Systematic Calculations of RIXS for the 3d Transition Metal Oxides by the Ab-initio Multiplet Methods

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11th International Conference on Inelastic X-ray Scattering (IXS2019)
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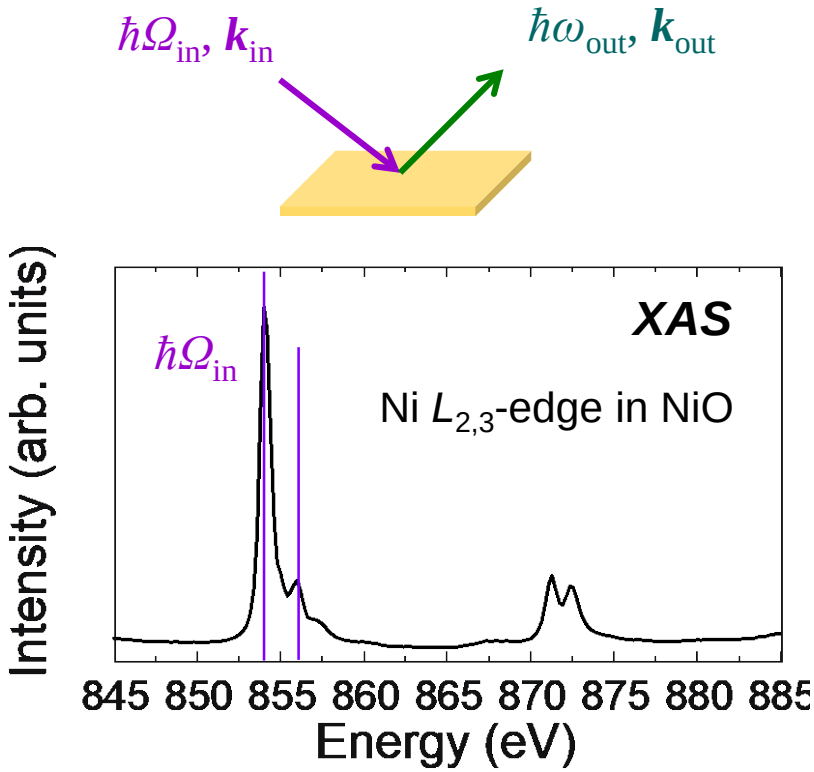
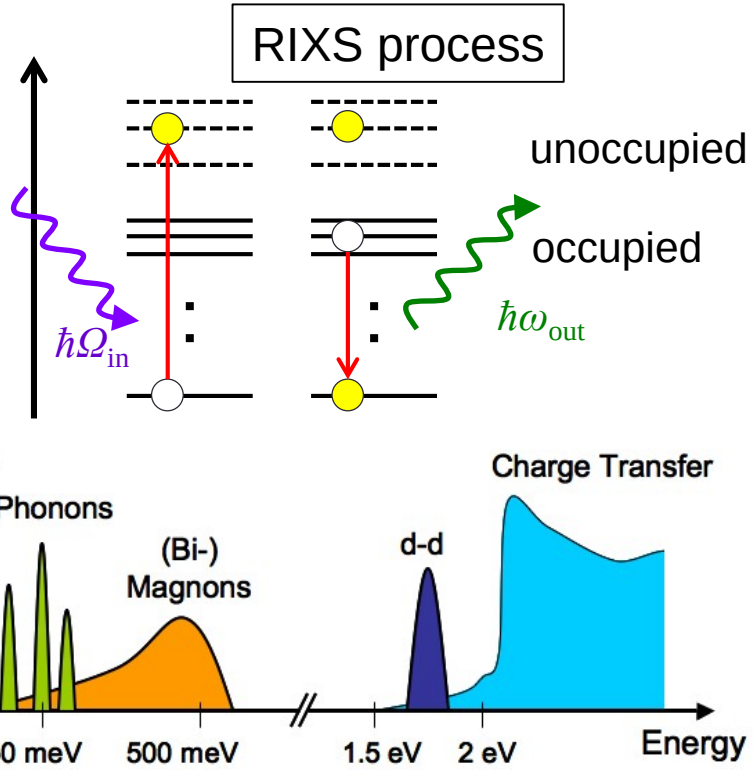
Resonant Inelastic X-ray Scattering (RIXS)





Ament *et al.*, Rev. Mod. Phys. 83, 705 (2011).

- Photon-in/Photon-out spectroscopy (**richer information than XAS**)
- Any elementary excitation can be observed

Establishment of an reliable theoretical procedure for interpretation of RIXS is highly desirable

Outline

The *ab-initio* multiplet method for XAS and RIXS

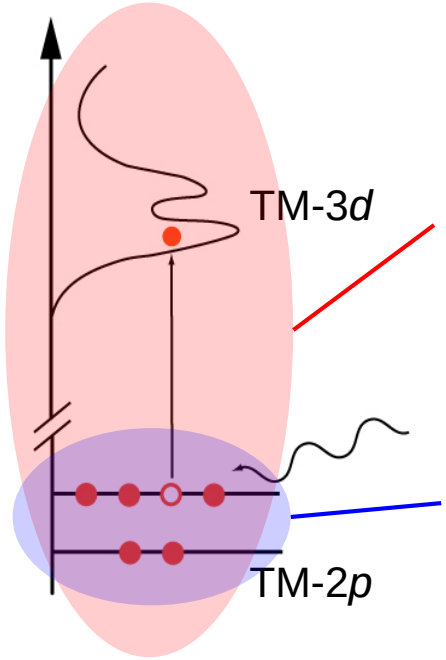
- Multiplet effects on XAS and RIXS
- An *ab-initio* quantum chemistry approach (RASCI/CASCI) for XAS and RIXS

Interpretation of RIXS: the use cases

- Angular dependence in Co *K*-pre-edge RIXS of CoO
- Site dependence in Fe *K*-pre-edge RIXS and RIXS-MCD of Fe_3O_4
- Effects of covalency and charge transfer in Fe-$L_{2,3}$ RIXS-MCD of α-Fe_2O_3

Multiplet Effects on TM $L_{2,3}$-edges

Transition metal (TM) $L_{2,3}$-edges ($2p \rightarrow 3d$)



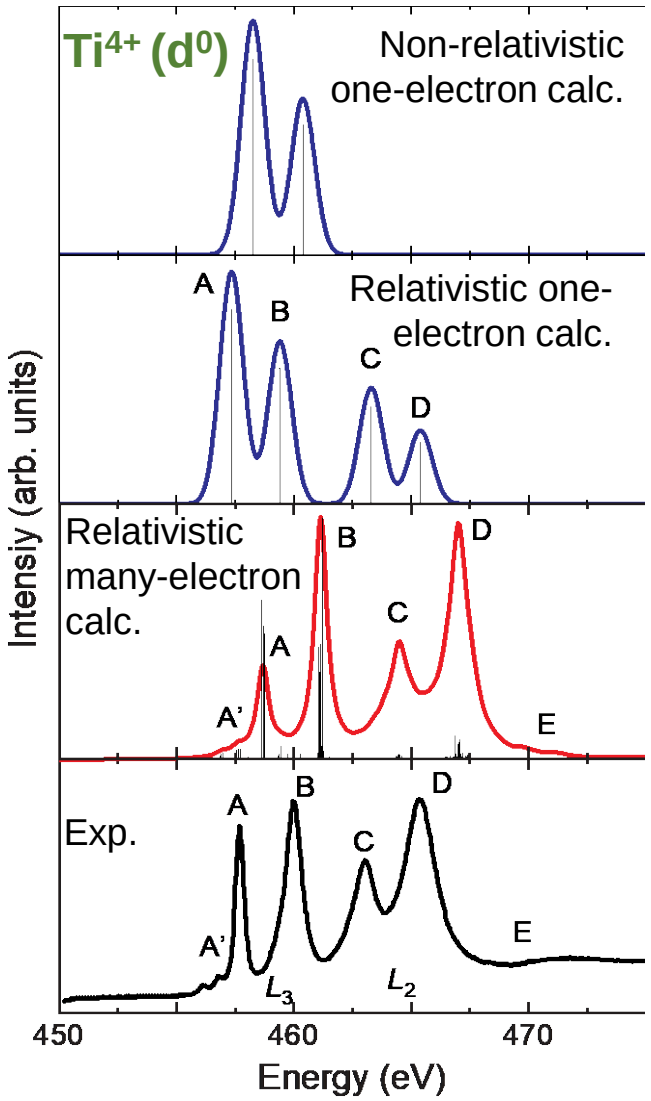
Strong correlations
core-hole & 3*d* electrons

Relativistic effects
e.g. spin-orbit coupling

Mulitplet structures originating from strong correlations between 2p and 3d electrons

TM 2p and 1s2p RIXS are also affected by multiplet effects

Ti-$L_{2,3}$ XAS of $SrTiO_3$



Go Beyond One-Electron Approximation

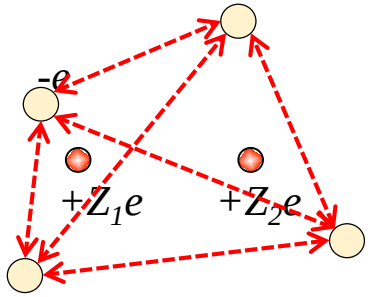
$$\hat{H}\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = E\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$$

Many-electron calc.

$$\hat{H} = \sum_{i=1}^{N}\left\{\hat{h}_{\mathrm{rel}}(\boldsymbol{r}_i) + v_{\mathrm{ext}}(\boldsymbol{r}_i)\right\} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ i\neq j}}^{N}\hat{g}(\boldsymbol{r}_i,\boldsymbol{r}_j)$$

Dirac (fully relativistic) operator
or
Non-rel. + spin-orbit coupling

Coulomb and exchange-correlation interactions among 2*p*, 3*d* (, ligand) electrons

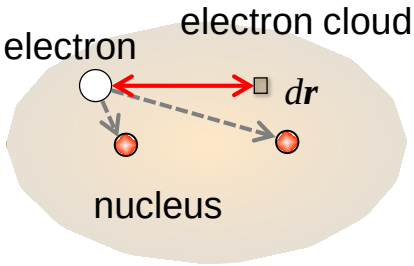


Origin of multiplet structures

One-electron calc.

$$\left[\hat{T} + v_{\mathrm{ext}}(\boldsymbol{r}) + v_{\mathrm{eff}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r})$$

Approximated *e*-*e* interactions via electron cloud (mean field)

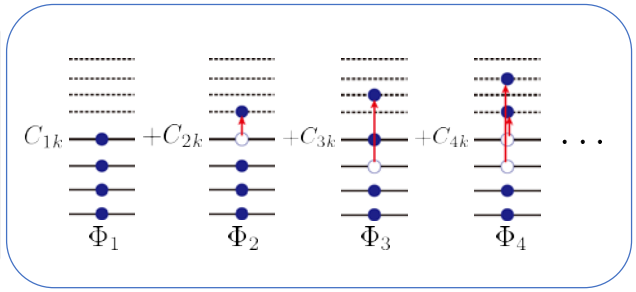


Ab-initio Multiplet Method

CASCI/RASCI using relativistic molecular orbitals

Many Electron Wavefunction

$$\Psi = \sum_{j=1}^{K} C_j \Phi_j,\ \Phi_j = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{j1}(\boldsymbol{r}_1) & \phi_{j1}(\boldsymbol{r}_2) & \cdots & \phi_{j1}(\boldsymbol{r}_N) \\ \phi_{j2}(\boldsymbol{r}_1) & \phi_{j2}(\boldsymbol{r}_2) & \cdots & \phi_{j2}(\boldsymbol{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{jN}(\boldsymbol{r}_1) & \phi_{jN}(\boldsymbol{r}_2) & \cdots & \phi_{jN}(\boldsymbol{r}_N) \end{vmatrix}$$



Including exchange-correlation interactions

Hamiltonian Matrix

$$\langle \Phi_p | \hat{H} | \Phi_q \rangle = \sum_{i,j} \langle \phi_i | \hat{h} | \phi_j \rangle \langle \Phi_p | a_i^\dagger a_j | \Phi_q \rangle + \frac{1}{2} \sum_{i,j,k,l} \langle \phi_i \phi_j | \hat{g} | \phi_k \phi_l \rangle \langle \Phi_p | a_i^\dagger a_j^\dagger a_l a_k | \Phi_q \rangle$$

One-electron integrals
kinetic energy, crystal field, hopping integrals, etc.

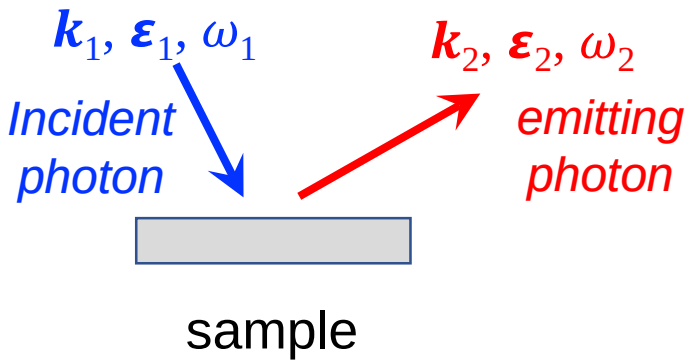
Two-electron integrals
e-e interactions

1. MO calculations using cluster models ***atomic structures as inputs***
2. Evaluate integral over MOs numerically
3. Diagonalize many-electron Hamiltonian to obtain $E_k, \Psi_k(\boldsymbol{C_k})$

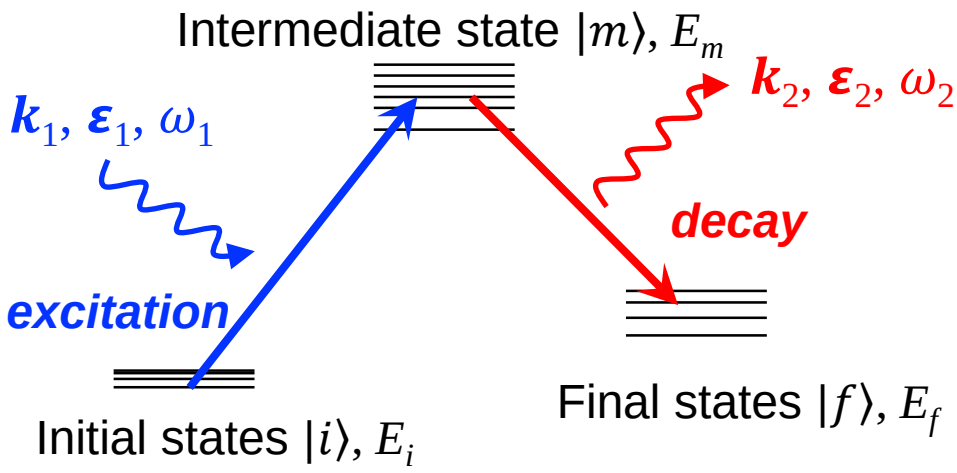
Initial, final & intermediate states

Ab-initio Multiplet Method

Geometry



Electronic transitions



Differential scattering cross-section (Kramers-Heisenberg formula)

Z. Phys. **24,** 681 (1924).

$$F(\omega_1,\omega_2)=\sum_f\left|\sum_m \frac{\langle f|T_2|m\rangle\langle m|T_1|i\rangle}{E_i+\hbar\omega_1-E_m+i\Gamma_m}\right|^2 \delta(E_i+\hbar\omega_1-E_f-\hbar\omega_2)$$

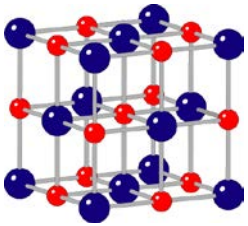
T_1, T_2: electric dipole (E_1) or electric quadrupole (E_2) operators

- **We can simulate RIXS in arbitrary geometries ($\epsilon_{in}, k_{in}, \epsilon_{out}, k_{out}$)**
- **RIXS-MCD can also be handled**

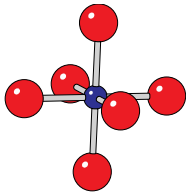
Ab-initio Multiplet Method

Map local atomic structures on spectral shapes

Atomic structures



Input

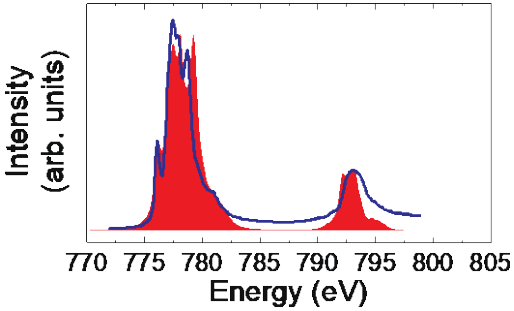


Electronic structures

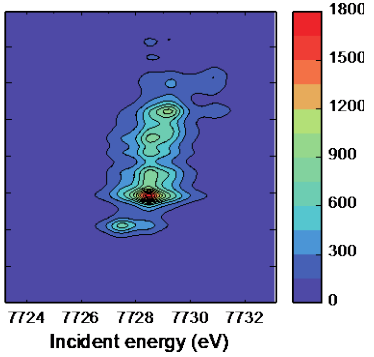
***Ab-initio* QC calc.**
RASCI/CASCI

$$\hat{H}\Psi = E\Psi$$

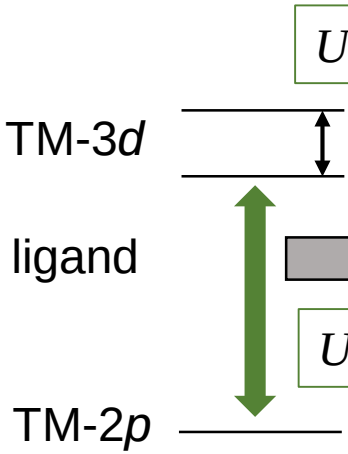
XAS, RIXS spectra



Output



c.f. Charge transfer multiplet method



Input: Adjustable parameters

Crystal field splitting

Charge transfer energy

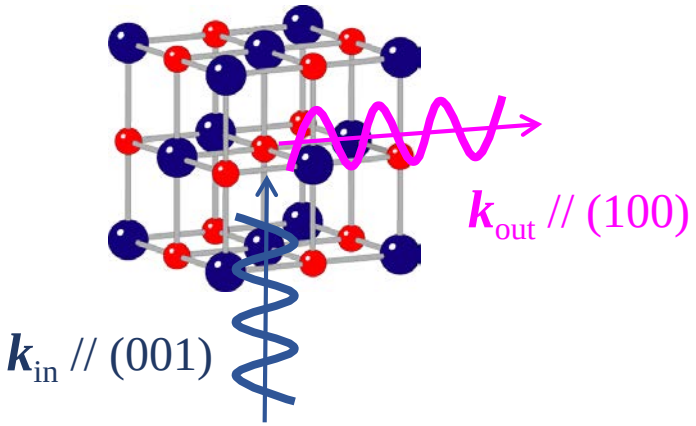
Hubbard parameters
(Coulomb interaction)

Fitting spectra

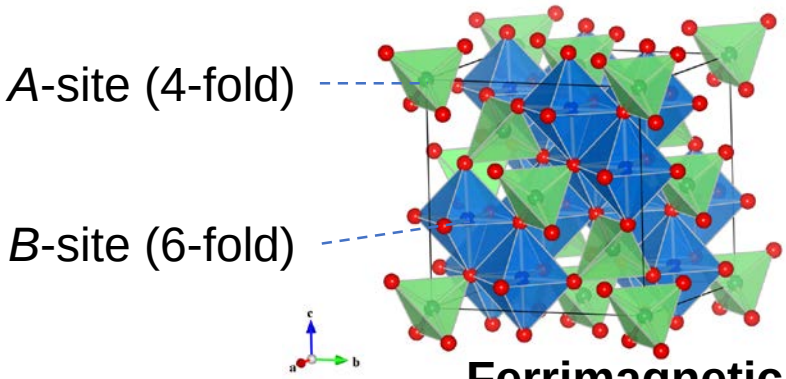
Use Cases of the Ab-Initio Multiplet Method

TM 1s2p RIXS(-MCD)

CoO — **Orientational dependence**



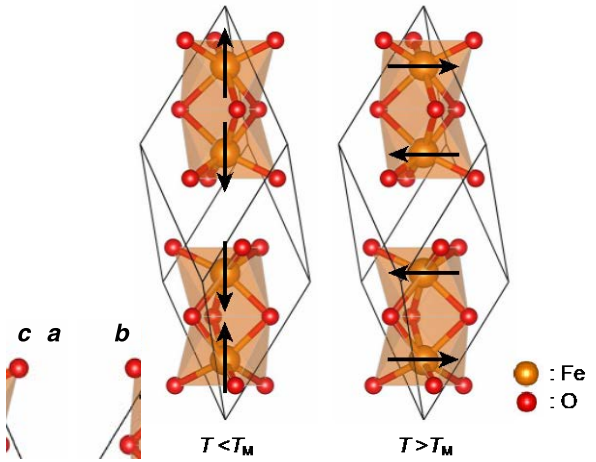
Fe_3O_4 — **Site dependencies**

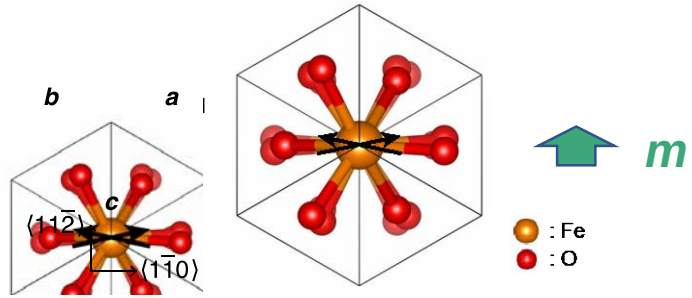


Ferrimagnetic

TM 2p RIXS(-MCD)

α-Fe_2O_3 — **RIXS-MCD originates from covalent bonding**



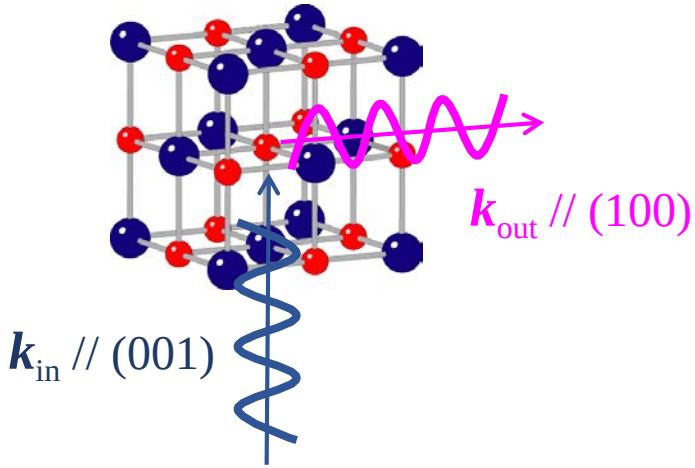


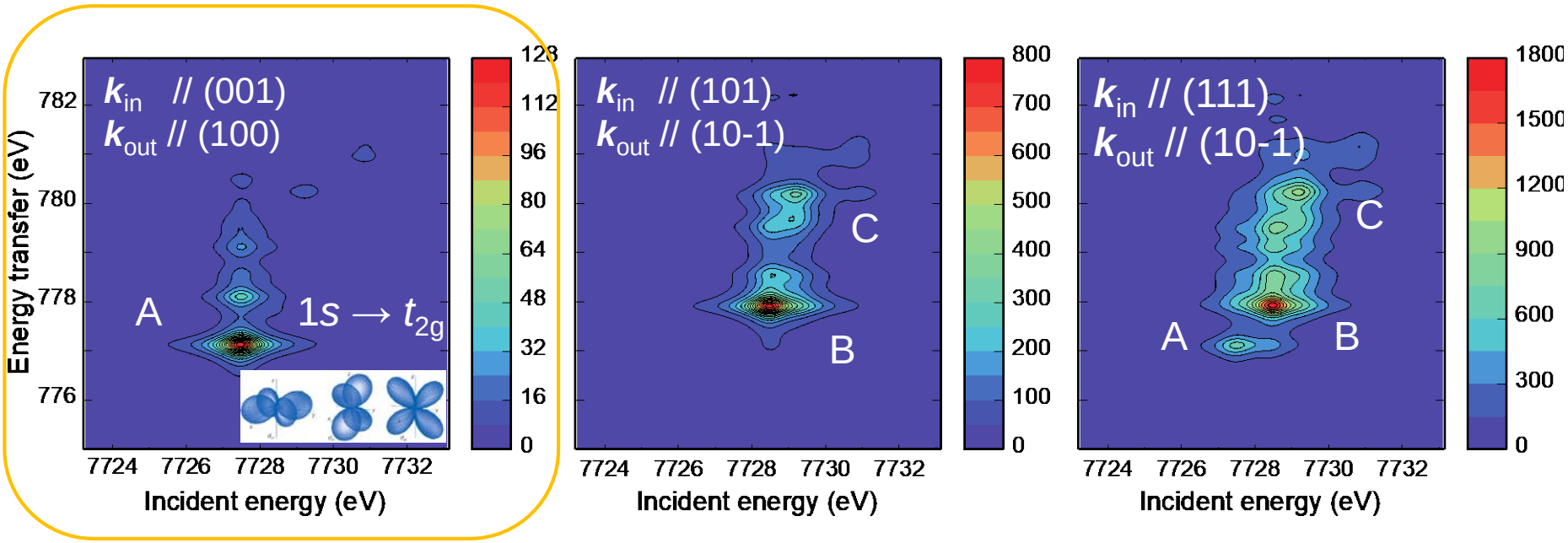
Weak ferromagnetic

Co 1*s*2*p* RIXS of CoO

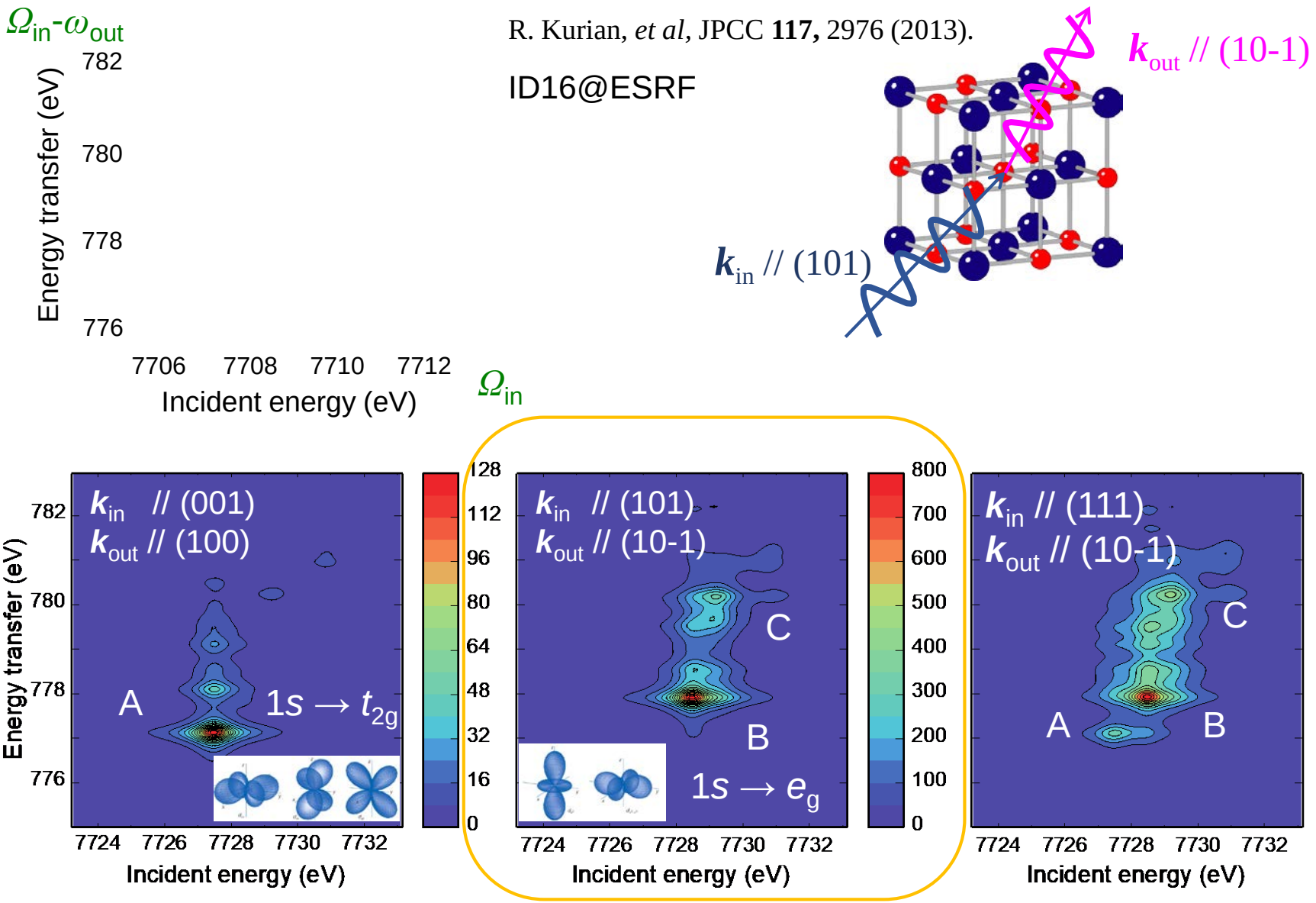
R. Kurian, *et al*, JPCC **117,** 2976 (2013).

ID16@ESRF





Co *K*-pre-edge RIXS of CoO



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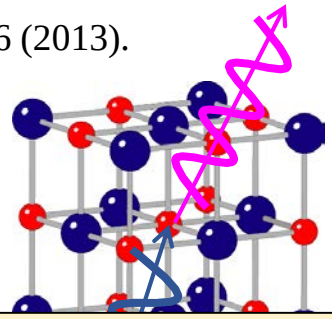


k_{out} // (10-1)

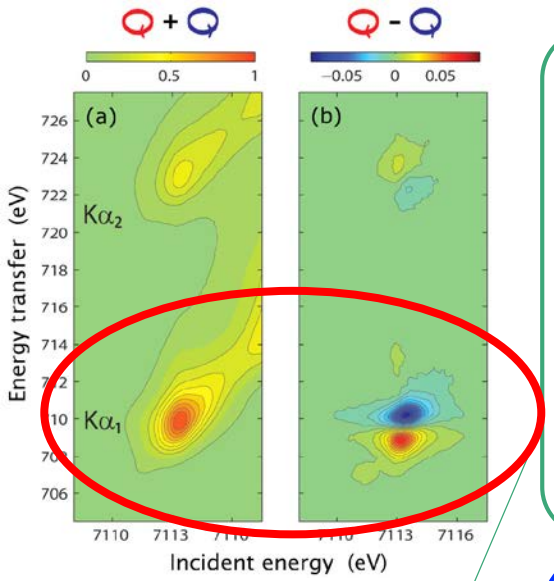
The 1s2p RIXS features are reproduced well by the *ab-initio* multiplet method.

We can simulate spectra in arbitrary experimental geometries ($\boldsymbol{k}_{in}$, $\boldsymbol{e}_{in}$, $\boldsymbol{k}_{out}$, $\boldsymbol{e}_{out}$).

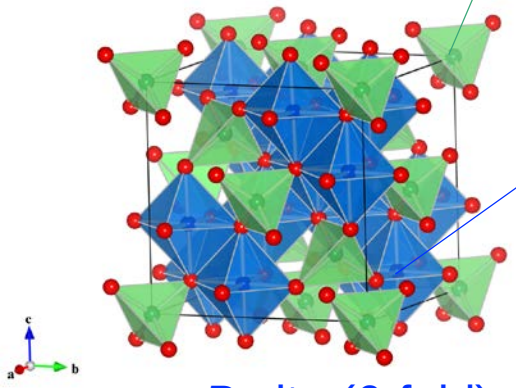
Analysis of orientational dependence of RIXS spectra is useful to clarify the origin of peaks.

Fe 1s2p RIXS and RIXS-MCD of Fe_3O_4

Experiment*



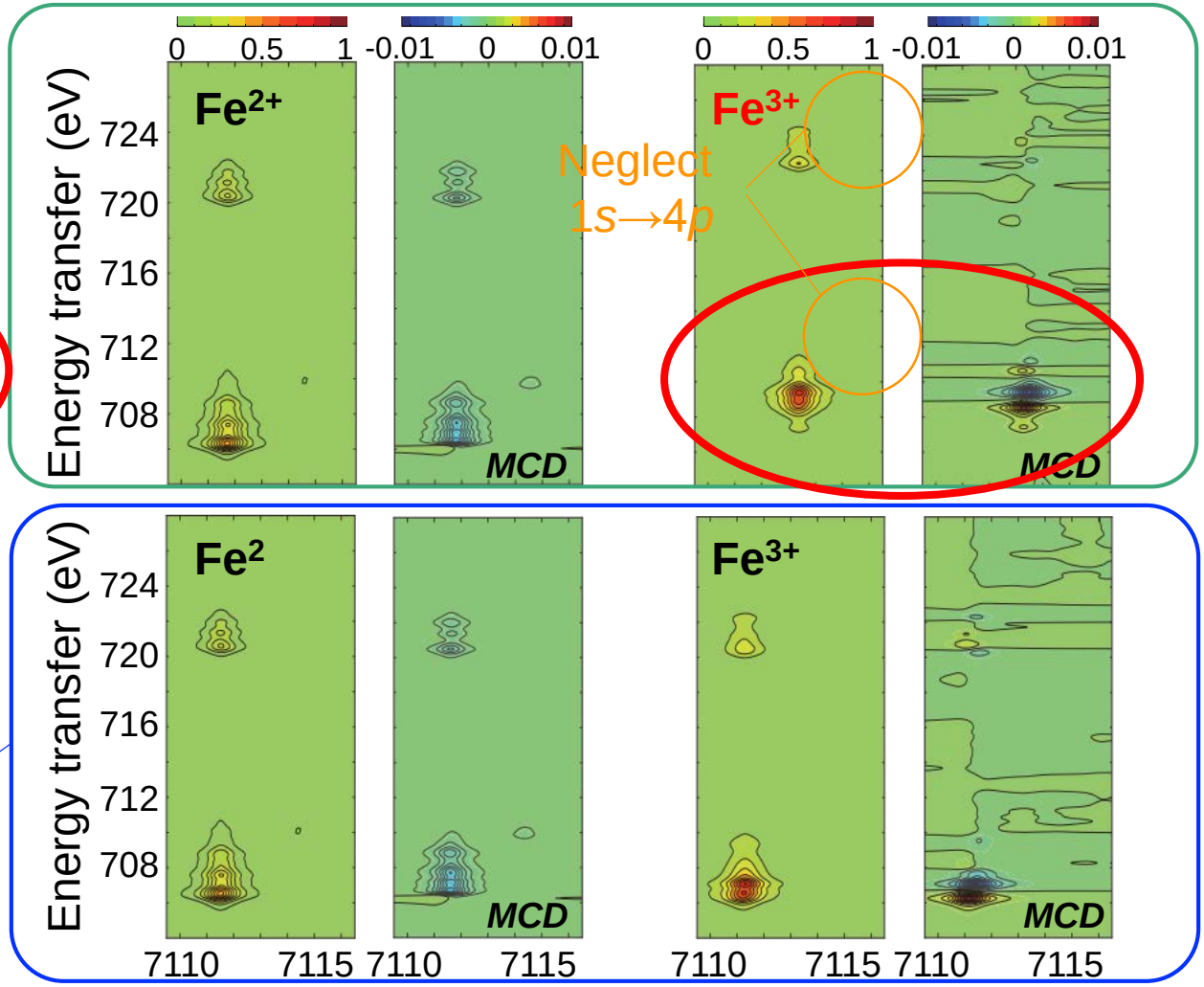
A-site (4-fold)



B-site (6-fold)

Calculations

Strong (dipole allowed)

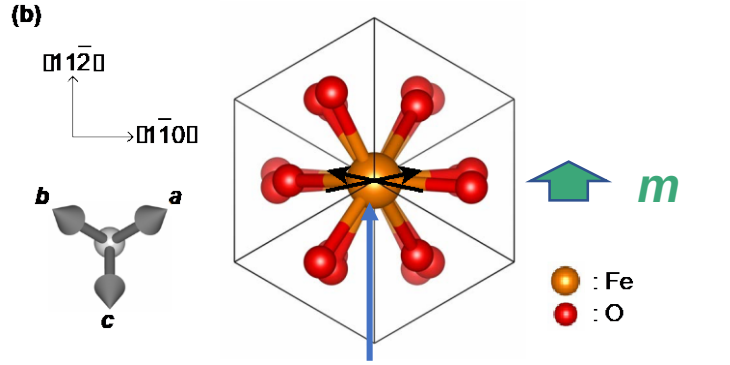


Weak (dipole forbidden)

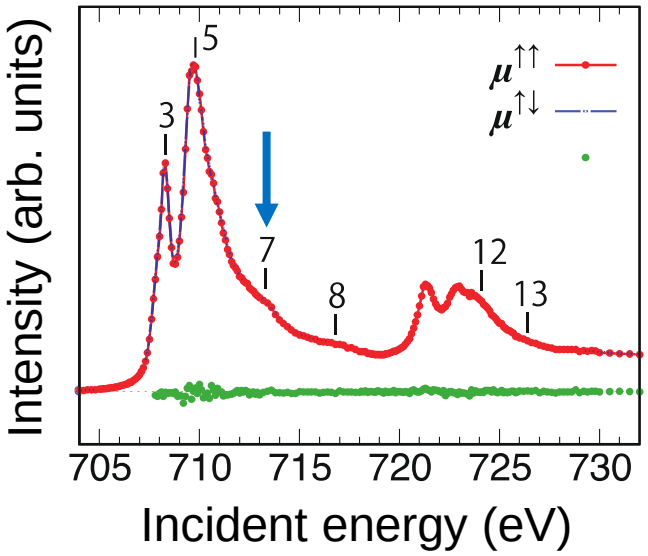
*Sikora *et al.*, Phys. Rev. Lett. **105,** 037202 (2010).

Fe-$L_{2,3}$ RIXS-MCD of α-Fe_2O_3 (Exp.)

α-Fe_2O_3 (weak ferromagnetic)



$\boldsymbol{k}_{in}$ // $\langle 1\bar{1}0 \rangle$, $\boldsymbol{k}_{out}$ // $\langle 111 \rangle$

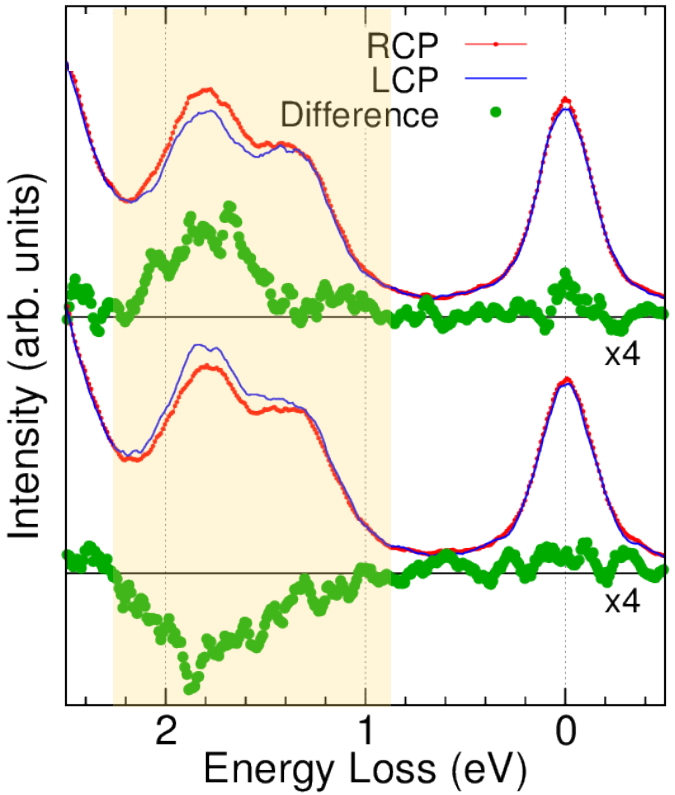


No discernible XMCD signal

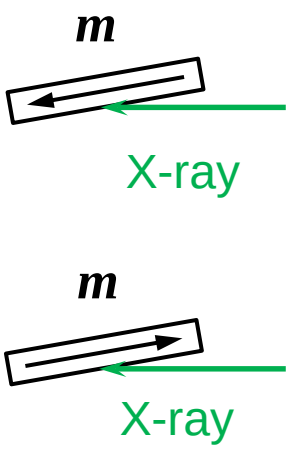
@SPring-8 BL07LSU

c.f. talk by Dr. Miyawaki (Mon.)

$h\nu_{in}$ = 713.25 eV (at peak 7)



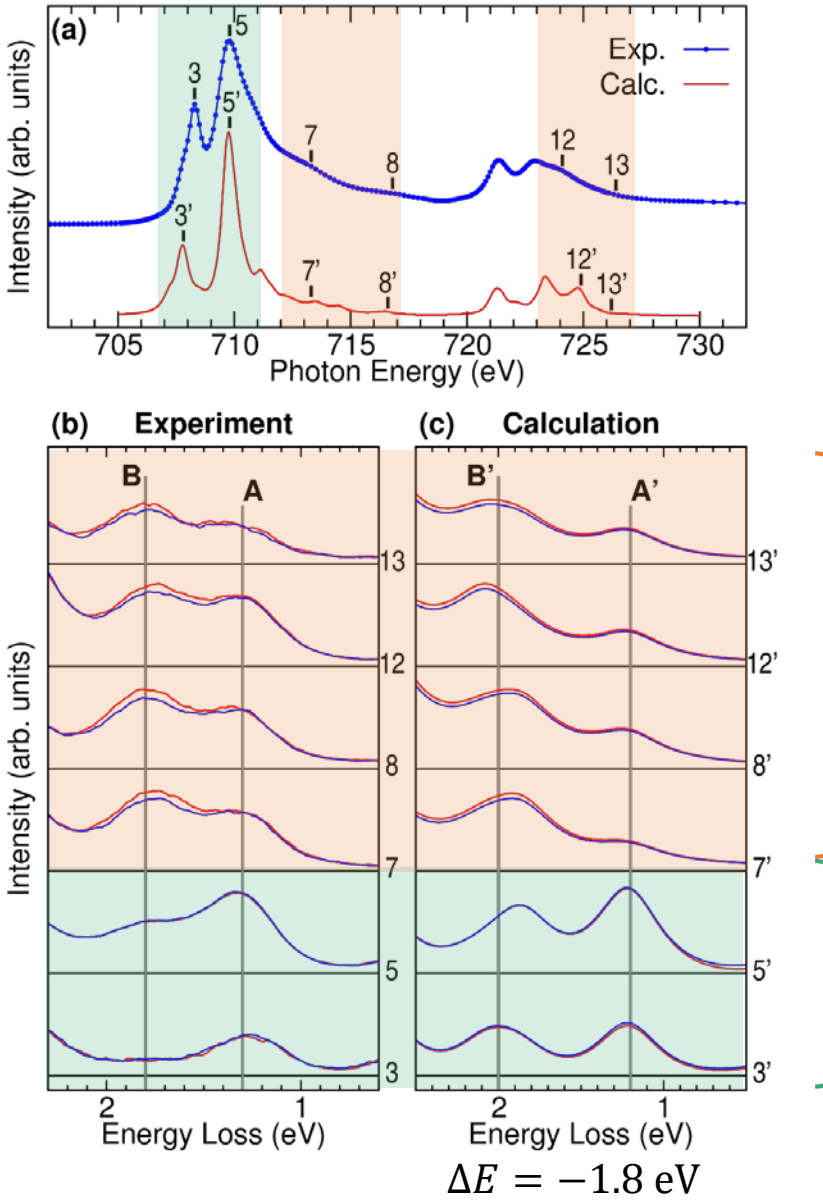
Miyawaki *et al.*, PRB **96,** 214420 (2017).



MCD signal in RIXS!

Revealing the origin of RIXS-MCD in α-Fe_2O_3 by the *ab-initio* multiplet calculations

Fe-$L_{2,3}$ RIXS-MCD of α-Fe_2O_3

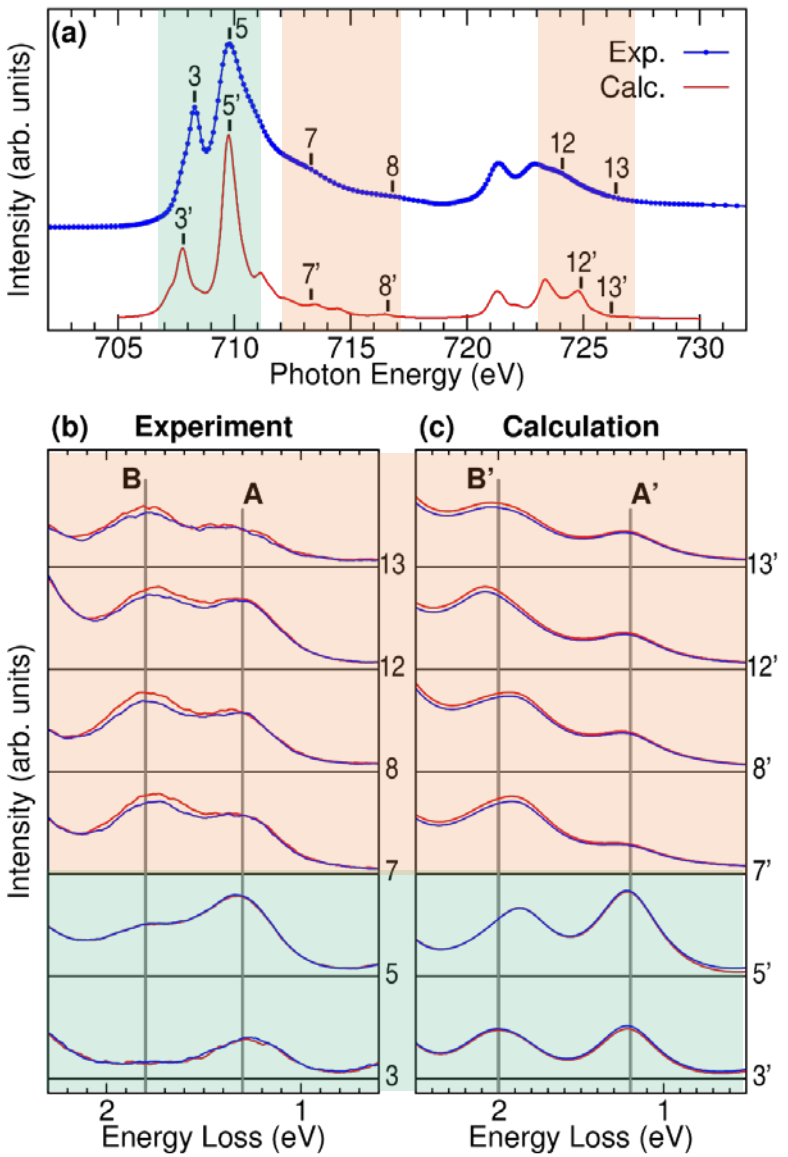


***Ab-initio* multiplet calculations reproduced the experimental RIXS-MCD features**

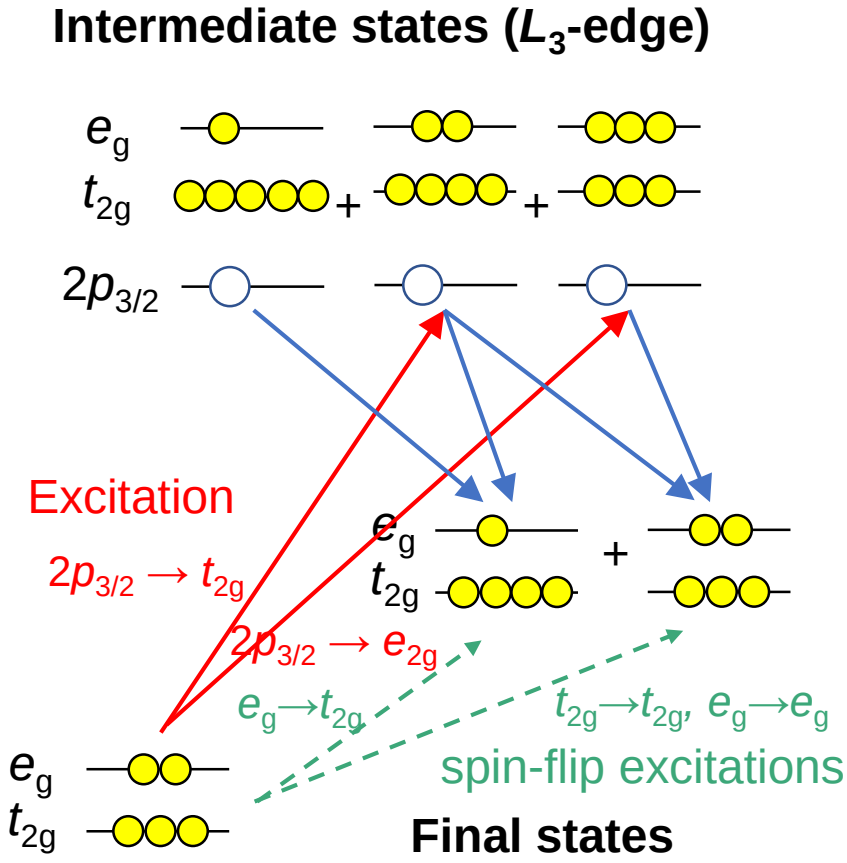
Clear RIXS-MCD signal is observed at the excitation above the main peak

No significant signal appears at the excitation on the main peaks

Fe-$L_{2,3}$ RIXS-MCD of α-Fe_2O_3



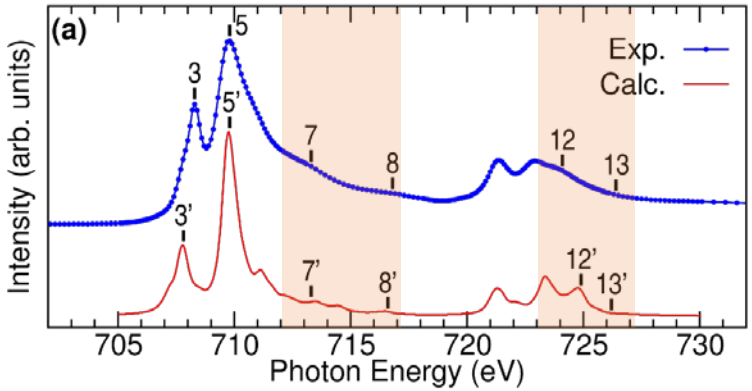
$\Delta E = -1.8$ eV

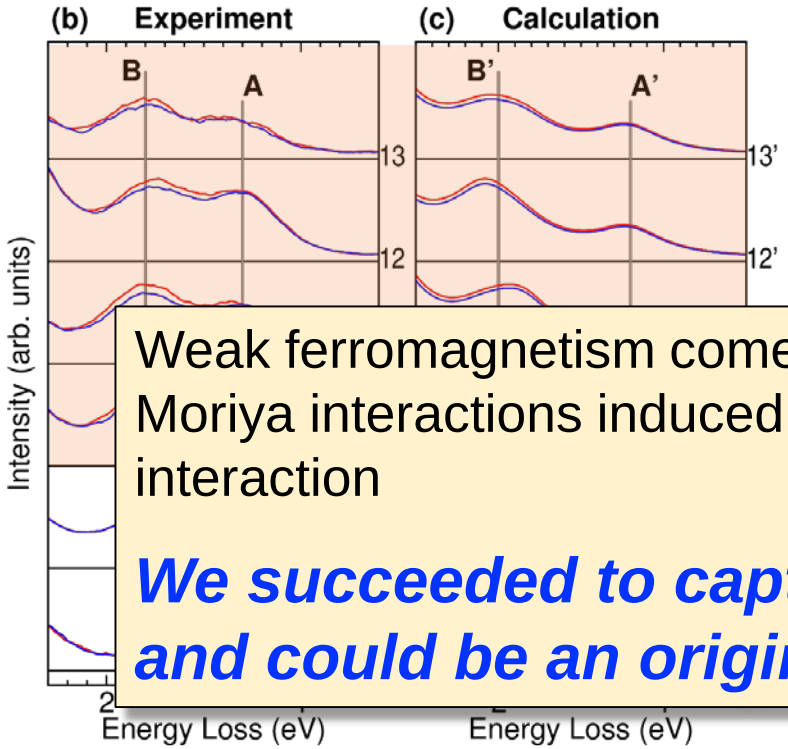


e_g: Strong covalent bonding
(9.7% O-2p population)

t_{2g}: Weak covalent bonding
(4.3% O-2p population)

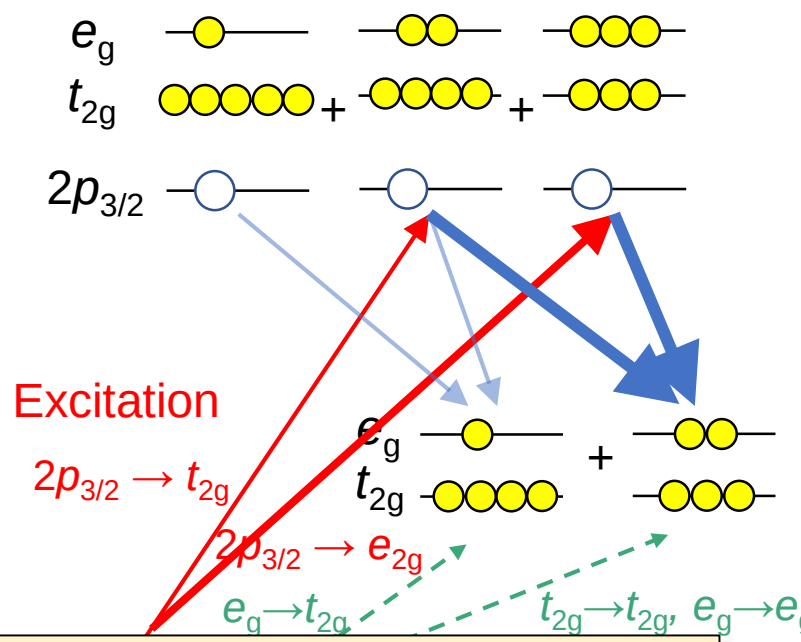
Fe-$L_{2,3}$ RIXS-MCD of α-Fe_2O_3





$\Delta E = -1.8$ eV

Intermediate states (L_3-edge)

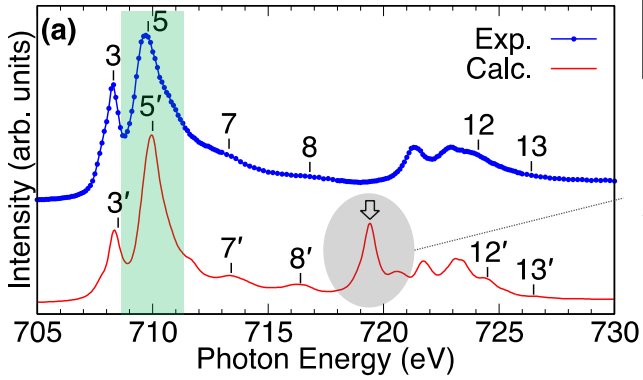


Weak ferromagnetism comes from the Dzyaloshinsky-Moriya interactions induced by the Fe-O-Fe super-exchange interaction

We succeeded to capture the D-M interactions and could be an origin of RIXS-MCD

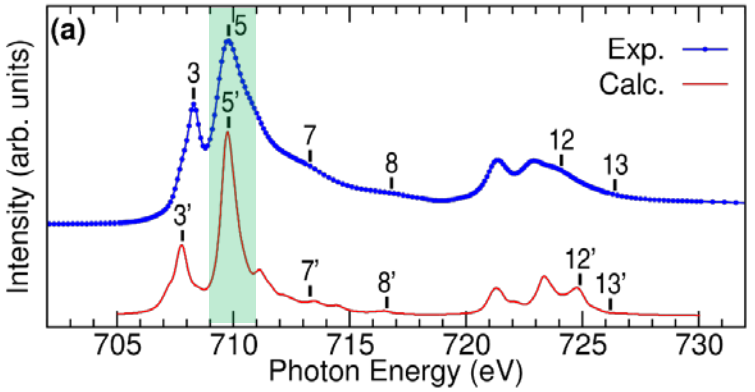
Charge Transfer Effects

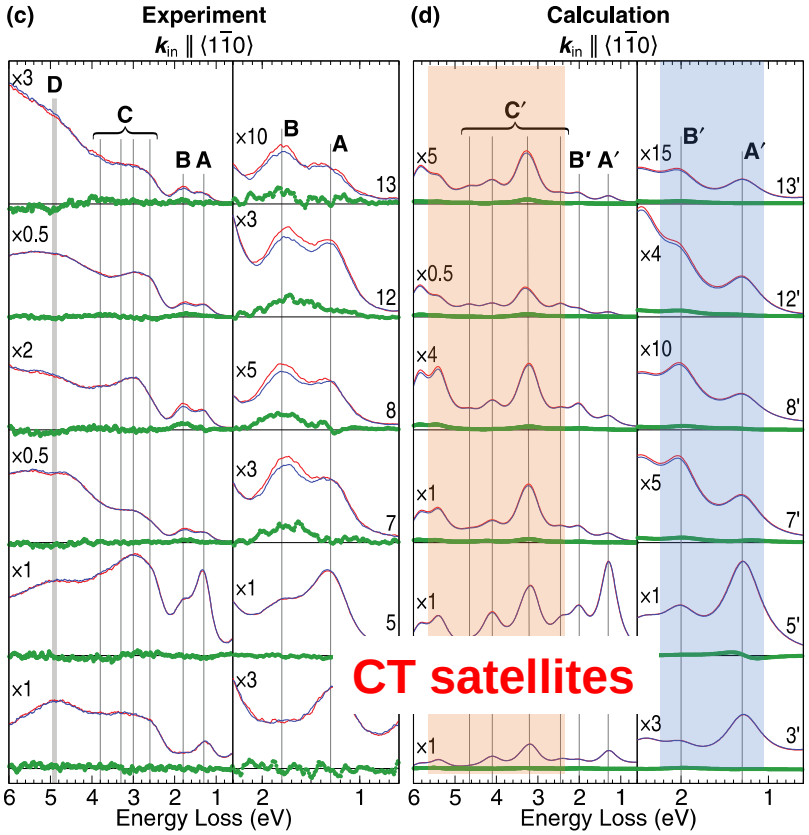
CT



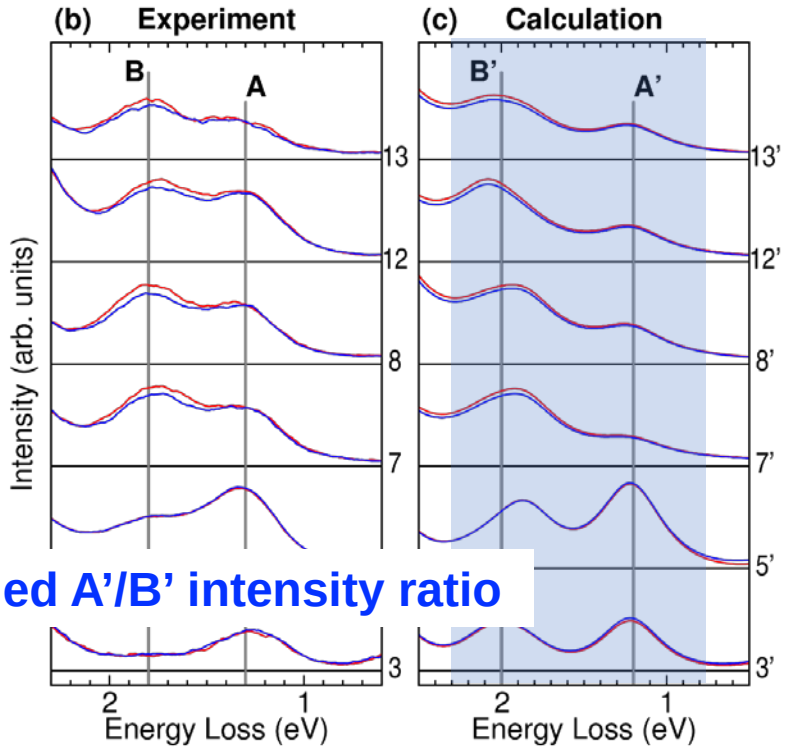
Artifact

w/o CT





CT satellites



Modified A’/B’ intensity ratio

Outlook

The *ab-initio* multiplet method for RIXS(-MCD)

- Simulate multiplet structures in RIXS of TM (and rare-earth) compounds **from atomic structures, *a priori***
- Works both TM *K*-pre-edge RIXS(-MCD) (*hard*) and TM-$L_{2,3}$ RIXS(-MCD) (*soft*)
- Charge transfer effects can be included
- Applicable to arbitrary atomic structures and geometries (no limitation about symmetries)

Detailed interpretation of RIXS spectra in terms of local atomic structures and electronic structures

Angular dependence, site dependence

Covalency and electronic configuration analysis

Acknowledgments

Collaborators

The University of Tokyo (ISSP)
- Jun Miyawaki
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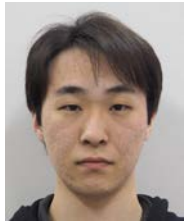
- Hisao Kiuchi

Osaka Prefecture University
- Masato Urasaki

Osaka University
- Shigemasa Suga
- Hidenori Fujiwara



Financial Supports

科研費 KAKENHI

MEXT/JSPS KAKENHI

PRESTO SAKIGAKE

JST PRESTO

Thank you for your kind attention!!

Ab-initio Multiplet Method

Input

- atomic numbers
- atomic coordinates

Solve Schrödinder (Dirac) equation

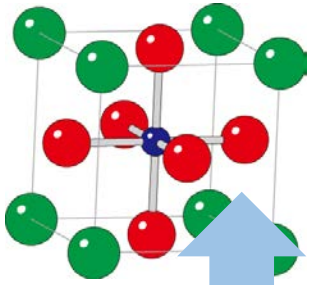
Electronic structure

- energy
- wave function
- charge density

Theoretical XAS *(& other properties)*

Fermi's golden rule

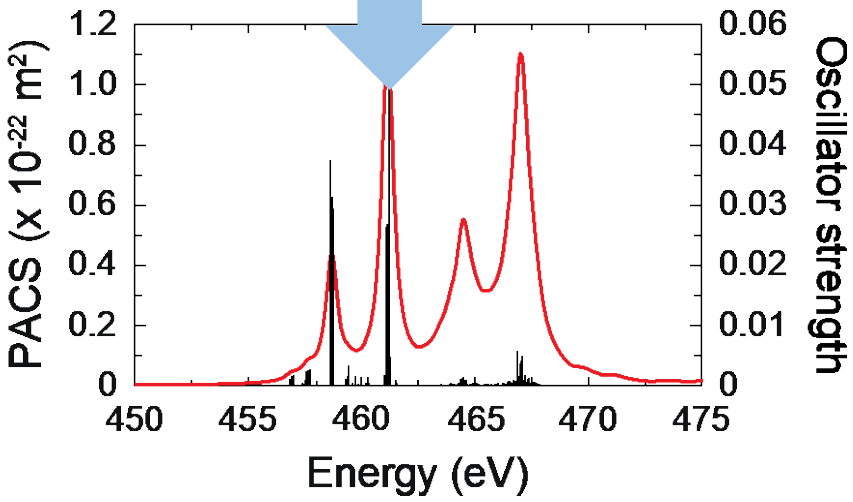
$$W_{fi} = \frac{2\pi}{\hbar} |\langle \Psi_f | T | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$



$SrTiO_3$ (perovskite)

Theoretical Fingerprints
(Local) structure to spectrum mapping

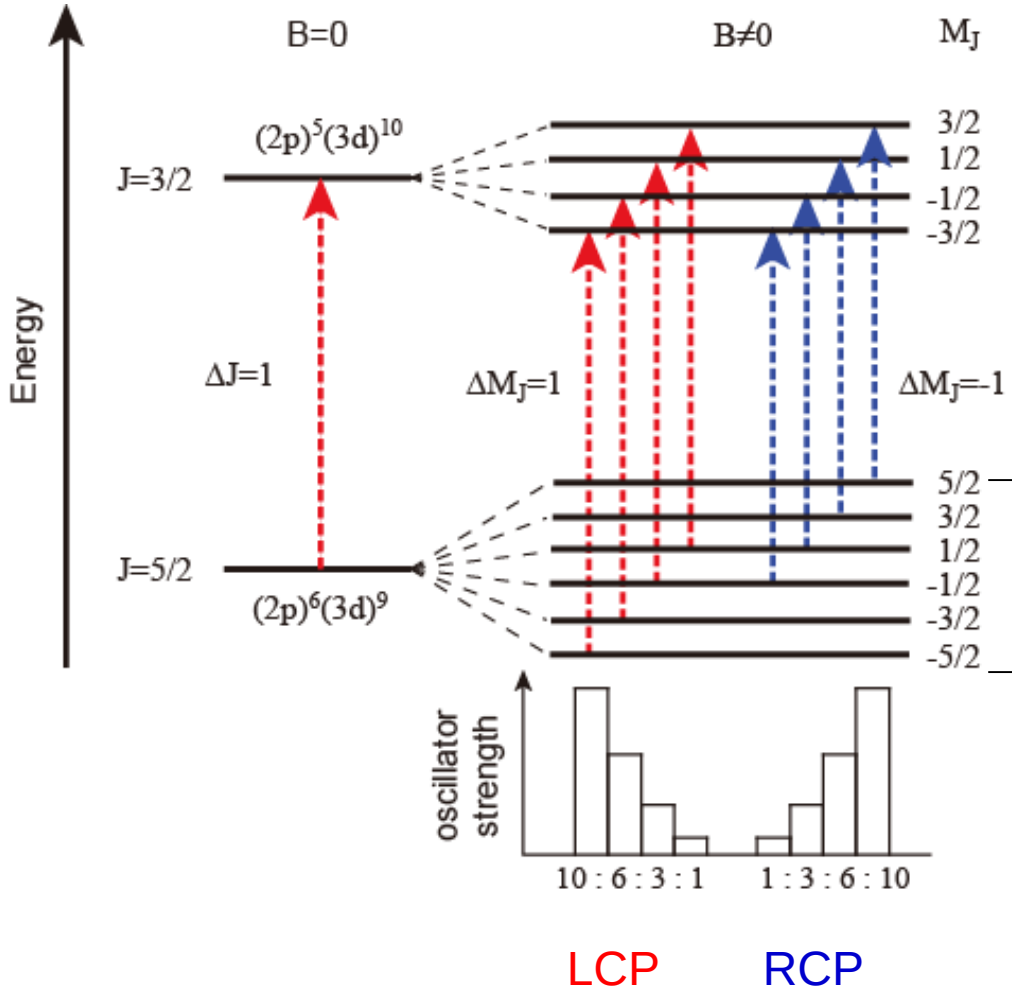
Ti-$L_{2,3}$ X[illegible] of $SrTiO_3$



Understand relationship between atomic structures and spectral shapes

Ab-Initio Multiplet Method for RIXS-MCD

Magnetic field and exchange interactions have affects on energy levels



Selection rule:

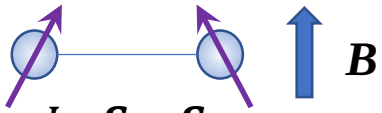
$\Delta J = \pm 1$

$\Delta M_J = +1$ (LCP)

$\Delta M_J = -1$ (RCP)

Zeeman splitting (external field)

Exchange splitting (interactions between magnetic moments)



$J_{ij}\, \boldsymbol{S}_i \cdot \boldsymbol{S}_j$

$\boldsymbol{D}_{ij} \cdot (\boldsymbol{S}_i \times \boldsymbol{S}_j)$

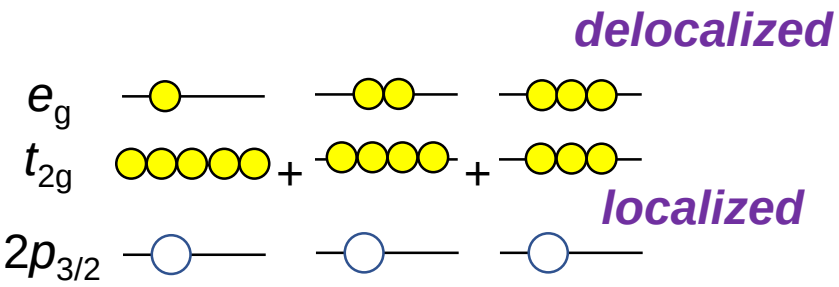
$\approx \mu_B B_m$

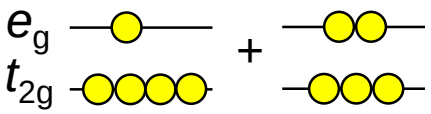
Molecular field approximation

B_m: adjustable parameter

Possible Transition Channels at Fe-$L_{2,3}$ RIXS

Intermediate states (L_3-edge)

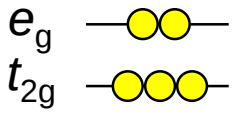




$e_g \rightarrow t_{2g}$

$t_{2g} \rightarrow t_{2g}$, $e_g \rightarrow e_g$

spin-flip excitations

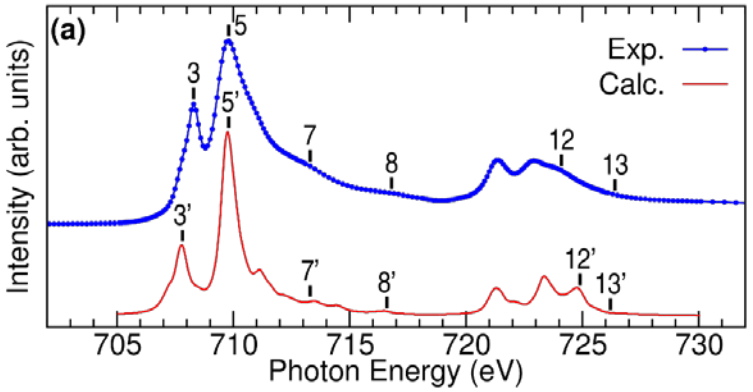


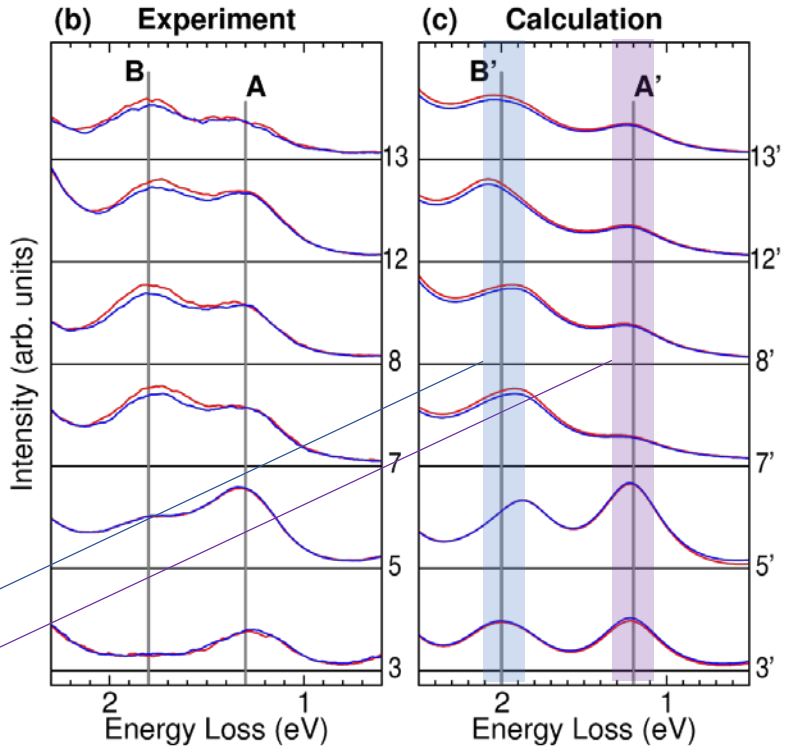
Initial states

d^5, high-spin

Final states

B': 65%	**25%**
A': 90%	**10%**





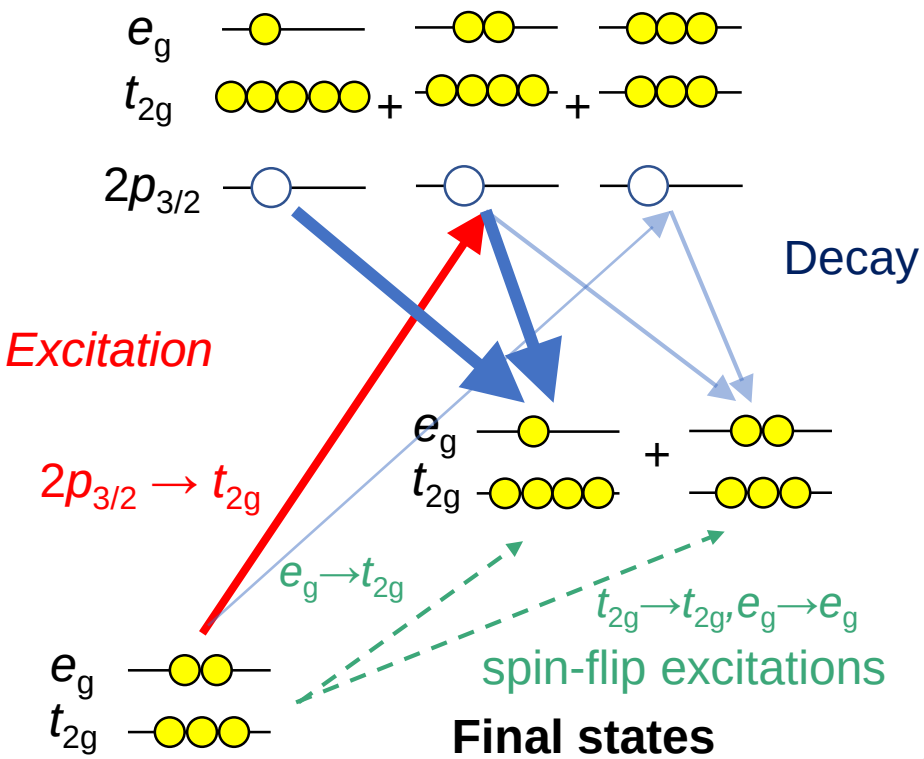
Miyawaki *et al.*, PRB **96,** 214420 (2017).

Possible Transition Channels at Fe-$L_{2,3}$ RIXS

Intermediate states (L_3-edge)

@L_3 main peak

5': 30-50% 30-50% 10-20%



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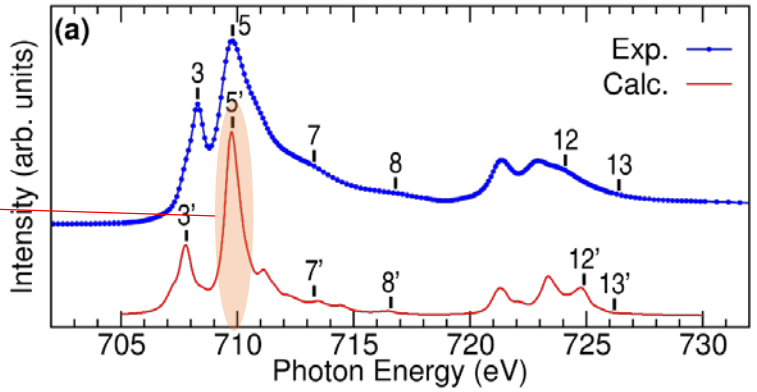

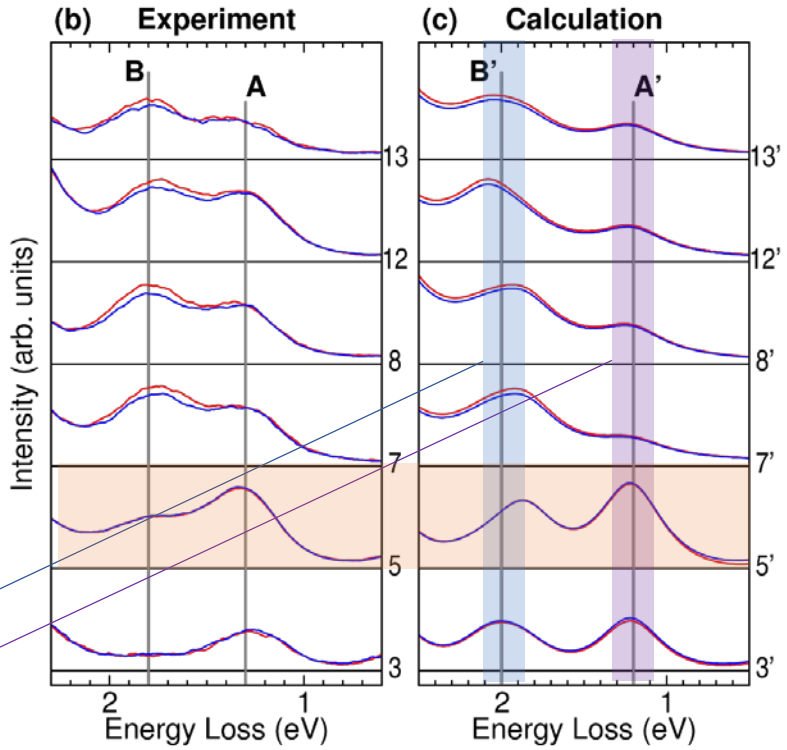

Miyawaki *et al.*, PRB **96,** 214420 (2017).

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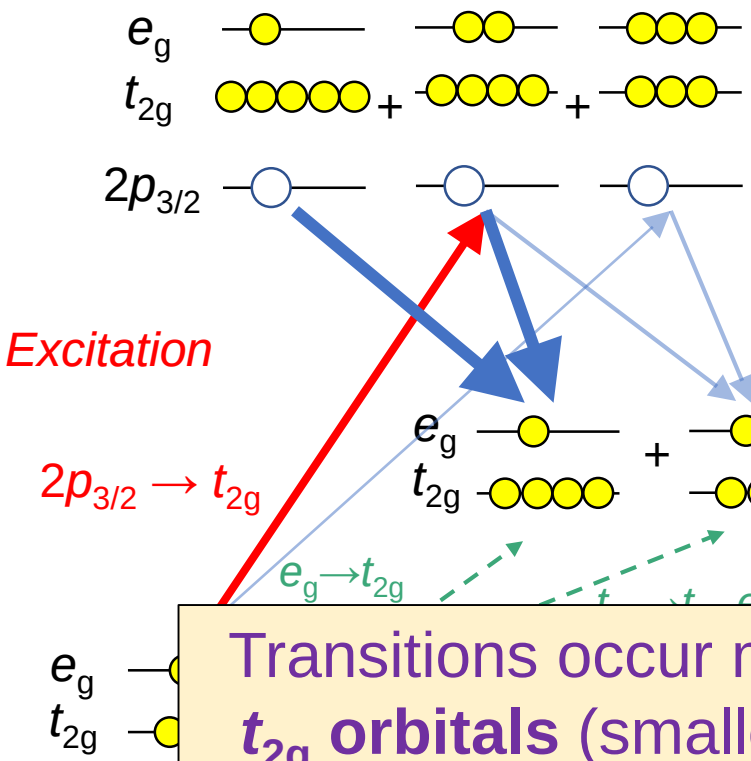
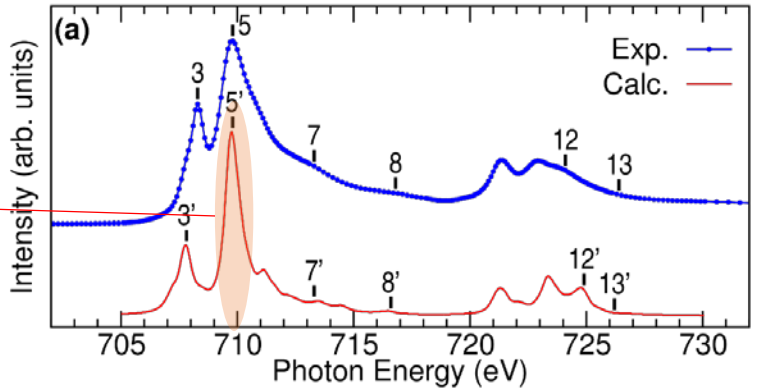
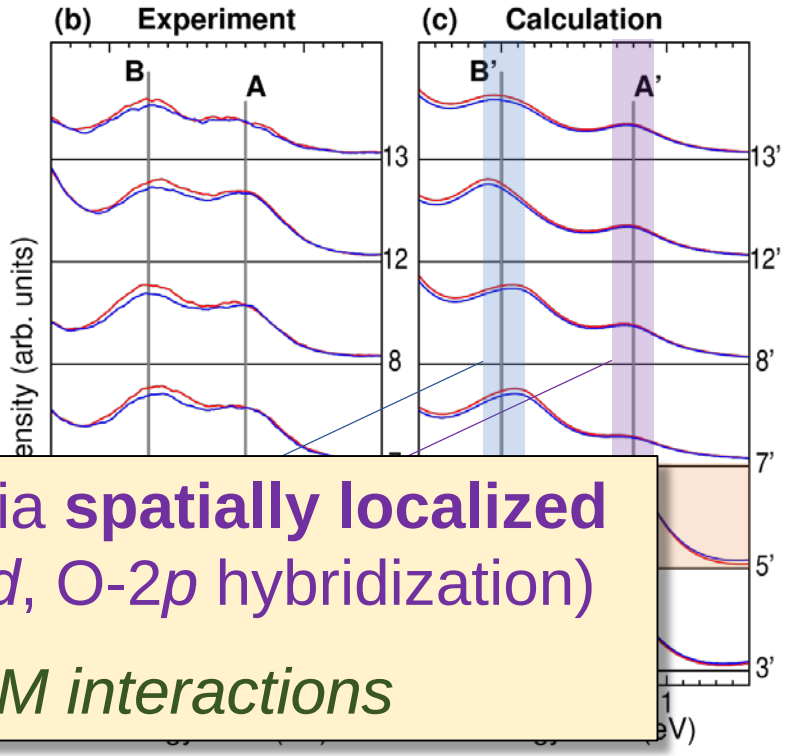






Transitions occur mainly via **spatially localized t_{2g} orbitals** (smaller Fe-3*d*, O-2*p* hybridization)

Cannot capture D-M interactions

Initial s

d^5, high-spin

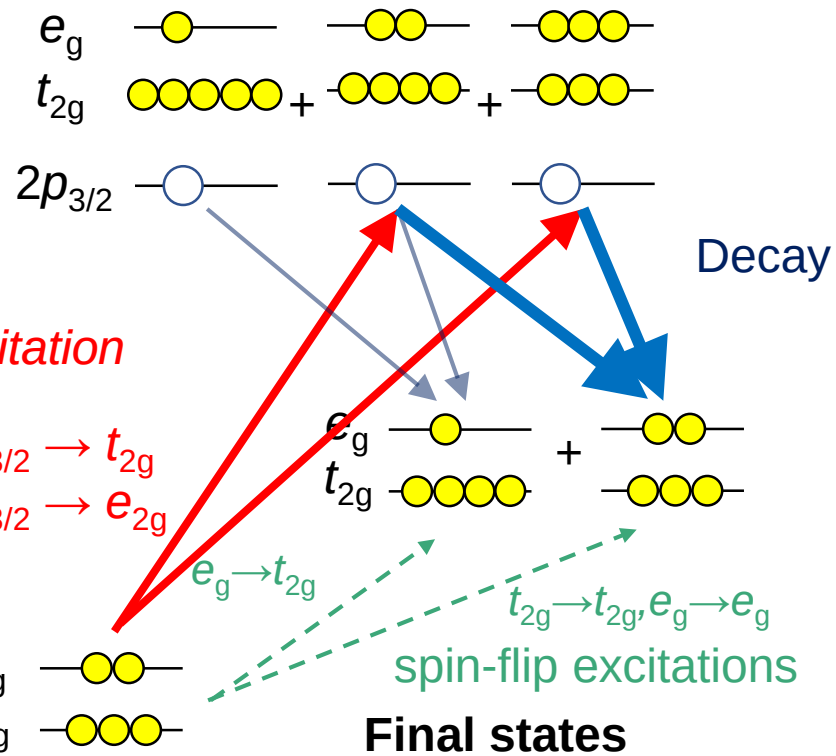
Miyawaki *et al.*, PRB **96,** 214420 (2017).

Possible Transition Channels at Fe-$L_{2,3}$ RIXS

Intermediate states (L_3-edge)

@L_3 shoulder (charge transferred) peak

7':	5%	**45%**	**45%**

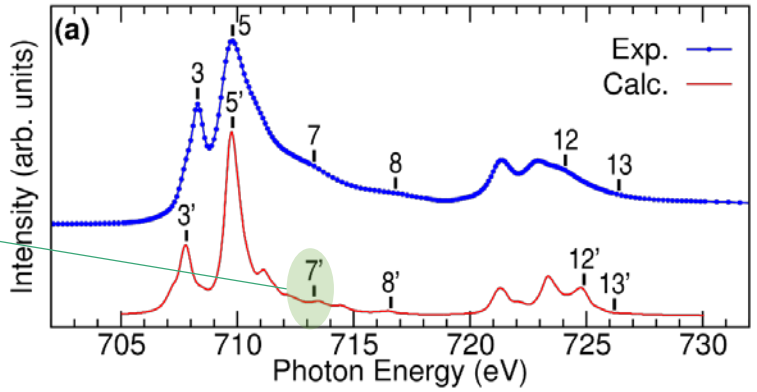


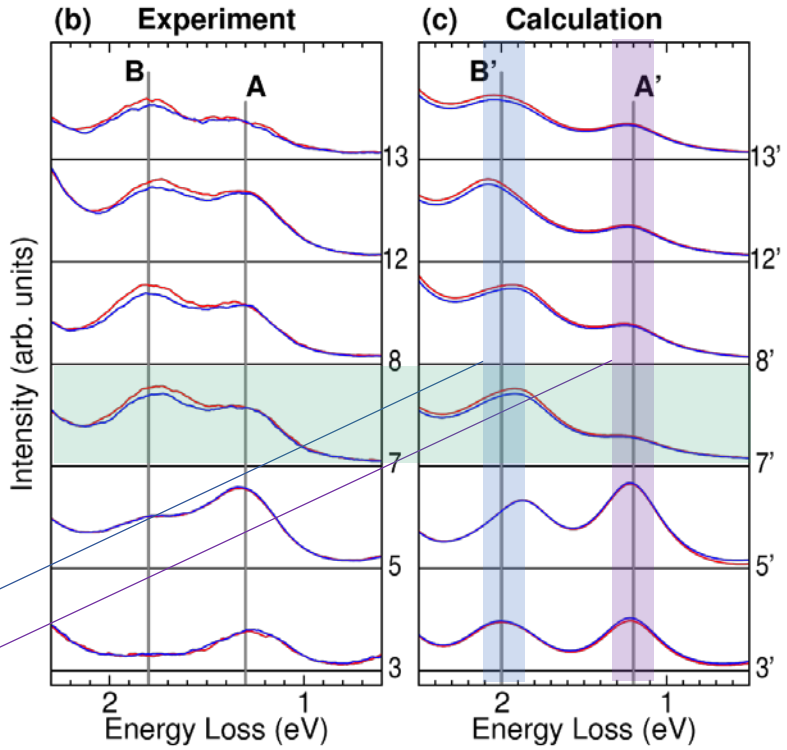
Initial states

d^5, high-spin

Final states

B':	65%	**25%**
A':	90%	**10%**





Miyawaki *et al.*, PRB **96,** 214420 (2017).

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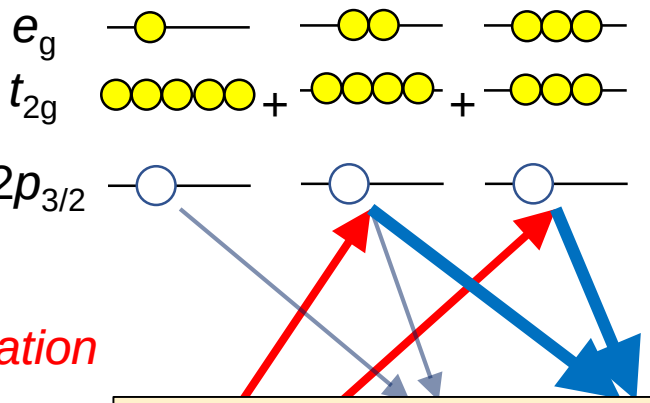
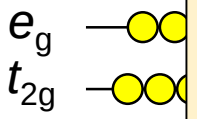


Decay

Excitation

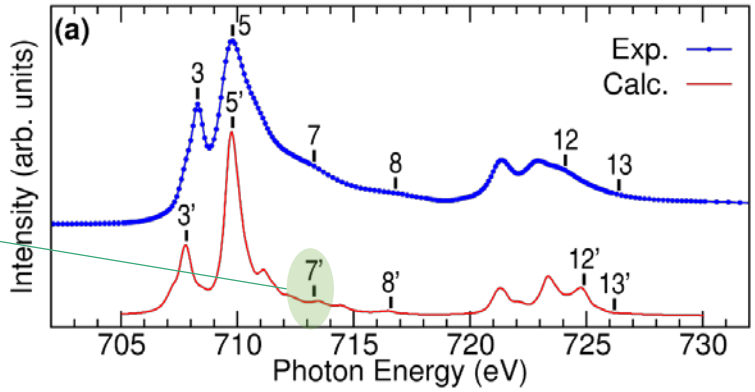
$2p_{3/2} \rightarrow t_{2}$

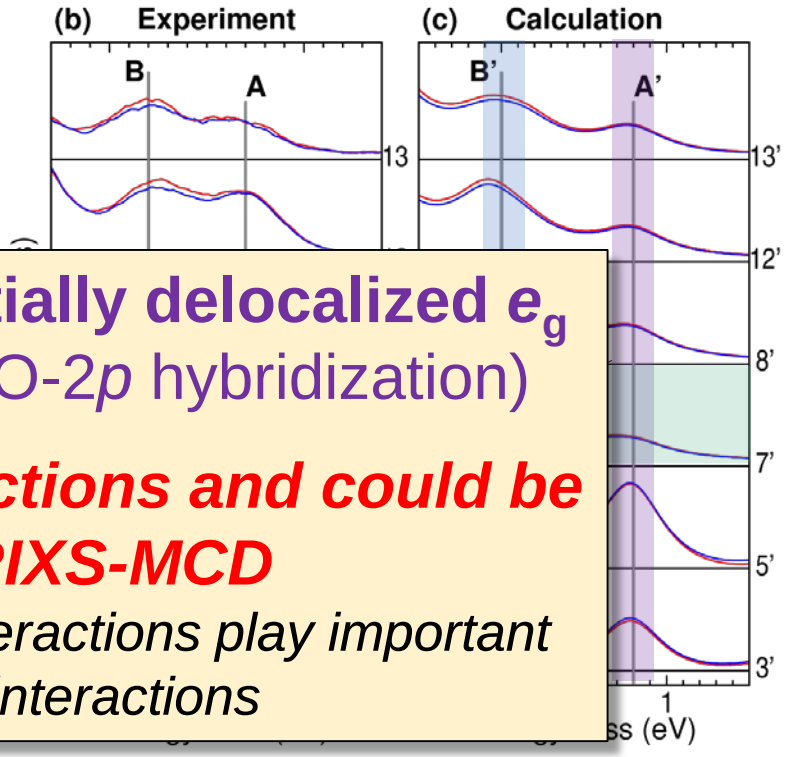
$2p_{3/2} \rightarrow e_{2}$



Initial stat

d^5, high-spin





More transitions via **spatially delocalized e_g orbitals** (larger Fe-3*d*, O-2*p* hybridization)

Can capture D-M interactions and could be an origin of RIXS-MCD

Fe-O-Fe super-exchange interactions play important role on the D-M interactions

Miyawaki *et al.*, PRB **96,** 214420 (2017).

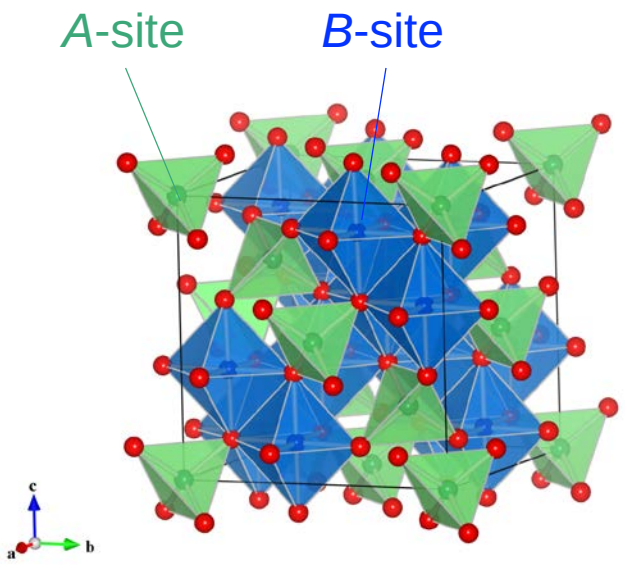
Fe *K*-pre-edge RIXS of Fe_3O_4

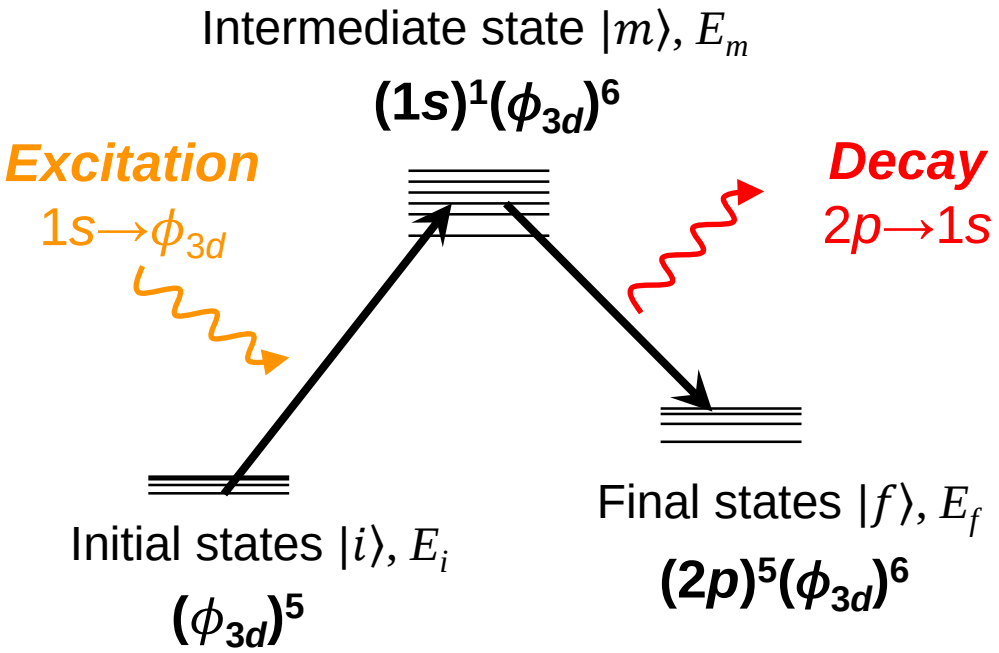
Spinel ferrite Fe_3O_4

Space group $Fd\bar{3}m$ (#227)

Ferrimagnetic (T_c = 860K)

$(Fe^{3+}\downarrow)[Ni^{2+}\uparrow,Fe^{3+}\uparrow]_2O^{2-}{}_4$





A-site (T_d):

$1s\rightarrow\phi_{3d}$: dipole **allowed**

strong intensity

B-site (O_h):

$1s\rightarrow\phi_{3d}$: dipole **forbidden**

weak intensity

Charge Transfer Multiplet Method

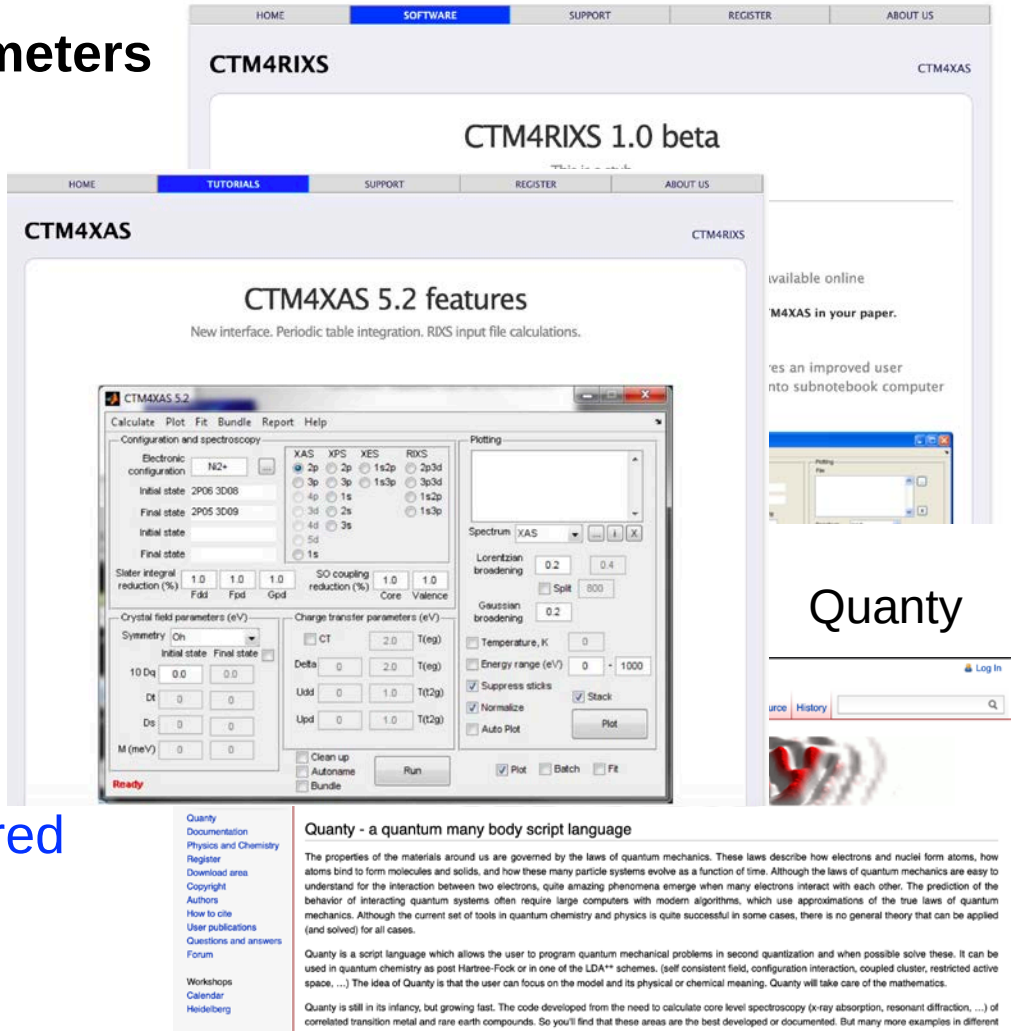
- Model Hamiltonian
- Fit spectra with **adjustable parameters**

Slater integrals: F^k, G^k
Crystal field splitting: $10Dq$
Hubbard parameter: U_{dd}, U_{pd}
Charge transfer energy: Δ

☺ Physically understandable
☺ Small computational cost (Fast!)
☹ Little predictive performance
☹ The lower the symmetry, more adjustable parameters are required

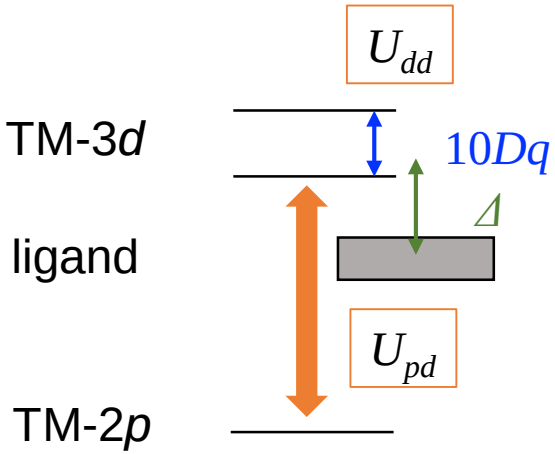
Part of those drawbacks can be overcome by the DMFT

CTM4XAS/RIXS



Charge Transfer Multiplet Method

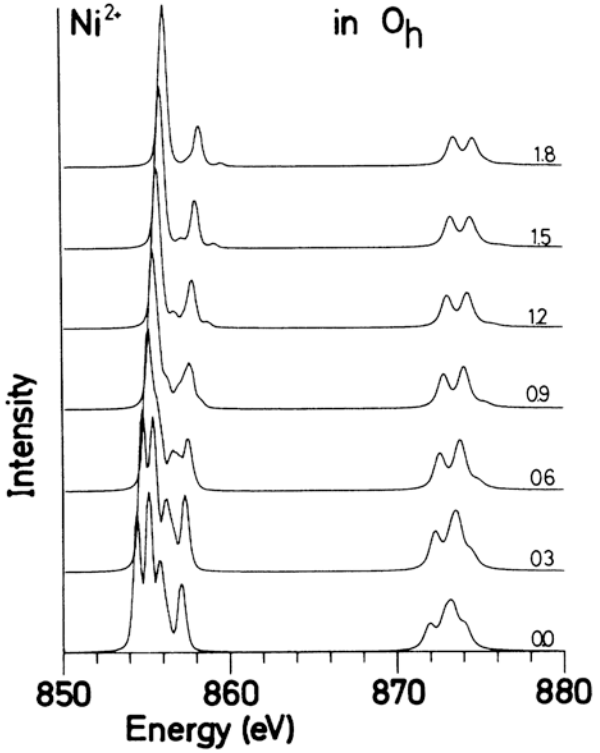
- Model Hamiltonian (Anderson impurity model)
- Fit spectra with adjustable parameter



Crystal field splitting

Charge transfer energy

Hubbard parameters
(Coulomb interaction)



de Groot *et al.*, Phys. Rev. B **42** (1990) 5459.

☺ Physically understandable

☺ Small computational cost (QUICK!)

☹ Little predictive performance

☹ The lower the symmetry, more adjustable parameters are required