Probing spin interactions in edge- and corner-shared cuprate systems by Resonant Inelastic Soft X-ray Scattering

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Workshop Quantum Magnets 2015

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C. Sekar ($CaCu_2O_3$)
A. Revcolevschi ($CuGeO_3$)

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Contents

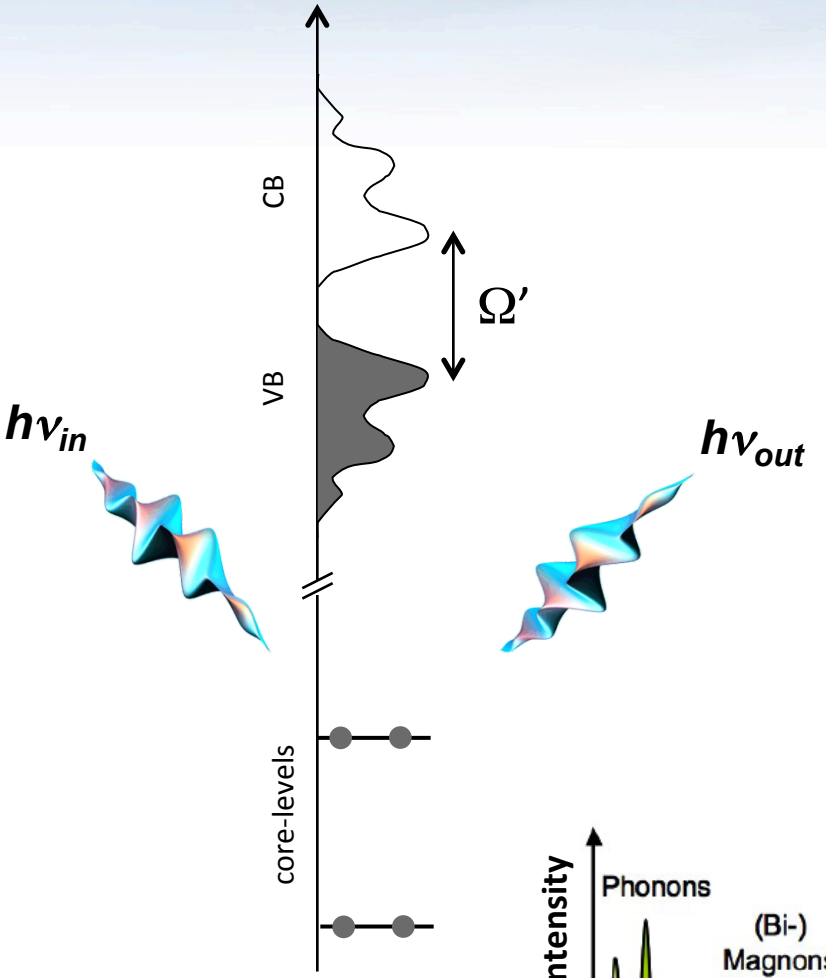
- Introduction to Resonant Inelastic (soft) X-ray Scattering
- Application to CuO_4 compounds:

  1. edge-shared CuO_4 chains with weak J

  2. corner-shared CuO_4 systems with strong J

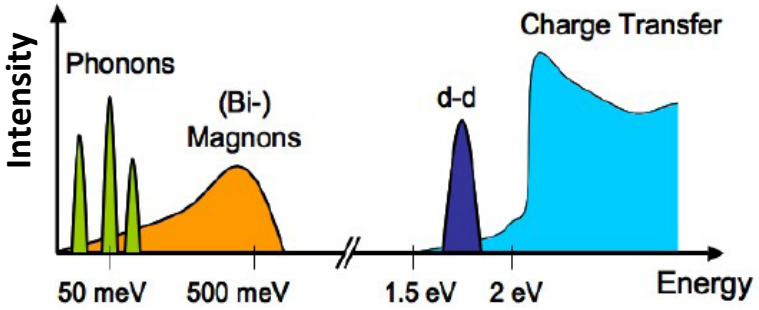
- New Experimental possibilities in soft-RIXS

Resonant Inelastic X-ray Scattering (RIXS)



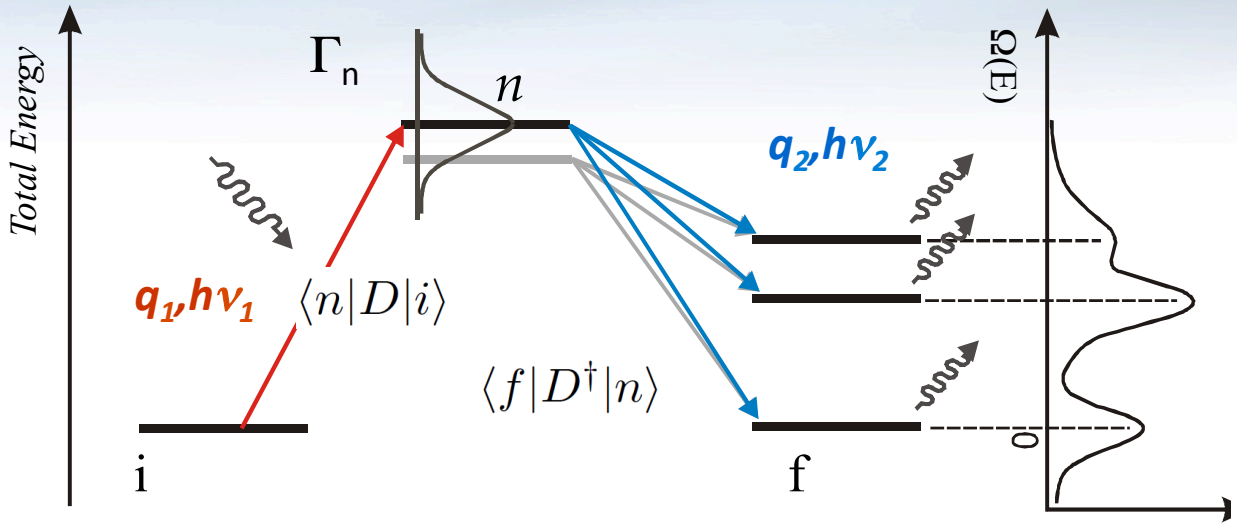
- photon *in* – photon *out*
- energy loss $\Omega(E) = h\nu_{in} - h\nu_{out}$ inelastic process
- resonance: site and chemically selective
- energy and momentum resolution

- sensitive to **lattice**, **spin, charge** and **orbital**
- **bulk** technique



♠ A. Kotani and S. Shin, *Rev. Mod. Phys*. 73, 203 (2001)
♣ L.J.P. Ament et al., *Rev. Mod. Phys*. **83**,705 (2011)

RIXS response

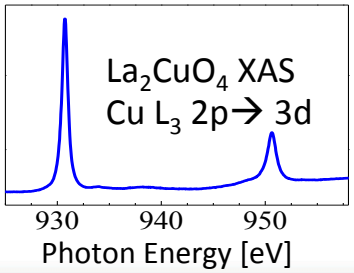


Kramers- Heisenberg formula

$$\frac{d^2\sigma}{d\Omega_2 d\hbar\omega_2} \propto \sum_f \left| \sum_n \frac{\langle f|D^\dagger|n\rangle\langle n|D|i\rangle}{E_i - E_n + \hbar\omega_1 - i\Gamma_n/2} \right|^2$$

Resonant excitation:

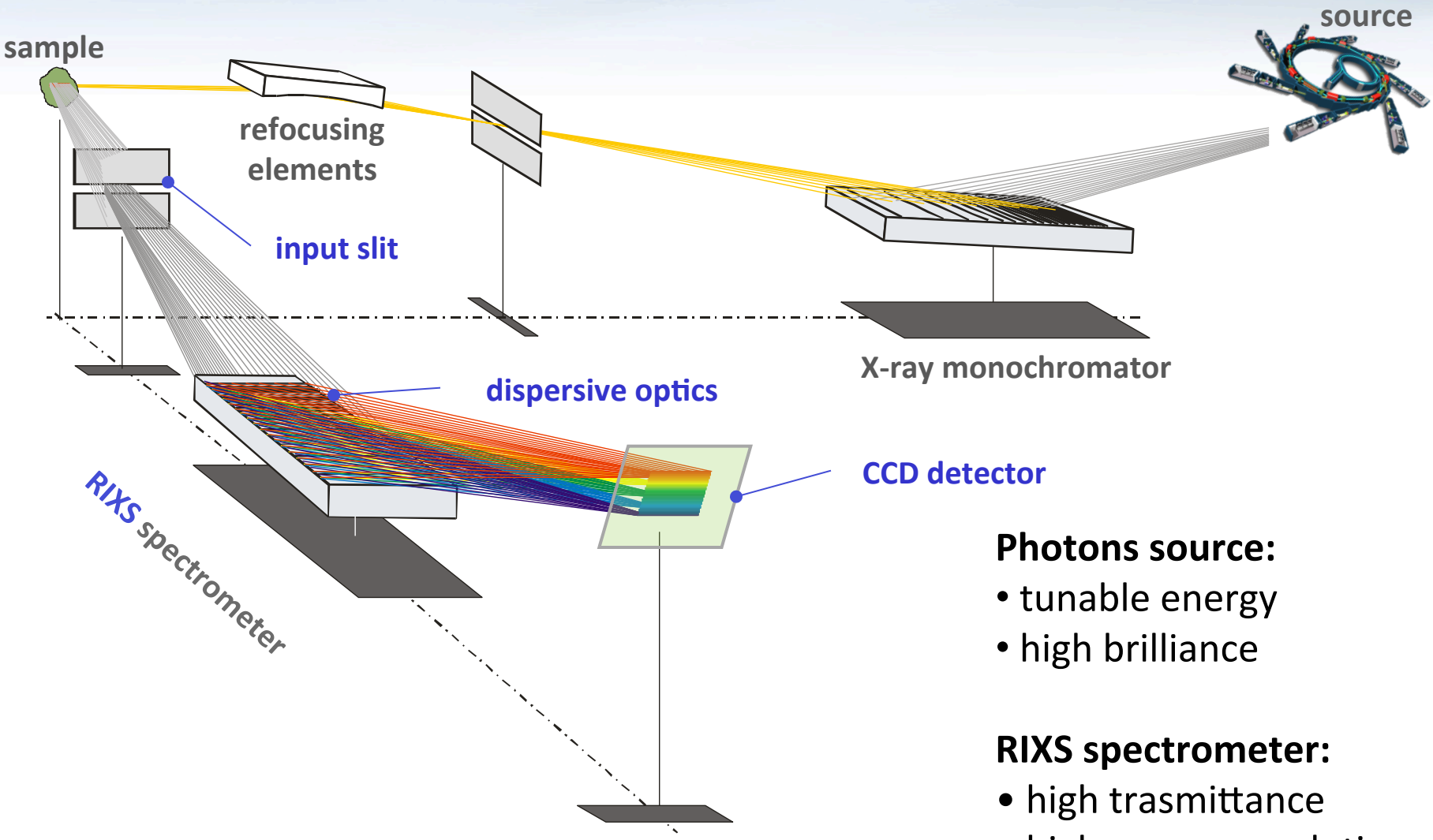
- element and site selective
- ehnancement of the RIXS response



Coherent de-excitation:

- core-hole lifetime $1/\Gamma_n$
- selection of the decay channel $h\nu_{out}$
- neutral final excitation
  (spin excitations, charge-transfer,
  intra- orbital dd-excitations, etc...)

RIXS Instrumentation



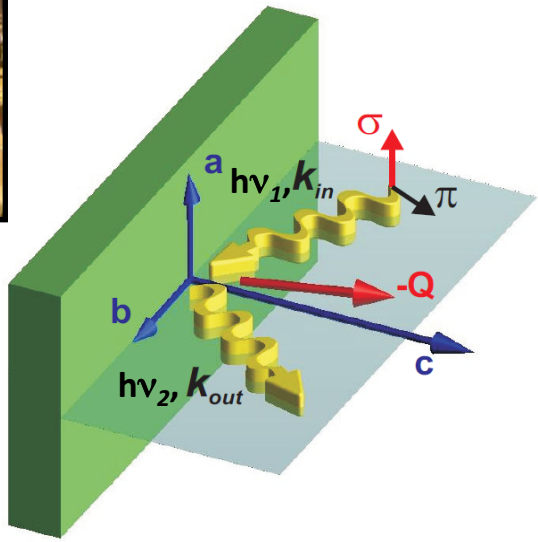
Photons source:
- tunable energy
- high brilliance

RIXS spectrometer:
- high trasmittance
- high energy resolution

RIXS instrumentation: SAXES

SAXES at ADRESS, PSI Villigen

$\Delta E_{Cu\text{-}L}$ = 130 meV
@ $h\nu_1$ = 930 eV



G. Ghiringhelli et al., Rev. Sci. Instrum. 77, 113108 (2006)

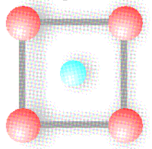
- ~ 5m long RIXS spectrometer
- variable scattering angle
- Energy range: 300 – 1600 eV

(all in-vacuum equipment)

A realization of quantum magnets: CuO_4 compounds

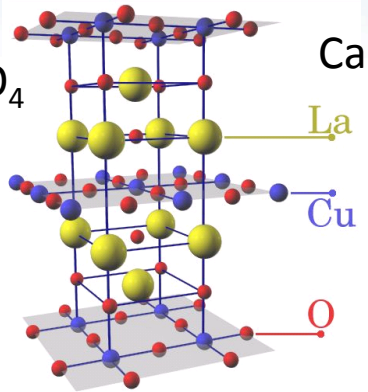
The **Cuprates family** (from 2D to 1D):

CuO_4 plaquette

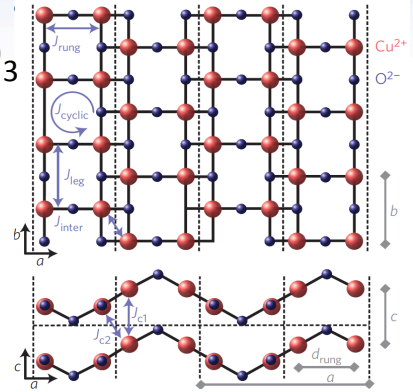


Cu^{2+}: $3d^9$ - S=1/2

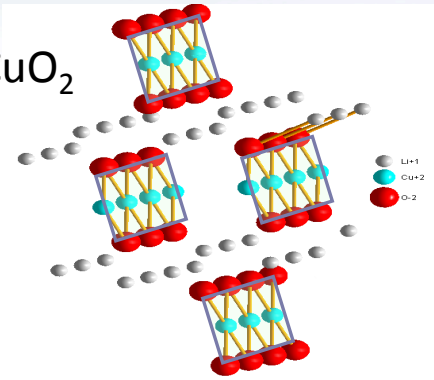
La_2CuO_4



$CaCu_2O_3$



Li_2CuO_2



- large variety of spin arrangements: 2D AFM plane, 1D AFM chain (corner-shared) up to frustrated 1D FM/AFM chain (edge-shared).

- very interesting systems, showing unconventional properties

(SC at high T_C, separation of spin - orbital - charge degrees of freedom, realizing frustrated magnetic structures)

- **test case** for RIXS: Cu $^{2+}$: $3d^9$ (x^2-y^2) → only n=1 possible intermediate state $3d^{10}$

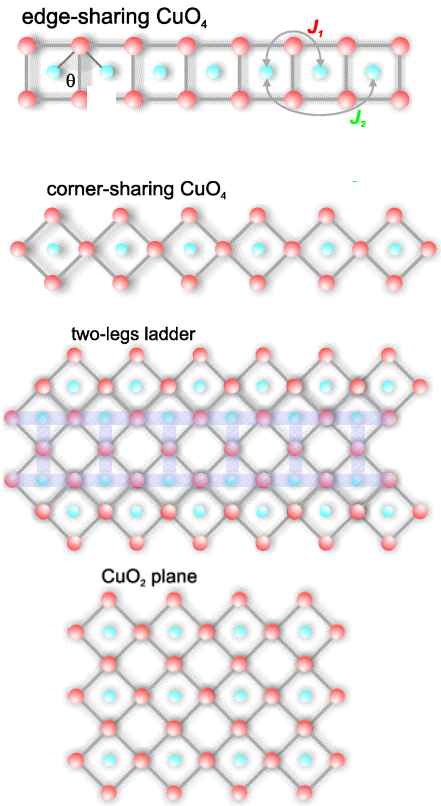
$$\frac{d^2\sigma}{d\Omega_2 d\hbar\omega_2} \propto \sum_f \left| \sum_n \frac{\langle f|D^\dagger|n\rangle\langle n|D|i\rangle}{E_i - E_n + \hbar\omega_1 - i\Gamma_n/2} \right|^2$$

RIXS on CuO_4 compounds

Spin correlations:

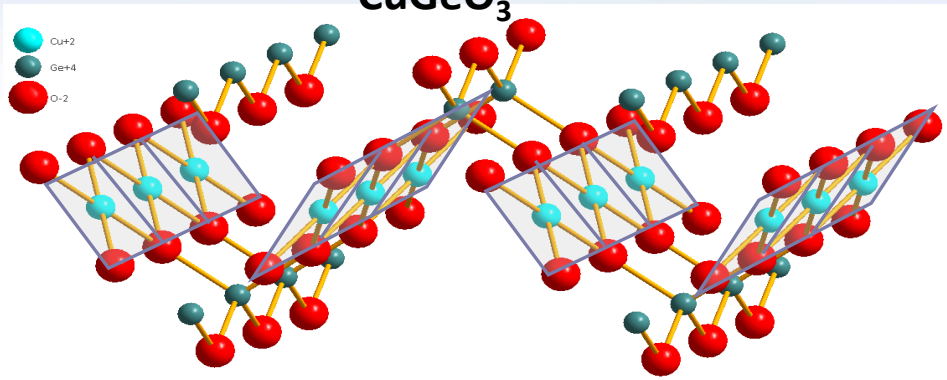
1. systems with small magnetic interaction J≈ 100K

2. systems with strong magnetic interaction J≈ 1500K

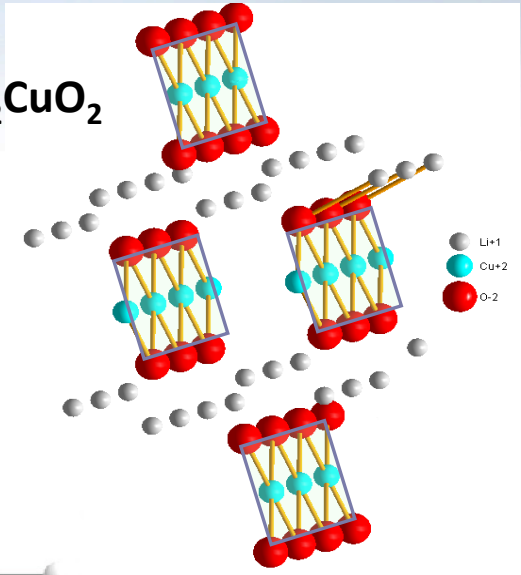


In-chain spin-correlations with J~100K

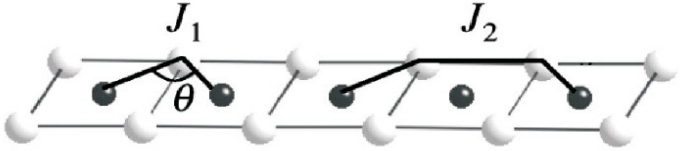
$CuGeO_3$



Li_2CuO_2



- edge-sharing CuO_4 chain (Cu^{2+}: S=1/2)



- $\theta \cong 90°$ → weak magnetic interaction ($J_1 \approx 100$ K)
- J_1 FM or AFM depending on θ
- $J_1 \approx J_2$ frustrated spin ½ chain

$CuGeO_3$ (θ ~ 99°)
- J_1 = 150 K♠ - AFM
- T_{SP} = 14 K

Li_2CuO_2 (θ ~ 94°)
- J_1 = -220 K♣ - FM
- $T_{N,3D}$ = 9 K

♠ K. Fabricius et al., *Phys. Rev. B* 57, 1102 (1998) ♣ W. Lorenz et al., *Eur. Phys. Lett.* 88, 37002 (2009)

In-chain spin-correlations with J~100K

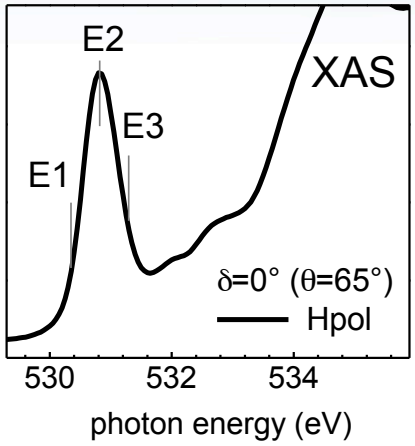
- state of art RIXS can NOT directly investigate spin modes in systems with J≈100 K (~ 10 meV) → limited by energy resolution ΔE= 100 meV *(more perspectives at the end…)*
- **high energy charge-transfer excitations are sensitive to short range spin correlation at the low energy scale**

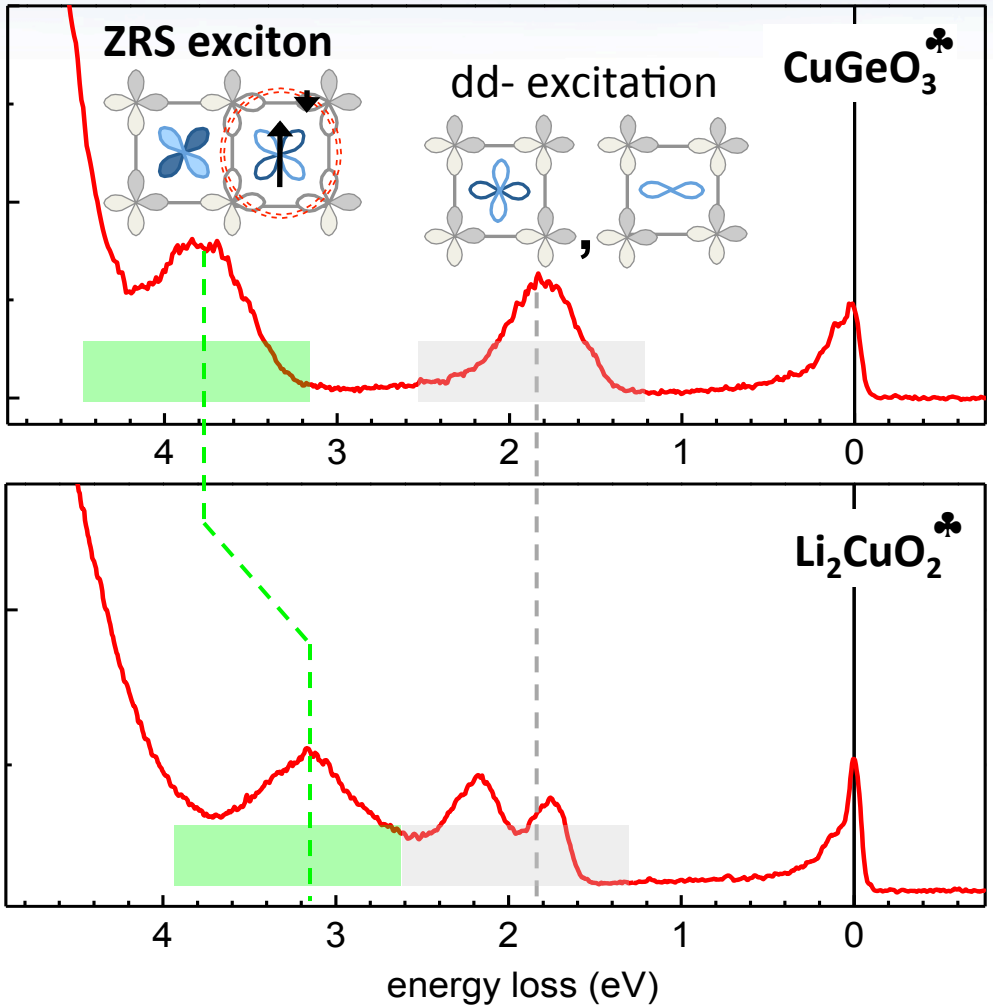
AFM Initial state: $d^9_{\downarrow}; d^9_{\uparrow}$ ⇨ Final state: $d^{10}; d^9 \underline{L}$

- ZR singlet exciton can be excited only if nearest neighbor spins are AFM (conservation of spin: no spin flip allowed)

In-chain spin-correlations with J~100K: $CuGeO_3$ and Li_2CuO_2

- **O-K RIXS** is strongly sensitive to ZRS exciton when $h\nu_{in} \approx$ 1s→ $3d^{10}$ <u>*L*</u>





ZRS exciton at:

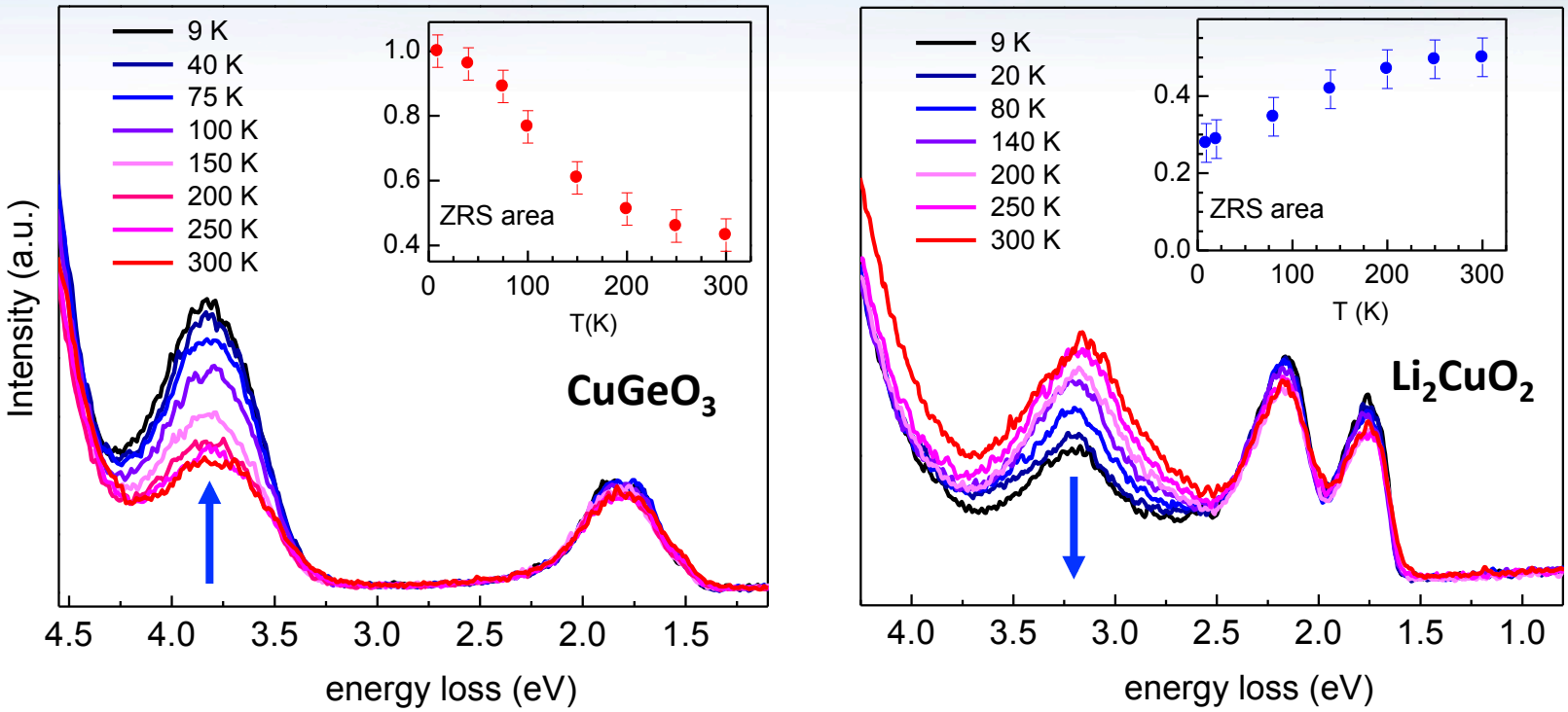
- 3.8 eV in $CuGeO_3$♦
- 3.1 eV in Li_2CuO_2

↑ first observation!!

♦ Atzkern et al., *Phys. Rev. B* 64, 075112 (2000); J. Kim et al., *Phys. Rev. B* 79, 094525 (2009)

♣ C. Monney, V. Bisogni et al., *PRL* 110, 087403 (2013)

In-chain spin-correlations with J~100K: $CuGeO_3$ and Li_2CuO_2



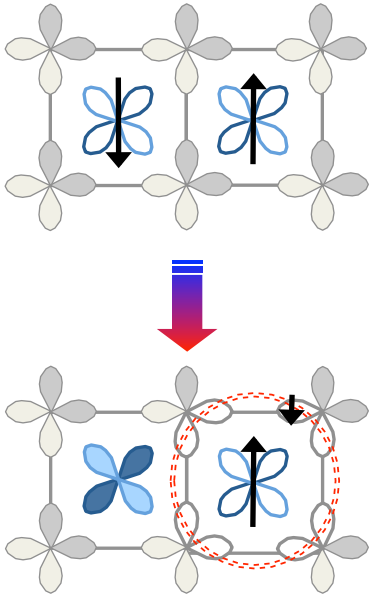
- ZRS exciton has a strong T dependence in the range 10 K < T< 300 K
  → sensitive to ~ 1 meV energy scale

- the T dependence is opposite between $CuGeO_3$ and Li_2CuO_2

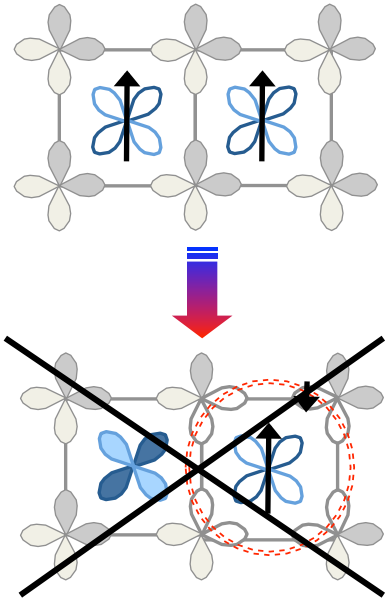
♣ C. Monney, V. Bisogni et al., *PRL* 110, 087403 (2013)

In-chain spin-correlations with J~100K: $CuGeO_3$ and Li_2CuO_2

AFM ground state



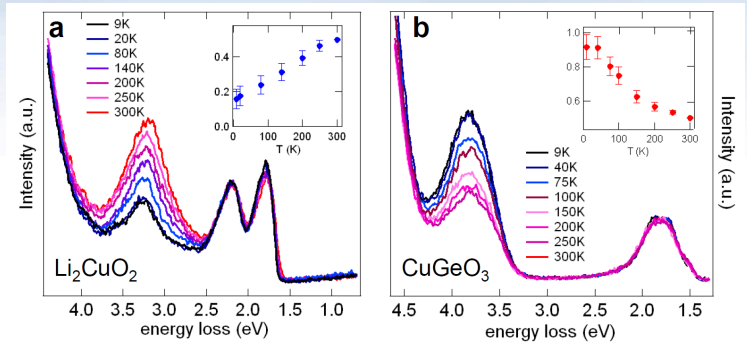
FM ground state



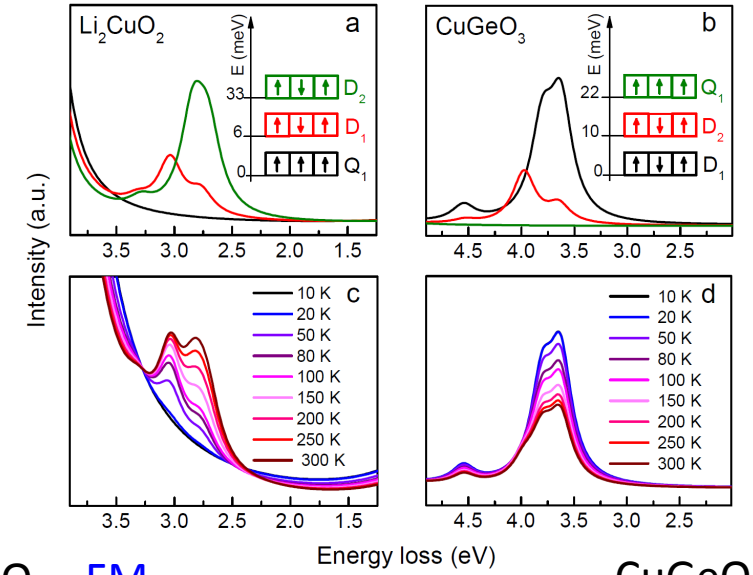
At low temperature, “only” the ground state is populated

♣ C. Monney, V. Bisogni et al., *PRL* 110, 087403 (2013)

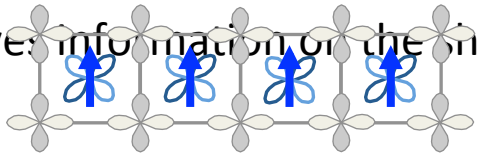
In-chain spin-correlations with J~100K: $CuGeO_3$ and Li_2CuO_2



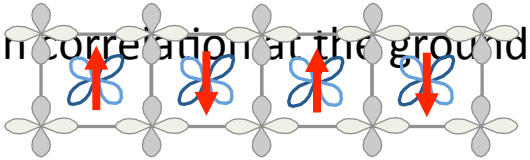
THEORY



Li_2CuO_2 - FM



$CuGeO_3$ - AFM



- ZRS *T* dep. gives information on the short range spin correlation at the ground state

♣ C. Monney, V. Bisogni et al., *PRL* 110, 087403 (2013)

Summary: spin-correlations with J~100K

- In systems with **small *J* (<100K)**, by probing the T dependence of localized ZR-excitations, O-K RIXS measures the short-range "nearest-neighbour" spin correlation at the ground state.

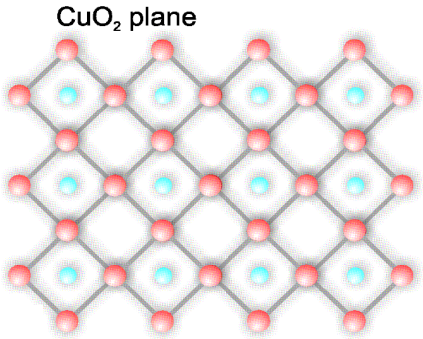
- high energy excitations at > 3 eV are strongly affected by thermal fluctuations corresponding to an energy scale of merely k_BT~ 1 meV, comparable to spin correlation.

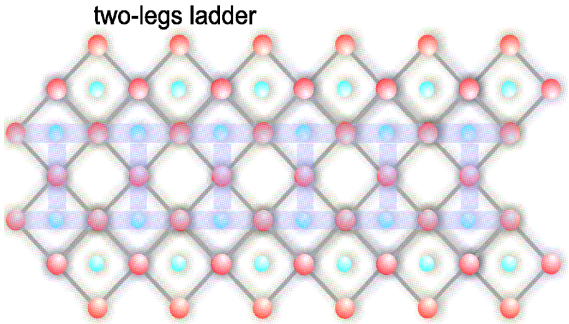
- the character of the magnetic correlations (FM or AFM) is immediately captured by the temperature dependence of the ZR-intensity.

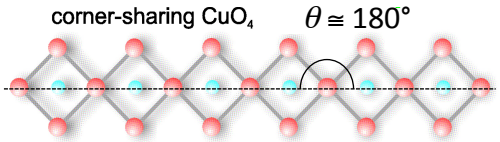
- both intra-chain and inter-chain magnetic correlations are probed with high sensitivity.

Spin-correlations with J~1500 K

- corner-shared arrangement of the CuO_4 building block unit
- $\theta \cong 180°$ → strong AFM interaction (J ≈1500 K)







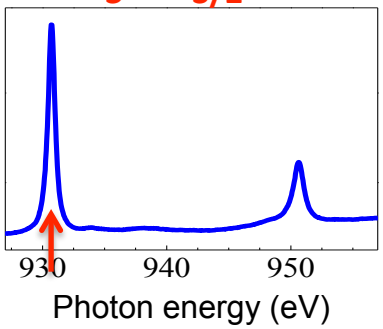
- corner-shared cuprates exist in different dimensionalities: from 2D to 1D

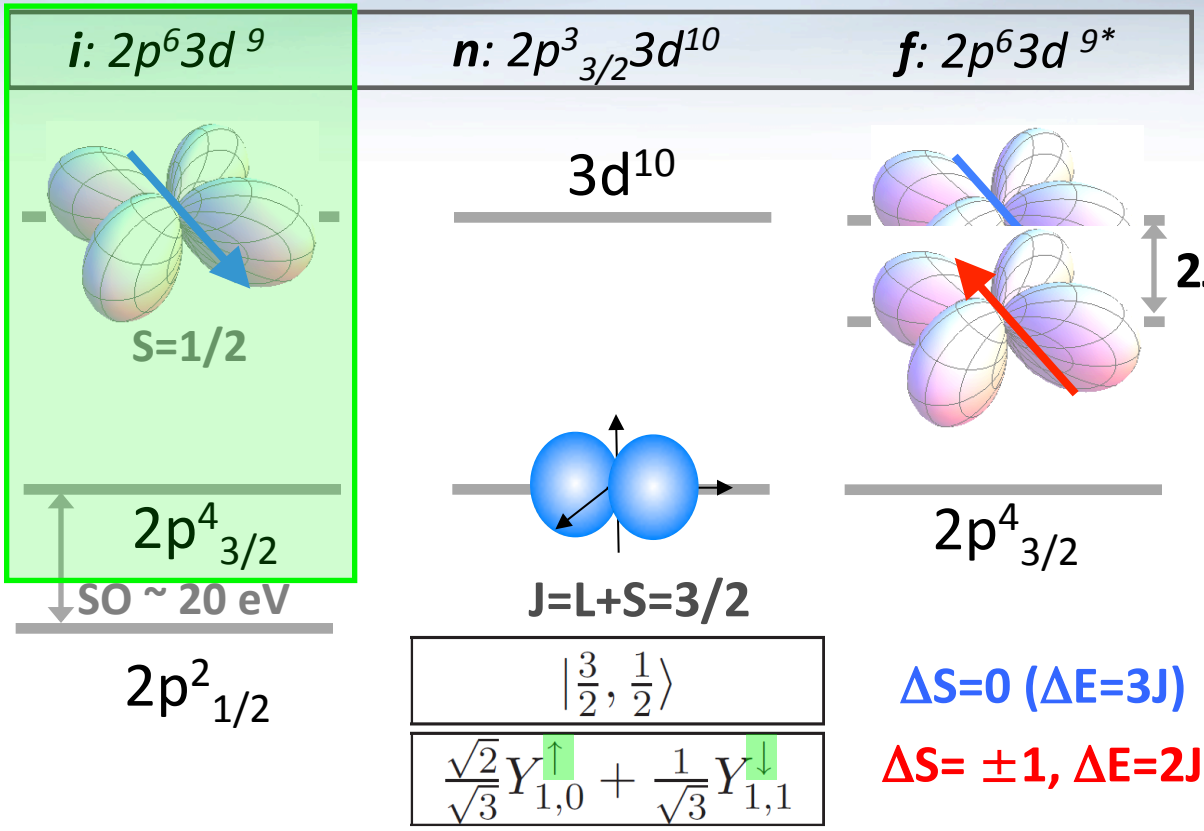
- ***J*** (130-150 meV) is comparable with RIXS energy resolution ΔE (~130 meV) → direct observation of spin excitations

Spin-correlations with J~1500 K

Cu^{2+}: $3d^9$ = 1 hole x^2-y^2

Cu L_3 $2p_{3/2}$ → 3d



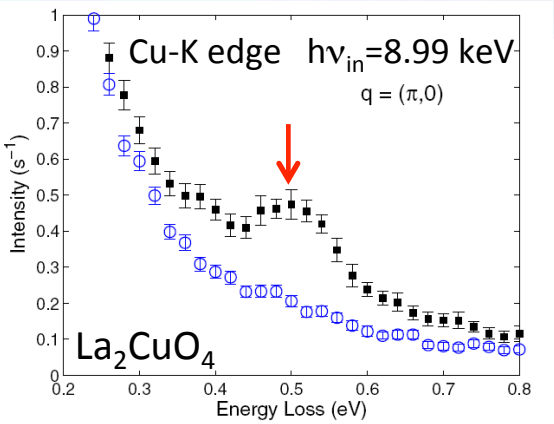


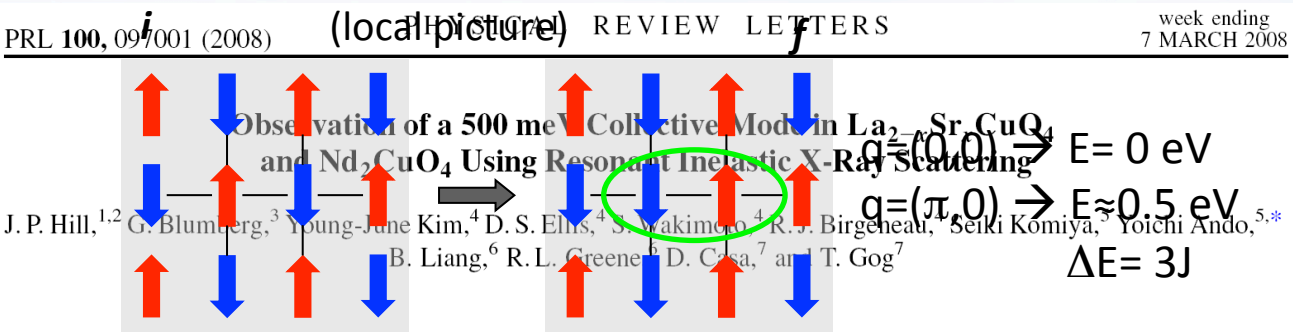
- **spin-orbit coupling** at *2p* core-hole → **S** is not a good quantum number
- RIXS couples to **odd**, **even** number of spin-flip processes: magnon (ΔS= ±1), bimagnon (ΔS=0)
- **no spin orbit couplit** at core-hole (1s) → RIXS couples to **even** number of spin-flips (ΔS=0)

L.J.P. Ament et al., *Phys. Rev. Lett*. 103 , 117003 (2009)

Spin-excitations accessed by RIXS (J~1500 K): ΔS=0

- Cu-K edge 1s→ 4p (8.99 keV): ΔS=0 spin excitation - **bimagnon**





(local picture)

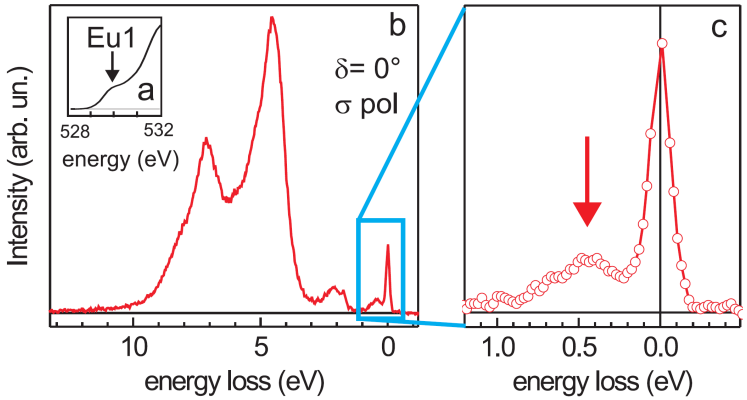
q=(0,0) → E= 0 eV

q=(π,0) → E≈0.5 eV

ΔE= 3J

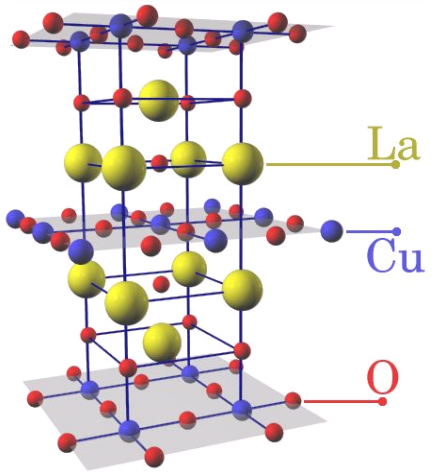
J. Hill et al., *Phys. Rev. Lett.* 100, 097001 (2008)

- O-K edge 1s → $3d^{10}\underline{L}$ (530 eV): ΔS=0 spin excitation - **bimagnon**



q=(0,0) → E=0.45 eV

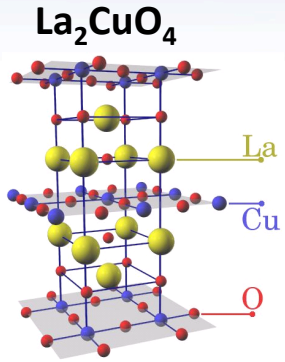
La_2CuO_4

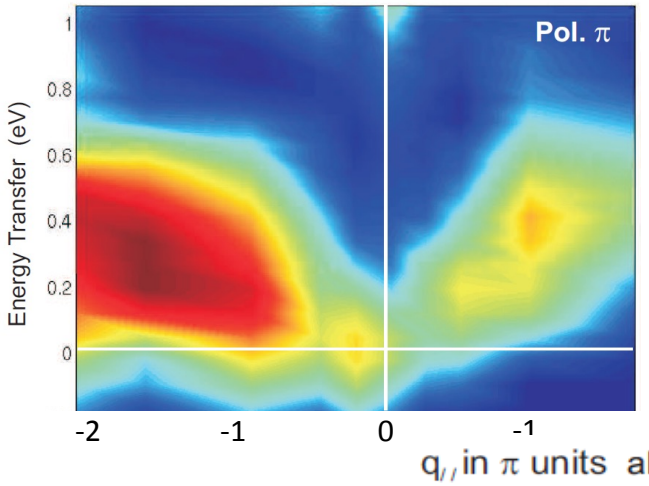


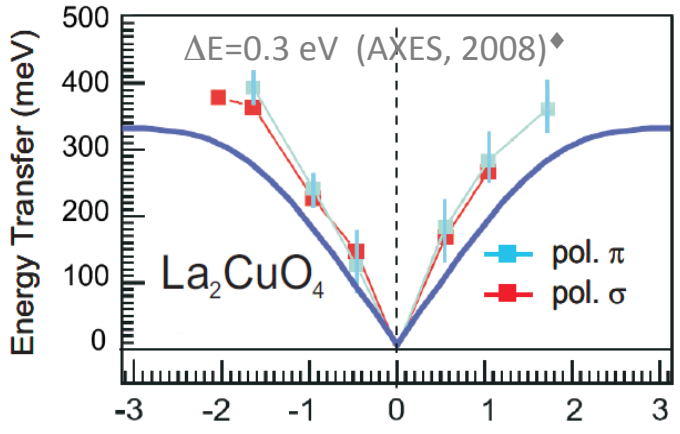
V. Bisogni et al., *Phys. Rev. B* 85, 214527 (2012)

Spin-excitations accessed by RIXS (J~1500 K): ΔS=1

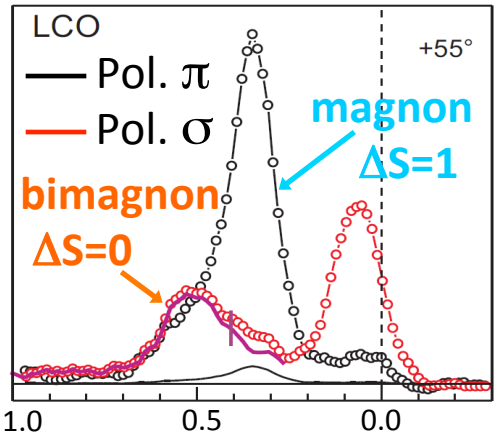
- Cu-L_3 edge $2p_{3/2}$ → 3d (930eV): ΔS=0 & ΔS=1 spin excitations – **bimagnon** & **magnon**

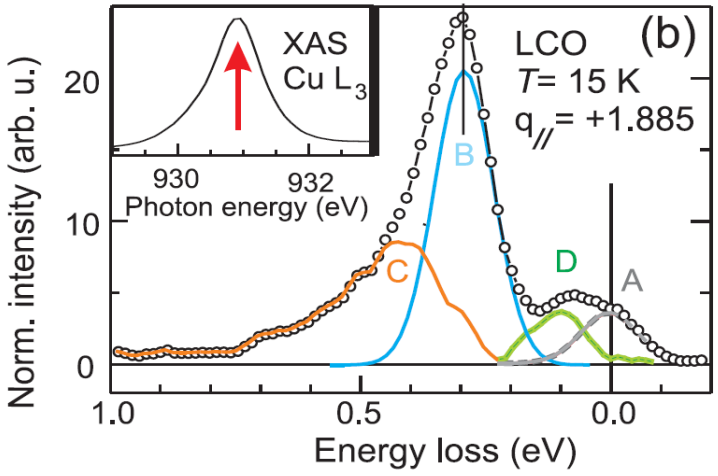


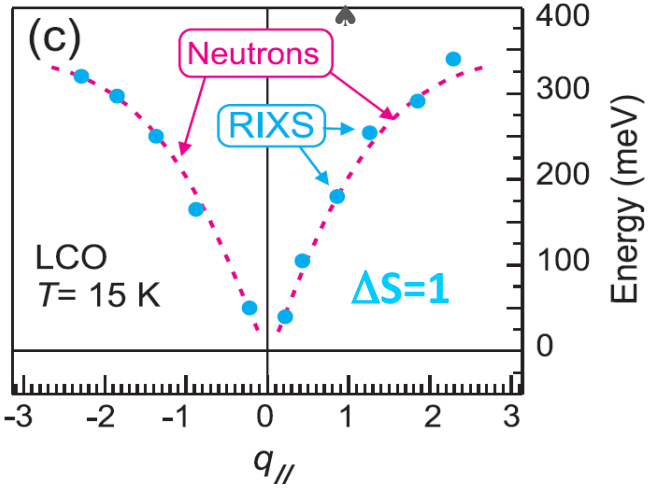




- Detailed spin excitations decomposition with ΔE≈130 meV ♣ (SAXES, 2009)







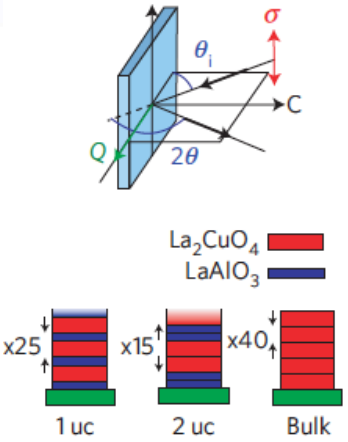
♣ L. Braicovich et al., *Phys. Rev. Lett.* 104, 077002 (2010)

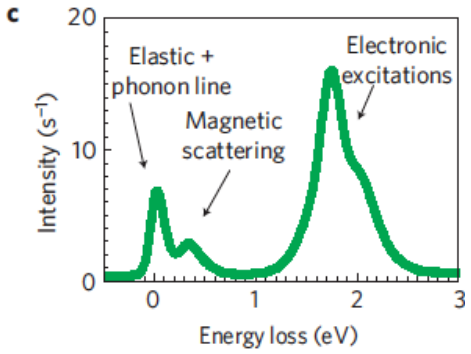
♠ R. Coldea et al., *Phys. Rev. Lett.* 86, 5377 (2001)

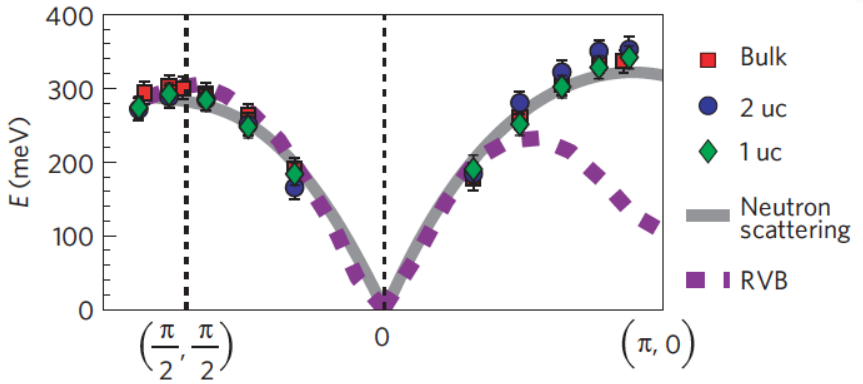
♦ L. Braicovich et al., *Phys. Rev. Lett.* 102, 167401 (2009)

Soft X-ray RIXS: tool to study *magnon* dispersion (J~1500 K)

- magnon dispersion in heterostructured systems of 1 or 2 uc of La_2CuO_4





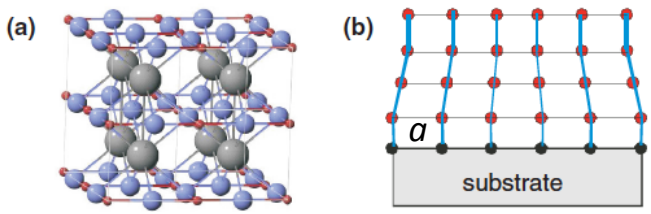


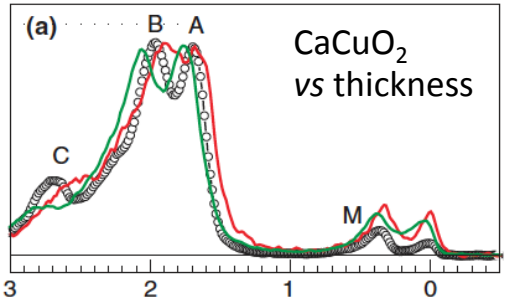
M.P.M. Dean et al., *Nat. Mat.* 3409 (2012)

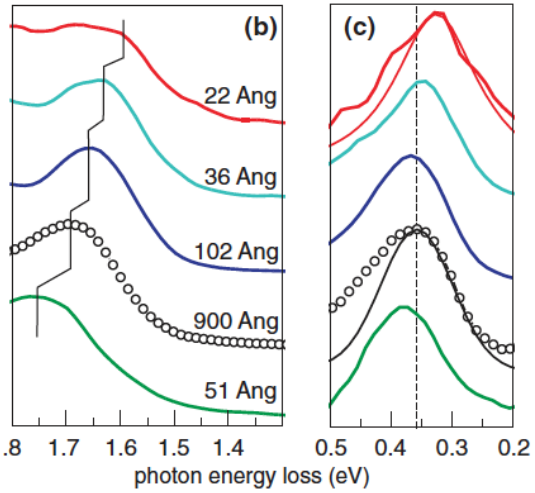
- magnon dispersion in strained thin films of $CaCuO_2$

→ scaling power law behaviour of ***J*** versus strain n~8

$$E \propto a^{-n} \qquad \frac{\delta E}{E_0} = -n \cdot \frac{\delta a}{a_0}.$$





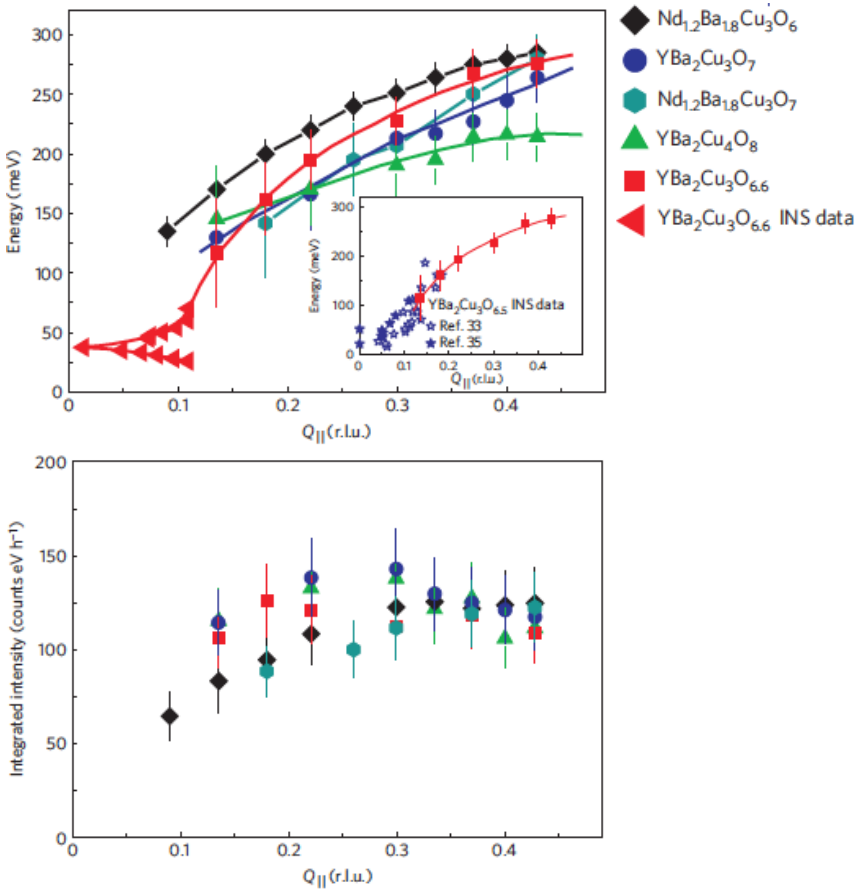


M. Minola et al., *Phys. Rev. B* 87, 085124 (2013)

Soft X-ray RIXS: tool to study *magnon* dispersion (J~1500 K)

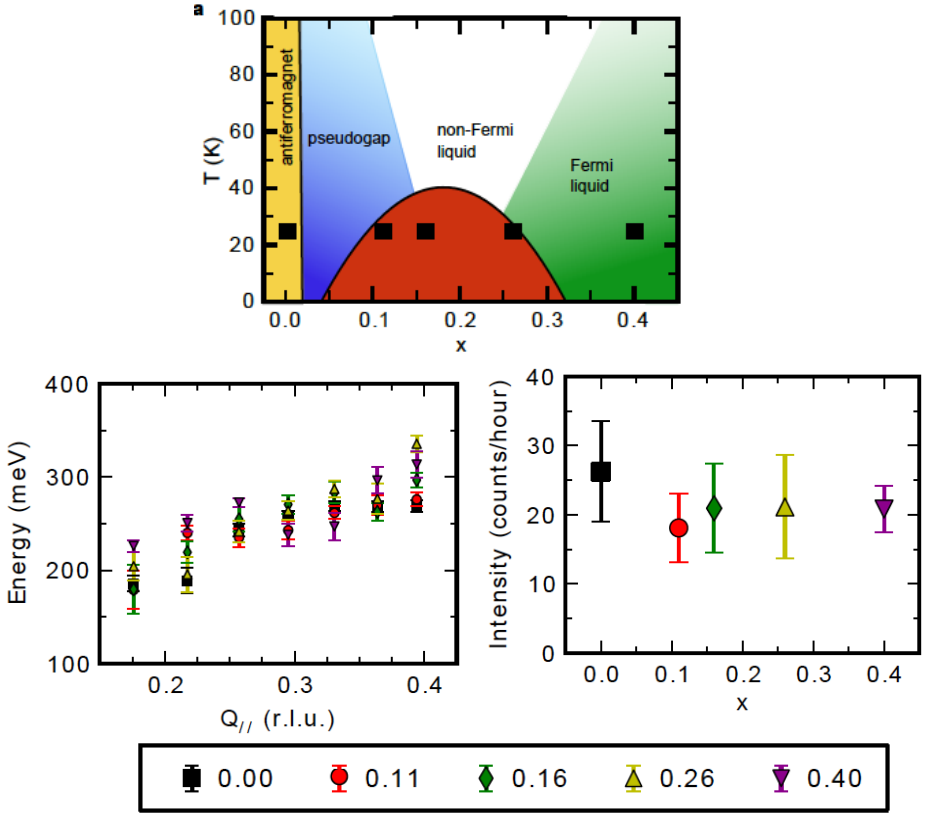
- magnon and paramagnon dispersion in doped cuprate systems

$Nd_{1.2}Ba_{1.8}Cu_3O_{6+x}$
$YBa_2Cu_3O_{6+x}$



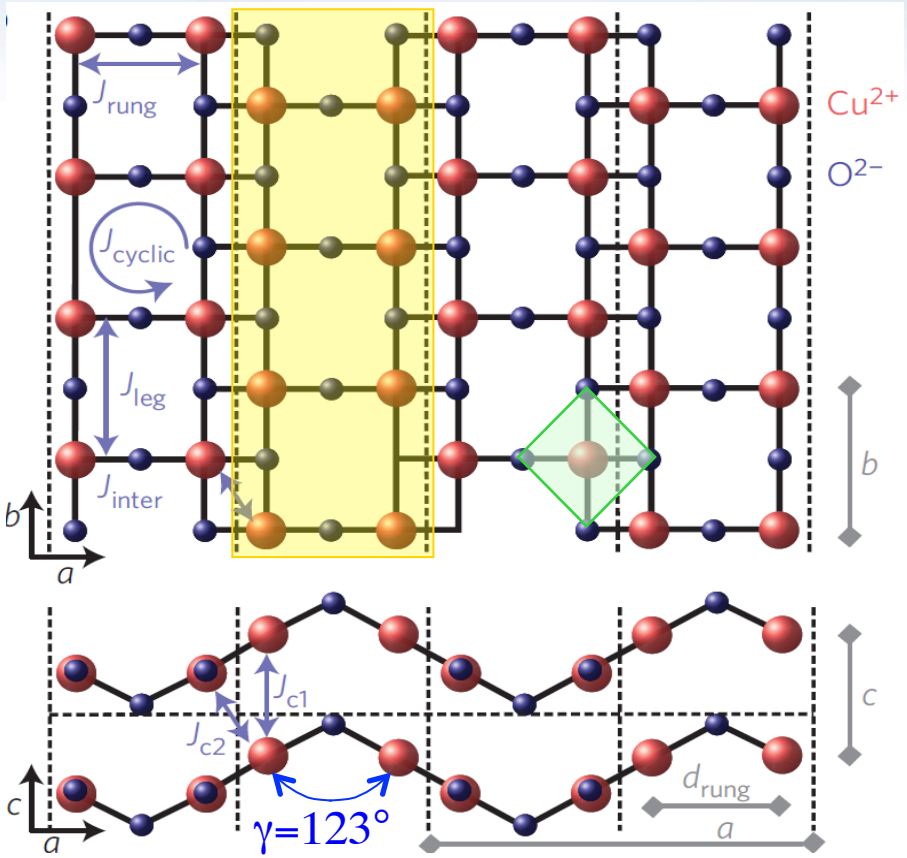
M. Le Tacon et al., *Nat. Phys.* 2041 (2011)

$La_{2-x}Sr_xCuO_4$



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

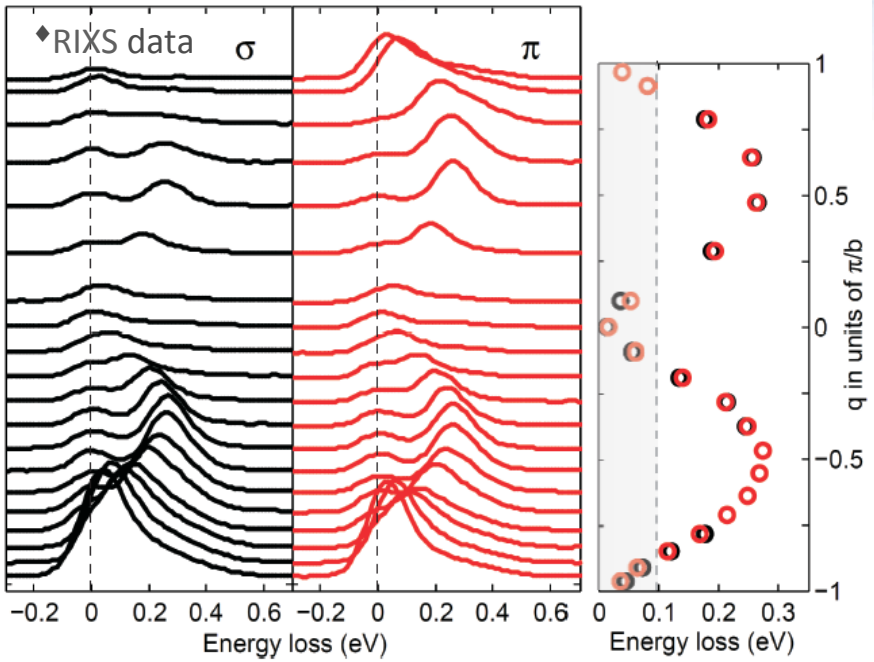
$CaCu_2O_3$: a buckled two-leg ladder system



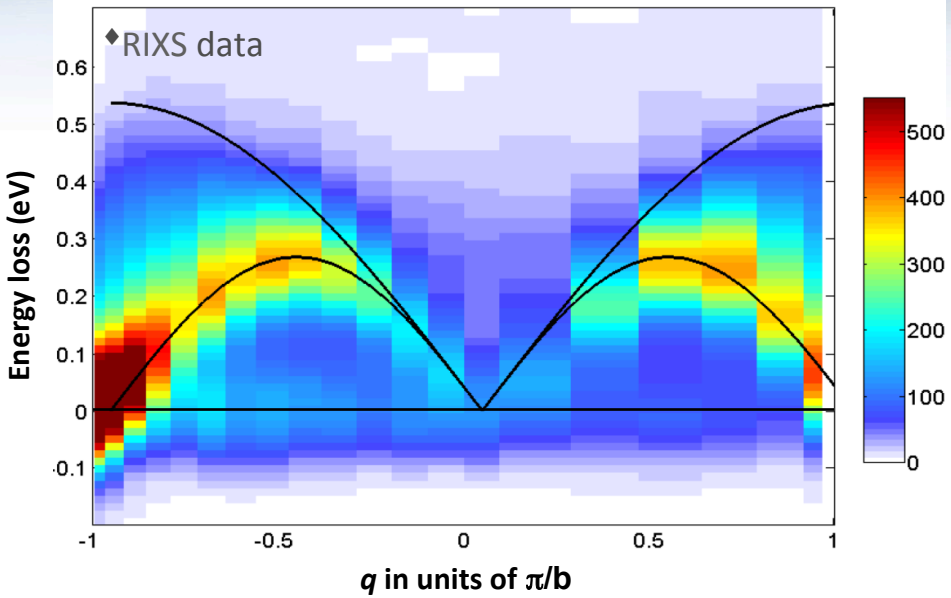
- **CuO_4** plaquette: Cu^{2+}: $3d^9$ and S=1/2
- **J_{leg}=162 meV – 168 meV** ♣, ♠, ♦
- **J_{rung}= J_{leg}/10≈ 15 meV** ♣, ♠, ♦

♣ B. Lake et al., *Nat. Phys* 6, 50 (2010)
♠ Bordas et al., *Phys. Rev. B* 71, 045108 (2005)
♦ Kiryukhin et al, *Phys. Rev. B* 63, 144418 (2001)

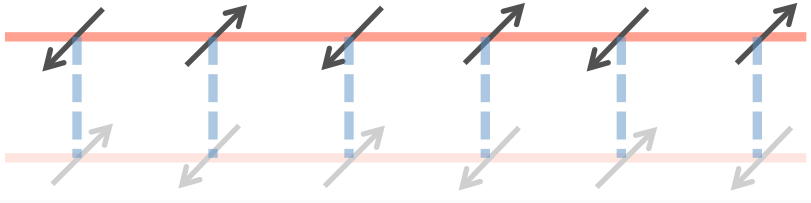
$CaCu_2O_3$: a buckled two-leg ladder system

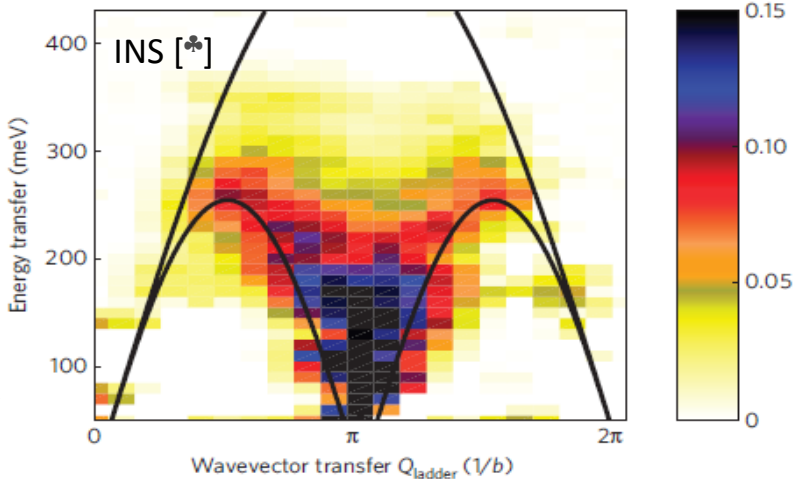


♦ V. Bisogni et al., *Phys. Rev. Lett.* 112, 147401 (2014)



- in agreement with INS data ♣
- **two-spinon** dispersion typical of 1D system
- two-spinon confinement ♣ – 2D effect ($E<J_{rung}$) – not visible within the RIXS resolution

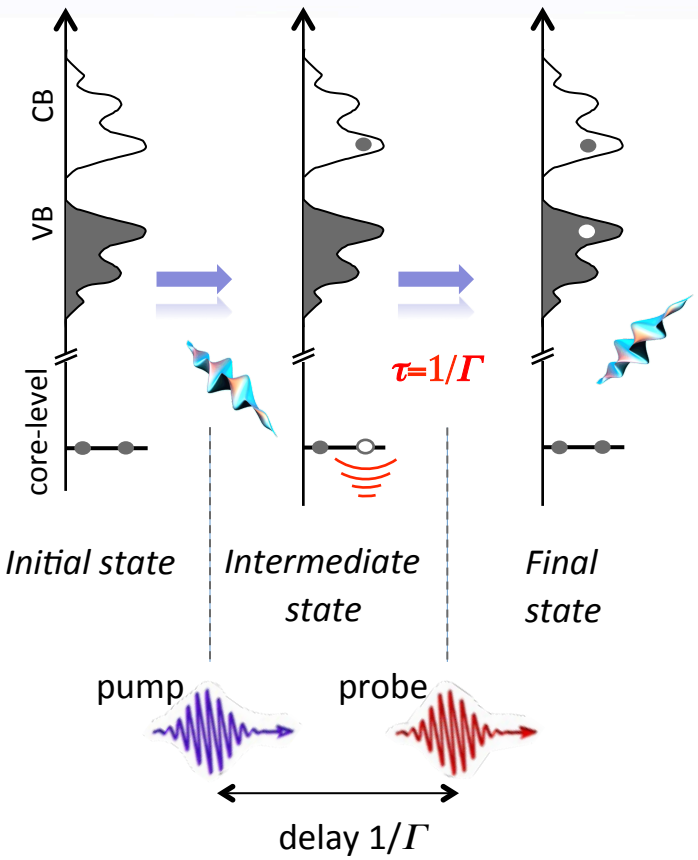




♣ B. Lake et al., *Nat .Phys.* 6, 50 (2010)

$CaCu_2O_3$: test case to explain RIXS magnetic intensity

- Core-hole clock concept



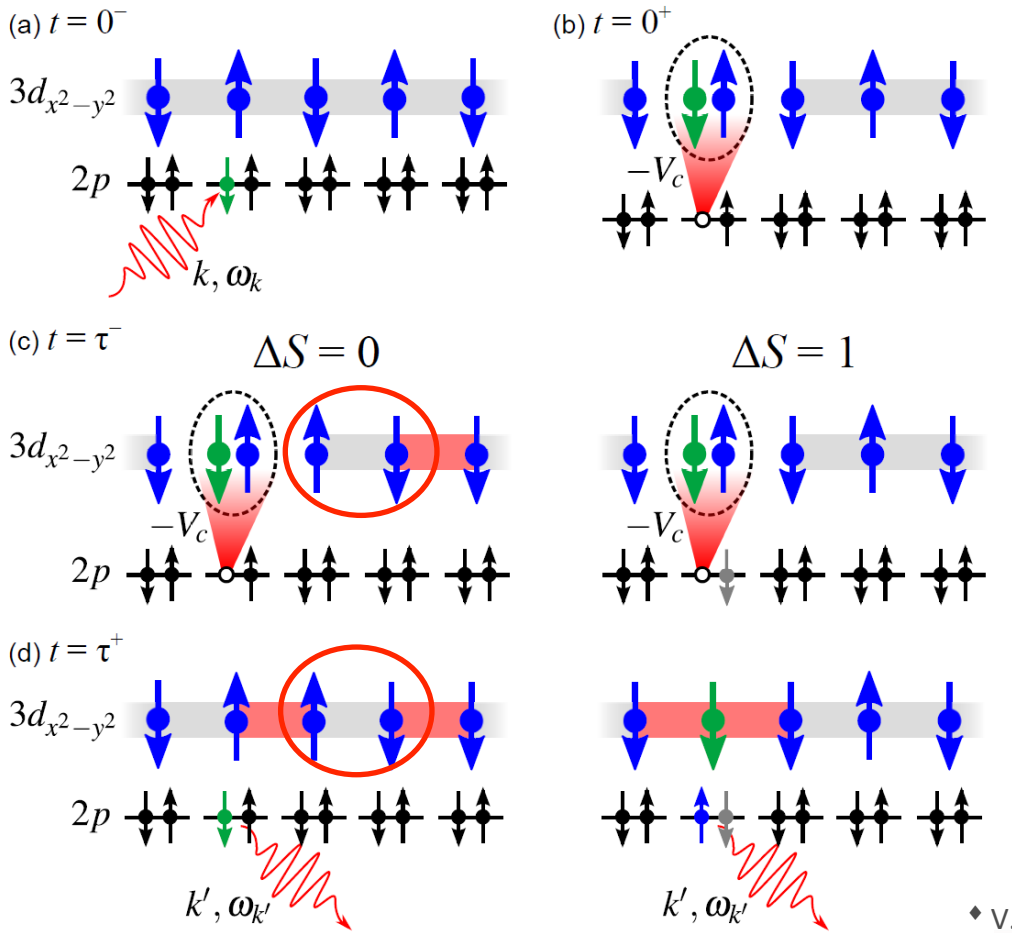
- Intermediate state lifetime given by core-hole clock $\tau = 1/\Gamma$ (Γ is the core-hole potential)
- Re-organization of electron within the core-hole lifetime
- Alternative to Pump & Probe experiment
- At L-edges (2p→3d) of **transition metal oxides**, τ = ~ *fs*
- RIXS can access the ***fs* dynamics** together with **momentum** and **energy** resolution

P. A. Bruhwiler et al., Rev. Mod. Phys. 74, 703 (2002)

$CaCu_2O_3$: test case to explain RIXS magnetic intensity

- taking spin excitations in $CaCu_2O_3$ as an example, we discuss the **RIXS magnetic intensity**
- total magnetic intensity: $I^{\varepsilon}(q,\omega,\tau) = I^{\varepsilon}_{S_0}(q,\omega,\tau) + I^{\varepsilon}_{S_1}(q,\omega,\tau)$

Cu L-edge



$\tau_{S0} \approx 1/J$

$\tau_{S1} \approx 0$

two magnetic domain walls created for both $\Delta S=0$ and $\Delta S=1$

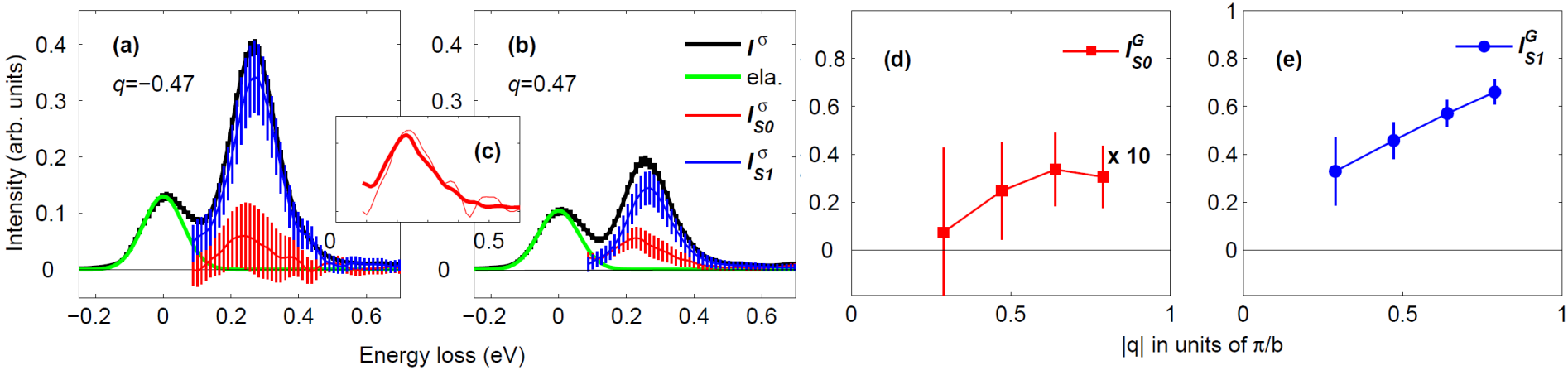
◆ V. Bisogni et al., PRL 112, 147401 (2014)

$CaCu_2O_3$: test case to explain RIXS magnetic intensity

- taking spin excitations in $CaCu_2O_3$ as an example, we discuss the **RIXS magnetic intensity**
- total magnetic intensity: $I^{\varepsilon}(q,\omega,\tau) = I^{\varepsilon}_{S_0}(q,\omega,\tau) + I^{\varepsilon}_{S_1}(q,\omega,\tau)$
- factorization of the intensity♣:

$$I^{\varepsilon}(q,\omega,\tau) = P^{\varepsilon}_{\mathrm{el}}(q)\cdot G_{S_0}(|q|,\omega,\tau) + P^{\varepsilon}_{\mathrm{sf}}(q)\cdot G_{S_1}(|q|,\omega,\tau)$$

- comparison of $I^{\sigma}(q)$ with $I^{\pi}(q)$
- experimental decomposition of $I^{\varepsilon}_{S0}/I^{\varepsilon}_{S1}$ and extraction of ω integrated G_{S0}/G_{S1} → I^{G}_{S0}/I^{G}_{S1}

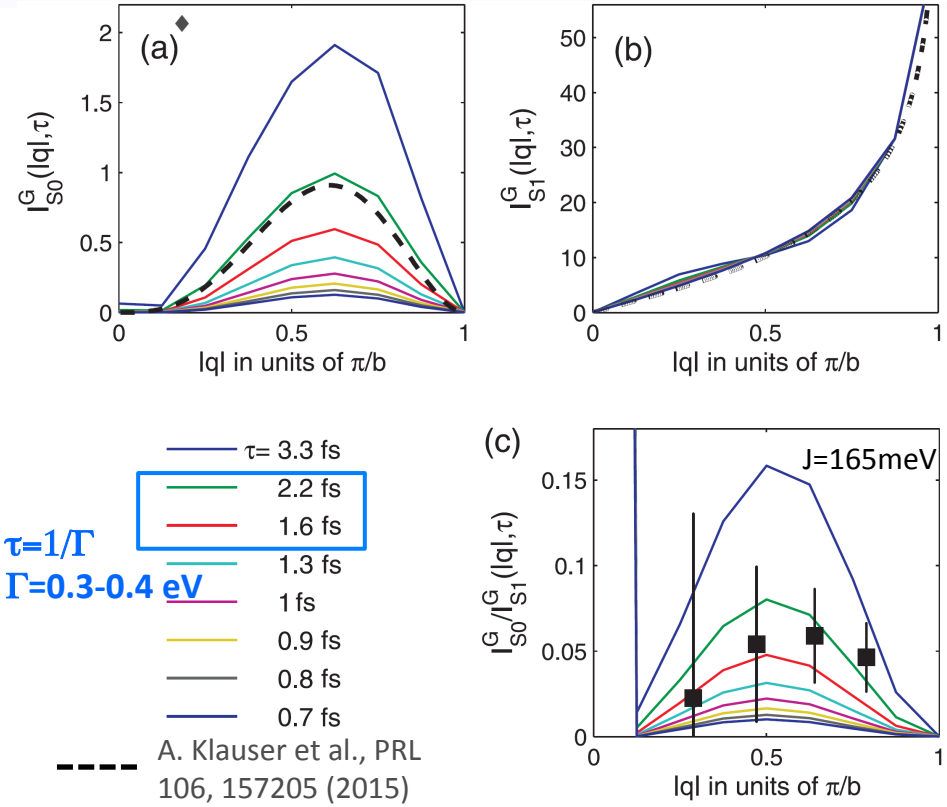


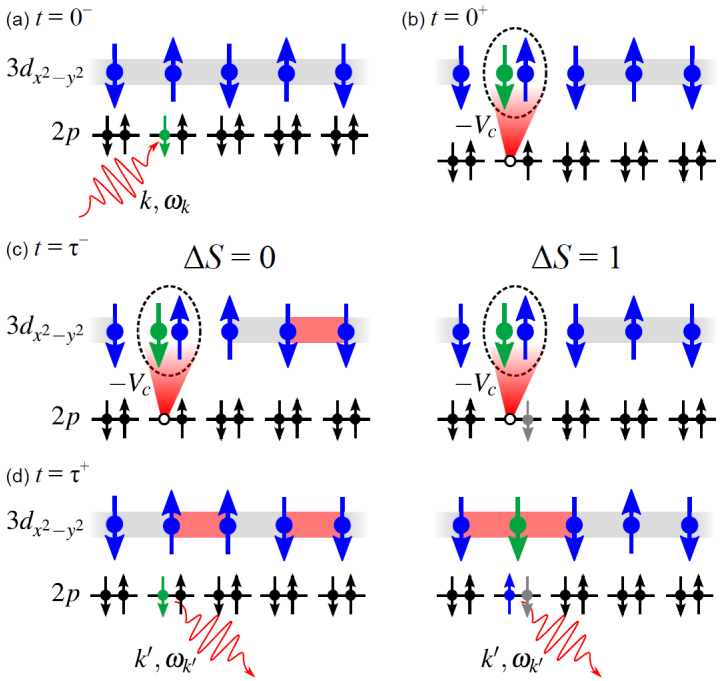
♦ V. Bisogni et al., PRL 112, 147401 (2014)

$CaCu_2O_3$: test case to explain RIXS magnetic intensity

- time evolution - core-hole lifetime τ - of RIXS magnetic response♦:

$$\mathcal{H}(t) = \mathcal{H}_{3d} + \Theta(t)\Theta(\tau - t)\mathcal{H}_{\text{corehole}}$$





- femtosecond dynamics of magnetic excitation probed by RIXS via **core-hole clock $\tau \approx 1/\Gamma$**
- *S1* excitation is mainly time independent
- *S0* is a slow process, with an intrinsic time scale $\tau_{S0} \approx 1/J$ (J=165 meV, $\tau_{S0} \approx 4$ fs)
- *S0* intensity is governed by the ratio $\tau/\tau_{S0} \approx J/\Gamma$

♦ V. Bisogni et al., PRL 112, 147401 (2014)

Summary: spin-excitations with J~1500K

- in systems with high J ($J \approx \Delta E$), RIXS can directly measure the momentum dispersion of spin excitations (magnons, bimagnons, paramagnons, two-spinons) in undoped and doped systems.

- RIXS does **not** need **big sample volumes** and can also be applied to very thin films.

- RIXS is sensitive to the femtosecond dynamics of magnetic excitations in solids: $\Delta S=1$ excitation is mainly time independent, while $\Delta S=0$ excitations are slow and depends on the ratio J/Γ.

- *time*-dependence can be used to discriminate between different excitations overlapping in energy.

New Experimental possibilities in soft-RIXS

- New **ERIXS spectrometer** at upgraded **ID32 beamline** of ESRF just entered in operation 7/2015
- Energy Range: 400 – 1600 eV
- 10-12 m long spectrometer arm
- 40'000 resolving power (4x present state-of-the-art)
- continuous arm rotation over 100° without breaking vacuum

Example:
@ Cu L_3 edge (930 eV)
SAXES, SLS → **ΔE~130 meV**
ERIXS, ESRF → **ΔE ~ 35 meV**

New Experimental possibilities in soft-RIXS

Coming Soon… 10/2016

BROOKHAVEN NATIONAL LABORATORY

- **Centurion spectrometer** and **SIX beamline** at the new NSLS-II synchrotron of Brookhaven National Laboratory
- Energy Range: 160 – 2300 eV
- 15 m long spectrometer arm
- 100'000 resolving power (10x present state-of-the-art)
- continuous arm rotation over 120° without breaking vacuum

Example:
@ Cu L_3 edge (930 eV)
SAXES, SLS → ΔE~130 meV
ERIXS, ESRF → ΔE ~ 35 meV
Centurion, NSLSII → ΔE ~ 13 meV

Thank you for the attention!