Mechanism of temperature dependence of RIXS spectra in charge transfer insulators

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Acknowledgment

- **Theory:**
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- **Experiment:**
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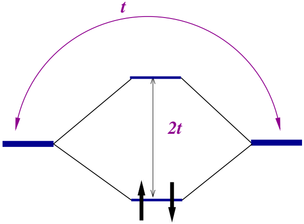
Overview

- T - dependence of charge response of strongly correlated systems
- O-K RIXS calculation
- Analytic consideration of "Cu-O-Cu" cluster
- RIXS spectra for ESC
- Conclusions

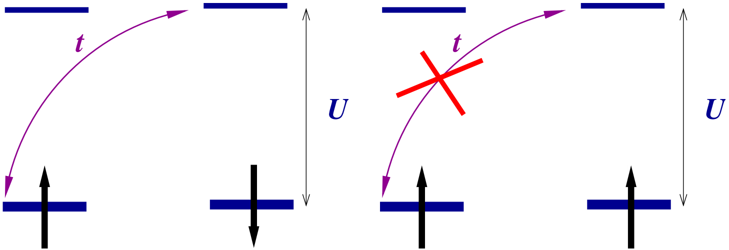
H_2 molecule, Hückel MO approach



$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}}[\phi_1(r) \pm \phi_2(r)],$$
$$|g\rangle = a^\dagger_{+,\uparrow} a^\dagger_{-,\downarrow} |vac\rangle$$
$$\Delta E = E_1 - E_0 = 2t$$
$$P_2 = P_{11}$$

Changes in charge response are expected at $T \sim 2t$

H_2 molecule, H-L approach

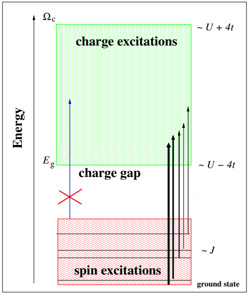


$$|g\rangle = \frac{1}{\sqrt{2}}\left[a^\dagger_{1,\uparrow}a^\dagger_{2,\downarrow} - a^\dagger_{1,\downarrow}a^\dagger_{2,\uparrow}\right]|vac\rangle - \frac{2t}{U}|s_i\rangle\,, \quad P_2 < P_{11}$$

$$|t\rangle = a^\dagger_{1,\uparrow}a^\dagger_{2,\uparrow}|vac\rangle\,, \quad \Delta E = E_1 - E_0 = \frac{4t^2}{U} = J \ll t$$

Changes in charge response are expected at $T \sim J$

Mott insulator

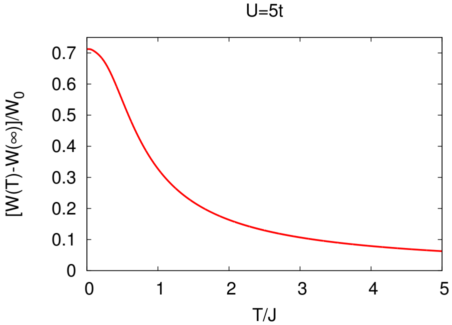


$$\hat{H} = \hat{K} + \hat{U},$$
$$\hat{K} = -t \sum_{\langle i,j \rangle,\sigma} d^{\dagger}_{i,\sigma} d_{j,\sigma},$$
$$\hat{U} = U \sum_{i} d^{\dagger}_{i,\uparrow} d_{i,\uparrow} d^{\dagger}_{i,\downarrow} d_{i,\downarrow}$$

$$\sigma_{\alpha\alpha}(\omega) = \frac{1}{V} \left\langle \left\langle \hat{P}^{\alpha} | \hat{J}^{\alpha} \right\rangle \right\rangle$$

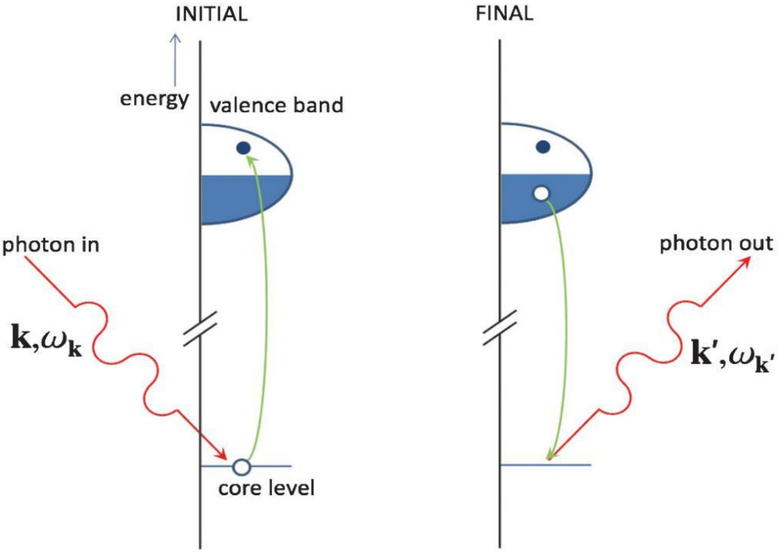
$$W(T) = \frac{\tilde{\omega}_p^2}{8} = \frac{\pi}{2V} \left\langle \left[\left[\hat{P}^{\alpha}, \hat{H} \right], \hat{P}^{\alpha} \right] \right\rangle = -\frac{\pi e^2 a \left\langle \hat{K} \right\rangle}{2Nd^2\hbar^2}$$

$$W(T) = -\frac{\pi e^2 a}{2d^2\hbar^2}(t\partial_t J)\left(C_\delta(T) - \frac{1}{4}\right),$$

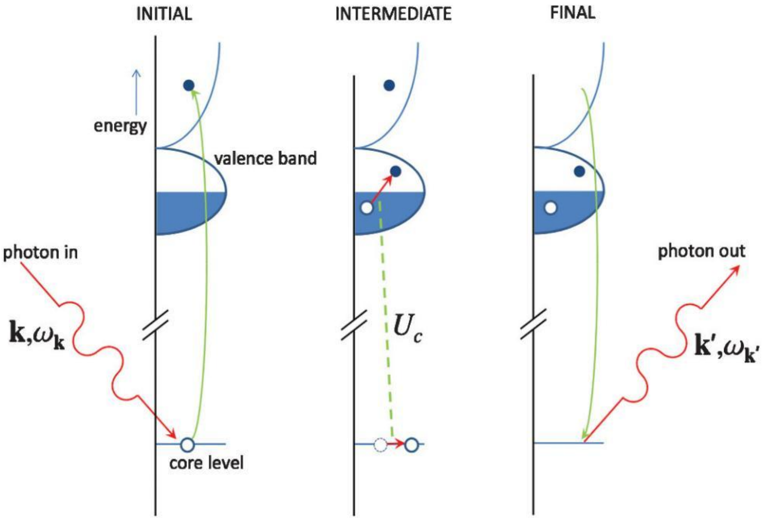


$$t\partial_t J = \frac{8t^2}{U} - \cdots .$$

Direct process



Indirect process



wrt the solid angle $\Omega_{\mathbf{k}_2}$ and energy ω

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}_2} d\omega} = \frac{\omega^2}{c^4}\left(\frac{1}{2\pi}\right)^3 W_{12},$$

$$W_{12} = \sum_f \frac{(2\pi)^3}{\Omega\omega}\left(\frac{e^2}{m}\right)^2 \delta\left(E_g + \Omega - E_f - \omega\right)$$

$$\times \left| \langle f|\, \rho_{\mathbf{k}_1 - \mathbf{k}_2} \,|g\rangle \sum_\mu \epsilon'_\mu \epsilon_\mu \right.$$

$$+ \frac{1}{m}\sum_{i,\mu,\nu}\left(\frac{\langle f|\, \epsilon'_\mu p_\mu\left(\mathbf{k}_2\right)|i\rangle \langle i|\, \epsilon_\nu p_\nu\left(-\mathbf{k}_1\right)|g\rangle}{E_i - \Omega - E_g}\right.$$

$$\left. + \frac{\langle f|\, \epsilon_\nu p_\nu\left(\mathbf{k}_1\right)|i\rangle \langle i|\, \epsilon'_\mu p_\mu\left(-\mathbf{k}_2\right)|g\rangle}{E_i + \omega - E_g}\right)\Bigg|^2,$$

$$\text{where } \mathbf{p}\left(\mathbf{k}\right) = \sum_n \mathbf{p}_n \exp\left(-\imath \mathbf{k}\cdot\mathbf{r}_n\right),\ \rho\left(\mathbf{k}\right) = \sum_n \exp\left(-\imath \mathbf{k}\cdot\mathbf{r}_n\right)$$

RIXS spectrum

$$
\begin{aligned}
I(\Omega,\omega,\vec{\epsilon},\vec{\epsilon}') &\propto \sum_f \left|F_{fg}(\Omega,\vec{\epsilon},\vec{\epsilon}')\right|^2 \delta\left[\Omega-\omega-(E_f-E_g)\right] \\
F_{fg}(\Omega,\vec{\epsilon},\vec{\epsilon}') &= \sum_i \frac{\langle f|\,\epsilon'_\mu p_\mu(\mathbf{k}_2)\,|i\rangle\,\langle i|\,\epsilon_\nu p_\nu(-\mathbf{k}_1)\,|g\rangle}{E_g+\Omega-E_i-\imath\Gamma} \\
&= \langle f|\,\hat{D}^\dagger\hat{G}(E_g+\Omega-\imath\Gamma)\hat{D}\,|g\rangle\,, \\
\hat{G}(z) &= \sum_i \frac{|i\rangle\,\langle i|}{z-E_i} = (z-\hat{H})^{-1}
\end{aligned}
$$

$\Gamma \sim 1$ eV is the spectral broadening due to the core- hole lifetime

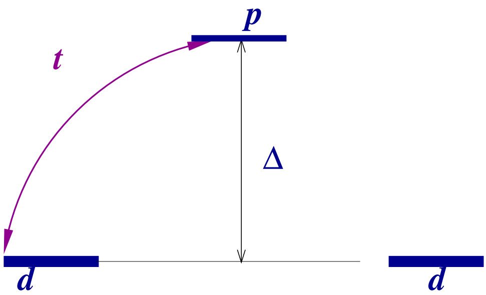
O K-edge RIXS spectrum

$$
\begin{aligned}
F_{fg}(\Omega,\vec{\epsilon},\vec{\epsilon}') &= \sum_{\mathbf{R},m,\mu,\nu} \frac{\langle \mathrm{f}|\,\epsilon'_\mu\,\hat{T}_{\mu,\mathbf{R}}\,|m,\mathbf{R}\rangle\,\langle m,\mathbf{R}|\,\epsilon_\nu\,\hat{T}_{\nu,\mathbf{R}}\,|\mathrm{g}\rangle}{E_g+\Omega-E_{m,\mathbf{R}}-\imath\Gamma} \\
\hat{T}_{\mu,\mathbf{R}} &= \sum_\sigma s^\dagger_{\mathbf{R}\sigma} p_{\mathbf{R}\mu\sigma} + h.c. \\
\hat{H}_{\mathbf{R}} &= \hat{H}_{pd} + \hat{H}_{C,\mathbf{R}}, \\
\hat{H}_{C,\mathbf{R}} &= \varepsilon_s \sum_\sigma s^\dagger_{\mathbf{R}\sigma} s_{\mathbf{R}\sigma} + U_C \sum_{\sigma,\sigma',\mu} s^\dagger_{\mathbf{R}\sigma} s_{\mathbf{R}\sigma} p^\dagger_{\mathbf{R}\mu\sigma'} p_{\mathbf{R}\mu\sigma'}.
\end{aligned}
$$

"Alchemical" approximation

$$\begin{aligned}
\hat{H}'_{pd,\mathbf{R}} &= \hat{H}_{pd} + U_C \sum_{\sigma,\alpha} p^{\dagger}_{\mathbf{R}\alpha\sigma} p_{\mathbf{R}\alpha\sigma} \\
U_C &\sim \varepsilon_{\mathrm{O},2p} - \varepsilon_{\mathrm{F},2p} \sim 3 - 5\ \mathrm{eV}, \\
I_g(\Omega, \omega, \vec{\epsilon}, \vec{\epsilon}') &= \sum_f \left| \sum_{\mathbf{R},\mu,\nu} \epsilon'_\mu \epsilon_\nu M^{fg}_{\mathbf{R}\mu\nu}(\Omega) \right|^2 \delta\left(E_g + \Omega - E_f - \omega\right), \\
M^{fg}_{\mathbf{R}\mu\nu}(\Omega) &= \sum_\sigma \langle f|\, p^{\dagger}_{\mathbf{R}\mu\sigma} \frac{1}{z - \hat{H}'_{pd,\mathbf{R}} - \varepsilon_s} p_{\mathbf{R}\nu\sigma} \,|g\rangle\,, \\
z &\equiv E_g + \Omega - \imath\Gamma.
\end{aligned}$$

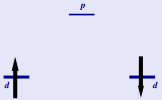
"Cu-O-Cu" cluster



$$\hat{H}_{pd} = \Delta \sum_{\sigma} p_{\sigma}^{\dagger} p_{\sigma} + t \sum_{i,\sigma} \left(\tilde{d}_{i,\sigma}^{\dagger} p_{\sigma} + p_{\sigma}^{\dagger} \tilde{d}_{i,\sigma} \right)$$

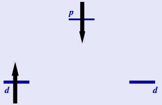
$$\tilde{d}_{i,\sigma} \equiv = d_{\sigma} \left(1 - d_{-\sigma}^{\dagger} d_{-\sigma} \right)$$

$$|s_d\rangle = \frac{1}{\sqrt{2}}\left(\tilde{d}^\dagger_{1,\uparrow}\tilde{d}^\dagger_{2,\downarrow} - \tilde{d}^\dagger_{1,\downarrow}\tilde{d}^\dagger_{2,\uparrow}\right)|vac\rangle + \cdots\,, \qquad \phi = \arcsin\frac{R}{\sqrt{Q^3}},$$



$$E_0 = \Delta - 2\sqrt{Q}\left(\frac{\sqrt{3}}{2}\cos\frac{\varphi}{3} + \frac{1}{2}\sin\frac{\varphi}{3}\right) \approx -\frac{2t^2}{\Delta},$$

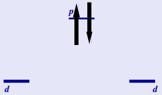
$$|ZRSs\rangle = \frac{1}{\sqrt{2}}\left[|ZRS,1\rangle + |ZRS,2\rangle\right] + \cdots\,, \qquad R = -t^2\Delta$$



$$|ZRS,i\rangle = \frac{1}{\sqrt{2}}\left(\tilde{d}^\dagger_{i,\uparrow}p^\dagger_\downarrow - \tilde{d}^\dagger_{i,\downarrow}p^\dagger_\uparrow\right)|vac\rangle$$

$$E_1 = \Delta + 2\sqrt{Q}\sin\frac{\varphi}{3} \approx \Delta - \frac{2t^2}{\Delta}\left(1 - \frac{6t^2}{\Delta^2}\right),$$

$$|s_p\rangle = p^\dagger_\uparrow p^\dagger_\downarrow|vac\rangle + \cdots\,, \qquad Q = \frac{1}{3}\left(\Delta^2 + 6t^2\right),$$

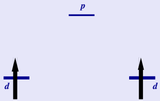


$$E_2 = \Delta + 2\sqrt{Q}\left(\frac{\sqrt{3}}{2}\cos\frac{\varphi}{3} - \frac{1}{2}\sin\frac{\varphi}{3}\right)$$

$$\approx 2\Delta + \frac{4t^2}{\Delta} - \frac{12t^4}{\Delta^3}.$$

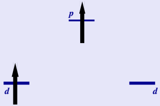
Triplet sector, $S = 1, S^z = 1$

$$|t_d\rangle = \tilde{d}^\dagger_{1,\uparrow}\tilde{d}^\dagger_{2,\uparrow}|vac\rangle + \cdots ,$$



$$E_{t,0} = \frac{\Delta}{2}\left(1 - R_t\right) \approx -\frac{2t^2}{\Delta} + \frac{4t^4}{\Delta^3},$$

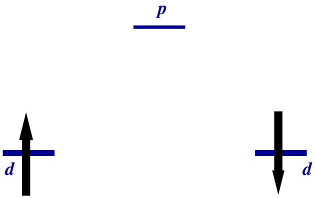
$$|ZRT\rangle = \frac{1}{\sqrt{2}} p^\dagger_\uparrow \left(\tilde{d}^\dagger_{2,\uparrow} - \tilde{d}^\dagger_{1,\uparrow}\right)|vac\rangle . + \cdots ,$$



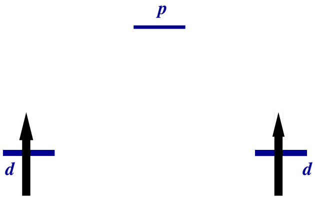
$$E_{t,1} = \frac{\Delta}{2}\left(1 + R_t\right) \approx \Delta + \frac{2t^2}{\Delta} - \frac{4t^4}{\Delta^3},$$

Low-enegry spectrum. "Magnetic" states

In the subspace of the states $|s_d\rangle$ and $|t_d\rangle \approx$,



, and



the system has only spin degrees of freedom, which are described by an effective Heisenberg Hamiltonian

$$\begin{aligned}\hat{J} &= J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + 2e_d, \\ J &= E_{t,0} - E_0 \approx 4t^4/\Delta^3 \ll t, \Delta, \\ 2e_d &= -2t^2/\Delta.\end{aligned}$$

Intermediate state

The eigenenergies of even states are

$$E_{\pm} = \frac{\Delta + U_C}{2} \pm \sqrt{1 + 8 \left[t / \left(\Delta + U_C \right) \right]^2},$$

An odd state

$$|\sigma, a\rangle = \frac{1}{\sqrt{2}} \left(\tilde{d}^{\dagger}_{1,\sigma 0} - \tilde{d}^{\dagger}_{2,\sigma 0} \right) |vac\rangle$$

has the energy

$$E_a = 0.$$

O K RIXS spectrum for finite temperature

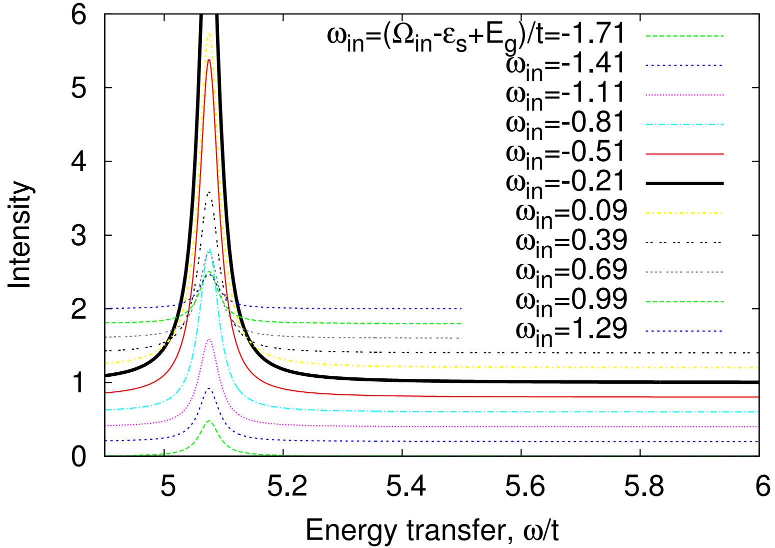
$$I(T,\Omega,\omega,\vec{\epsilon},\vec{\epsilon}') = \left\langle I_g(\Omega,\omega,\vec{\epsilon},\vec{\epsilon}')\right\rangle_T$$
$$= \frac{\sum_g \exp(-E_g/kT) I_g(\Omega,\omega,\vec{\epsilon},\vec{\epsilon}')}{\sum_g \exp(-E_g/kT)},$$

For $T \sim J \ll \Delta$

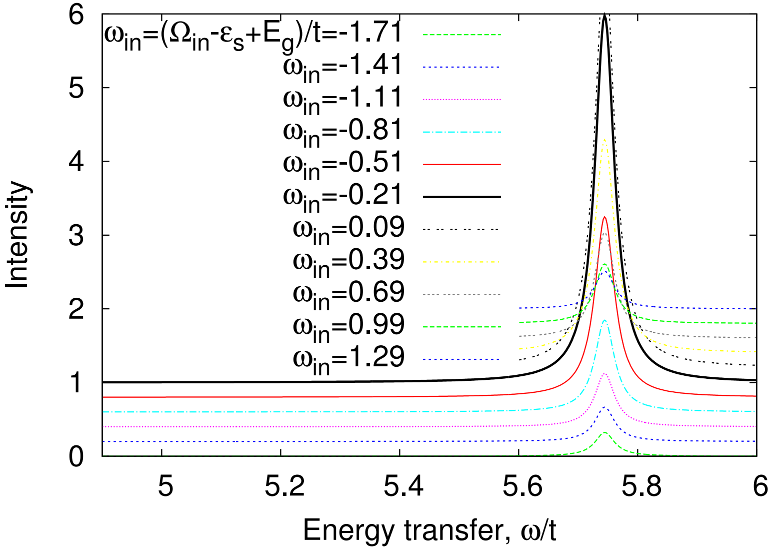
$$I(T,\Omega,\omega) = w_s I_0(\Omega,\omega) + w_t I_t(\Omega,\omega),$$

where $w_s = 1/Q(T)$, $w_t = 3\exp(-J/kT)/Q(T)$,
$Q(T) = 1 + 3\exp(-J/kT)$.

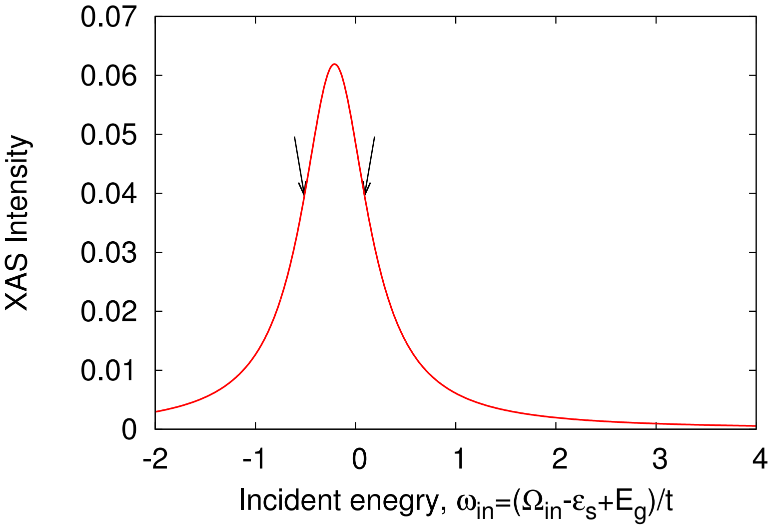
$|s_d\rangle$ starting state



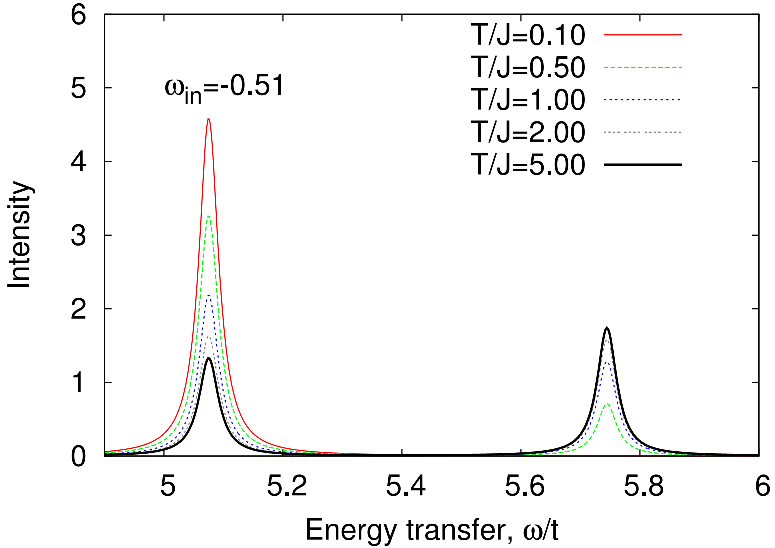
$|t_d\rangle$ starting state



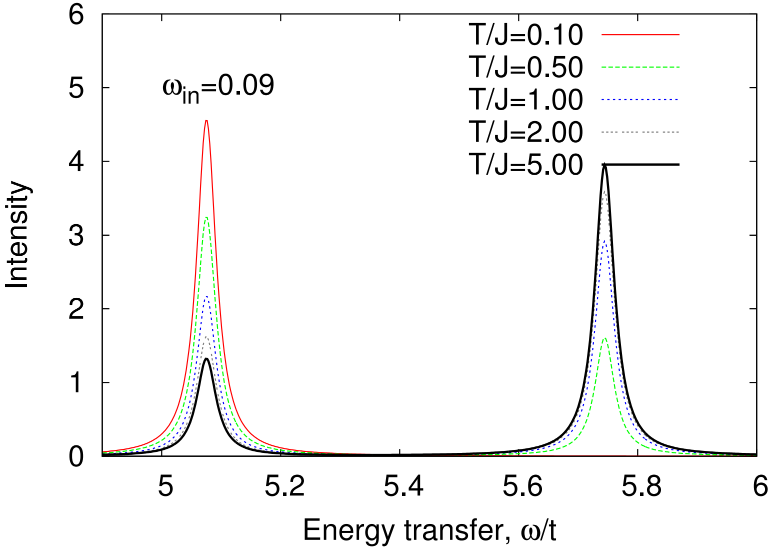
XAS spectrum



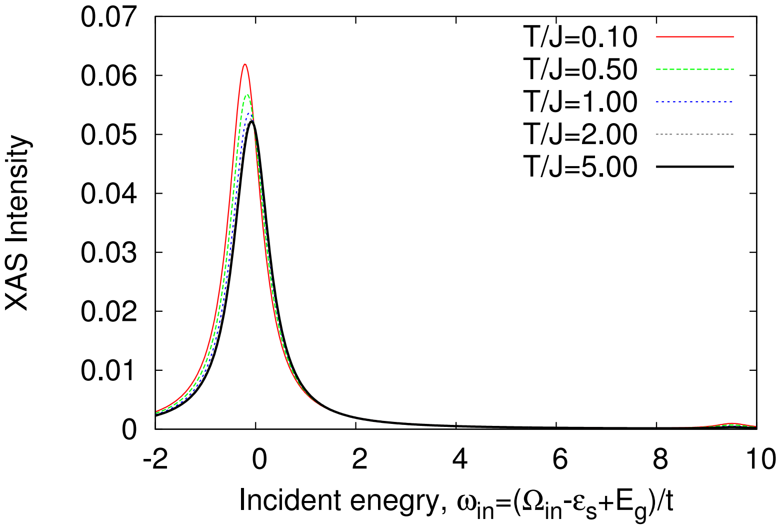
T-dependence of RIXS spectra



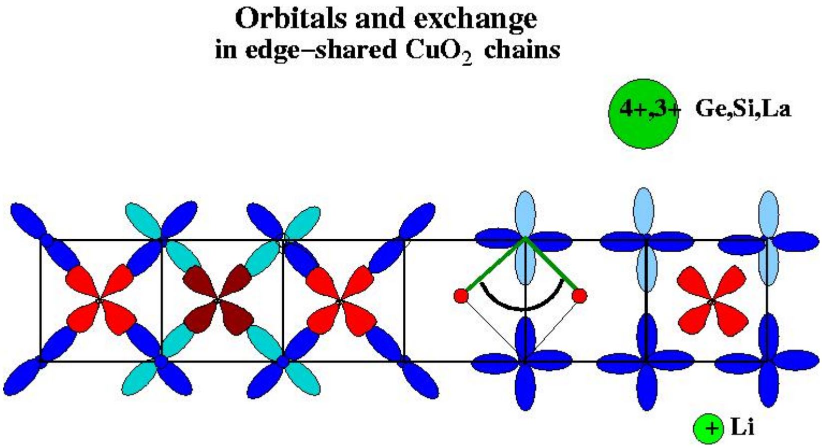
T-dependence of RIXS spectra



T-dependence of XAS spectrum



Edge-shared CuO_2 chains

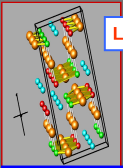


Edge-shared CuO_2 chains: large variety of ground states

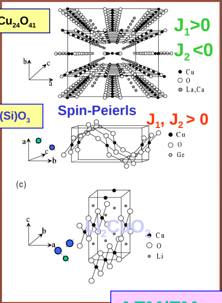
Different embeddings *(Interchain coupling,crystal field)* Cu-O-Cu bond angles, spin anisotropies

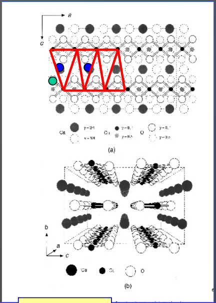
inchain-spiral

off-chain spiral



Li(Na)Cu_2O_2





$Ca_2Y_2Cu_5O_{10}$

AFM/FM
$J_1<0$, $J_2>0$

1. 1. fm in-chain & afm off-chain ordering: Li_2CuO_2, $Ca_8La_6Cu_{24}O_{41}$ $Ca_2Y_2Cu_5O_{10}$
2. No spiral ordering, but frustrated : Li_2ZrCuO_4, $Rb(Cs)_2Cu_2Mo_3O_{12}$
3. Incommensurable (IC) in-chain ordering :in-chain helix: Li(Na)Cu_2O_2, $LiVCuO_4$, $CuSiO_3$
4. Incommensurable off-chain

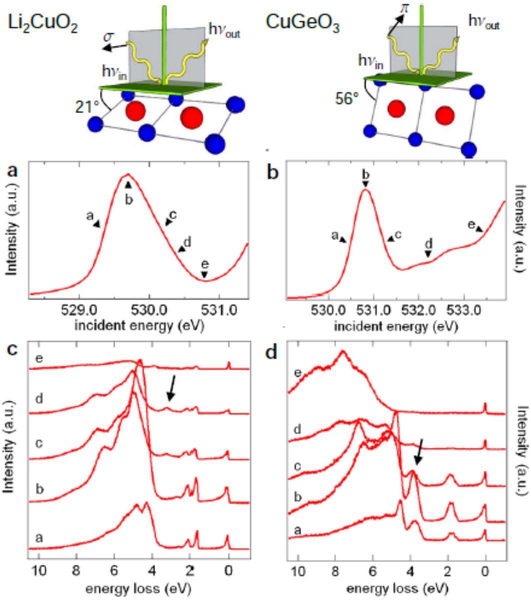
1D-spiral:

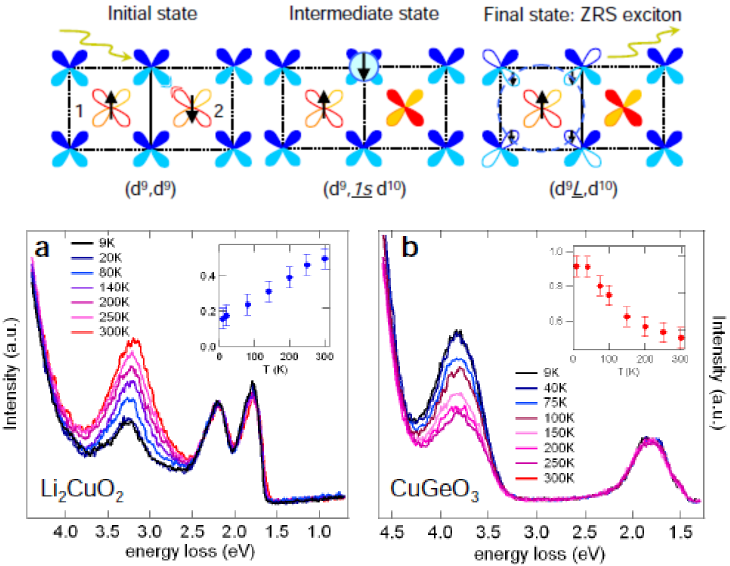
$\alpha=|J_2/J_1|\geq 1/4$, cos $\varphi = - J_1/4J_2$

if $J_2/|J_1| >> 1$, $\varphi \approx \pi/2$

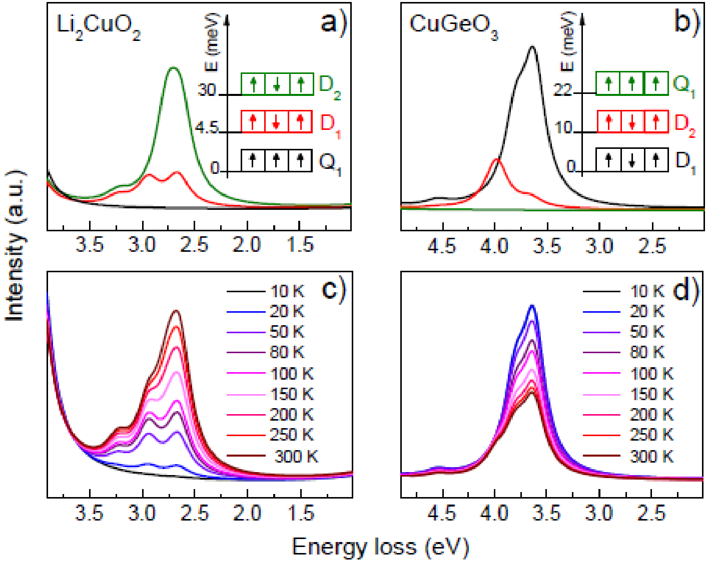
3D: FM maybe stabilized by specific AFM interchain coupling and easy-axis spin anisotropy

O *K*-edge, C. Monney et al., PRL **110**,087403 (2013)




Initial state
Intermediate state
Final state: ZRS exciton
1
2
(d9,d9)
(d9,1s d10)
(d9L,d10)
a
9K
20K
80K
140K
200K
250K
300K
T (K)
Li2CuO2
Intensity (a.u.)
energy loss (eV)
b
9K
40K
75K
100K
150K
200K
250K
300K
T (K)
CuGeO3
Intensity (a.u.)
energy loss (eV)

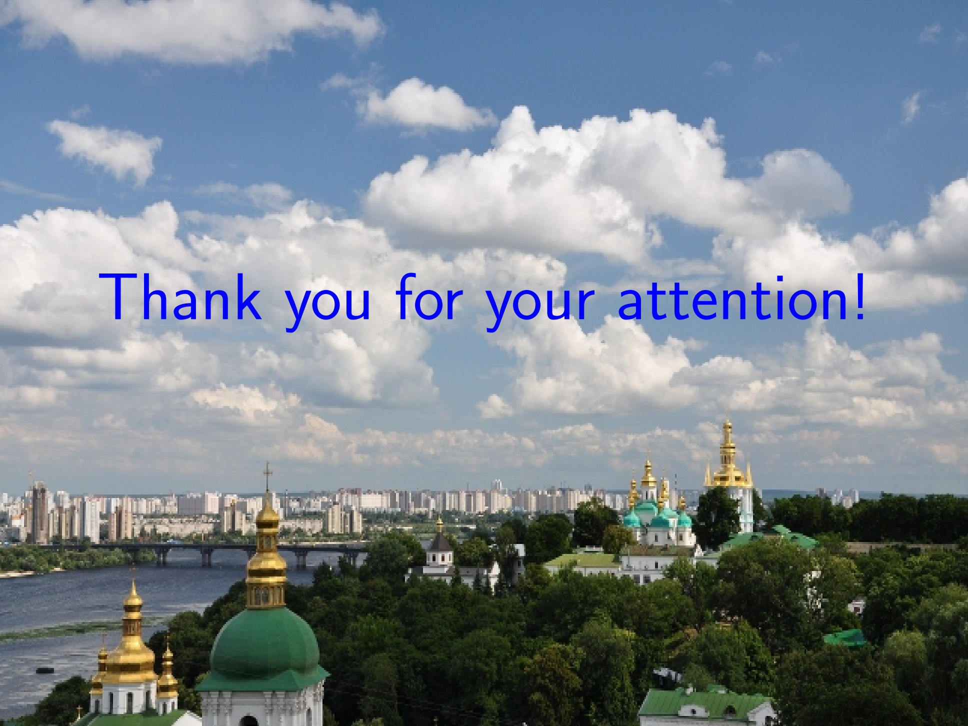
Theory



Li_2CuO_2
a)
E (meV)
30
4.5
0
D_2
D_1
Q_1
$CuGeO_3$
b)
E (meV)
22
10
0
Q_1
D_2
D_1
3.5 3.0 2.5 2.0 1.5
4.5 4.0 3.5 3.0 2.5
c)
d)
10 K
20 K
50 K
80 K
100 K
150 K
200 K
250 K
300 K
Intensity (a.u.)
Energy loss (eV)

Conclusions

- In strongly correlated systems, the probability of charge-transfer excitations depends on the magnetic state of the system.
- RIXS spectra of antiferromagnetic CTI strongly change in the temperature interval between zero and several J



Thank you for your attention!