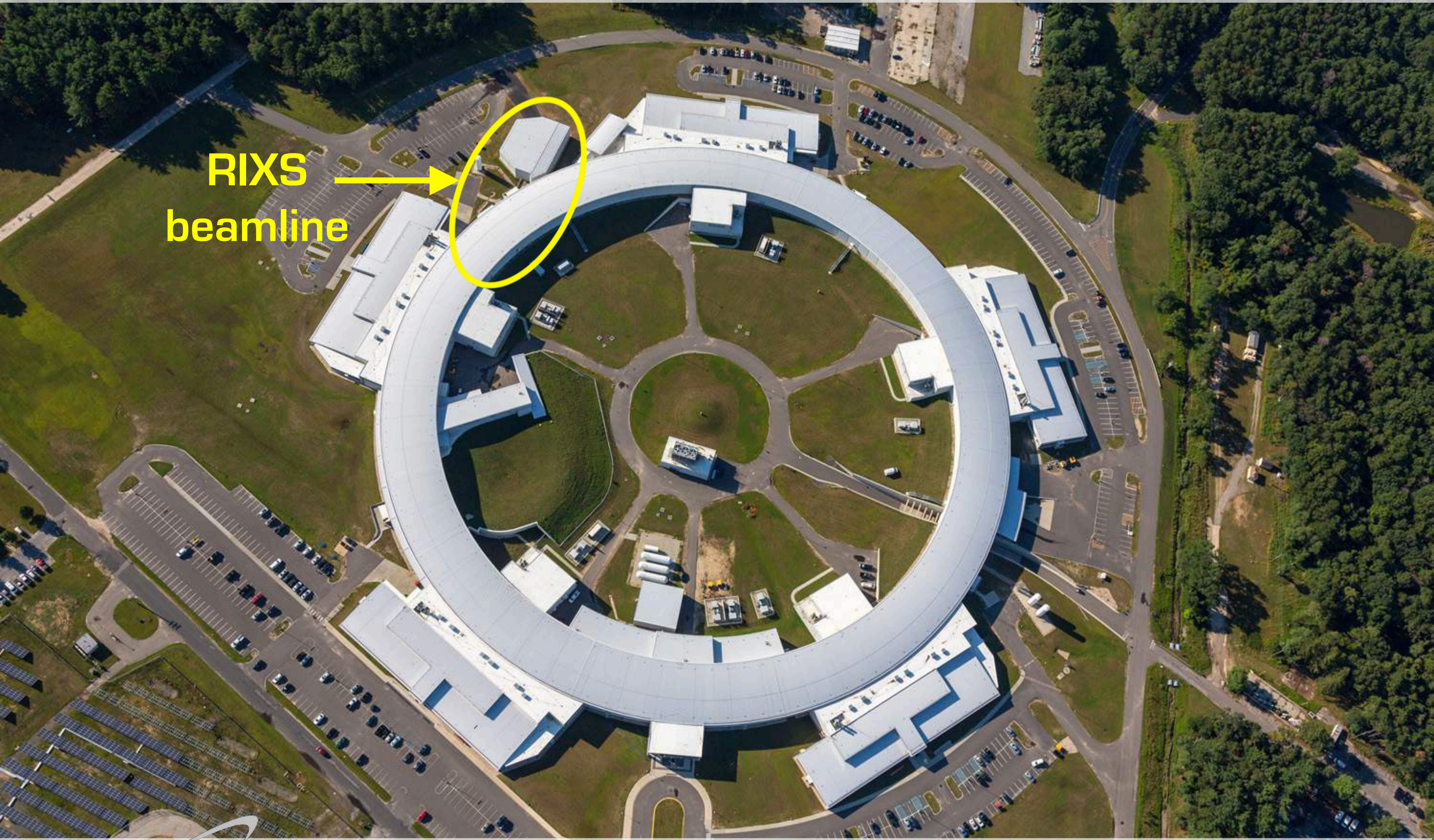
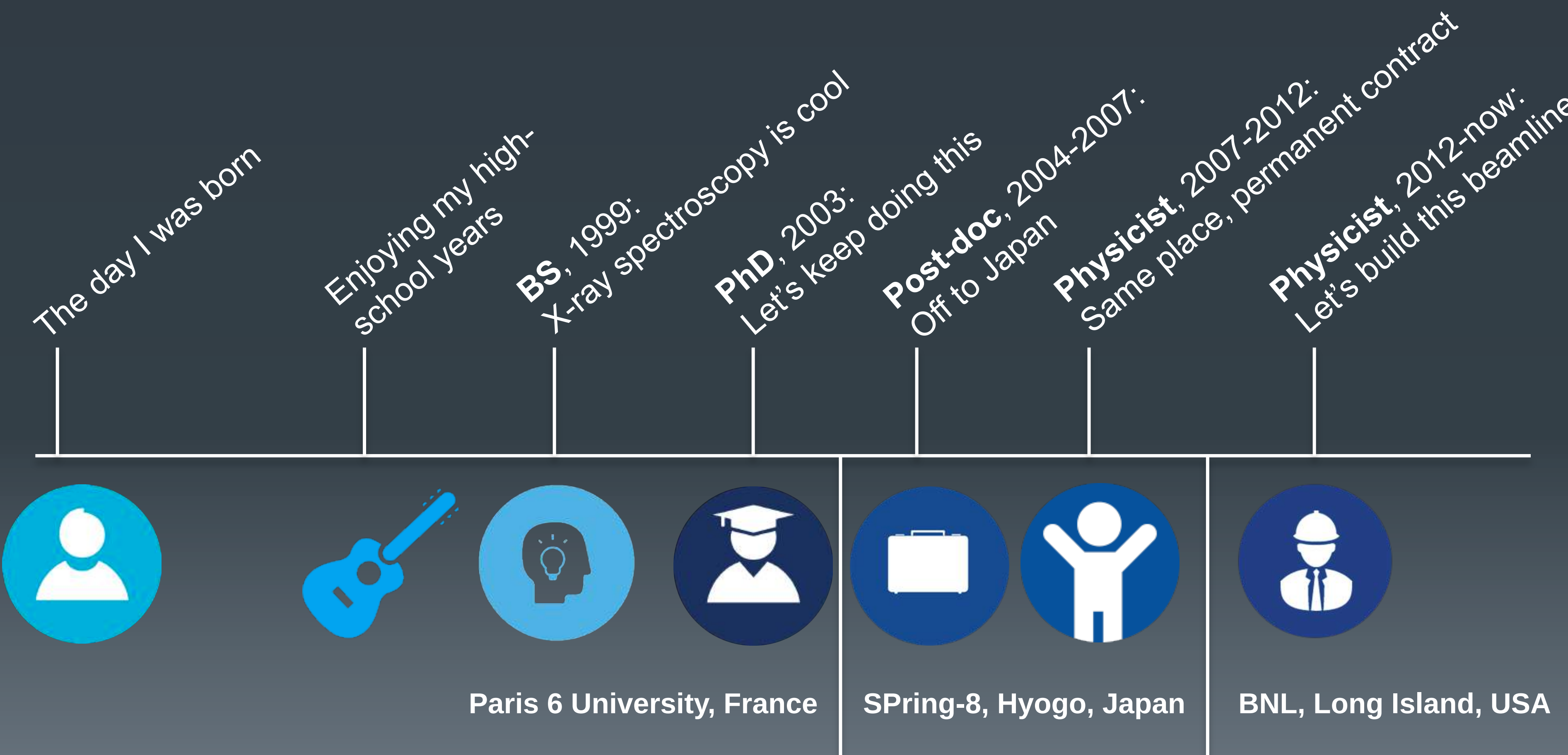
Resonant Inelastic X-ray Scattering (RIXS)

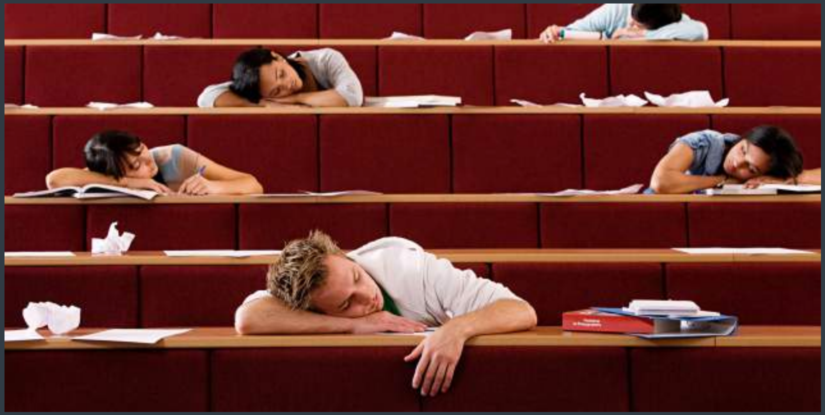


BROOKHAVEN NATIONAL LABORATORY
Ignace Jarrige, Email: jarrige@bnl.gov, Phone: 631-344-8814

And here is my **Life Timeline**:



Because this could be you at 6:40 pm today:



And because this is you right now:

Let me already give you…

The *take away message* of this lecture:

- Why do we use RIXS?

RIXS probes the behavior of the valence electrons (the most important electrons for physics and chemistry!), both local and collective

- How does RIXS work?

RIXS measures energy change (spectroscopy) and momentum change (scattering) of photons scattered from the sample

- Why does RIXS need light sources?

RIXS is photon hungry, and needs tunability of photon energy

- Who uses RIXS?

Bulk of users are physicists, but interest from material scientists and chemists is rapidly growing

The *take away message* of this lecture:

- And also, RIXS instruments look **COOL**:

ID32 at the ESRF (Grenoble, France), 12 meters. A similar spectrometer, 15 meters in length, is currently in construction at NSLS-II.

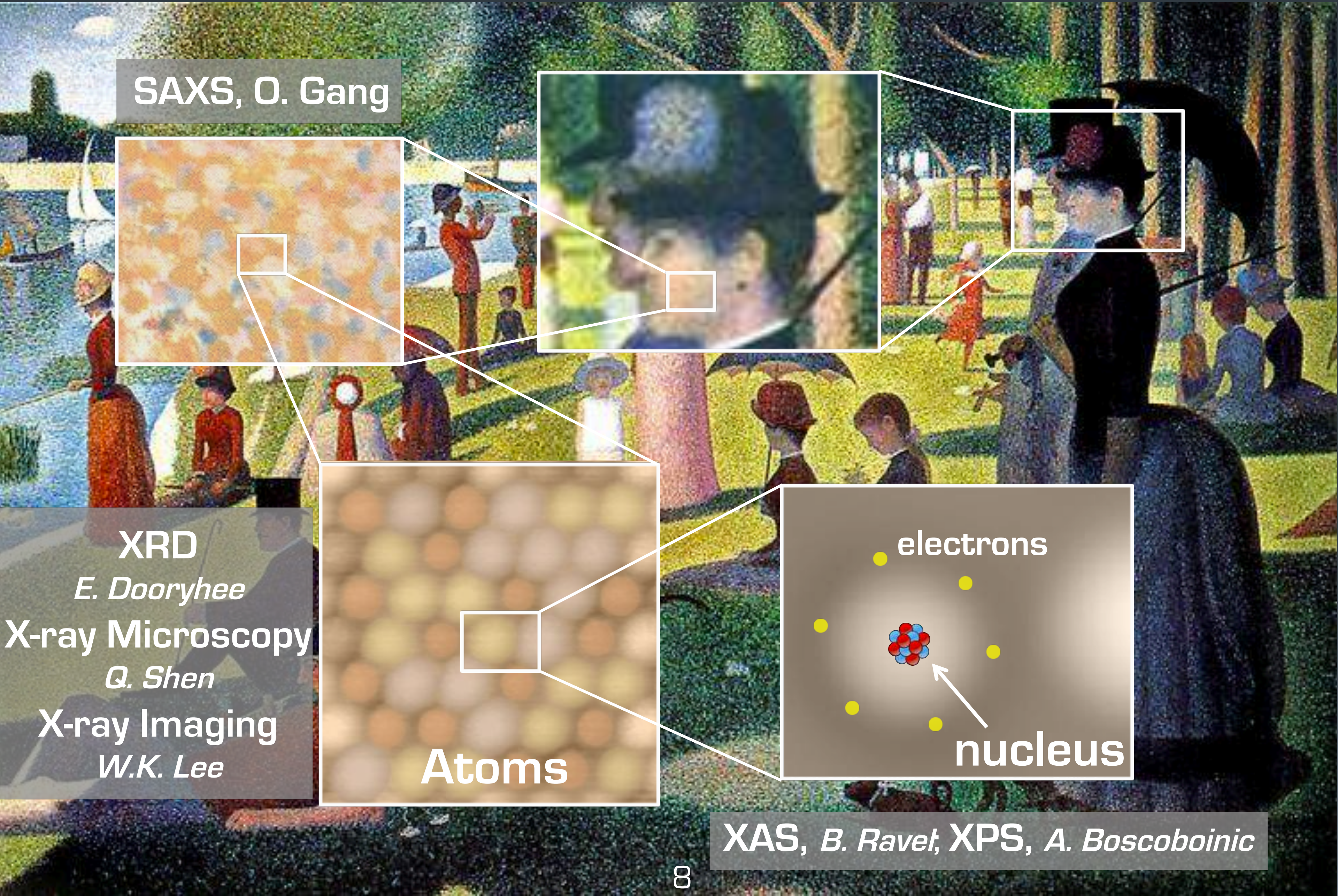
… And because every lecture needs an outline:

- Section 1: What's the big deal with electron behavior?
- Section 2: From band structure to electron behavior
- Section 3: Probing the band structure
- Section 4: How does RIXS work?
- Section 5: Examples of RIXS studies
- Section 6: RIXS at NSLS-II

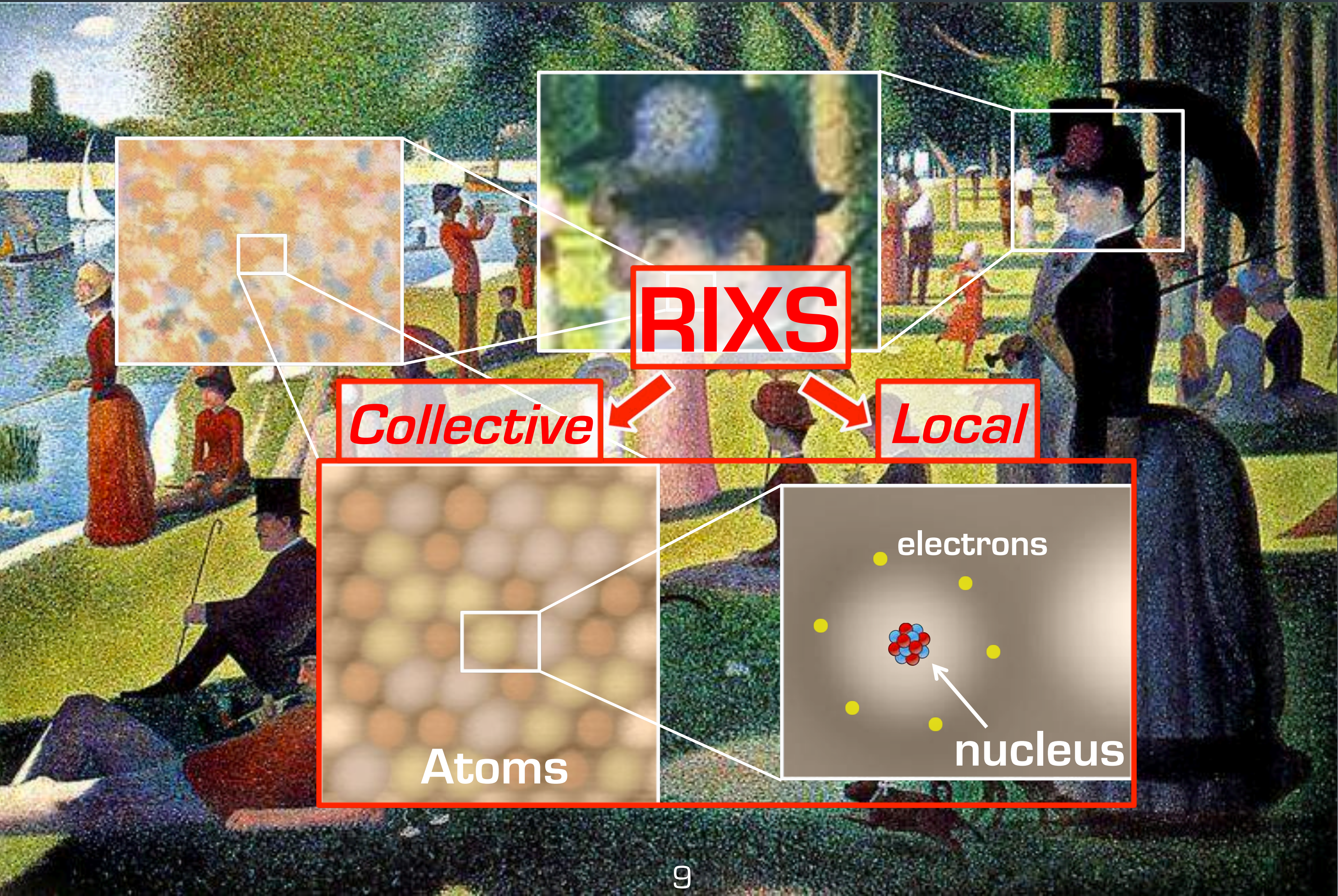
Section 1:

What's the big deal with electron behavior?

Different Probes for Different Scales



RIXS Probes Local and Collective Electron Behavior



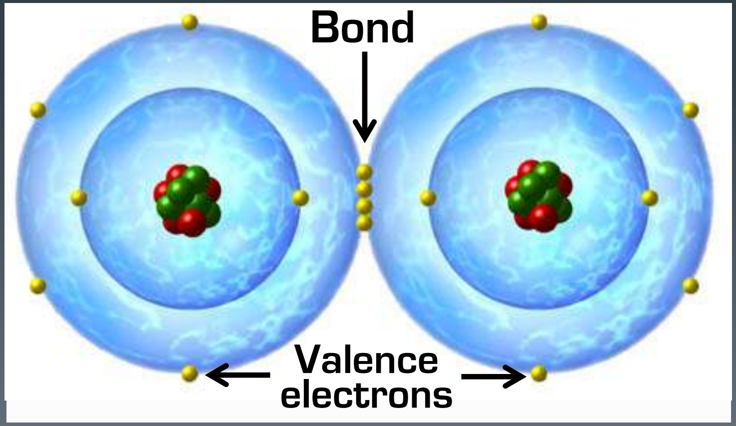
All the Electrons? No, the Valence Electrons.

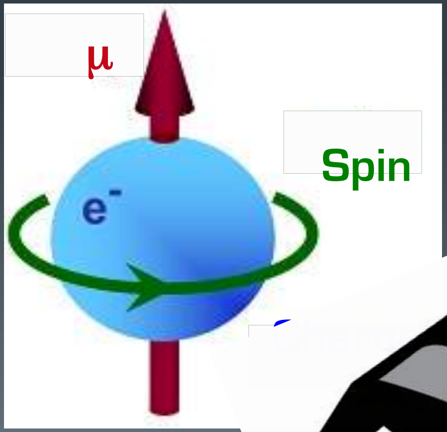
The color of the **outer shell** determines which candy I want to eat first:

The **Valence Electrons** Determine:

Chemical Reactivity and **Bonding** Between Atoms

Electrical and **Magnetic** Properties of Matter

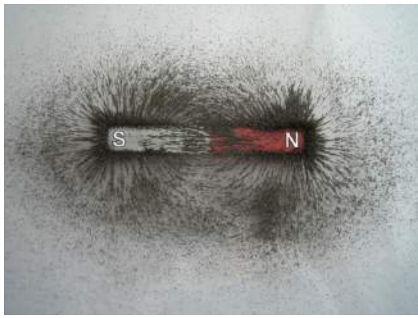


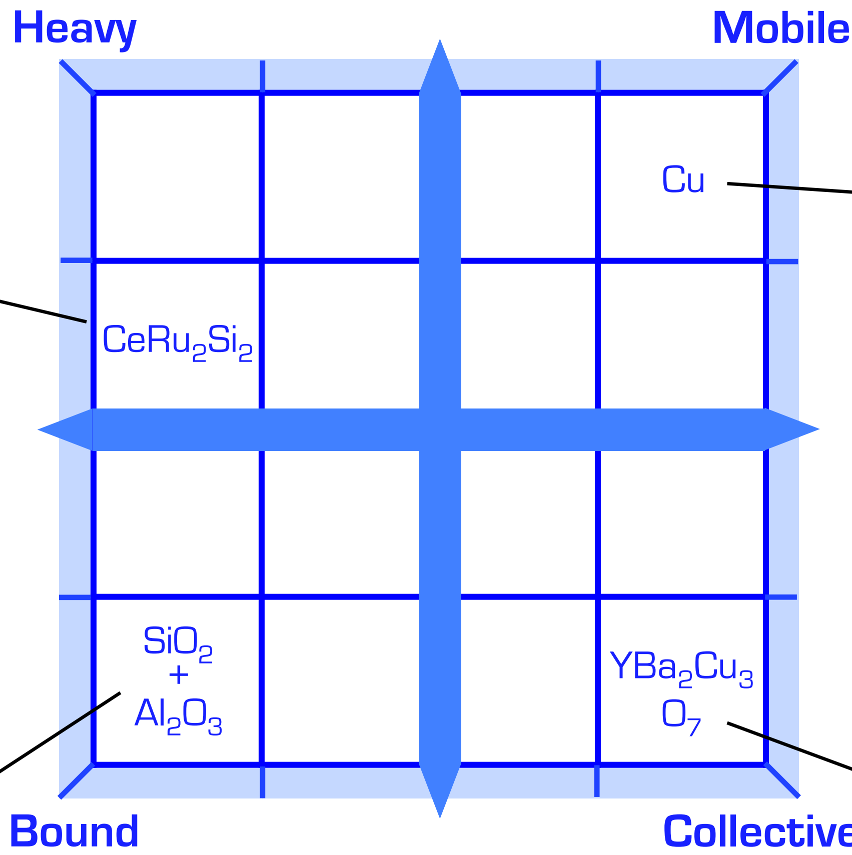


Electrons also have an ‘Attitude’, a **Behavior**

The Social Behavior of the Valence Electrons in Materials

Metamagnet

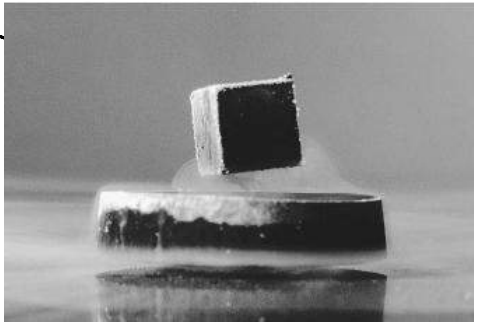




Copper Wire

Ceramic Insulator

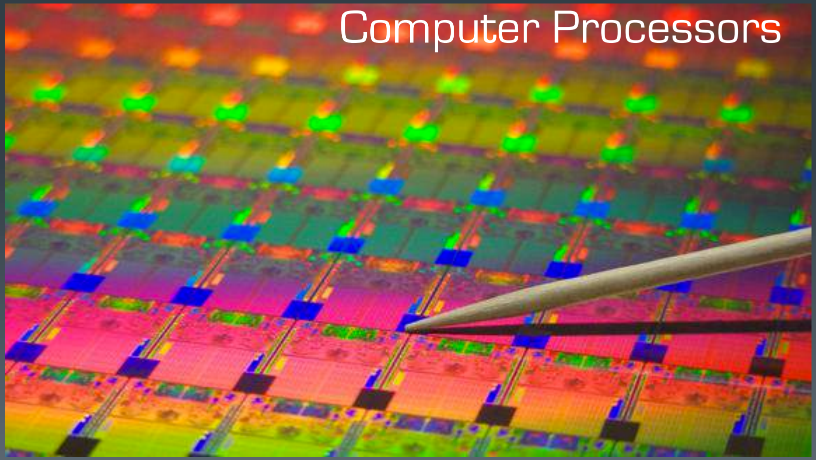
Superconductor



Valence Electron Behavior Making Our Life ***Easy***

'Sea' of mobile electrons

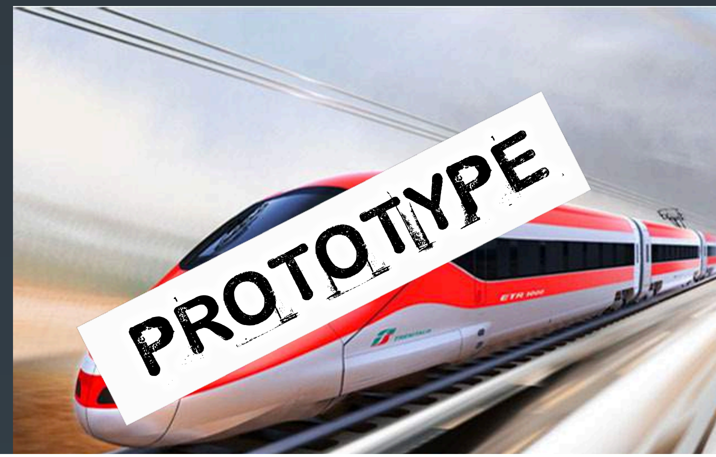
Bound electrons



Mobile and Bound Electrons

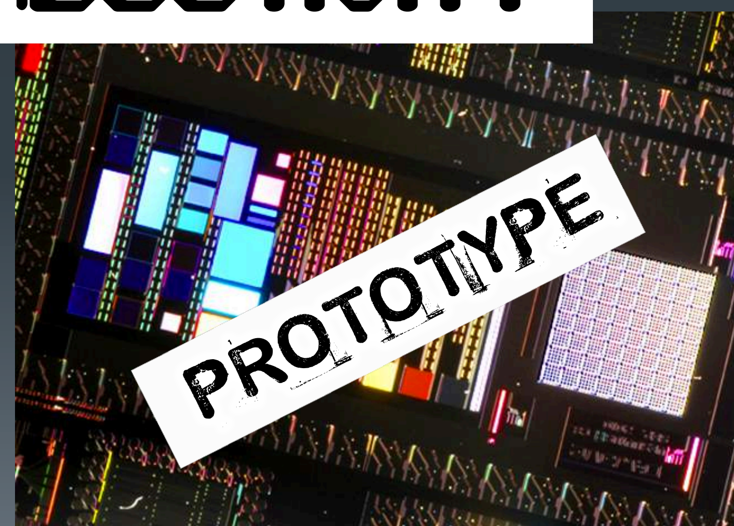
Collective Valence Electron Behavior Making Our Life ***Easier***

NYC a 10 min ride from BNL



SUPERCONDUCTIVITY

$20 billion / year savings in the US



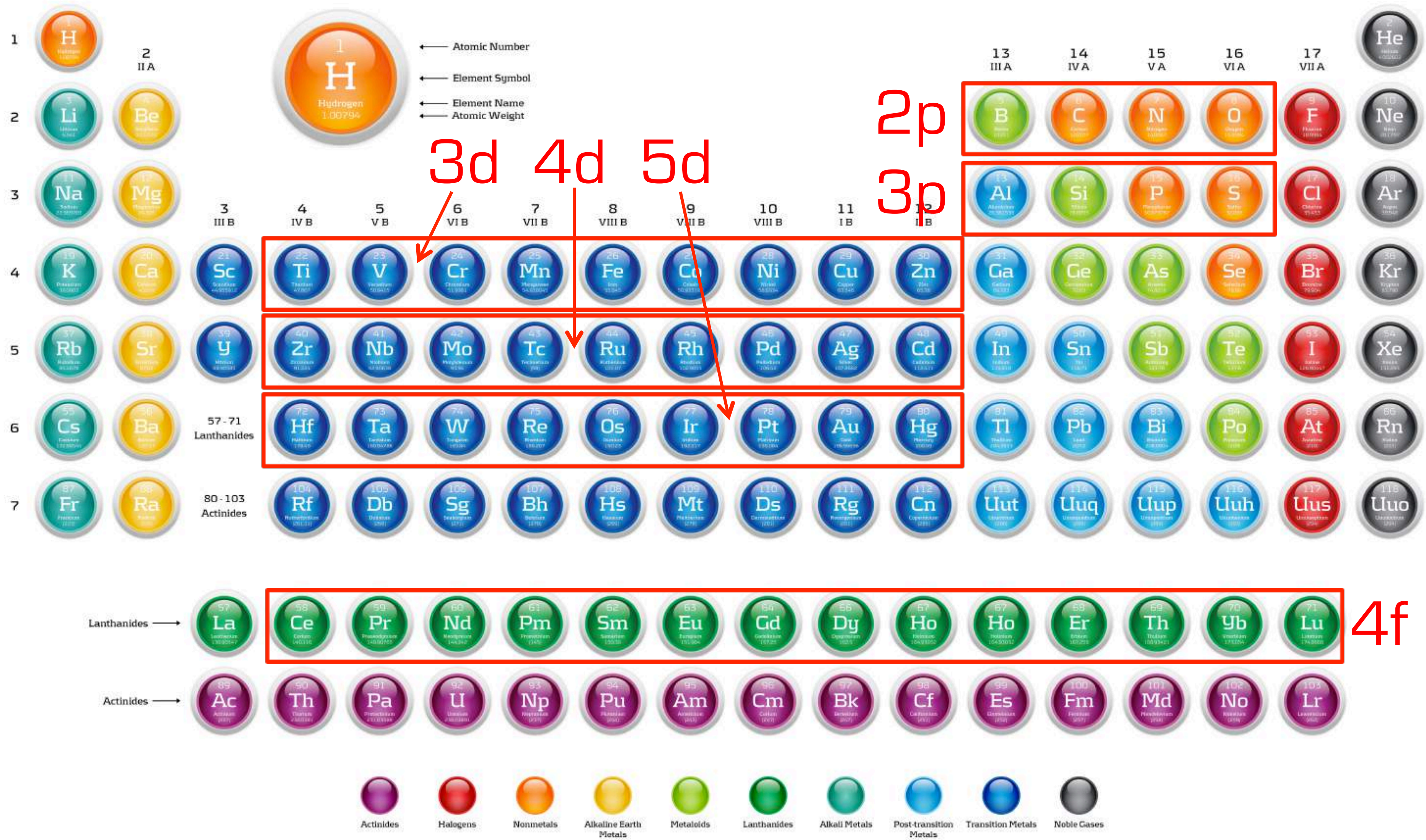
Chip 500 x faster than Iphone 6's

Section 2:

From band structure to electron behavior

The Valence Electrons on the Element Map

Are these valence “states”, or valence “bands”…?

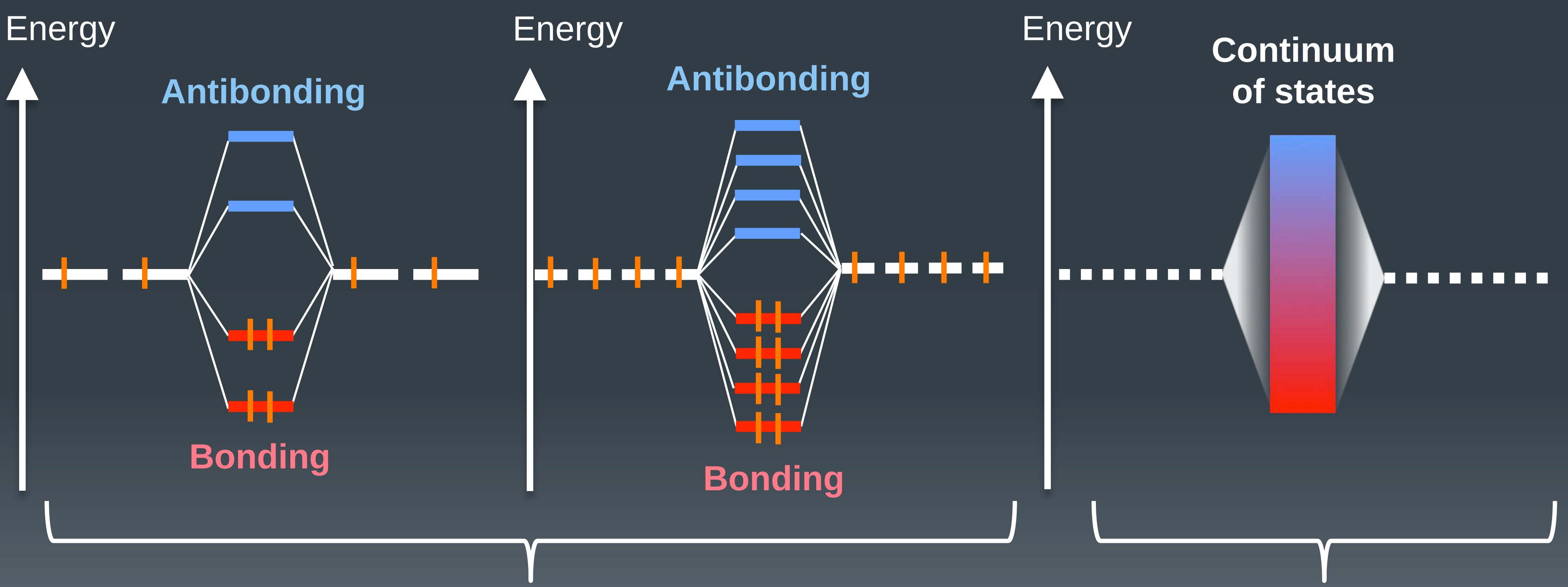


How Do Valence Bands Form?

Forming a chemical bond between **two** atoms:

Forming a chemical bond between **four** atoms:

Forming an energy band with **many** atoms in a solid:

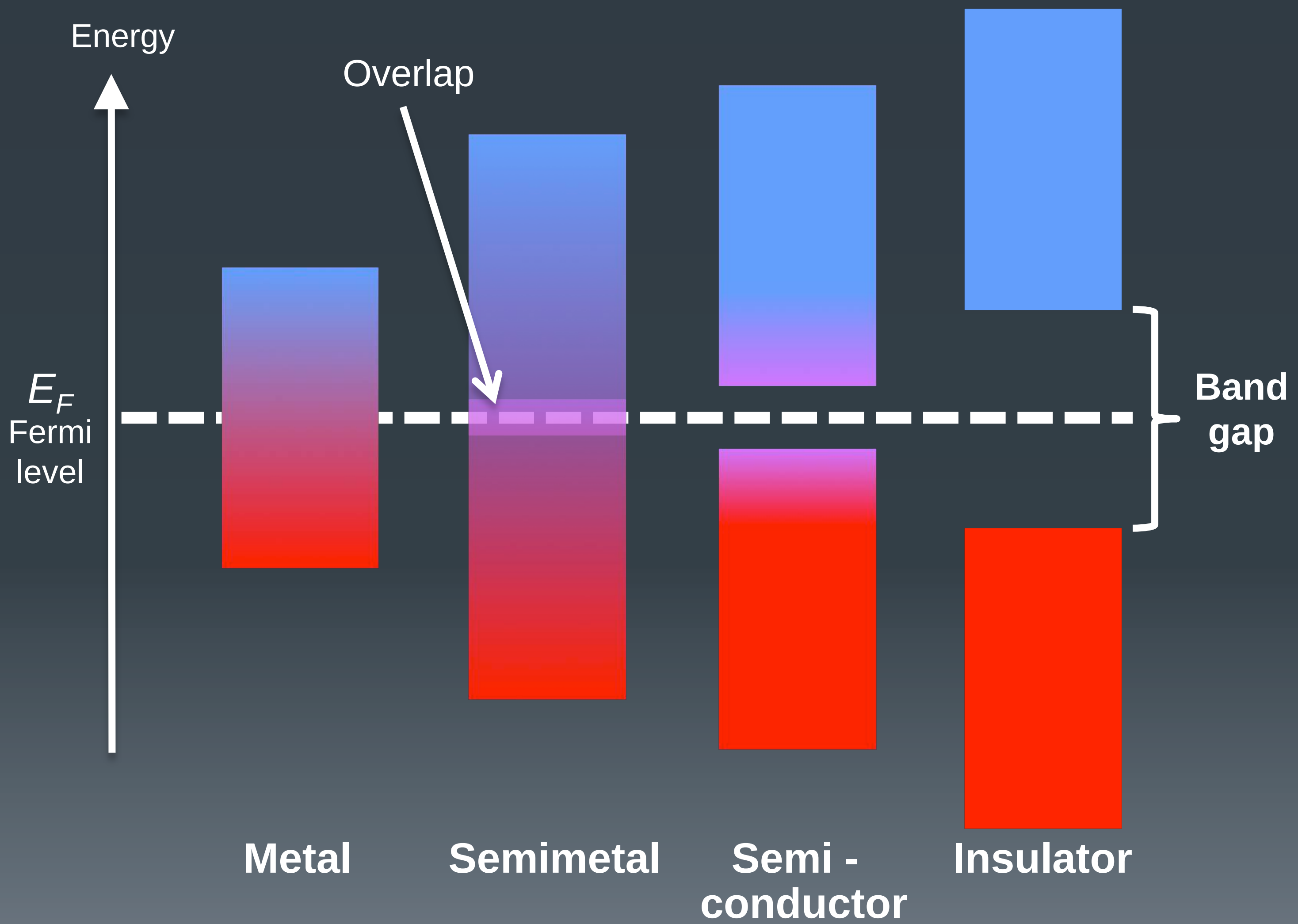


Molecular Orbitals

Valence Band

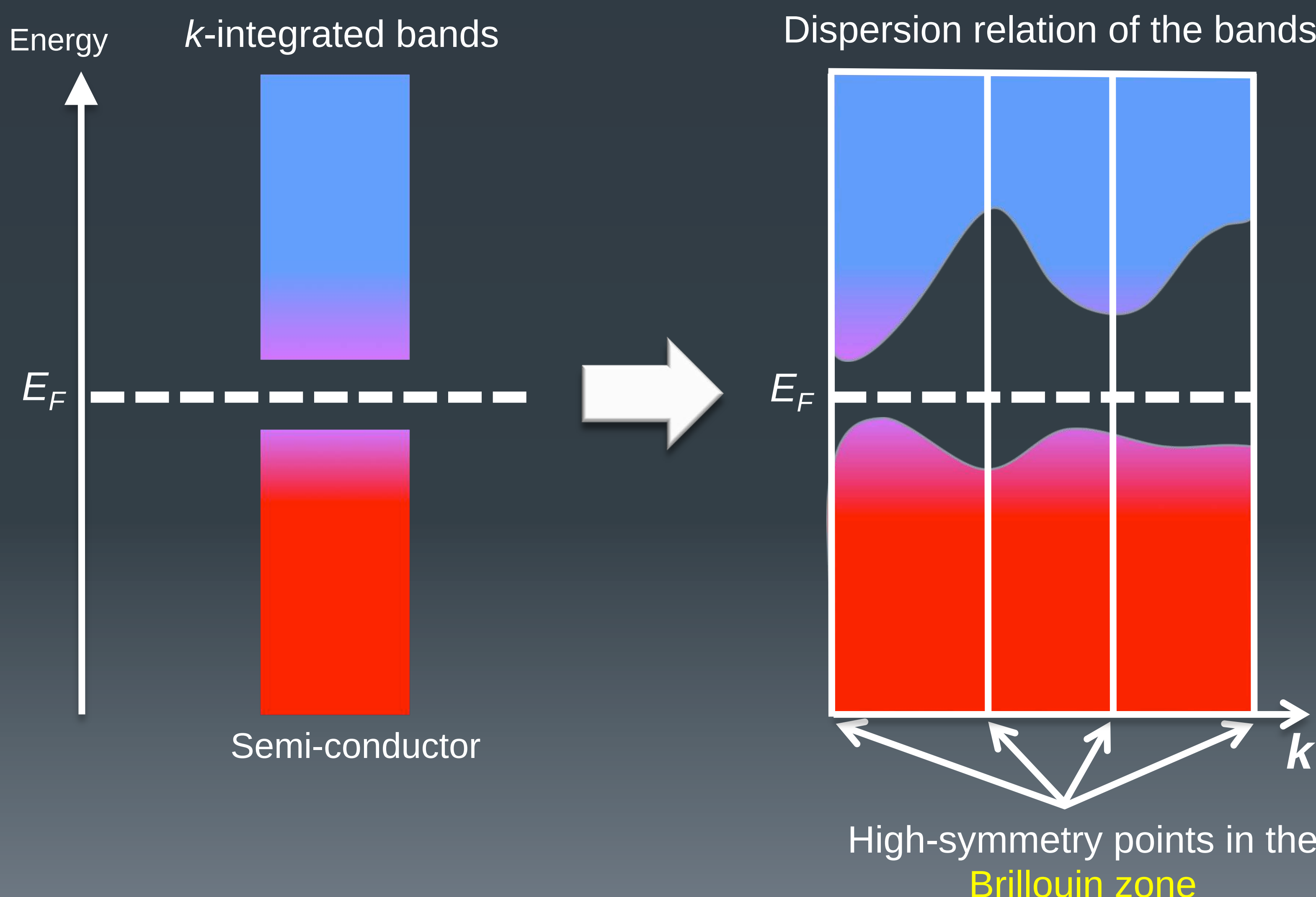
From Band Structure to Electron Behavior

Filling of the valence band, red=occupied, blue=unoccupied



From Band Structure to Electron Behavior

Each band has a dispersion relation, which is the energy of the band as a function of the electron's wavevector k ($k = q/\hbar$ where q is the momentum)



Why Use the Reciprocal Space?

- ## Crystals in real space are big!

  Crystal lattices of macroscopic dimension have about 10^7 unit cells in each dimension. Rather than exploring each of them, exploit their periodicity

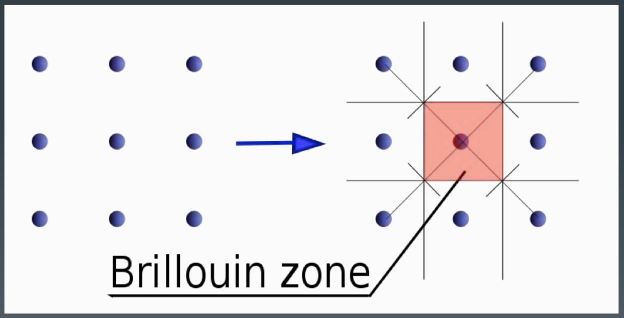
- ## Periodicity is key

  Observable functions related to a crystal lattice (charge and spin densities, electric potential, …) are all periodic because of the lattice vectors

- ## Mathematical description of crystal structure

  Reciprocal lattice is a Fourier transform of the lattice in the real space:

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}$$



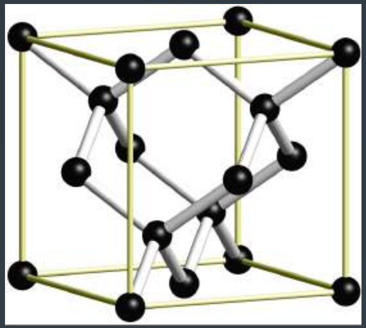
- ## Infinity contained in one cell

  The first unit cell in the reciprocal space (the first Brillouin zone), contains all the information we need about an infinitely periodic crystal

The Link between Electron Behavior and Band Structure

Copper versus Silicon:

Same single crystal structure (face-cubic centered)

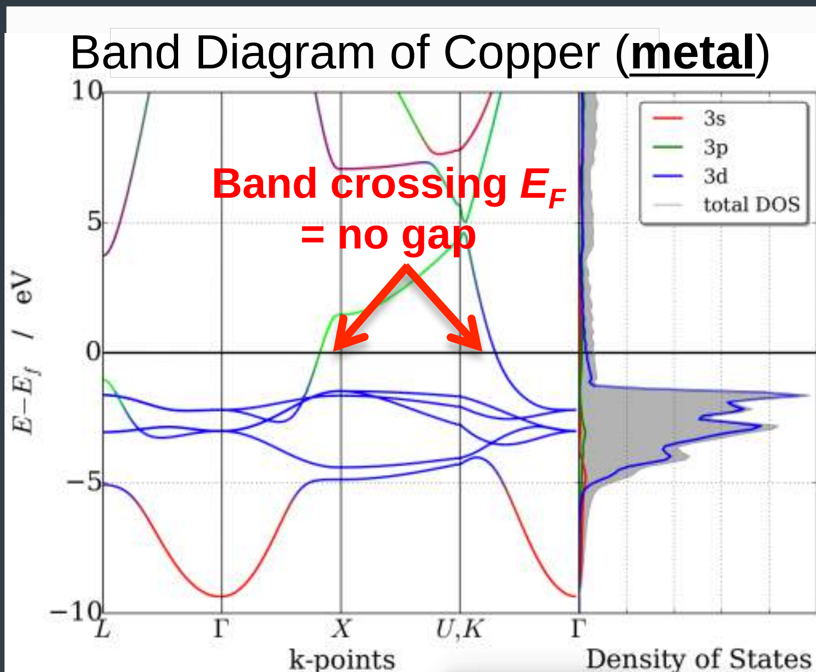


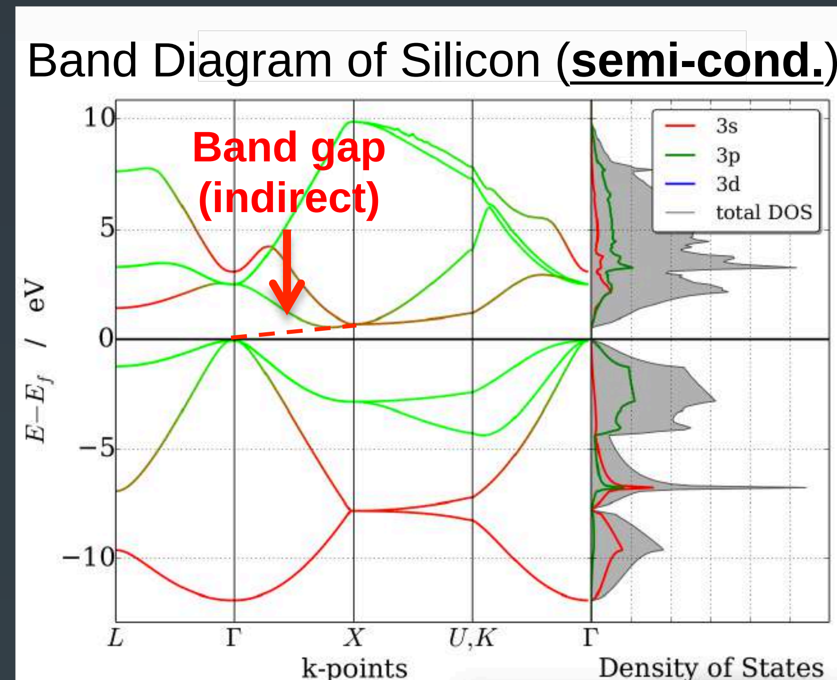
Yet very different properties (and appearances):

The origin of these differences is in the band structure!

The Link between Electron Behavior and Band Structure

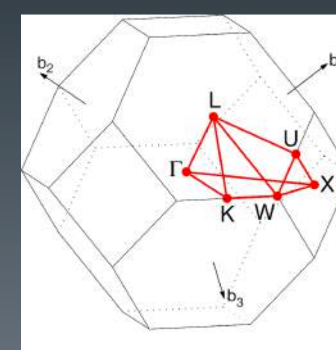
Different valence orbitals, forming different bands:





Germain Salvato-Vallverdu, VASP calculations

The band structure contains precious information about the electron behavior, which governs the material properties



FCC path: Γ-X-W-K-Γ-L-U-W-L-K|U-X

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

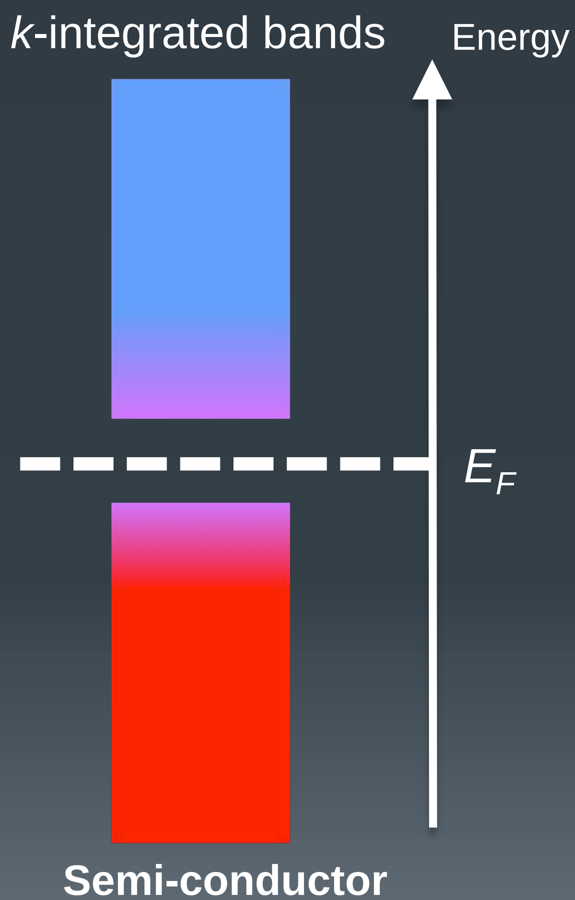
So, now… how do I probe the band structure??

Section 3:

Probing the band structure

How does spectroscopy probe valence bands?

Let's make an analogy between valence bands and bowling ball racks:

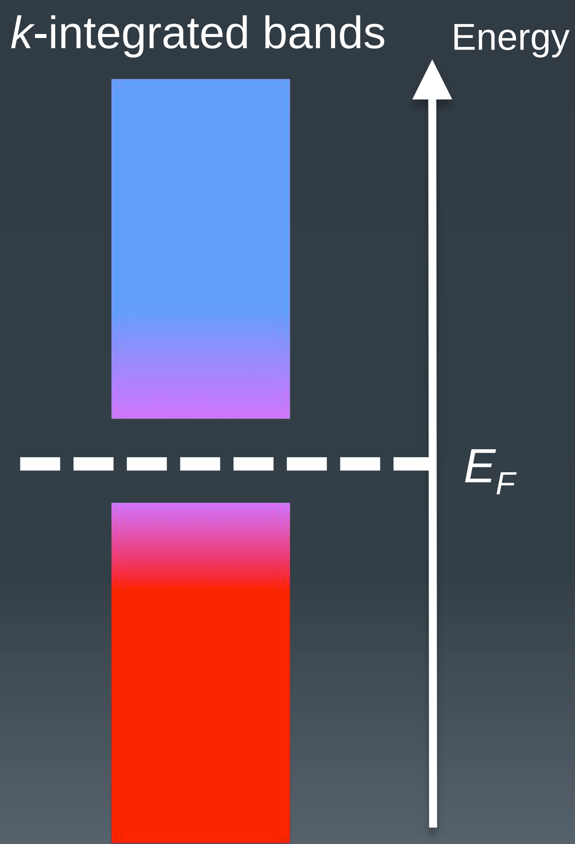


Empty states

Occupied states

How does spectroscopy probe valence bands?

Let’s make an analogy between <u>valence bands</u> and <u>bowling ball racks</u>:

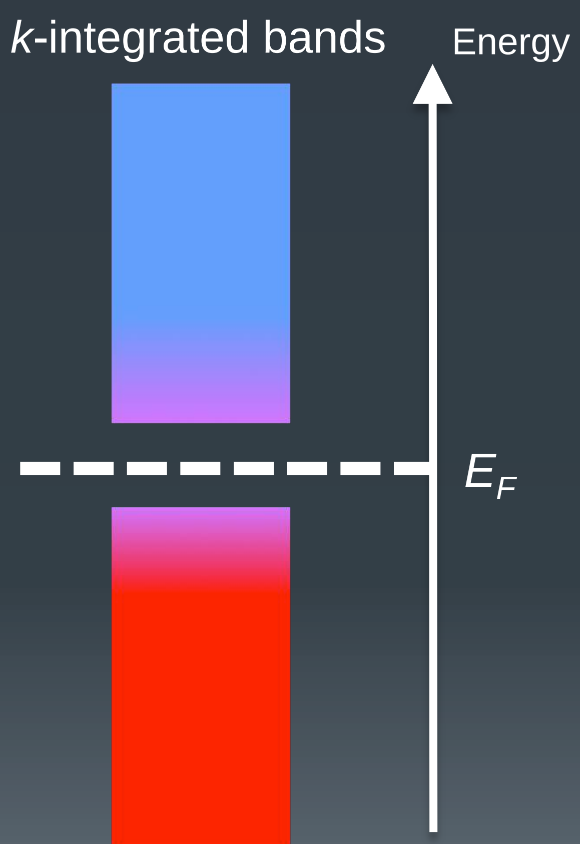


Semi-conductor

If I know the energy it takes to bring the ball up, I know the <u>energy difference between the two levels</u>

How does spectroscopy probe valence bands?

Let's make an analogy between valence bands and bowling ball racks:



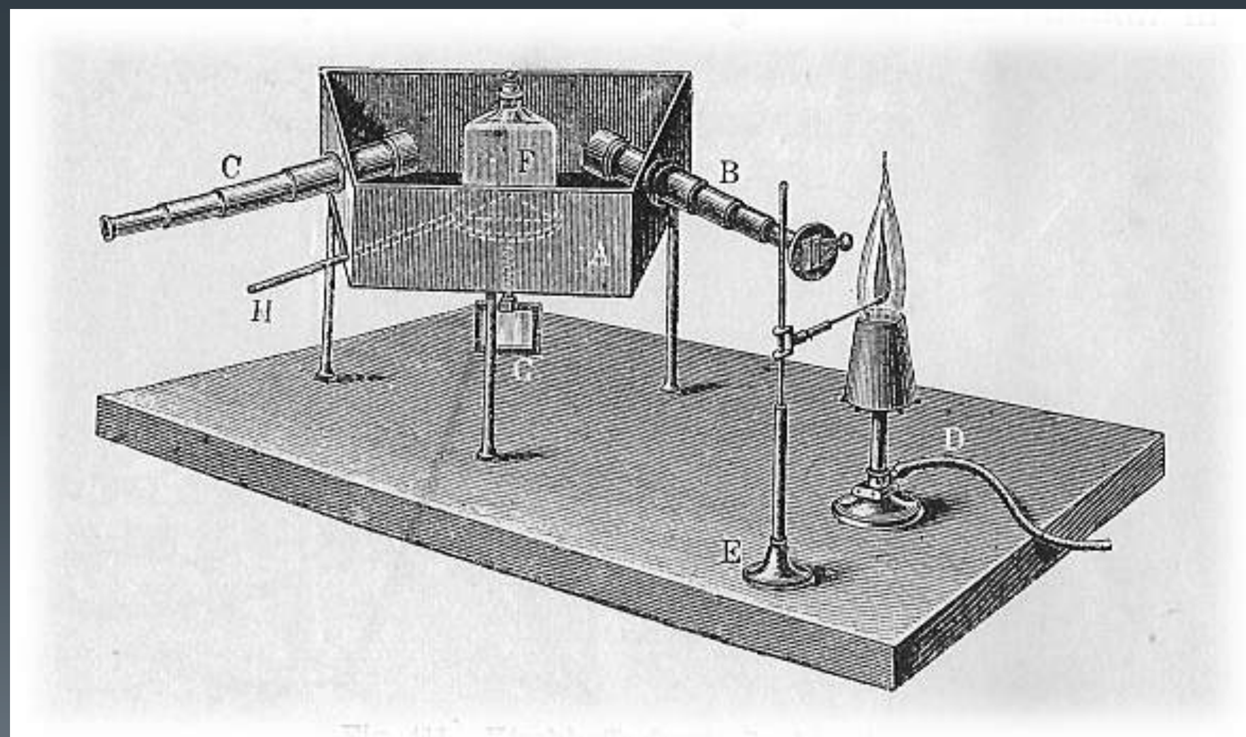
Semi-conductor

If I know the number of balls that are able to go up, I know the density of states (DOS)

Great, we've rediscovered optical spectroscopy!

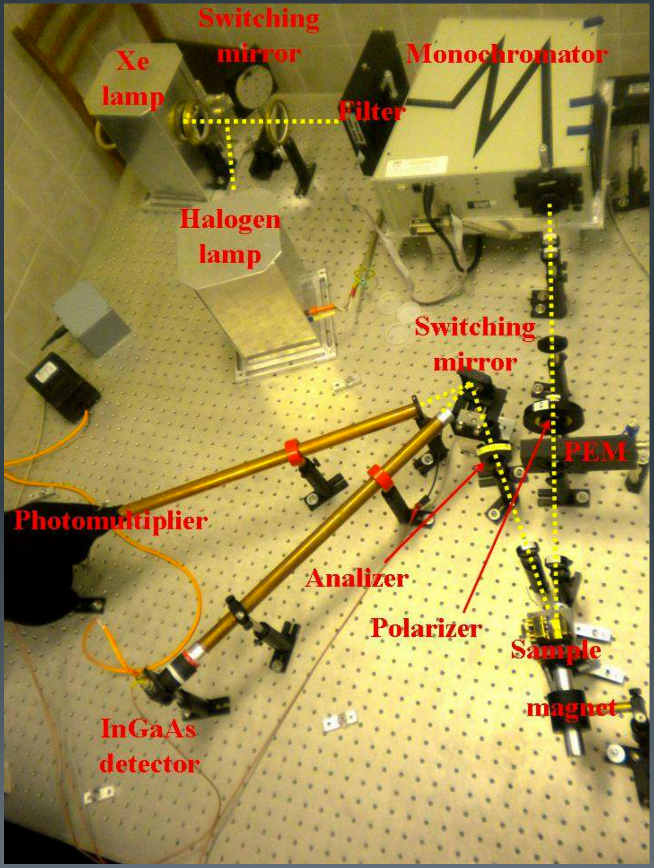
The Early Days of Optical Spectroscopy:
First attribution of spectra to chemical elements by Kirchhoff and Bunsen in 1860 with their spectroscope

(to continue with the analogy, and because history is fun:
The first indoor bowling alley worldwide opened in New-York in 1840!)



Great, we've rediscovered optical spectroscopy!

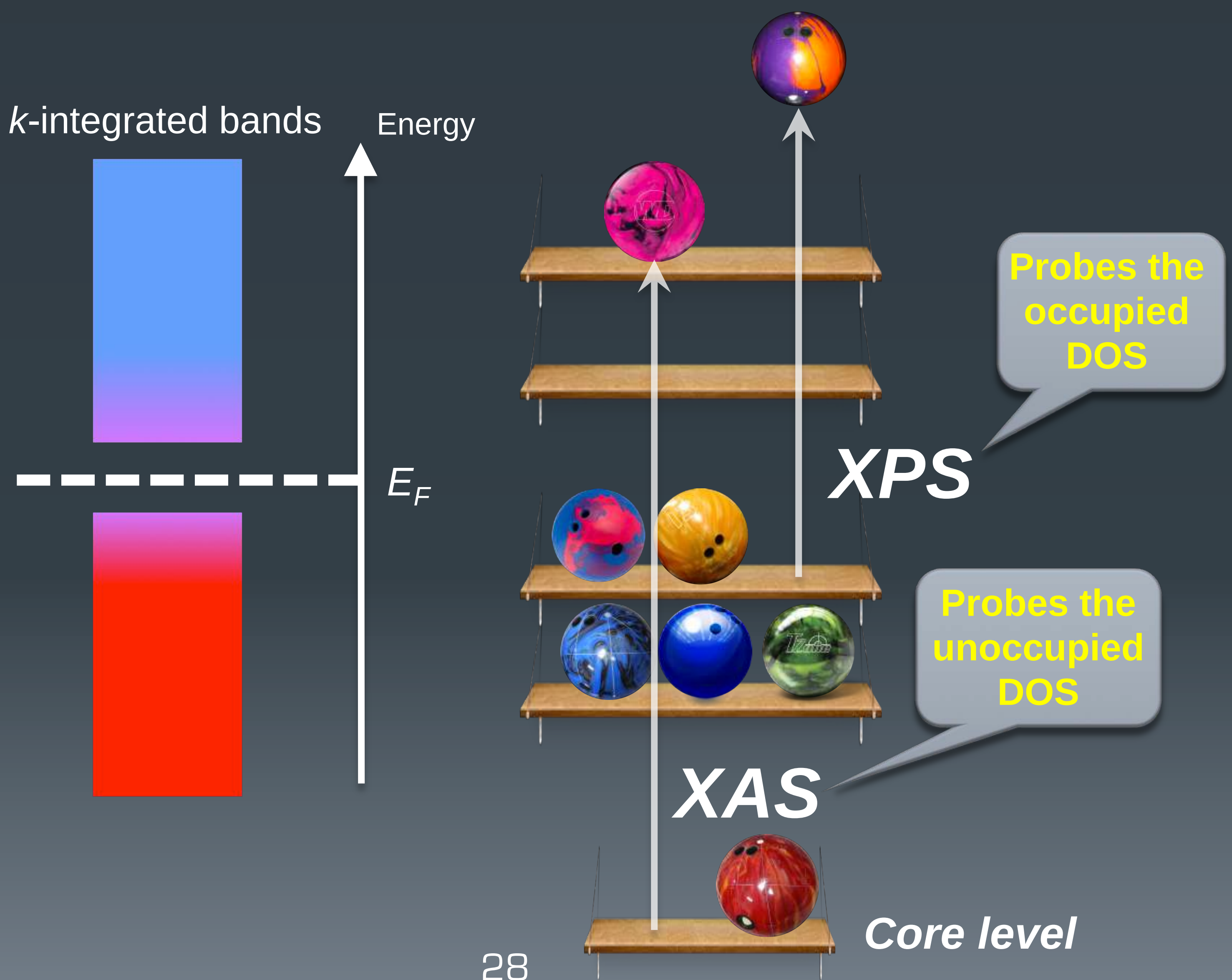
State-of-the art Optical Spectroscopy:
Magneto-optical Spectrometer
Can detect transitions between near IR (0.8 eV) to UV (6 eV)



Sandor Bordacs, University of Budapest

What about x-ray spectroscopy?

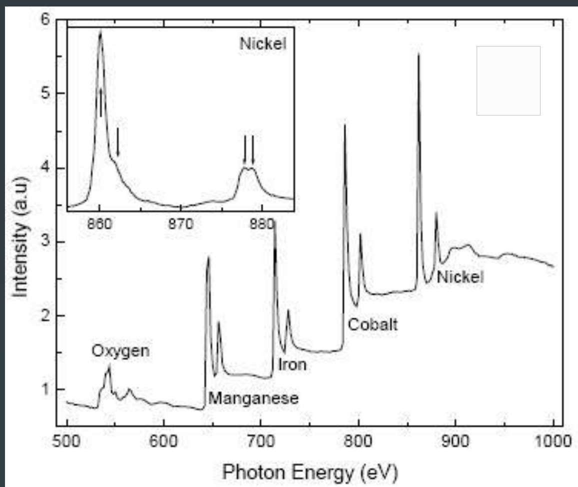
Another way to do it: *use x-rays* to excite core-level electrons



What about x-ray spectroscopy?

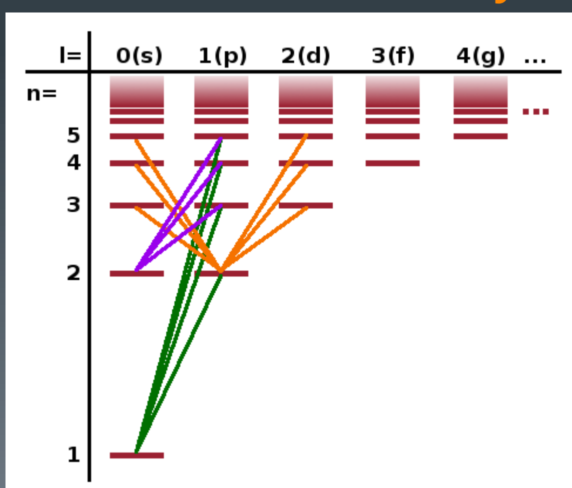
Use of monochromatic x-rays to probe valence bands offers (1/2):

Element Selectivity:



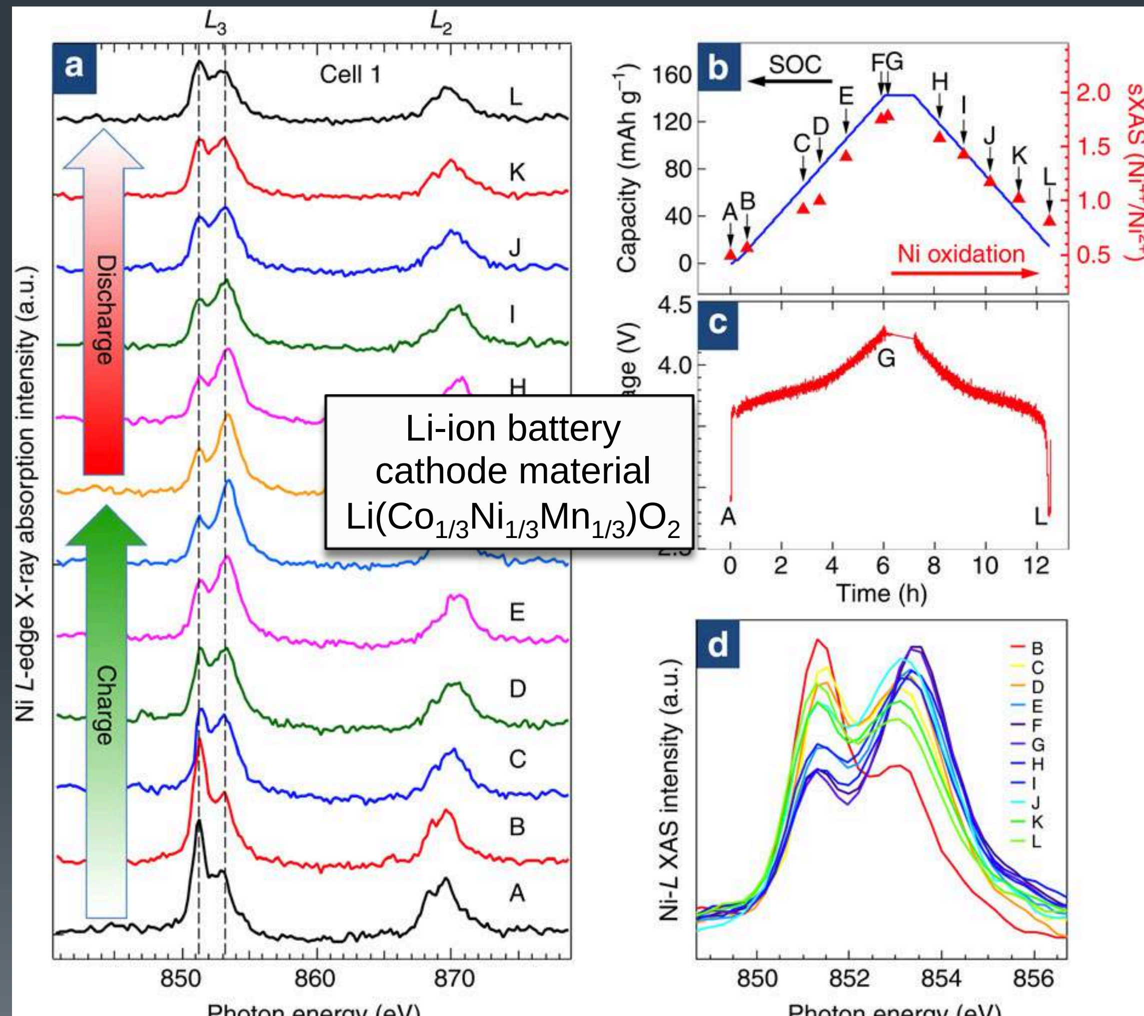
ALSHub Tutorial

Orbital Selectivity:



users.aber.ac.uk/

Charge Selectivity:



X. Liu et al., Nature Comm., 2013

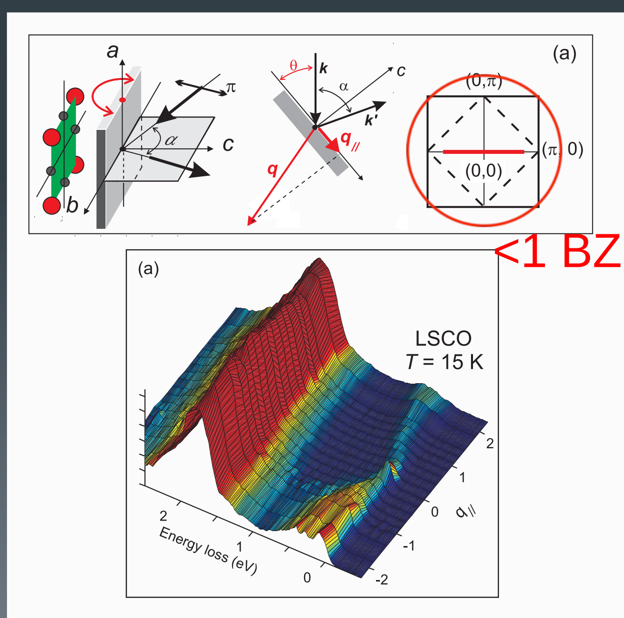
What about x-ray spectroscopy?

Use of monochromatic x-rays to probe valence bands offers (2/2):

q=E/c
Momentum
Increases with
Energy!

- Optical light momentum negligible in spectroscopy
- Soft x-rays RIXS gets close to BZ boundary
- Hard x-rays RIXS covers several BZ

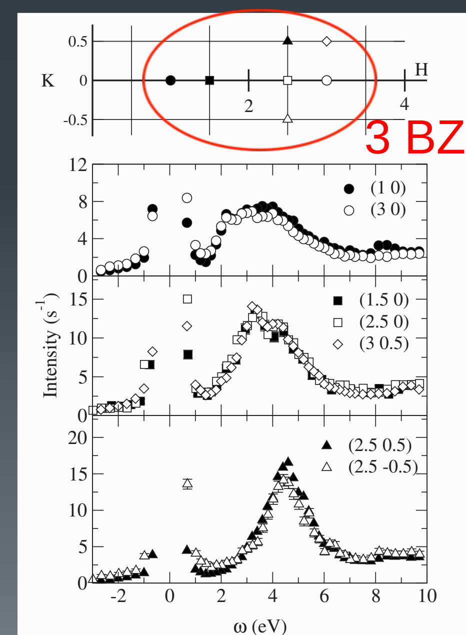
<u>SOFT</u> x-ray RIXS on La_2CuO_4
$Cu-L_3$ edge (~930 eV)



<1 BZ

L. Braicovich et al., PRL, 2010

<u>HARD</u> x-ray RIXS on La_2CuO_4
Cu-K edge (~8990 eV)

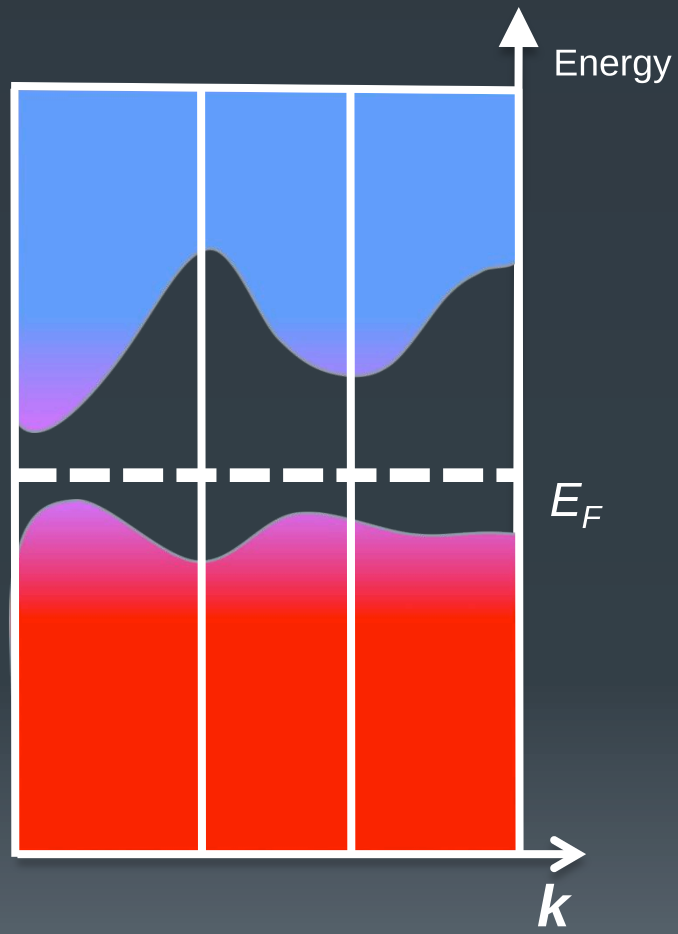


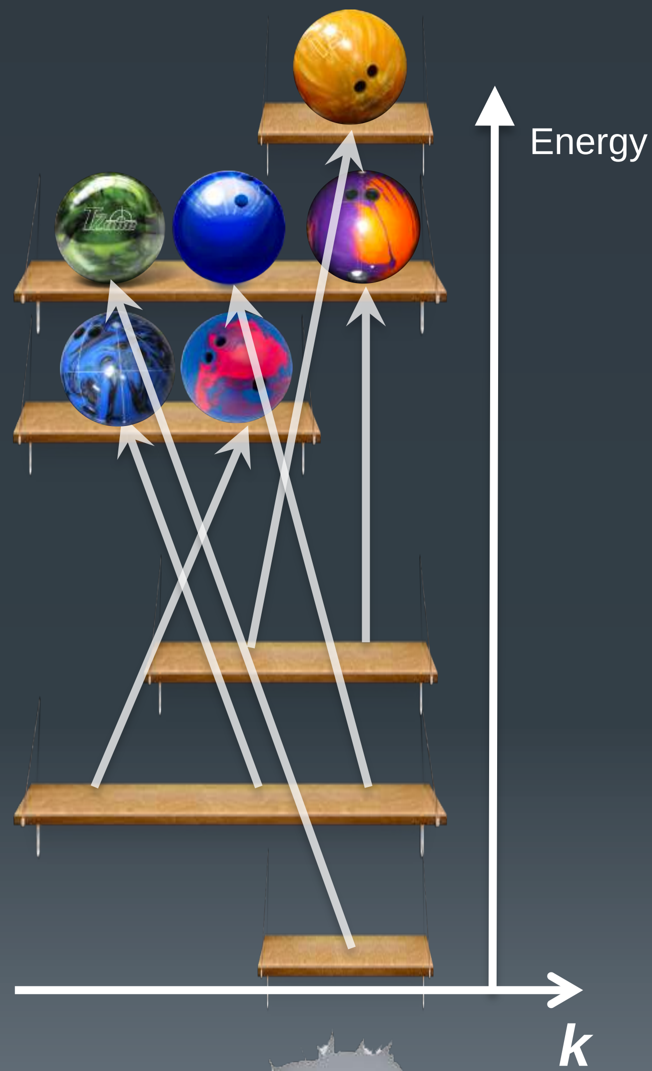
3 BZ

Y.J. Kim et al., PRB, 2007

What about x-ray spectroscopy?

X-ray spectroscopy can explore **energy** *and* **momentum** of the bands





One more ingredient for RIXS: the **core-hole** →

It’s about time to reveal RIXS!!!

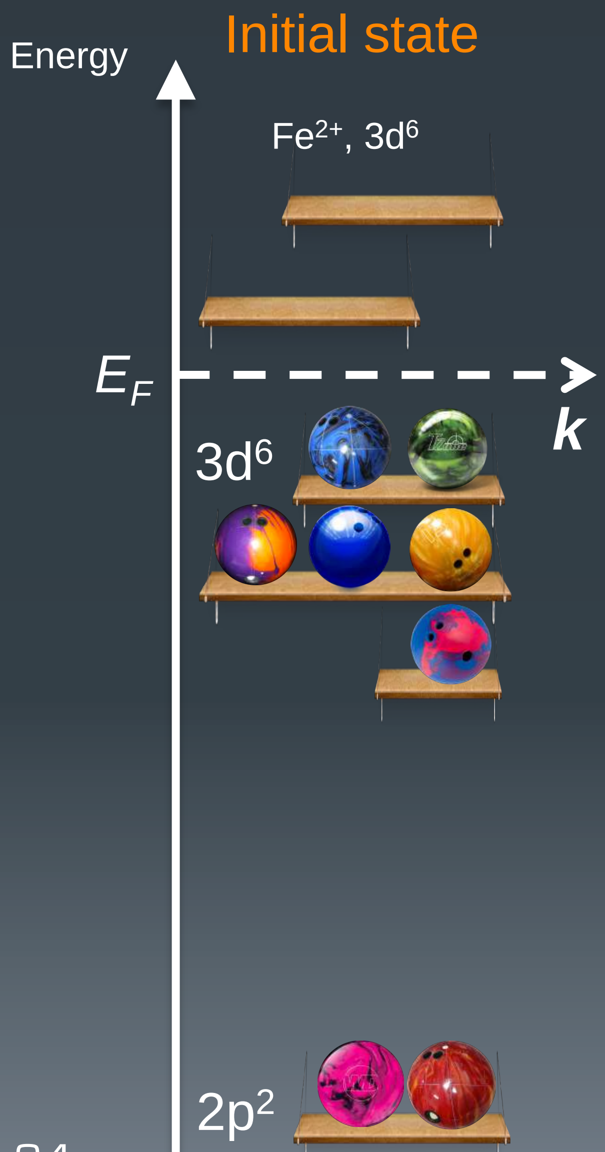
Drum roll please……

Section 4:

How does RIXS work?

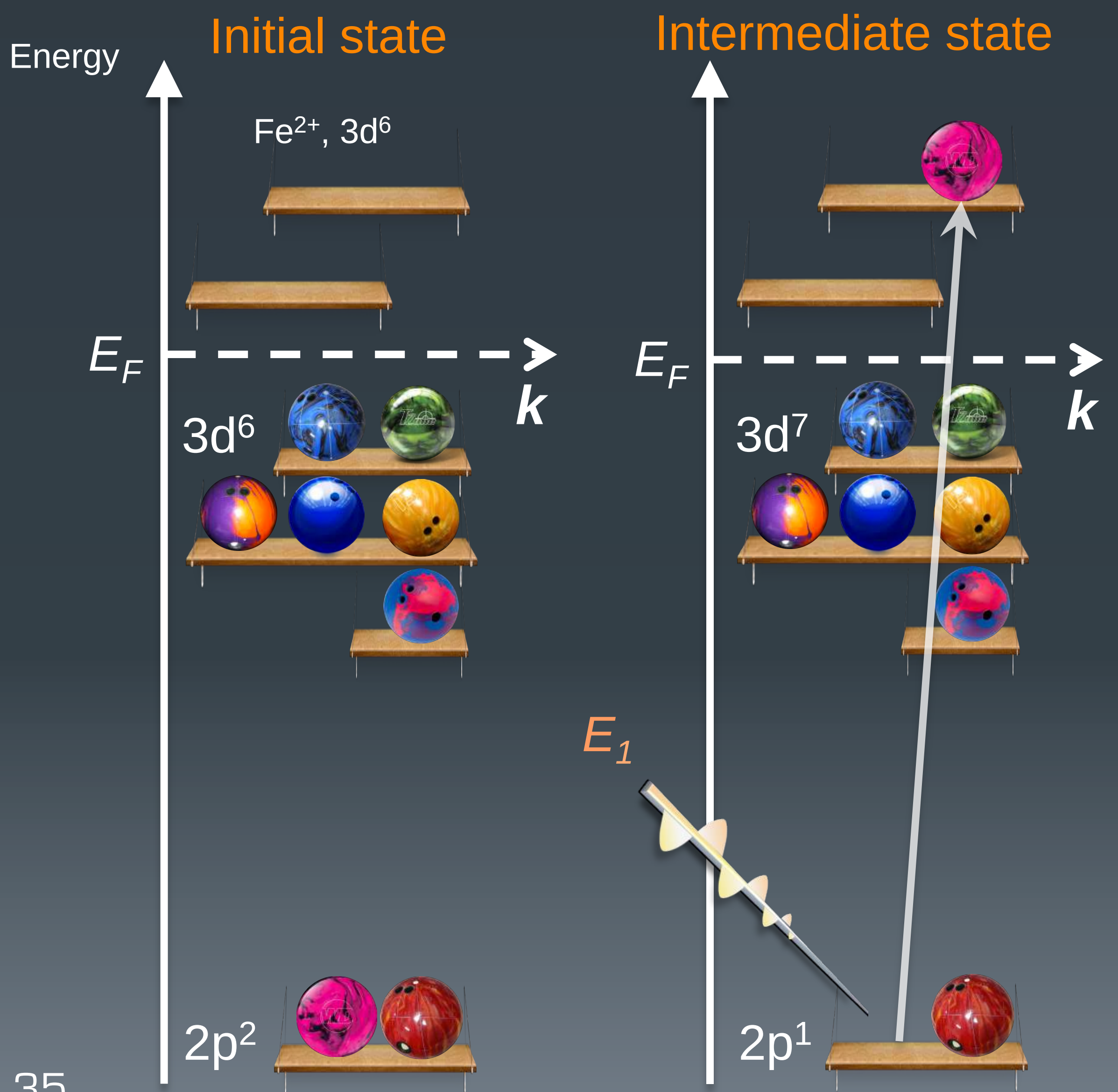
The RIXS process revealed

Three steps involved via photon-in photon-out process:



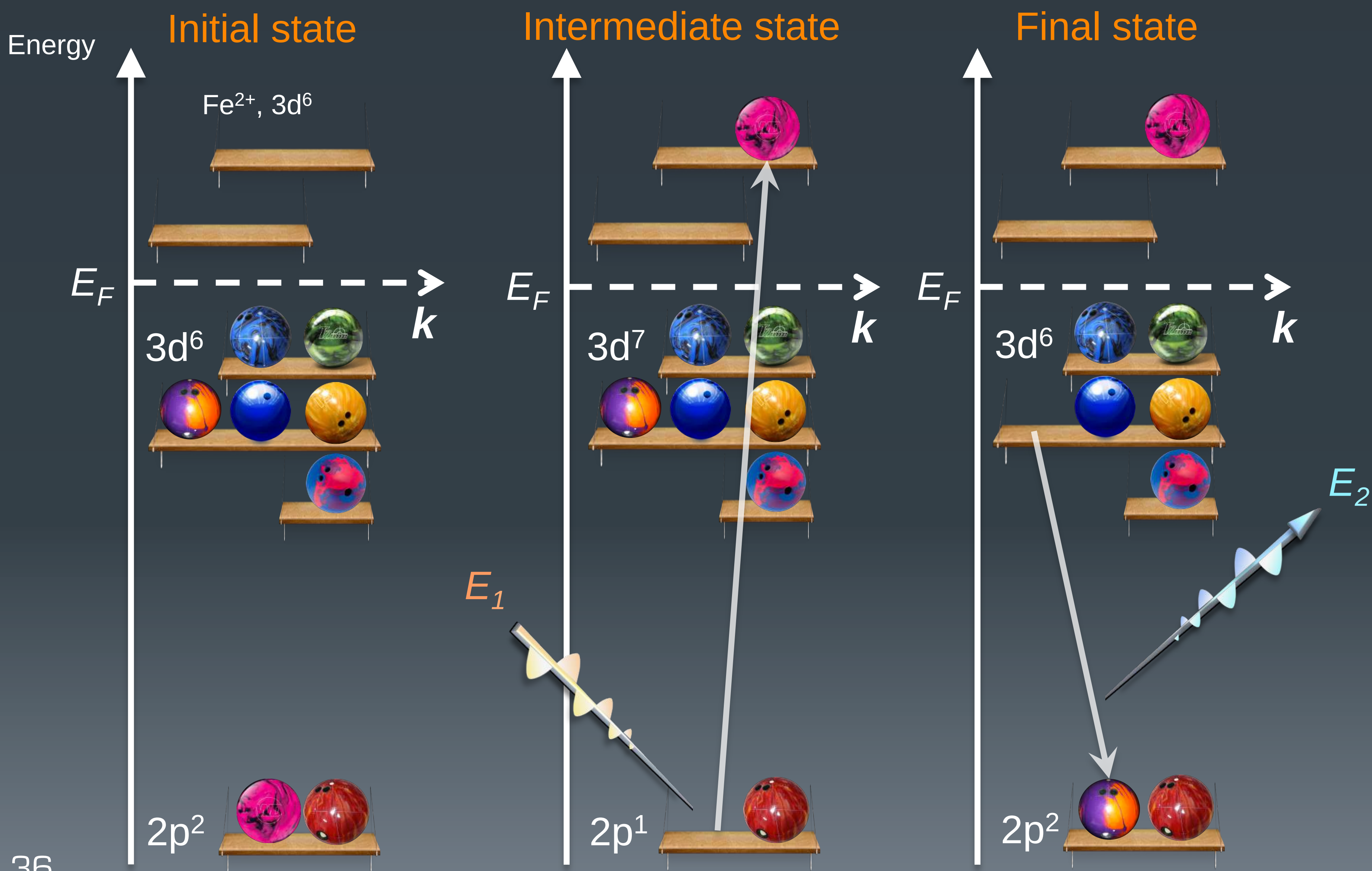
The RIXS process revealed

Three steps involved via photon-in photon-out process:



The RIXS process revealed

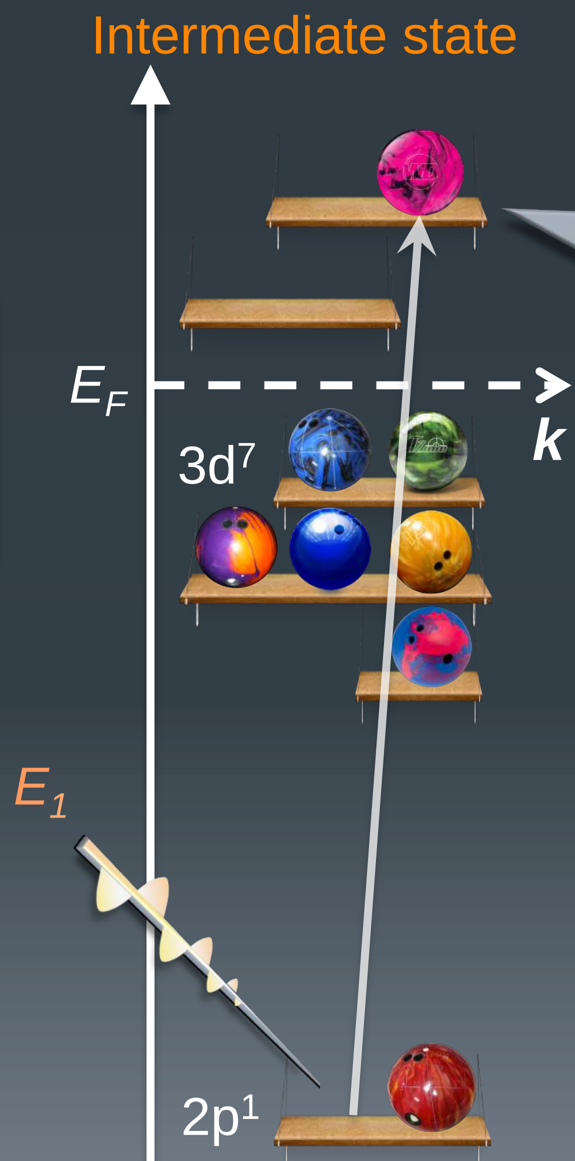
Three steps involved via photon-in photon-out process:



The RIXS process revealed

Three steps involved via photon-in photon-out process:

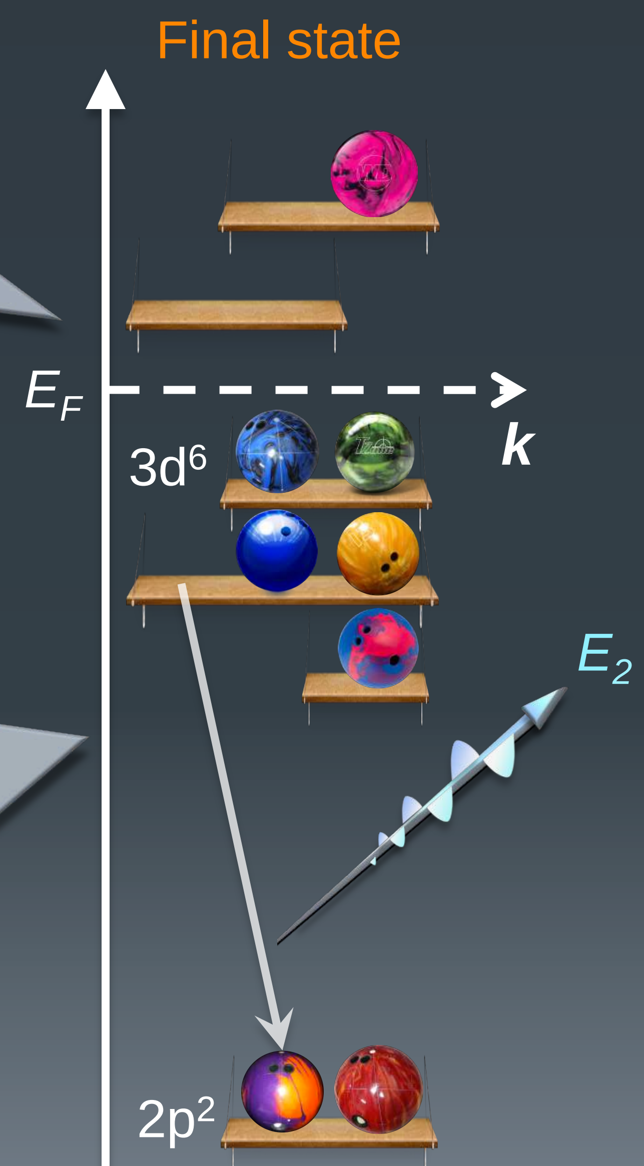
Creation of the core-hole provides **element, orbital and charge selectivity**



Sensitivity to **unoccupied states** through promotion of a core-level electron

The RIXS process revealed

Three steps involved via photon-in photon-out process:



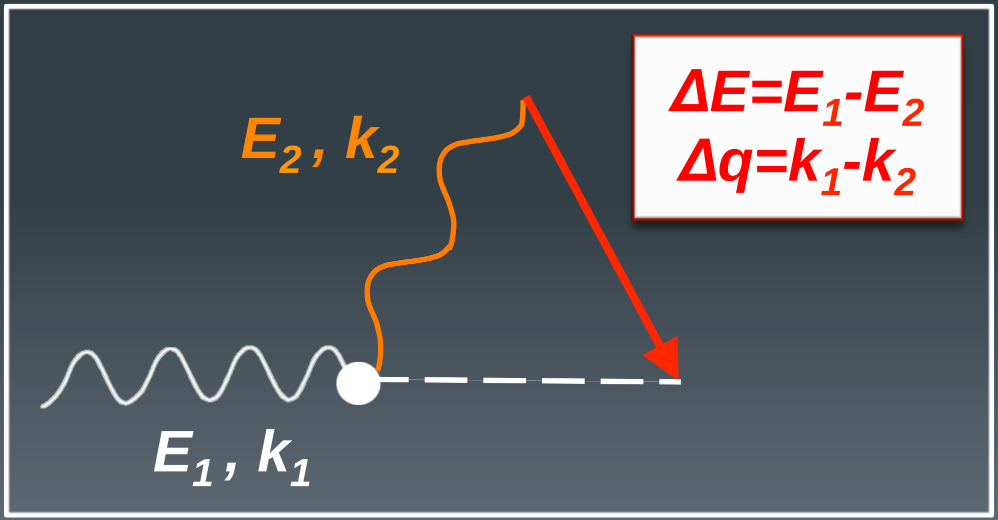
Non-dipole excitations, like here (d-d) allowed!

Sensitivity to **occupied states** through recombination of core hole with a participator valence electron

The RIXS process revealed: Summary

- RIXS measures energy and momentum transfers (ΔE, Δq) from light to electrons

- It probes local and cooperative electronic effects between the excited and decayed valence electrons and also the neighboring electrons = RIXS probes electronic correlations



Our big 'light bulb': NSLS-II

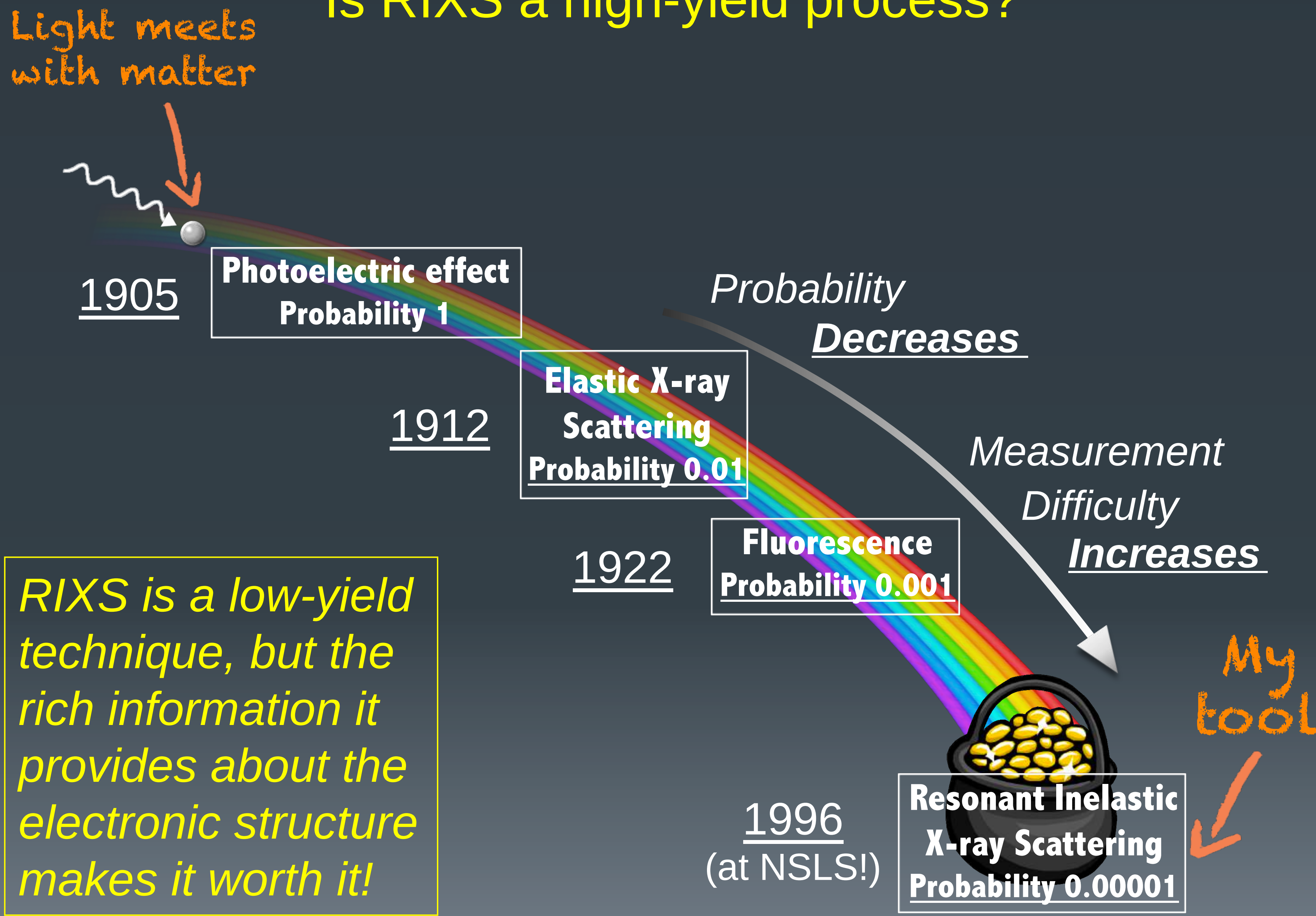
One Light Source…

Many Beamlines: Lights of different color (energy), size, brightness

Optics used to split the light into a rainbow of energies

NSLS-II makes the electrons glow!

Is RIXS a high-yield process?



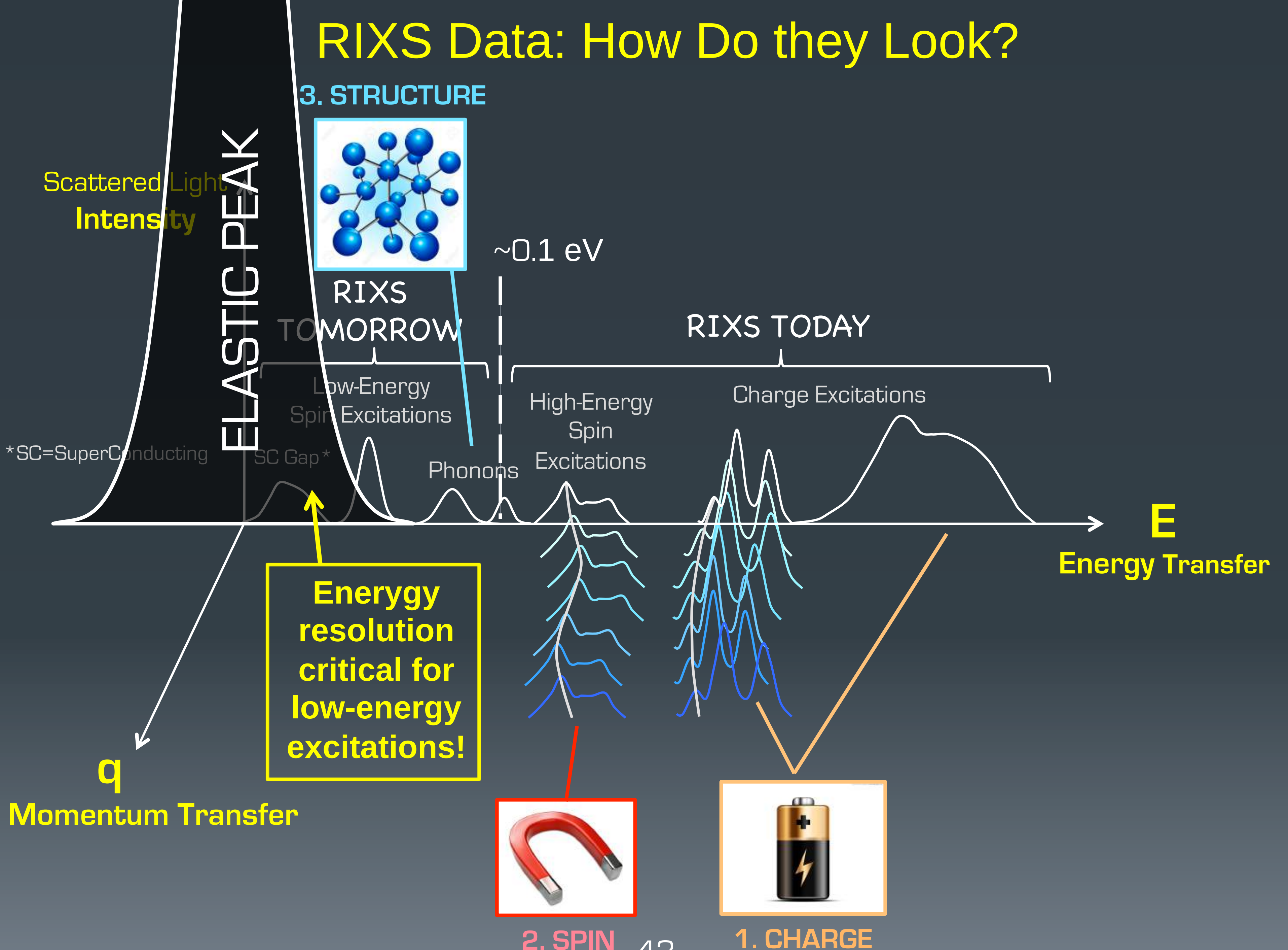
RIXS is a low-yield technique, but the rich information it provides about the electronic structure makes it worth it!

RIXS vs XAS, XPS

RIXS
XAS
XPS

- Probes both Occupied and Unoccupied States ✔
- Element and Orbital Selective ✔
- Dipole Selection Rules Non Essential ✔
- Charge Neutral ✔
- Applicable to All Sample Environments ✔
- Bulk Sensitive ✔
- Compatible with Microscopy ✔

RIXS Data: How Do they Look?



Section 5:

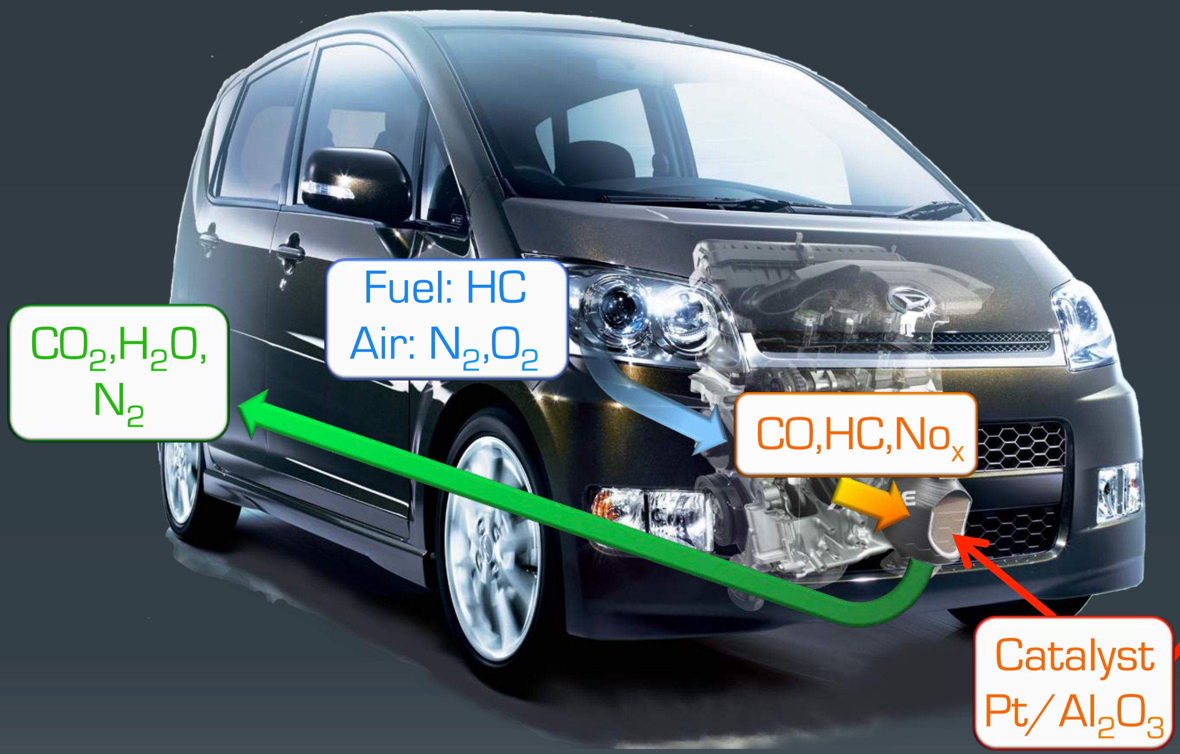
Examples of RIXS Studies

RIXS STUDY 1/2

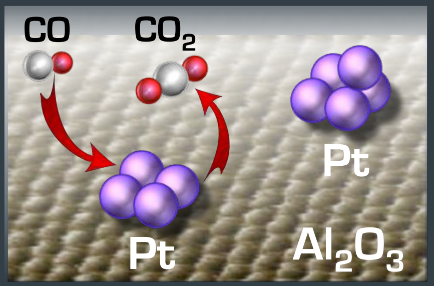
CATALYTIC CONVERTERS

A RIXS study about chemistry

What is a catalytic converter?

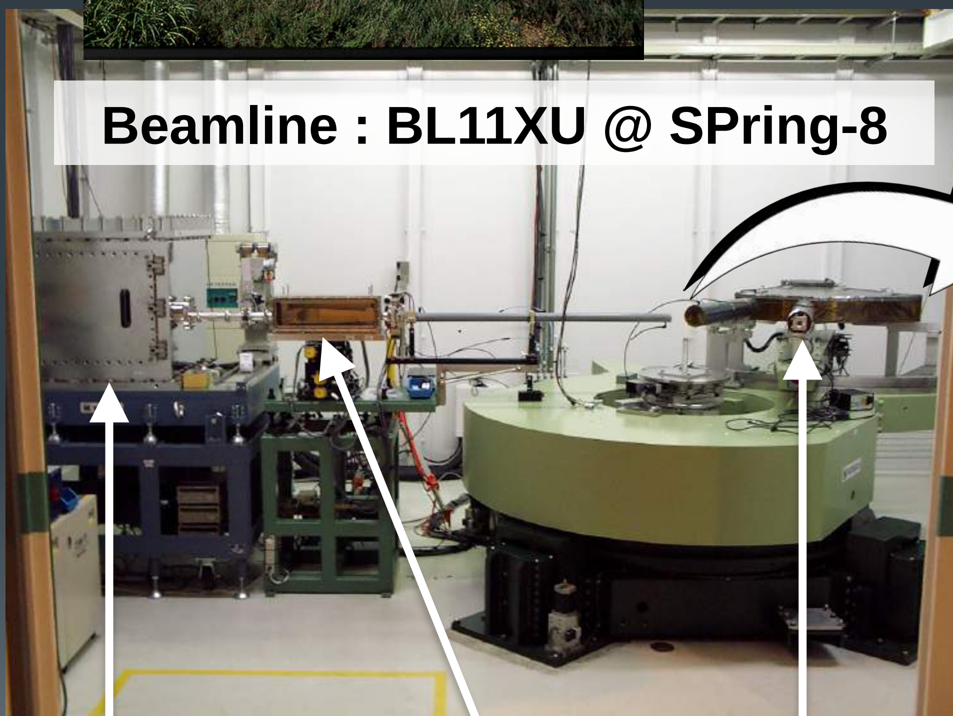


Operation Temperature
≈ 350~900 °C



Today let's focus on the reference samples: Pt, PtO_2

Experimental Setup: Hard X-ray RIXS



High-resolution monochromator

Focusing optics

Spectrometer + Detector

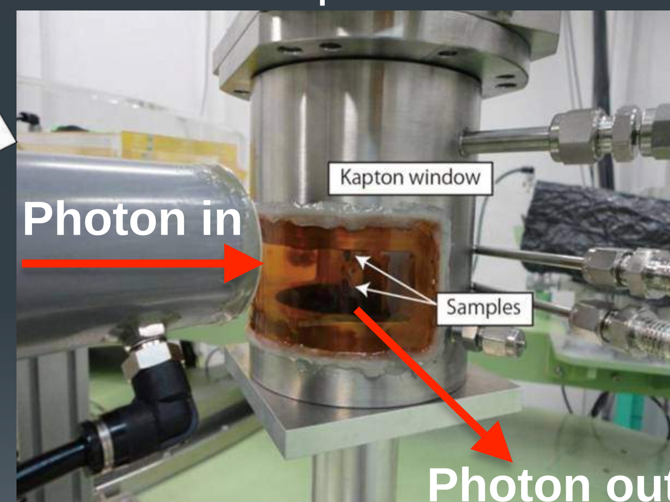
RIXS exp. conditions

Pt-L_3 : E_1=11564 eV

Energy resolution = 700 meV

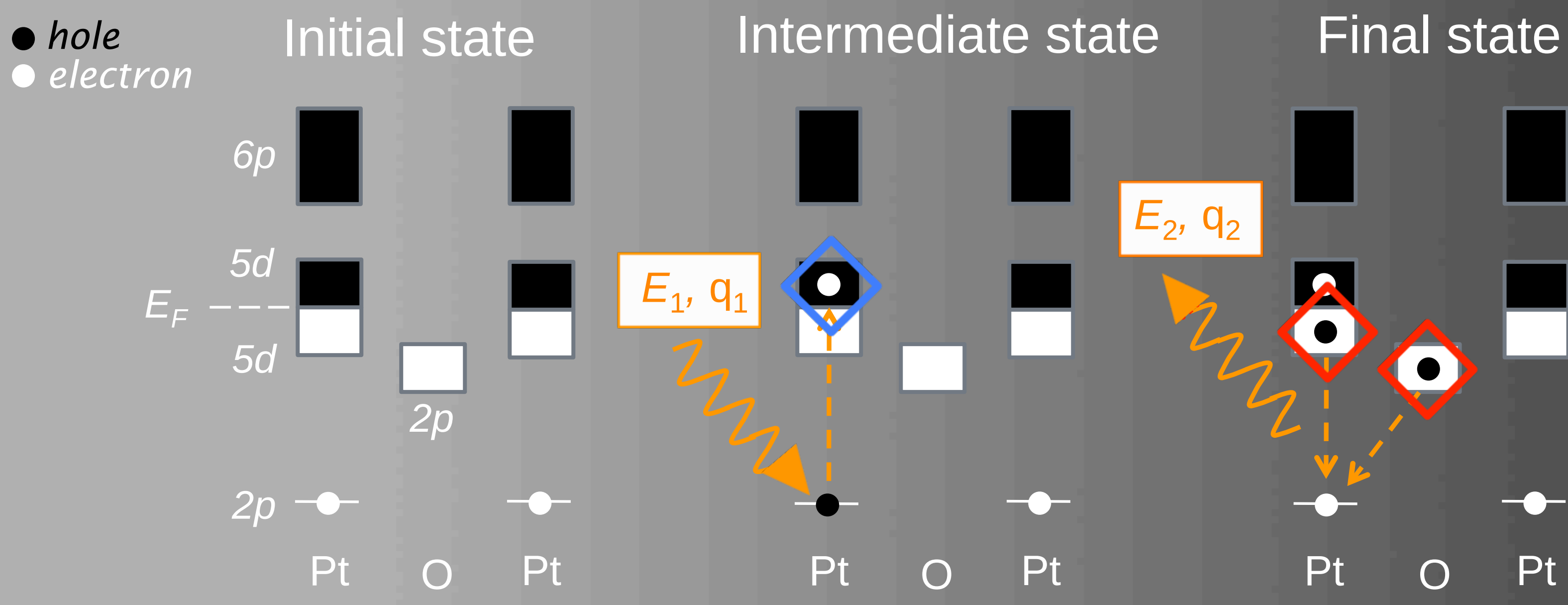
Samples: Polycrystalline Pt, PtO_2

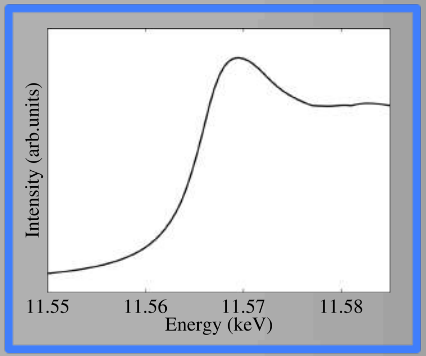
Sample Cell



Fully compatible with *in-situ* and *operando* environments!

The RIXS Process on Pt Catalysts





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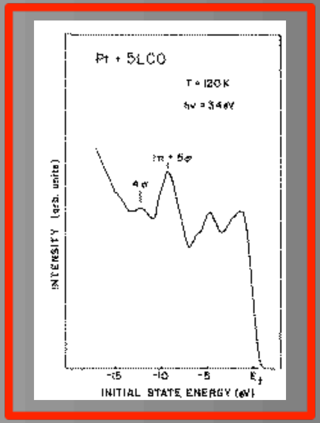

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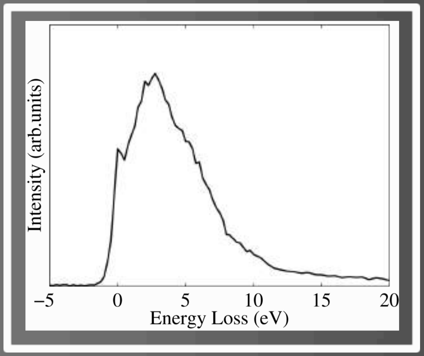


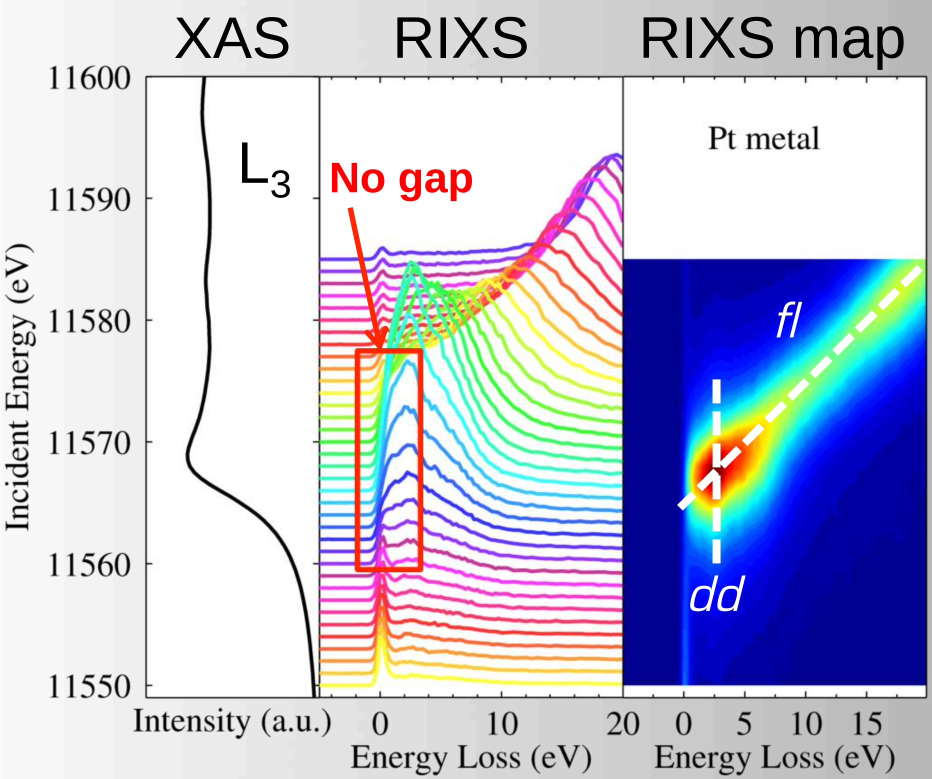
Unoccupied VB (XAS)

Occupied VB (XES)

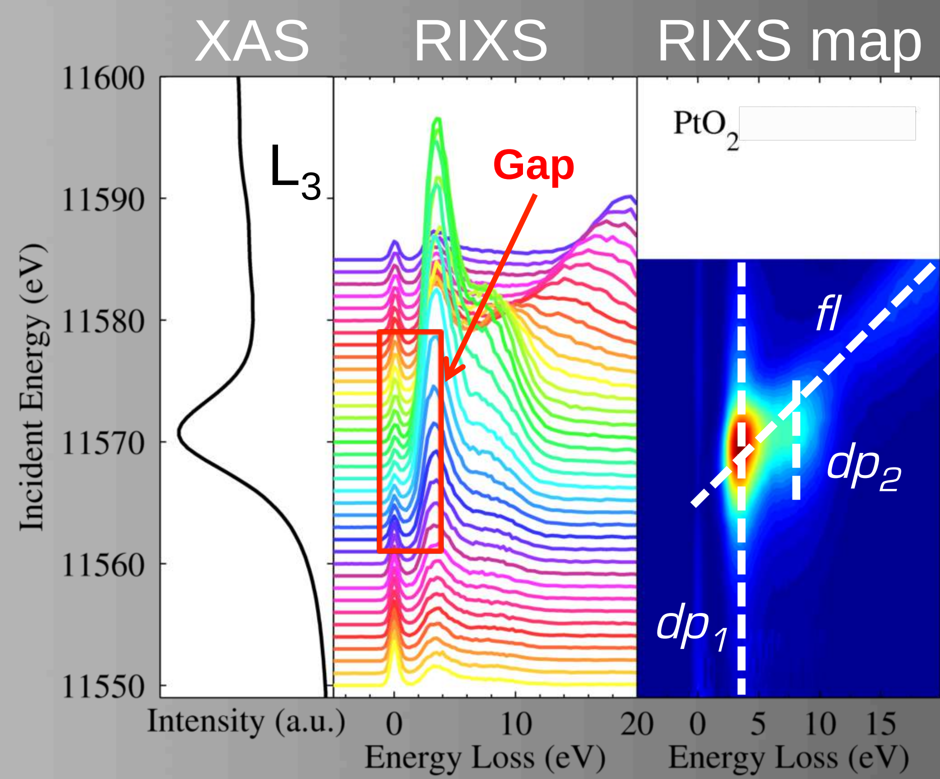
RIXS

The RIXS Process on Pt Catalysts

Pt (metal)



PtO_2 (insulator)



Feature Assignments:

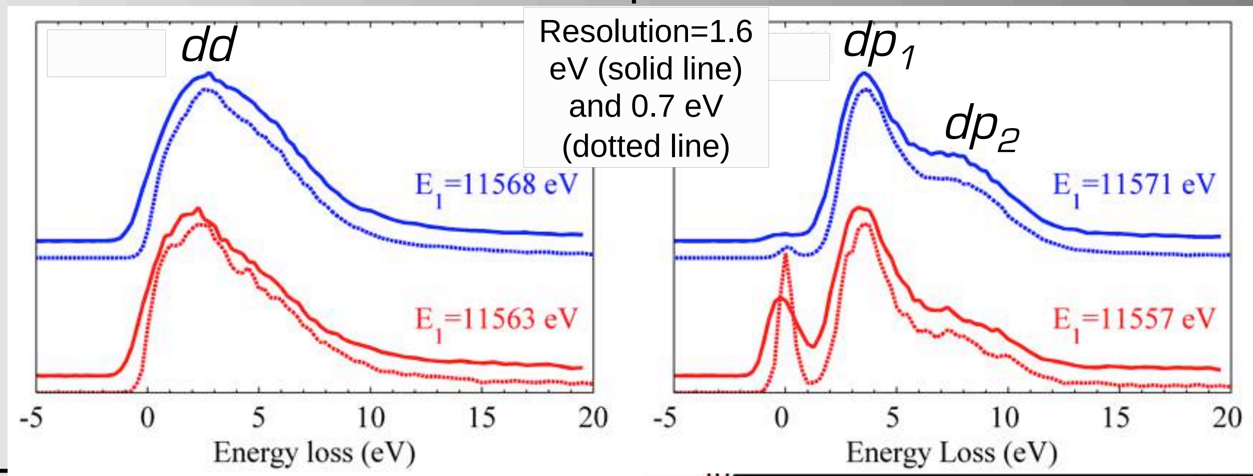
dd ➔ ????
dp ➔ ????
fl ➔ ????

If you don’t know, look at the DOS!

The RIXS Process on Pt Catalysts

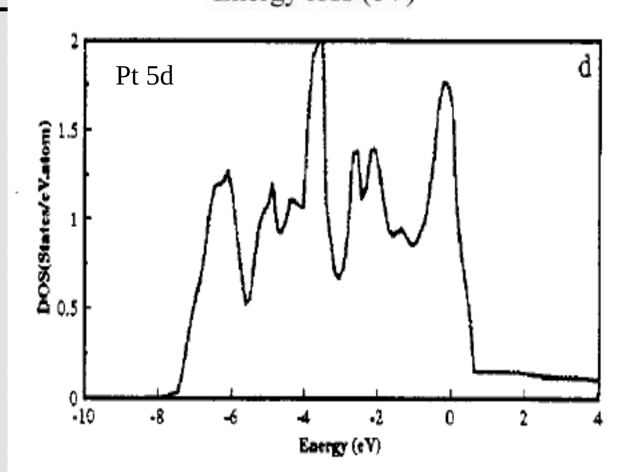
Pt (metal) | **PtO_2 (insulator)**

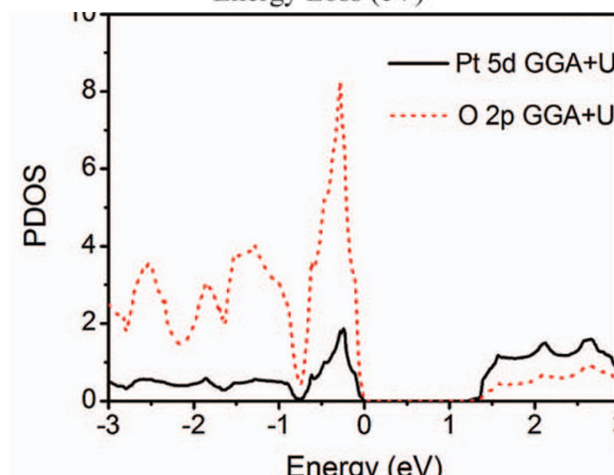
RIXS (exp.)



DOS (calc.)

W. Chen et al., Phys. Scripta, 1996



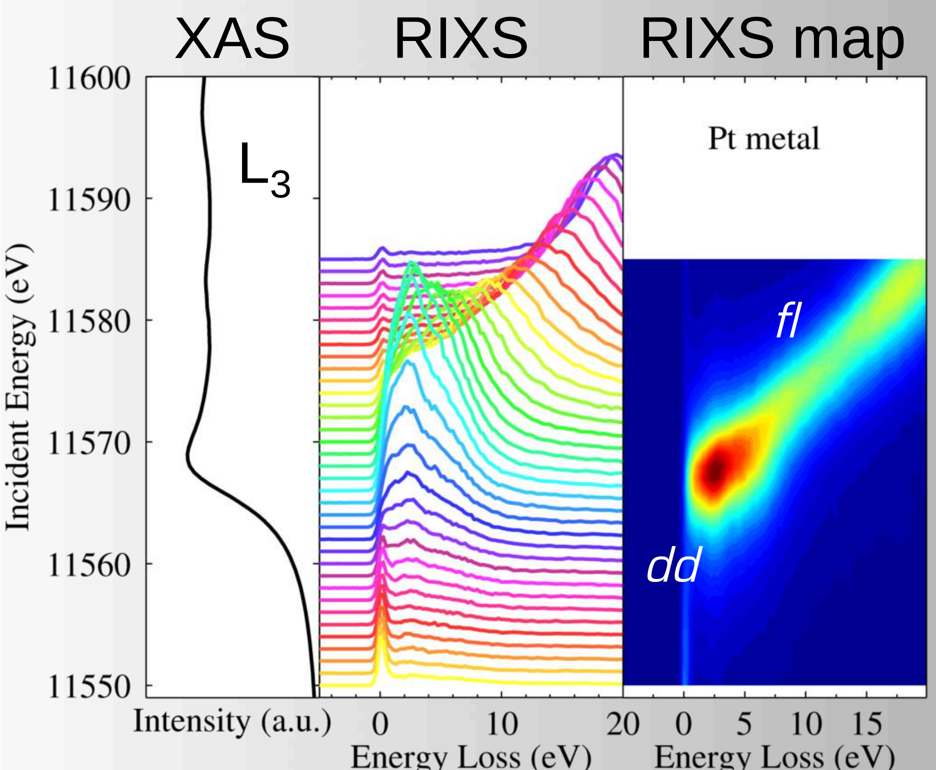


Y. Yang et al., AIP Advances, 2012

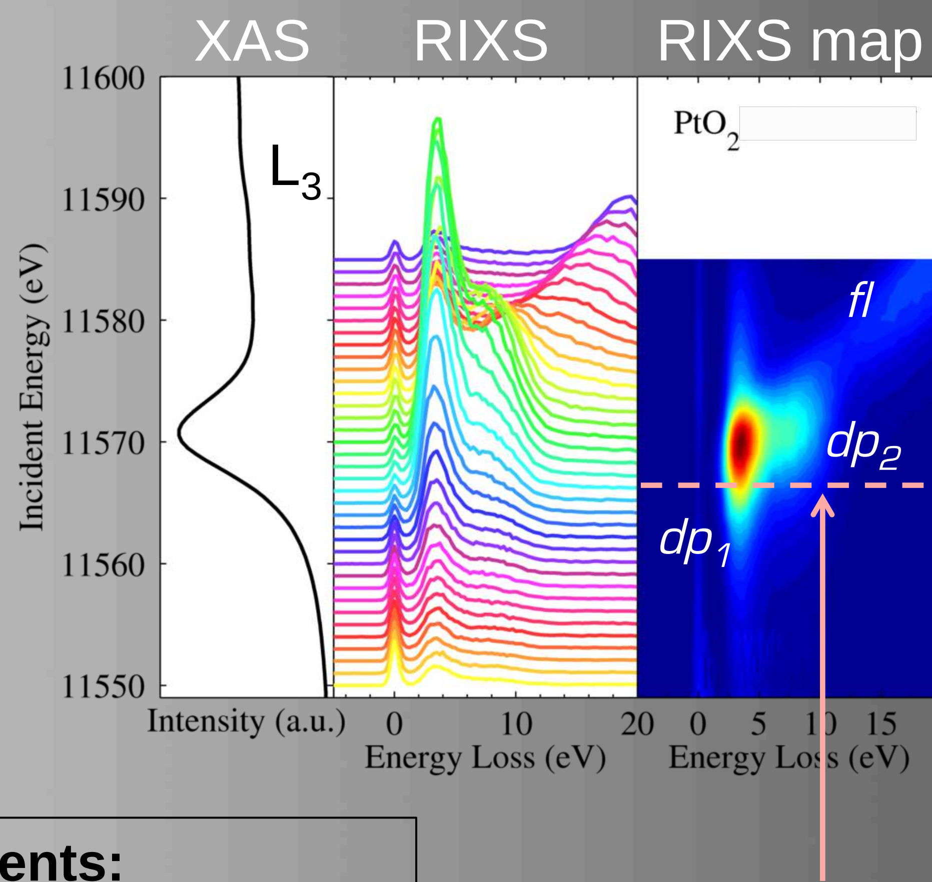
The RIXS spectra really reflect the *k*-integrated convoluted occupied and unoccupied DOS! Pure 5d for Pt metal, and mixed Pt5d-O2p for PtO_2

The RIXS Process on Pt Catalysts

Pt (metal)



PtO_2 (insulator)



Feature Assignments:

dd ➔ Pt5d - Pt5d transitions (RIXS)

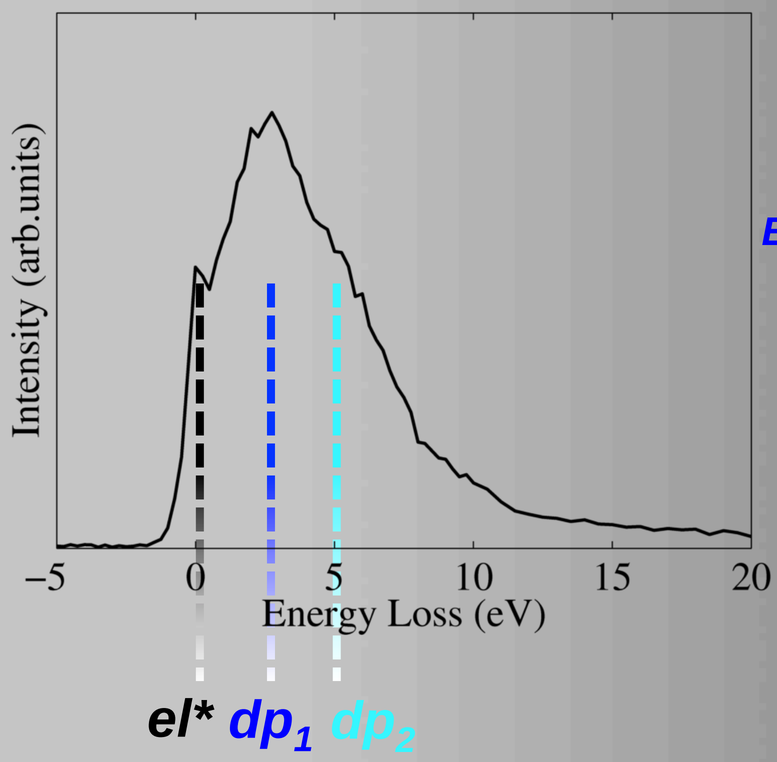
dp ➔ Pt5d/O2p - Pt5d/O2p transitions (RIXS)

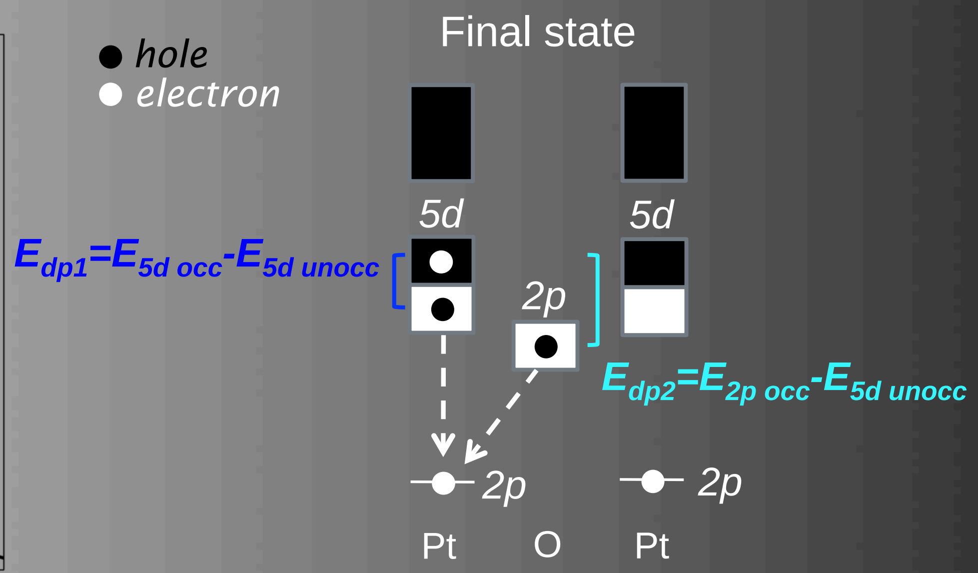
fl ➔ Fluorescence (XES)

NEXT SLIDE:
Take a slice here

The RIXS Process on Pt Catalysts

el* = elastic peak

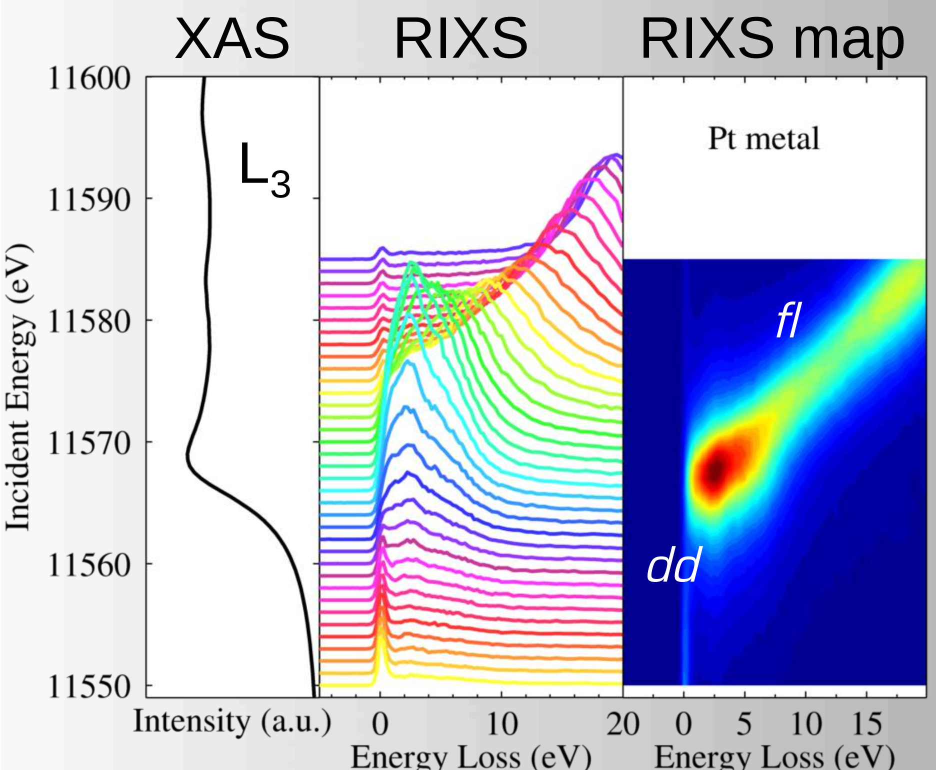




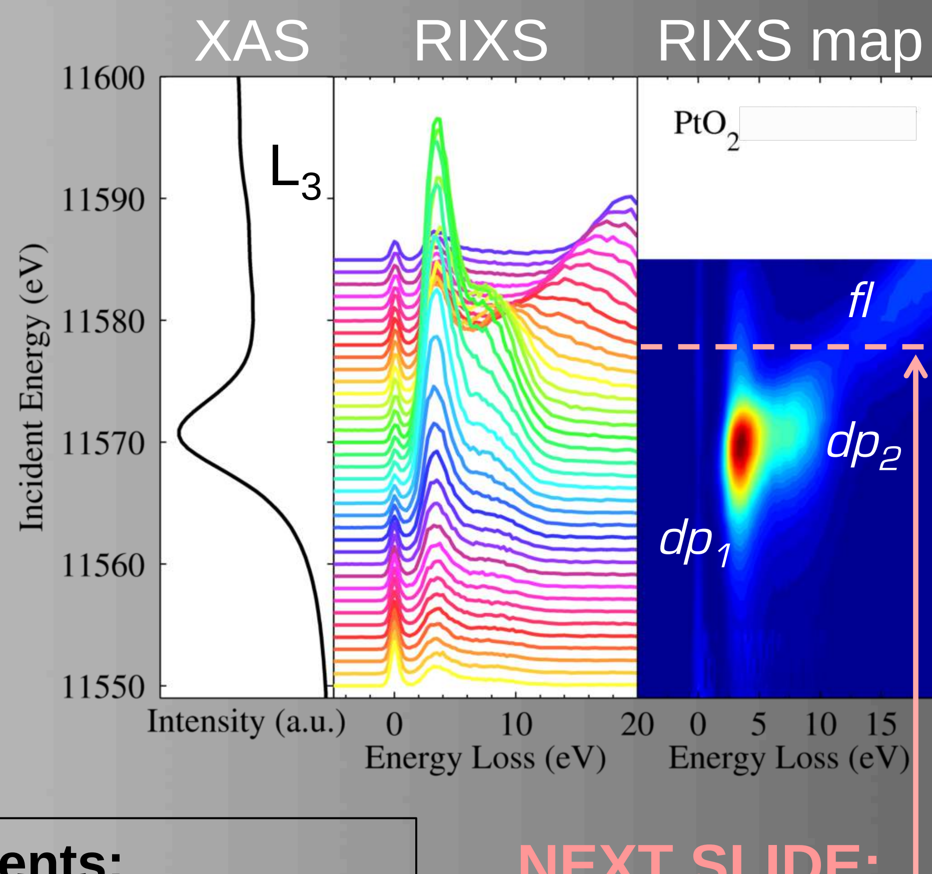
Unoccupied VB * Occupied VB = <u>RIXS</u>, E loss constant

The RIXS Process on Pt Catalysts

Pt (metal)



PtO_2 (insulator)



Feature Assignments:

dd ➔ Pt5d - Pt5d transitions (RIXS)

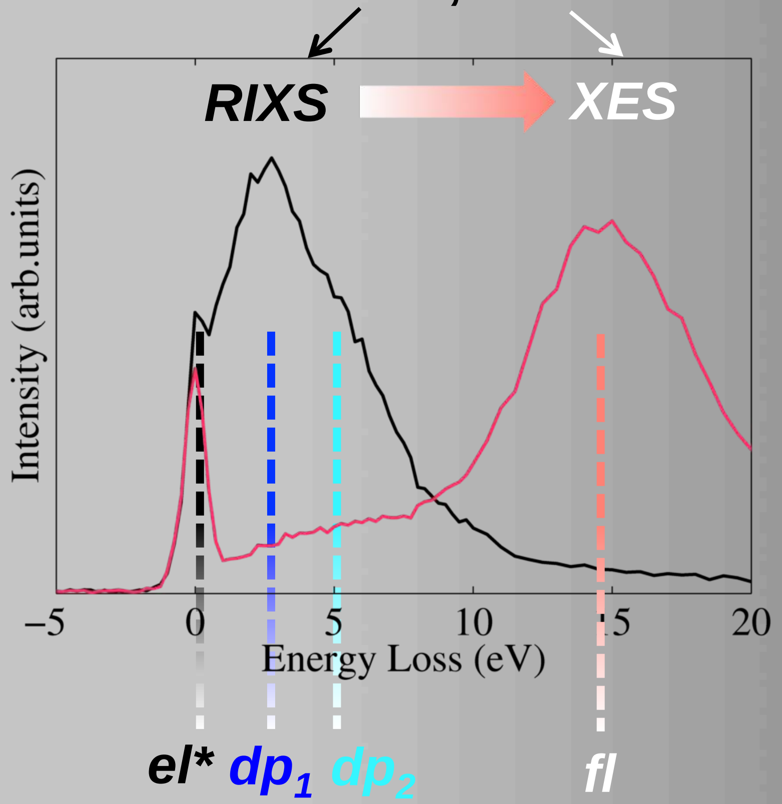
dp ➔ Pt5d/O2p - Pt5d/O2p transitions (RIXS)

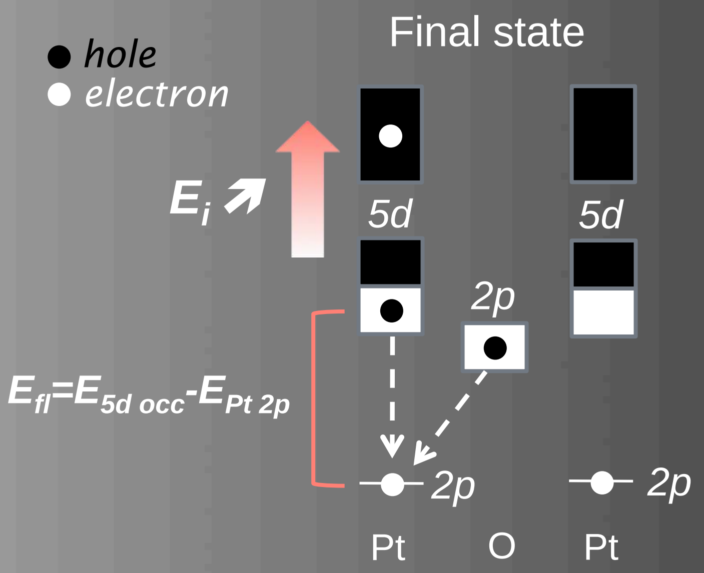
fl ➔ Fluorescence (XES)

NEXT SLIDE:
Take a slice here

The RIXS Process on Pt Catalysts

Two spectroscopic processes intertwined: Raman, Fluorescence



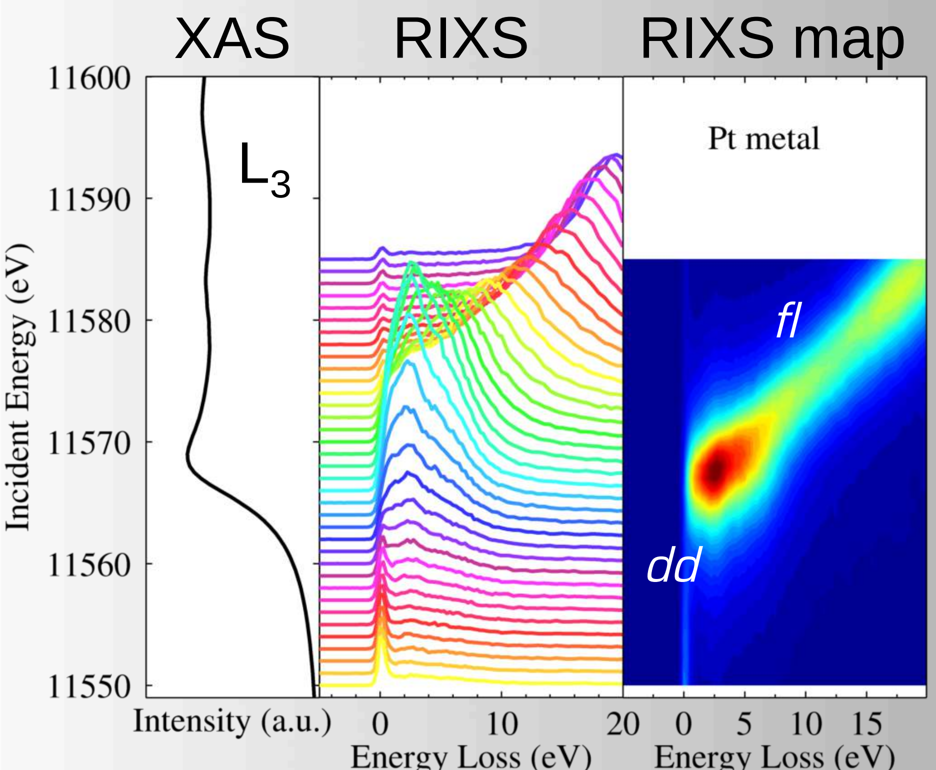


Unoccupied VB * Occupied VB = RIXS, E loss constant

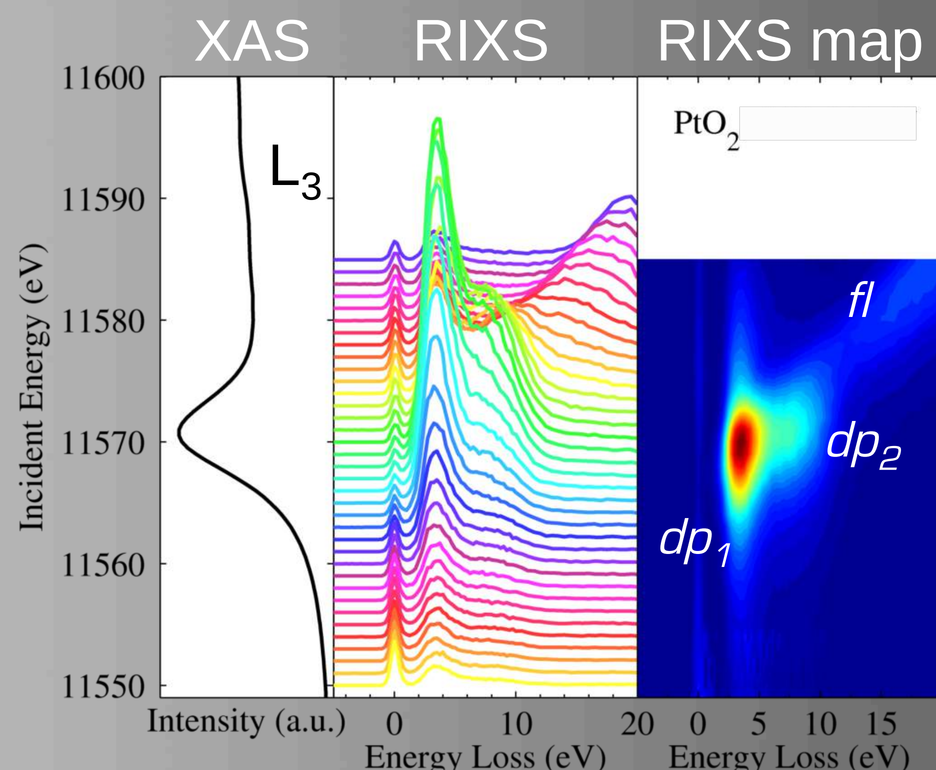
Occupied VB: XES, E photon constant (E loss drifts!)

The RIXS Process on Pt Catalysts

Pt (metal)



PtO_2 (insulator)



XES (fluores.) stronger than RIXS

RIXS (Raman) stronger than XES

Metallicity ↗

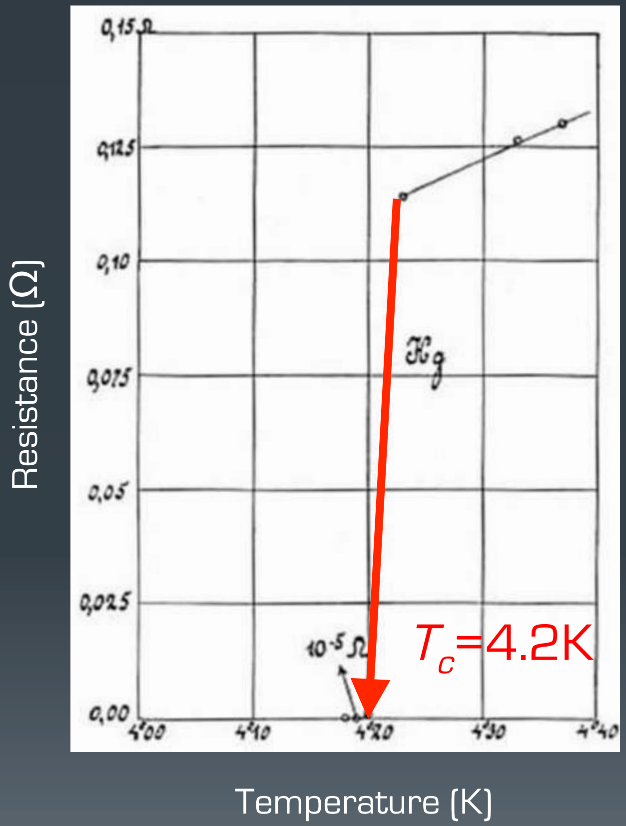
RIXS is weaker in metals where conduction states are more delocalized, and lifetime of excited photoelectron in intermediate state is shorter

High-T_C SUPERCONDUCTIVITY

A RIXS study about physics

How It Began

1911: First Observation of Superconductivity, in Mercury
(H.K. Onnes)

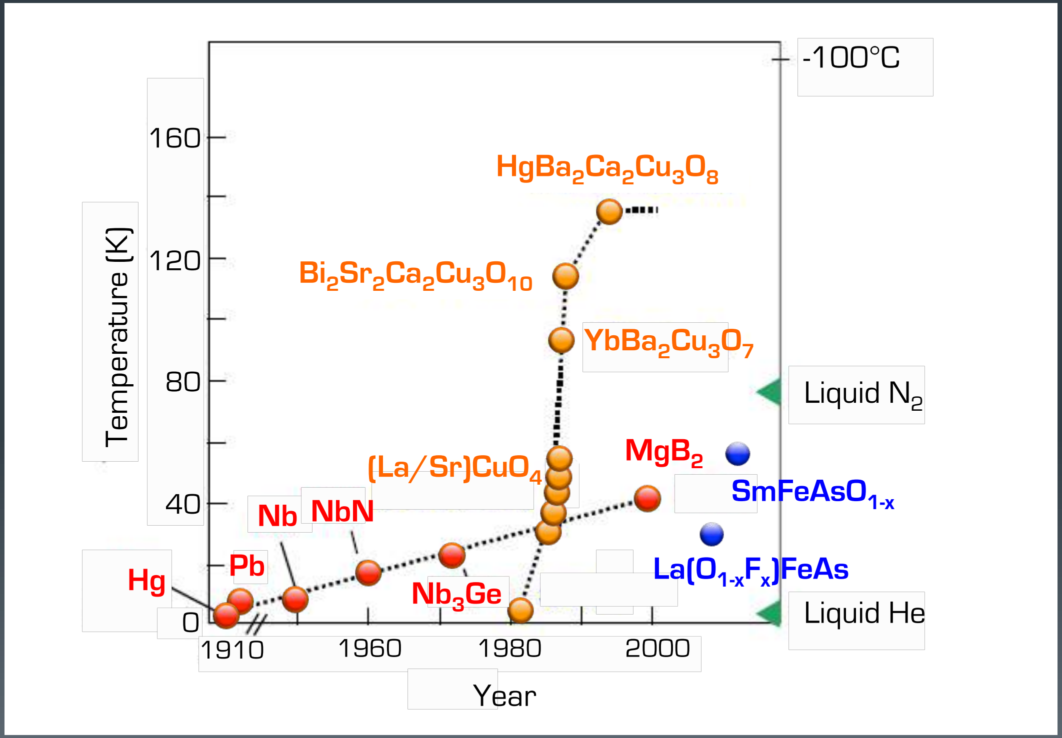


How It Took Off

1911 - … : Conventional Superconductors

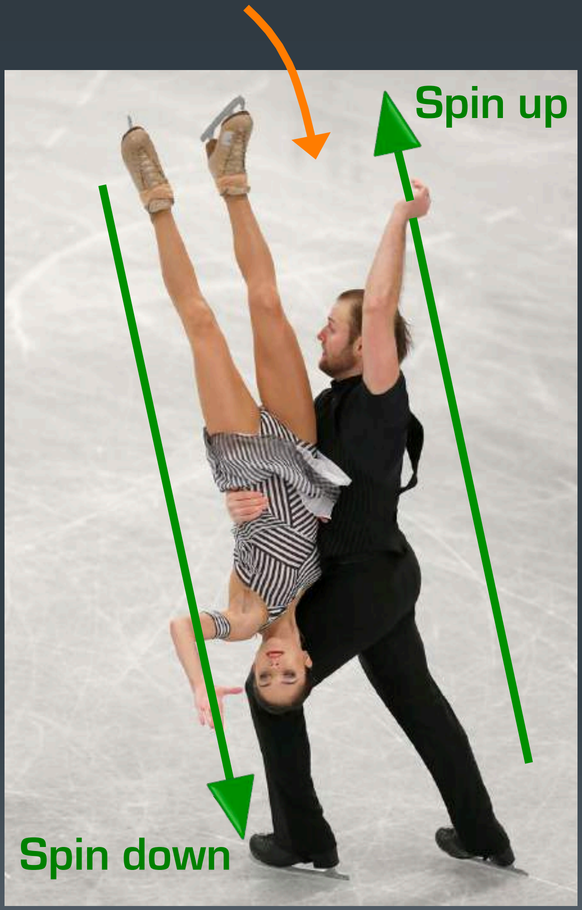
1986 - … : Cuprates Superconductors (High-T_C)

2008 - … : Iron-based Superconductors (High-T_C)

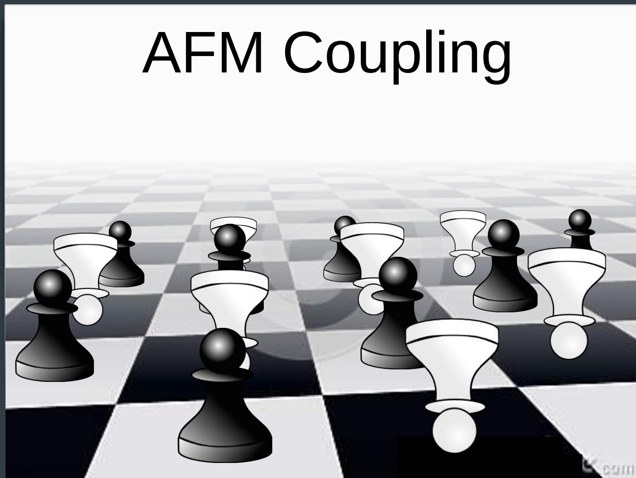


Superconductivity Is About Cooper Pairs

If these people were electrons, to superconduct they would need to form pairs like this



How Do Cooper Pairs Form In Cuprates?



AFM=AntiFerroMagnetic

T↘
+
Electron doping

Antiferromagnetic Interactions Likely At The Origin of Cooper Pair Formation In Cuprates: How do we Know?

BNL study that uses RIXS

nature materials

LETTERS

PUBLISHED ONLINE: 4 AUGUST 2013 | DOI: 10.1038/NMAT3723

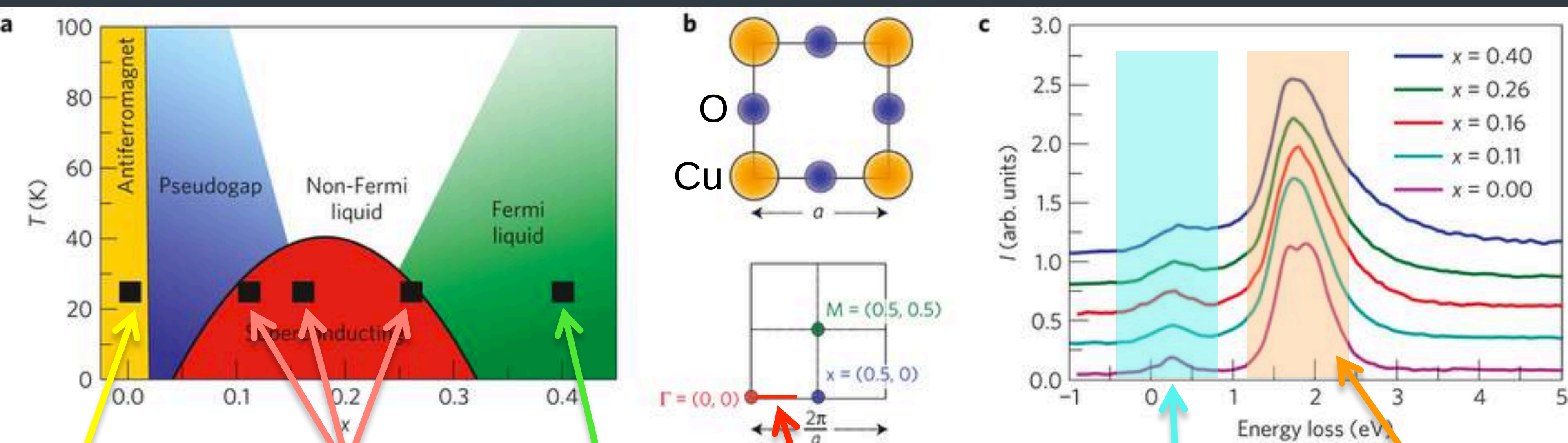
Persistence of magnetic excitations in $La_{2-x}Sr_xCuO_4$ from the undoped insulator to the heavily overdoped non-superconducting metal

M. P. M. Dean[1]*, G. Dellea[2], R. S. Springell[3], F. Yakhou-Harris[4], K. Kummer[4], N. B. Brookes[4], X. Liu[1,5], Y-J. Sun[1,5], J. Strle[1,6], T. Schmitt[7], L. Braicovich[2,8], G. Ghiringhelli[2,8], I. Božović[1] and J. P. Hill[1]*

Using RIXS To Detect Spin Excitations

Exploring the phase diagram of a superconductor with RIXS:

Phase diagram of $La_{2-x}Sr_xCuO_4$ | CuO_2 plaquette | RIXS Data



Underdoped

Superconducting

Overdoped

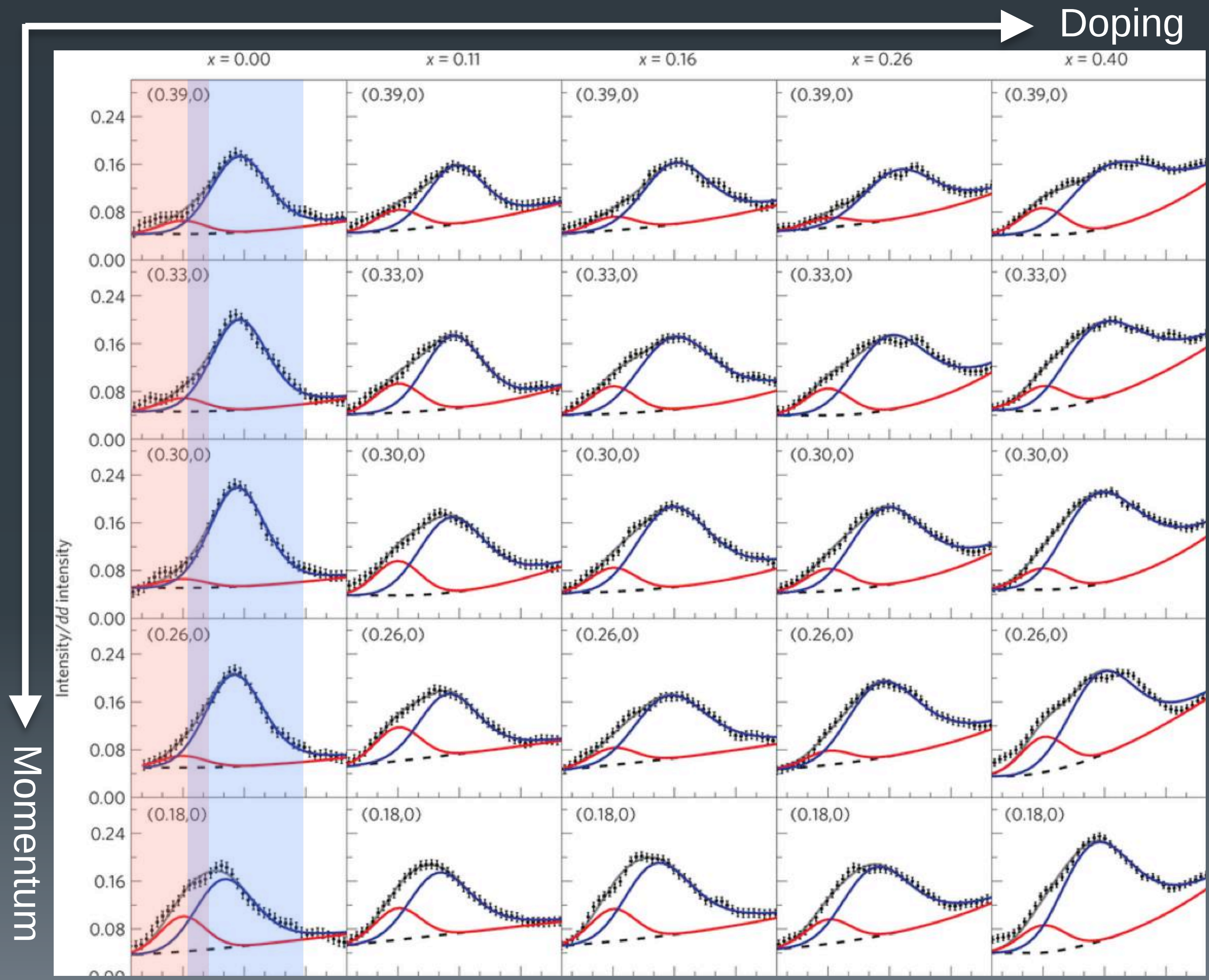
Momentum range of soft RIXS experiment

Elastic peak + spin excitation

Charge excitations (d-d)

Using RIXS To Detect Spin Excitations

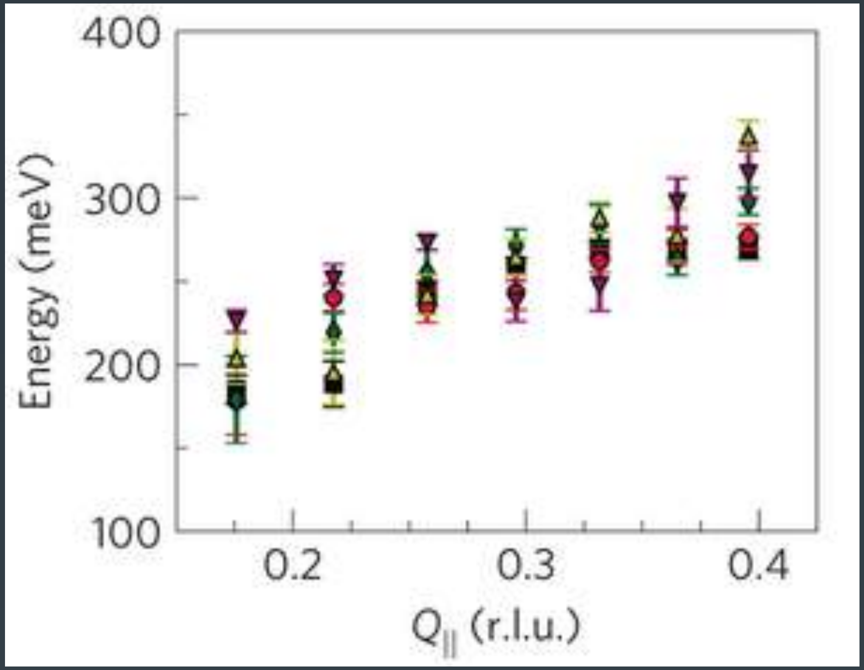
Spin excitations found to persist in superconducting state!



Elastic peak **Spin excitation**

Using RIXS To Detect Spin Excitations

Dispersion of the spin excitation measured by RIXS:



Good agreement with Inelastic Neutron Scattering (INS).

<u>RIXS can be used on small crystals</u> (beam size down to ~10 μm nowadays)

Neutrons need BIG crystals,
or a LOT of small ones:

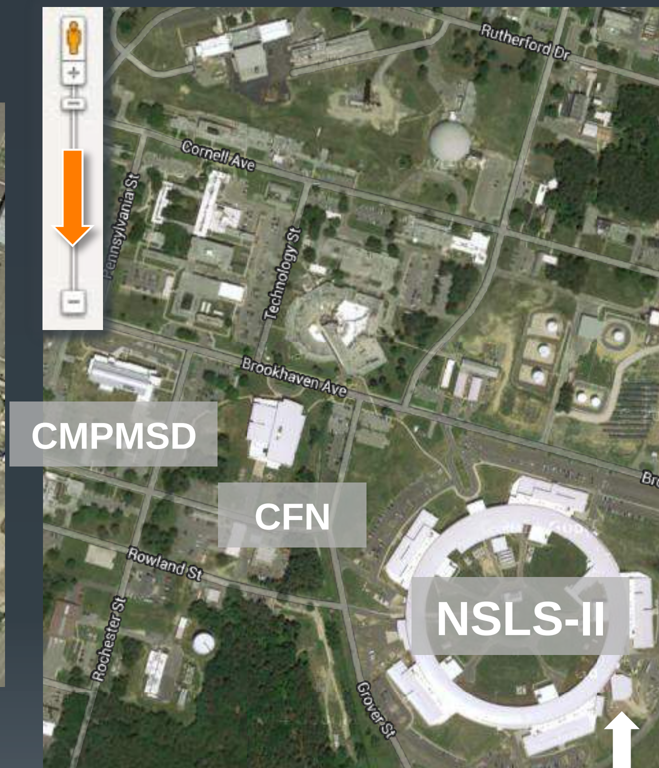
AMES Laboratory

Section 6:

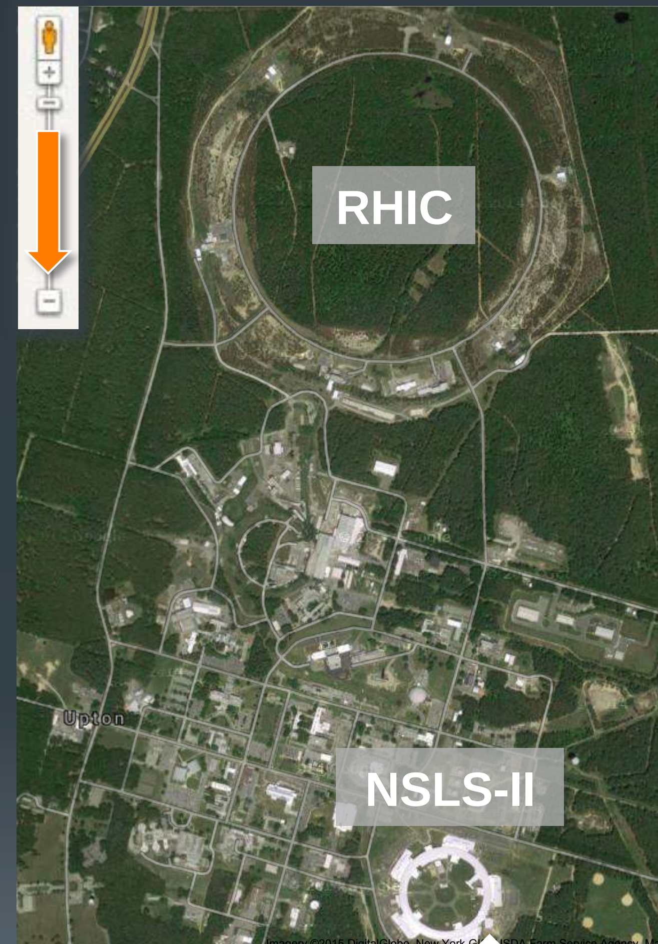
RIXS at NSLS-II

The SIX Beamline at NSLS-II, and the Neighborhood at BNL

SIX



SIX



SIX

SIX in Four Words

SOFT

INELASTIC

X-RAY

SCATTERING

SIX in One Number

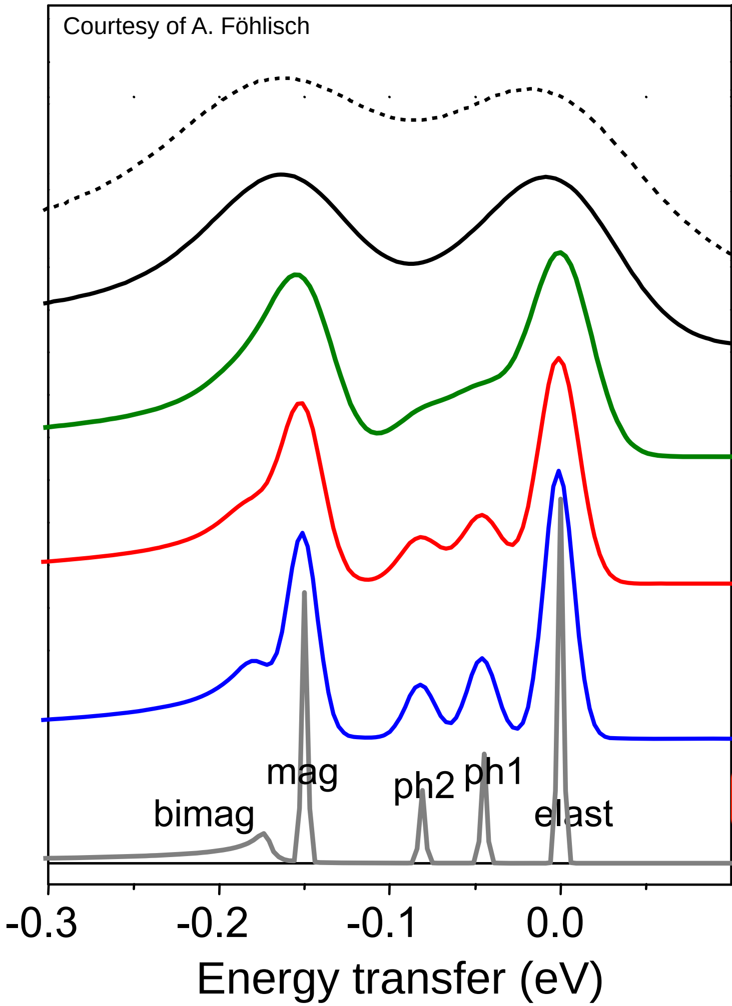
A Resolving Power Of

100,000

Ability to Distinguish Photons With a Difference in Energy of 0.001%

World-Wide Resolution Race in RIXS

RIXS Spectrum Shown for Different Energy Resolutions



RIXS Instruments Around the World

E/Δ*E*

Operations

- 7000 – ARHEA @ SOLEIL; Hornet @ SPring-8; qRIXS @ ALS
- 10000 ← ADRESS @ SLS

20000

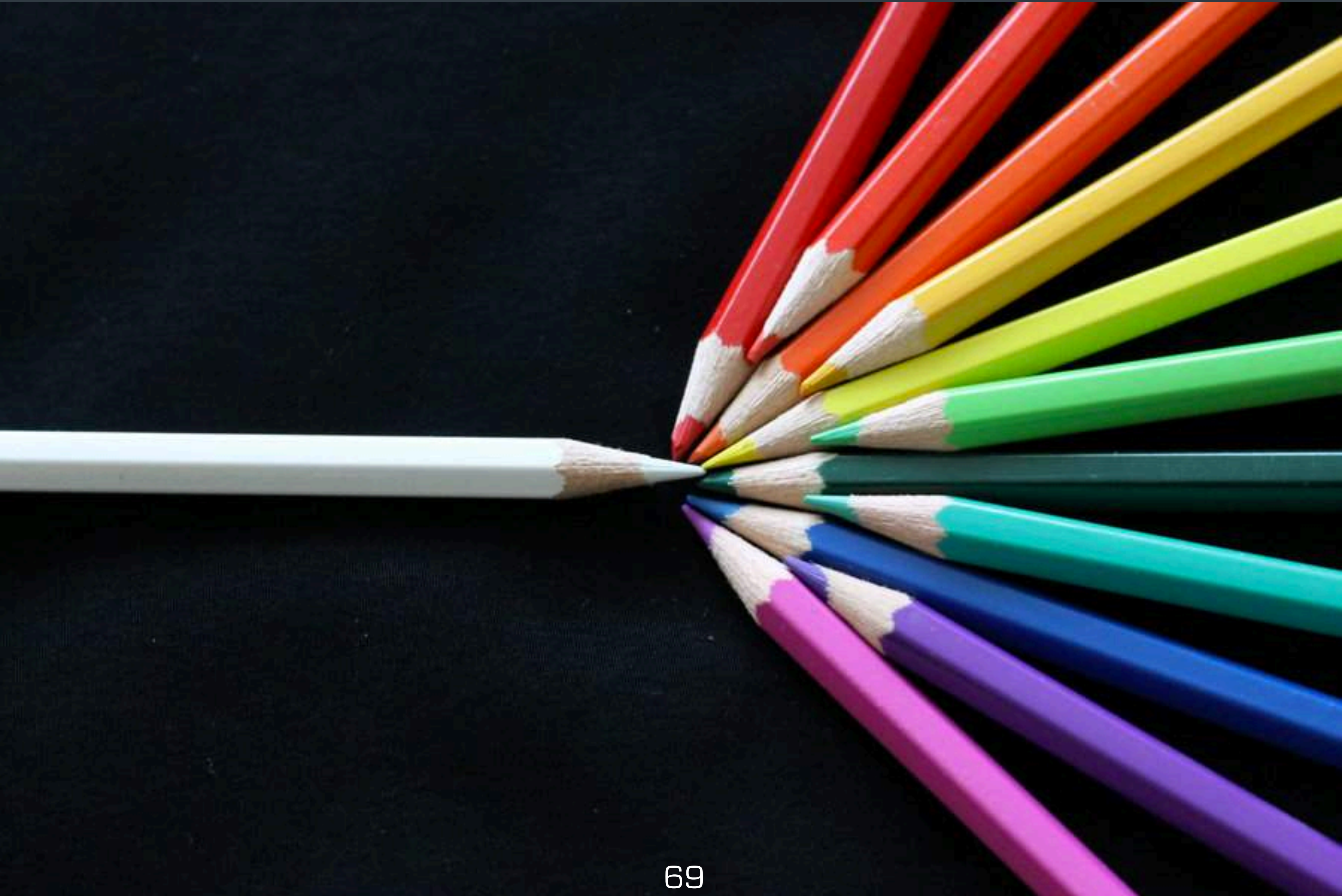
Under Construction

- 30000 – eRIXS @ ESRF; Veritas @ MaxLab4; AGS-AGM @ TPS; I21 @ Diamond

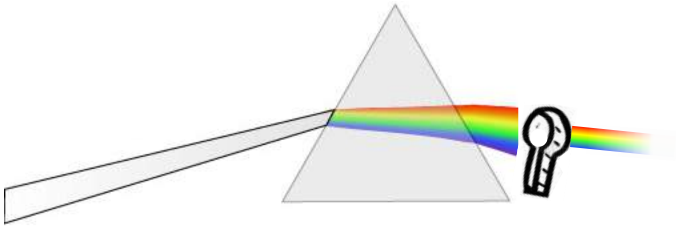
40000

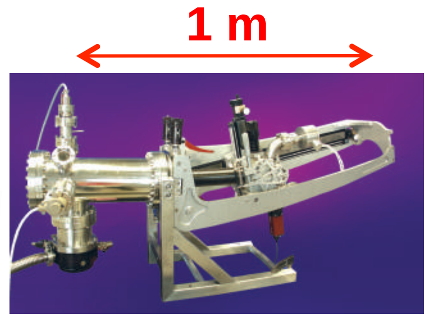
- **100000 ← SIX @ NSLS-II**
- ∞ ← **Ideal (theory)**

SIX Needs To Be Loooooong (100000)

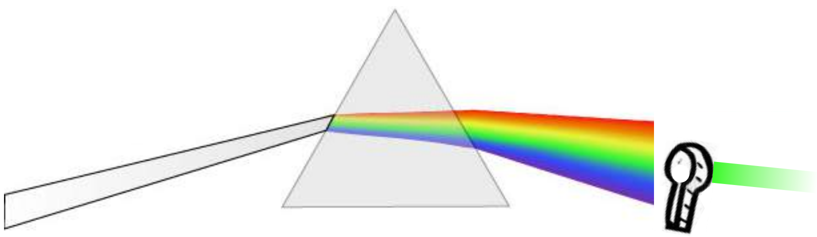


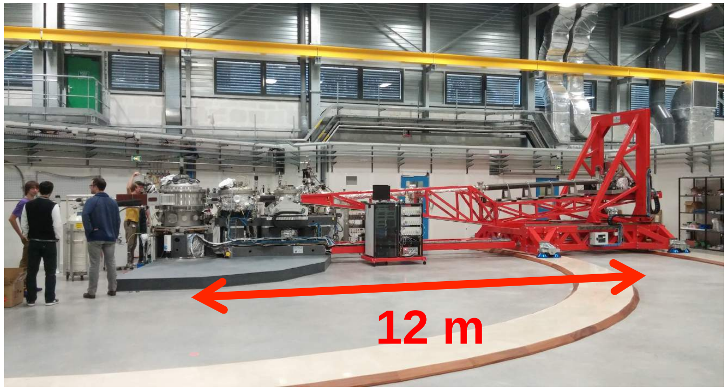
Spectrometer: How Long is Long?



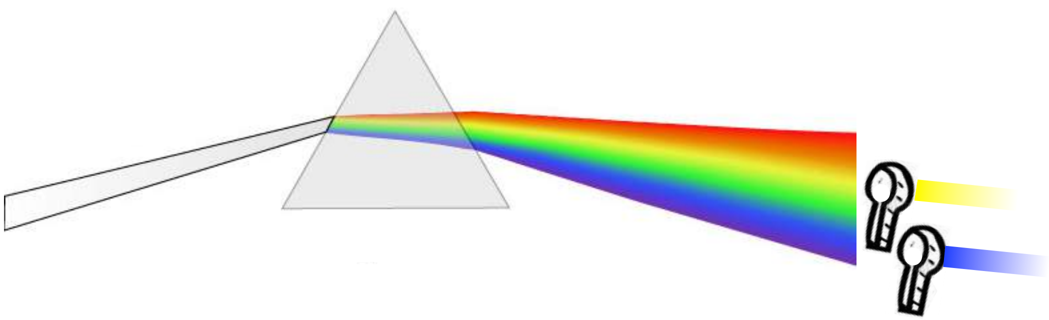


Commercial Spectrometer

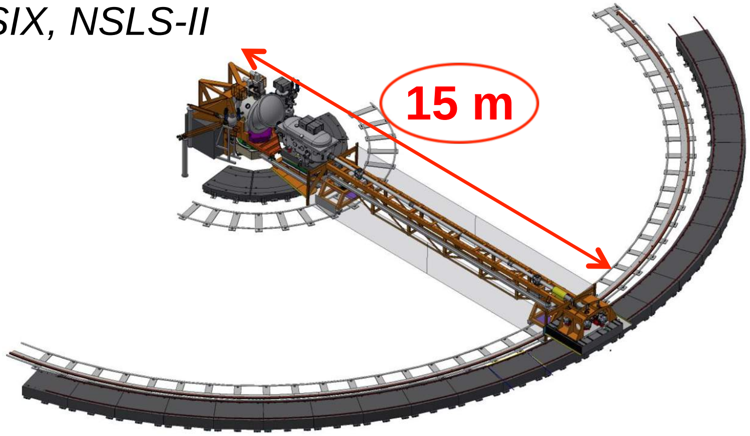




ID32
ESRF (France)

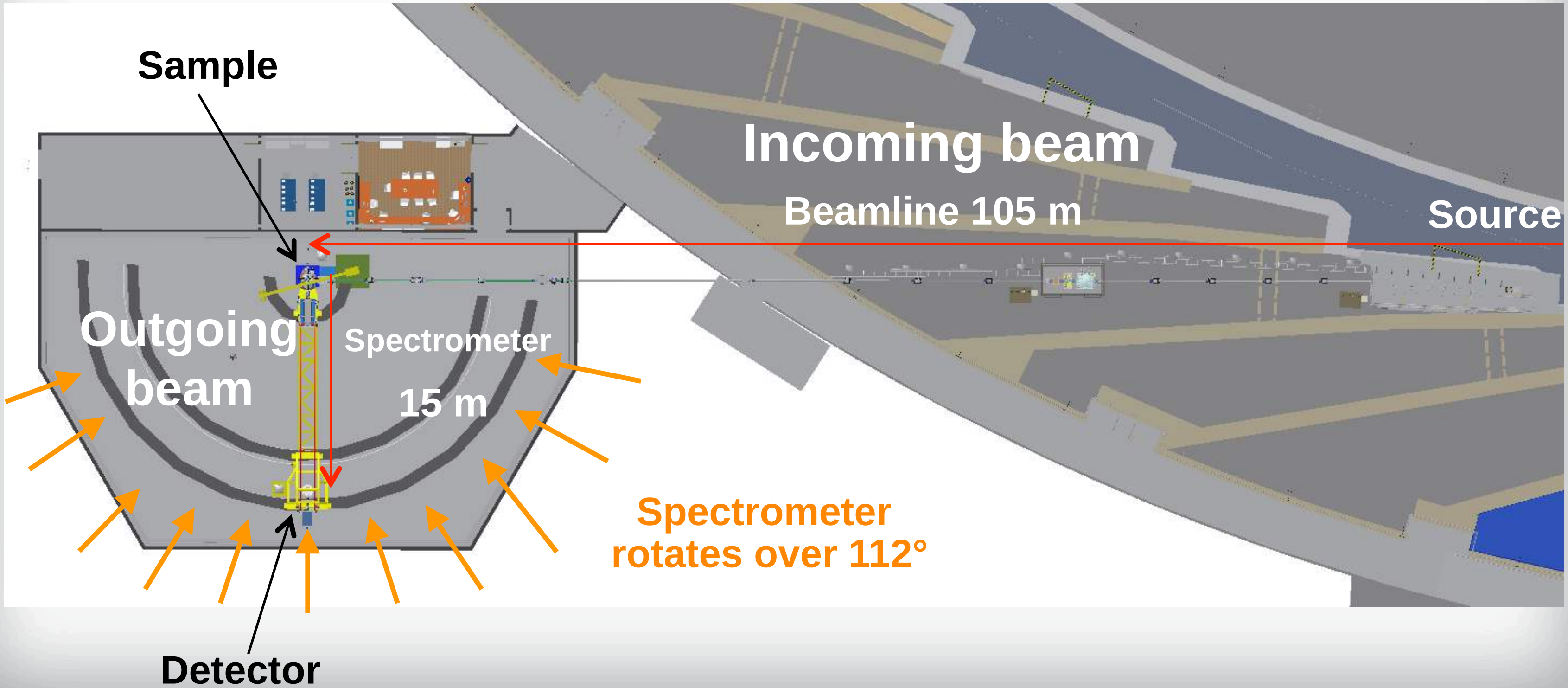


SIX, NSLS-II



Beamline: How Long is Long?

SIX, NSLS-II



SIX is Too Long for NSLS-II Experimental Hall

Google Map 2012

Google Map 2013

Google Map 2014

The SIX Spectrometer Building

May 2013 - Start of contract

August 2013 - Footings

September 2013 - Floor slab

The SIX Spectrometer Building

November 2013 - Steel

The SIX Spectrometer Building

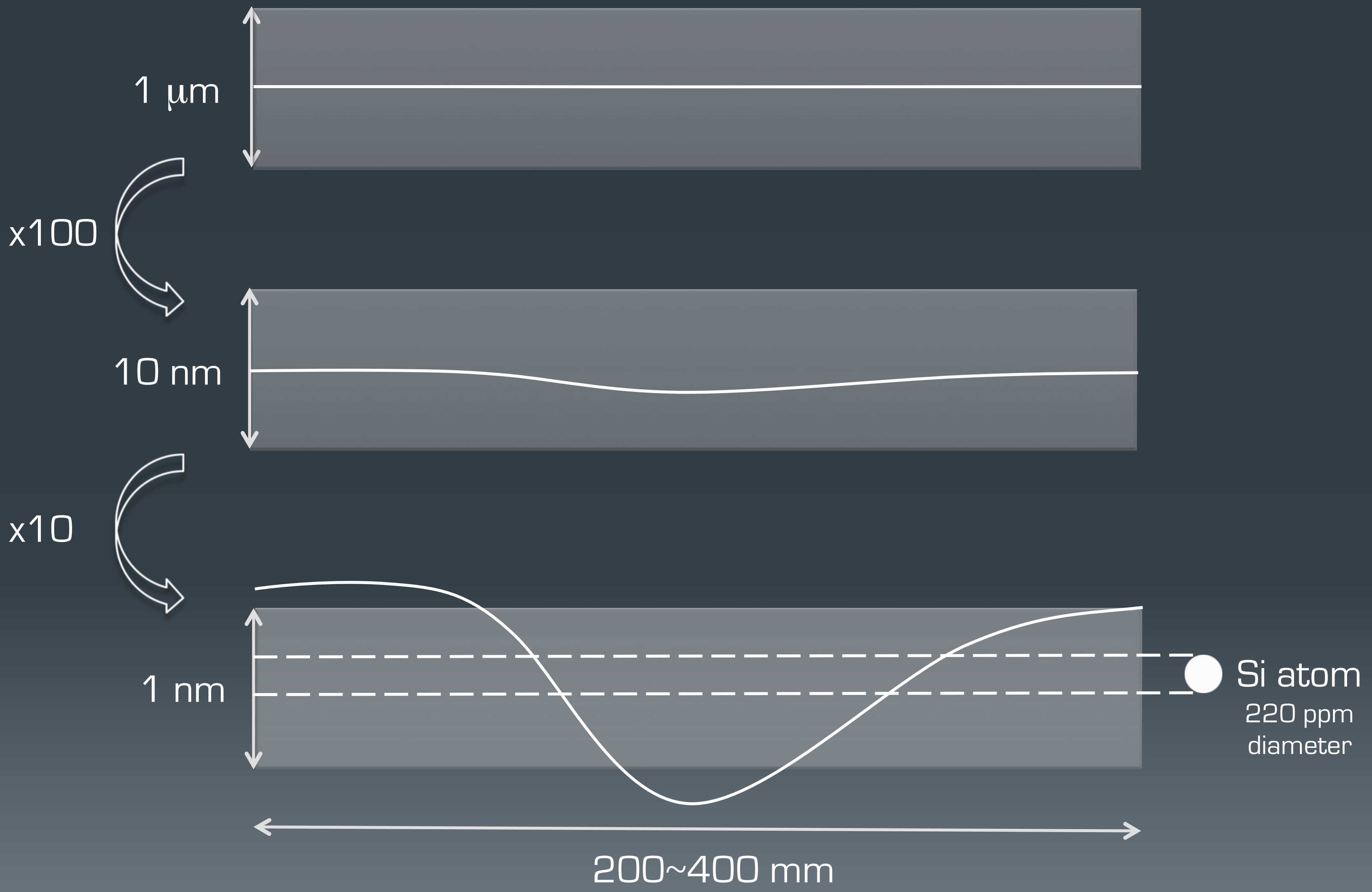
February 2014 - Weather Tight

June 2014 - Complete

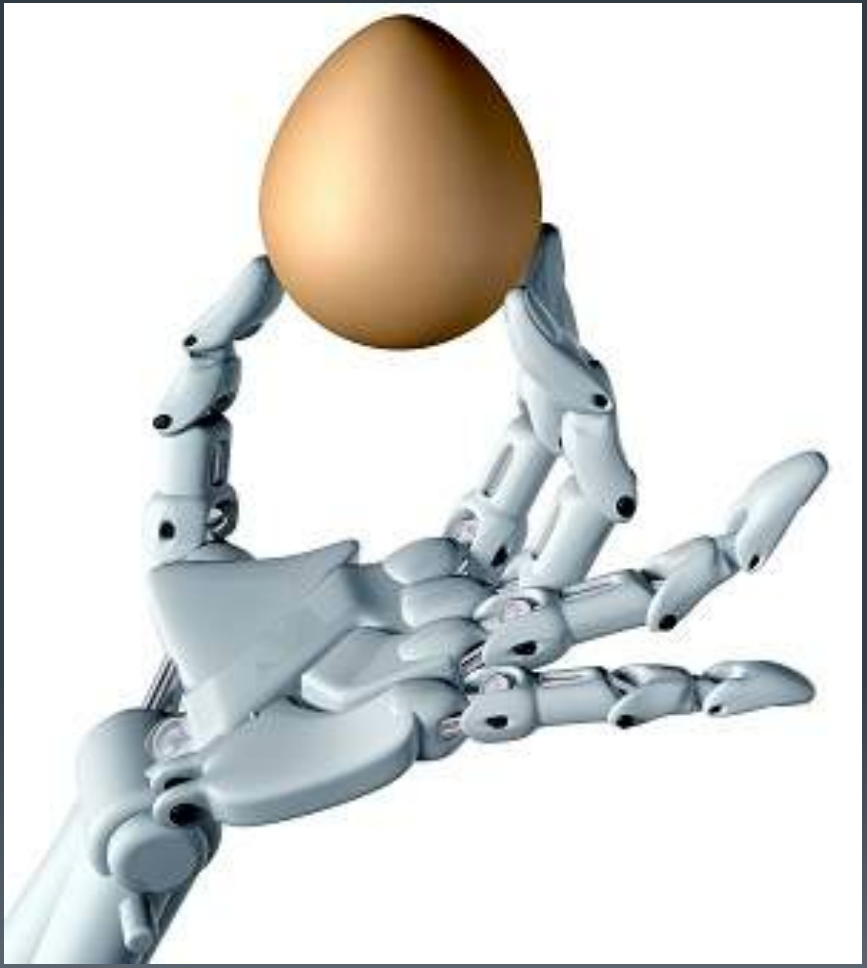
And nowadays?...


SIX
UNDER
CONSTRUCTION

Optics Polishing for SIX Down to Atoms

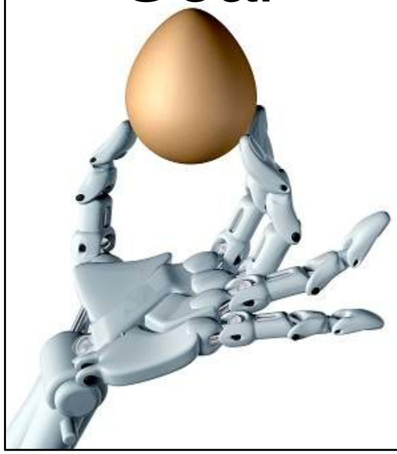


SIX Needs To Be Stable



SIX Needs To Be Stable

Goal



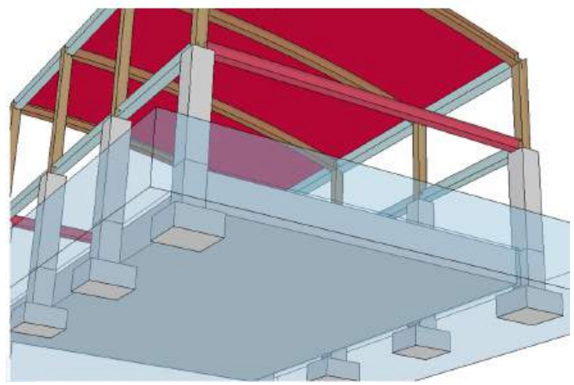
Environment

LIE (0.8 miles)

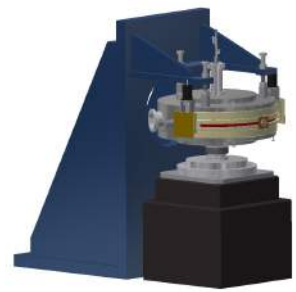
LIRR (1 mile)

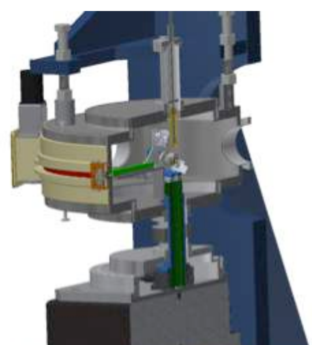
Shore (8 miles)

Our design



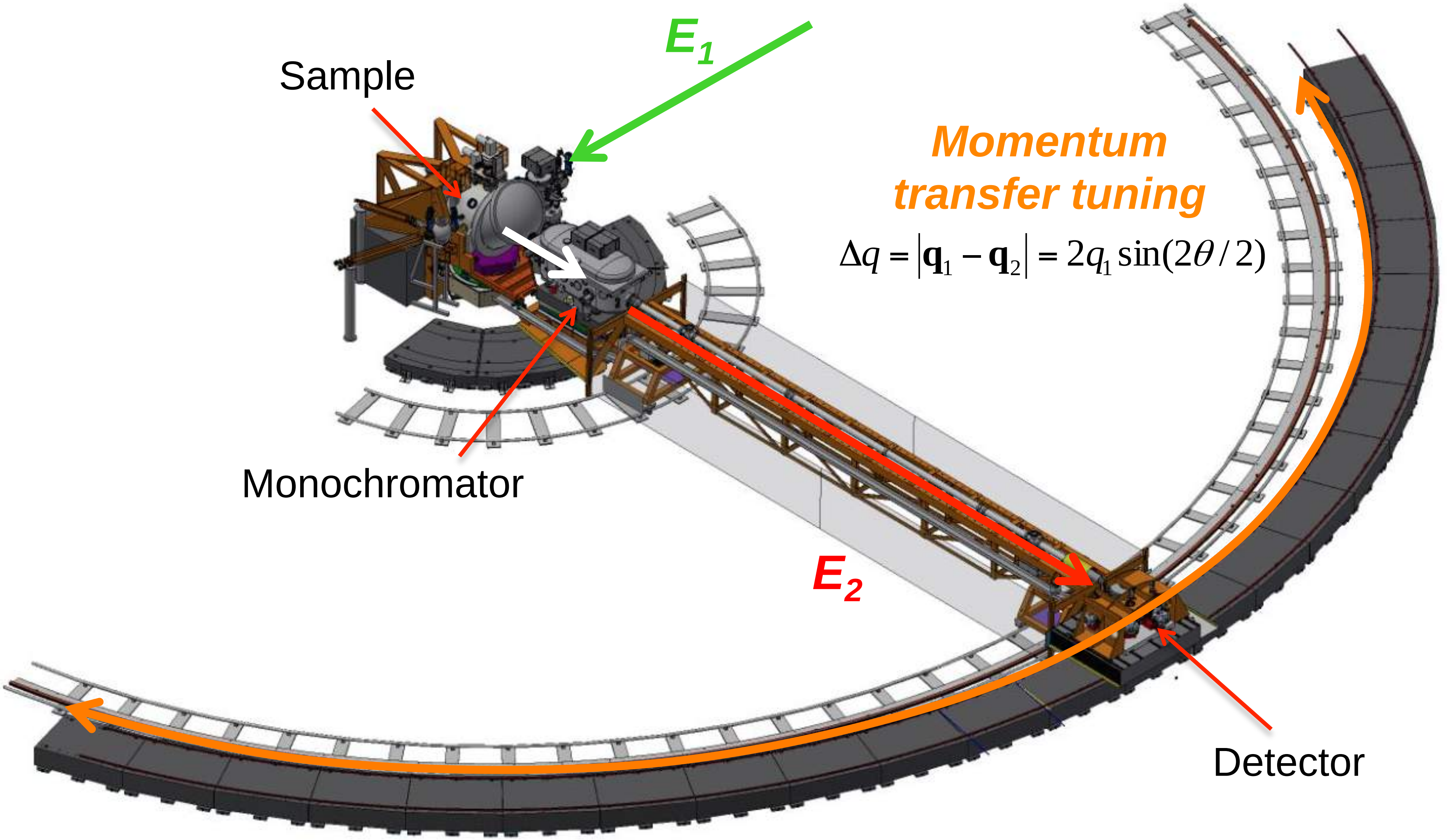
Concrete slab isolated from the ‘rest of the world’





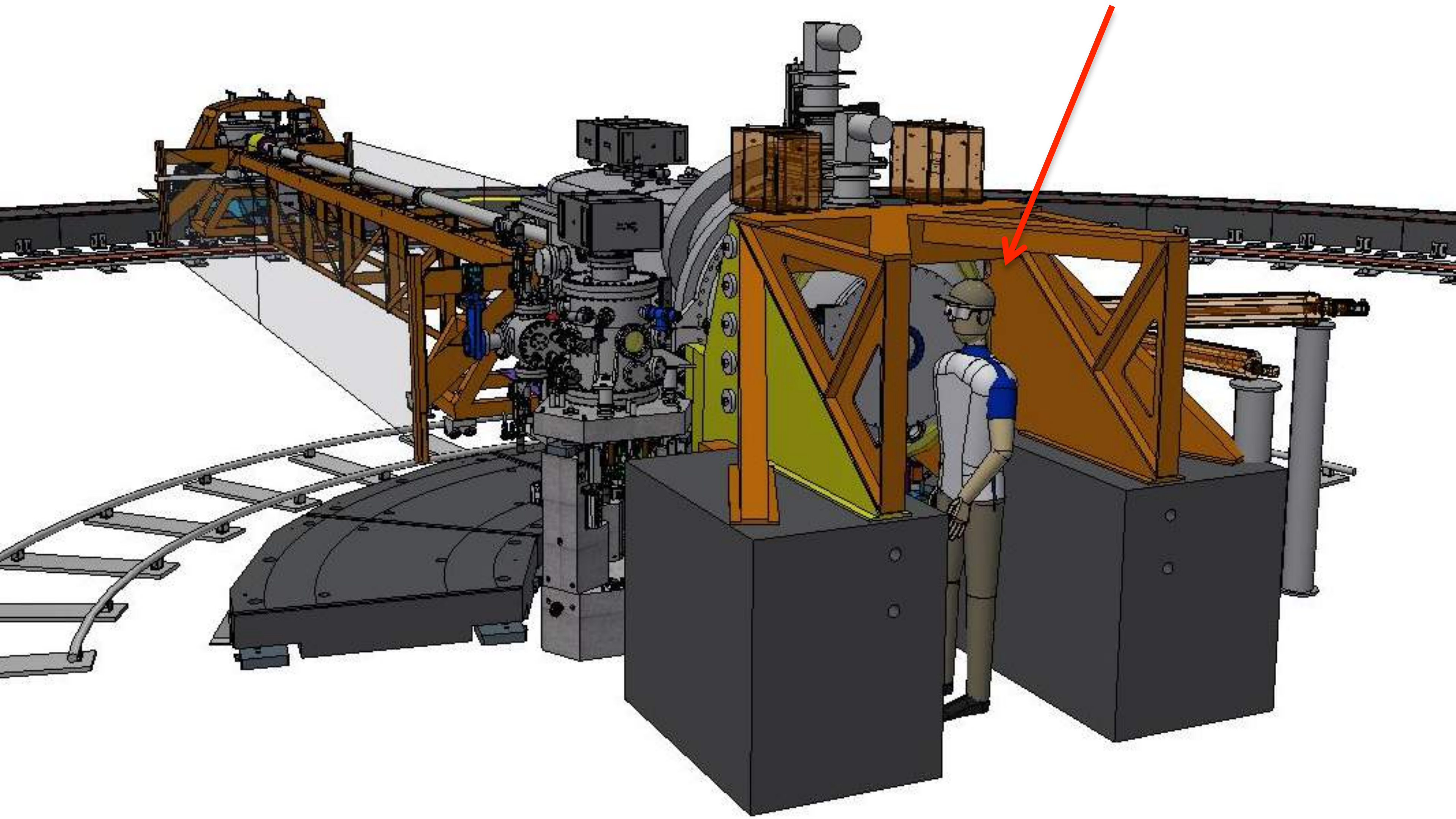
Sample and optics on granite blocks, decoupled from chamber

Doing a RIXS experiment at SIX



Doing a RIXS experiment at SIX

You in a couple of years…?



First Light For SIX End of 2016

Questions?