



POLITECNICO  
MILANO 1863



# Una nuova spettroscopia di raggi X per lo studio dei “materiali quantistici”



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CLASSE DI SCIENZE FISICHE, MATEMATICHE E NATURALI

Venerdì 14 gennaio 2021 ore 11

# Introduction

## Career

Milano – Laurea Ingegneria. Nucleare  
Paris – ENSTA Diplome d'Engenieur

2001 – Grenoble  
ESRF – PhD in physics

Milano POLIMI (RTI, PA, PO)

Since 2001 – ESRF (collab.)

2005-2012 – PSI (collab.)

2011, 2019 – Stanford

XFEL.EU – Hamburg

2018 - Europhysics Prize CMD-EPS

## Scientific interests

Synchrotron radiation

X-ray resonant spectroscopy

X-ray instrumentation

Strongly correlated electrons

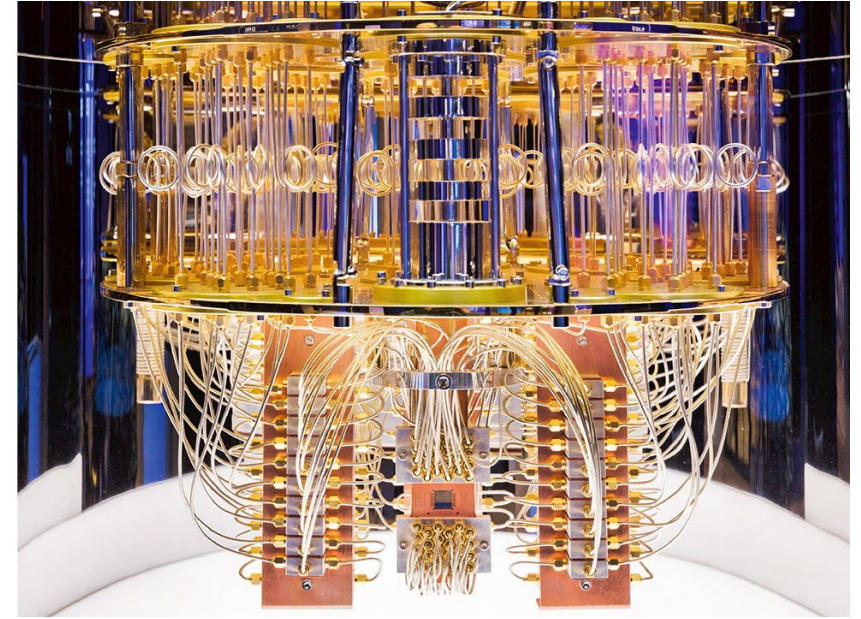
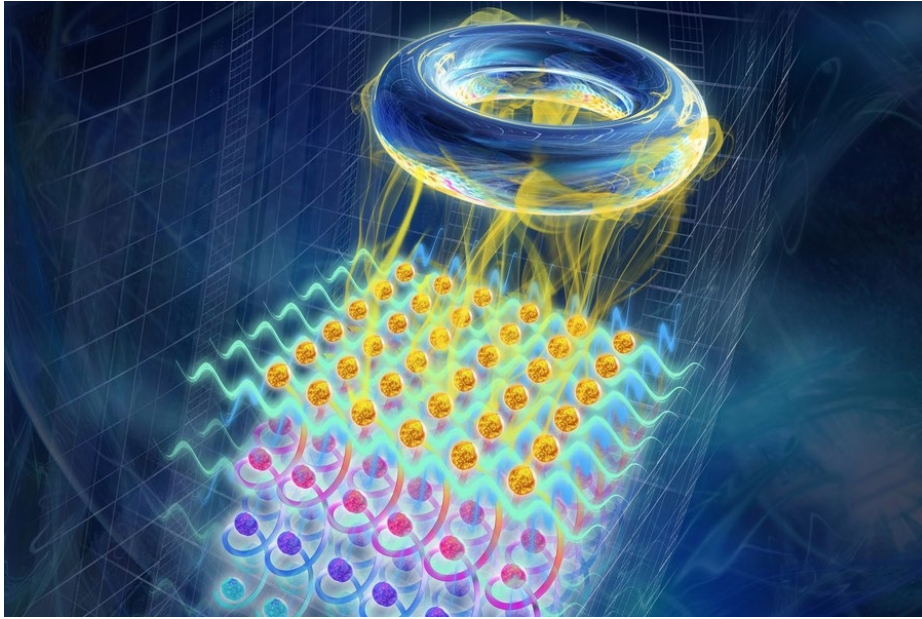
Cuprate superconductors

## Resonant Inelastic X-ray Scattering

Diffusione  
Anelastica  
Risonante di  
Raggi X

- Una spettroscopia per i materiali complessi
- Luce, Raggi X e neutroni
- Come funziona il RIXS
- Le difficoltà tecniche nella strumentazione per RIXS
- 2 risultati sui cuprati superconduttori ad alta T<sub>c</sub>

# Quantum matter, quantum materials, quantum technology



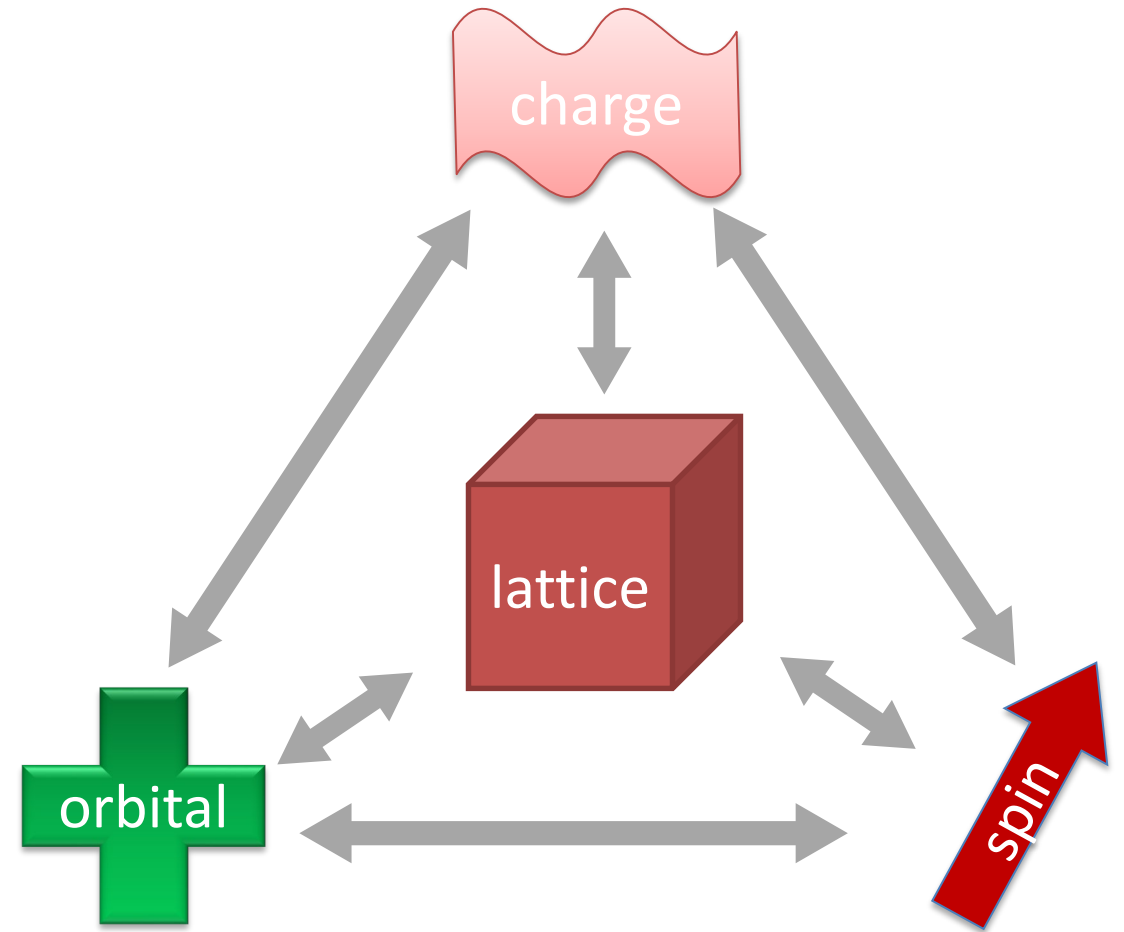
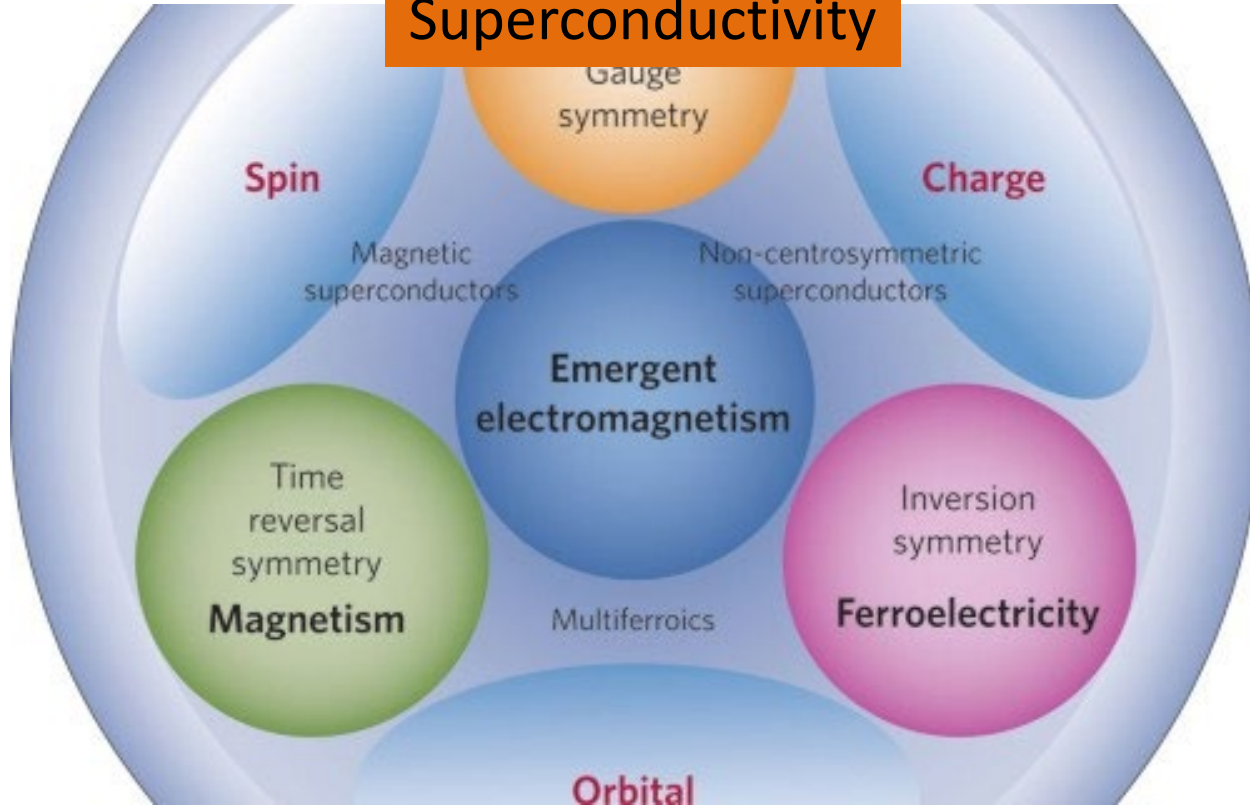
All matter, all materials, all technologies are ultimately governed by quantum physics laws, at microscopic level. But often quantum aspects can be hidden in macroscopic laws proper to classical physics (eg semiconductor electronics)



**QUANTUM-SOMETHING**  
When particle-wave duality is unresolved  
When typical quantum mechanical phenomena emerge at macroscopic scale  
When wave-physics is purposely exploited

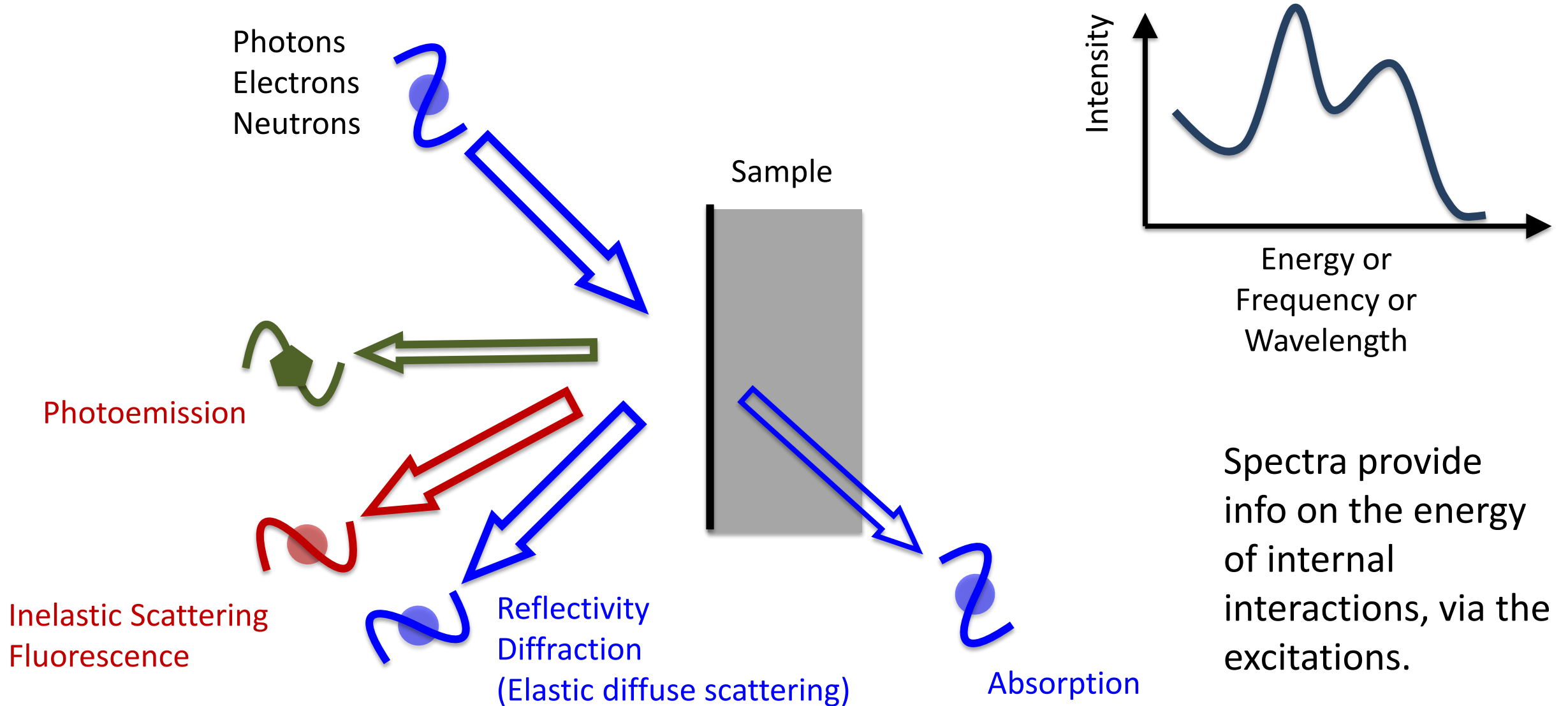
# Electronic correlation in condensed matter

## Superconductivity

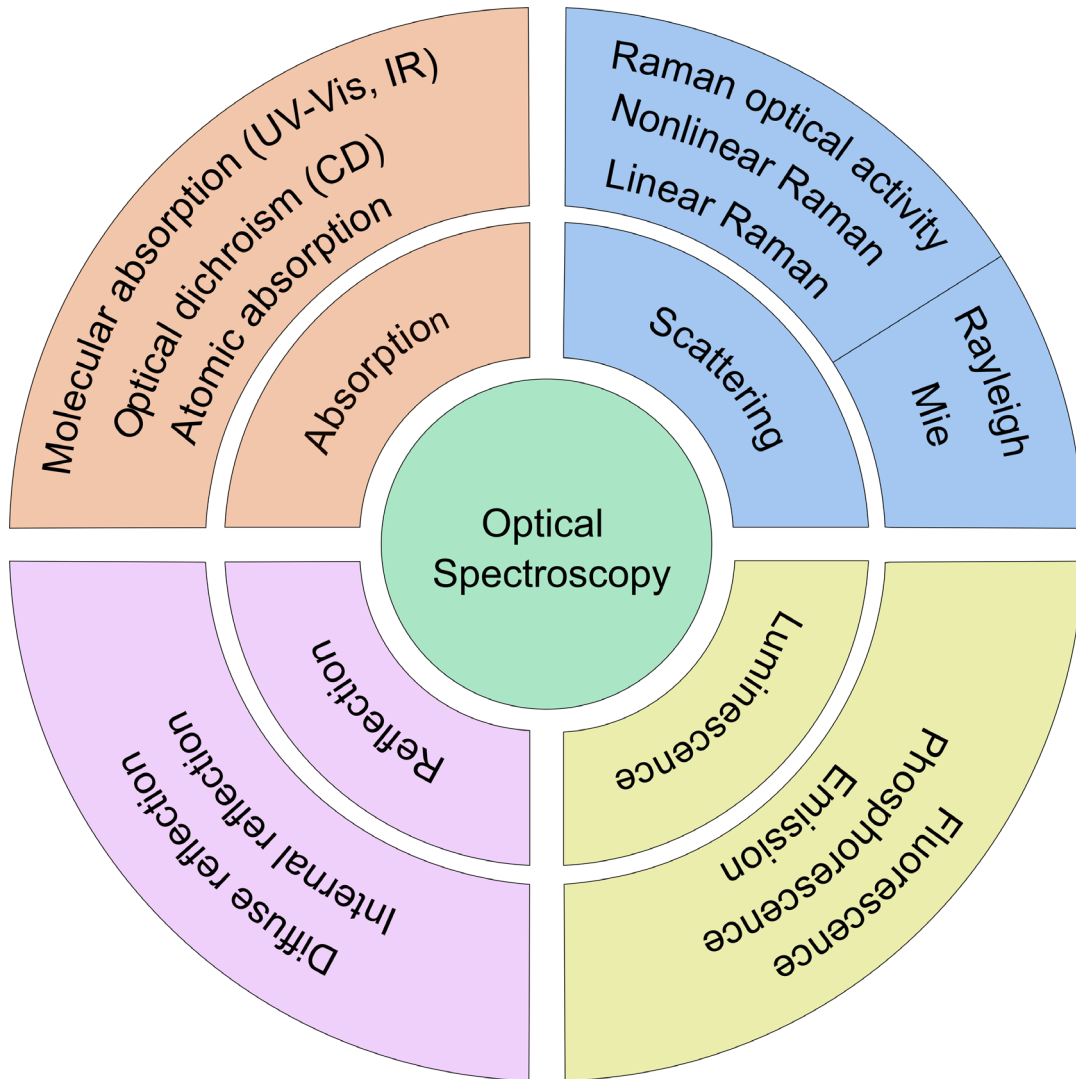


# Spectroscopy for condensed matter

The energy/frequency dimension in the description of materials

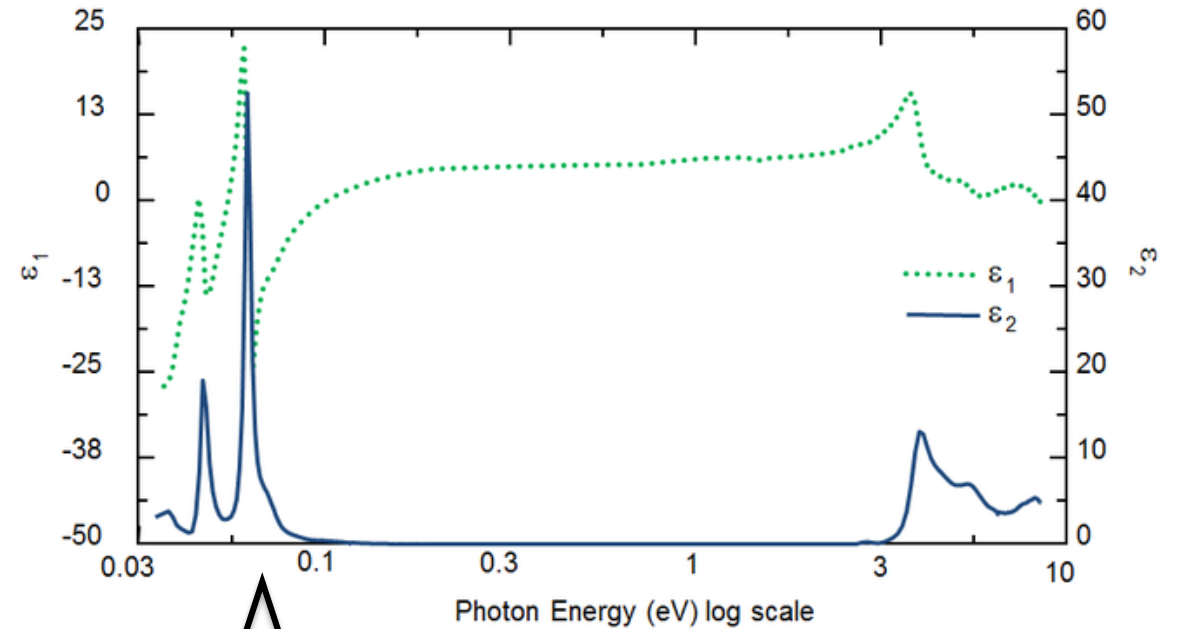


# Optical Spectroscopy



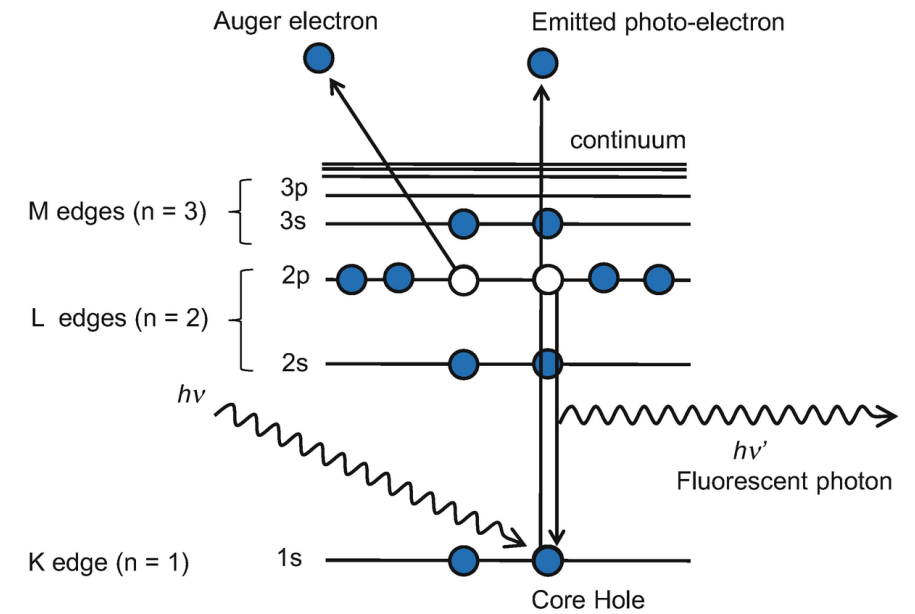
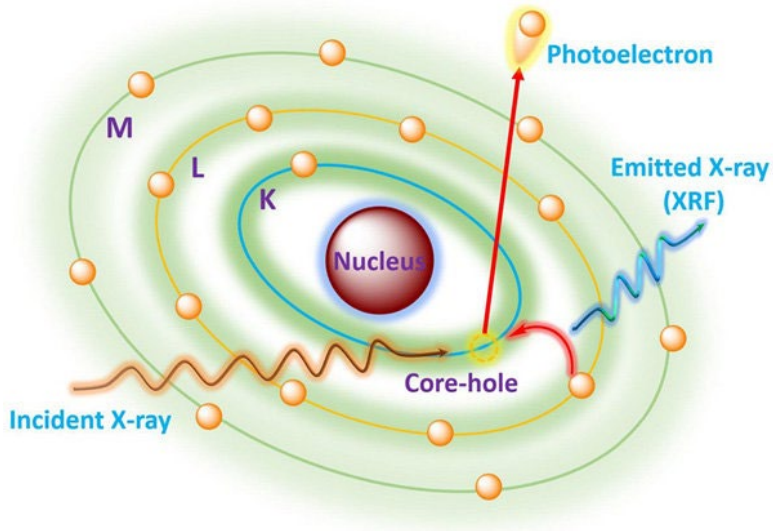
Complex optical constants:

$$\epsilon_r(\omega) = \epsilon_1(\omega) + i \epsilon_2(\omega)$$

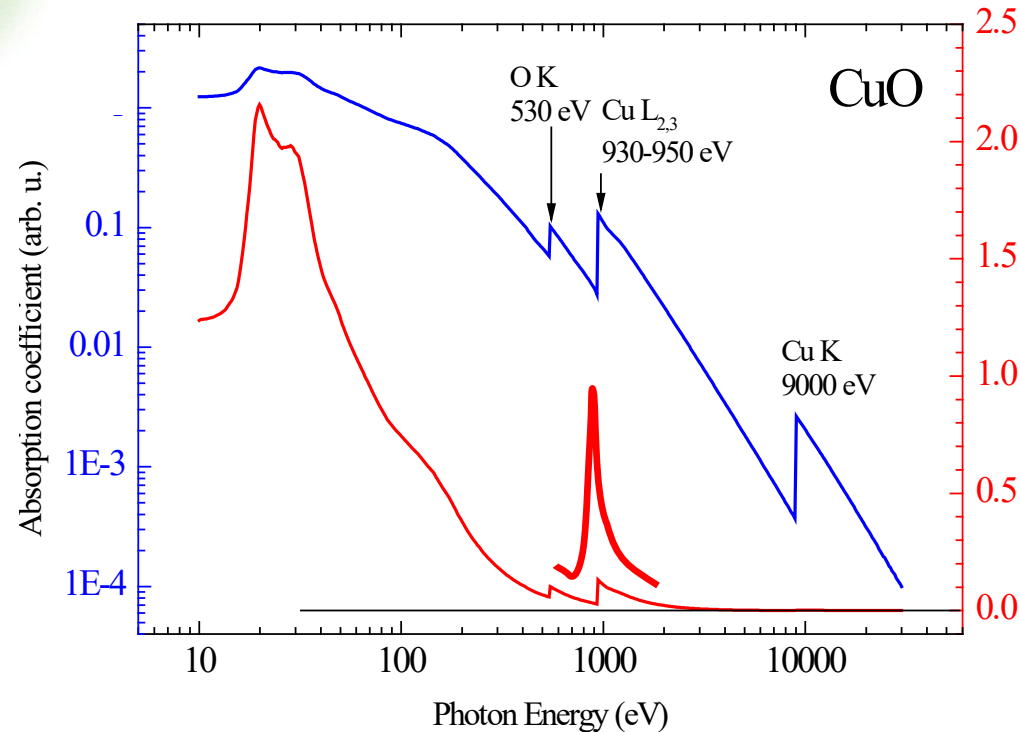


Absorption peaks  
=  
Excitation resonances

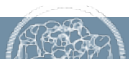
# X-ray spectroscopy



Dipole selection rule:  $\Delta l = \pm 1$   
(e.g.  $ns \leftrightarrow np$  transition)



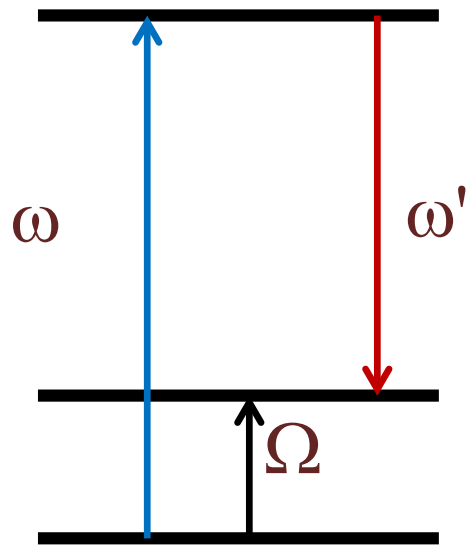
Peaks and edges in absorption provide info on the electron binding energies. And resonance to enhance scattering



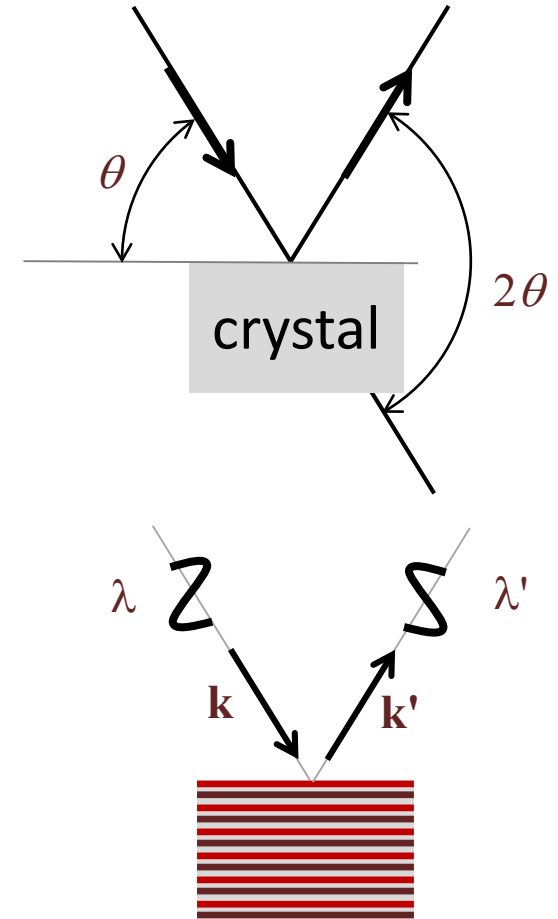
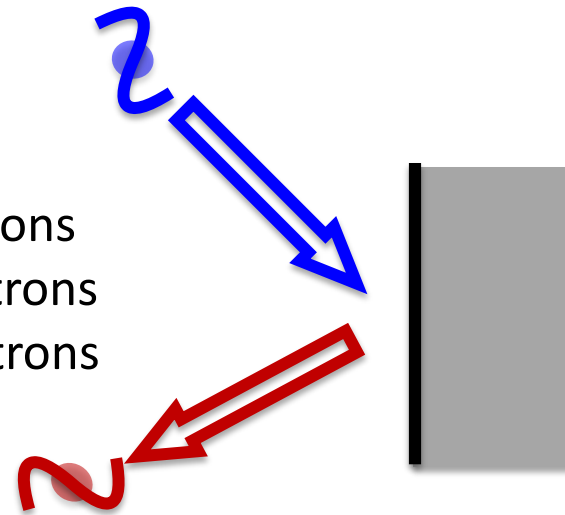


# Energy loss spectroscopy

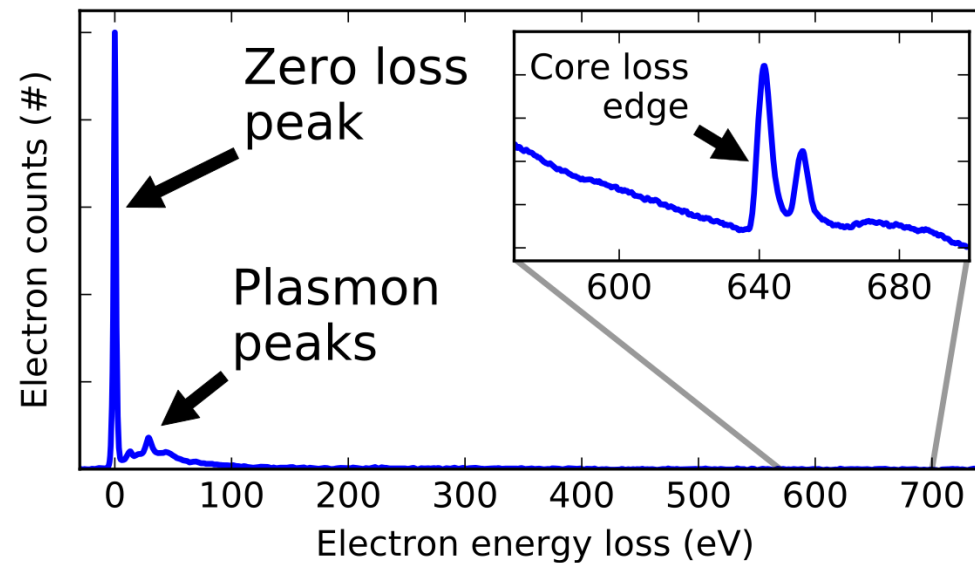
Raman light scattering



Photons  
Electrons  
Neutrons



Electron Energy Loss Spectroscopy (EELS)

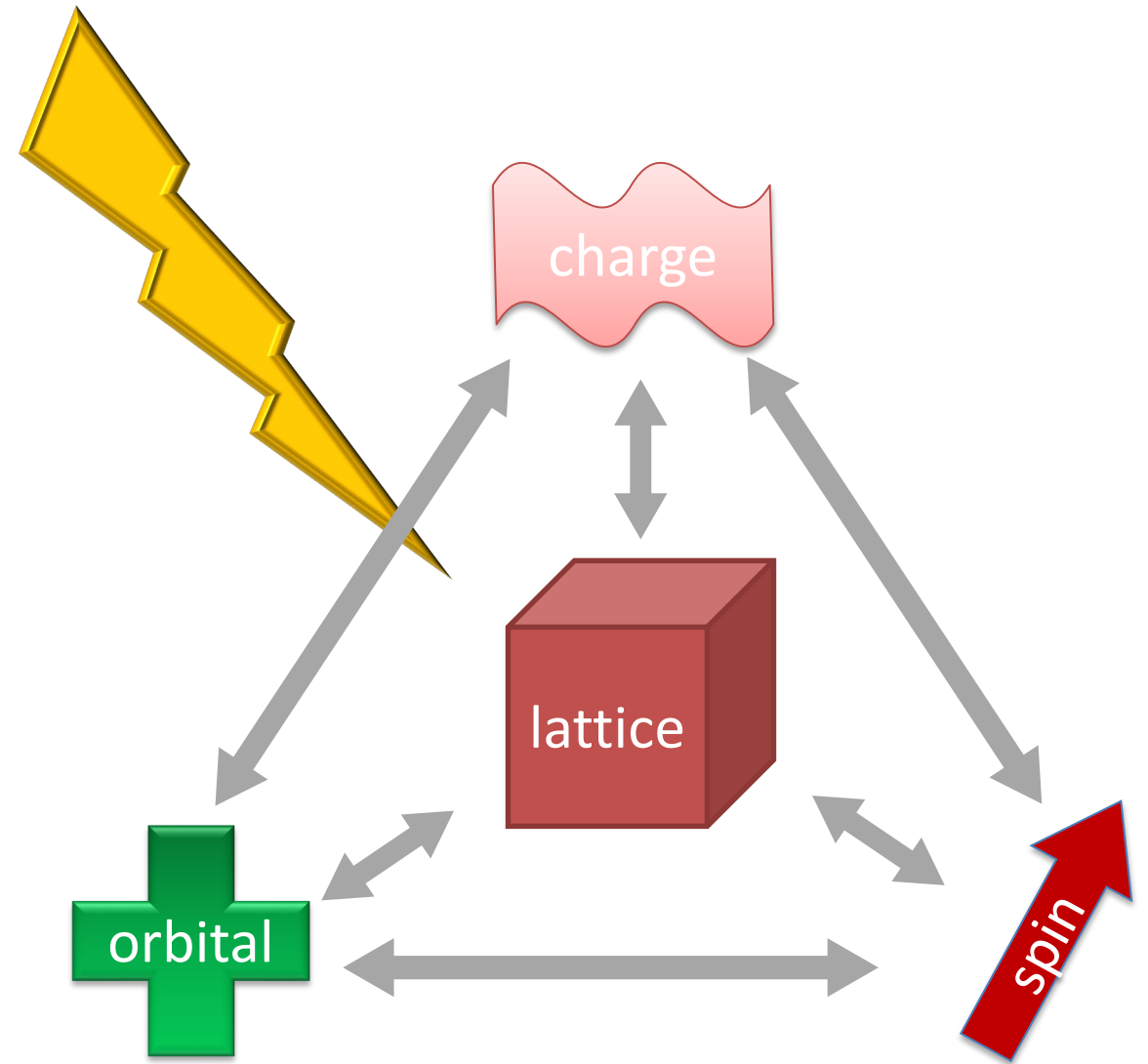


Energy and momentum!

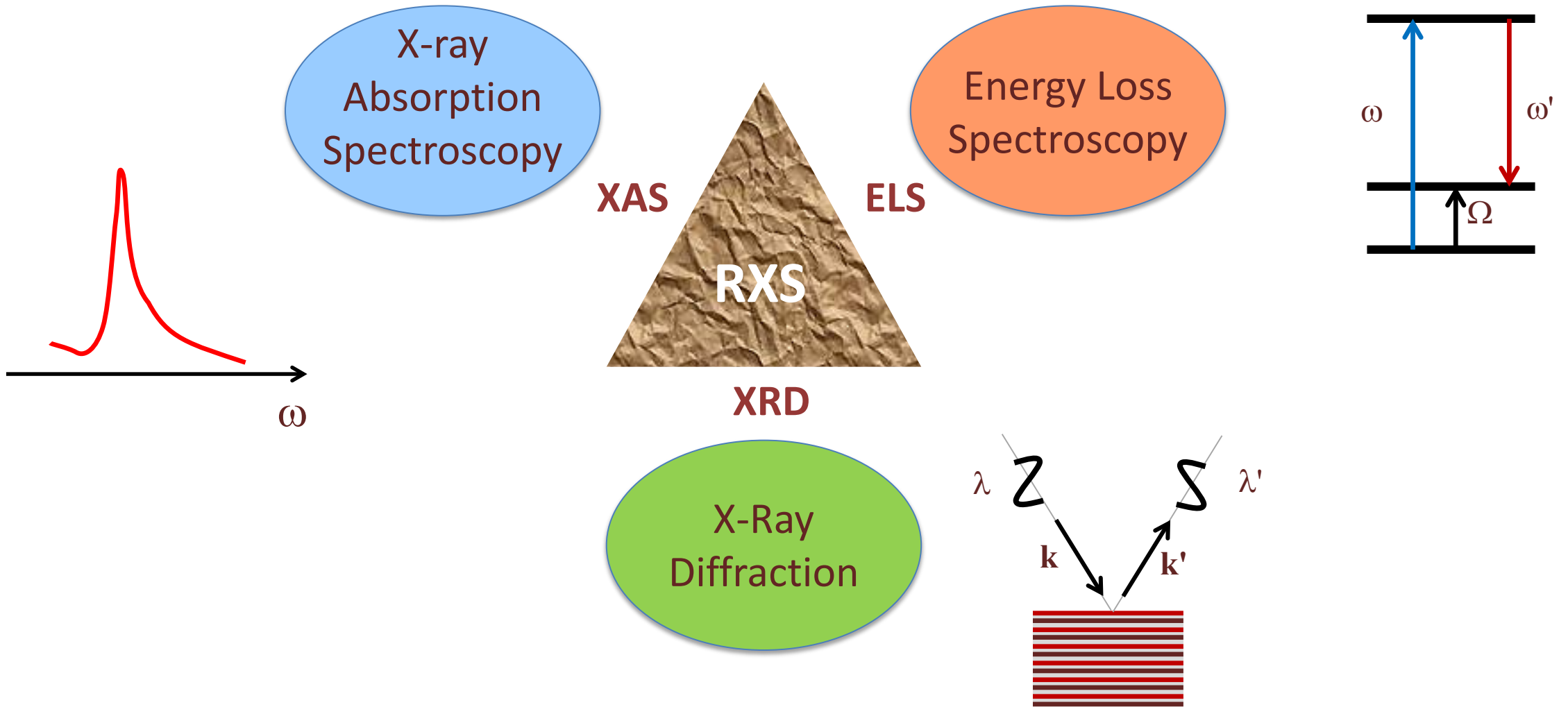
# One probe for several degrees of freedom

1. Energy loss spectroscopy
2. Momentum resolution
3. Coupling to
  - a. Charge
  - b. Spin
  - c. Orbital
  - d. Lattice
4. Bulk sensitivity
5. Good energy resolution
6. Decent count rate

electrons	(1, 2, 3, 5, 6)
neutrons	(1, 2, 3b, 3d, 4, 5)
photons	(1, 2, 3a, 3c, 3d, 4, 5, 6)



# Resonant X-ray Scattering

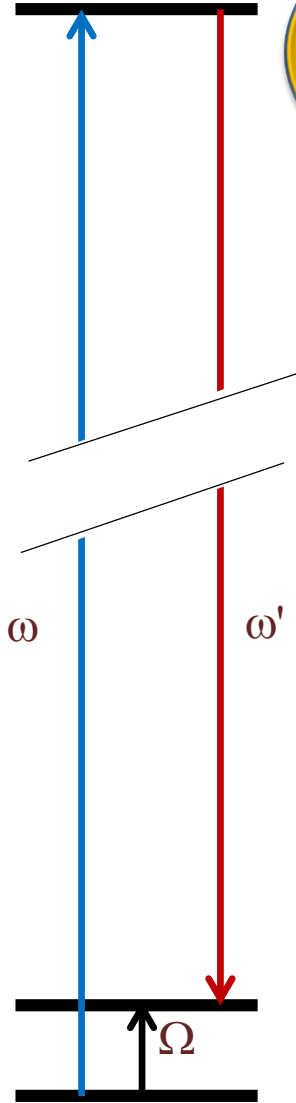
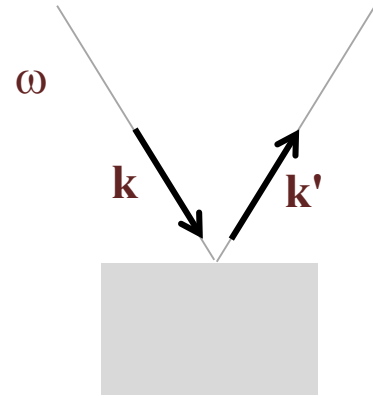


# A Raman scattering with X-rays

Energy Loss Spectroscopy

Inelastic X-ray Scattering

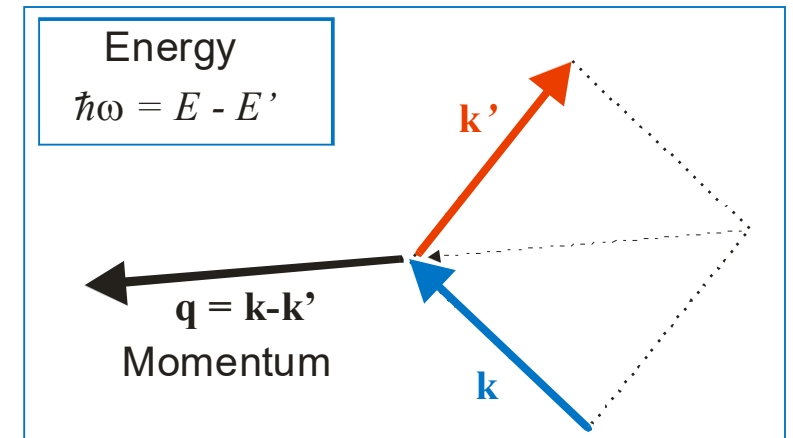
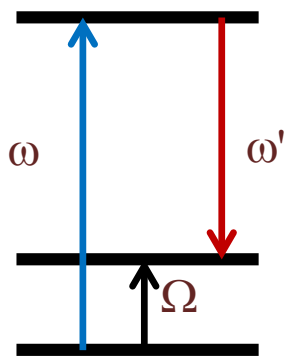
Raman light scattering



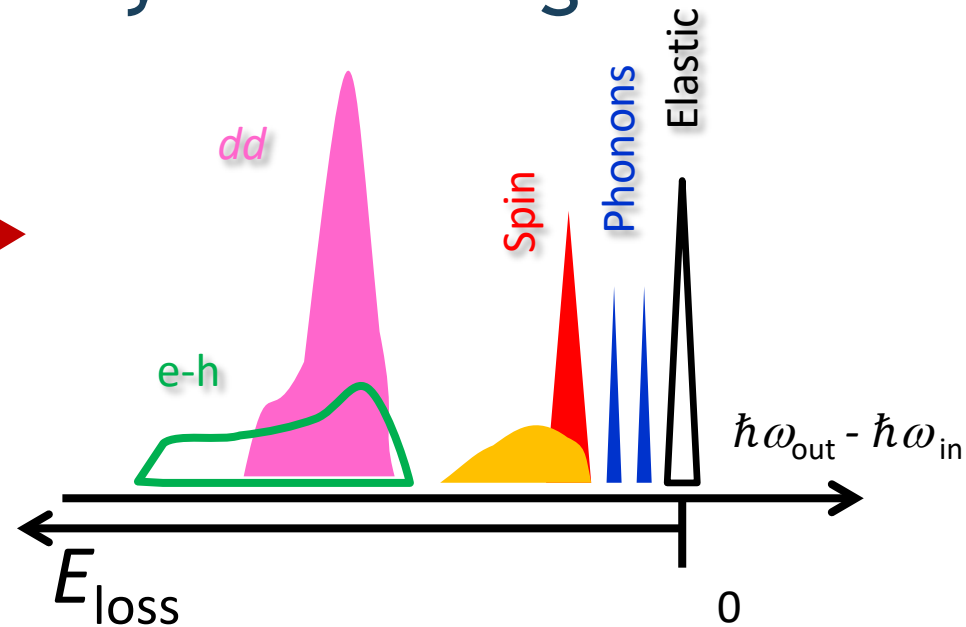
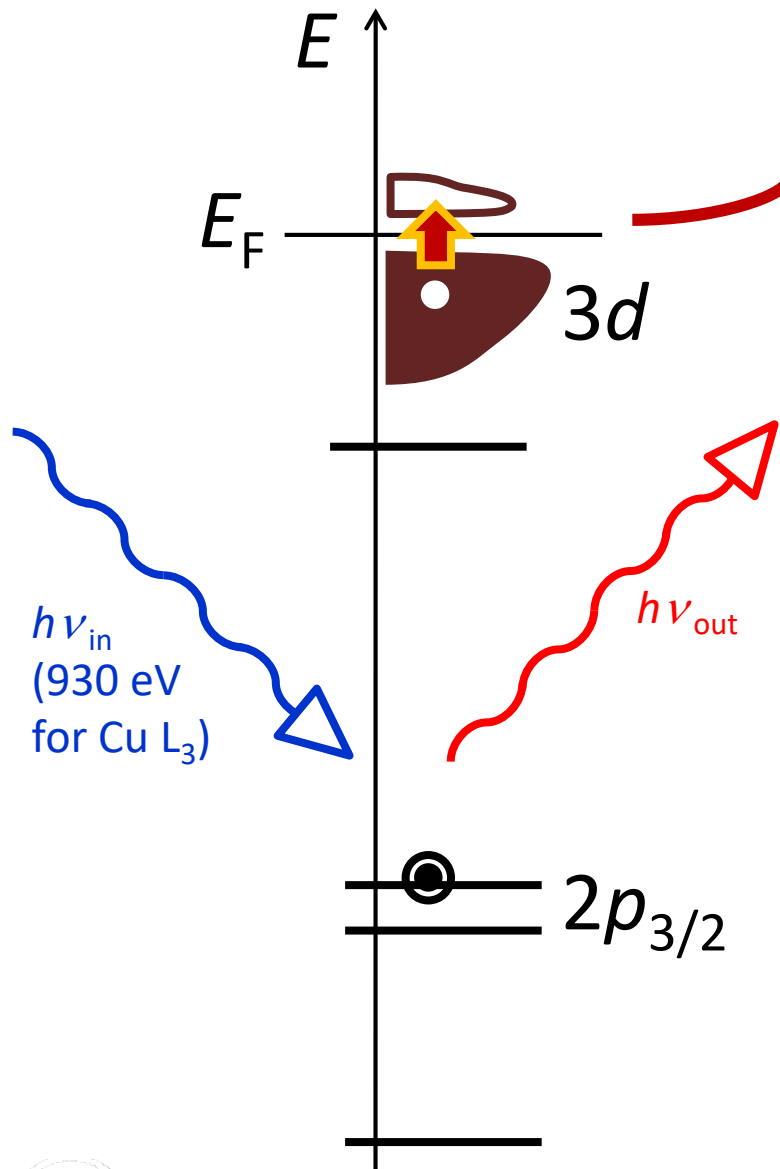
$k \approx 0, q \approx 0,$   
 $\Omega = \omega - \omega'$

$\Omega = \omega - \omega'$

$q = k' - k$



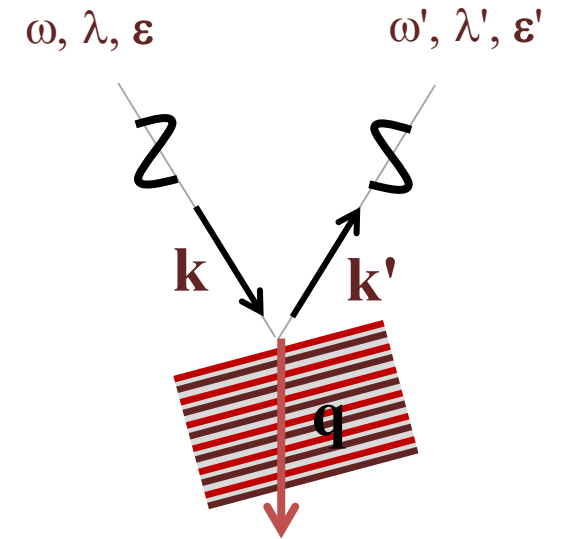
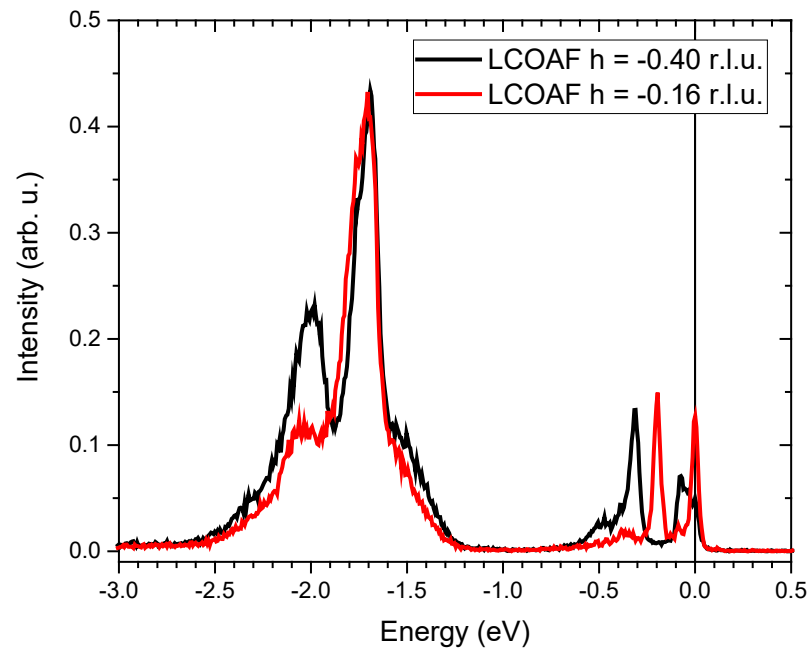
# RIXS, Resonant Inelastic X-ray Scattering



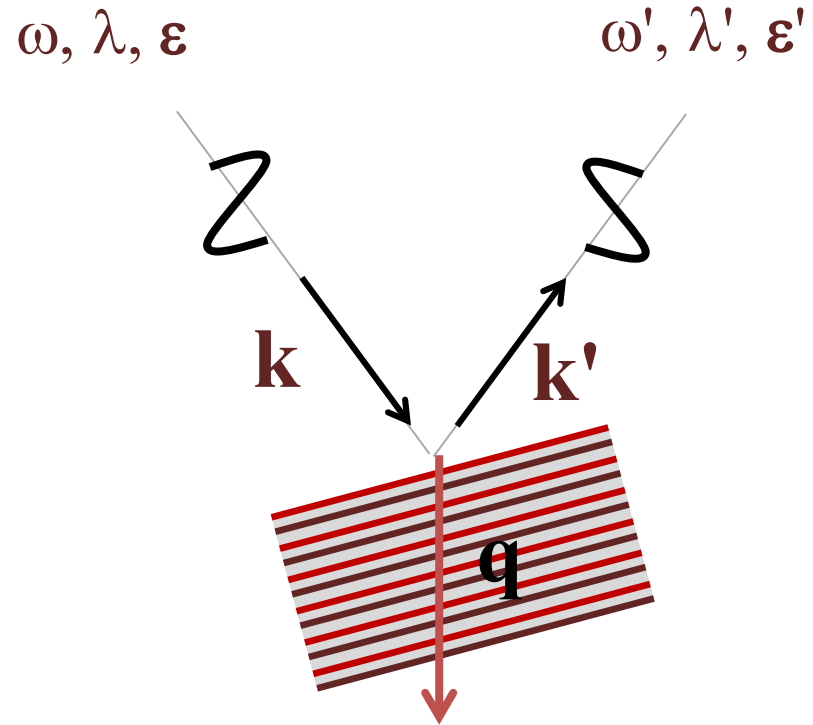
$$\Omega = \omega - \omega'$$

$$\mathbf{q} = \mathbf{k}' - \mathbf{k}$$

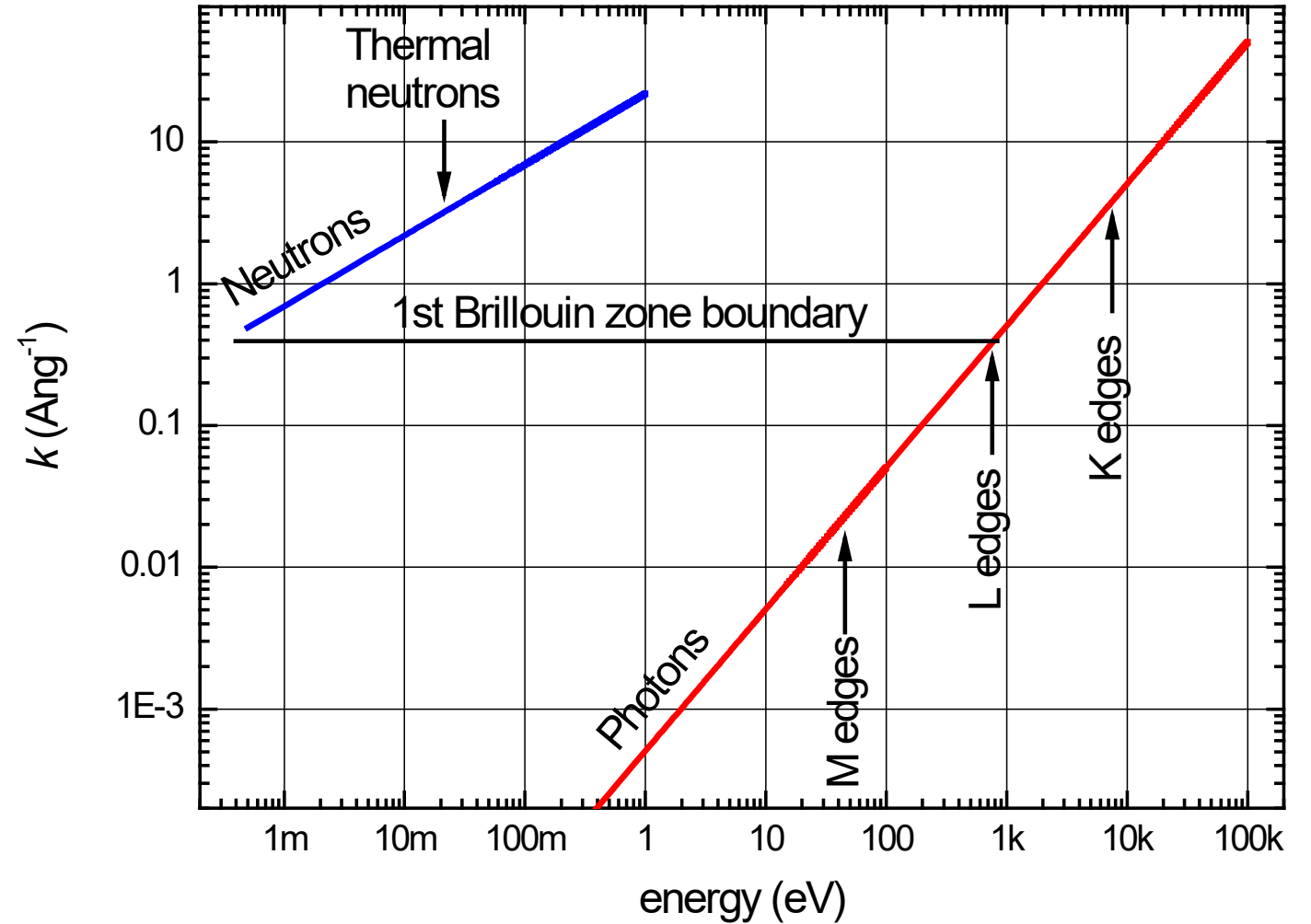
$\varepsilon, \varepsilon'$ : polarization



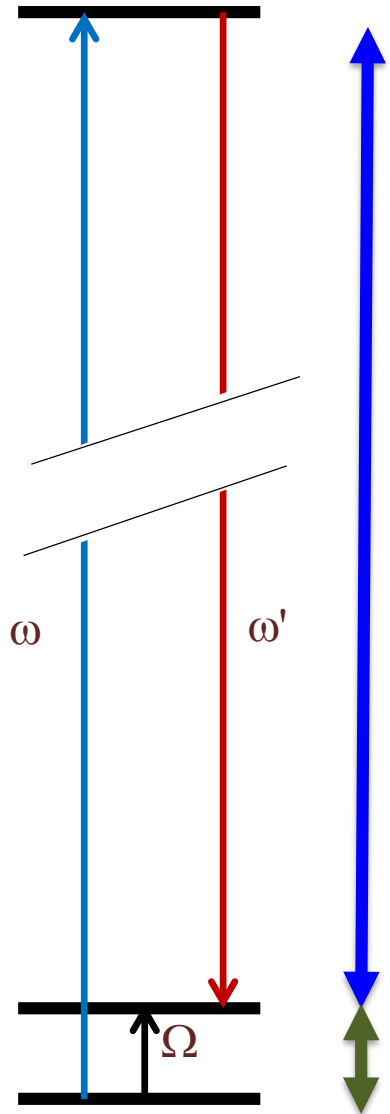
# Energy and momentum



Wavevector of particles used in inelastic scattering



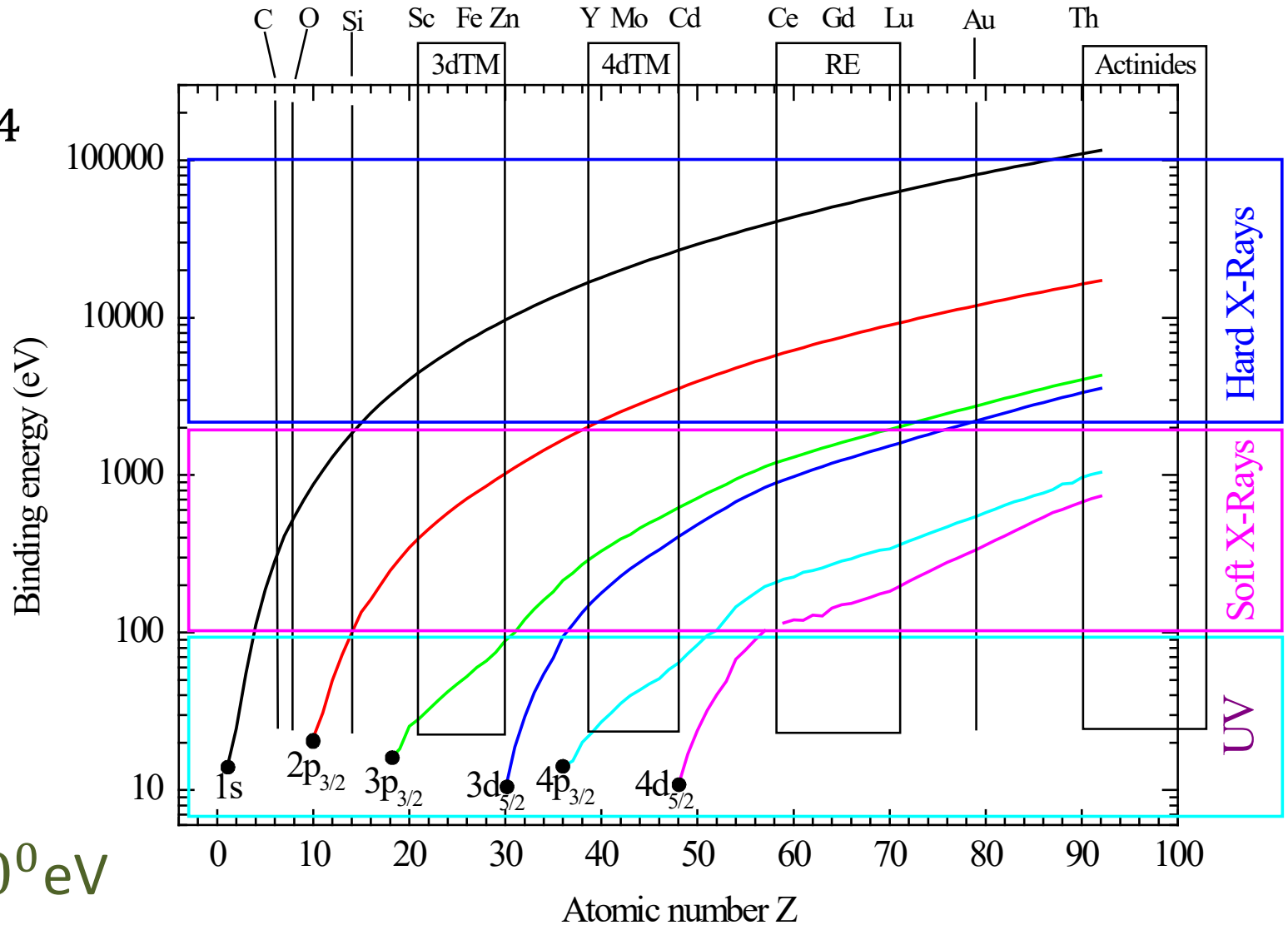
# Ultra high resolving power is needed



$$\frac{E}{\Delta E} > 10^4$$

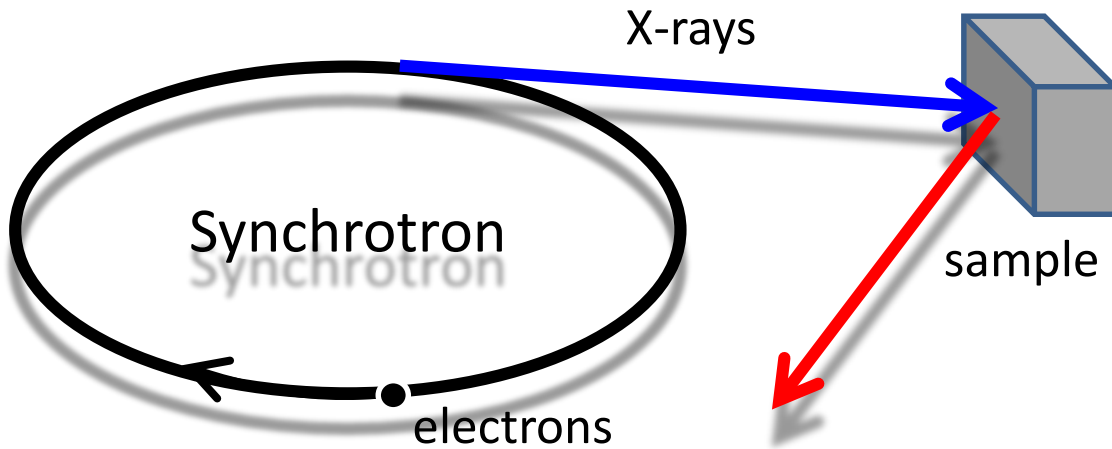
$$\hbar\omega \sim 10^3 \text{ eV}$$

$$\hbar\Omega \sim 10^{-2} - 10^0 \text{ eV}$$

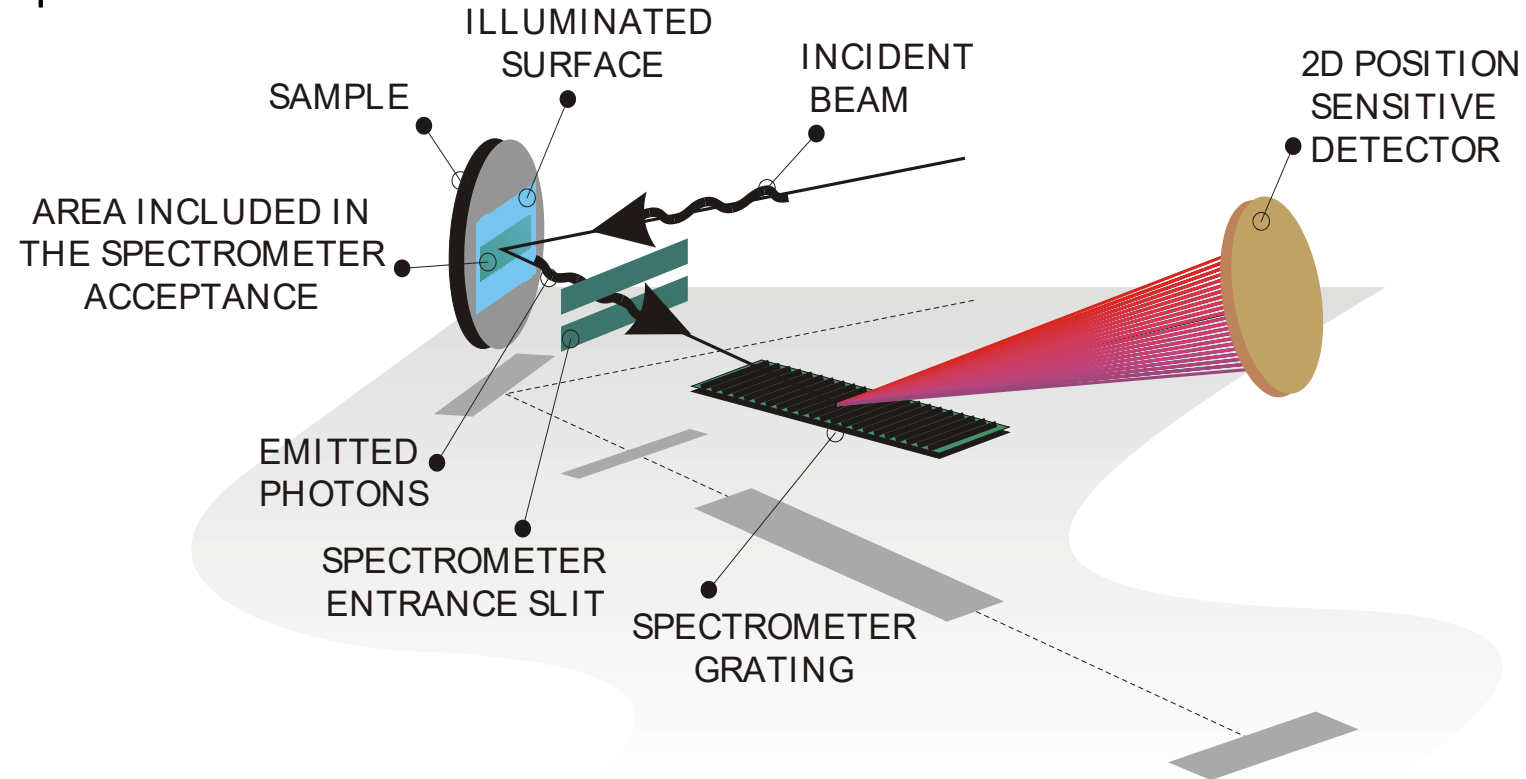


# RIXS measurements: the technical challenge

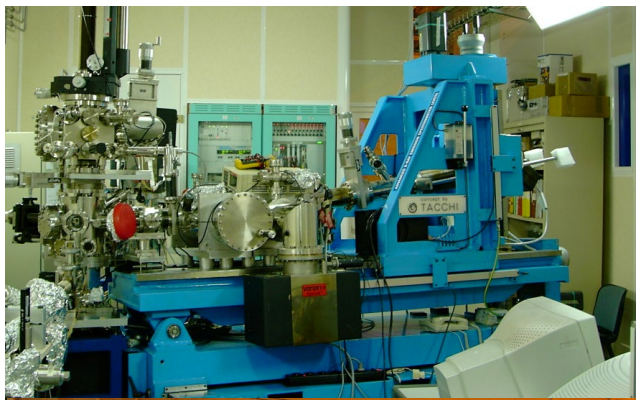
Tunable and brilliant source of x-rays is needed



In the soft x-rays (100-1500 eV) a grating spectrometer is used





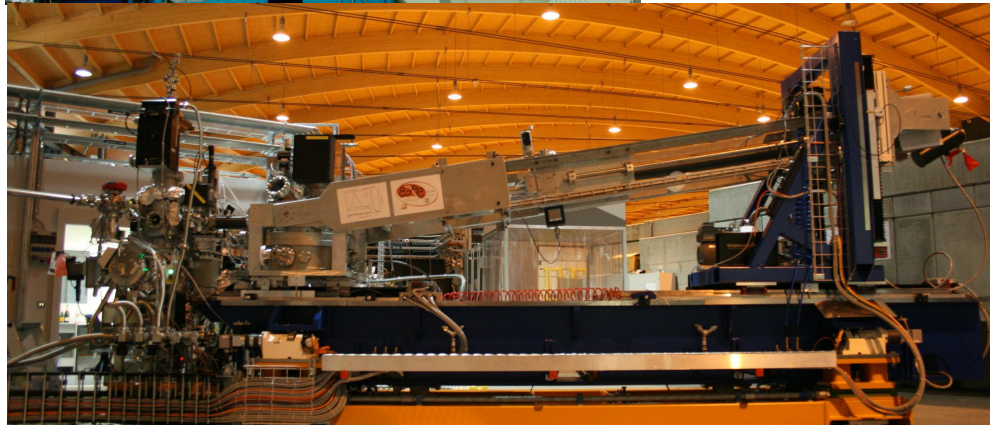


AXES, ESRF: **2.2 m**

1994 – 2012

$E/\Delta E \sim 3000$

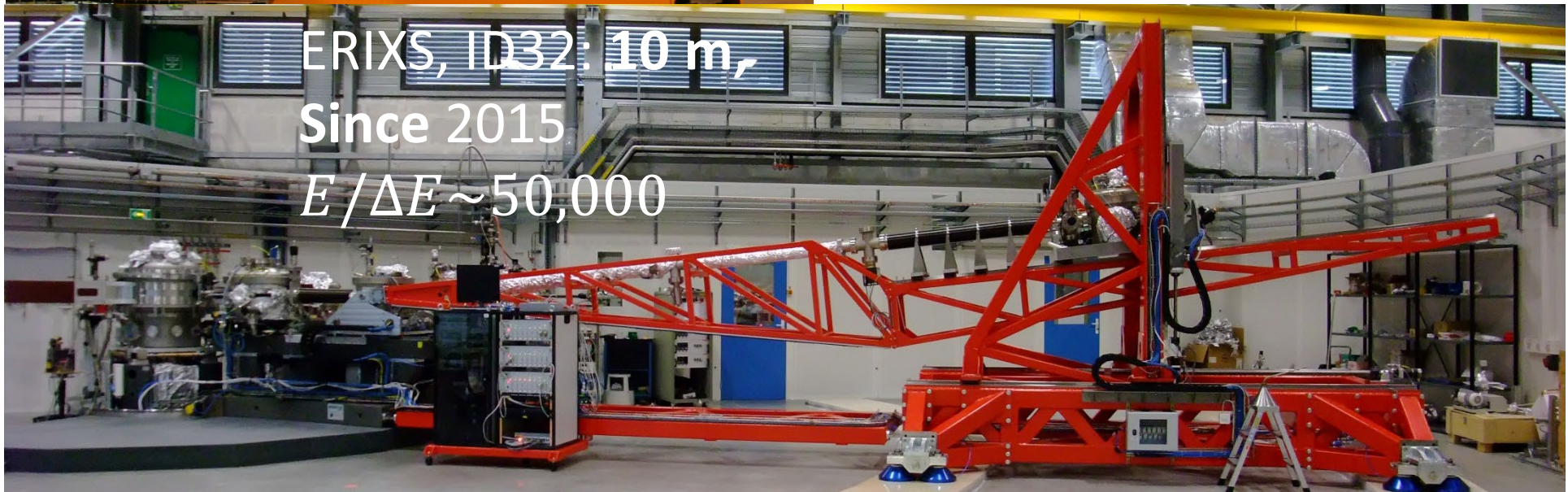
Lucio Braicovich



SAXES, SLS: **5 m**

Since 2007

$E/\Delta E \sim 10,000$

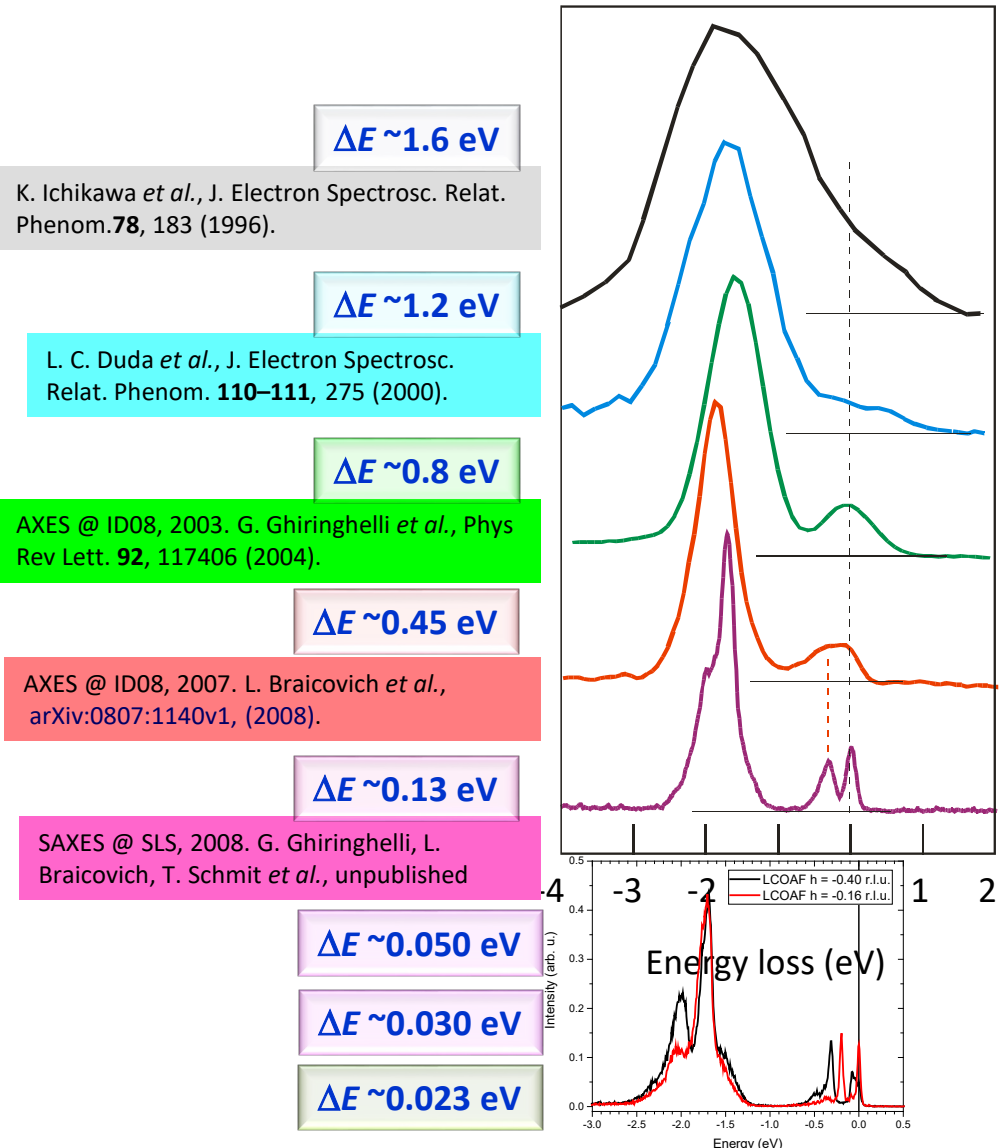


ERIXS, ID32: **10 m,**

Since 2015

$E/\Delta E \sim 50,000$

# ENERGY RESOLUTION: progress in 20 years



$\Delta E \sim 1.6 \text{ eV}$   
 K. Ichikawa *et al.*, J. Electron Spectrosc. Relat. Phenom. **78**, 183 (1996).

$\Delta E \sim 1.2 \text{ eV}$   
 L. C. Duda *et al.*, J. Electron Spectrosc. Relat. Phenom. **110–111**, 275 (2000).

$\Delta E \sim 0.8 \text{ eV}$   
 AXES @ ID08, 2003. G. Ghiringhelli *et al.*, Phys Rev Lett. **92**, 117406 (2004).

$\Delta E \sim 0.45 \text{ eV}$   
 AXES @ ID08, 2007. L. Braicovich *et al.*, arXiv:0807:1140v1, (2008).

$\Delta E \sim 0.13 \text{ eV}$   
 SAXES @ SLS, 2008. G. Ghiringhelli, L. Braicovich, T. Schmit *et al.*, unpublished

$\Delta E \sim 0.050 \text{ eV}$   
 $\Delta E \sim 0.030 \text{ eV}$   
 $\Delta E \sim 0.023 \text{ eV}$

$\text{La}_2\text{CuO}_4$   
 $\text{Cu } 2p \rightarrow 3d$   
 Photon energy  $\sim 931 \text{ eV}$

2000 Uppsala

2003 ESRF + AXES

2007

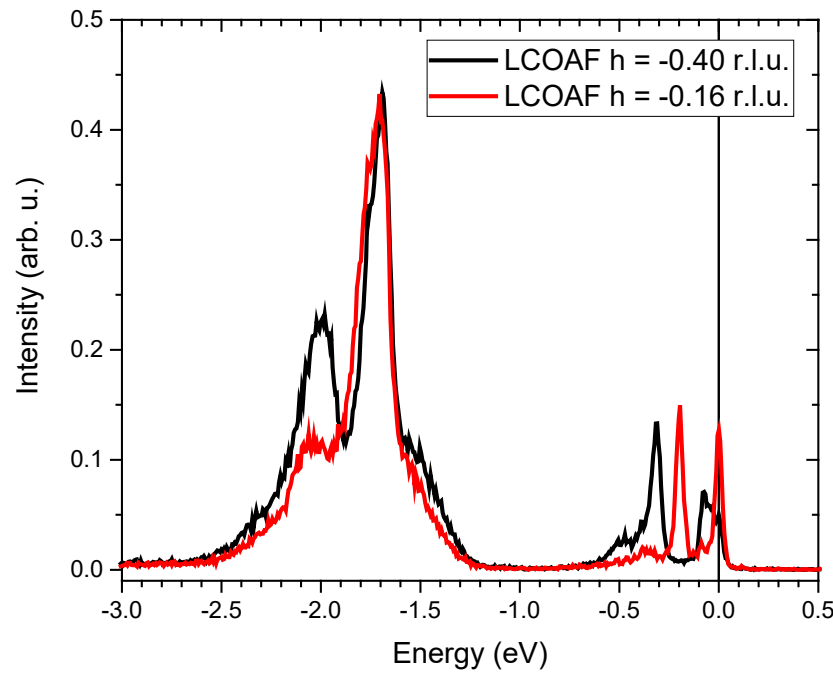
2008 SLS + SAXES

2015 ESRF + ERIXS

2016

2019 NSLS II + SIX

2021 ESRF + ERIXS



Combined resolving power has increased by a factor 70

# RIXS instruments growing in many synchrotrons

Some high level projects



## Soft X-rays:

ESRF

Diamond Light Source (UK)

MAX IV (Sweden)

SLS-PSI (Switzerland)

BESSY II (HZB, Berlin)

European XFEL

Taiwan Photon Source

Brookhaven NSLS II (US)

Stanford LCLS II (US)

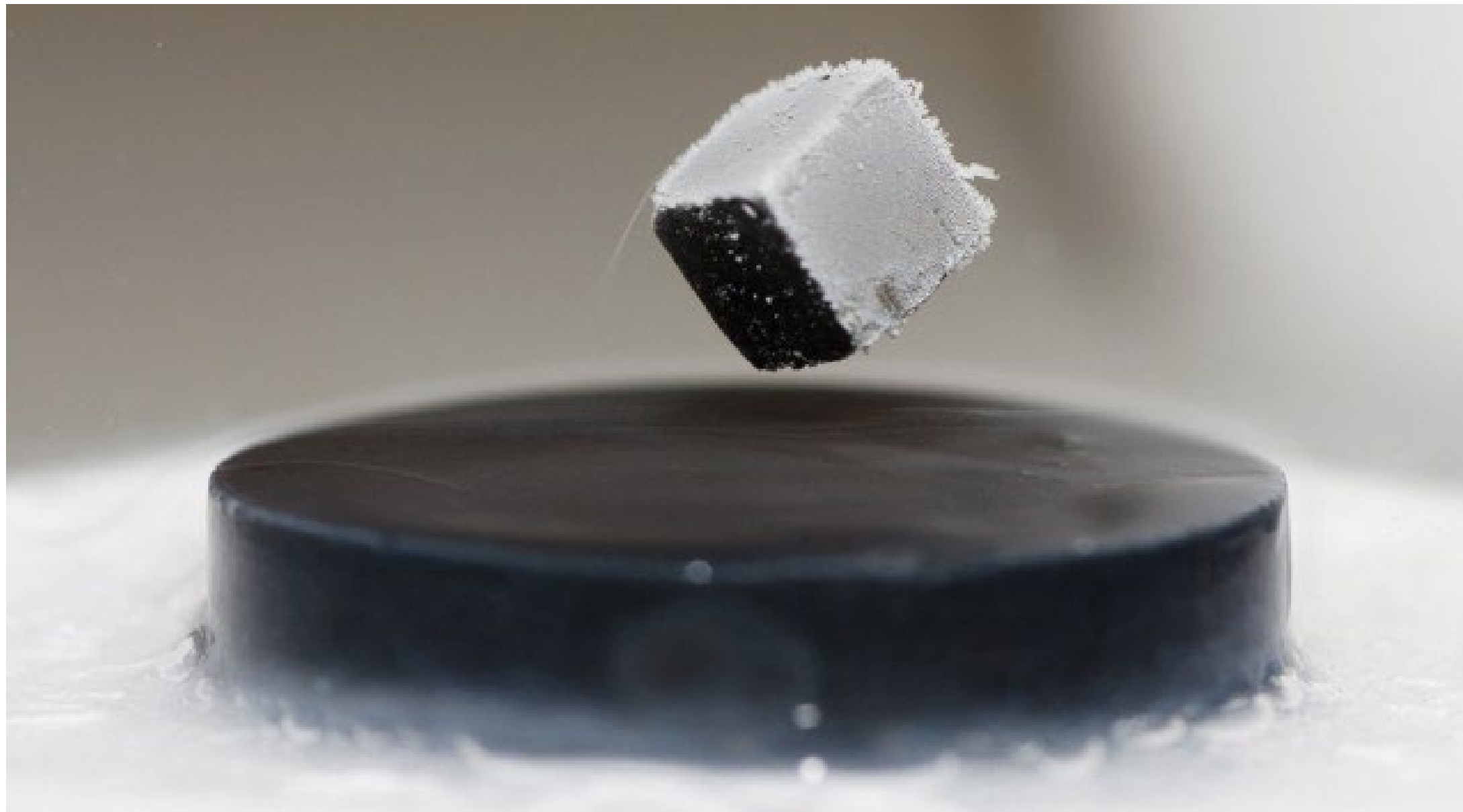
## Hard/Intermediate X-rays:

ESRF

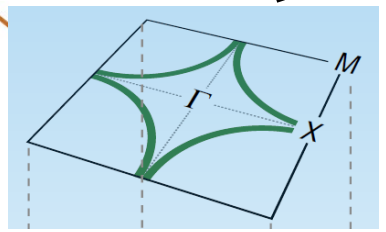
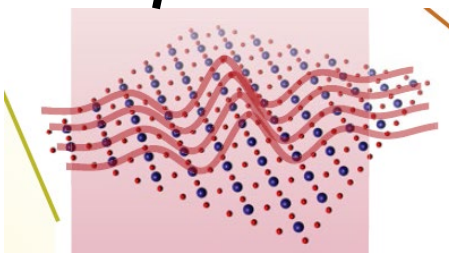
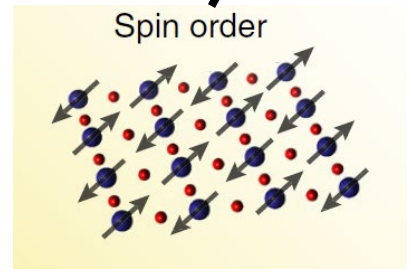
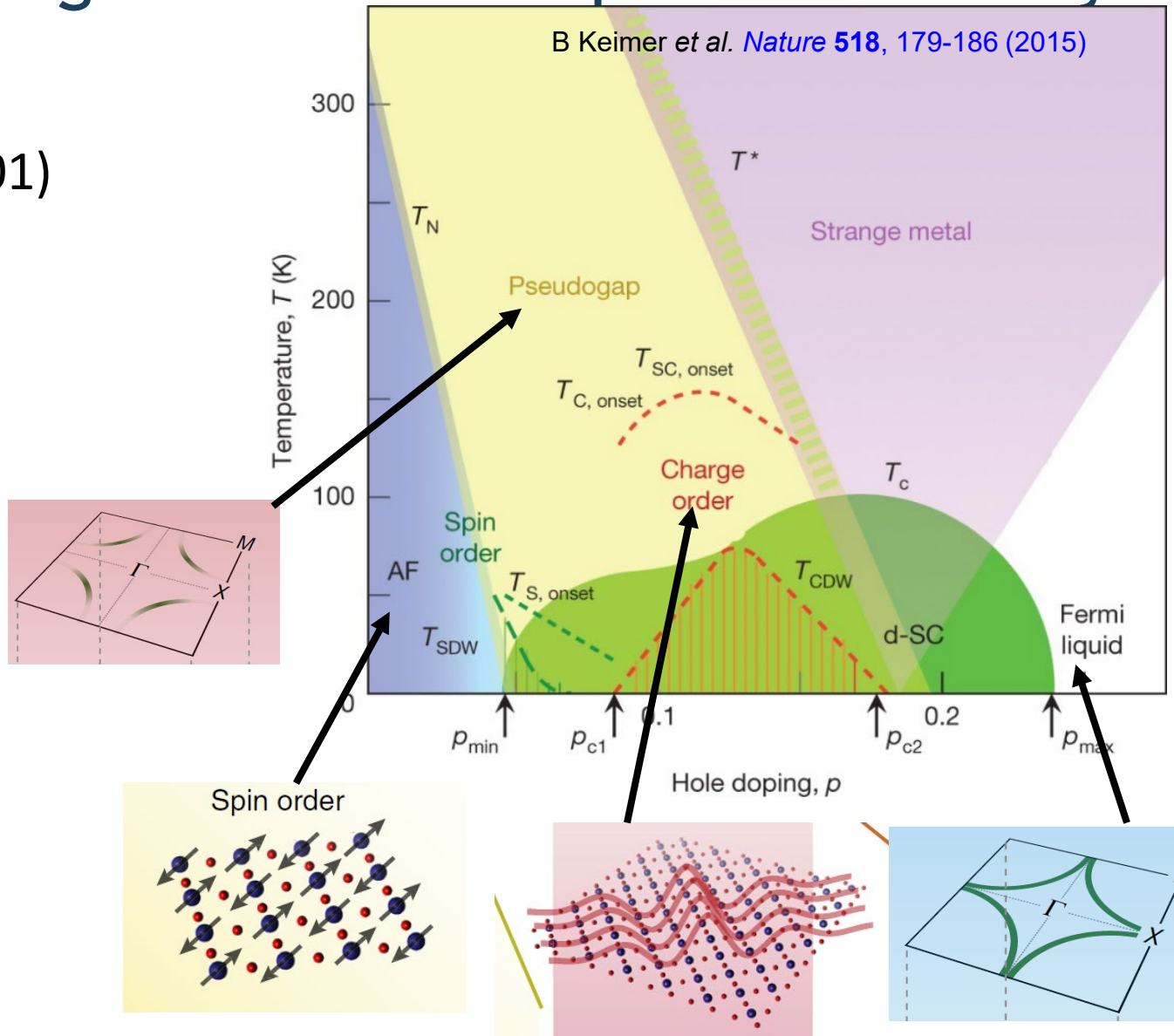
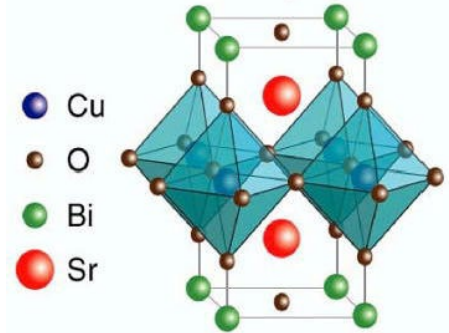
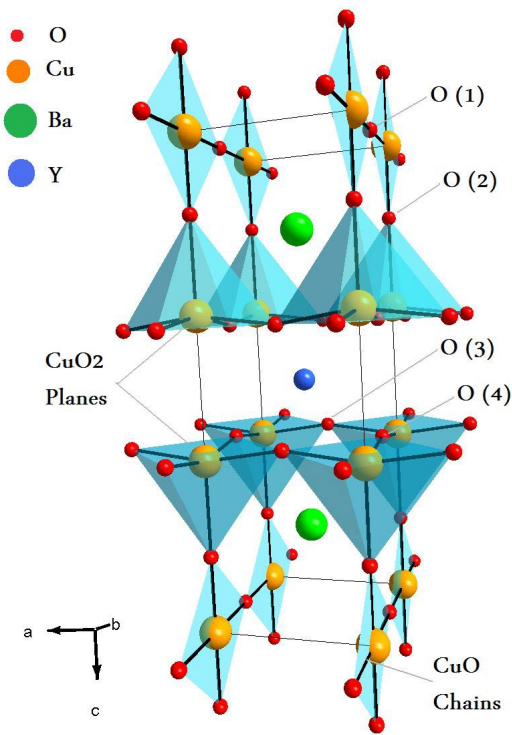
APS (US)

DESY (Hamburg)

# High Tc Superconducting cuprates

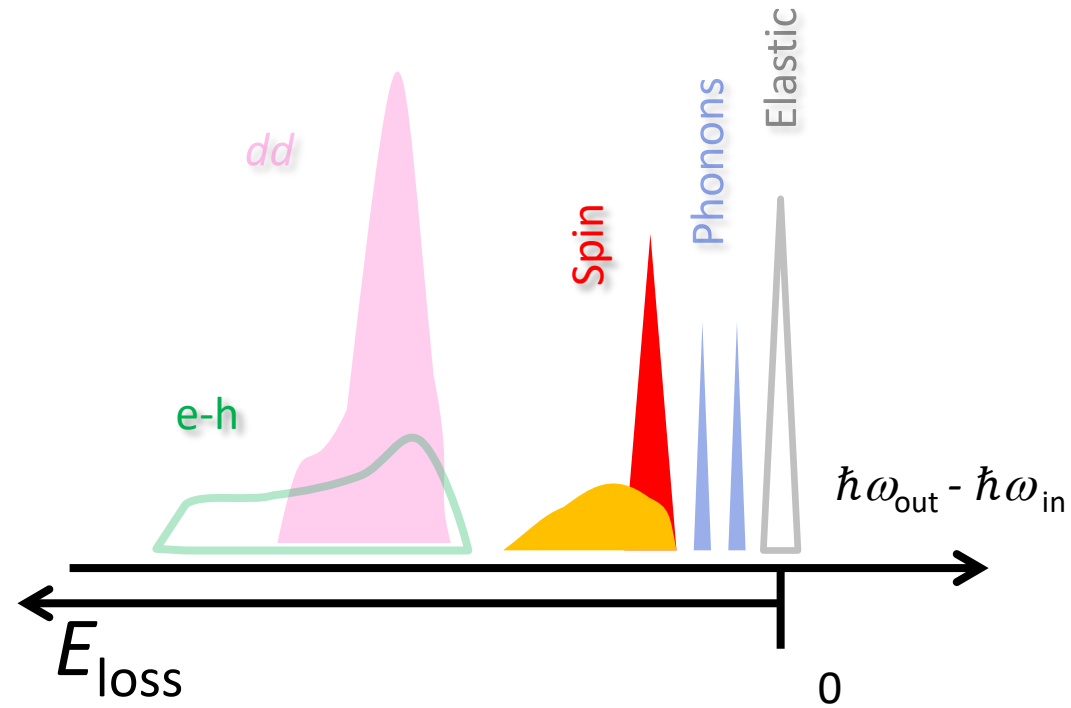
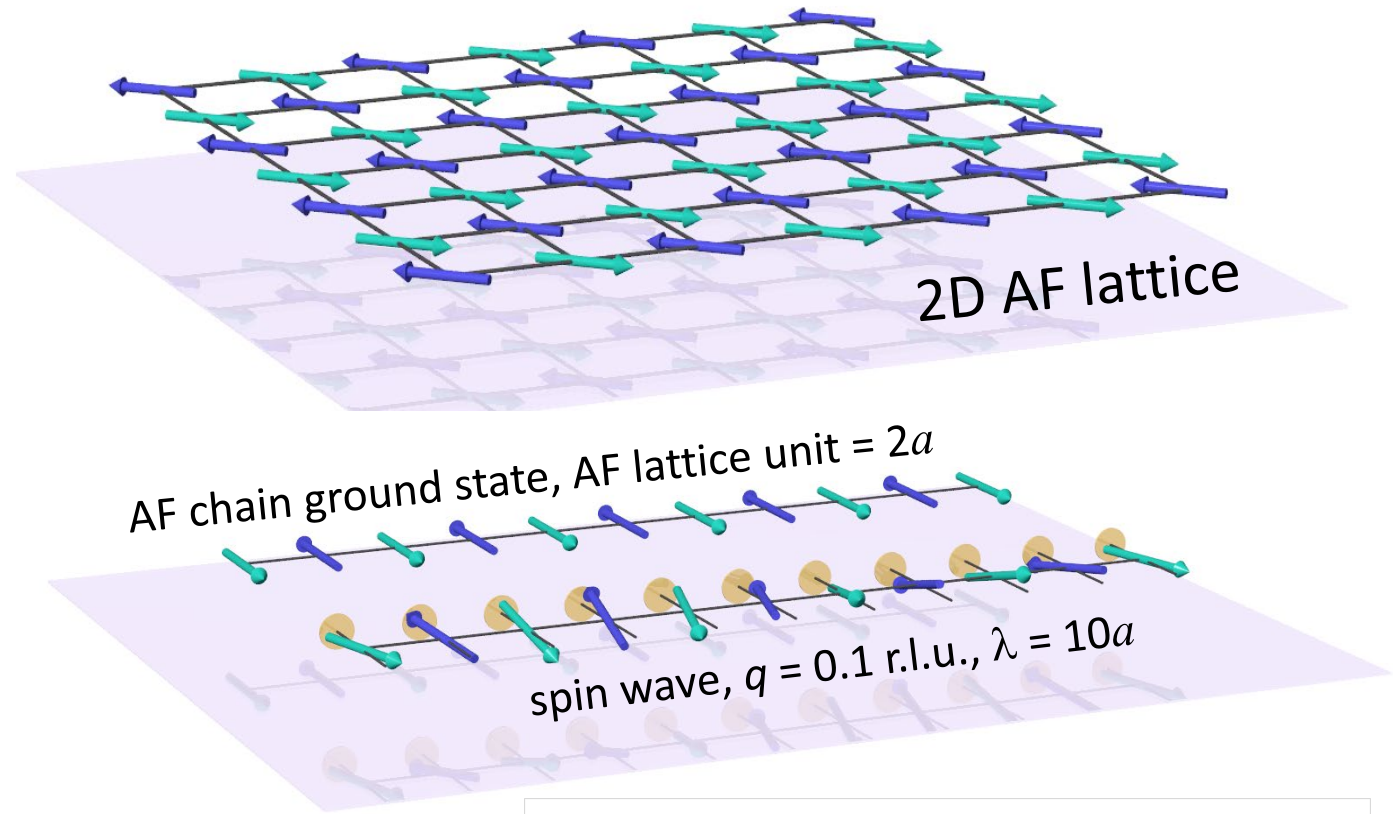


# Cuprates: Magnetism, Charge Order and Superconductivity



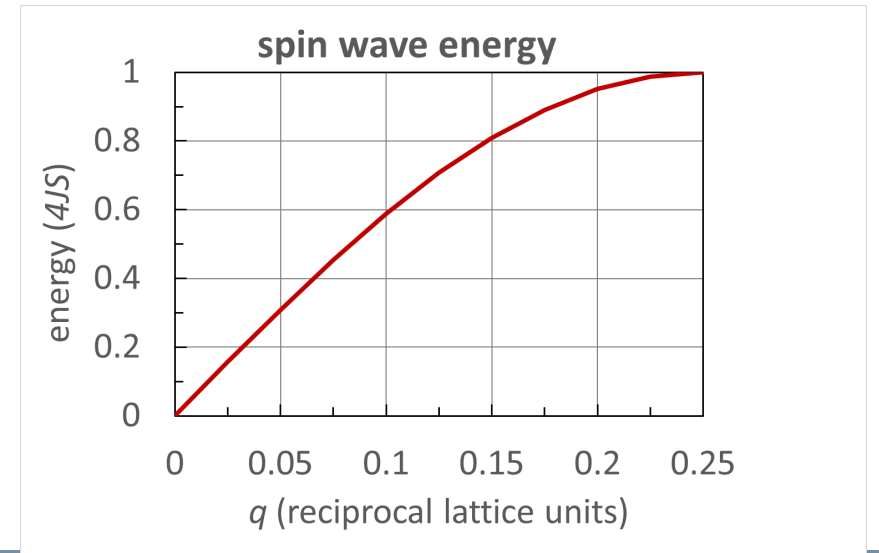
J. Pellicciari and R. Comin *Nature Materials* **17**, 661 (2018)

# Spin excitations



Single magnon: Lorentzian peak

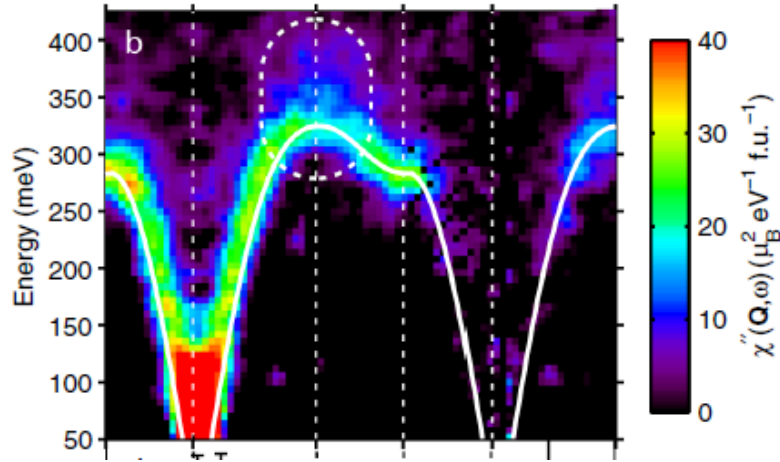
Double magnons: continuum



# Spin excitations: neutron vs x-ray scattering

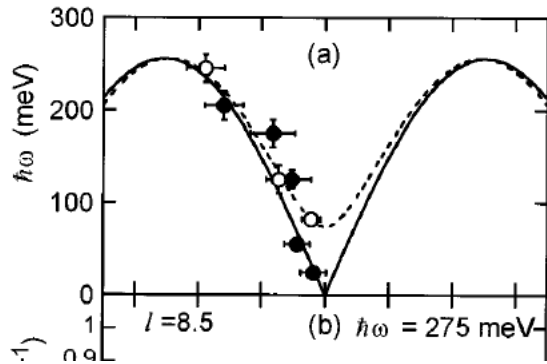
10 orders of magnitude higher sensitivity than INS

$\text{La}_2\text{CuO}_4 - 10^3 \text{ mm}^3$  single crystal



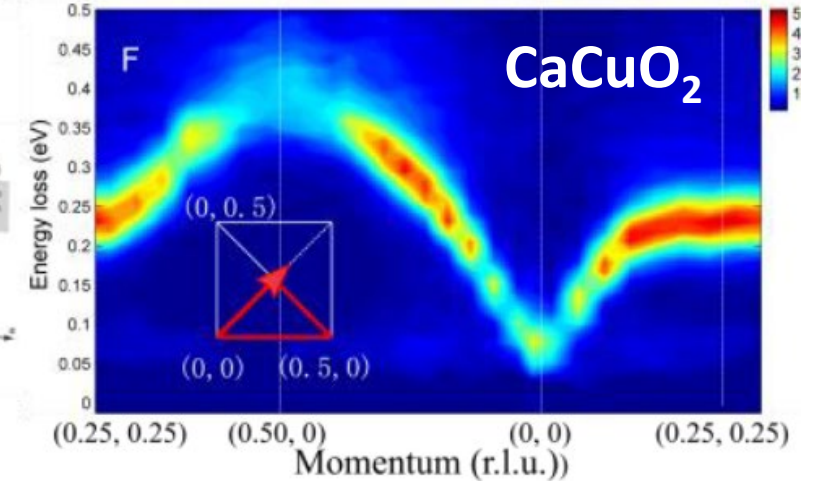
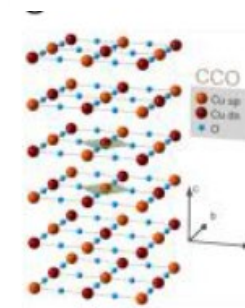
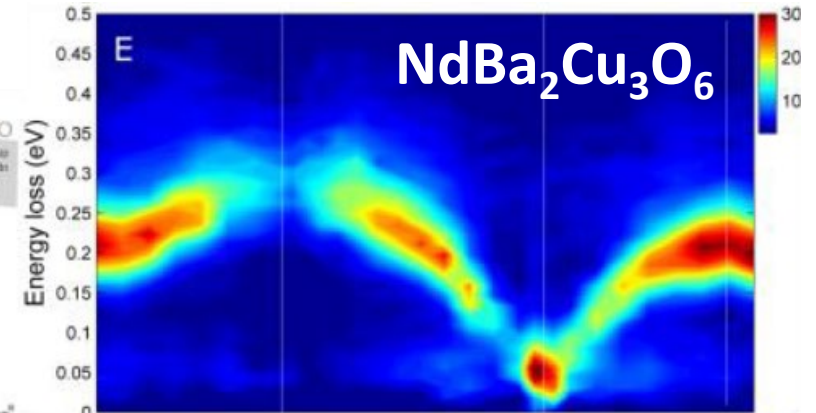
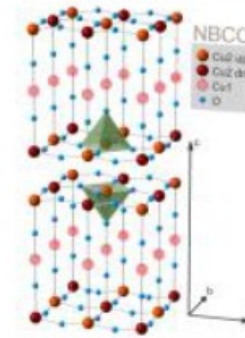
Inelastic Neutron Scattering (since 1960s)

$\text{YBa}_2\text{Cu}_3\text{O}_6 - 1 \text{ mm}^3$  single crystal



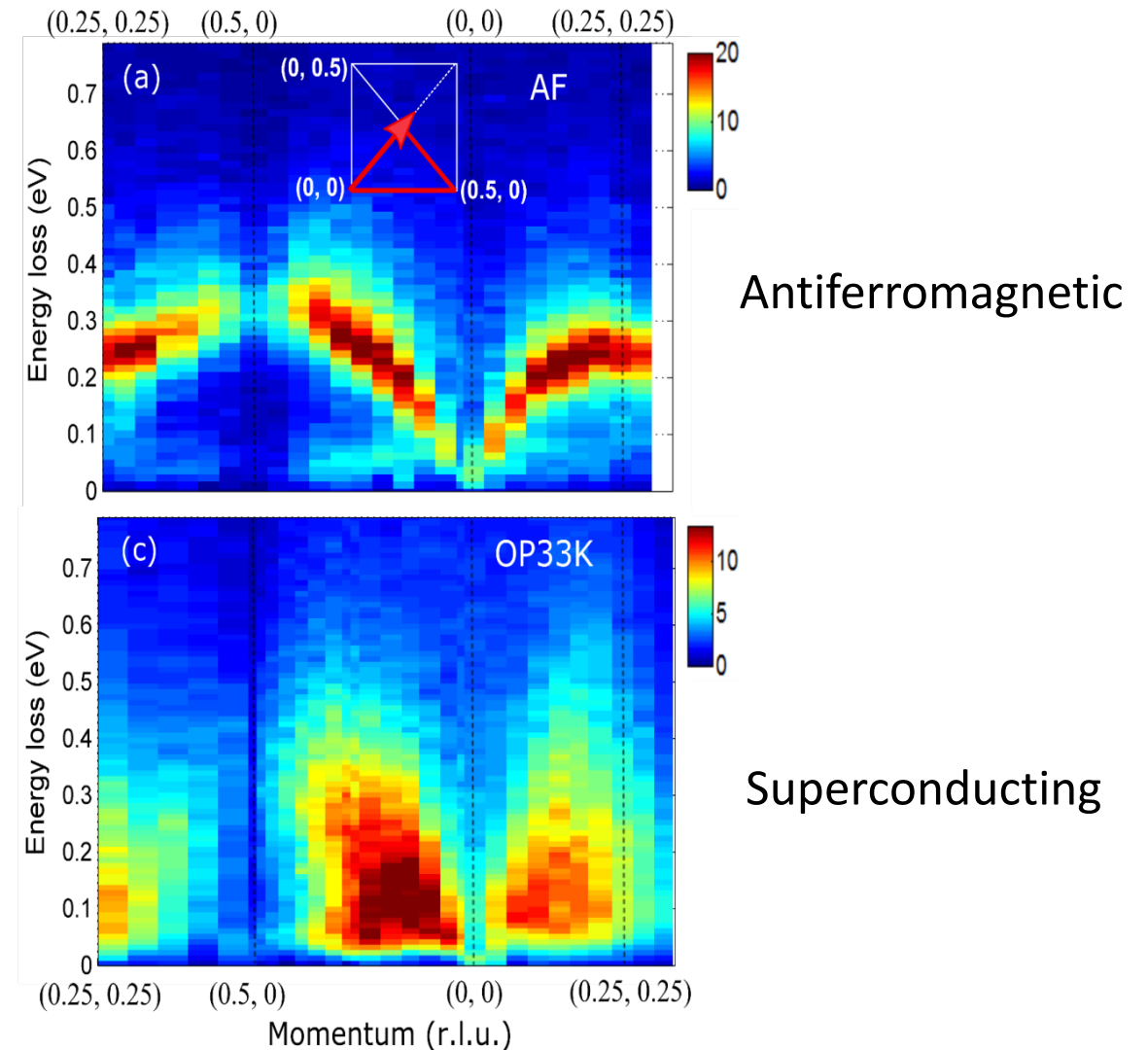
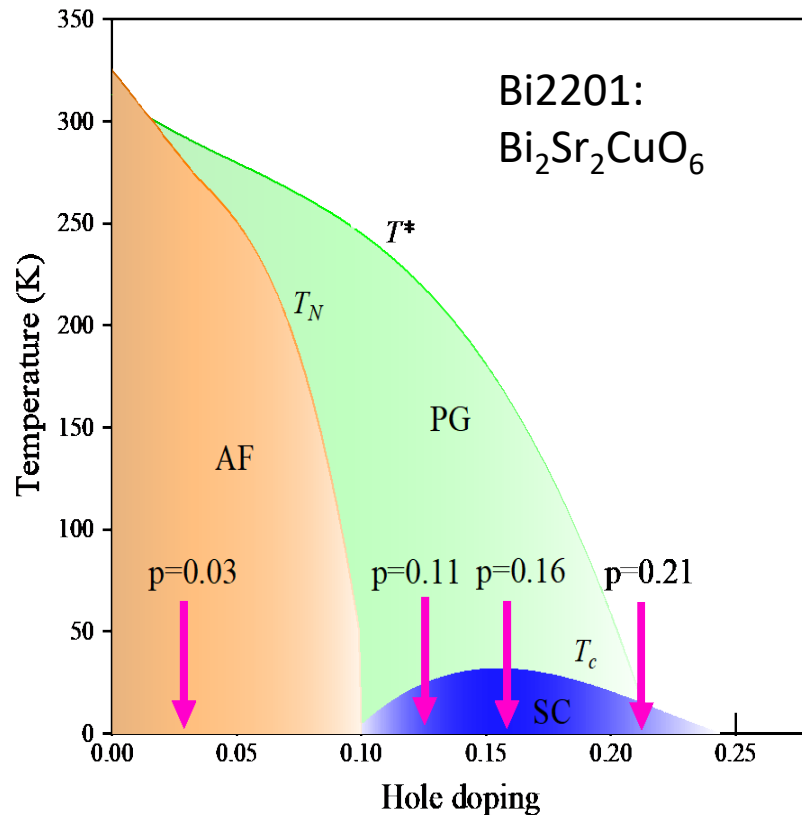
RIXS (since 2010s)

Thin films -  $10^{-7} \text{ mm}^3$  interaction volume



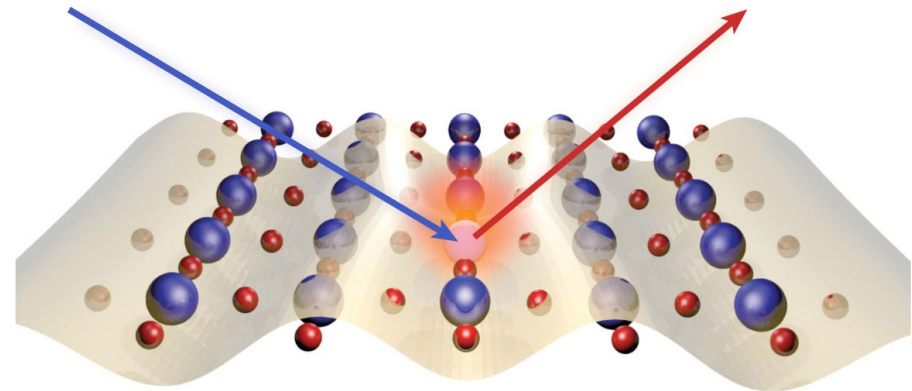
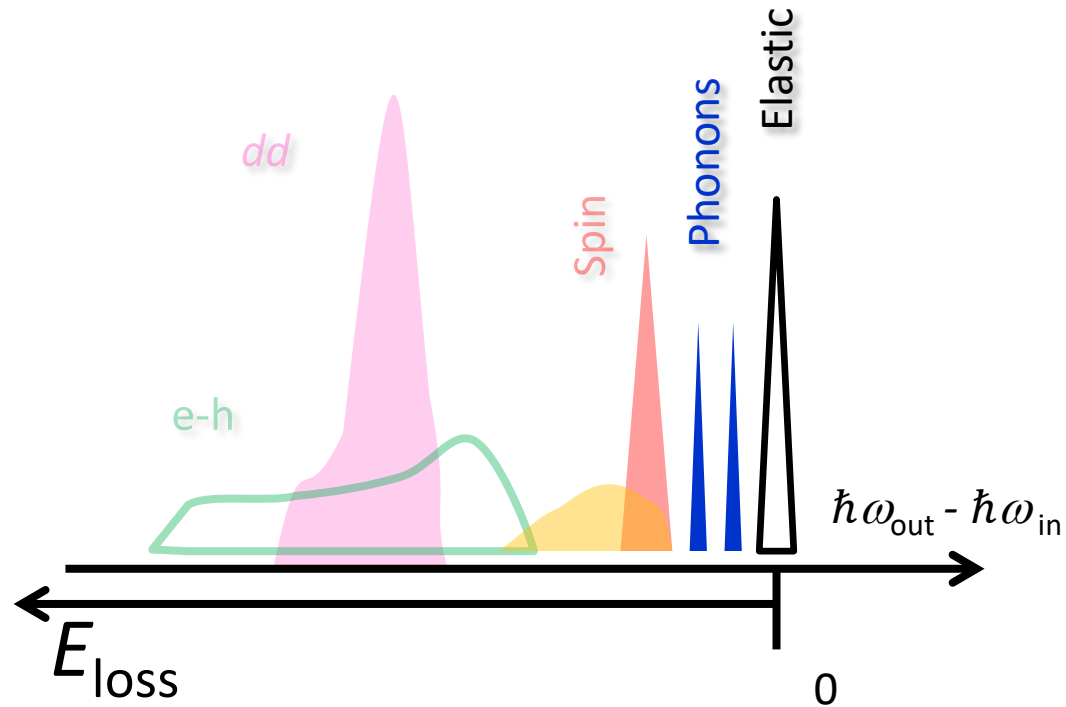
# RIXS demonstrated that magnetism is present also in the superconducting state of cuprates

Doping destroys AF order, but not spin excitations:  
damped magnons = paramagnons



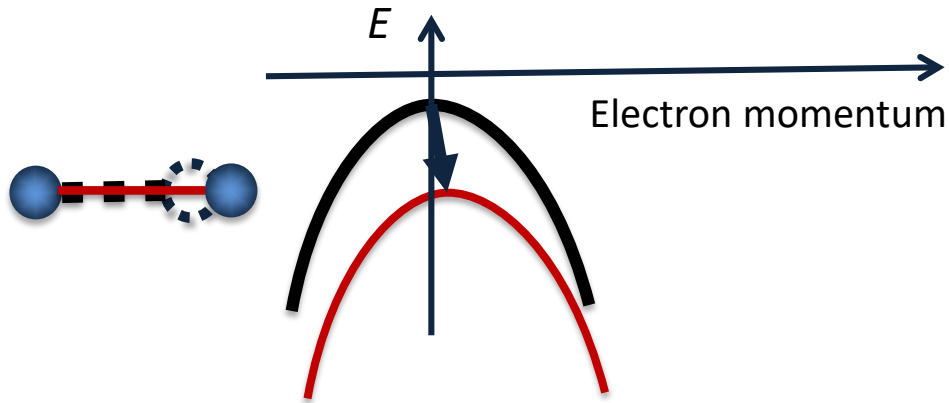


# RIXS for phonons and charge order



- Elastic scattering is related to order parameters
- RIXS: enhancing charge-order scattering

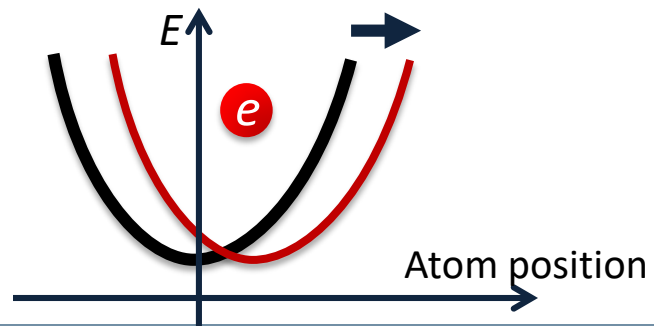
# Phonons: Electron phonon coupling in cuprates



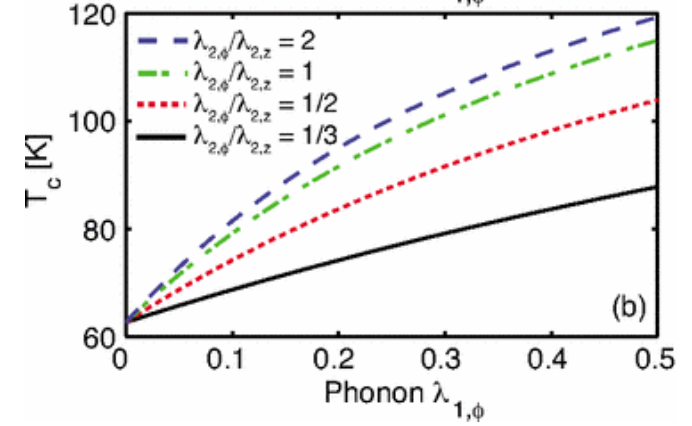
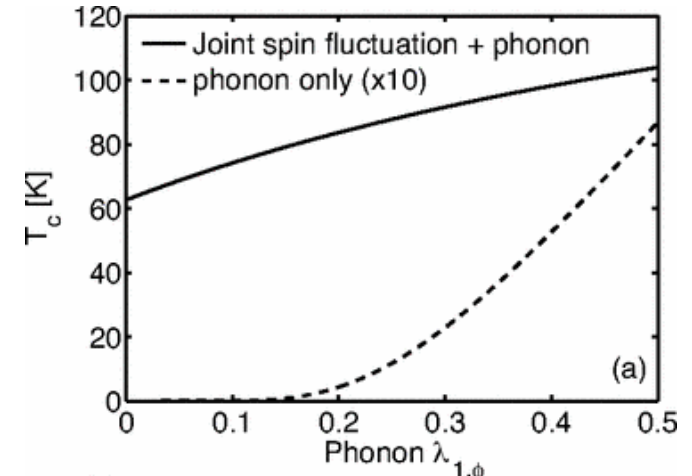
How  $\mathcal{H}$  is modified by an atomic displacement

≡

How lattice is deformed by the presence of a valence electron



EPC: cooperative effect of phonons in SC pairing in cuprates

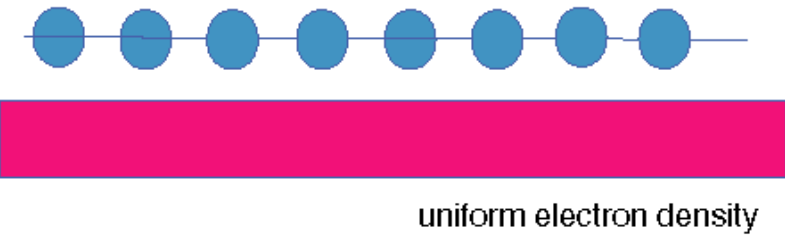


Phys. Rev. B 82, 064513 (2010)

# Charge order and phonons

Charge density waves emerge because the atom position is influenced by the non uniform distribution of valence charge

Ions uniformly spaced



uniform electron density

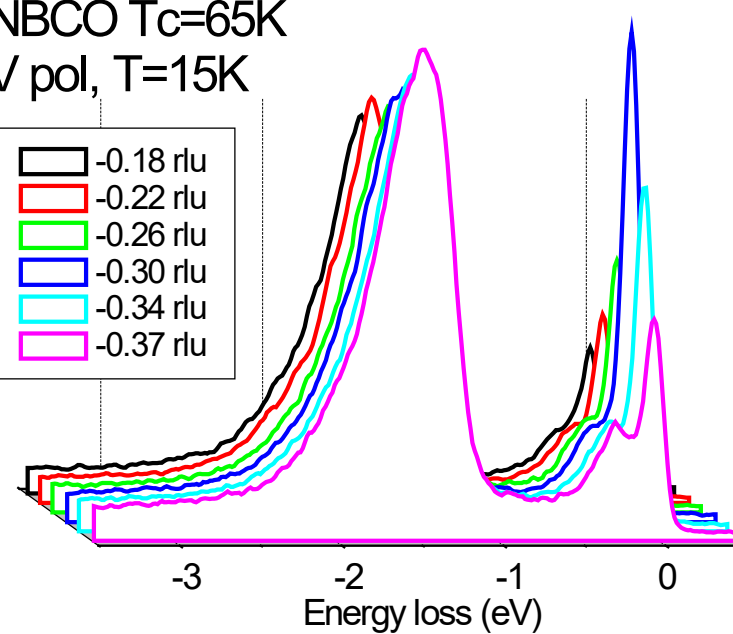
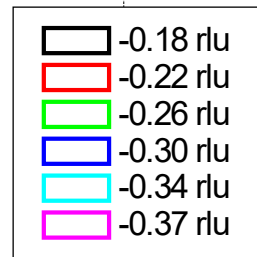
Ions develop static periodic distortion



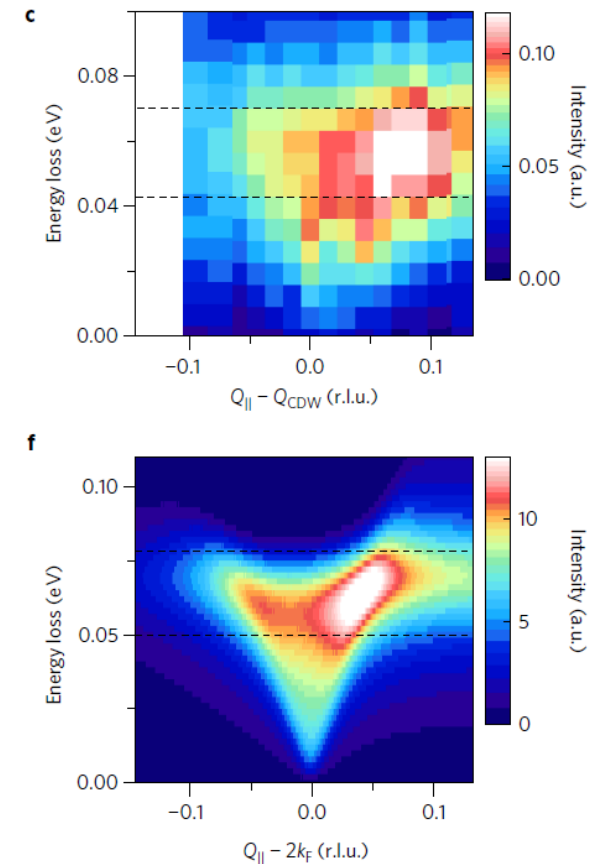
electron density modulated (charge density wave)

With R(I)XS charge order was observed directly in all hole doped cuprates

NBCO  $T_c=65K$   
V pol,  $T=15K$



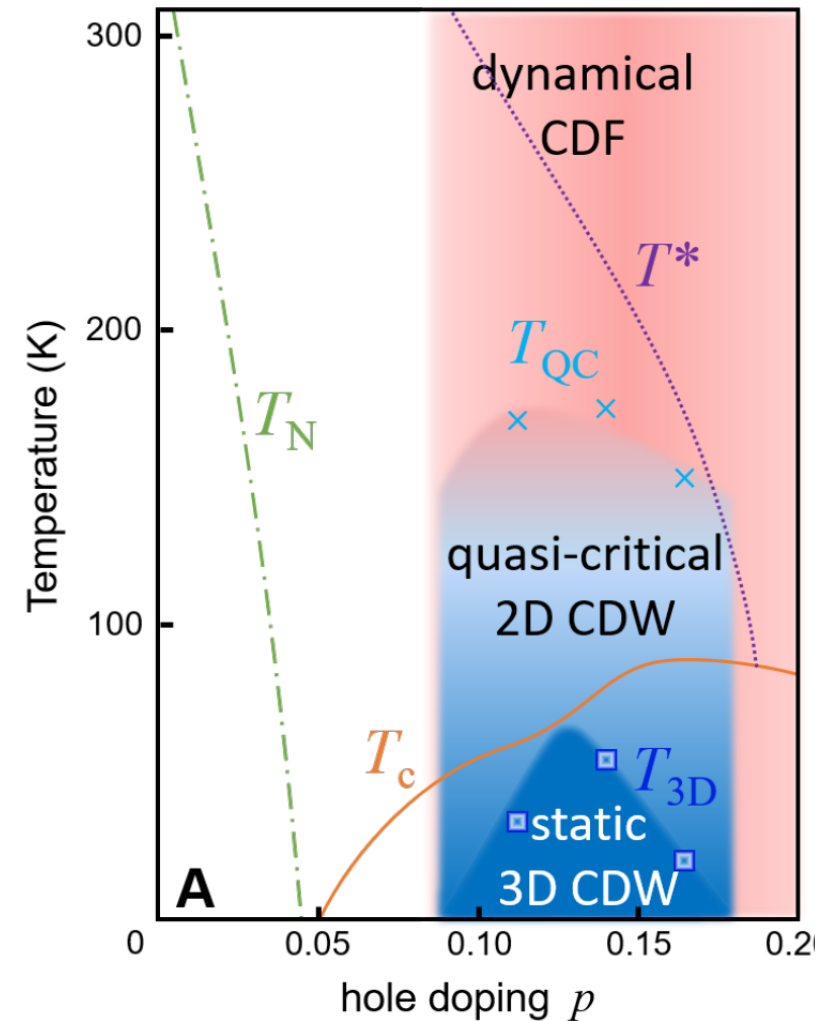
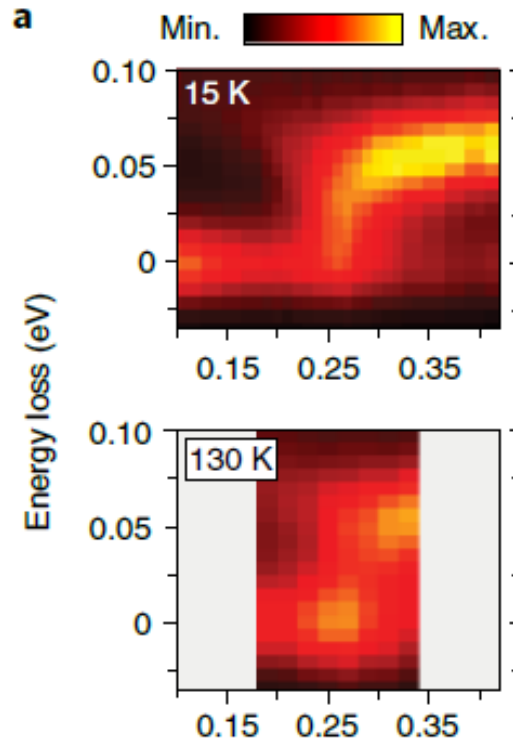
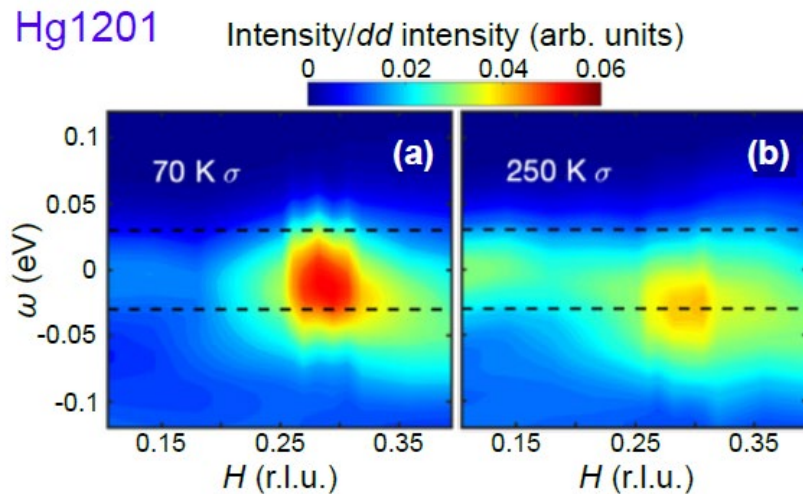
RIXS can see also that charge order couples with phonons



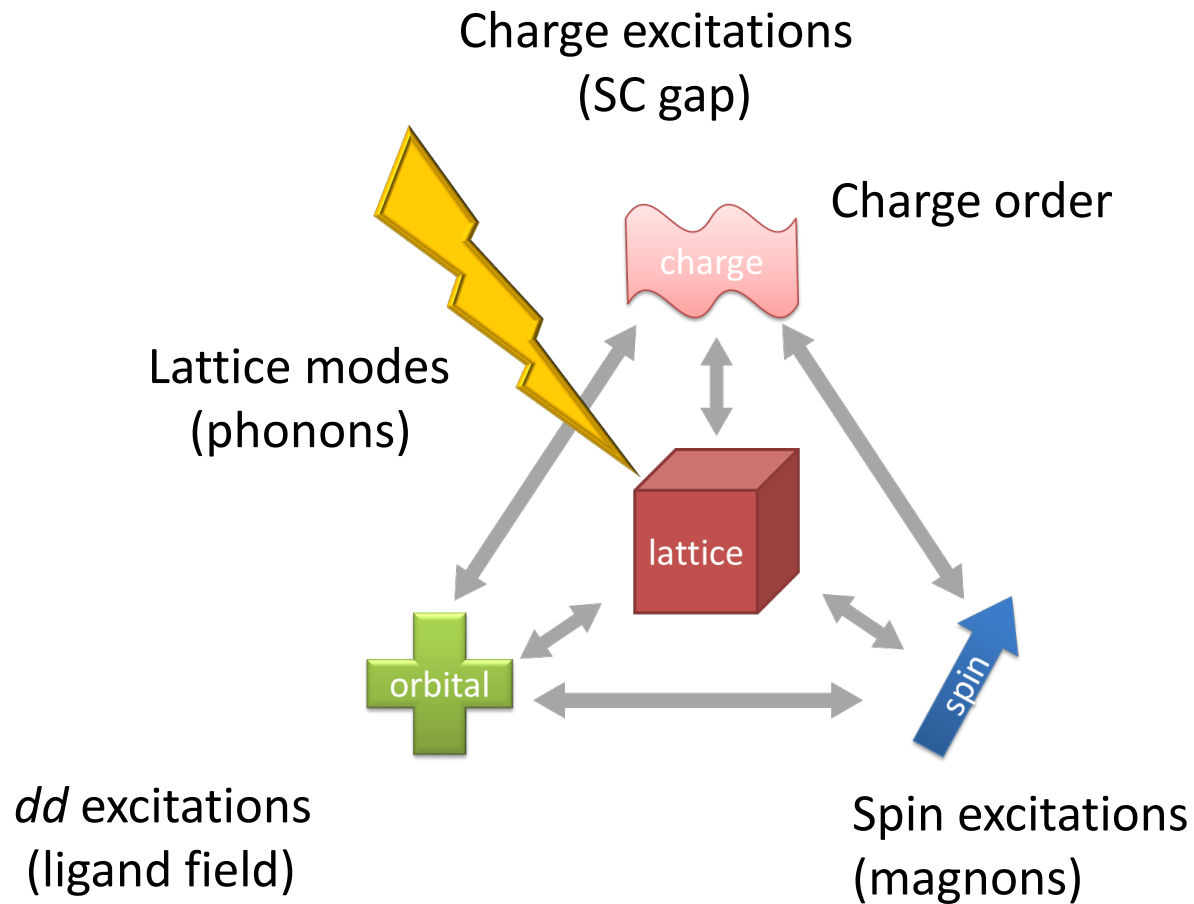
# RIXS has redefined the phase diagram of cuprates

RIXS was used to determine:

- 1) that charge order is a general property of cuprates
- 2) how charge order is coupled to phonons
- 3) that charge order is dominated by charge density fluctuations



# RIXS outlook



RIXS is sensitive to all degrees of freedom and can be used to determine interplay and entwining that are at the origin of the complex behavior of quantum materials

RIXS research has been driven by remarkable technical improvements, leading to several discoveries.

Better resolution, polarization dependence and time dependence will bring more

# Special acknowledgements



**Lucio  
Braicovich**

**Nick  
Brookes**



**Riccardo  
Arpaia**



**Marco  
Moretti**



**Marco  
Salluzzo**



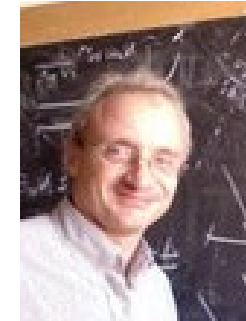
**Leonardo  
Martinelli**



**Carlo  
Di Castro**



**Tom  
Devereaux**



**Marco  
Grilli**



**Bernhard  
Keimer**



**Sergio  
Caprara**

