# Charge dynamics in $CuGeO_3$: a combined RIXS study at O-K and Cu-$L_3$ edges

V. Bisogni, C. Monney, J. MalèK, S.-L. Drechsler, R. Kraus, K.J. Zhou, V. Strocov, J. van den Brink, B. Büchner, T. Schmitt and J. Geck

Funding:

# Acknowledgments


**IFF Dresden:**
Jochen Geck
Roberto Kraus
Martin Knupfer
Bernd Büchner

**ITF Dresden:**
Jiri Malèk
Krzysztoff Wohlfeld
Liviu Hozoi
Roman Kuziak
Satoshi Nishimoto
Stephan-L. Drechsler
Jeroen van den Brink

Emmy Noether-Programm
Deutsche Forschungsgemeinschaft DFG

Funding:
DFG
Leibniz Gemeinschaft

**SLS - PSI Villigen:**
Claude Monney
Kejin Zhou
Vladimir Strokov
Thorsten Schmitt

PAUL SCHERRER INSTITUT PSI
SWISS LIGHT SOURCE SLS
MaNEP SWITZERLAND

**Université Paris-Sud :**
Alexandre Revcoleshi

ICMMO

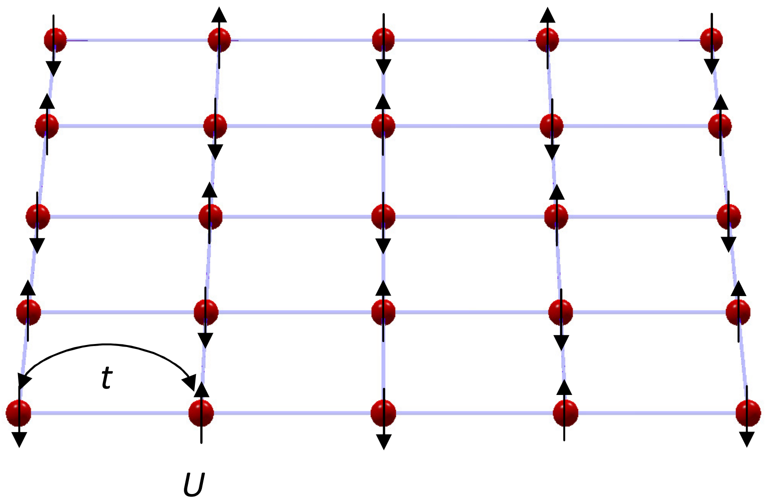
**ICAM-I2CAM :** Travel expenses have been supported by I2CAM trough the **NSF grant number DMR-0844115**.
(ICAM-I2CAM, 1 Shields Avenue, Davis, CA 95616)

ICAM-I2CAM Institute for Complex Adaptive Matter
NSF

# Outline

- Introduction to the case of $CuO_2$ plane
- System under study: $CuGeO_3$
- Experimental method: Resonant Inelastic X-ray Scattering (RIXS)
- Motivations: *d-d* excitations and Zhang-Rice singlet excitons
- Conclusions

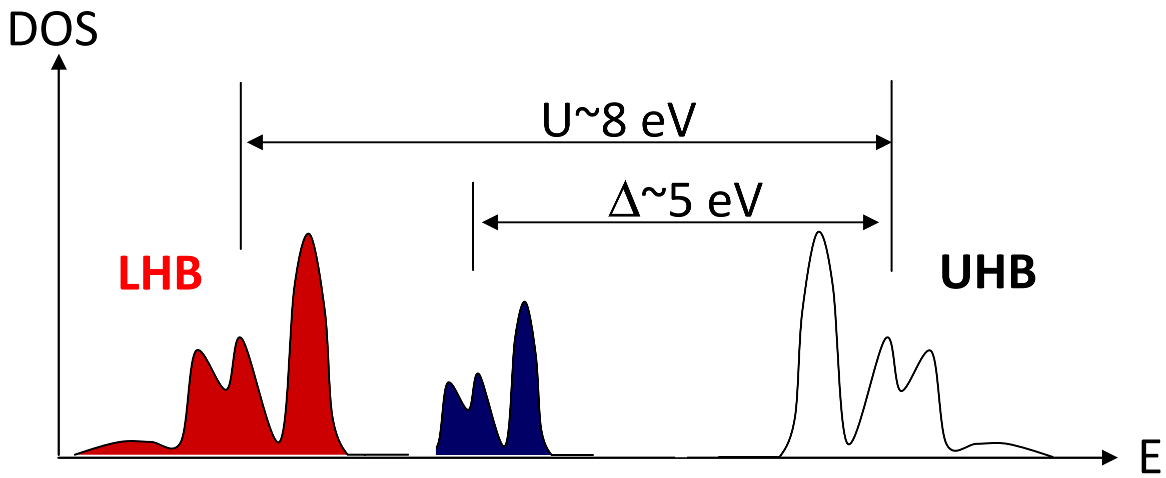
## Correlated electron systems: example of a $CuO_2$-plane

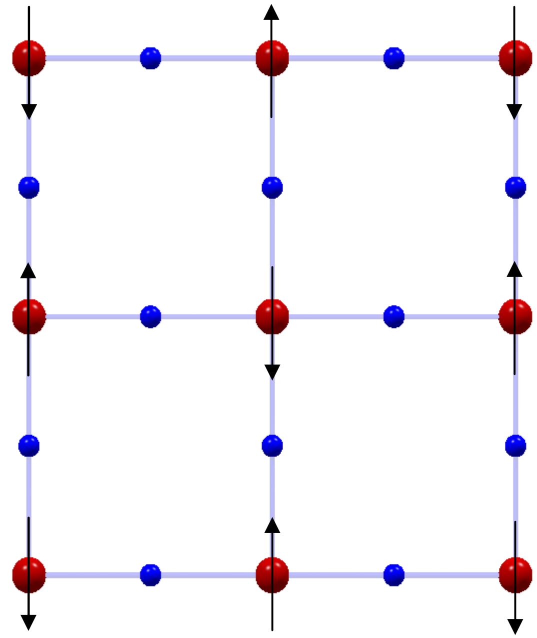



Cu:$d^9$ →one hole per Cu

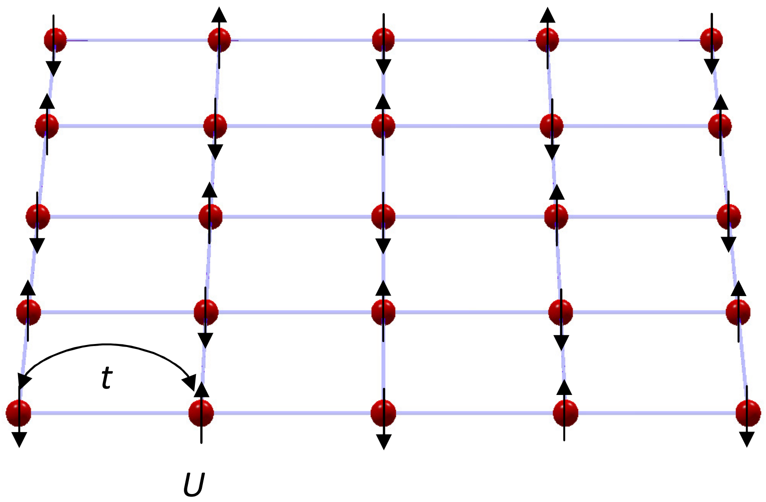
single band Mott-Hubbard ($U$~8 eV, $t$~0.4 eV)

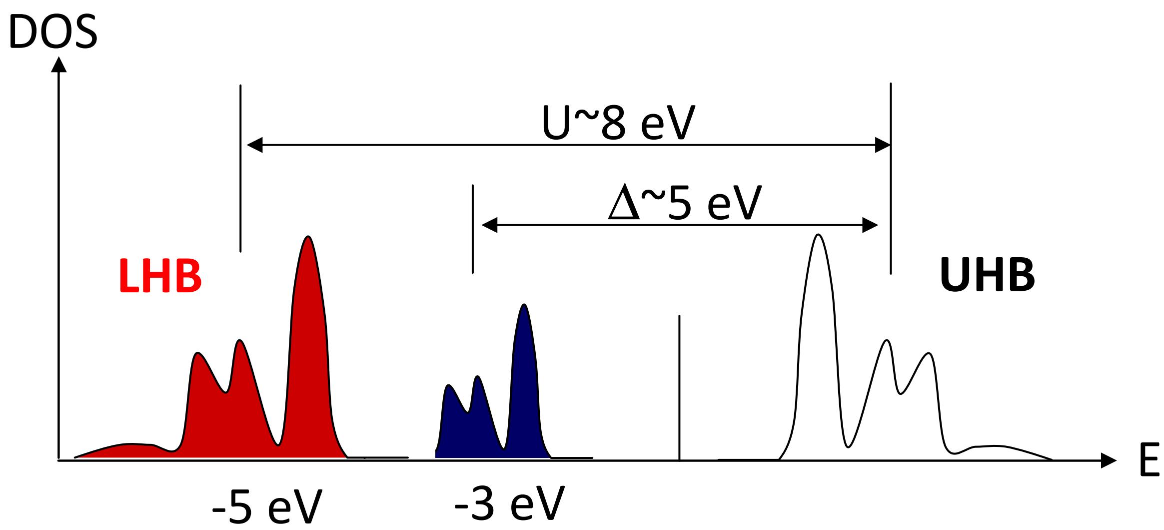
$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} (c^\dagger_{i\sigma} c_{j\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$



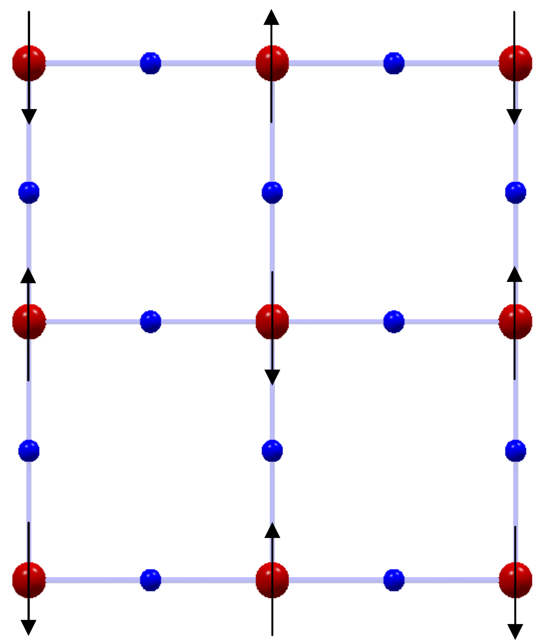



## Correlated electron systems: example of a $CuO_2$-plane

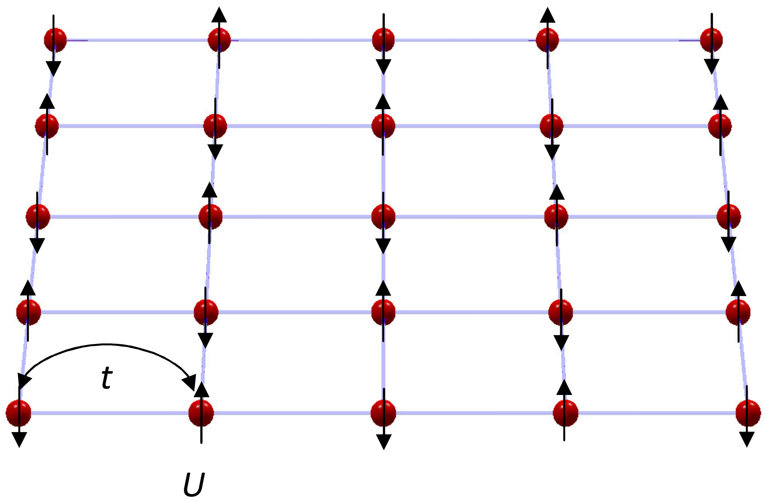



**Multi-band Mott-Hubbard model:**
**O:2p + TM:3d bands**

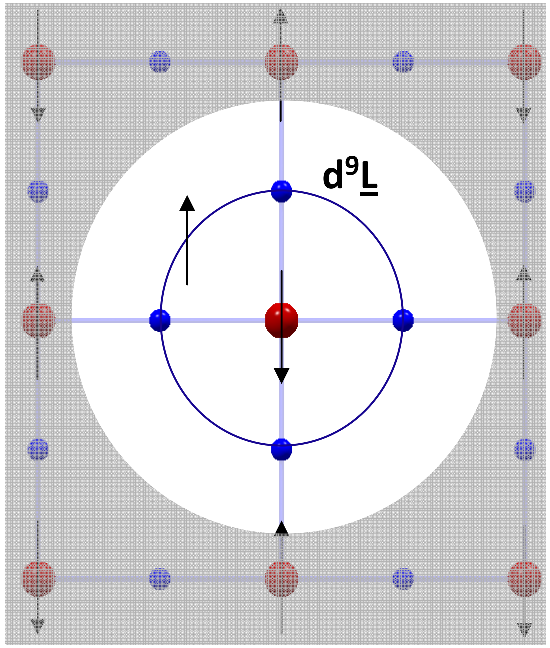


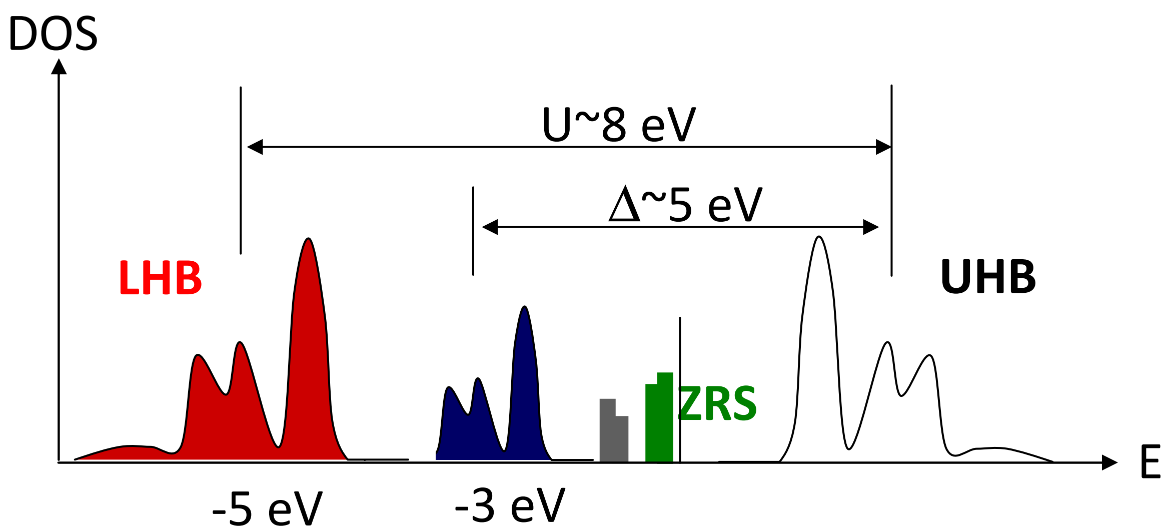
## Correlated electron systems: example of a $CuO_2$-plane



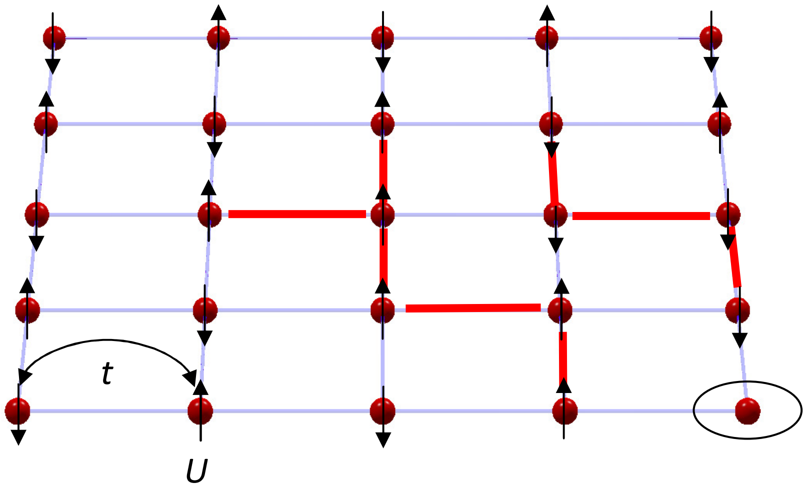

**Multi-band Mott-Hubbard model:**
**O:2p + TM:3d bands**

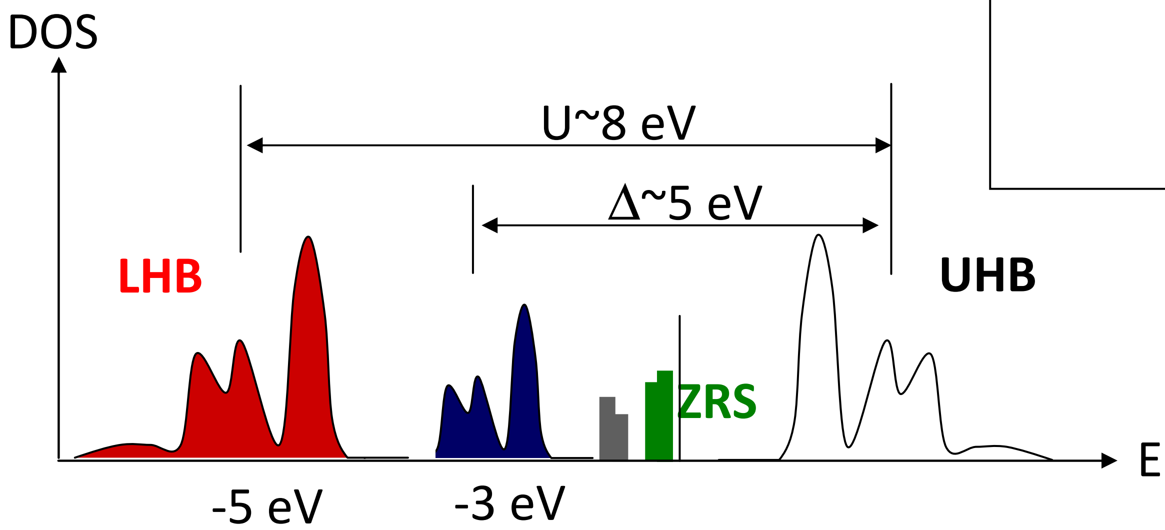
**Zhang-Rice Singlet**



## Correlated electron systems: example of a $CuO_2$-plane



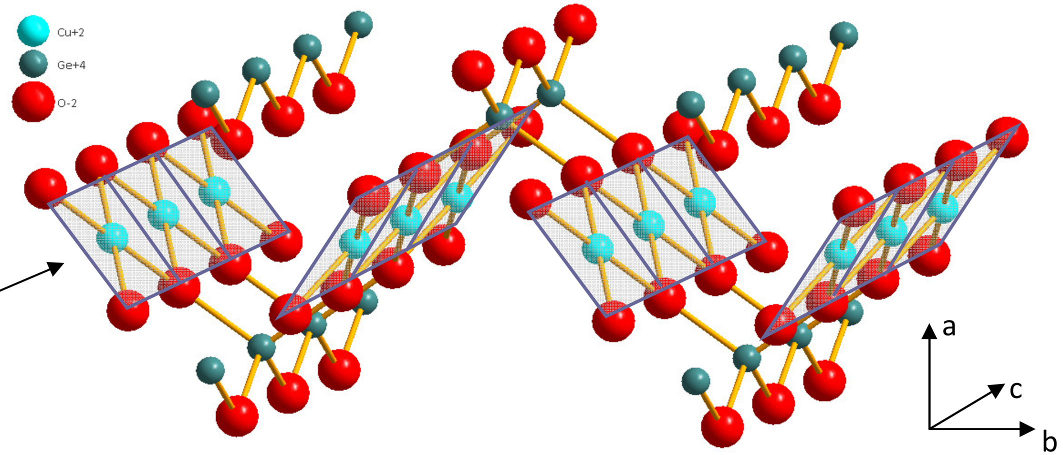

**high energy** interactions (U,Δ,t) are connected to **low energy** excitations:

- **ZRS** states close to $E_F$
- localized spins→**spin dynamics**

Further:

- QP couple to magnons/phonons
- phonons/magnons can influence high energy scales

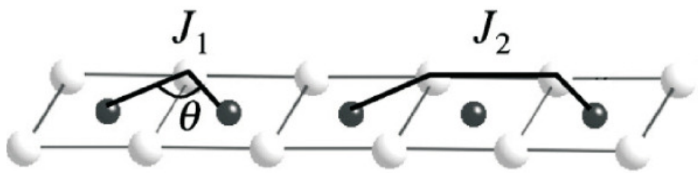
# $CuGeO_3$




$CuO_2$- chain

- model compound of one-dimensional edge-sharing cuprate
- composed by the same unit as the high-$T_c$ cuprates: $CuO_4$ plaquette
- $Cu^{2+}$: $3d^9$ S=1/2

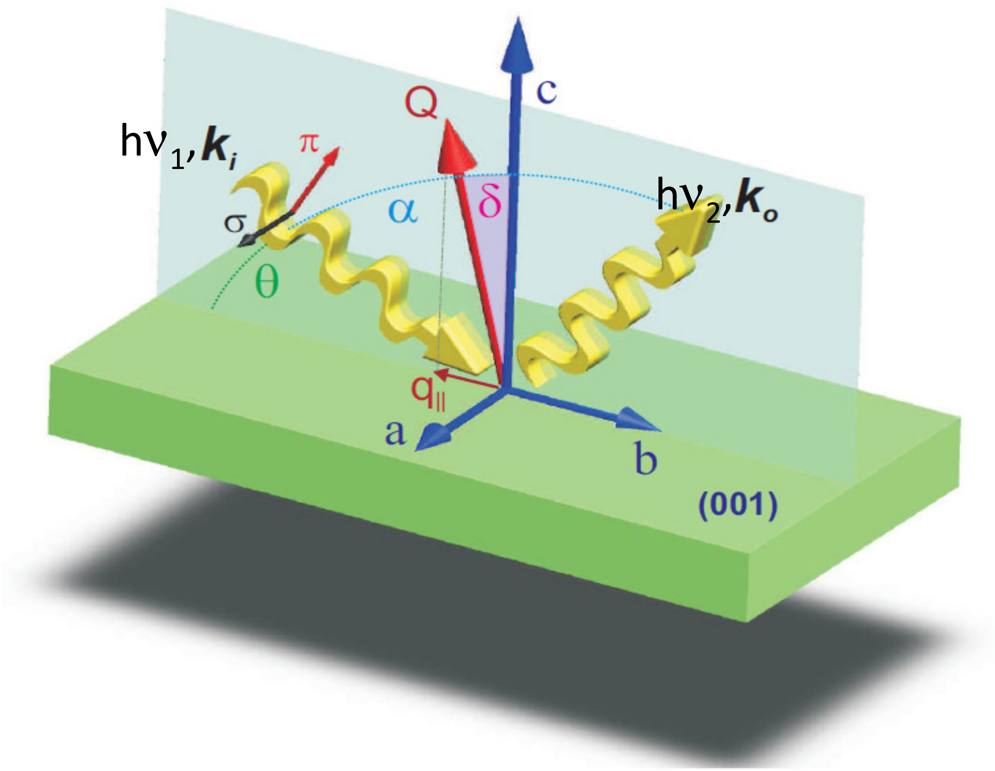
$CuO_2$ chain



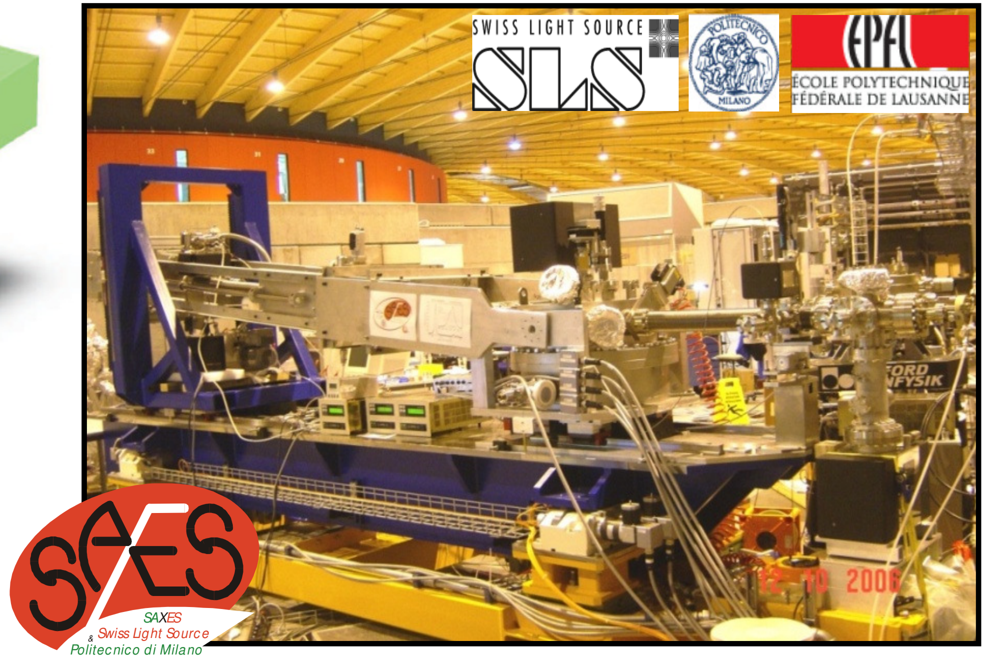

- $\theta$ = 99° ⇨ AFM $J_1$ (~160 K) and AFM $J_2$ ($\alpha \cdot J_1$~ 56 K)*
- Spin-Peierls transition at $T_{SP}$=14 K and dimerization starting at T<60K

*Fabricius et al., PRB **57**, 1102 (1998)

## Resonant Inelastic X-ray Scattering (RIXS)

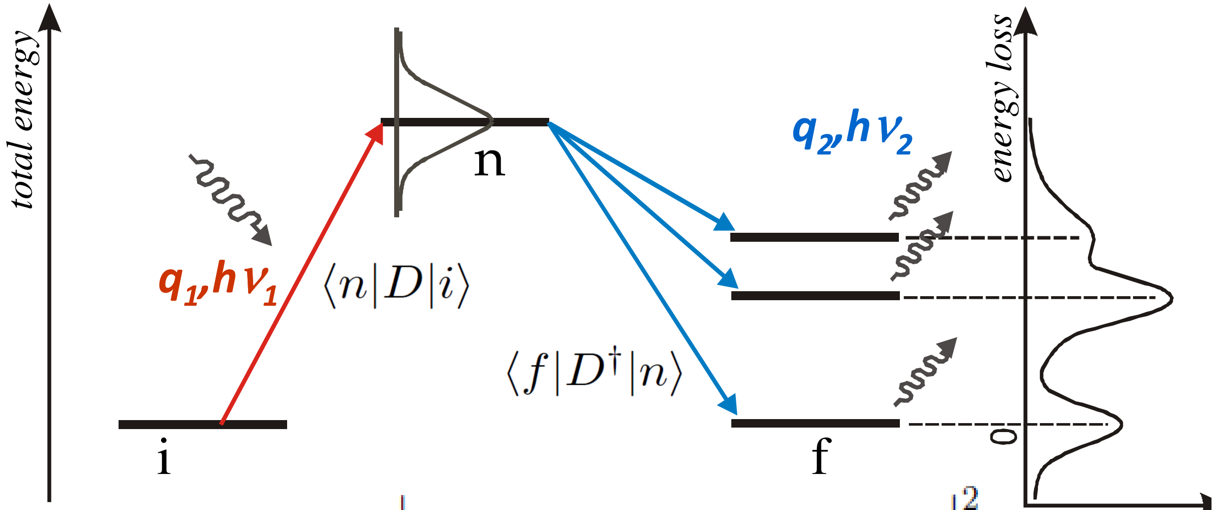



- photon *in* – photon *out*
- site and chemical selective
- energy loss: $\Delta E = h\nu_2 - h\nu_1$
- momentum transfer $\boldsymbol{Q}=\boldsymbol{k_o}-\boldsymbol{k_i}$
- in-plane Q projection: $\boldsymbol{q_{//}} \propto \boldsymbol{Q} \cdot \sin\delta$



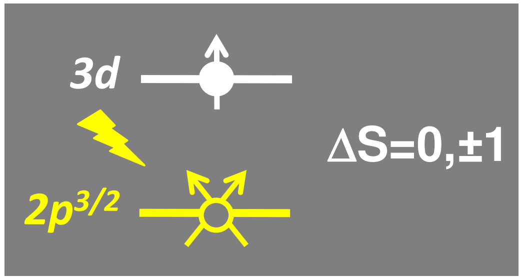

G. Ghiringhelli et al., Rev. Sci. Instrum. **77**, 113108 (2006)

*RIXS Review: L.J.K. Ament et al., arXiv1009.3630 (2010)



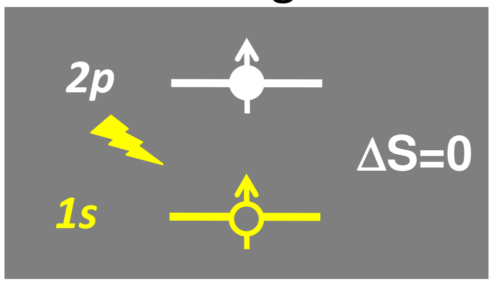

$$\frac{d^2\sigma}{d\Omega_2 d\hbar\omega_2} \propto \sum_f \left| \sum_n \frac{\langle f|D^\dagger|n\rangle\langle n|D|i\rangle}{E_i - E_n + \hbar\omega_1 - i\Gamma_n/2} \right|^2$$

**Cu-$L_3$** edge




- *d-d* excitations
- magnetic excitations (ΔS=0,1)

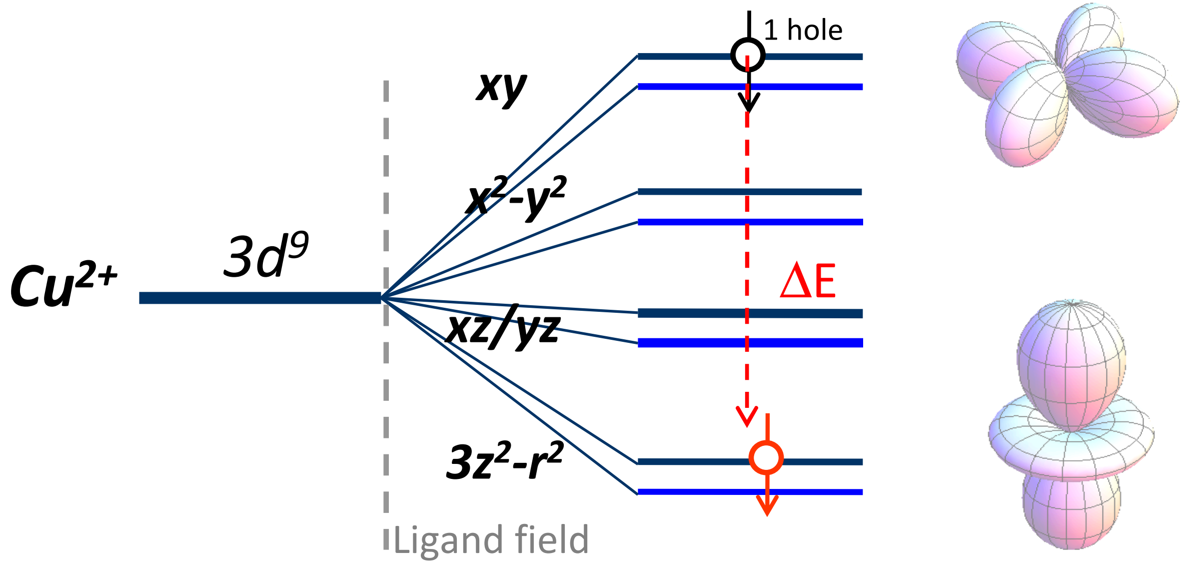
**O-K** edge




- *charge-transfer* excitations
- magnetic excitations (ΔS=0)
- *d-d* excitations

# Motivations

- intra-site *d-d* orbital excitations give information on the 3d valence band



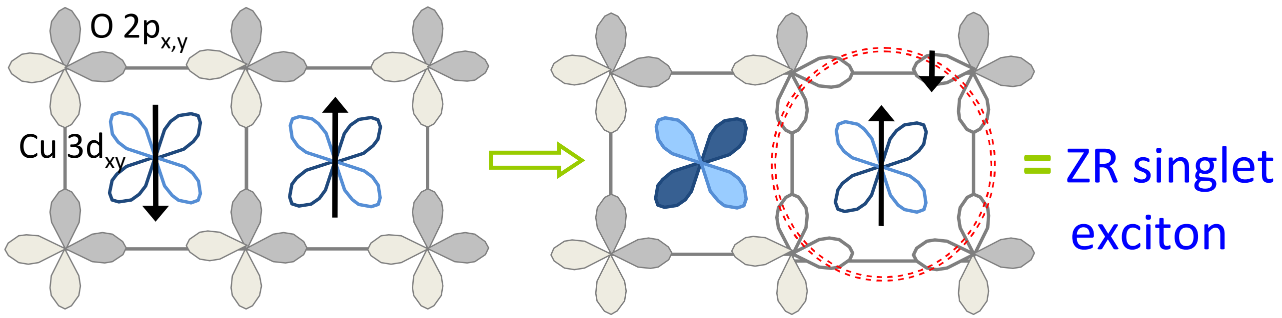

In high-$T_c$ cuprate, the $E_{x2-y2}$-$E_{z2}$ split is connected to $T_c$

PRL 105, 057003 (2010)

- inter-site charge-transfer excitations (Zhang-Rice singlet exciton) give information on the magnetic correlation at the low energy scale

AFM Initial state: $d^9{}_{\downarrow}$; $d^9{}_{\uparrow}$

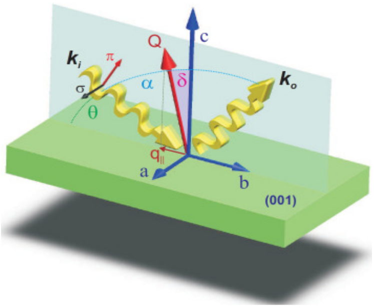
Final state: $d^9{}_{\downarrow}\underline{L}_{\uparrow}$; $d^{10}$

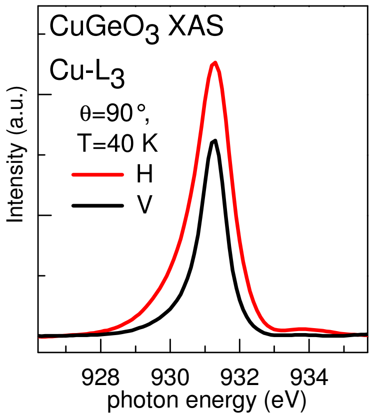


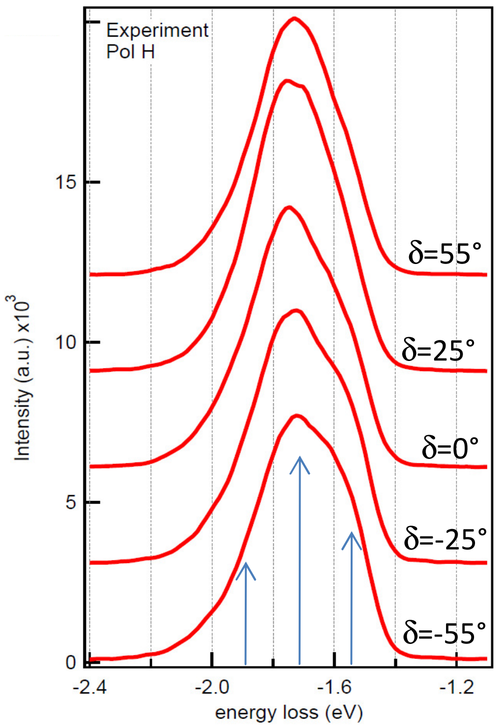
# *d-d* excitations at Cu-$L_3$ edge

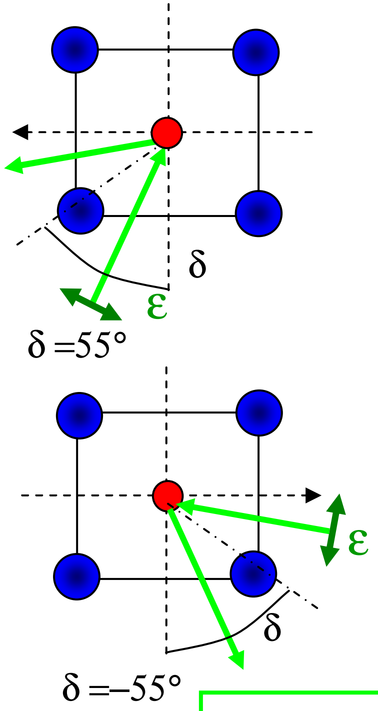
- *d-orbitals have strong spatial anysotropy*

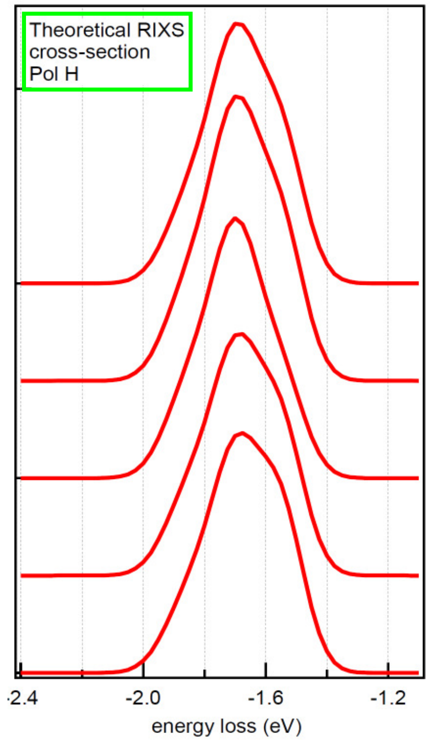
  *→ d-d excitations have strong ε dependence*
- single ion model *+ *ab-initio* quantum chemical calculations**



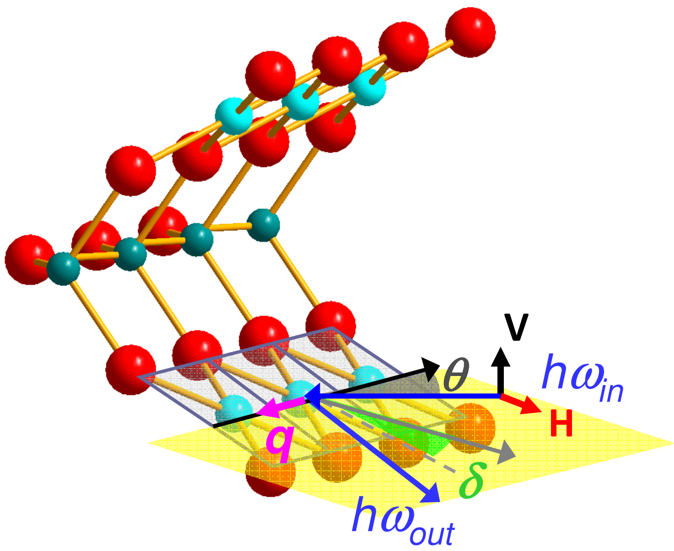



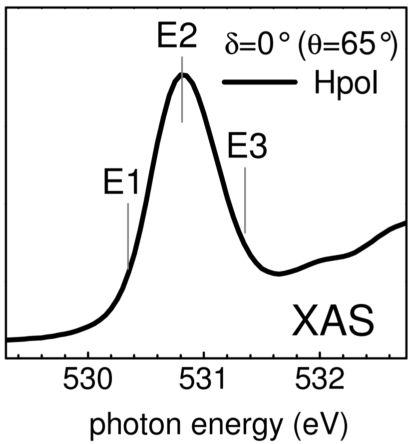

RIXS Energy resolution ΔE=120 meV

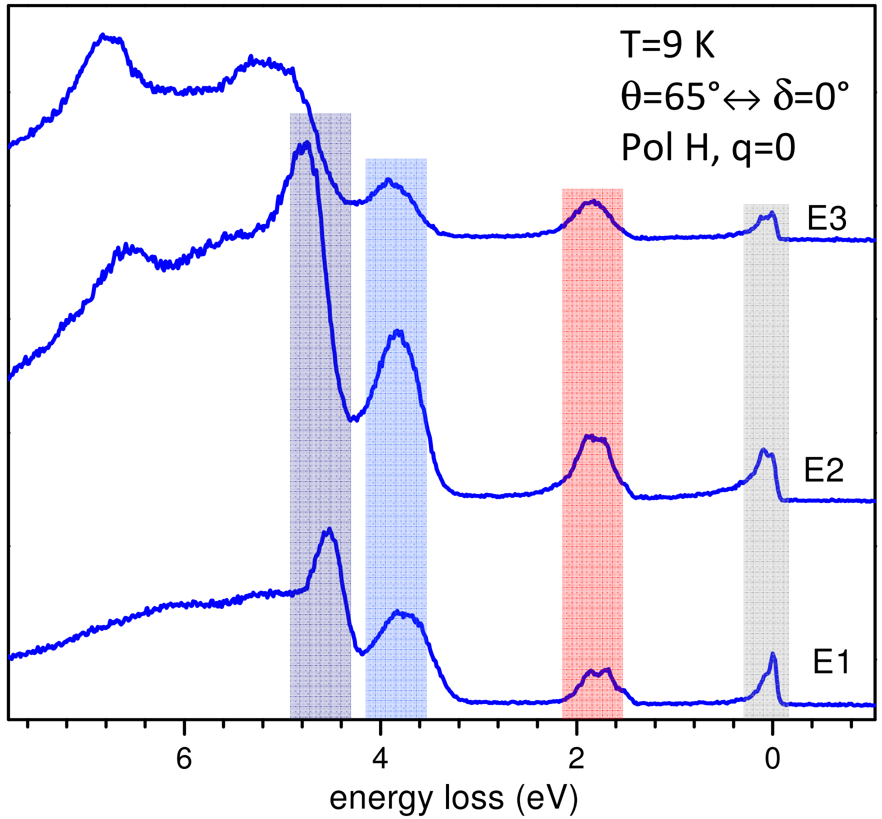
| | |
|---|---|
| $E_{xy}$=0 eV | |
| $E_{x^2-y^2}$=1.55 eV | $\Gamma_{x^2-y^2}$=0.12 eV |
| $E_{xz/yz}$=1.7 eV | $\Gamma_{xz/yz}$=0.125 eV |
| $E_{z^2}$=1.85 eV | $\Gamma_{z^2}$=0.14 eV |

* M. Moretti Sala et al., NJPhys **13**, 043026 (2011);

** L. Hozoi et al., ariXiv:**1012.3603** (2010)

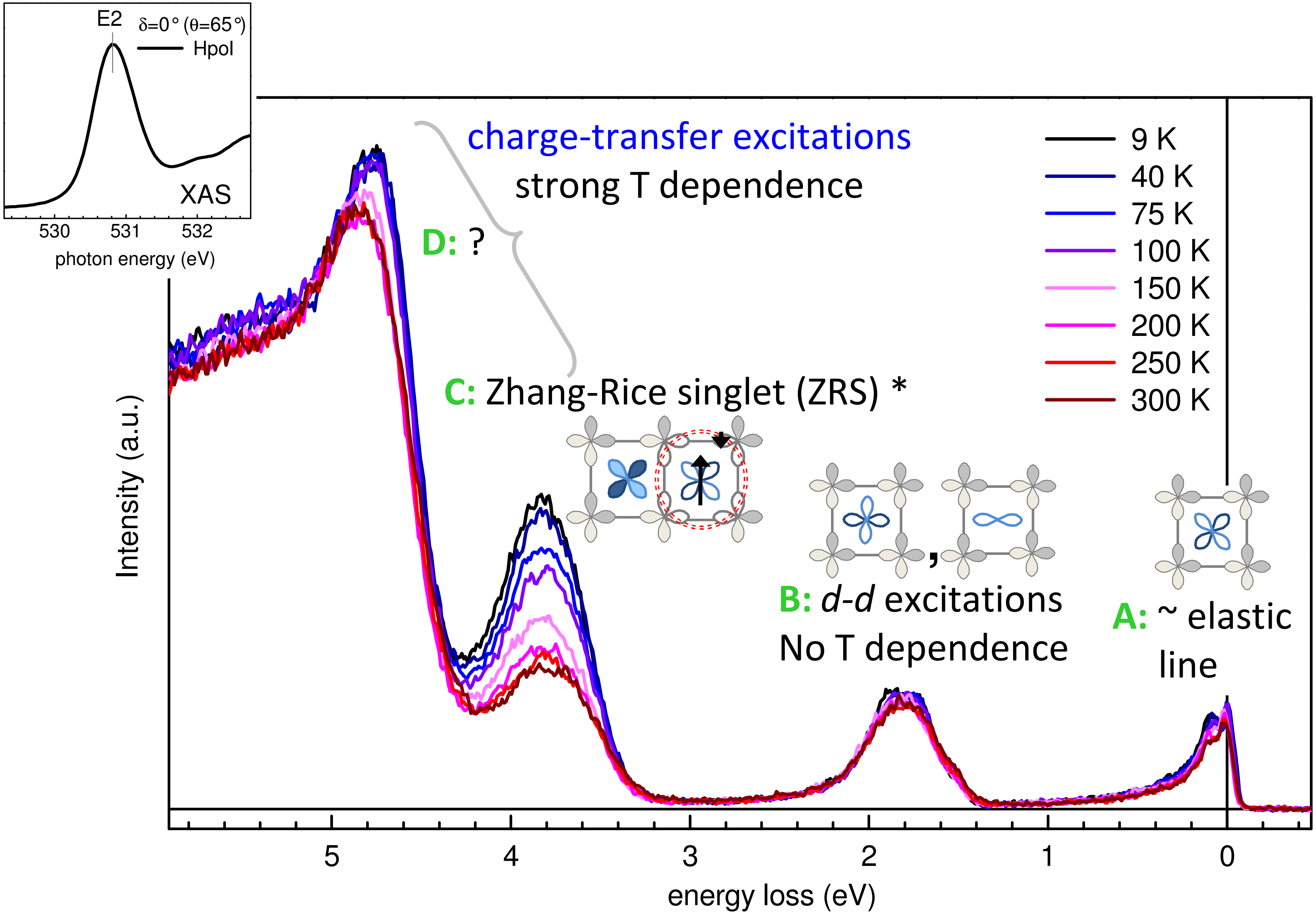


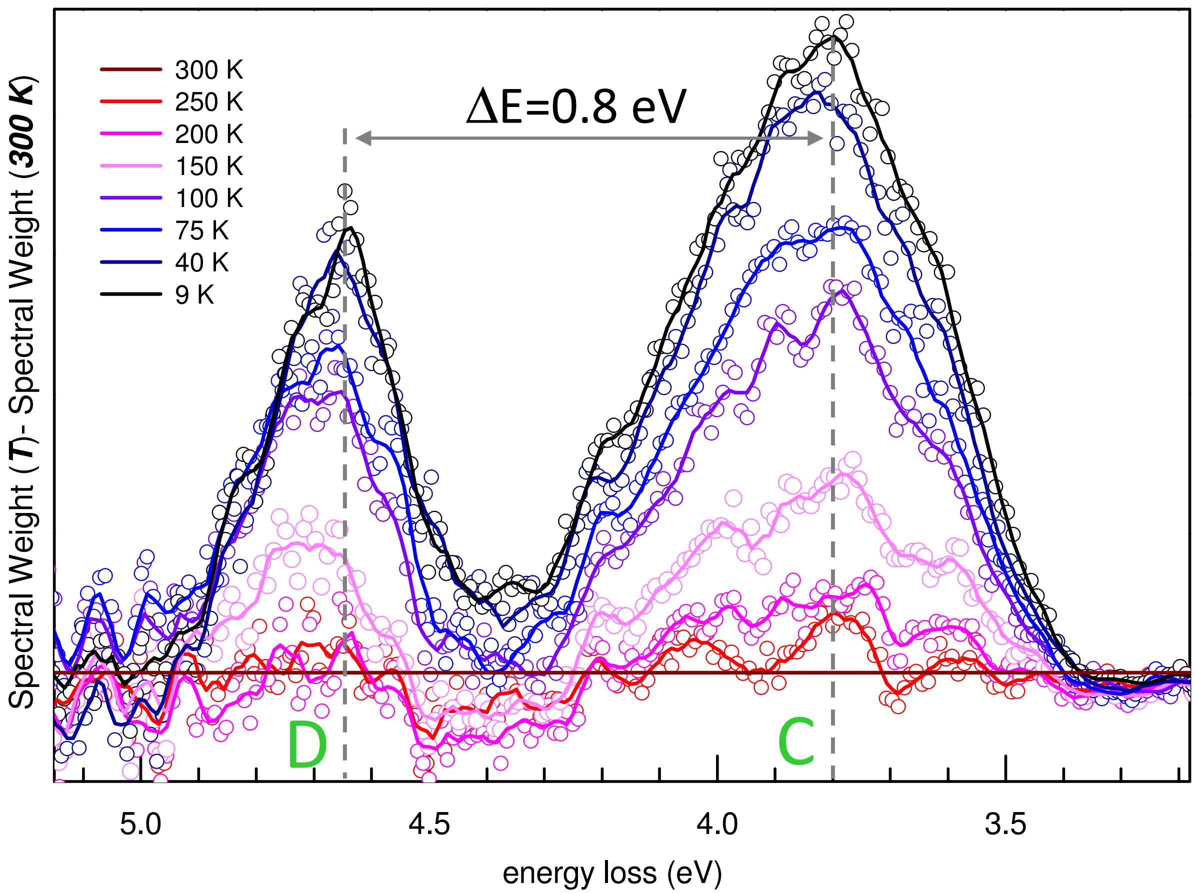

RIXS Energy resolution ΔE=60 meV

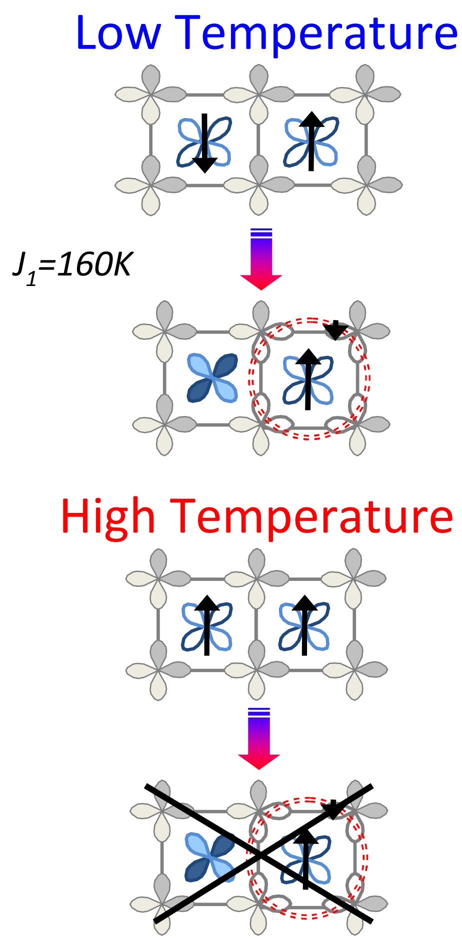
# Temperature dependence




* S. Atzkern et al., PRB **64**, 075112 (2001); J.Kim et al., PRB **79**, 094525 (2009)

# ZRS excitons T dependence



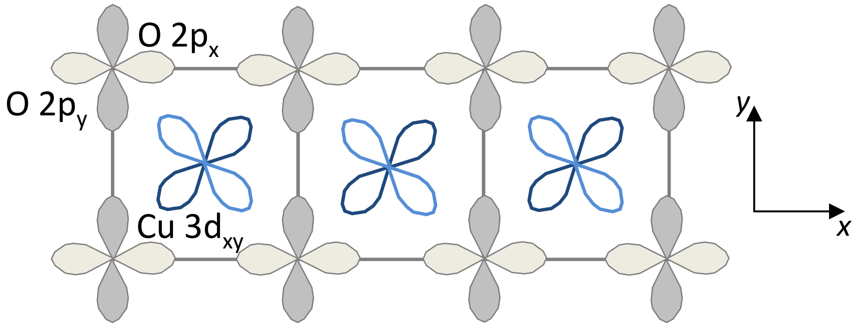

Peak C at 3.8 eV:

- Zhang-Rice singlet exciton*
- spectral weight depends on the nearest neighbor (NN) spin-spin correlation

Peak D at 4.6 eV

- Zhang-Rice object ⇔ same T trend as peak C
- What kind of ZR exciton?


* S. Atzkern et al., PRB **64**, 075112 (2001); J.Kim et al., PRB **79**, 094525 (2009)



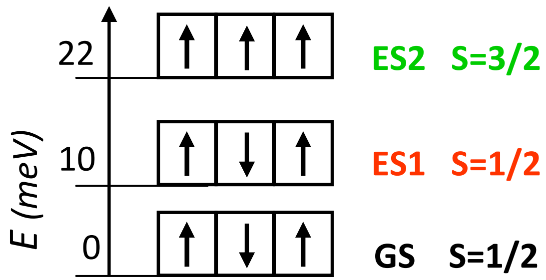

**Model:**

- cluster of 3 plaquettes with open boundary conditions;
- *pd*-Hamiltonian* based on $2p_x$ and $2p_y$ orbitals for O and $3d_{x2-y2}$ orbital for Cu;
- RIXS cross-section **:

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

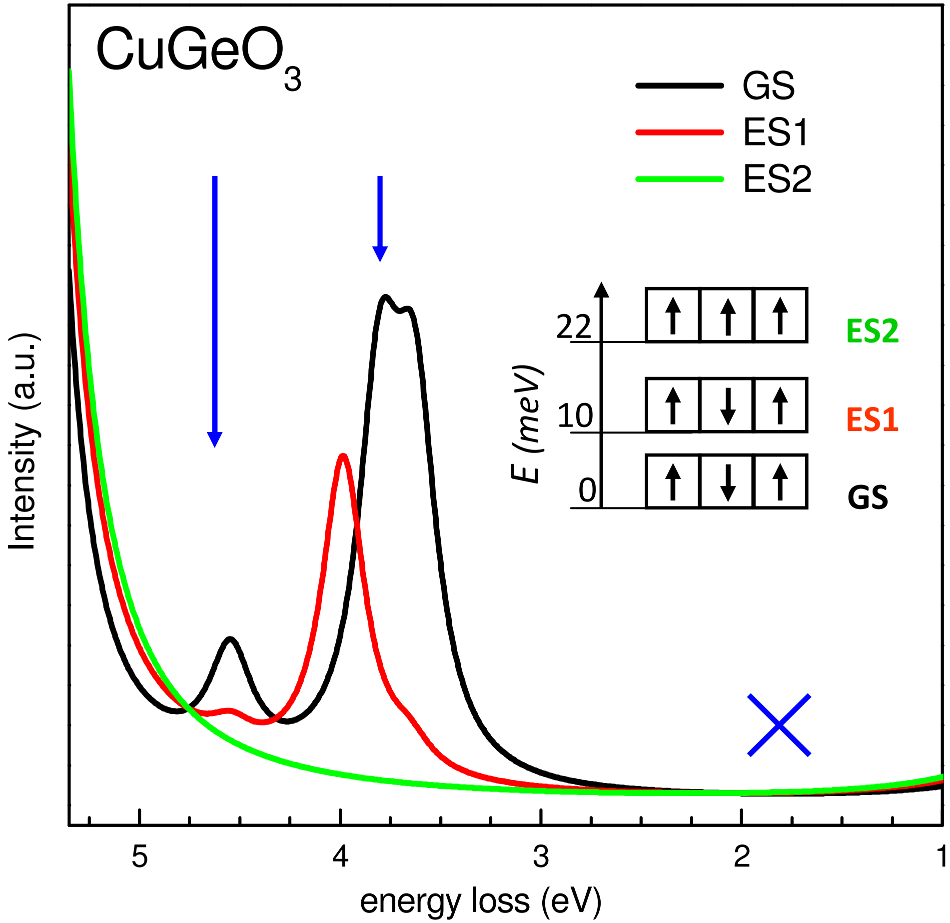
**Temperature dependence:**

- RIXS initial states ⇔ eigenstates which can be thermally polutated
- $\Delta S$=0 at the O-K edge

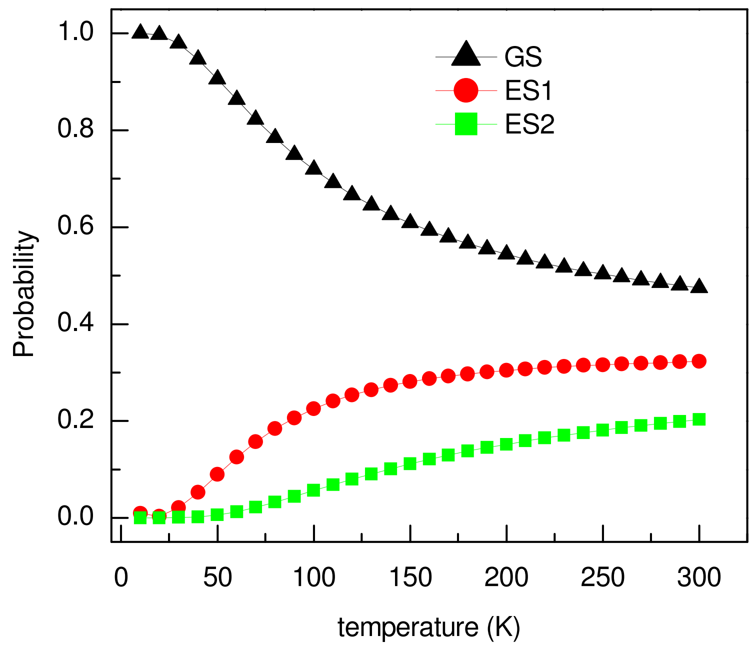



* Y. Mizuno et al., PRB **57**, 5326 (1998)
** K. Okada et al., JPJS **76**, 123706 (2007)

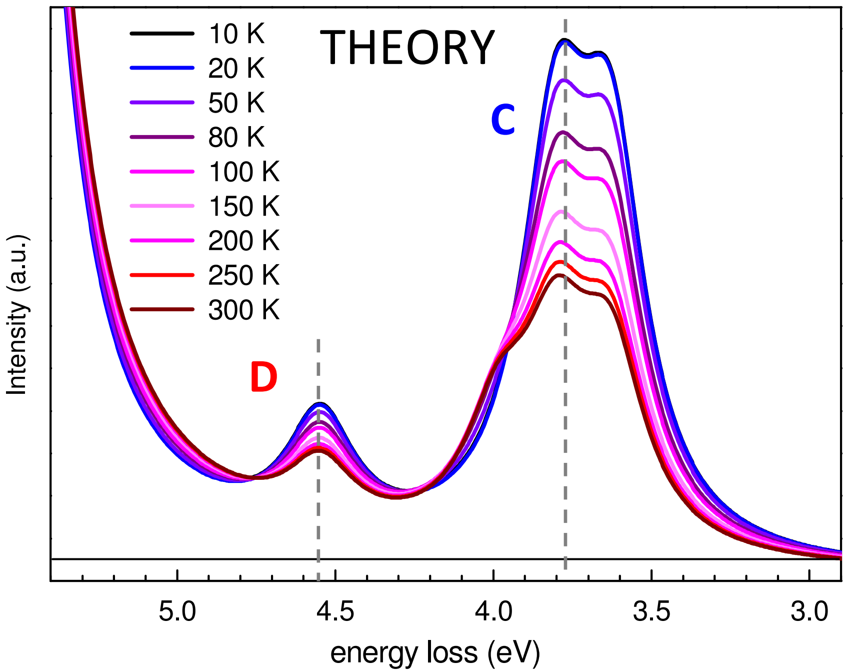
- fundamental RIXS spectra for $CuGeO_3$

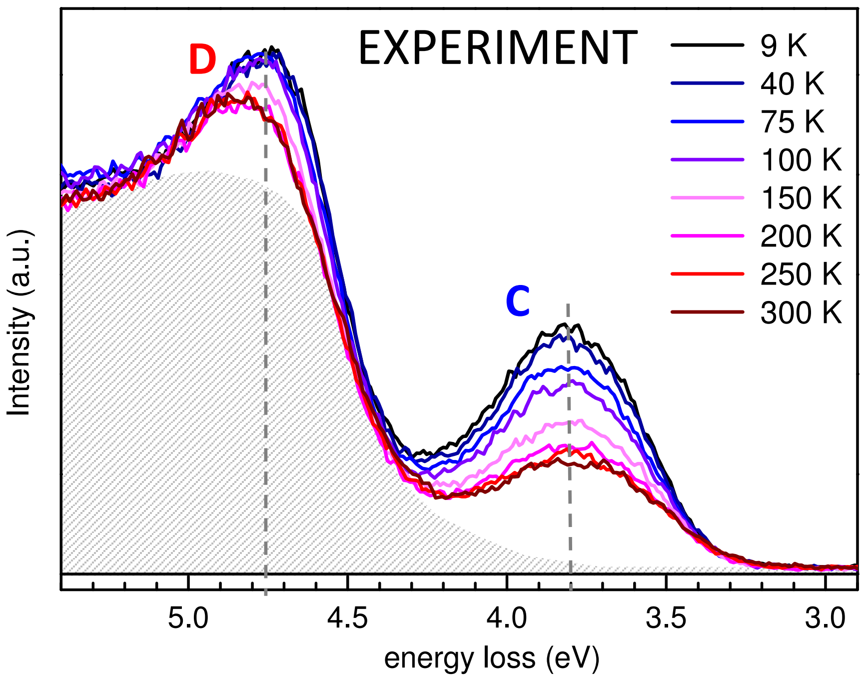


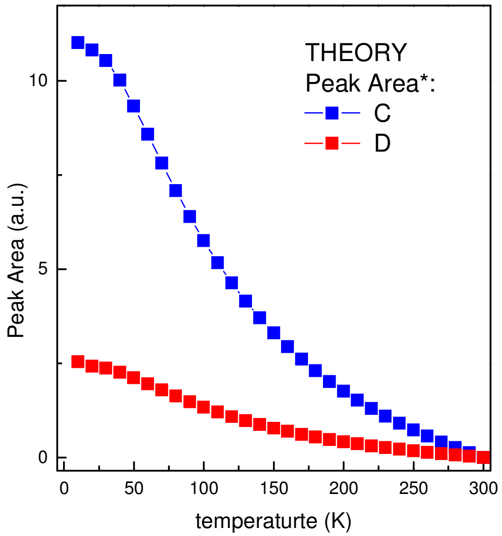

- weights for T dependence

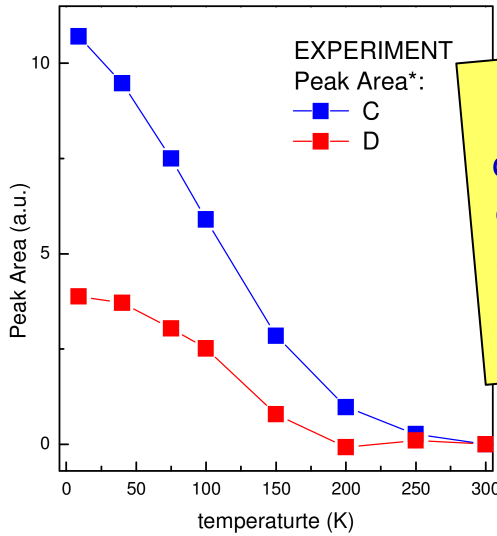


# O-K RIXS theory



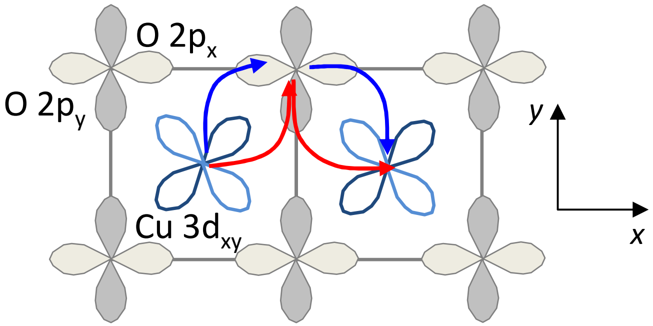




Temperature dependence of ZRS depends on the spin configuration at the ground state

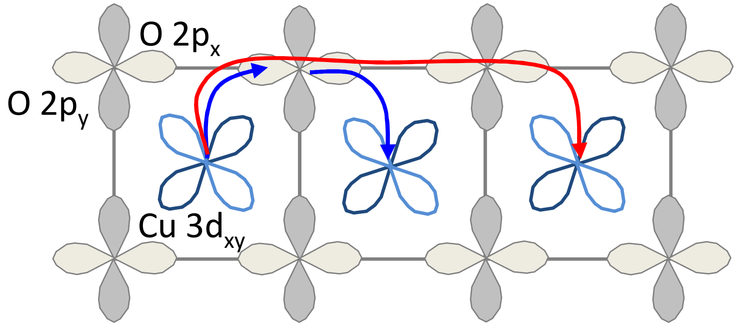
* After subtraction of the spectrum at 300 K

**Explanation 1:**




Two ZRS peaks →
charge-transfer paths through Op$_x$ and Op$_y$

**Explanation 2:**

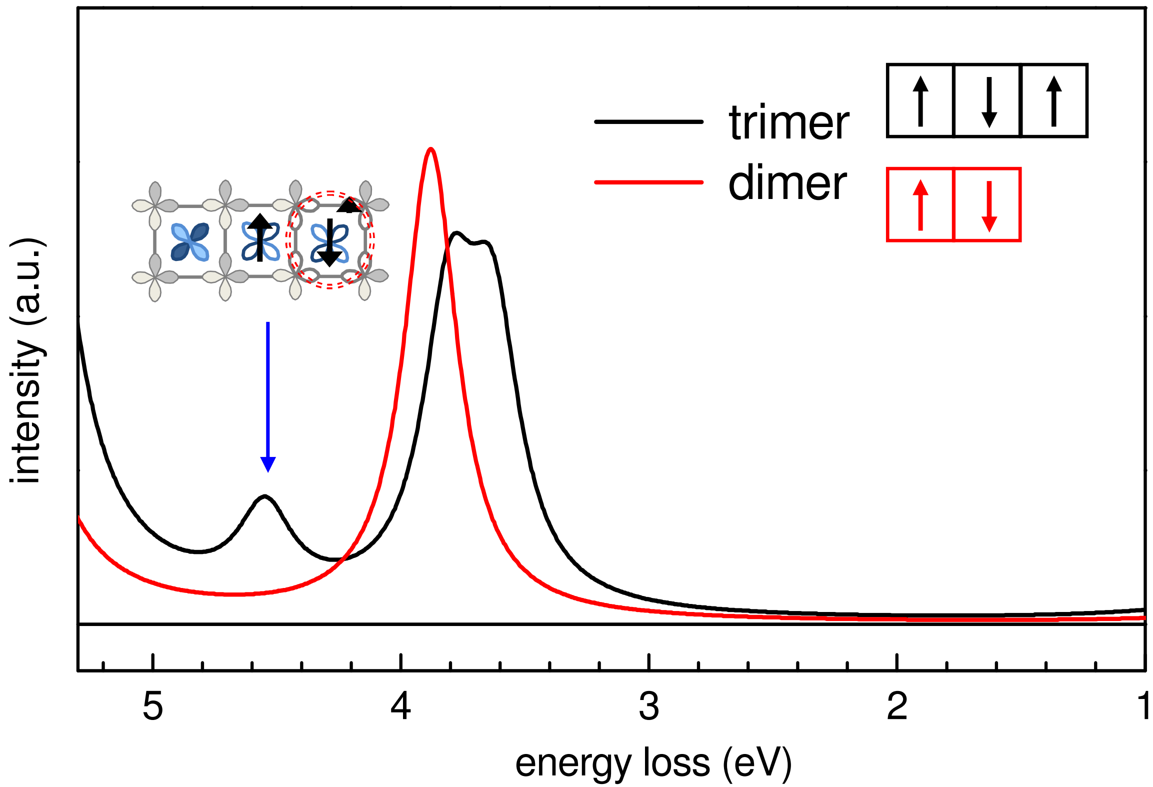



Two ZRS peak→
charge transfer path between nearest-neighbor (NN) and next-nearest neighbor (NNN)*

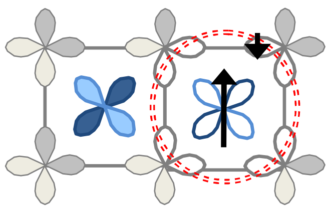
RIXS calculation on a dimer (two-plaquette cluster)

* Y. Matiks et al., PRL **103**,187401 (2009)

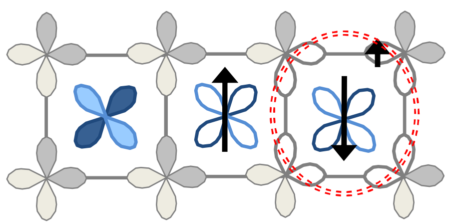
# O-K RIXS theory




- **4.5 eV peak** is present only in the trimer
  → **NNN ZRS exciton**
- **trimer** is the smallest cluster which describes



and



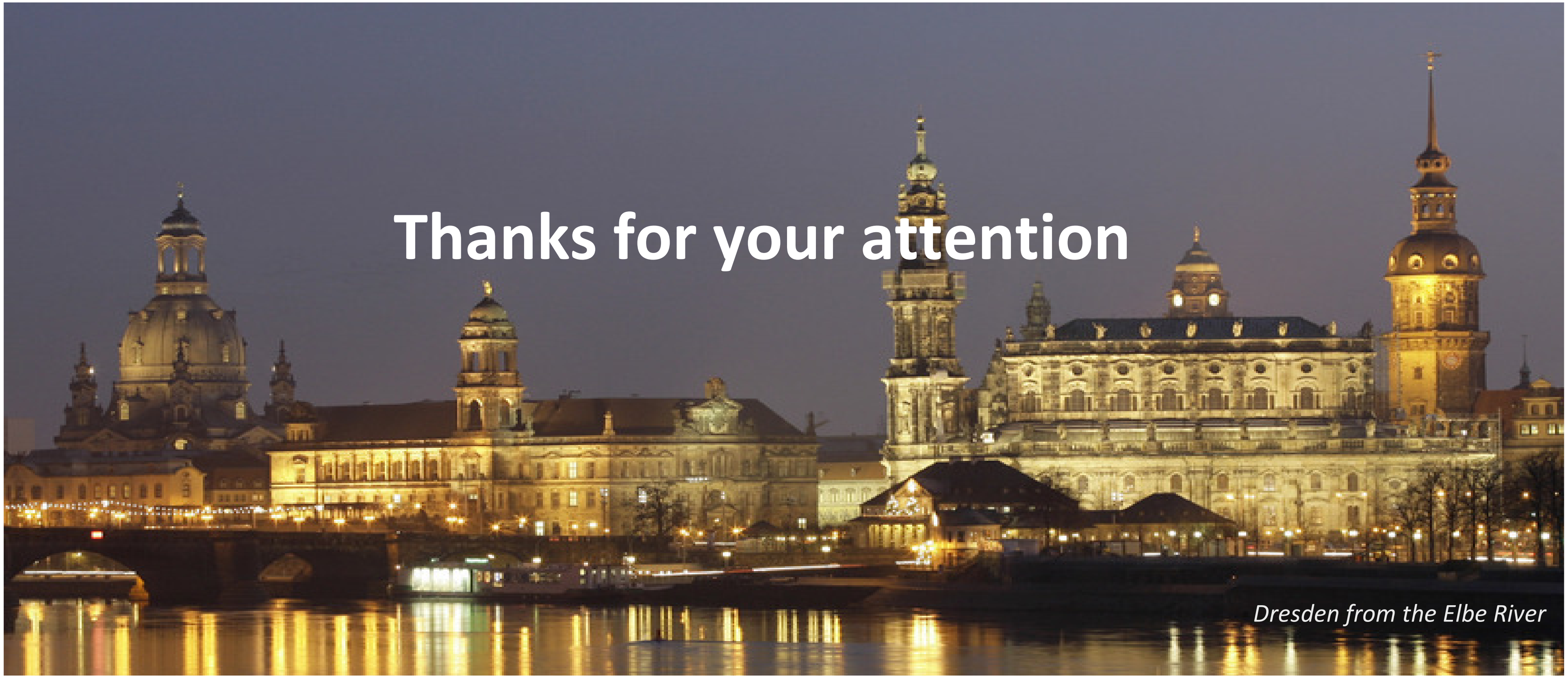
# Conclusions

• deep understanding of *d-d* excitations energy and symmetry in $CuGeO_3$ by Cu-$L_3$ RIXS

• clear evidence of NN and NNN Zhang-Rice singlet excitons enhanced by O-K RIXS

• the temperature dependence of the ZRS excitons is linked to the local magnetic correlation at the ground state

• high-energy charge-transfer excitations (~4 eV) are directly connected to the magnetic phenomena at much lower energy scale ($J_1$~10 meV)



*Dresden from the Elbe River*