(Resonant) Inealstic X-ray Scattering

Brian Moritz
SLAC National Accelerator Laboratory and Stanford University

UXSS19
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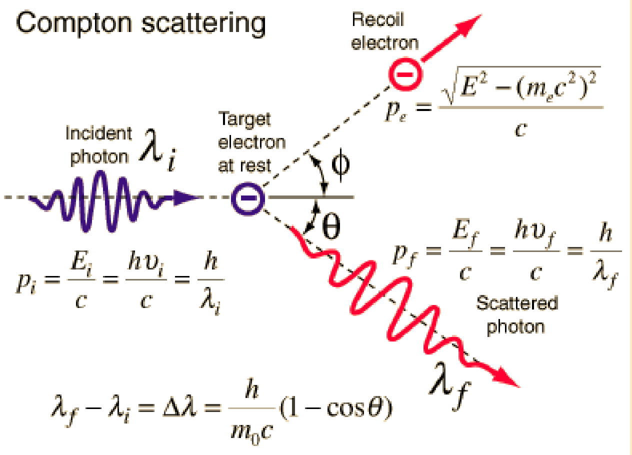
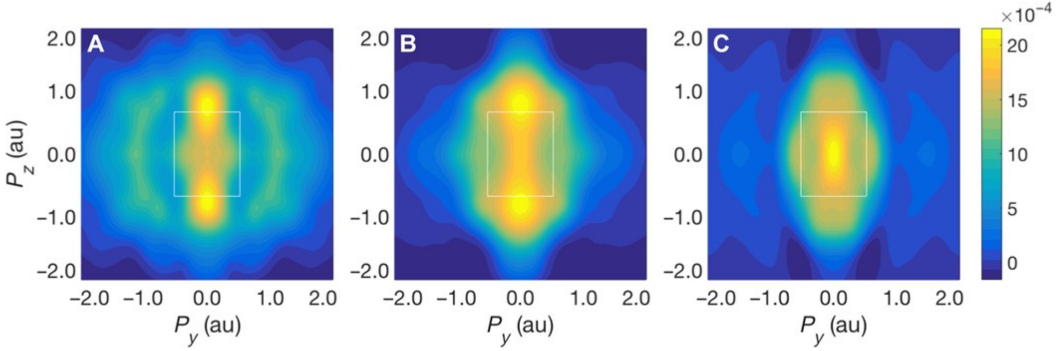
SLAC NATIONAL ACCELERATOR LABORATORY

U.S. DEPARTMENT OF ENERGY
Office of Science

Compton Scattering

Arthur Compton

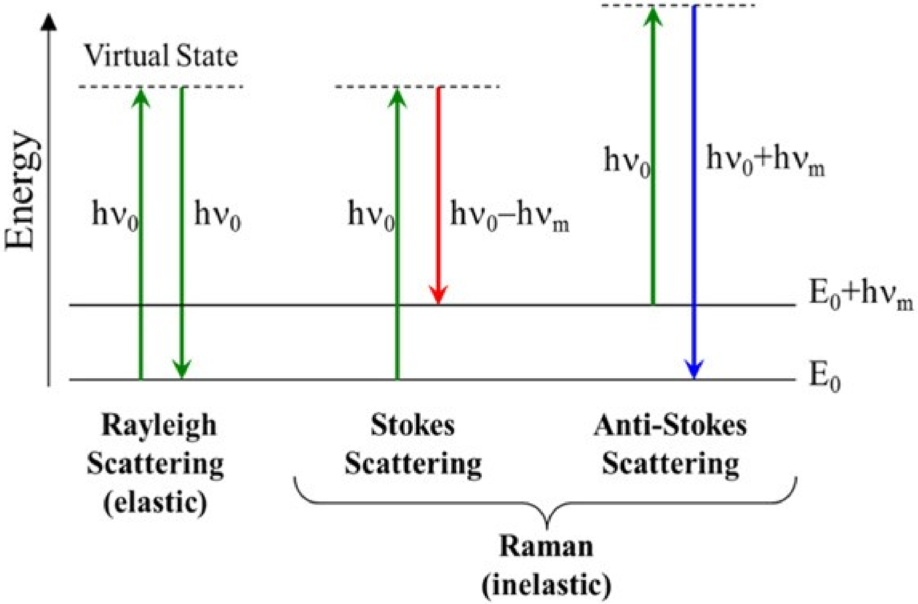




Hafiz *et al*, Science Adv. **3**, e1700971 (2017)

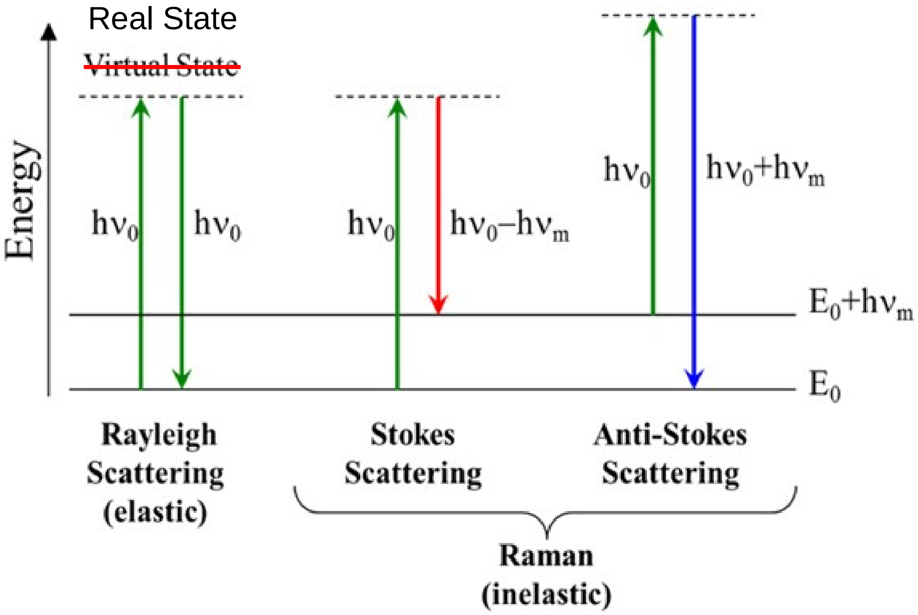
Raman Scattering

C. V. Raman



Resonant Raman Scattering

C. V. Raman



Question #1

Raman and his student K.S. Krishnan performed the measurements to identify what became known as the Raman effect in solids, liquids, and gases. Did Krishnan receive the Nobel Prize along with Raman in 1930?

Yes 🟦

No ⬟

Detector Improvements

1920s

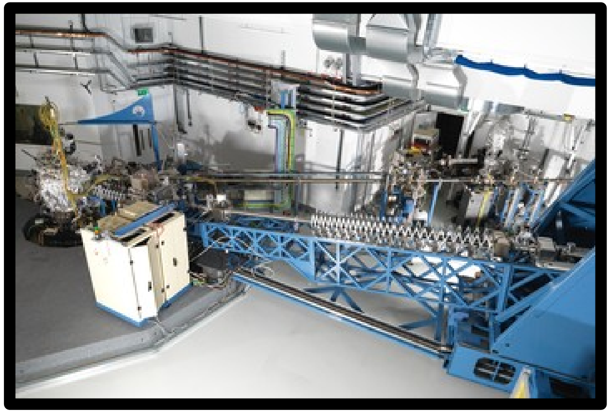
From 2014:

$\Delta E = 50$ meV at $Cu\text{-}L_3$

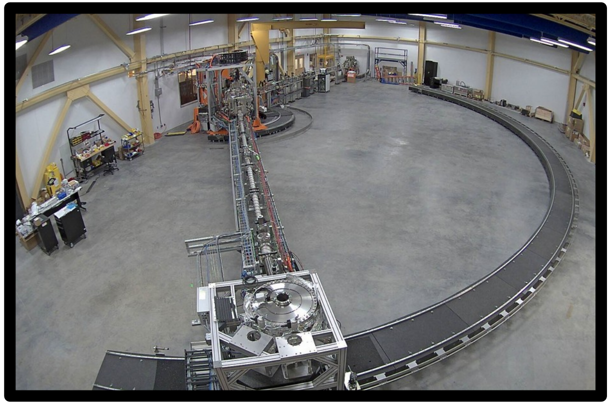
2010s

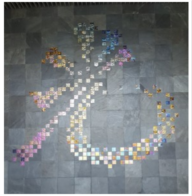
“New” Facilities

diamond



NSLS-II
National Synchrotron Light Source II



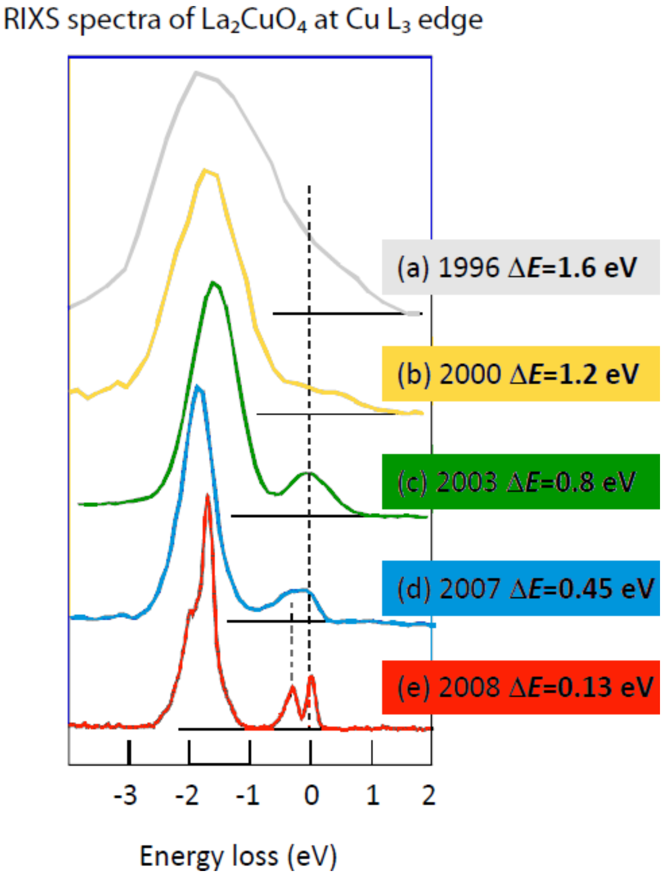


ESRF
The European Synchrotron

https://youtu.be/ccf2sdXypQk

Improvements in Resolution

a) Ichikawa *et al*, JESRP **78**, 183 (1996)
b) Duda *et al*, JESRP **110-111**, 275 (2000)
c) Ghiringhelli *et al*, PRL **92**, 117406 (2004)
d) Braicovich *et al*, PRL **102**, 167401 (2009)
e) Braicovich *et al*, PRL **104**, 077002 (2010)


RIXS spectra of La_2CuO_4 at Cu L_3 edge

BL-2B, Photon Factory

BW3, HASYLAB

AXES – ID08, ESRF

AXES – ID08, ESRF

SAXES – ADRESS, SLS

Courtesy of G. Ghiringhelli

Question #2

You use a detector with a resolving power of 30,000 to detect photons at 900 eV. What is the resolution (considering only the detector)?

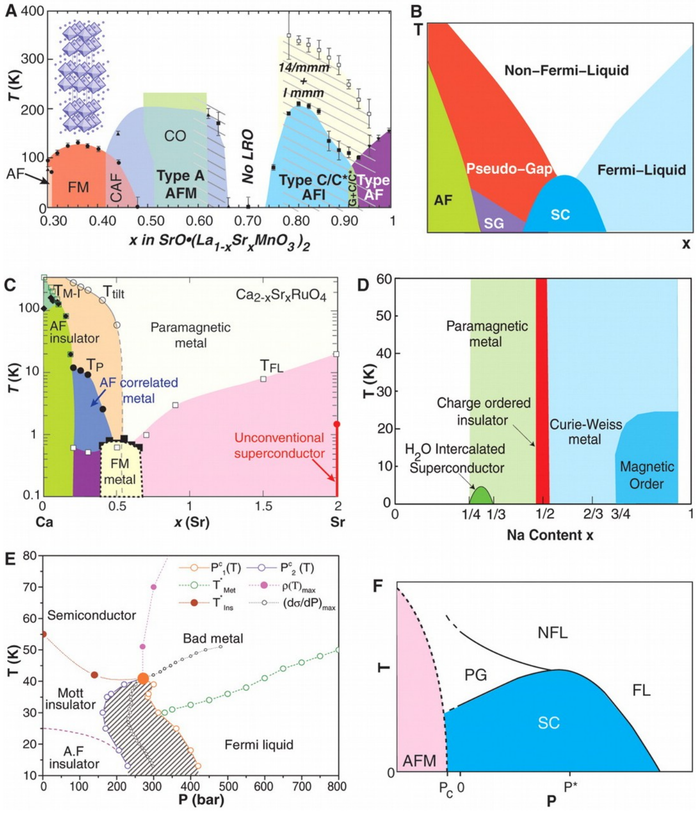
3 meV ■

30 meV ●

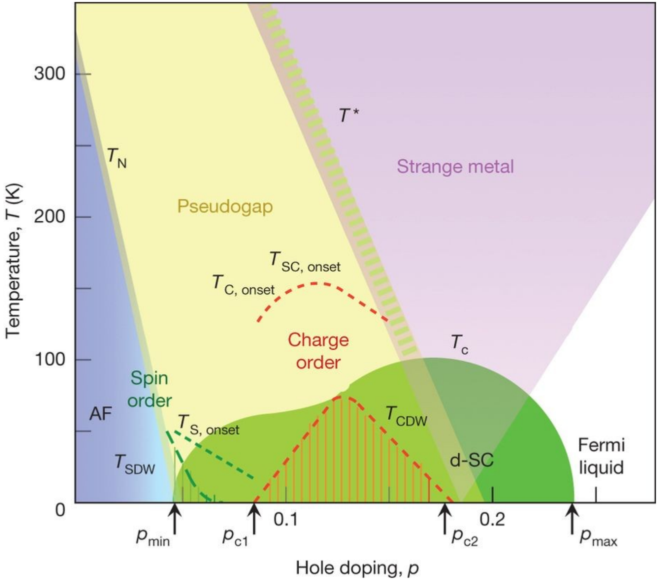
300 meV ▲

100 meV ⬟

Complexity in Transition Metal Materials (Oxides)



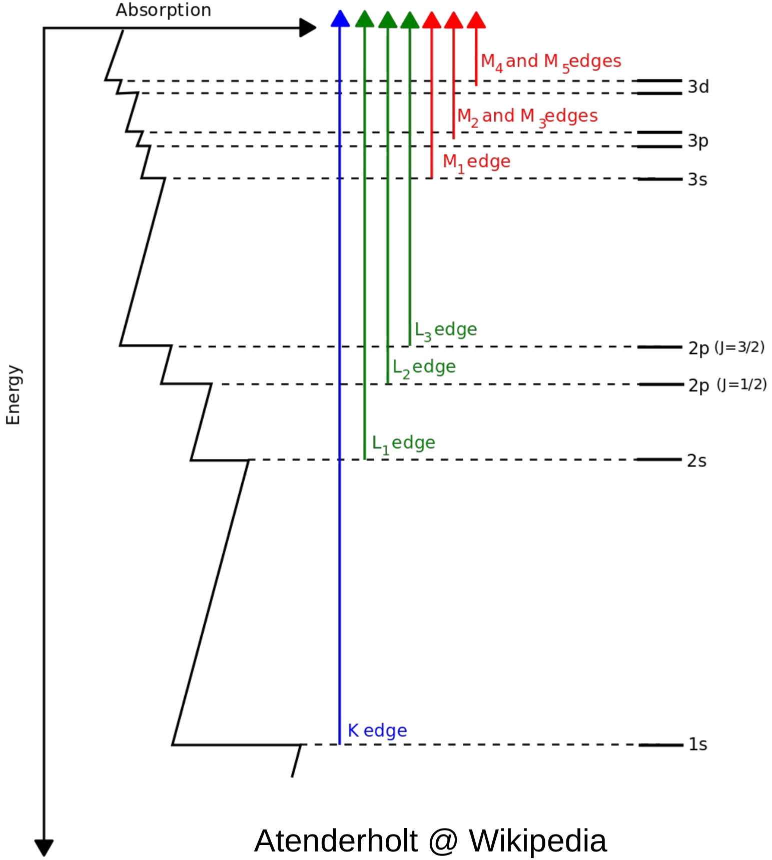
Dagotto *et al*, Science **309**, 257-262 (2005)



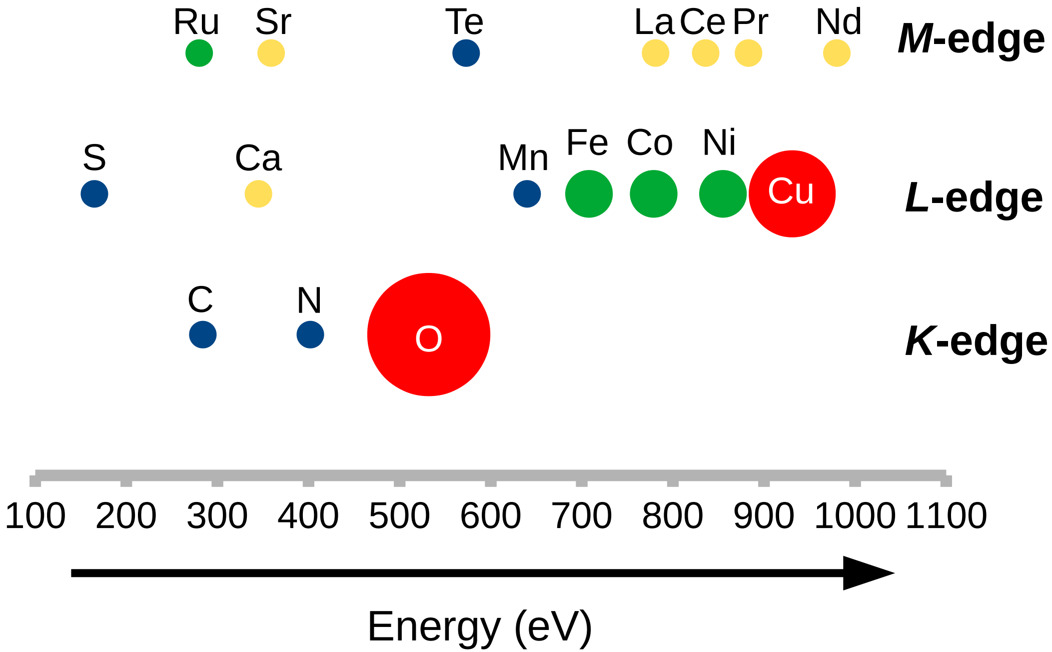
Keimer *et al*, Nature **518**, 179-186 (2015)

Our examples will involve cuprates as their electron configurations make them somewhat better template systems

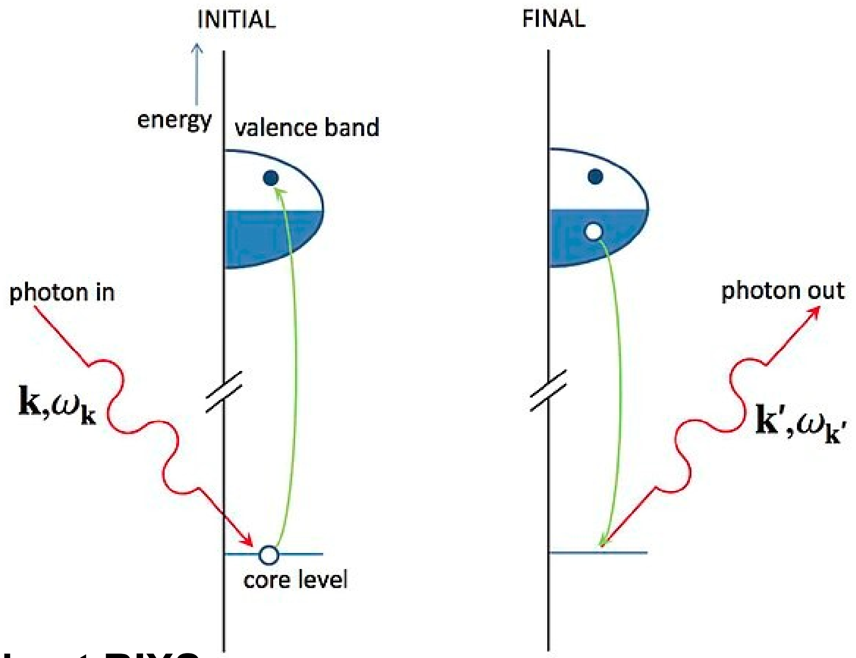
X-ray *K*-, *L*-, and *M*-edges



Atenderholt @ Wikipedia



Resonant Inelastic X-ray Scattering (RIXS)



<u>Direct RIXS</u>

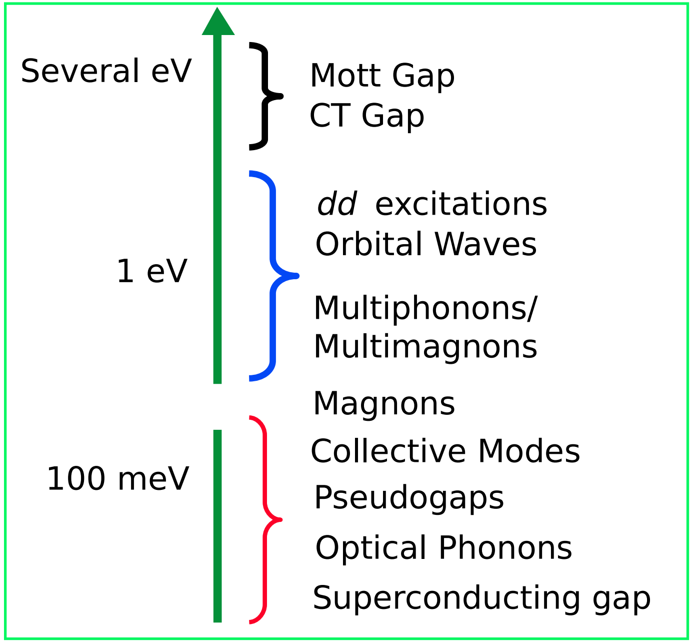
Transition Metal *L*-edge & *M*-edges, O *K*-edge

<u>Indirect RIXS</u>

Transition Metal *K*-edges

- Photon-in/Photon-out
- Bulk Sensitive
- Chemical Specific
- Resonant –
  Enhanced Cross-sections
- High Resolution
- Polarization Control

Elementary and Collective Excitations



Several eV

Mott Gap
CT Gap

1 eV

dd excitations
Orbital Waves

Multiphonons/
Multimagnons

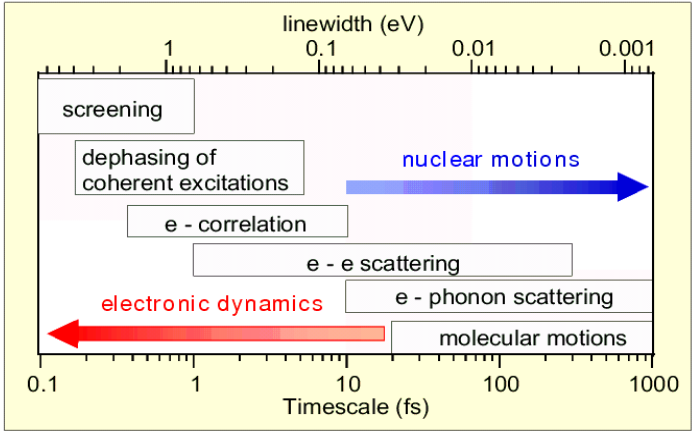
100 meV

Magnons
Collective Modes
Pseudogaps
Optical Phonons
Superconducting gap

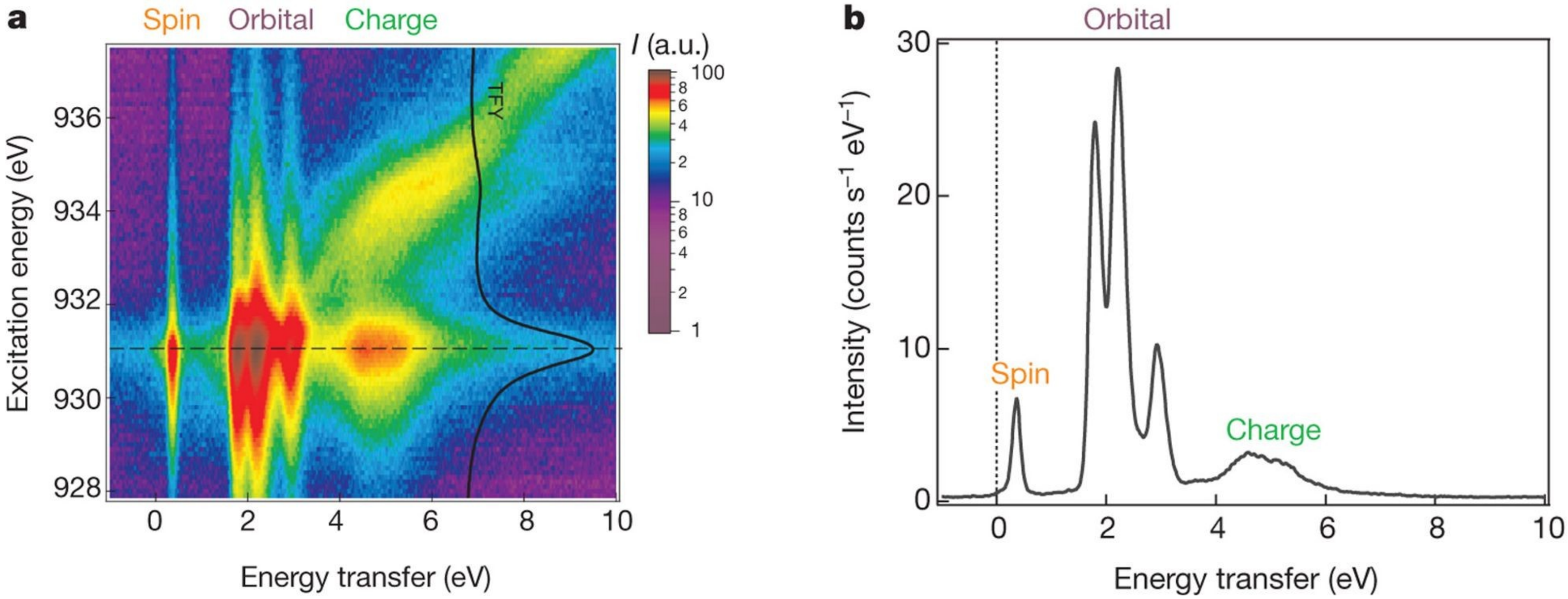
- Orbital fluctuations: ~ 100 meV - 1.5 eV
- Multiphonons/magnons ~ 50-500 meV
- Pseudogaps ~ 30-300 meV
- Quasi e-h pairs ~ 1-250 meV
- Collective modes ~ 1-150 meV
- Optical Phonons: ~ 10 - 70 meV
- Single Magnons: ~ 10 meV - 400 meV
- Superconducting gaps ~ 1 – 35meV

Techniques:

Raman Scattering
Inelastic X-ray Scattering
ARPES …

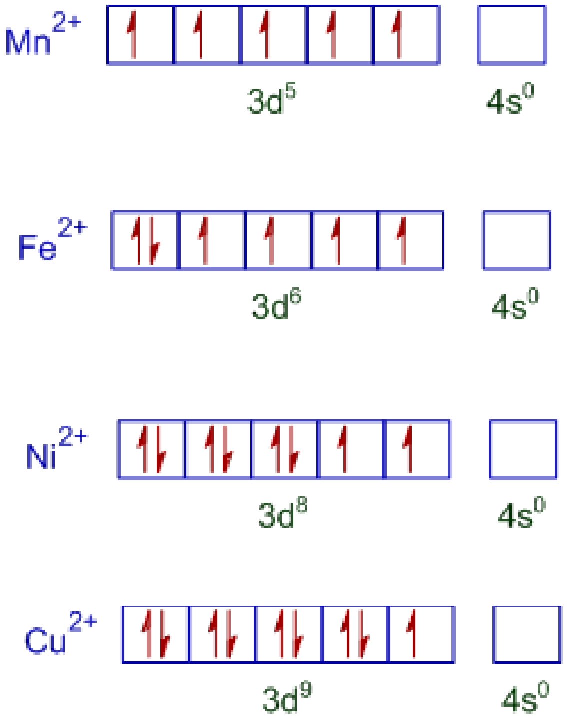


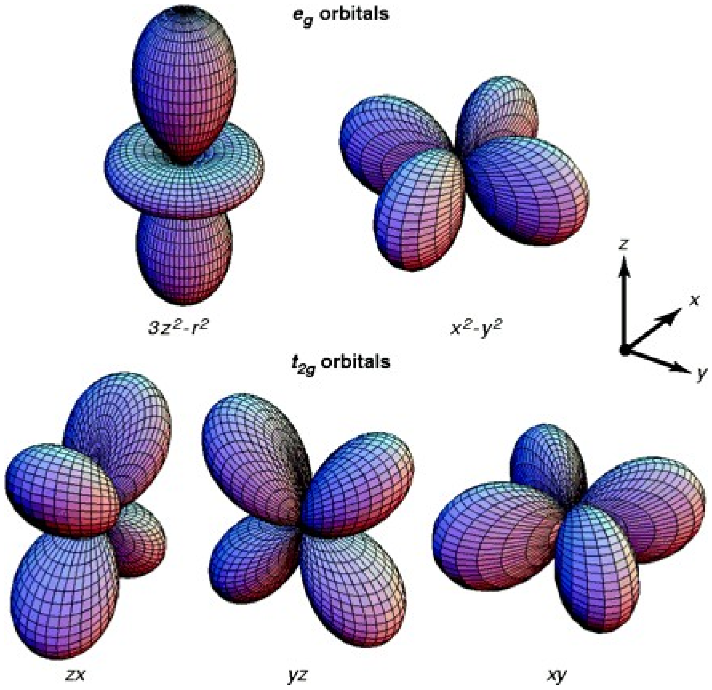
RIXS Map



Schlappa *et al*, Nature **485**, 82-85 (2012)

Why Cu^{2+} ($3d^9$) Is Special





Tokura *et al*, Science **288**, 462-468 (2000)

Question #3

In the atomic limit and an octahedral environment with an elongated *c*-axis, which *d*-orbital is partially filled in a $3d^9$ configuration due to crystal field effects?

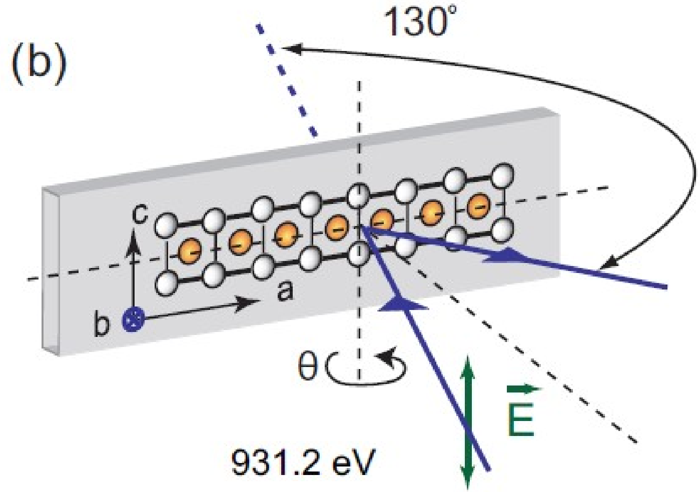
d_{x2-y2} 🟦

d_{3z2-r2} 🟢

d_{xy} ▲

d_{xz}/d_{yz} ⬟

Cu *L*-edge *dd* excitations in $Ca_2Y_2Cu_5O_{10}$



- Align scattering plane along *a*-axis
- Scattering angle fixed at 50°
- Incident polarization along c
- Out-going polarization along c or in the *a*-*b* plane
- At half-filling, ~ Cu $3d^9$ chains

Cu 3*d* states

$$
\begin{aligned}
d_{x^2-y^2} &= \frac{1}{\sqrt{2}}(Y_{22}+Y_{22}) \\
d_{3z^2-r^2} &= Y_{20} \\
d_{xy} &= -\frac{i}{\sqrt{2}}(Y_{22}-Y_{22}) \\
d_{yz} &= -\frac{i}{\sqrt{2}}(Y_{21}+Y_{2\bar{1}}) \\
d_{xz} &= \frac{1}{\sqrt{2}}(Y_{21}-Y_{2\bar{1}})
\end{aligned}
$$

Cu 2*p* $j_{3/2}$ states

$$
\begin{aligned}
p_{\frac{3}{2},-\frac{3}{2}} &= Y_{1\bar{1}}^{\downarrow} \\
p_{\frac{3}{2},-\frac{1}{2}} &= \sqrt{\frac{1}{3}}Y_{1\bar{1}}^{\uparrow} + \sqrt{\frac{2}{3}}Y_{10}^{\downarrow} \\
p_{\frac{3}{2},\frac{1}{2}} &= \sqrt{\frac{2}{3}}Y_{10}^{\uparrow} + \sqrt{\frac{1}{3}}Y_{11}^{\downarrow} \\
p_{\frac{3}{2},\frac{3}{2}} &= Y_{11}^{\uparrow}
\end{aligned}
$$

M. Moretti-Sala *et al*, *NJP* **13**, 043026 (2011)

RIXS cross-section for each transition

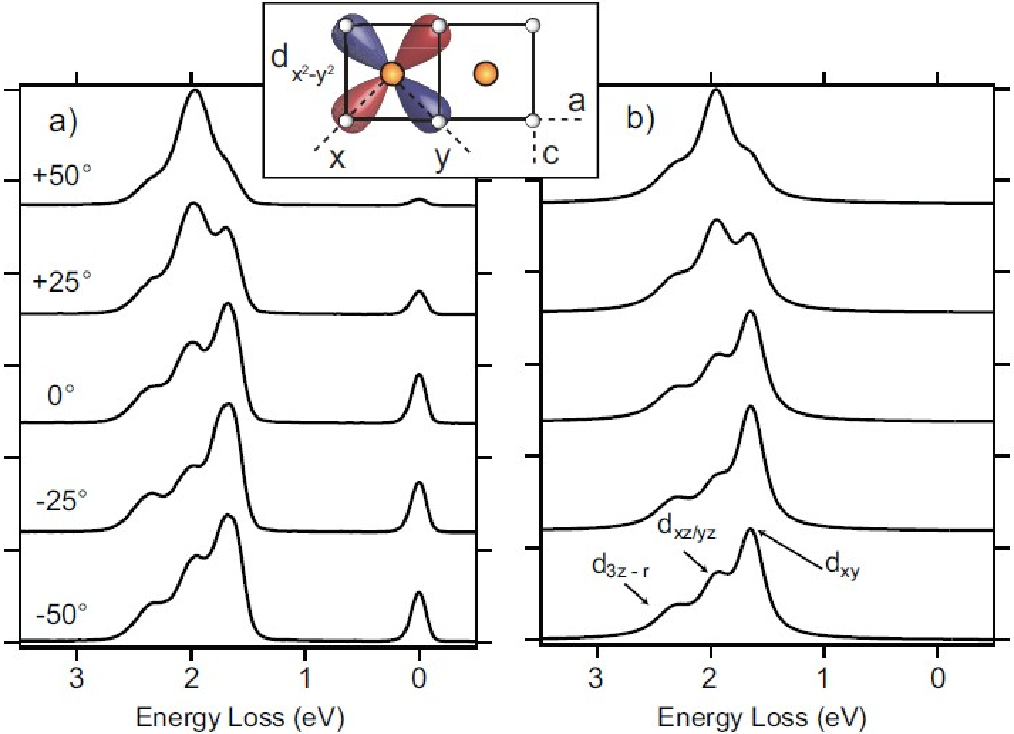
$$\sigma_{3z^2-r^2}^{\downarrow(\uparrow)} \propto \sum_{q'} \left| \sum_{m} \langle d_{3z^2-r^2}^{\downarrow(\uparrow)} | T_{q'}^{\dagger} | p_{\frac{3}{2},m} \rangle \langle p_{\frac{3}{2},m} | T_q | d_{x^2-y^2}^{\downarrow} \rangle \right|^2$$

- Include linear polarization
- 3*j*-symbols
- Straightforward evaluation

Question #4

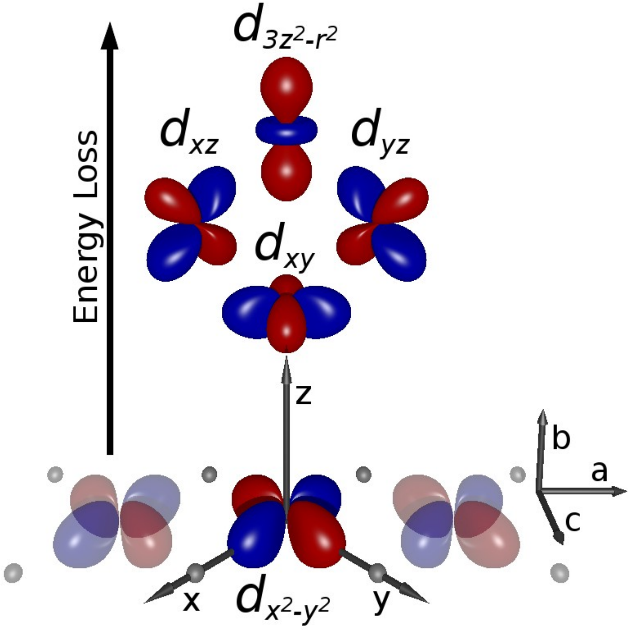
Which side is the experimental data on?

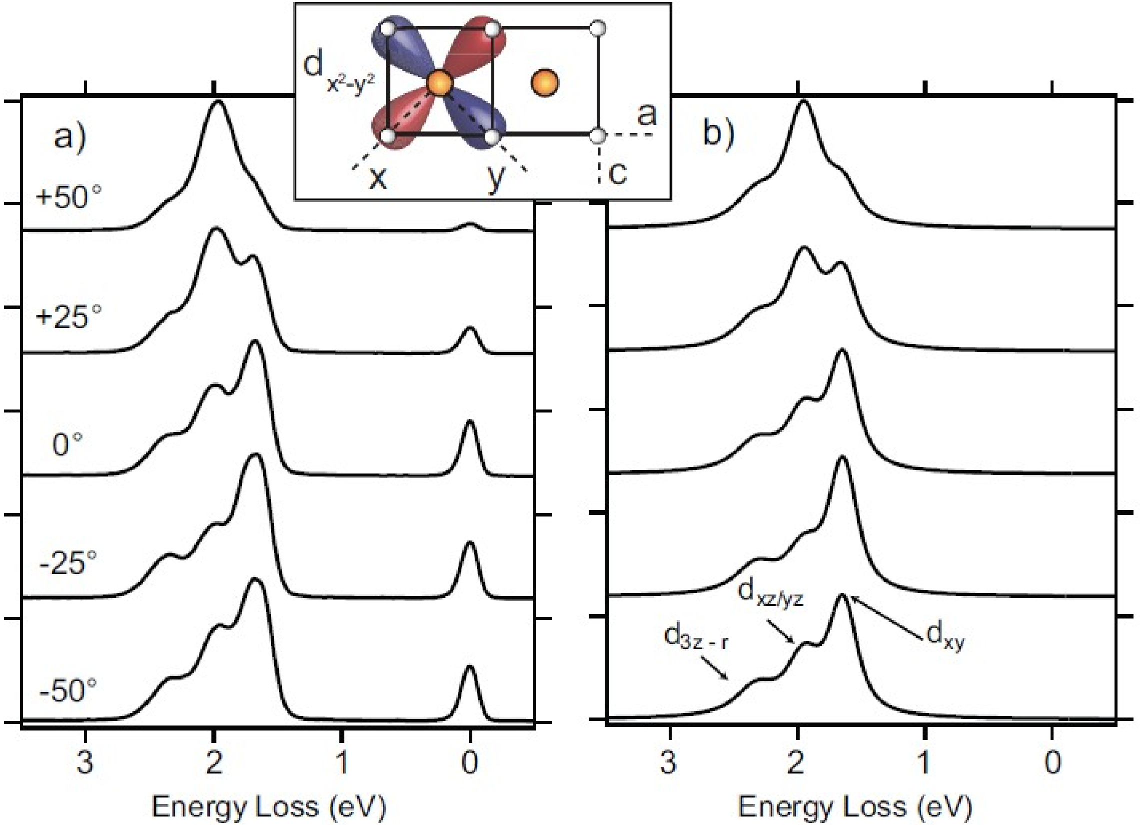
🟦



⬟

Crystal Field Energies for *d*-orbitals





Lee *et al*, *Phys. Rev. B* **89**, 041104(R) (2014)

Question #5

Typically in a cubic or tetragonal system the binding energy for $d_{eg} < d_{t2g}$. Why does the d_{3z2-r2} orbital have the highest loss energy?

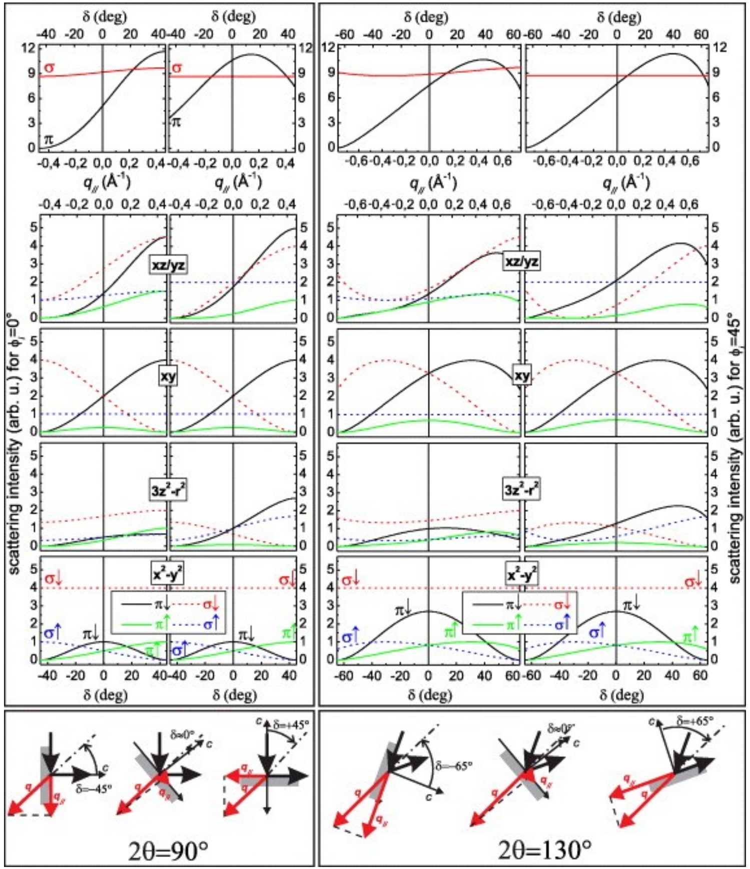
🟦 Other atoms (+ charge) in the crystal push it down to higher energy loss

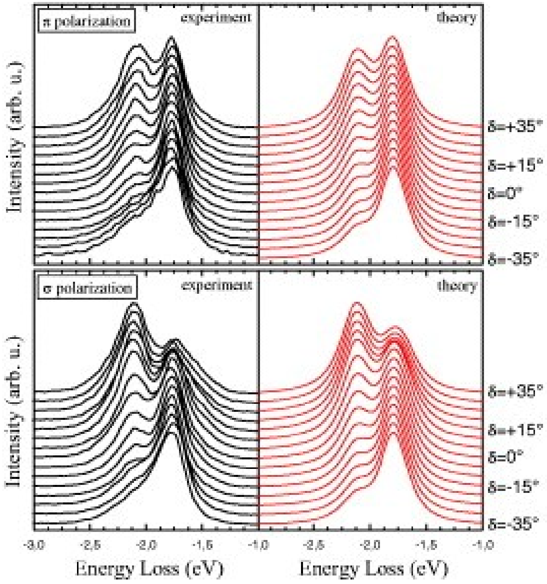
🟢 The lack of apical oxygen ligands make it a more favorable orbital for electron occupation, giving it a higher binding energy (energy loss)

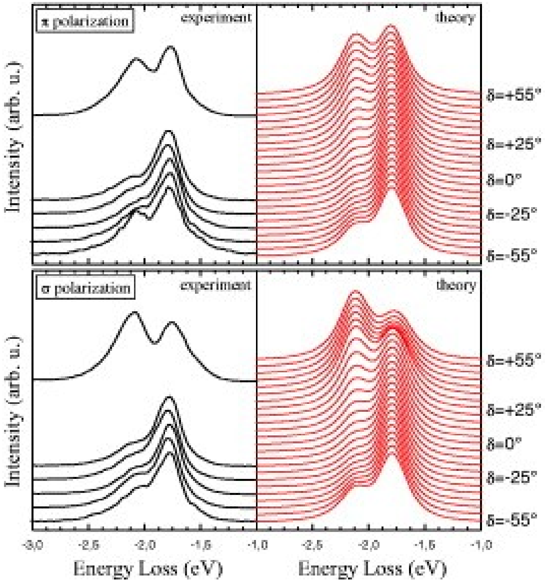
▲ Spin-orbit coupling in the valence shell

⬟ The core-hole potential

Crystal Field Energies for any Cu 3d^9







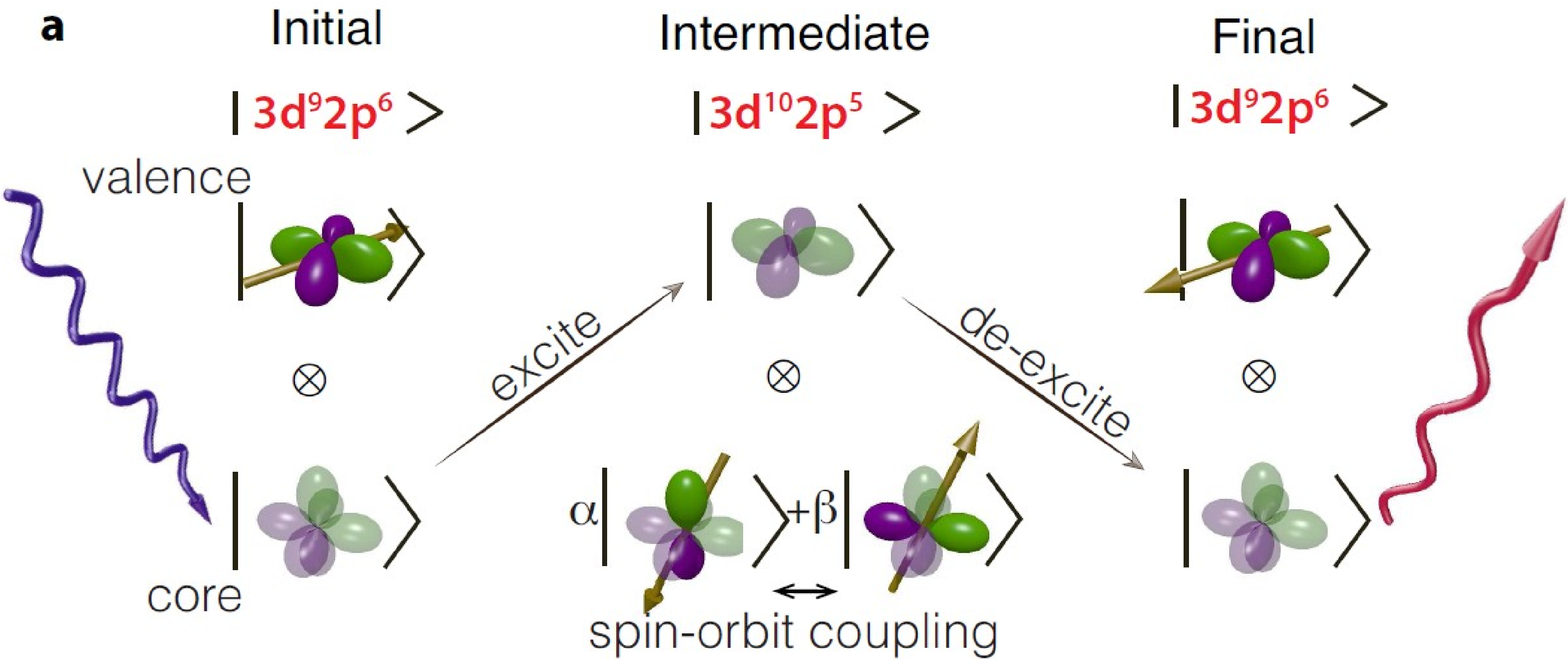
M. Moretti-Sala *et al*, *NJP* **13**, 043026 (2011)

Question #6

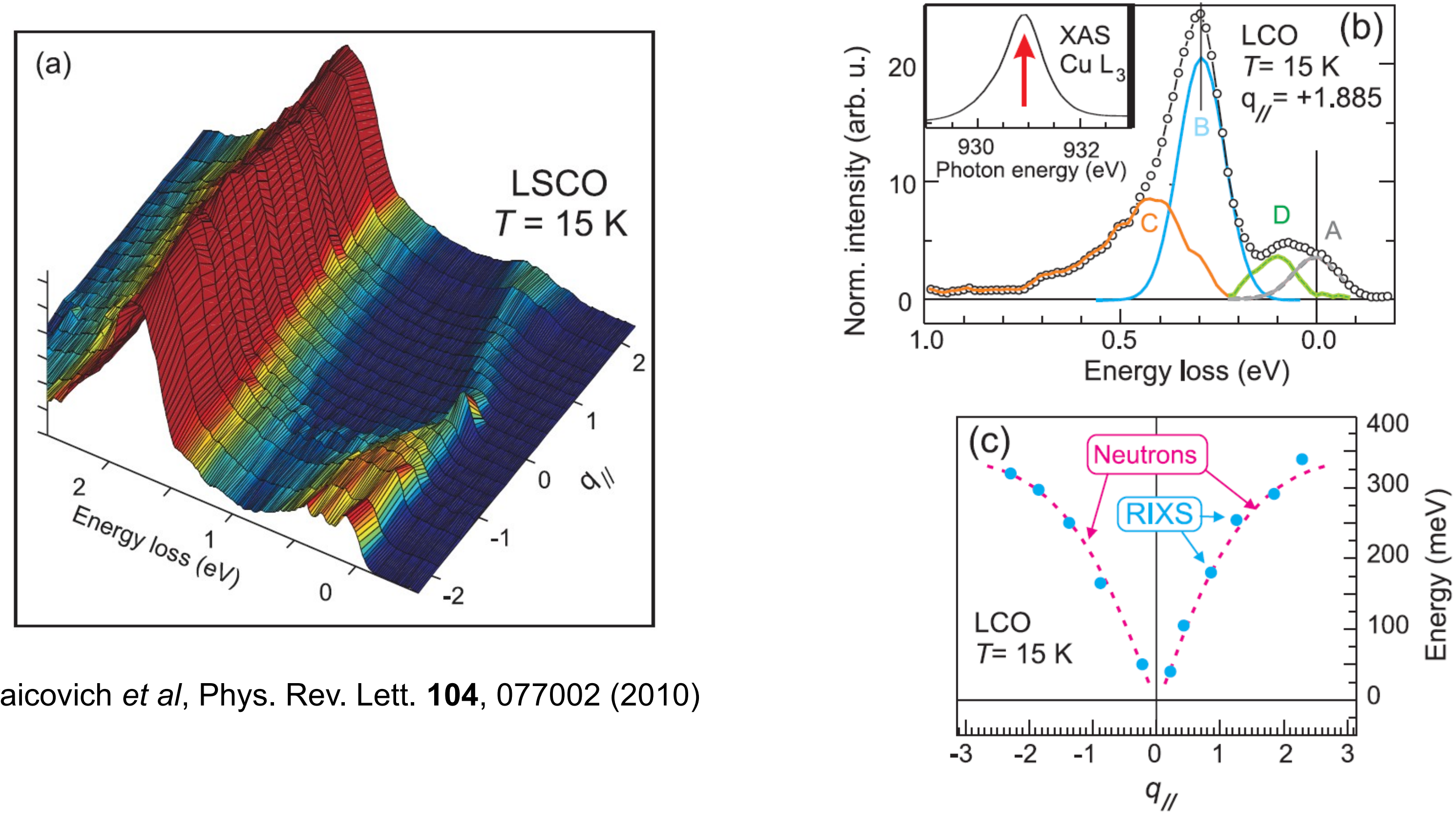
Can you use RIXS to measure spin excitations?

- 🟦 No. X-rays AREN'T sensitive to the electrons spin degree of freedom
- 🟢 Yes. X-rays ARE sensitive to the electrons spin degree of freedom
- ▲ It depends on the spin orientation and core-level spin-orbit coupling
- ⬟ I don't know

Core Spin-Orbit Coupling Allows Access to Spin

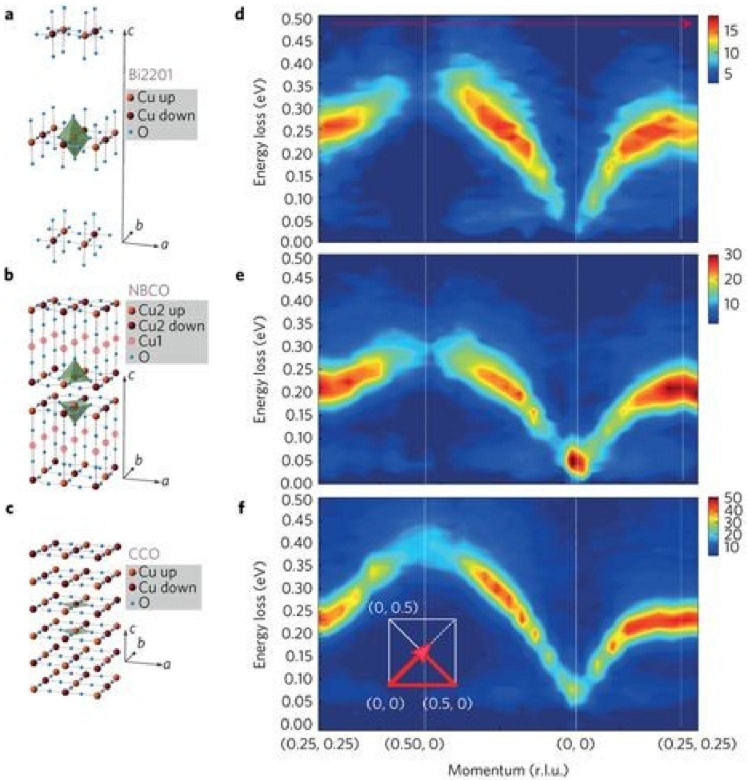


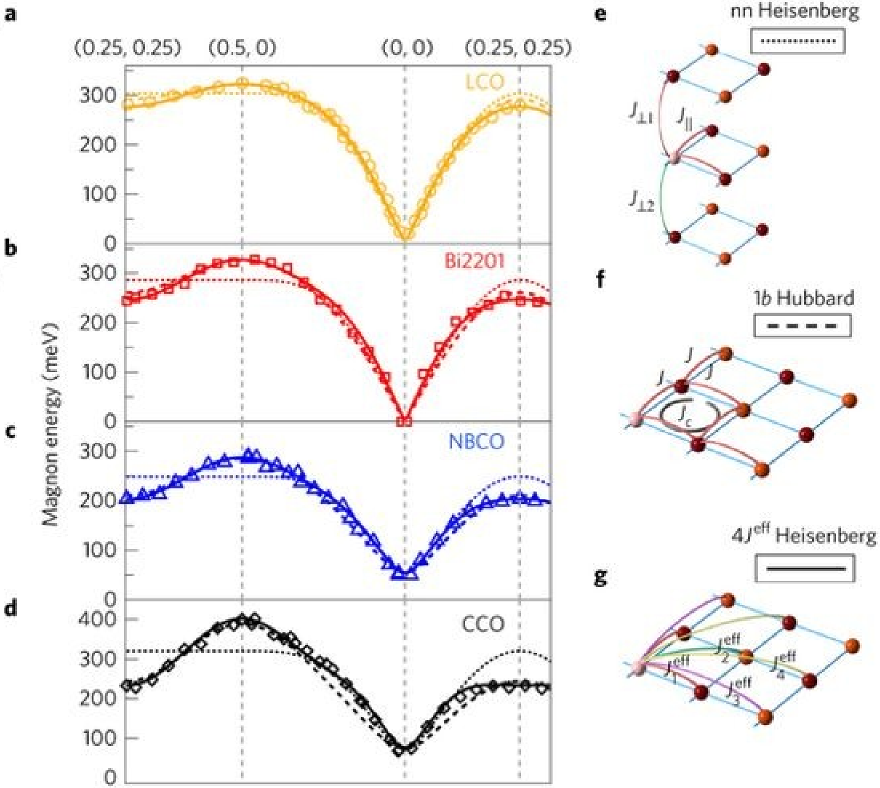
RIXS Measures Spin Excitations



Braicovich *et al*, Phys. Rev. Lett. **104**, 077002 (2010)

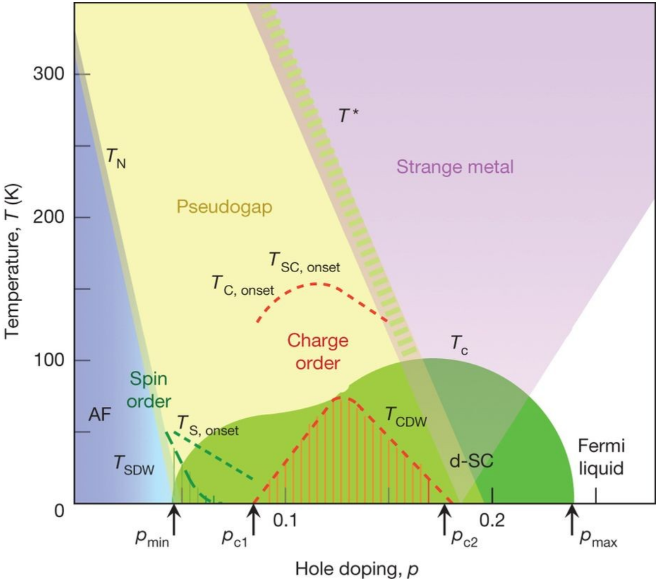
Spin Excitations across Multiple Compounds





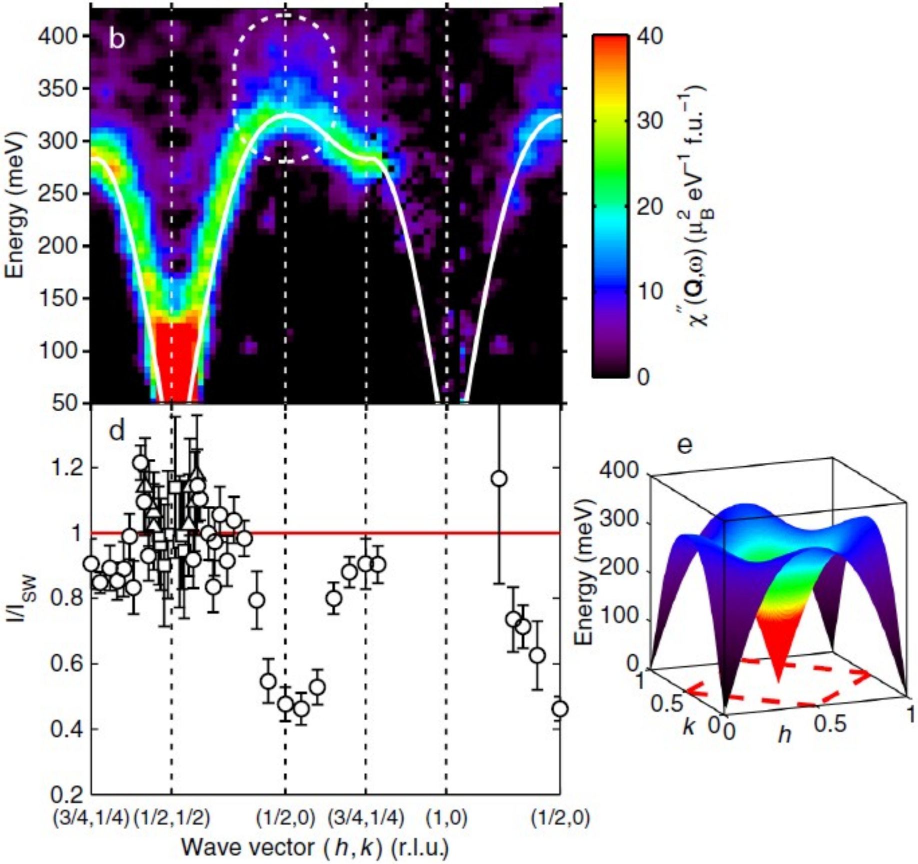
Peng *et al*, *Nature Physics* **13**, 1201-1206 (2017)

Do Spin Excitations Persist with Doping?



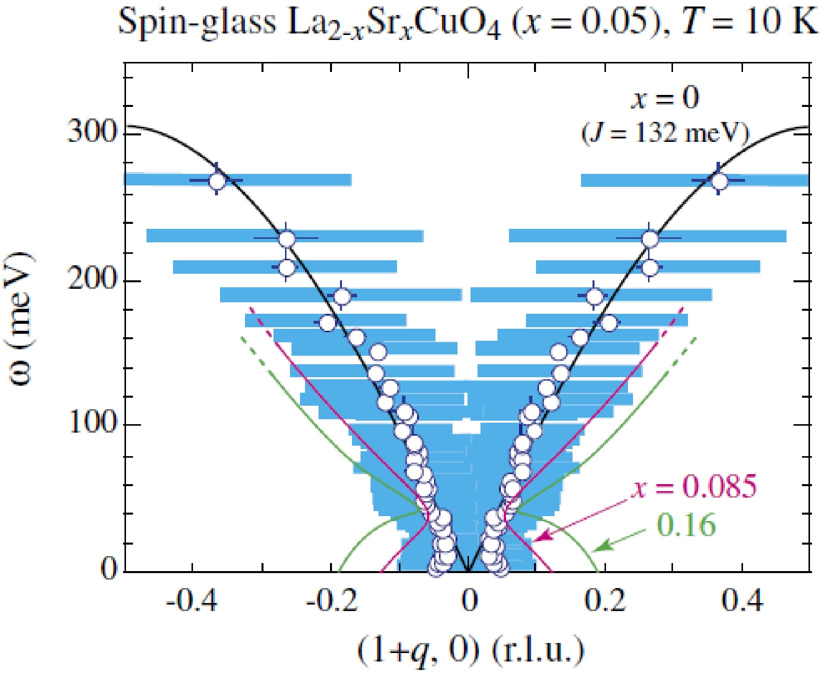
Keimer *et al*, Nature **518**, 179-186 (2015)

Headings *et al*, *PRL* **105**, 247001 (2010)

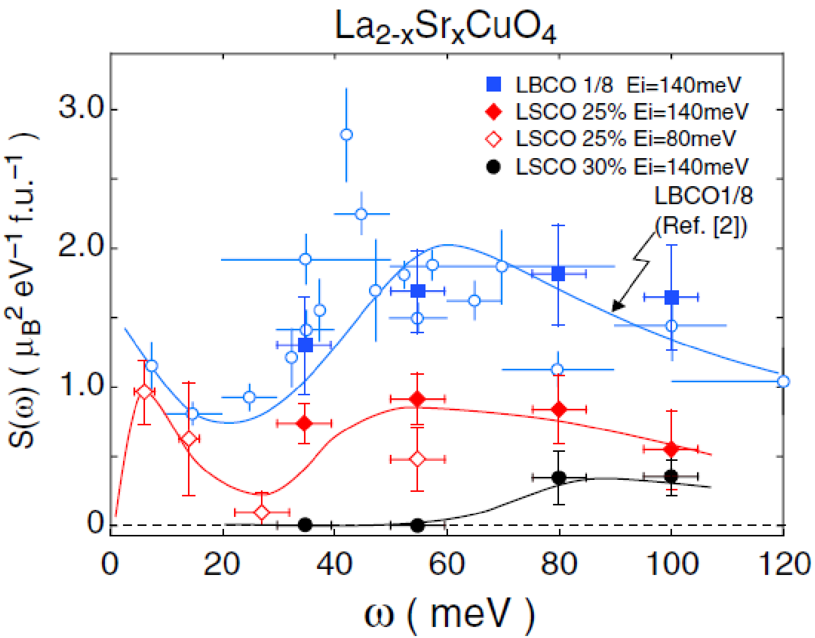


Do Spin Excitations Persist with Doping?

SLAC

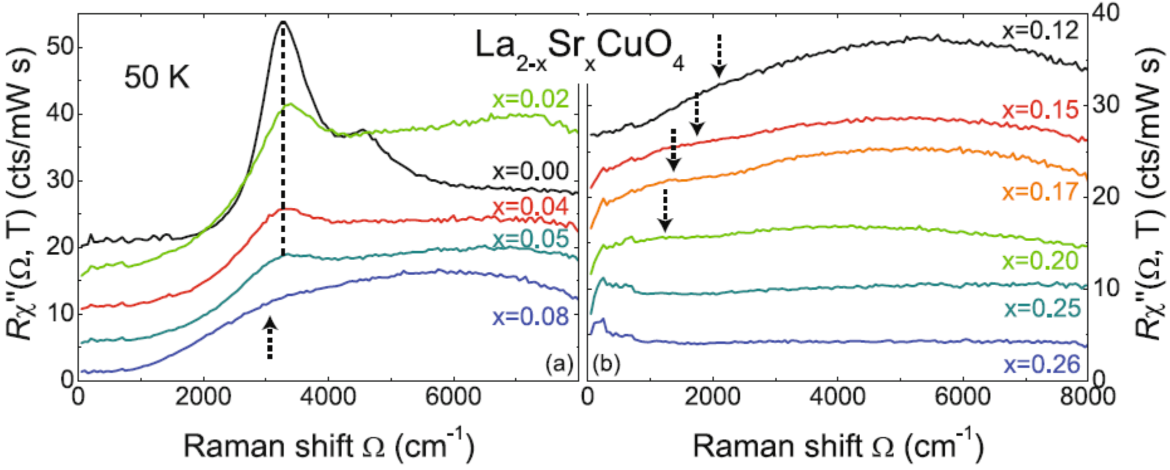


Fujita *et al*, JPSJ **81**, 011007 (2012)

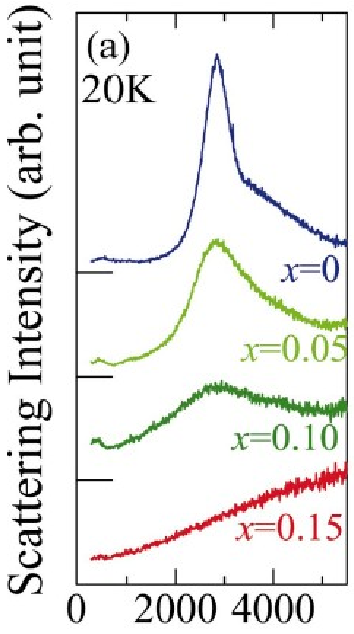


Wakimoto *et al, Phys. Rev. Lett.* **98**, 247003 (2007)

Do Spin Excitations Persist with Doping?



Muschler *et al*, EPJ: Special Topics **188**, 131 (2010)



- Well defined AFM excitations in the undoped compounds
- An “hourglass” shape emerges, intensity rapidly decreases
- Rapid suppression of the two-magnon response

Y. Onose *et al*, Phys. Rev. B **69**, 024504 (2004)

Question #7

Is RIXS capable of detecting magnon-like excitations in doped cuprates?

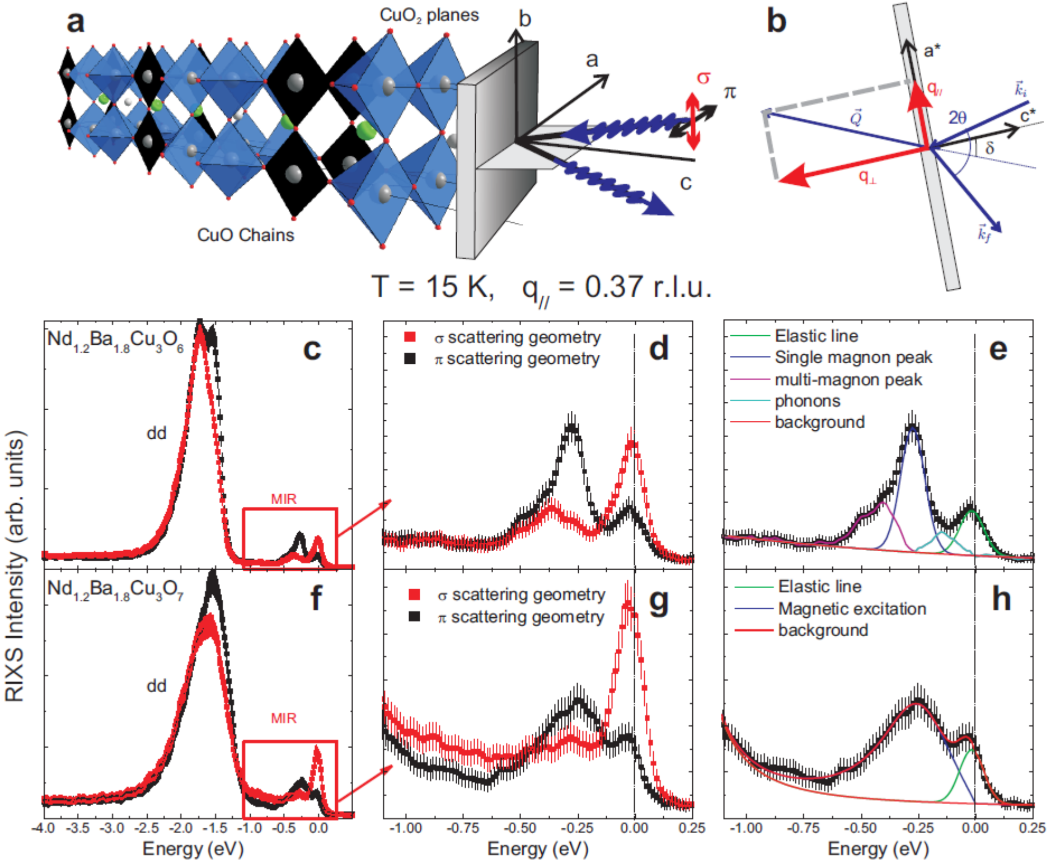
🟦 No

🟢 Yes

▲ Maybe

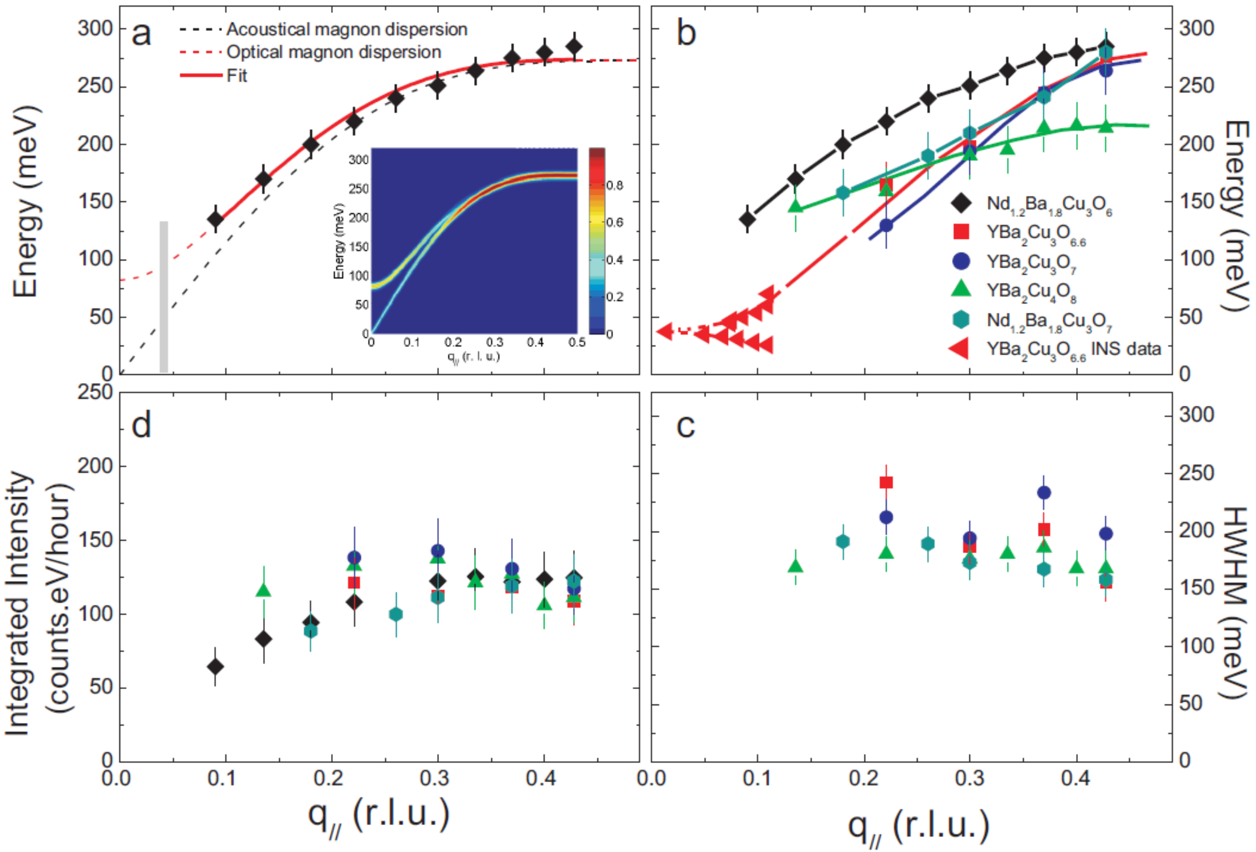
⬟ I don’t know

Do Spin Excitations Persist with Doping: Yes!



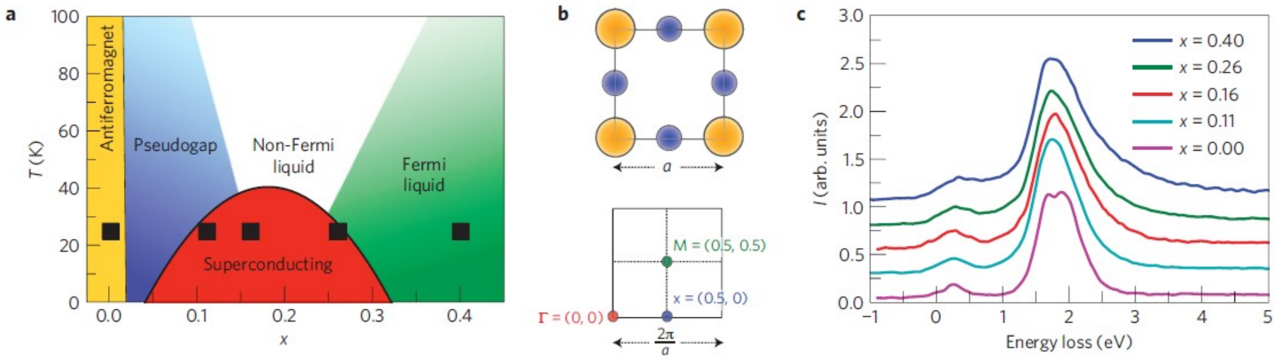
M. Le Tacon *et al*,
Nature Phys. **7**, 725-730 (2011)

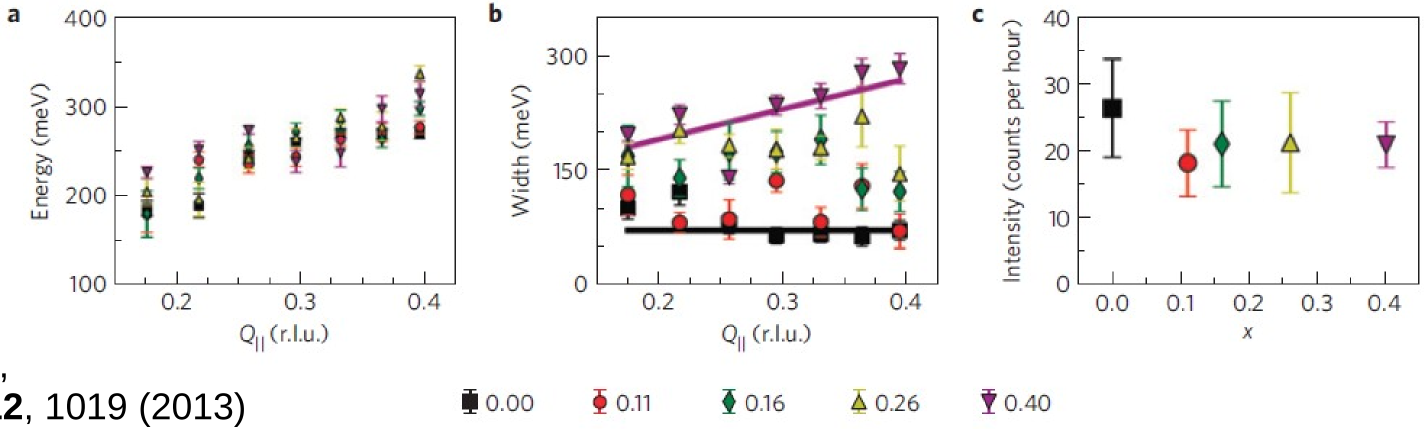
Do Spin Excitations Persist with Doping: Yes



M. Le Tacon *et al*,
Nature Phys. **7**, 725-730 (2011)

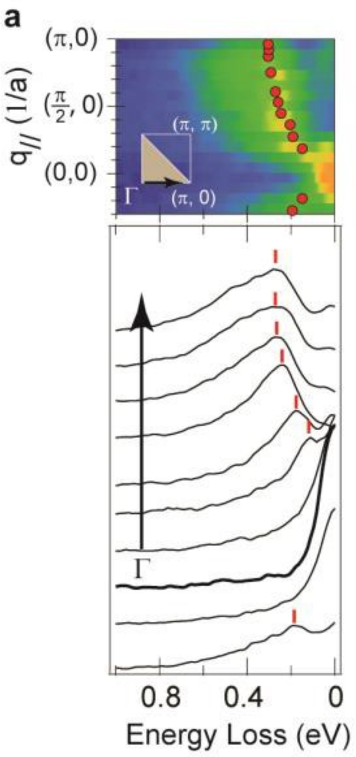
Do Spin Excitations Persist with Doping: Yes



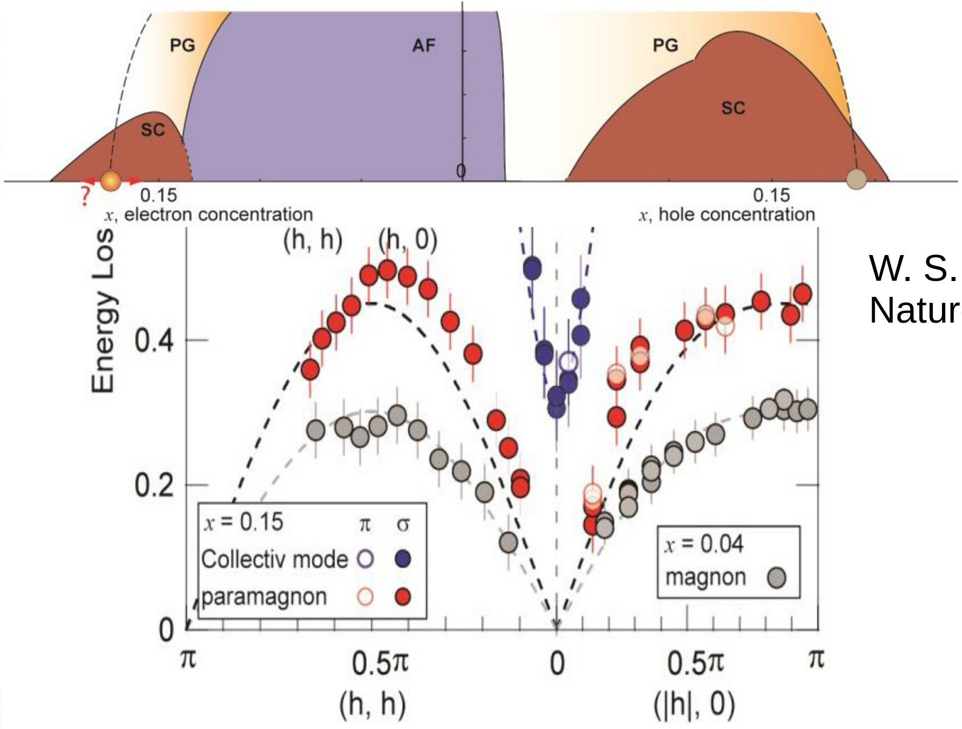


M. Dean *et al*,
Nature Mat. **12**, 1019 (2013)

Spin Excitations Harden with Doping?

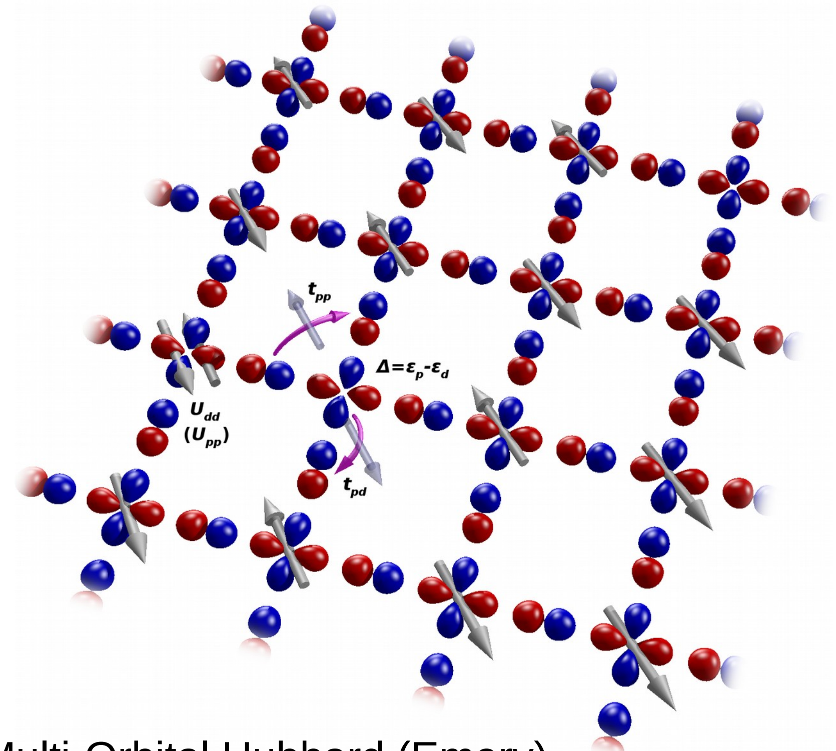


$Nd_{2-x}Ce_xCuO_4$ (NCCO)

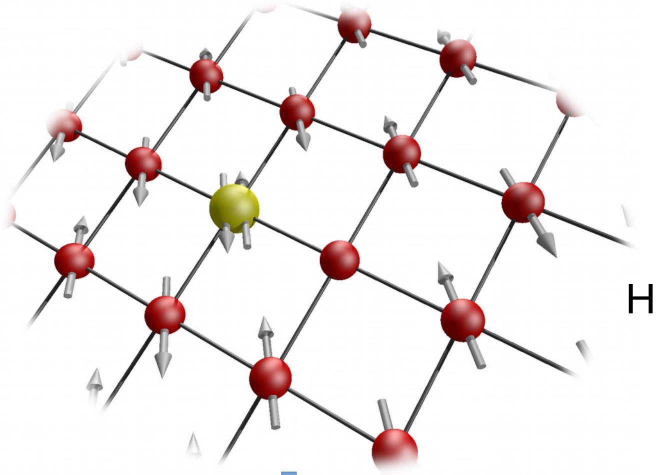


W. S. Lee *et al*,
Nature Phys. **10**, 883-889 (2014)

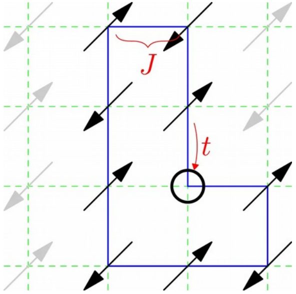
The Condensed Matter “Fruit Fly”



Multi-Orbital Hubbard (Emery)



Hubbard



t-J + ...

Question #8

Is the Hubbard model exactly solvable?

🟦 Yes, using the Bethe Ansatz in 1-D

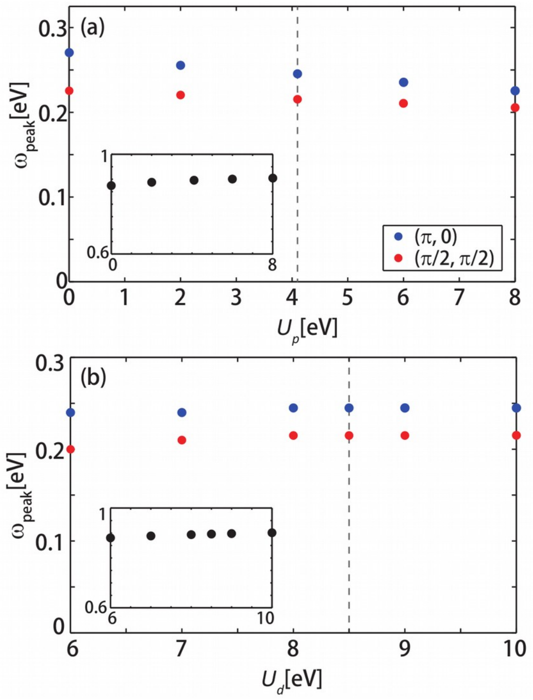
🟢 It’s an NP hard problem with no exact solution for dimensions D>1

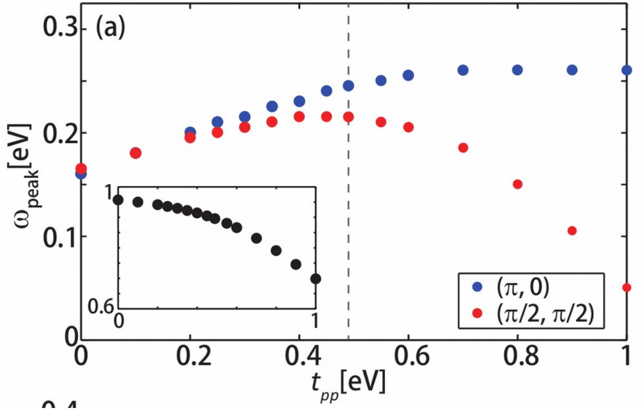
▲ Both of the above

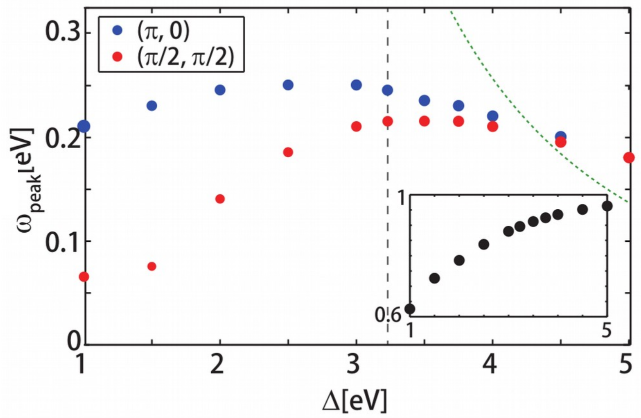
⬟ I’ll just use mean-field theory!

Spin Structure Factor

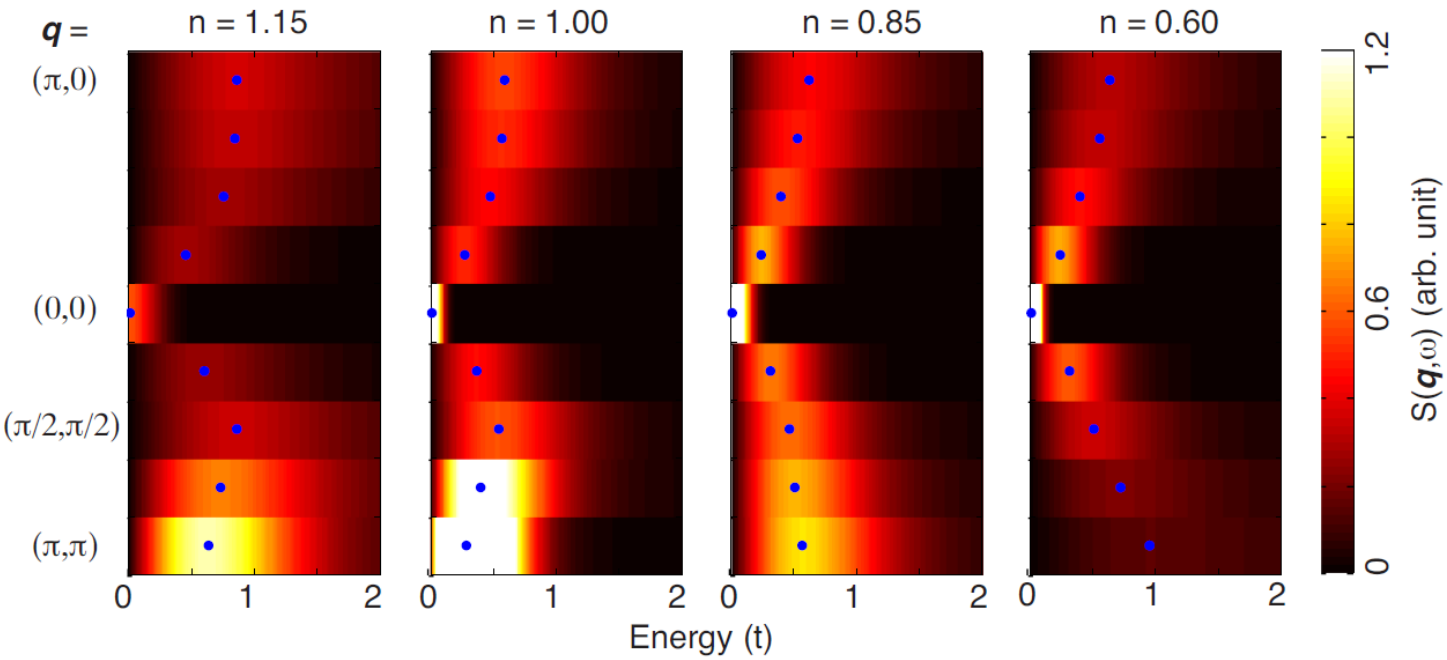
$|t_{pd}| = 1.13$ eV
$|t_{pp}| = 0.49$ eV
$\Delta = 3.23$ eV
$U_d = 8.5$ eV
$U_p = 4.1$ eV







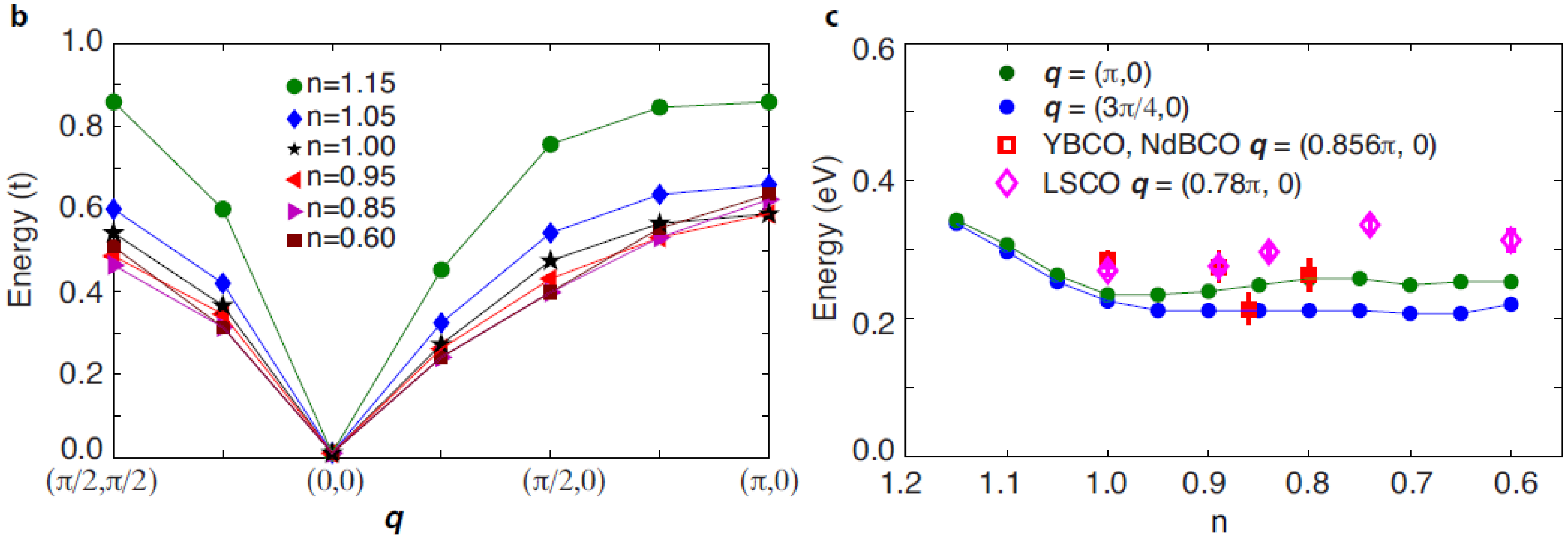
Spin Structure Factor with Doping



- S(q,w) from DQMC and MEM
- Results at $T=t/3$
- t'/t = -0.3 bandstructure with $U=W=8t$

White et al, *Phys. Rev. B* **40**, 506 (1989)
Jarrell and Gubernatis, *Phys. Rep.* **269**, 133 (1996)

Spin Structure Factor with Doping



- Weak softening on the hole-doped side
- Significant hardening with electron-doping
- Decent comparison for *t*~400 meV

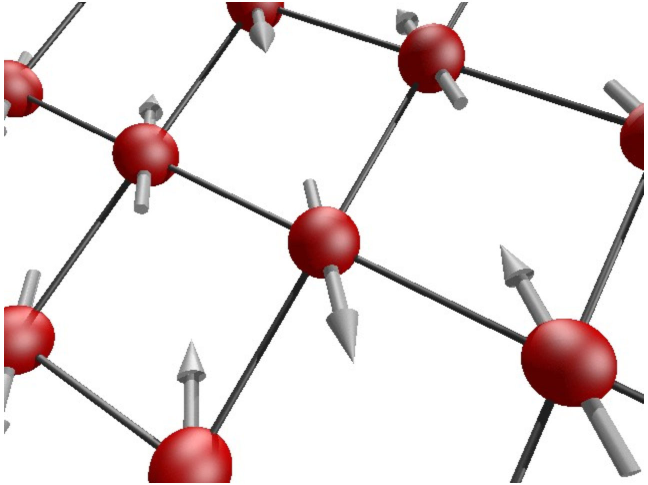
Braicovich *et al*, Phys. Rev. Lett. **104**, 077002 (2010)

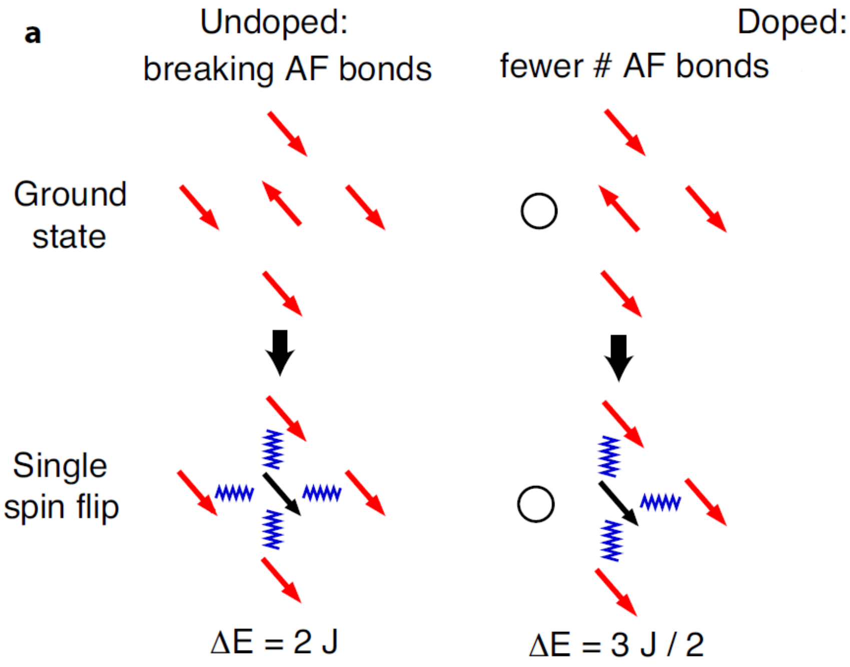
Le Tacon *et al*, Nature Phys. **7**, 725-730 (2011)

Dean *et al*, Nature Mat. **12**, 1019 (2013)

Microscopic Physics

- Super-exchange – *J*
- Undoped: Broken AF bonds ~ 2*J*
- Doped: Fewer AF bonds
  Lose a delocalization path
  (3-site terms)





Bała, Oleś, Zaanen,
Phys. Rev. B **52**, 4597 (1995)

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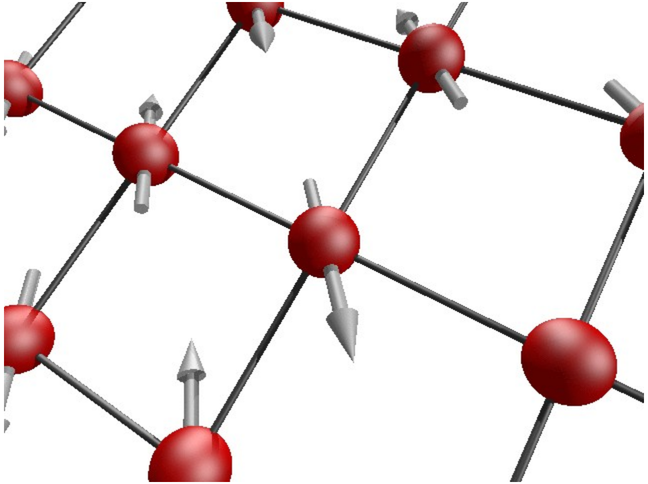

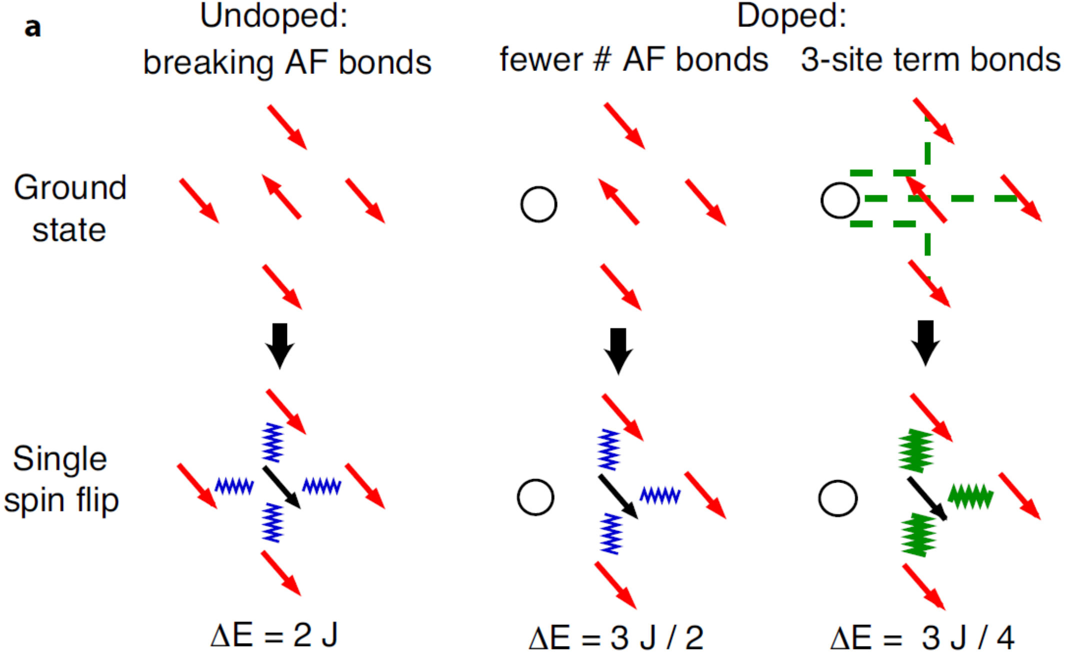

Bała, Oleś, Zaanen,
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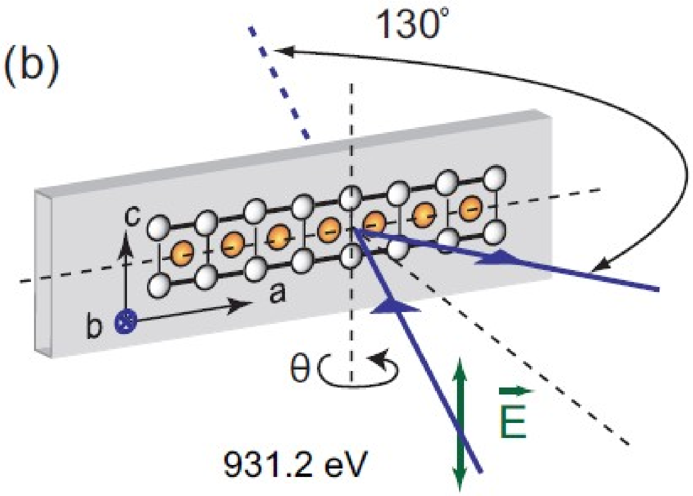
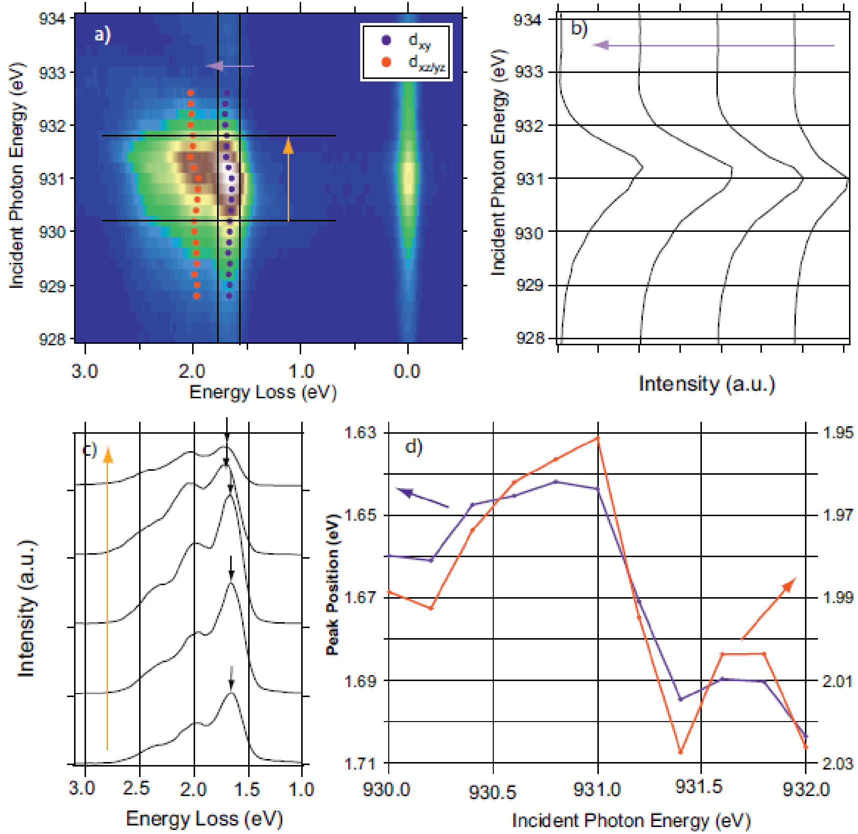
Question #9

For spin excitations in RIXS from doped cuprates, which of the following is flase?

- 🟦 J (the super exchange energy) decreases rapidly
- 🟢 Paramagnons are broad, but persist due to short-range spin correlations
- ▲ With doping, higher order exchange and delocalization become important
- ⬟ Only the first one is false!

Return to the 1-D Chain Compound





Question #10

What could cause this kind of “kink” in the RIXS spectrum?

- 🟦 Intersecting an emission line
- 🟢 Magnetic excitations
- ▲ Phonons
- ⬟ Something’s wrong with the spectrometer

Phonons in RIXS (Indirect)

Franck-Condon

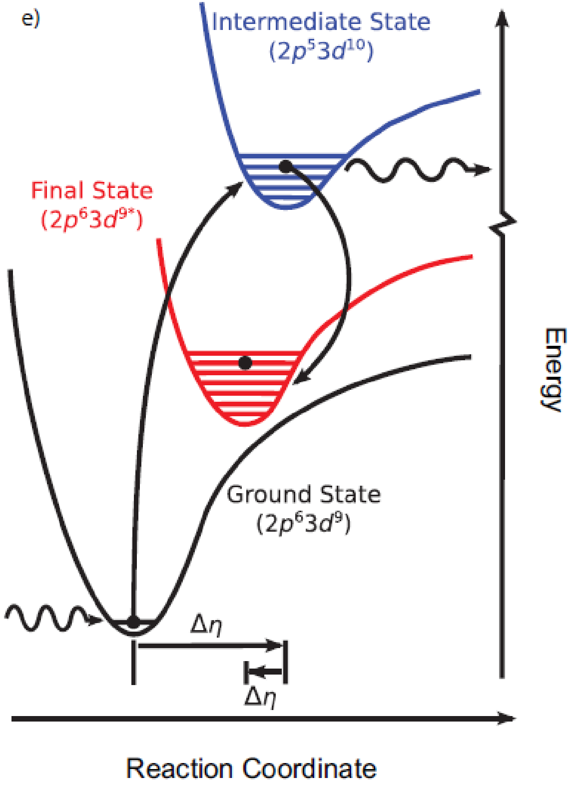
J. Hancock et al,
New Journal of Physics **12** (2010) 033001

$$\frac{d\sigma}{d\Omega} \propto \sum_{m=0}^{\infty} |\mathcal{M}|^2 \delta(\hbar(\nu_{\mathrm{in}} - \nu_{\mathrm{sc}}) - (E_{\mathrm{MO}} + m_{\mathrm{MO}}\hbar\omega_0 - E_{\mathrm{g}}))$$

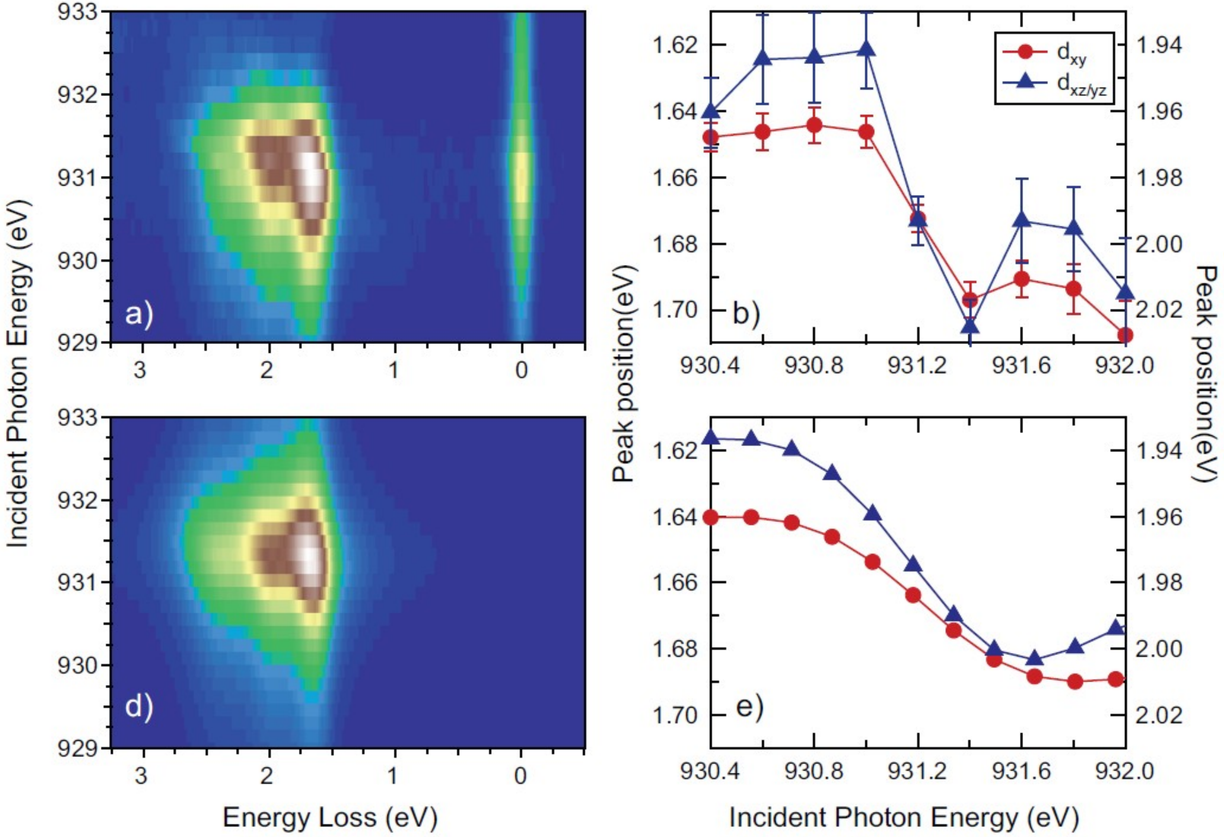
$$\mathcal{M} = \sum_{n=0}^{\infty} \sum_{i=\mathrm{WS,PS}} \frac{[\langle \mathrm{MO}|i\rangle\langle i|g\rangle]_{\mathrm{e}}[\langle m_{\mathrm{MO}}|n_i\rangle\langle n_i|0_{\mathrm{g}}\rangle]_{\mathrm{v}}}{\hbar\nu_{\mathrm{in}} - (E_{\mathrm{i}}^{e} + \hbar\omega_0 n_i - E_{\mathrm{g}}) - i\Gamma}$$

$$[\langle m_a|n_b\rangle]_{\mathrm{v}} = \mathrm{e}^{-\gamma_{a\to b}^2/2} \frac{(-1)^{n-N}\sqrt{m!n!}\,\gamma_{a\to b}^{n+m-2N}}{(n+m-N)!} L_N^{n+m-2N}(\gamma_{ba}^2)$$

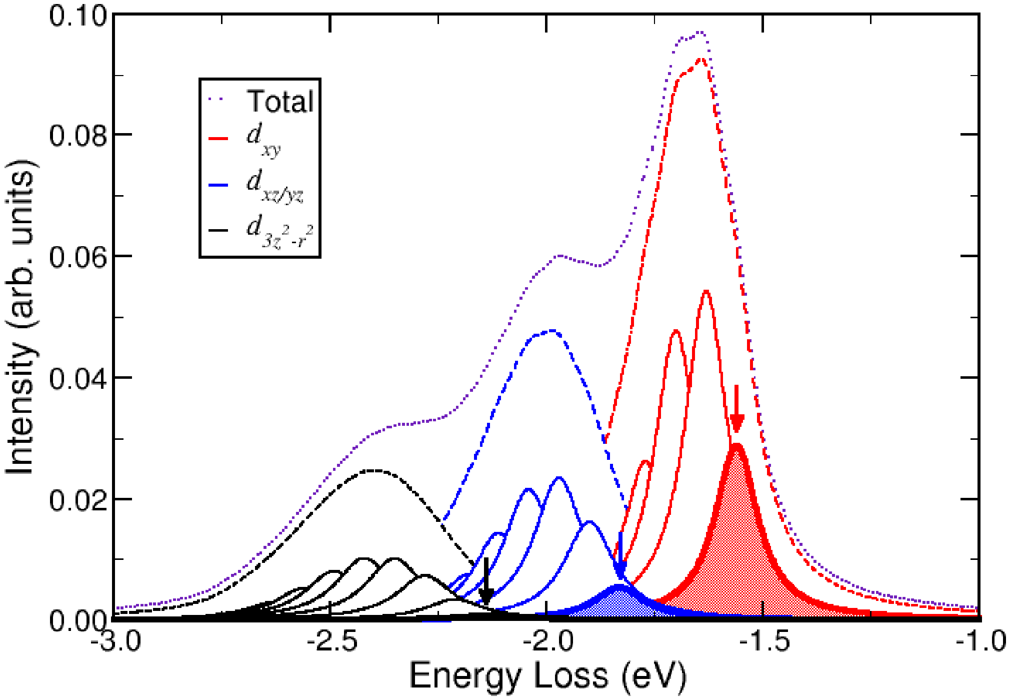
$$\gamma_{a\to b} = \sqrt{\frac{\mu\omega_0}{2\hbar}}(x_b - x_a)$$



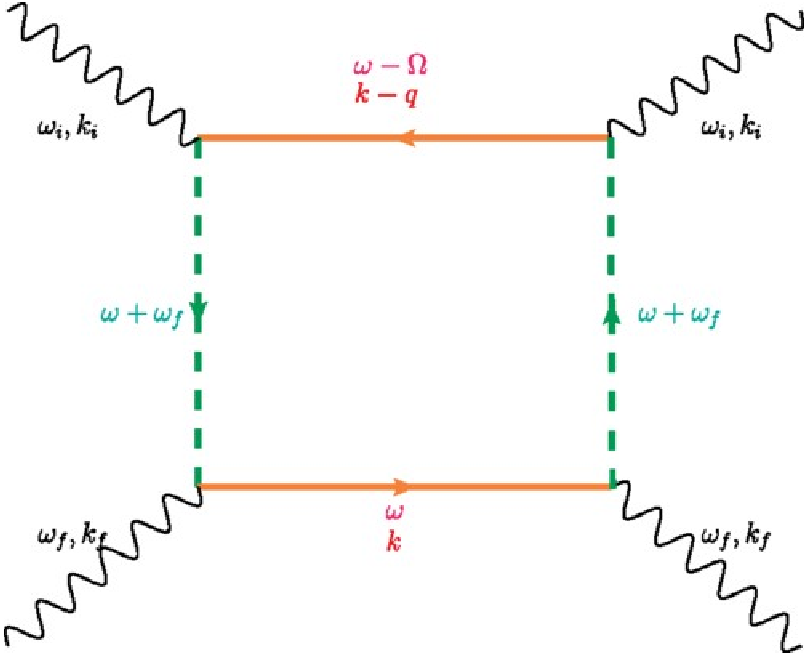
Franck-Condon Simulation



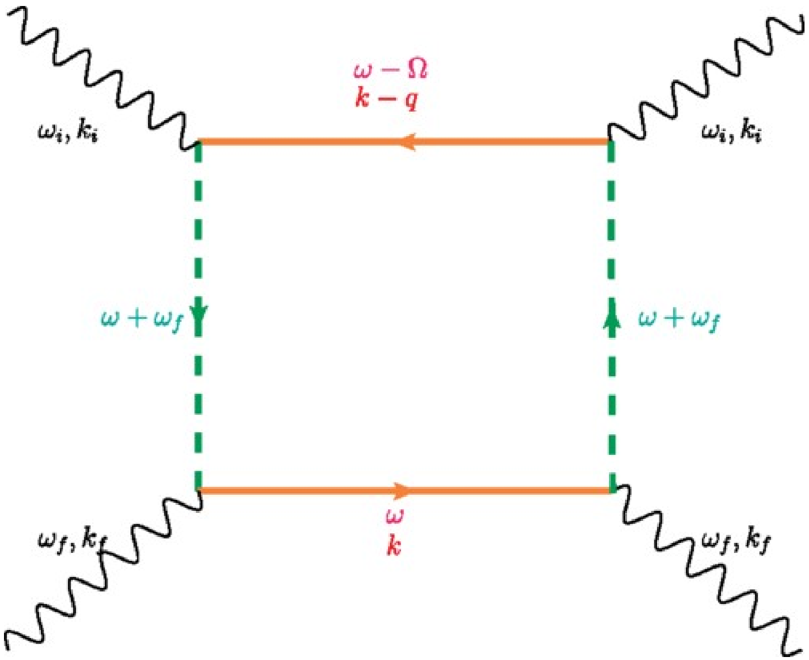
Phonon Contributions to Energy/Linewidth

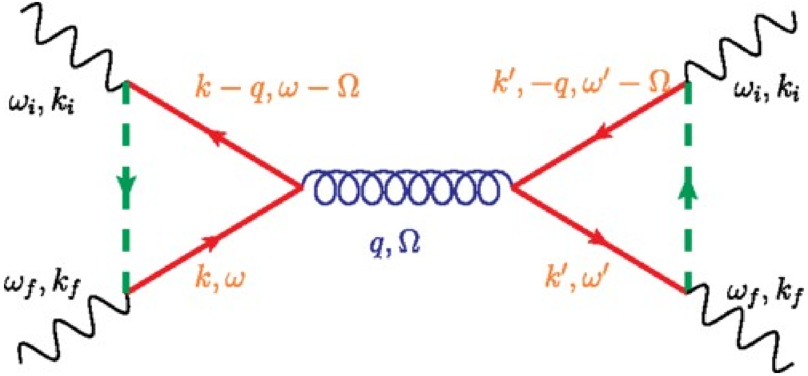


Direct Phonon RIXS



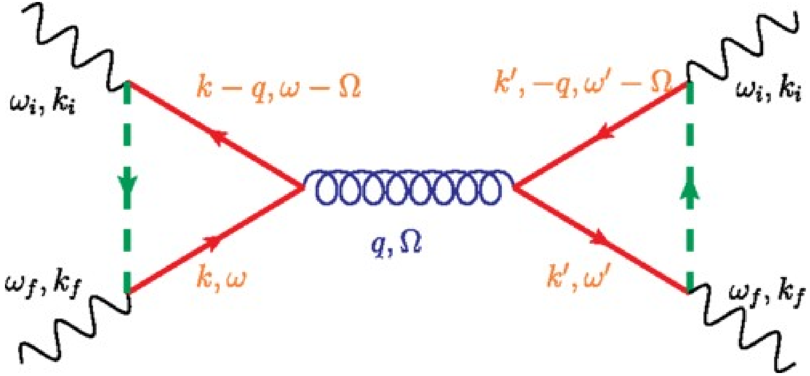
Direct Phonon RIXS



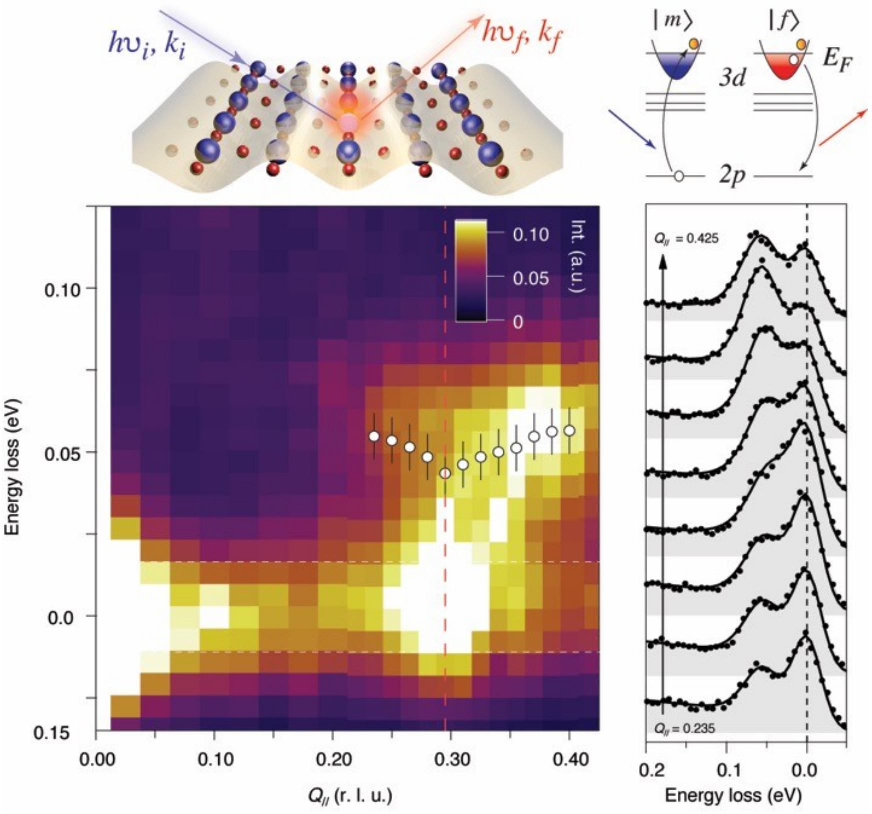


Directly Access the Electron-Phonon Coupling

$$\begin{aligned}\chi_{\text{phonon}}(\mathbf{k_i},\mathbf{k_f},\mathbf{q}|\omega_i,\omega_f,\Omega) = {} & \sum_{\nu}\frac{1}{N}\sum_{\mathbf{p}}\frac{1}{N}\sum_{\mathbf{p}'}[\mathbf{e_i}\cdot\mathbf{d}_{3d,2p}(\mathbf{p}+\mathbf{q},\mathbf{p}-\mathbf{k_f})][\mathbf{e_f}\cdot\mathbf{d}_{2p,3d}(\mathbf{p}-\mathbf{k_f},\mathbf{p})]g_{\nu}^{3d,3d}(\mathbf{p},\mathbf{p}+\mathbf{q}) \\ & \times|\phi_{3d}(\mathbf{p})|^2|\phi_{3d}(\mathbf{p}+\mathbf{q})|^2\left[\frac{f(-\epsilon_{\mathbf{p}})}{\epsilon_{\mathbf{p}}-\omega_f-E_{2p,3d}-i\Gamma}-\frac{f(-\epsilon_{\mathbf{p}+\mathbf{q}})}{\epsilon_{\mathbf{p}+\mathbf{q}}-\omega_i-E_{2p,3d}-i\Gamma}\right] \\ & \times[\mathbf{e_i}\cdot\mathbf{d}_{2p,3d}(\mathbf{p}'-\mathbf{k_f},\mathbf{p}'+\mathbf{q})][\mathbf{e_f}\cdot\mathbf{d}_{3d,2p}(\mathbf{p}',\mathbf{p}'-\mathbf{k_f})]g_{\nu}^{3d,3d}(\mathbf{p}'+\mathbf{q},\mathbf{p}') \\ & \times|\phi_{3d}(\mathbf{p}')|^2|\phi_{3d}(\mathbf{p}'+\mathbf{q})|^2\left[\frac{f(-\epsilon_{\mathbf{p}'})}{\epsilon_{\mathbf{p}'}-\omega_f-E_{2p,3d}+i\Gamma}-\frac{f(-\epsilon_{\mathbf{p}'+\mathbf{q}})}{\epsilon_{\mathbf{p}'+\mathbf{q}}-\omega_i-E_{2p,3d}+i\Gamma}\right] \\ & \times\frac{1}{\pi}\Im\left\{\frac{1}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}+\mathbf{q}}+\Omega+i\gamma_e}\tilde{D}_{\nu}(\mathbf{q},\Omega)\frac{1}{\epsilon_{\mathbf{p}'}-\epsilon_{\mathbf{p}'+\mathbf{q}}+\Omega+i\gamma_e}\right\}.\end{aligned}$$



Electron-Phonon Coupling

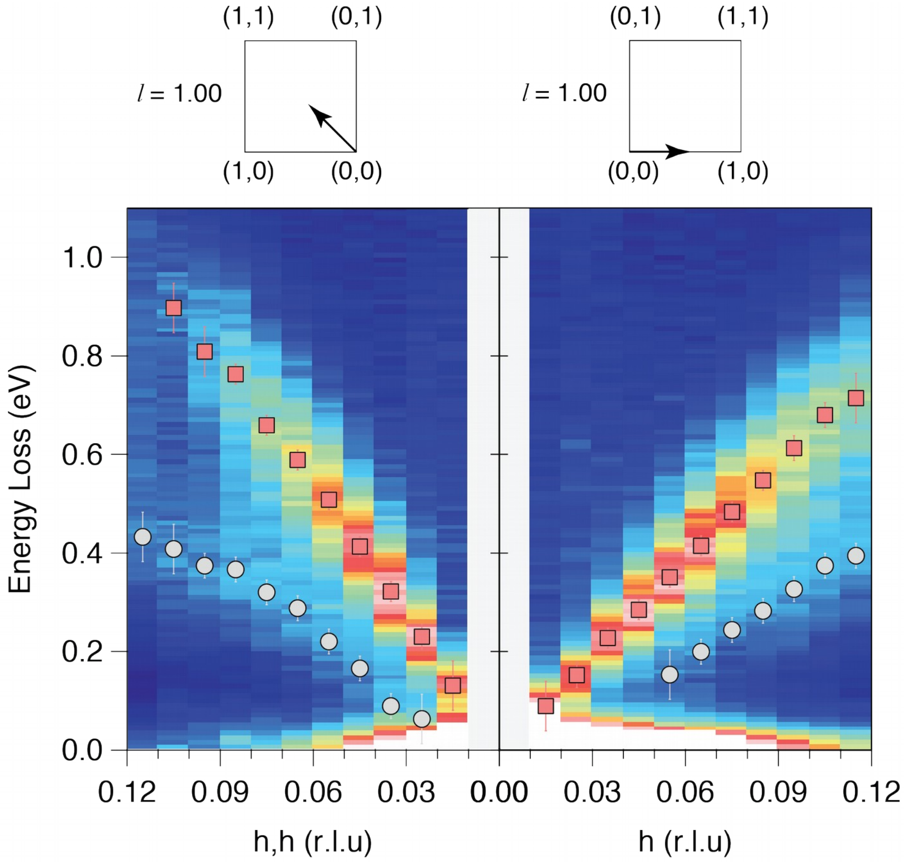


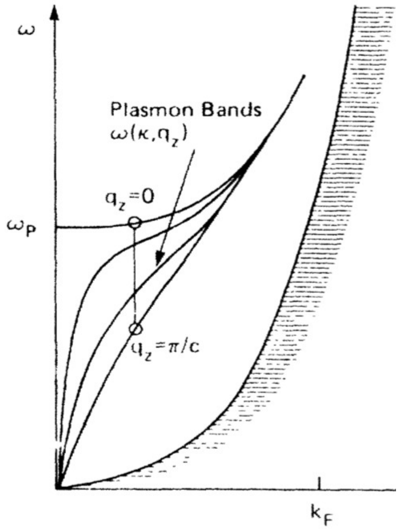
- A comprehensive energy-momentum space picture of the interplay between CDW, charge, and phonon.
- Bond stretching phonon softens at the CDW wavevector.
- Anomalous phonon intensity enhancement due to the “Fano” interference between the CDW excitations and phonon.

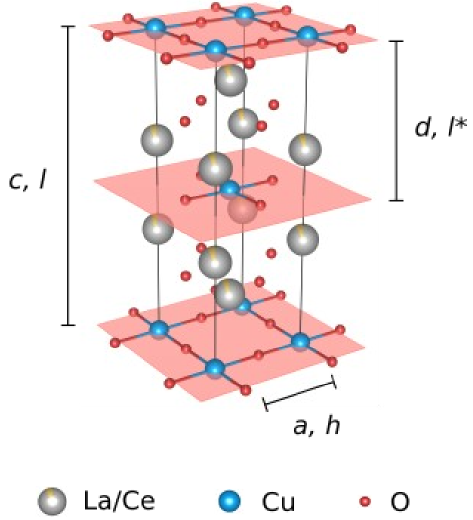
First evidence of dispersive CDW excitations in cuprates, enabling access to the dynamics of CDW.

L. Chaix *et al.*, *Nature Physics* ***13****, 952-956 (2017)*

Plasmons



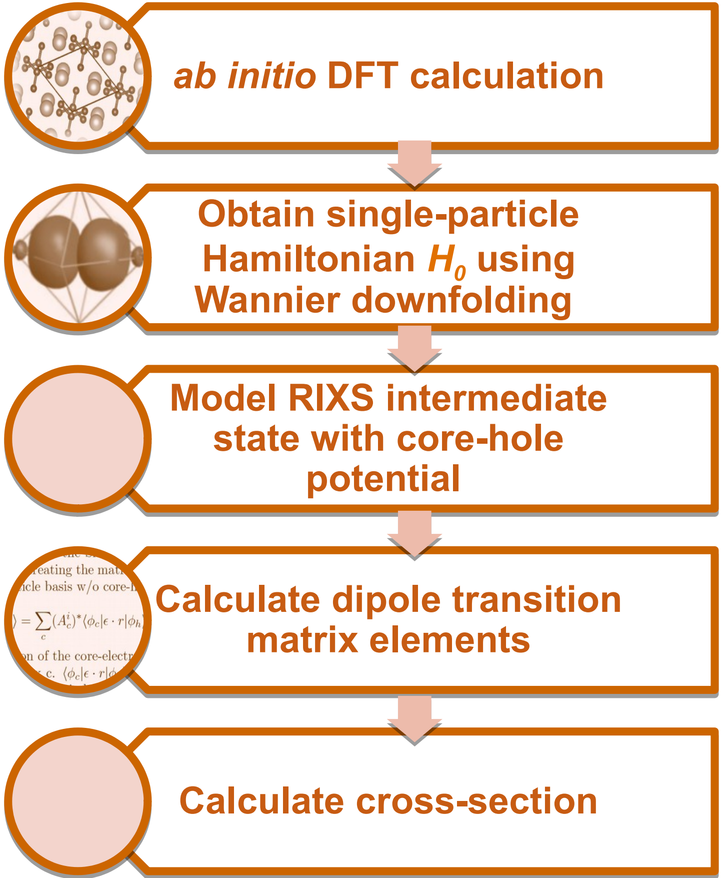




Visscher and Falicov, Phys. Rev. B **3**, 2541 (1971)
Fetter, Ann. Phys (N.Y.) **88**, 1 (1974)

M. Hepting *et al, Nature* **563**, 374-378 (2018)

Wannier Orbital Based Method for XAS/RIXS



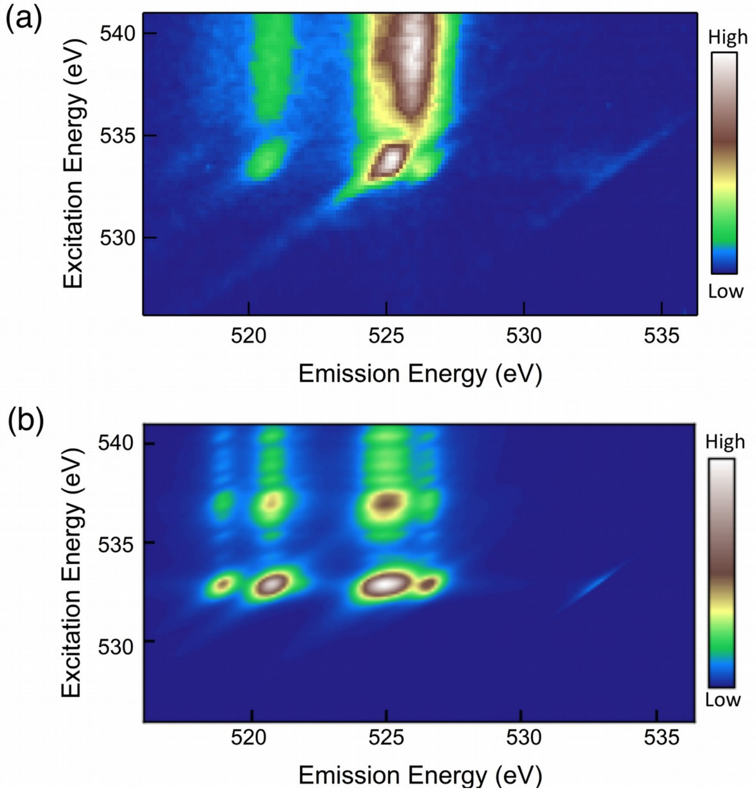
ab initio DFT calculation

Obtain single-particle Hamiltonian H_0 using Wannier downfolding

Model RIXS intermediate state with core-hole potential

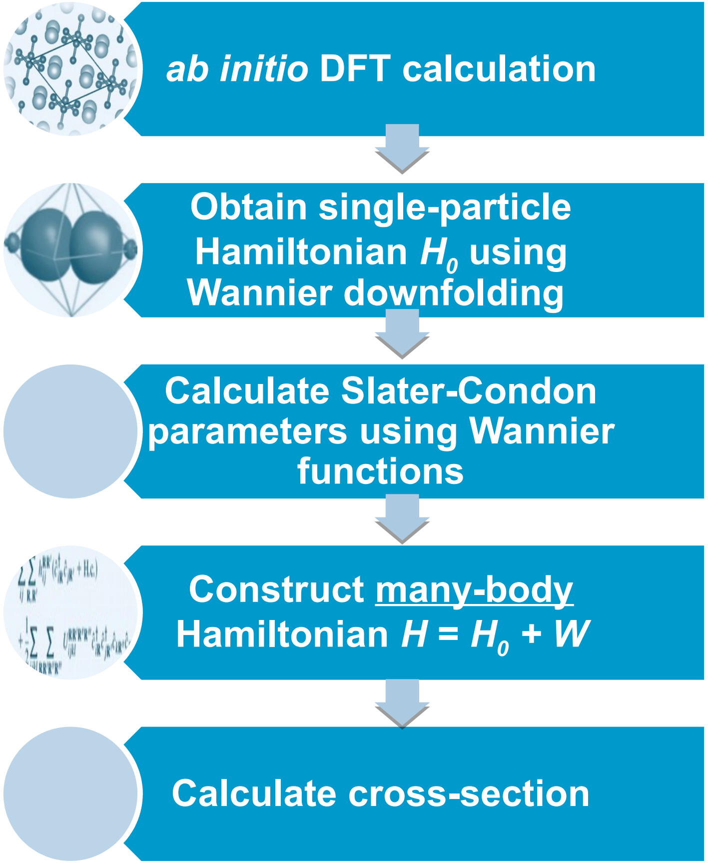
Calculate dipole transition matrix elements

Calculate cross-section



C. J. Jia to appear in Comp. Phys. Comm.

Charge Transfer Atomic Multiplet Calculation



ab initio DFT calculation

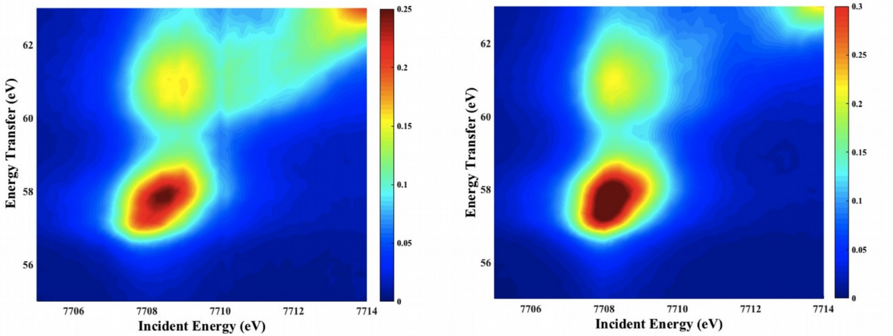
Obtain single-particle Hamiltonian H_0 using Wannier downfolding

Calculate Slater-Condon parameters using Wannier functions

Construct <u>many-body</u> Hamiltonian $H = H_0 + W$

Calculate cross-section

(a)Co(phen)(3,5-DBSQ)$_2$ at 298K (b) Co(tmeda)(3,5-DBSQ)$_2$ at 298K



(c) Co(phen)(3,5-DBSQ)$_2$ Simulation (d) Co(tmeda)(3,5-DBSQ)$_2$ Simulation