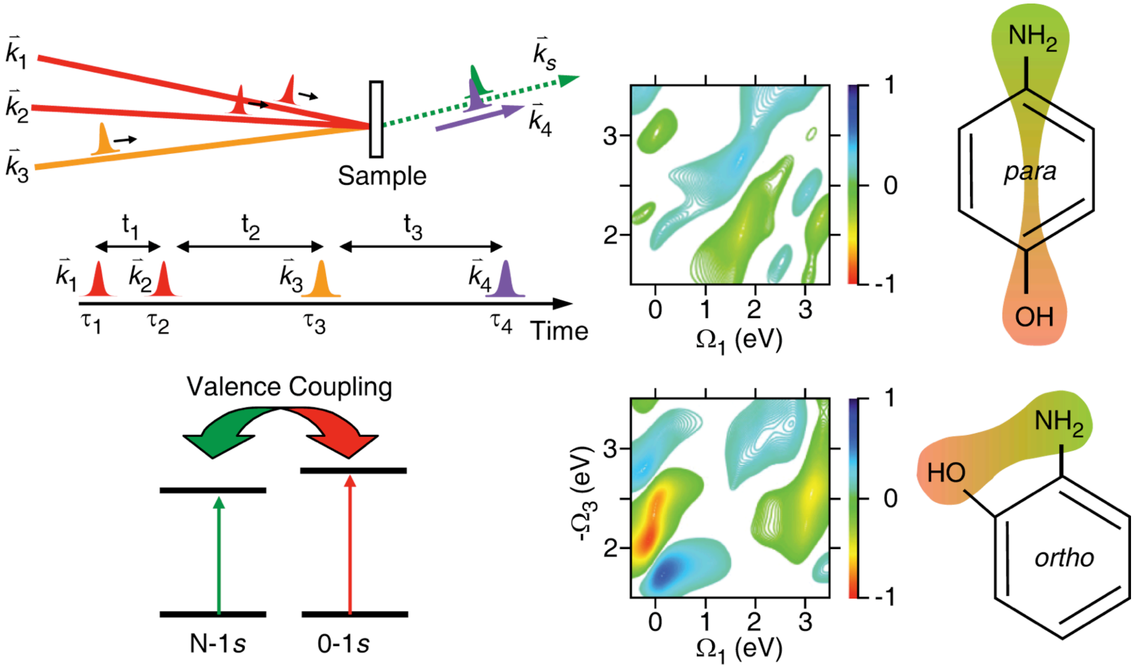
1. $La_{2-x}Sr_xNiO_4$, x=1/3 a special doping where $Q_{SDW}=Q_{CDW}$ (point F).
2. Only at F, there is extra energy loss feature connected with the elastic peak (at the energy range of 0 to 1 eV). At other momentum positions, it is a dip at similar energy range.

There are some intriguing energy loss features at the ordering wave vector.

Resolution ~ 150 meV
Spring8

Wakimoto et al, arXiv: 0806.3302 (2008)

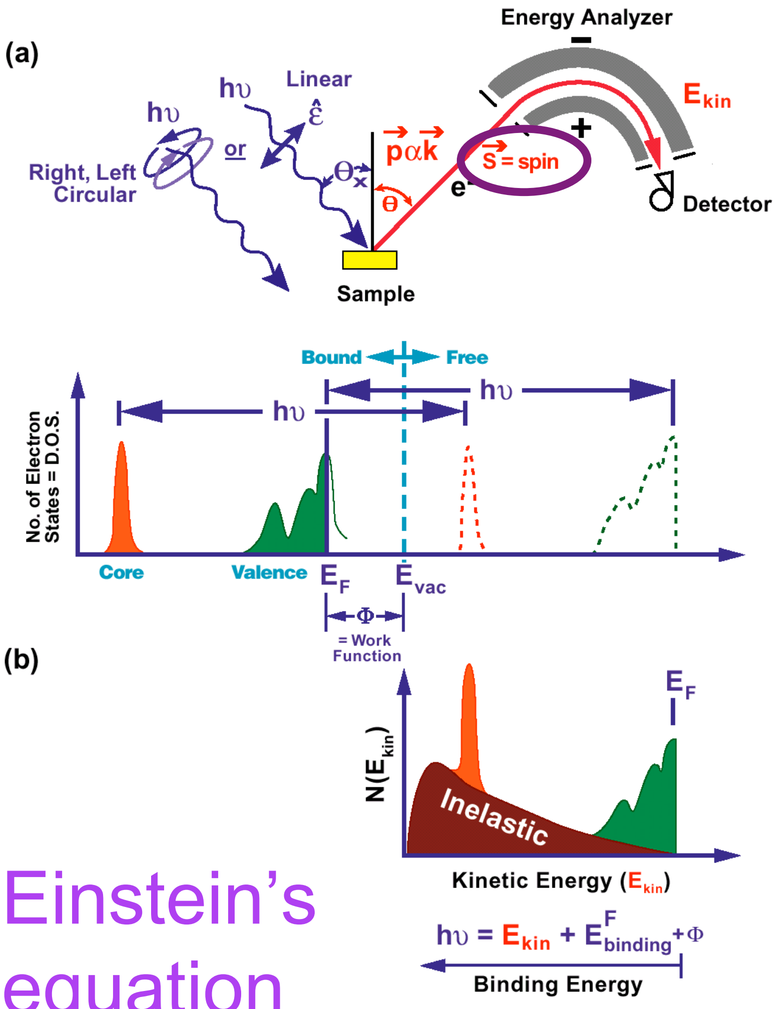
The Ultimate Experiment: Multidimensional Spectroscopy



9-2008
8777A14

Left: Proposed four-wave mixing of ultrashort x-ray pulses resonant with the O-1*s* and N-1*s* levels; Middle: theoretically predicted two-dimensional spectra the lower of which exhibits the coupling of excitations on the oxygen with those of the nitrogen in para and ortho-aminophenol molecules at right. [Source: S. Mukamel]

Photoelectron Spectroscopy



ag.zh/photospectros1/7-97

Einstein's equation

X-ray Spectroscopy of Condensed Matter

Quantum Number Selectivity:

- ✓ Absorption

$$\omega\ \varepsilon_2 \Rightarrow \Delta E = E_f - E_\iota$$

Study *unoccupied* states

- ✓ Angle-integrated photoemission

$$N(E,\hbar\omega) \Rightarrow E_f, E_\iota$$

Study *occupied* states

- ✓ Angle-resolved photoemission

(also inelastic scattering)

$$N(E,\hbar\omega,\theta,\varphi) \Rightarrow E_f, E_\iota, \vec{\kappa}$$

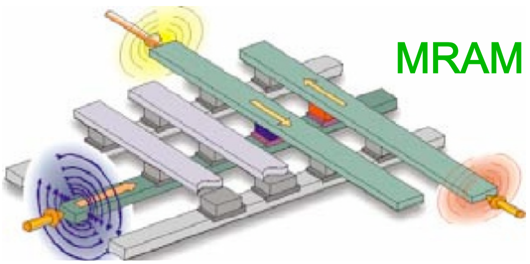
!!! Spin-polarized photoemission

$$(N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow) \Rightarrow E_f, E_\iota, \vec{\kappa}, \enclose{circle}{\vec{\sigma}}$$

Femto-sec control of nanoscale electron & spin distribution

Present Status:

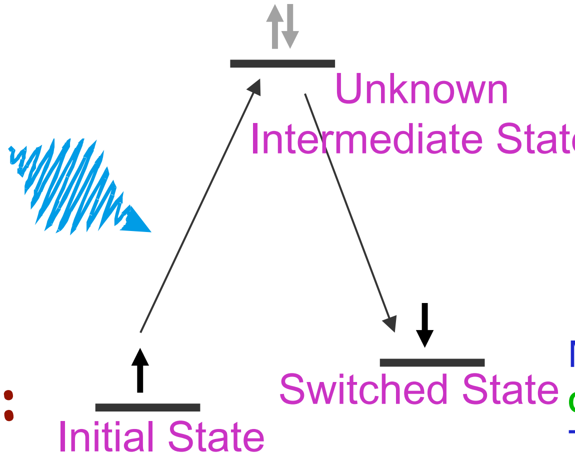
Coherent magnetization switching runs into a ‘speed limit‘ ~2ps; decoherence determined by angular momentum dissipation

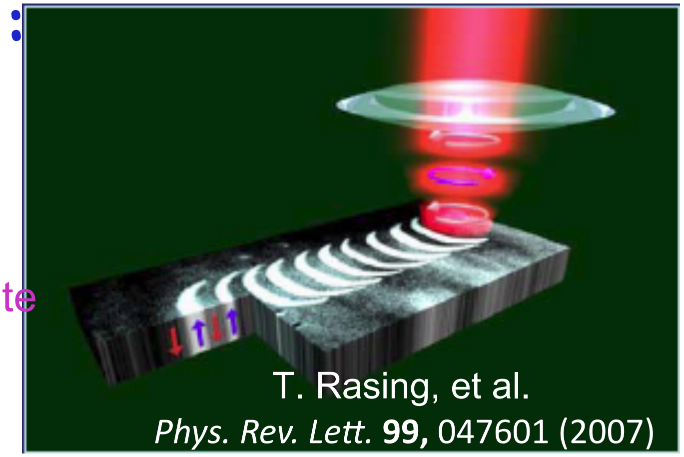


Future prospects:

Control materials function by:

- spin currents
- polarized light
- Thz electrical fields





T. Rasing, et al.
Phys. Rev. Lett. **99,** 047601 (2007)

Magnetic domain pattern (top) written by circularly polarized optical laser pulses. The magnetization reversal is thought to proceed by a coherently excited intermediate state (left)

challenge:

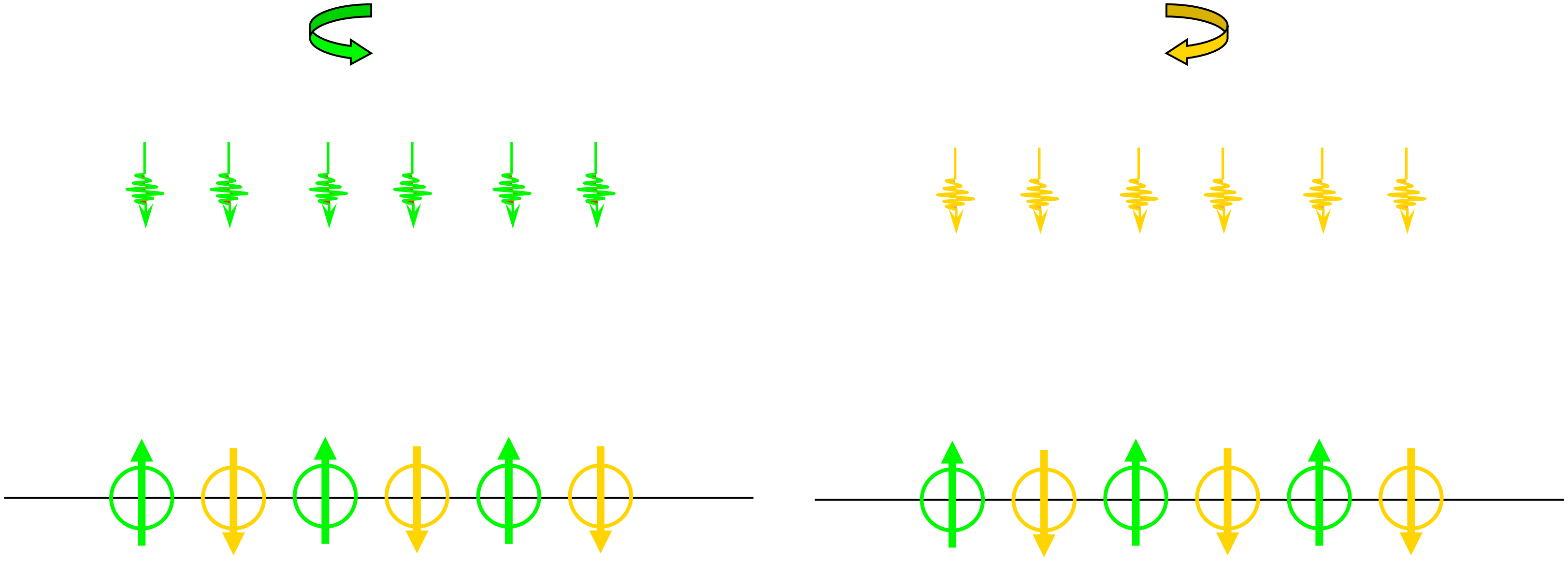
identify nature (charge, spin, orbital), temporal evolution and coherence of excited state

Courtesy: BES workshop on New Era Science

Photoemission with circularly polarized light and spin detection

Selective excitations

(use of elliptically polarizing undulator)

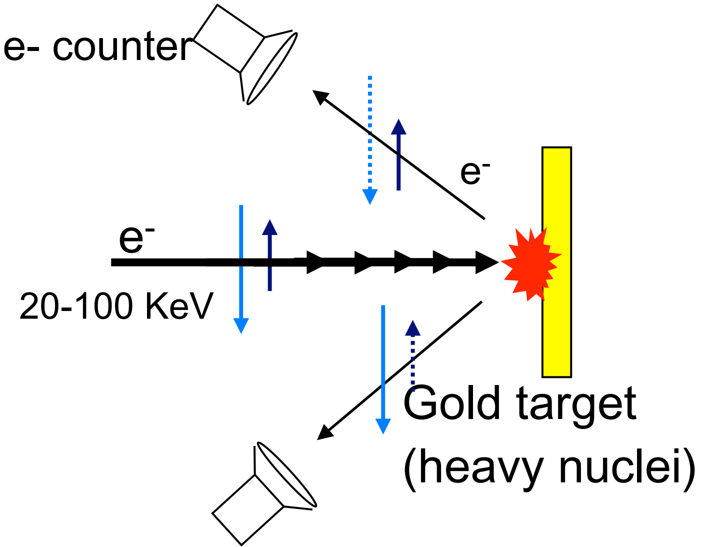


Spin detection (two schemes)

Mott Detector

Spin-orbit interaction

Hint = L · S



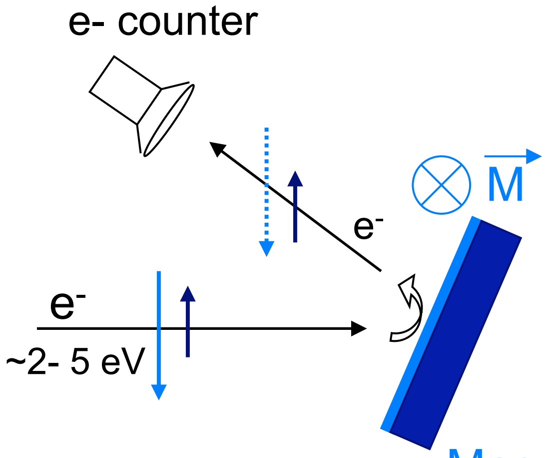
D.T. Pierce et al. 1988 +….

FOM ≤ 10^{-4}

Exchange scattering interaction

Reflectivity contains a term:

α P · M



Magnetized thin film

(e.g.,Co/W(110))

R. Bertacco et al. 2001

x 100 →

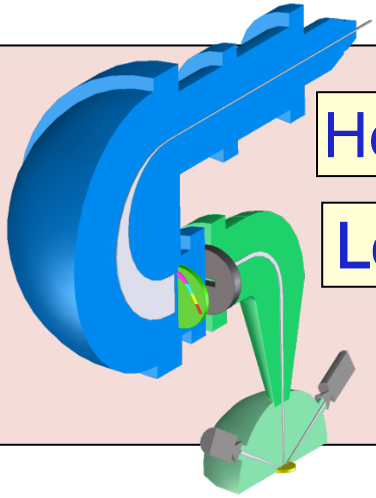
FOM ~ 10^{-2}

Exchange scattering spin detection with TOF analyzer
>1000 times more efficient than Mott detector with Scienta analyzer

Graf, Schmid, Jozwiak, Hussain, Lanzara et al, PRB, 71, 144429 (2005)

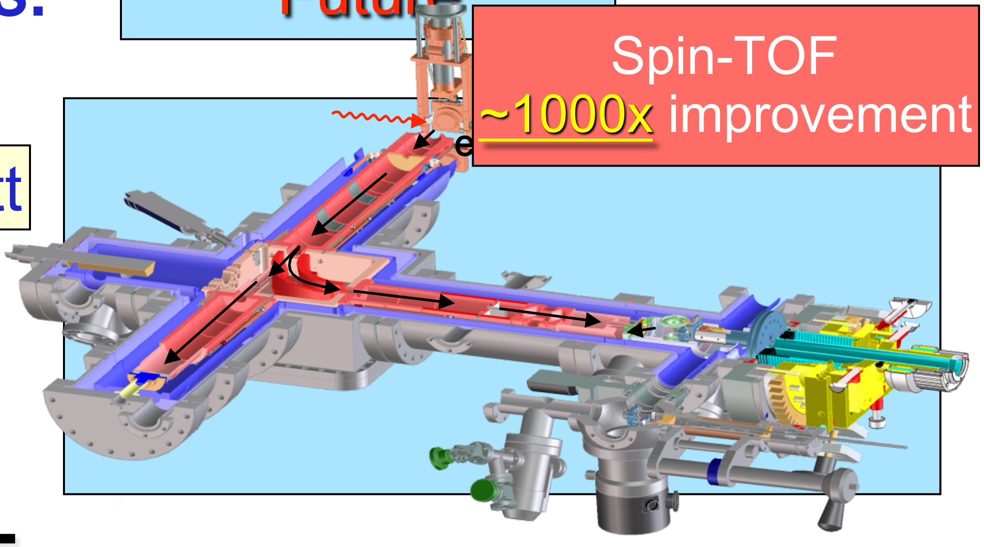
Spin-ARPES w/ spin-TOF analyzer

Present vs. Future



Hemisphere + Mott

Low Efficiency



Spin-TOF

~1000x improvement

=

Spin Analysis

Spin-Orbit Scattering (Mott detector)

Exchange Scattering

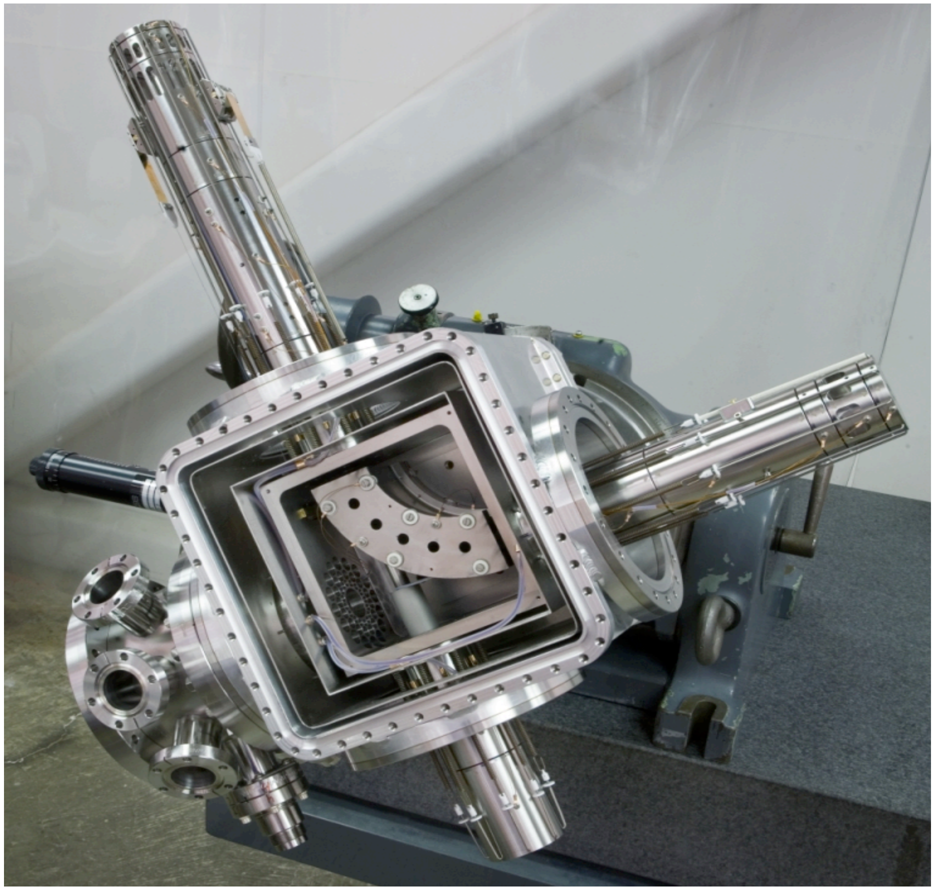
+

Energy Analysis

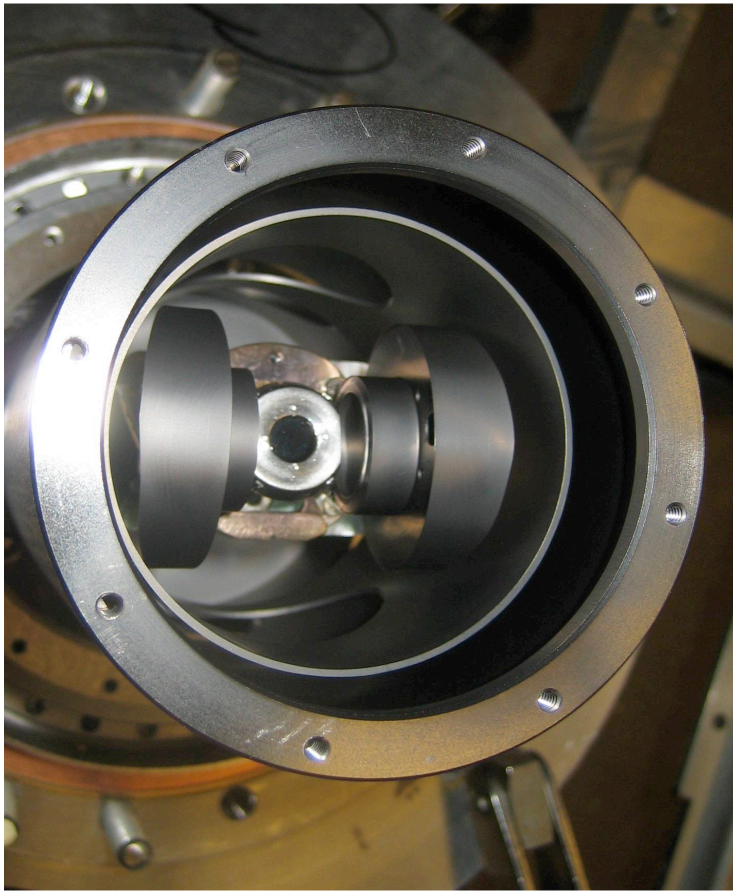
Hemispherical Analyzer

Time-of-Flight Analyzer

SPIN TOF

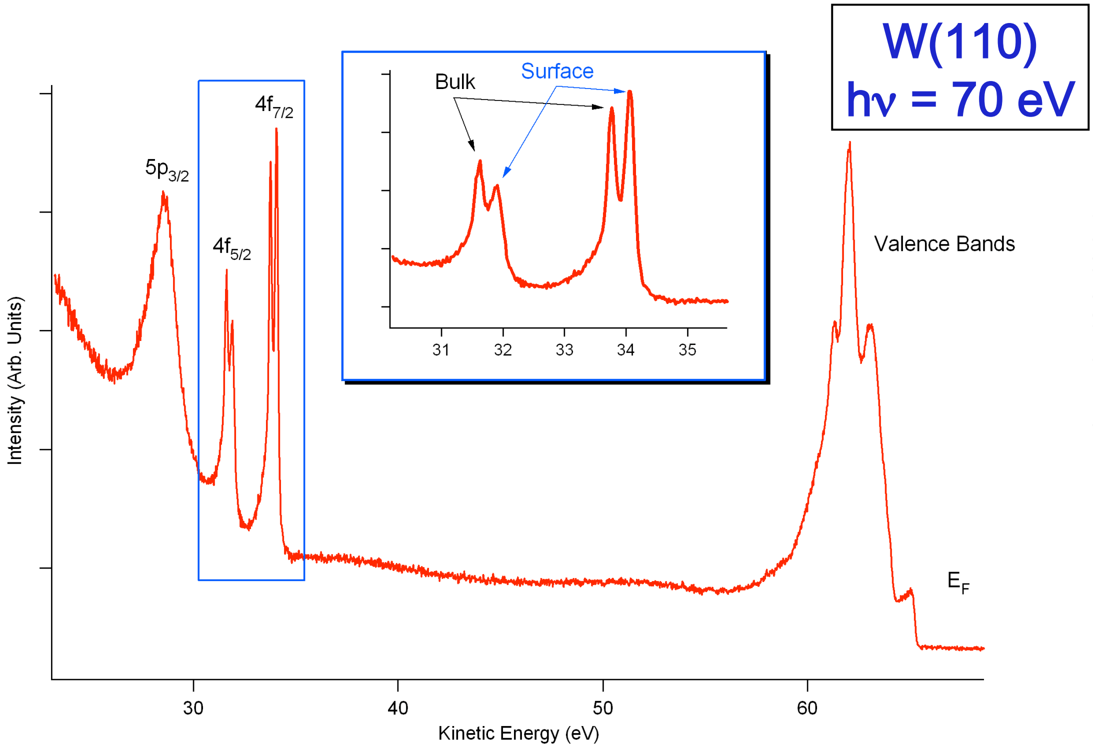


Precision Lens system
>2,000 parts!

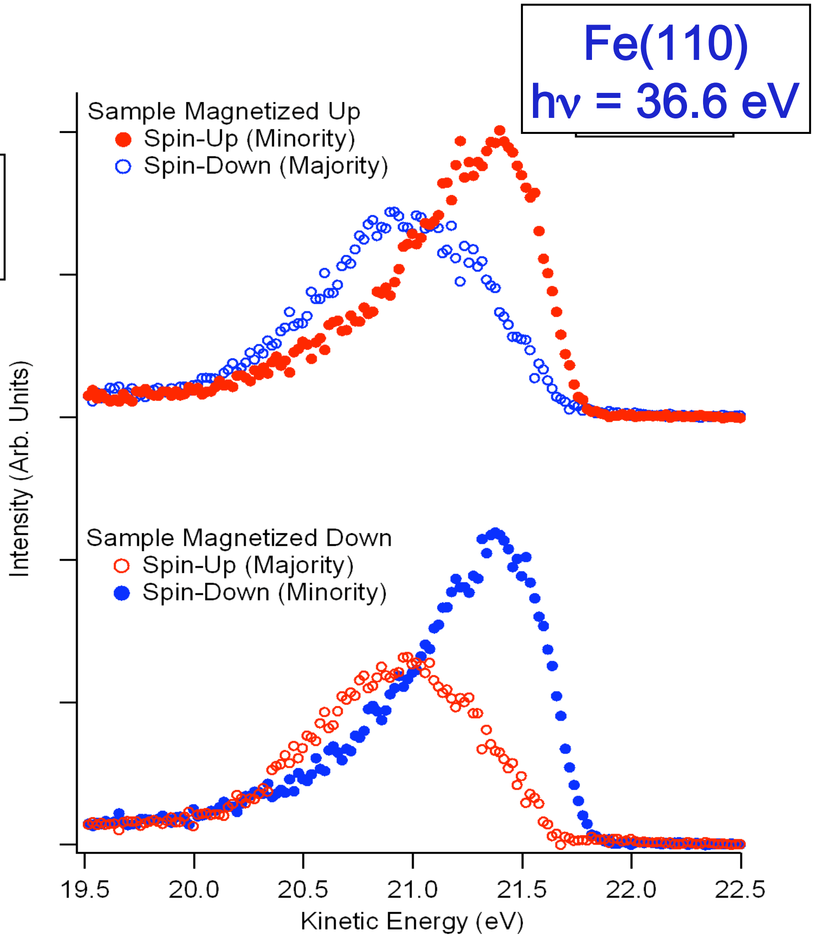


Spin Polarimeter:
target and coils

Calibrating Spin-TOF Analyzer with ALS 2-bunch

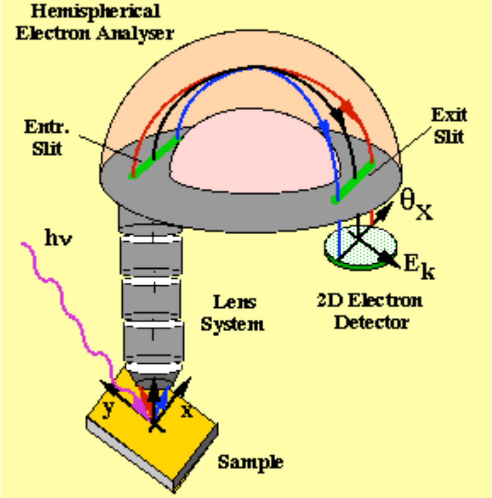


Straight path: Spin-integrated



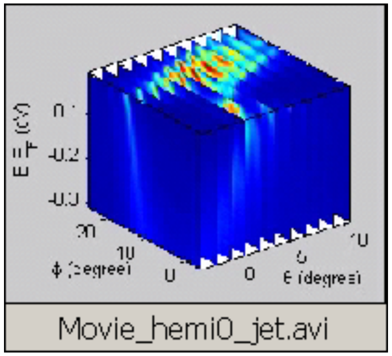
90° path: Spin-resolved

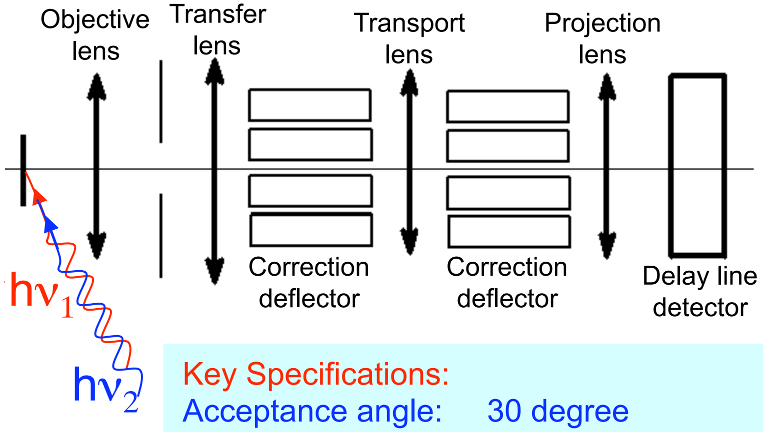
Time-Resolved Photoemission
Comparison of the Hemispherical Analyzer and the TOF Analyzer



Currently used Hemispherical Analyzer (2D detection)

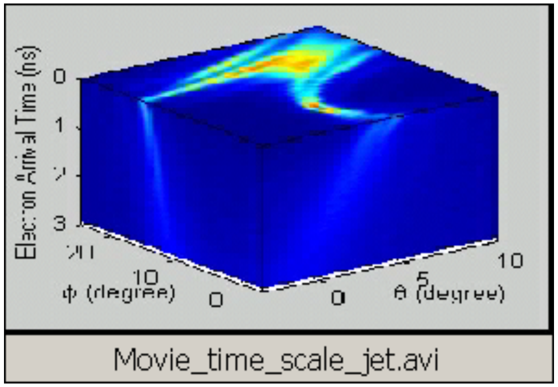
(Bi2212 Bi-layer splitting)





TOF Analyzer Proposed (3D detection)

(Bi2212 Bi-layer splitting)



Key Specifications:

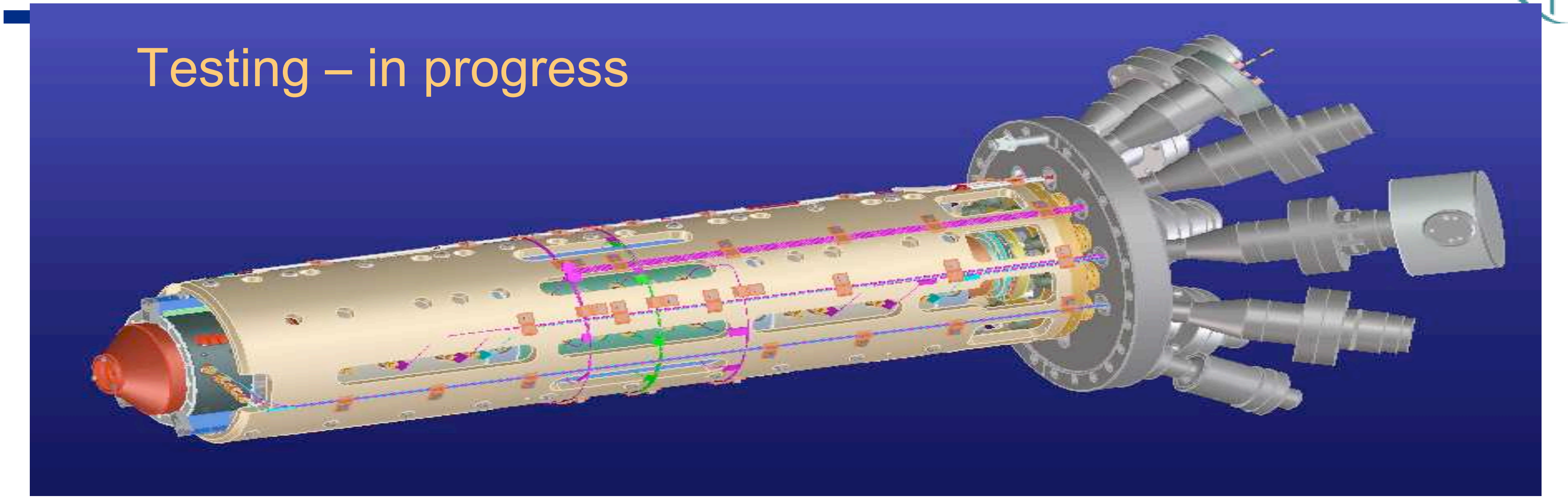
Acceptance angle:	30 degree
Energy resolution:	<=2meV (5eV Pass Energy)
Angular resolution:	<=0.1 degree (~2mrad)

(comparable to Scienta analyzer but 100 times faster)

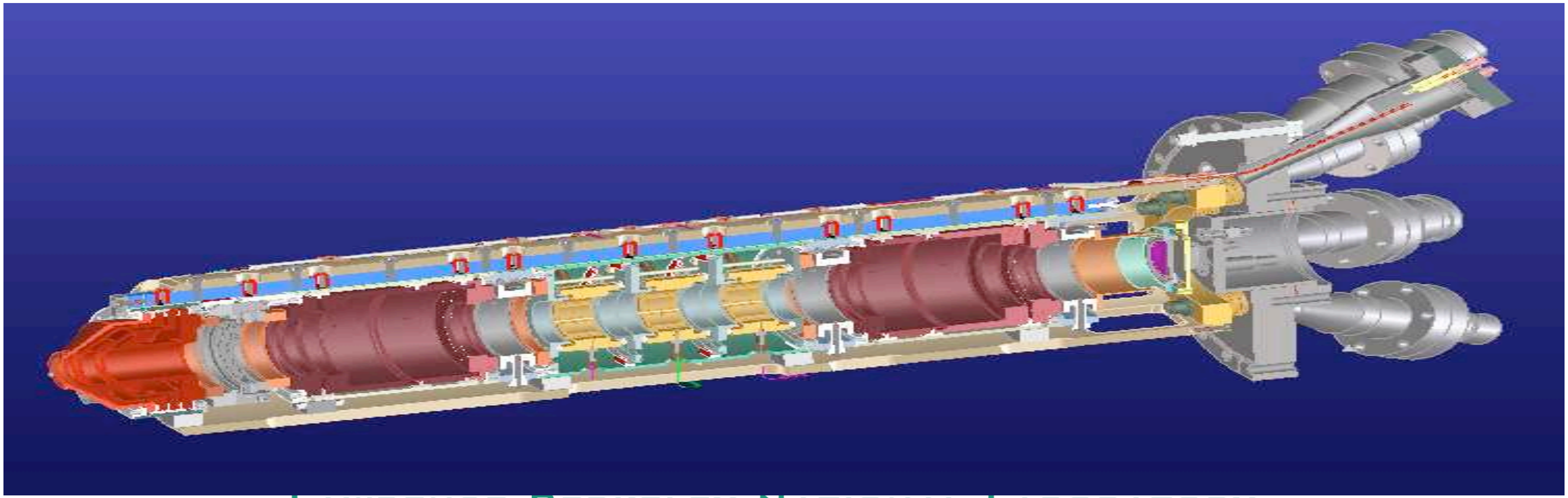
Commissioning– in progress

Next step: nano-ARPES with TOF analyzer

TOF 3D ARPES Analyzer

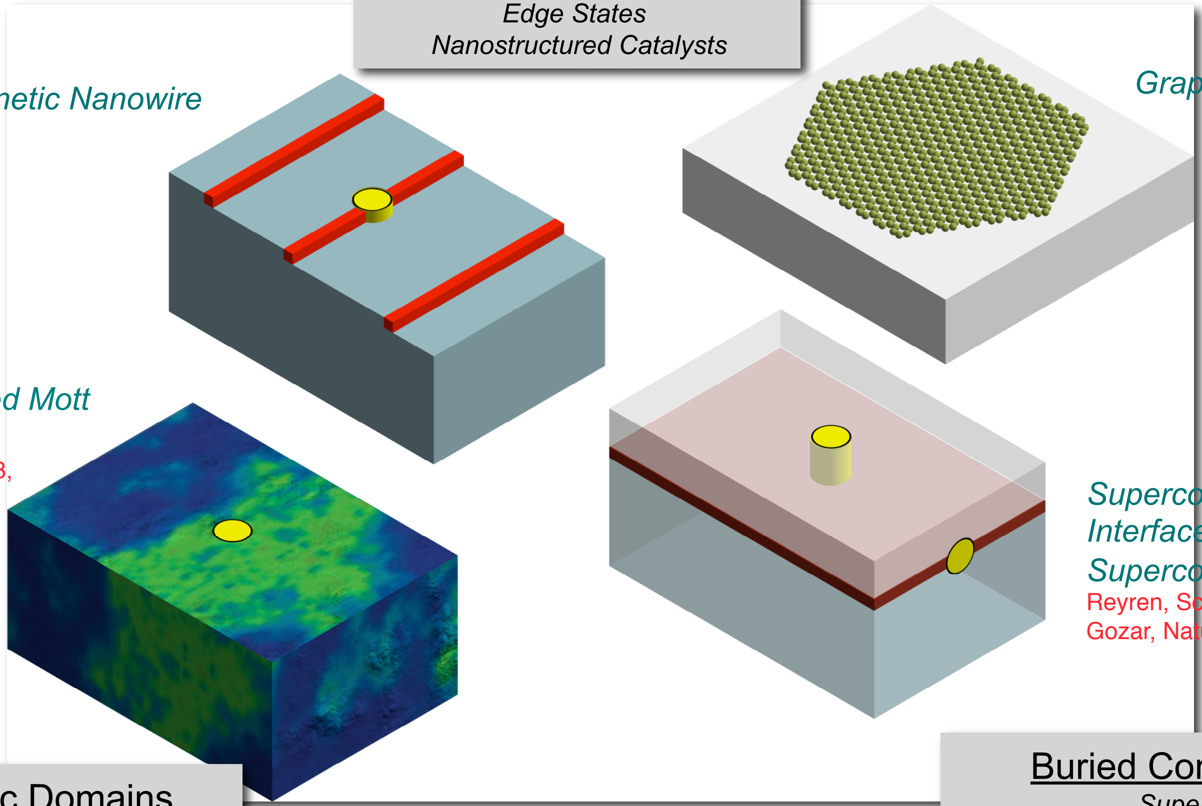


Testing – in progress



NanoARPES: A Tool For Nanoscale Electronic Structure Characterization

Simultaneous Spatial + Energy + Momentum Resolution for the First Time



Individual NanoObjects

Atomic Wires at Step Edges
Quantum Dots
Edge States
Nanostructured Catalysts

Magnetic Nanowire

Graphene Nanocrystal

Spatially-Resolved Mott Transition in VO_2

Qazilbash, Science,318, 1750, 2007

Superconductivity at the Interface Between Non-Superconductors

Reyren, Science, 317,1196, 2007.
Gozar, Nature, 455, 782, 2008.

Electronic Domains

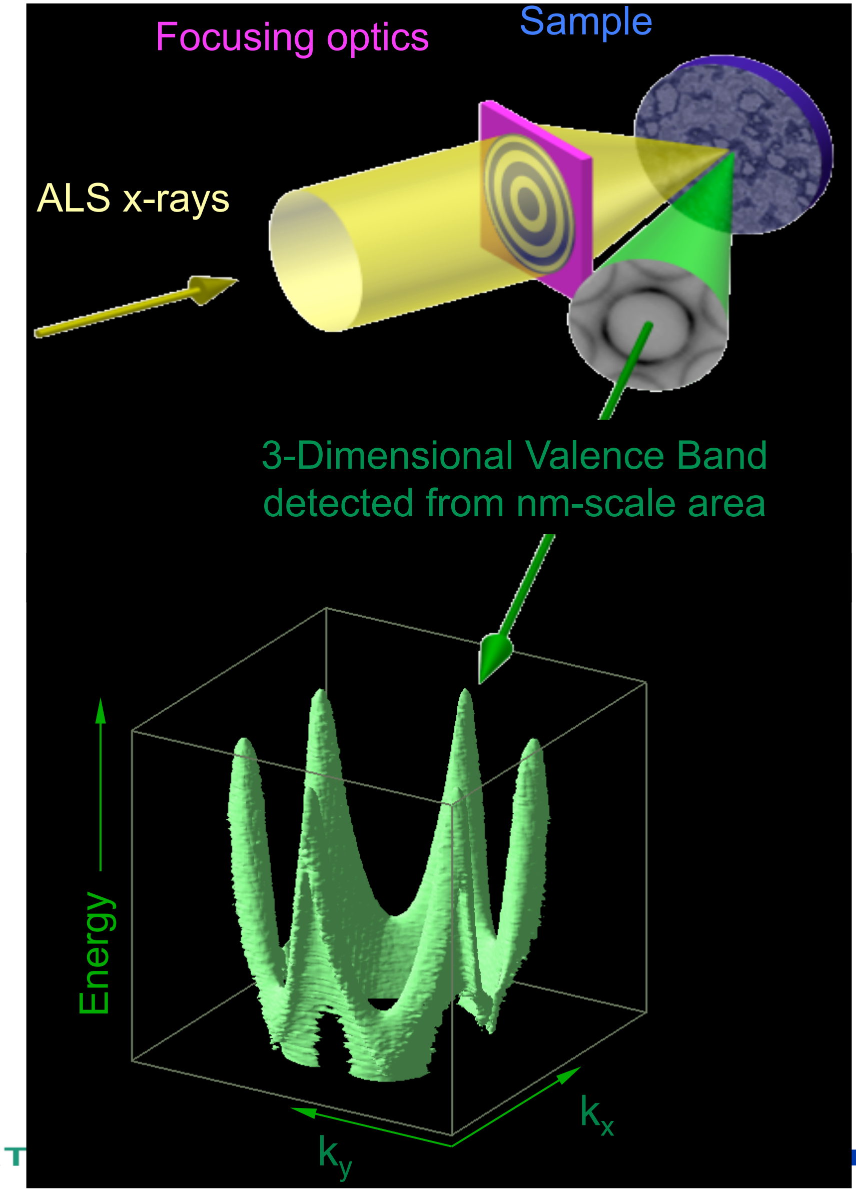
Metal-Insulator Transition
High-T_c Superconductivity
Collosal Magnetoresistance

Buried Complex Materials

Superconductivity
Solar Energy
Novel Electronics
Two-Dimensional Electron Gases

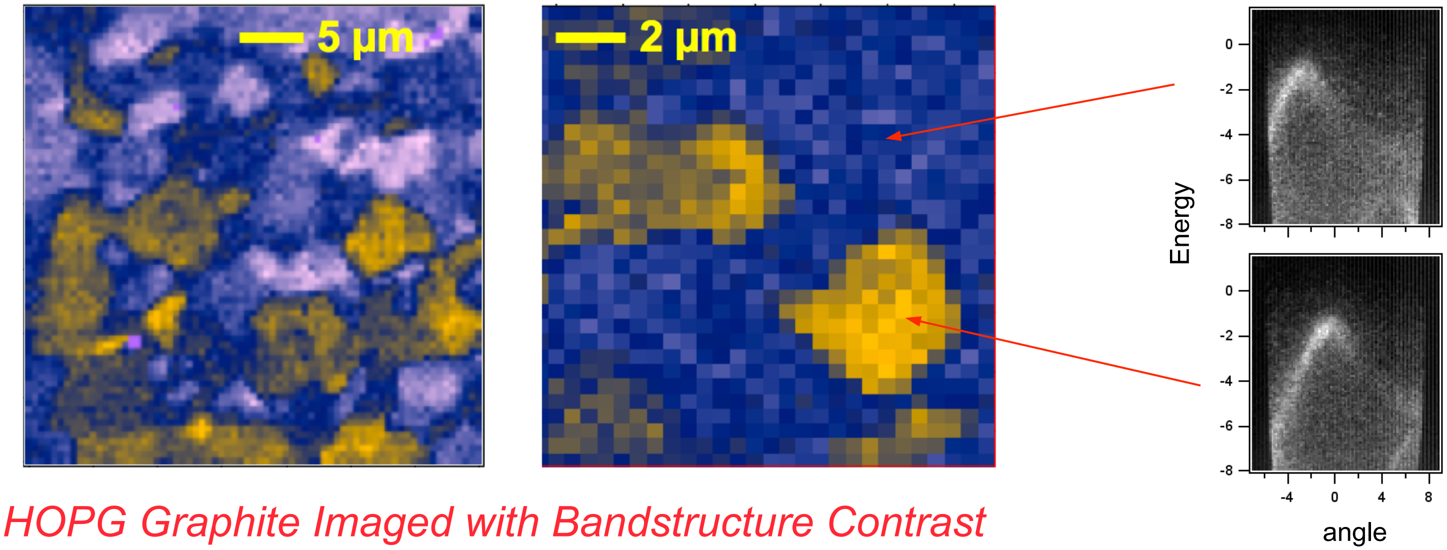
NanoARPES: A New Microscope for Electronic Structure Measurements

- *Why ARPES?*
  - The only general method for bandstructure determination of bulk materials, surfaces, with combined chemical, structural, and magnetic sensitivity.
- *Why nanoARPES?*
  - Small Samples
  - Samples in device conditions
  - Electronic segregation
  - Complex Thin Films
- *Near-term capabilities*
  - Soft-xray instrument with ~50 nm spatial resolution and 10 meV energy resolution
- *Future Storage Ring: <10 nm*
  - *highest rep rate possible, 1-10 MHz*
  - *photon energy 20-2000 eV*
  - *highest brightness*
  - *narrow bandwidth <10 meV*



NanoARPES: First Results @ ALS

First Electronic Bandstructure Determination From a Polycrystalline Material

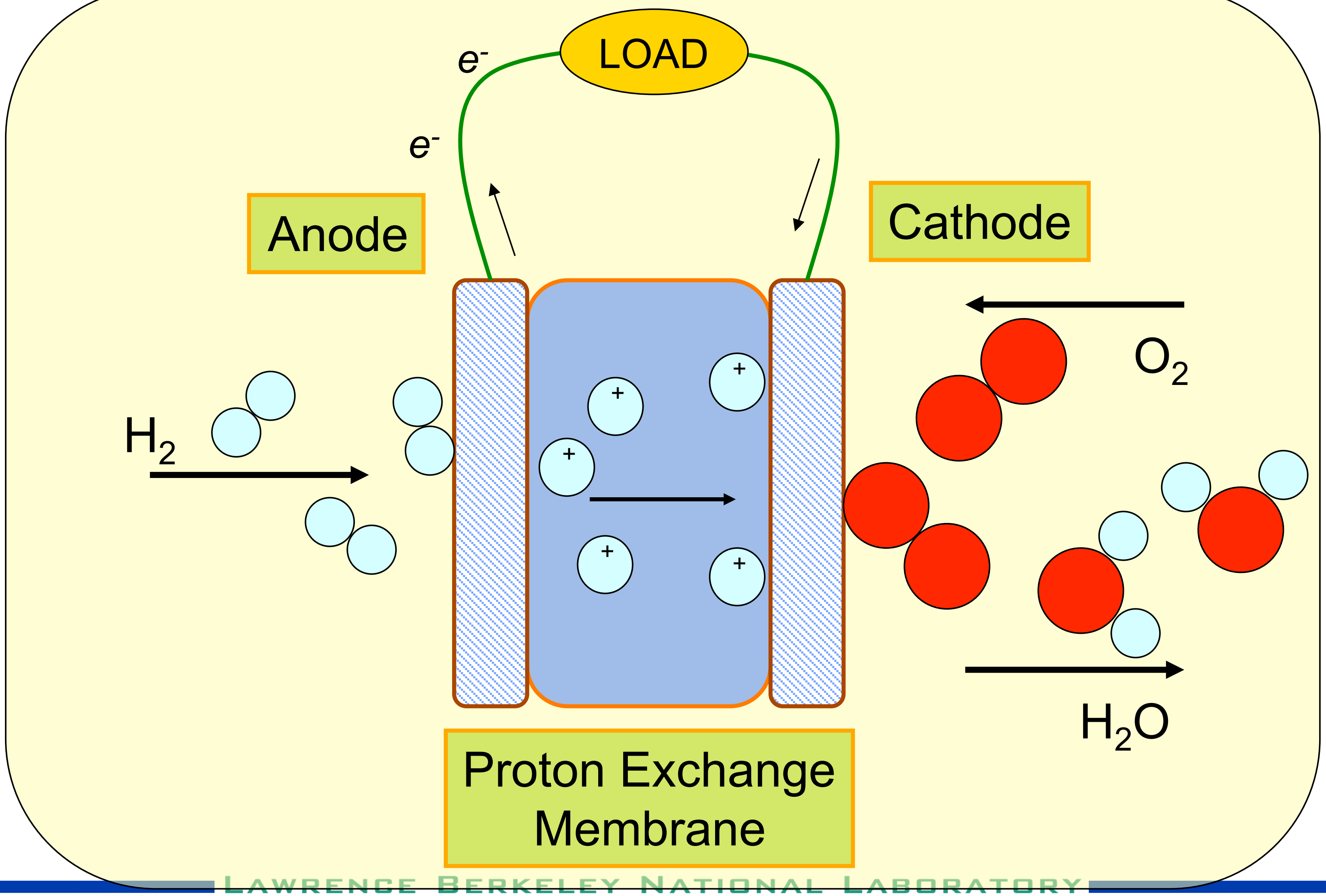


HOPG Graphite Imaged with Bandstructure Contrast

What are new opportunities with core level photoemission ?

In-Situ & ***dynamical*** studies of chemical reactions at surfaces

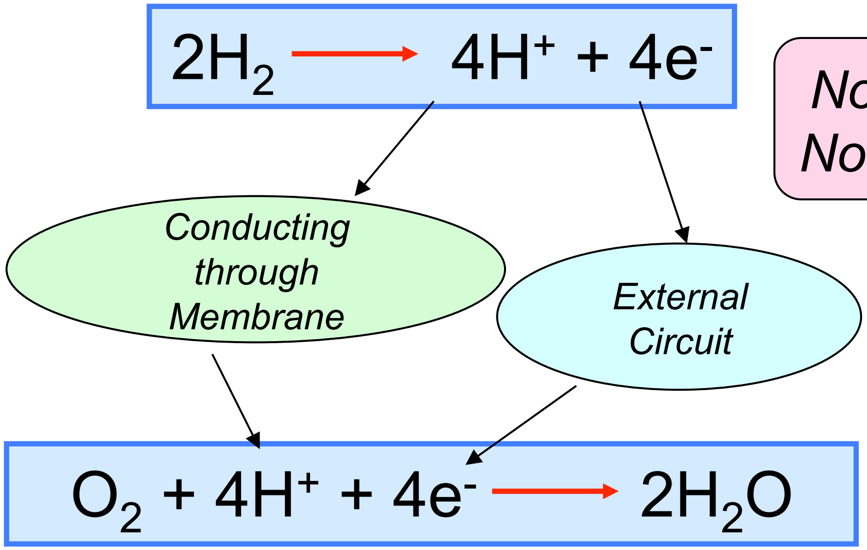
Fuel Cell (101) - Schematic



Proton Exchange Membrane

Anode : Hydrogen oxidation

Hydrogen gas = Hydrogen Ions + Electrons



$2H_2 \rightarrow 4H^+ + 4e^-$

Conducting through Membrane

External Circuit

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Not too weak!
Not too strong!

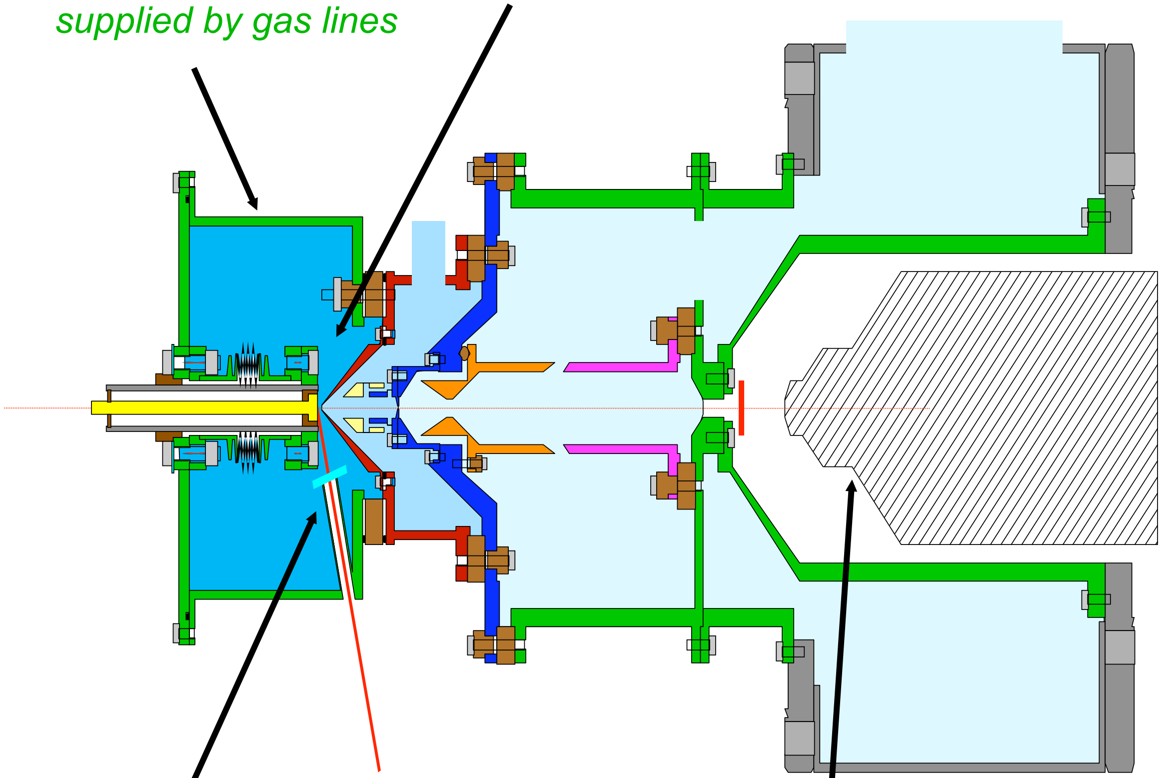
Cathode : Oxygen reduction

Oxygen gas + Protons + Electrons = Water

In both cathode and anode, Pt based catalysts are applied to increase the rate of each chemical reactions. Need better material than presently used Pt.

Cathode : the performance of polymer electrolyte membrane fuel cells is limited by the slow rate of O_2 reduction (ORR) at Cathode, ~5 orders of magnitude slower than H_2 oxidation at Anode

The Schematic Pictures of Electron Optical System of Ambient Pressure X-ray Photoelectron Spectroscopy (XPS)



Experimental cell supplied by gas lines

Sample with Z motion, cold finger and resistive heater

X-rays incident at 15° through a 100 nm Al/or SiN window

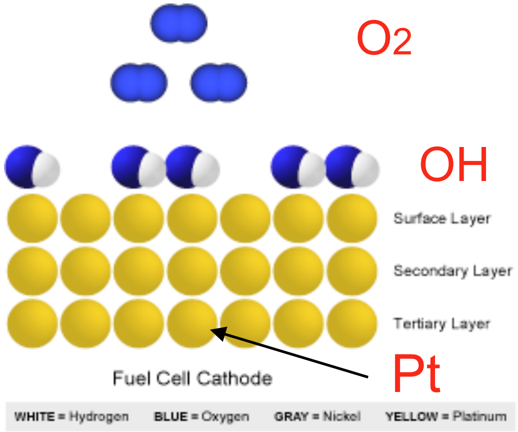
Analyzer lens, pumped independently

HP-PES Differentially Pumped Optics

BL 9.3.2

Ogletree, Bluhm, Lebedev, Fadley, Hussain, Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

80% of All Important Chemical Reactions Take Place on Interfaces



NEWS OF THE WEEK

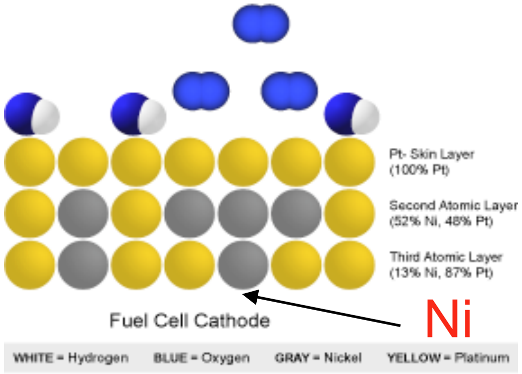
Science AAAS

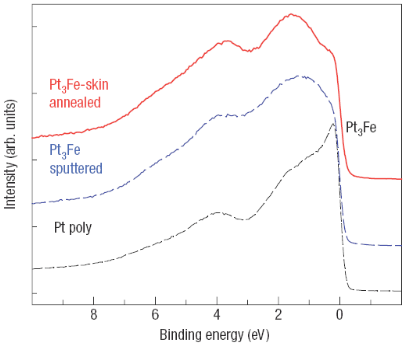
CHEMISTRY

Science 315 Jan 2007

Platinum in Fuel Cells Gets a Helping Hand

The discovery of a unique *platinum-nickel alloy* represents a breakthrough in catalyst research: it is *90 times more active* than state-of-the-art platinum catalysts currently used.





Top: In standard Pt catalysts absorption of oxygen on the surface is hindered by the binding of other molecules, such as OH.

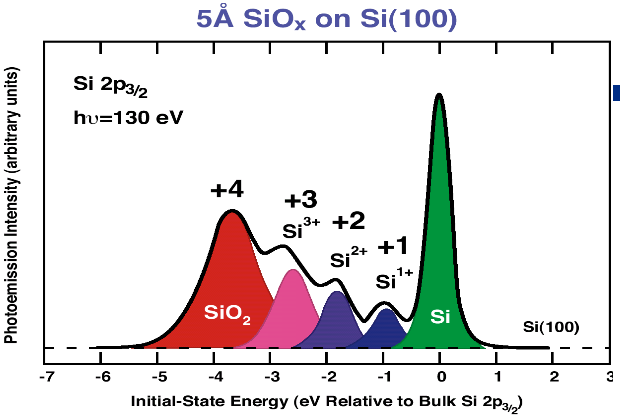
Bottom: In the new material The nickel atoms change the surface properties such that OH cannot bind as well, leaving room for oxygen.

Research team includes: Argonne and Berkeley National Labs, U. South Carolina.

nature materials | VOL 6 | MARCH 2007 |

BL 9.3.2

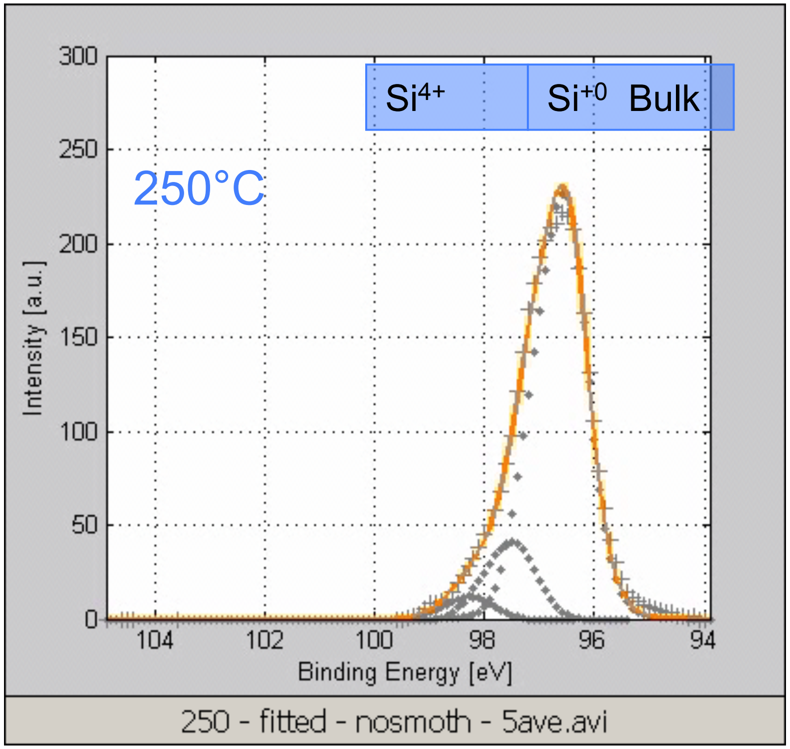
in-situ real-time study of ultra-thin Si gate oxide: Oxidation dynamics



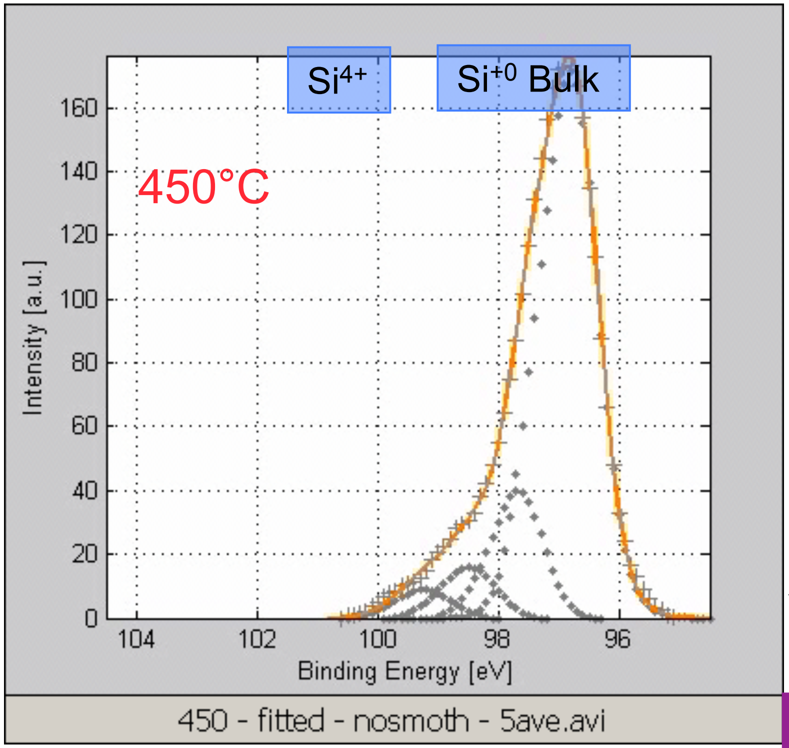
Himpsel PRB 1988

Strong temperature dependence

Excitation energy	350 eV
Acquisition	1 spectrum / 8 sec



250 - fitted - nosmoth - 5ave.avi



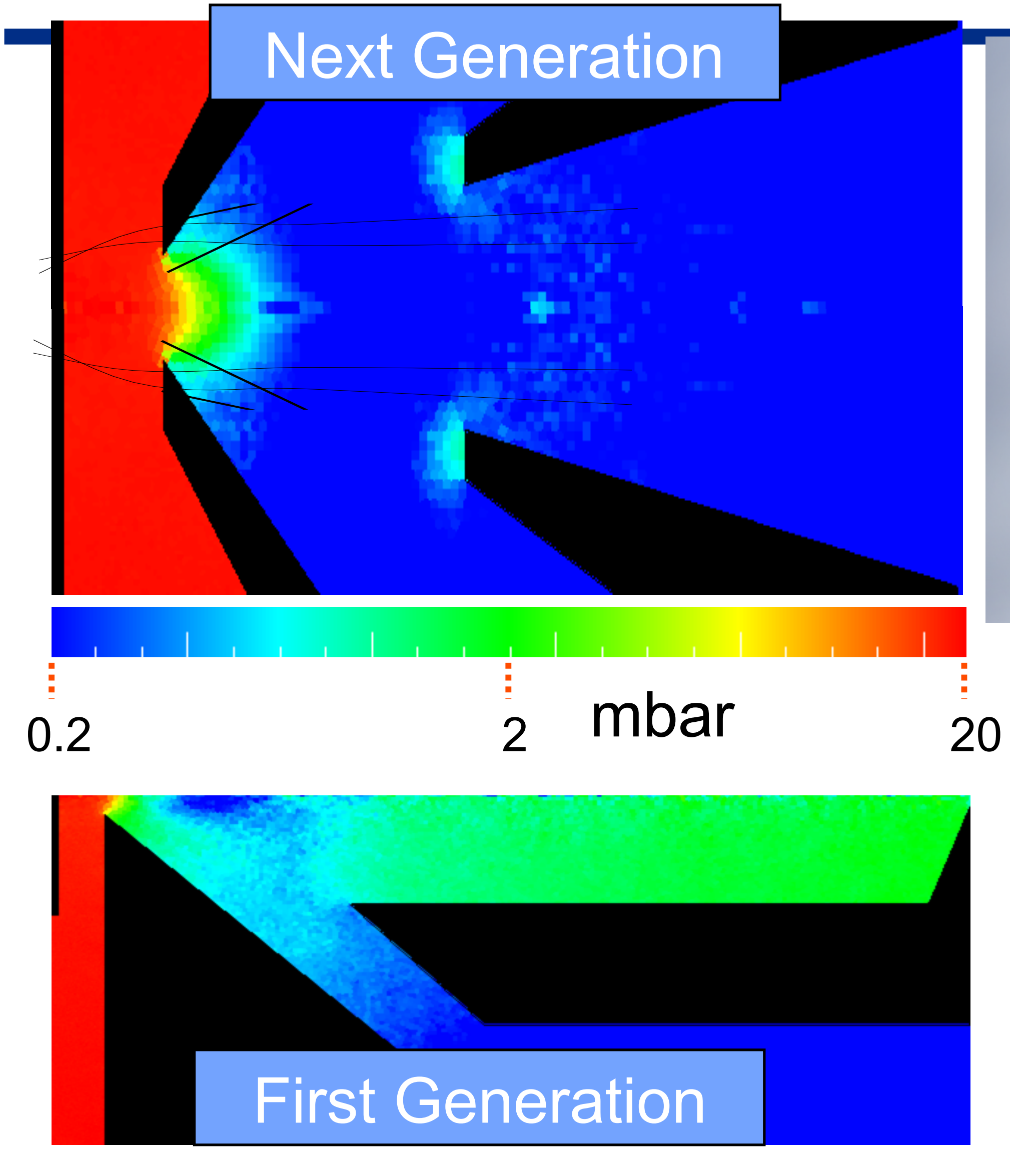
450 - fitted - nosmoth - 5ave.avi

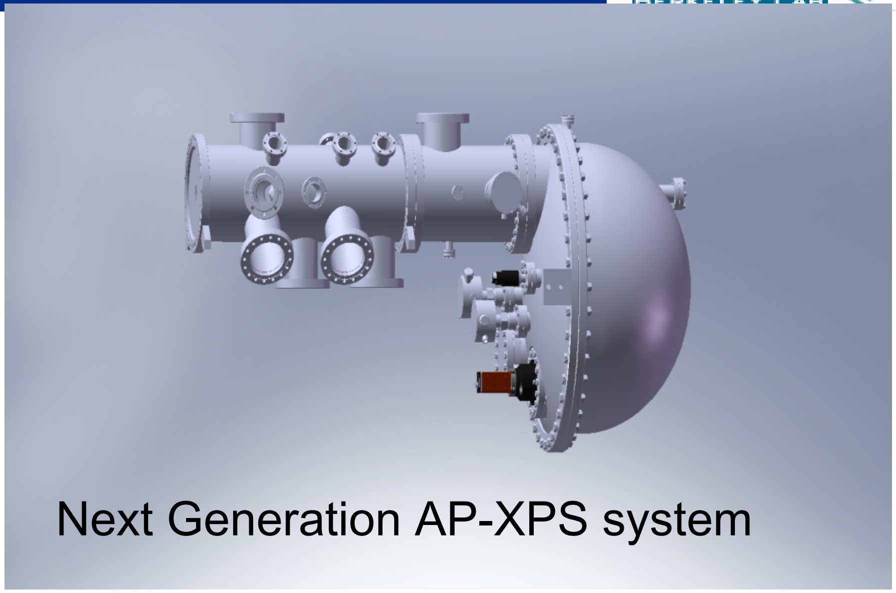
Enta, Mun Fadley, Hussain et al. App. Phys. Lett. 92,012110 (2008)

BL 9.3.2

Si(100) oxidized by water vapour @ .1 torr

Efficient Detection is necessary for study of Dynamics of Chemical Reactions & Radiation Sensitive Samples




Next Generation AP-XPS system

- •New Scienta 4000 AP-XPS system (A collaborative project between ALS(SSG) and VGScienta):
- •Optimization using gas dynamics calculations

- •Will be delivered in May, 2008

BL 9.3.2

Outlook

- Resonant soft x-ray scattering is a powerful but simple technique to measure charge ordering in complex materials.

- Soft x-ray resonant inelastic scattering (RIXS) is a technique of choice for the study of low energy *coupled* excitations.

- Future light sources (FEL) will enable ultra-high resolution (< 5-10 meV) q-resolved RIXS near the 2p edges of transition metals.
- Need to manage radiation damage and perturbation of ground state properties with high intensity electromagnetic radiation

Spatial-, Spin-, and Time-Resolved Photoemission with the use of *FEL (high repetition rate) and TOF* analyzers will keep ARPES as an important technique for study of strongly correlated electron systems.

- In-situ dynamical photoemission spectroscopy will help in understanding and control of electronic structures and tailoring properties of complex materials for energy application.
- High rep rate and low photon energy helps to avoid space charge problem

Collaborators

- ALS, Lawrence Berkeley National Laboratory
  - Yi-De Chuang, Bob Schoenlein
  - Chris Jozwiak, A. Lanzara (MSD, UCB)
- Stanford University and SIMES
  - Z. X. Shen, Wei-Sheng Lee
  - T. P. Devereaux, theory
- Princeton University
  - Zahid Hasan
- University of British Columbia
  - Suman Hossain, Andreas Damascelli

What are the ideal characteristics of FEL for study of condensed matter physics?

- Transform limited source
- Timing resolution ~ ps – 10 fs…
- Tunable photon energy range ~ 6 eV – ~ 3 keV
- Repetition rate ~ 1MHz – 10 MHz

  (100kHz ok, for day one)
- Photon flux (<~10^8 photon/pulse at sample, avoids sample perturbation/damage, space charge effect)