遷移金属$L_{2,3}$端X線吸収分光と多電子系第一原理計算による正極材料の化学状態解析

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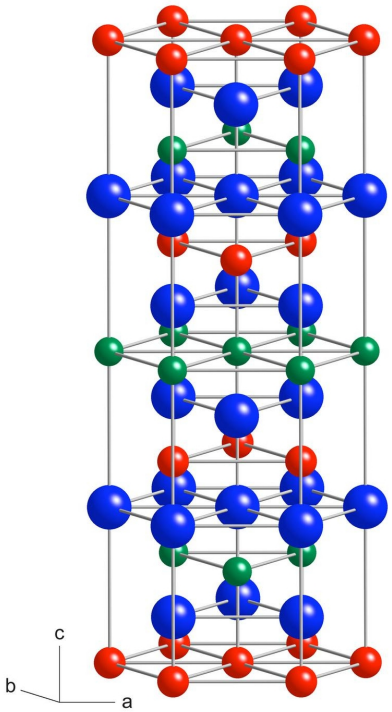
立命館SRセンター公開シンポジウム

～ 軟X線分光を用いた二次電池研究の最前線 ～

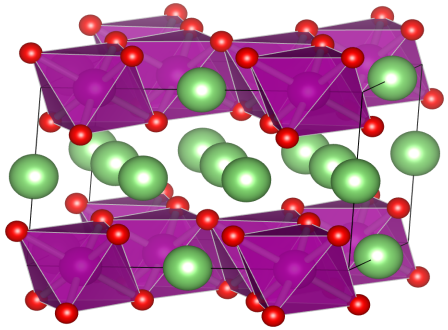
2016年11月11日

Characterization of Cathode Materials via Soft X-ray Absorption Spectroscopy

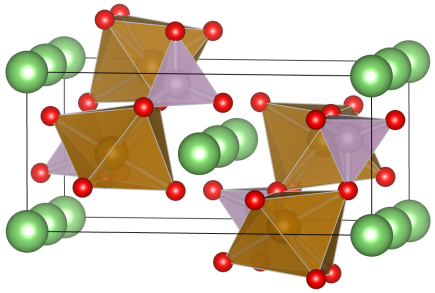
$LiCoO_2$

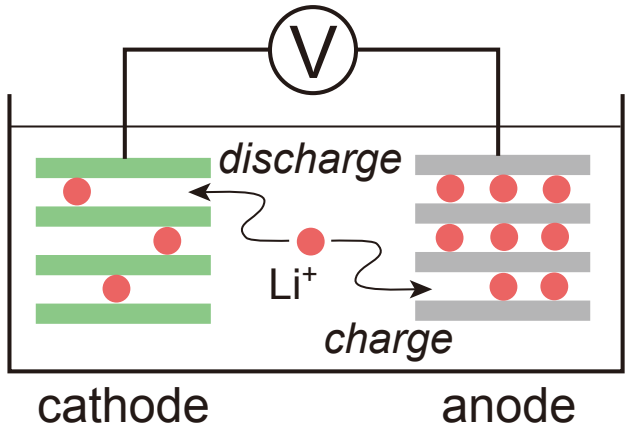


Li_2MnO_3



$LiFePO_4$





Redox behavior during charge/discharge cycle?

Soft X-ray Absorption Spectroscopy (XAS) give us direct information of valence electrons

- Transition metal (TM) $L_{2,3}$-edges : $2p \rightarrow$ **3*d*,** (4*s*)
- Oxygen *K*-edge : 1s → **2*p*,** 3*p*

Ab-initio Calculations of XAS

Input

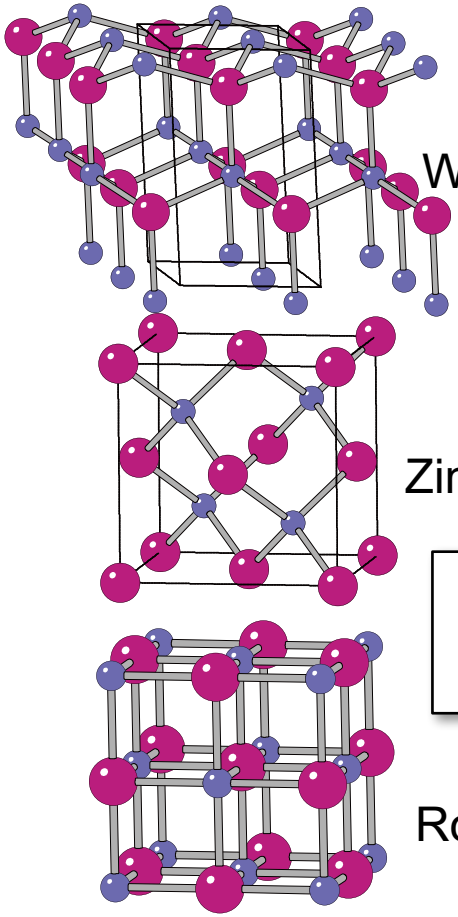
- atomic numbers
- atomic coordinates

Quantum mechanics

$$H\Psi_k = E_k\Psi_k$$

Theoretical spectra

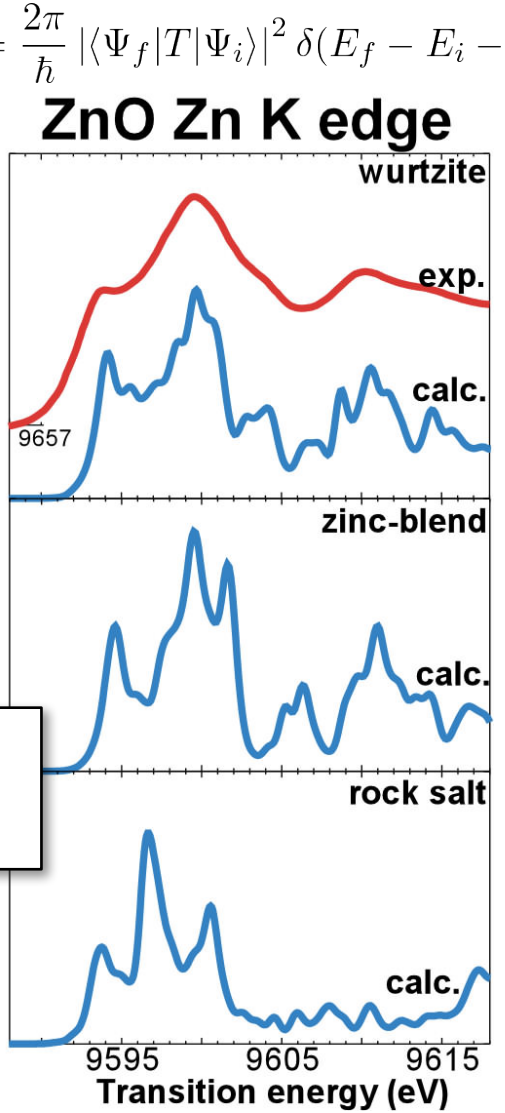
$$W_{fi} = \frac{2\pi}{\hbar}\left|\langle\Psi_f|T|\Psi_i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$



No adjustable parameter

Theoretical fingerprints

Map local structure to a spectrum



Mizoguchi *et al.*, Phys. Rev. B **70,** 045103 (2004).

Ab-Initio Methods for XANES/ELNES

No universal method for simulating all edges of all elements!

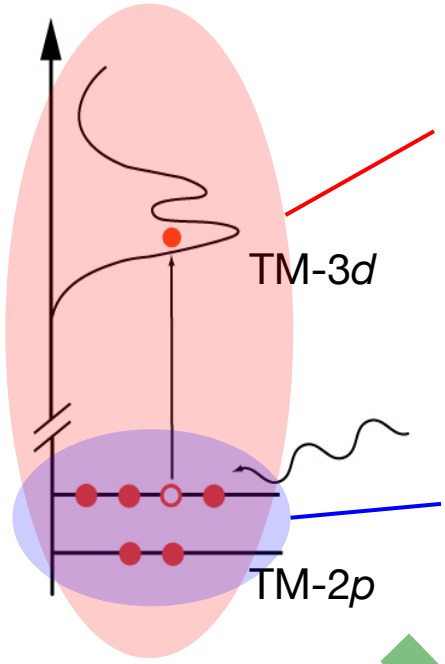
Typical element

- *K*-edge, *L*-edge [deep core]
  - *independent particle approximation*
    - Supercell + DFT + core-hole
    - Multiple scattering theory
- *K*-edge, *L*-edge [shallow core (< 100eV)]
  - *two-particle theory* – strong excitonic effects
    - Bethe-Salpeter Equation (BSE)

Transition metal
Rare-earth

- *K*-edge (main features)
  - Supercell + DFT + core-hole
  - Multiple scattering theory
- $L_{2,3}$-edge, $M_{4,5}$-edge, *K*-pre-edge
  - *many-electron theory – multiplet effects*
    - Configuration Interaction (CI)

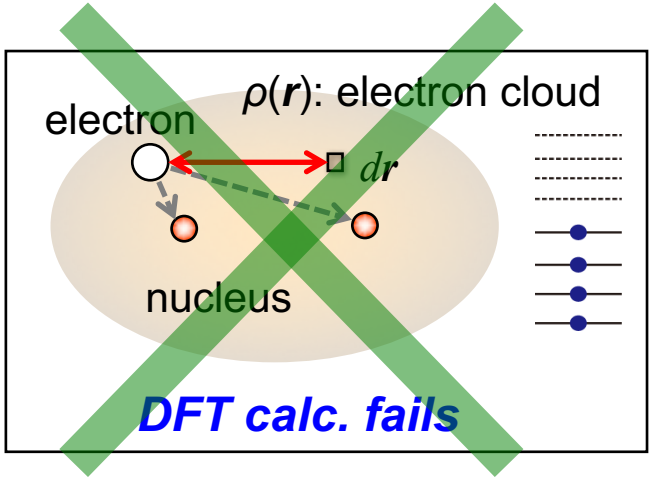
Multiplet Effects on TM-$L_{2,3}$ XAS

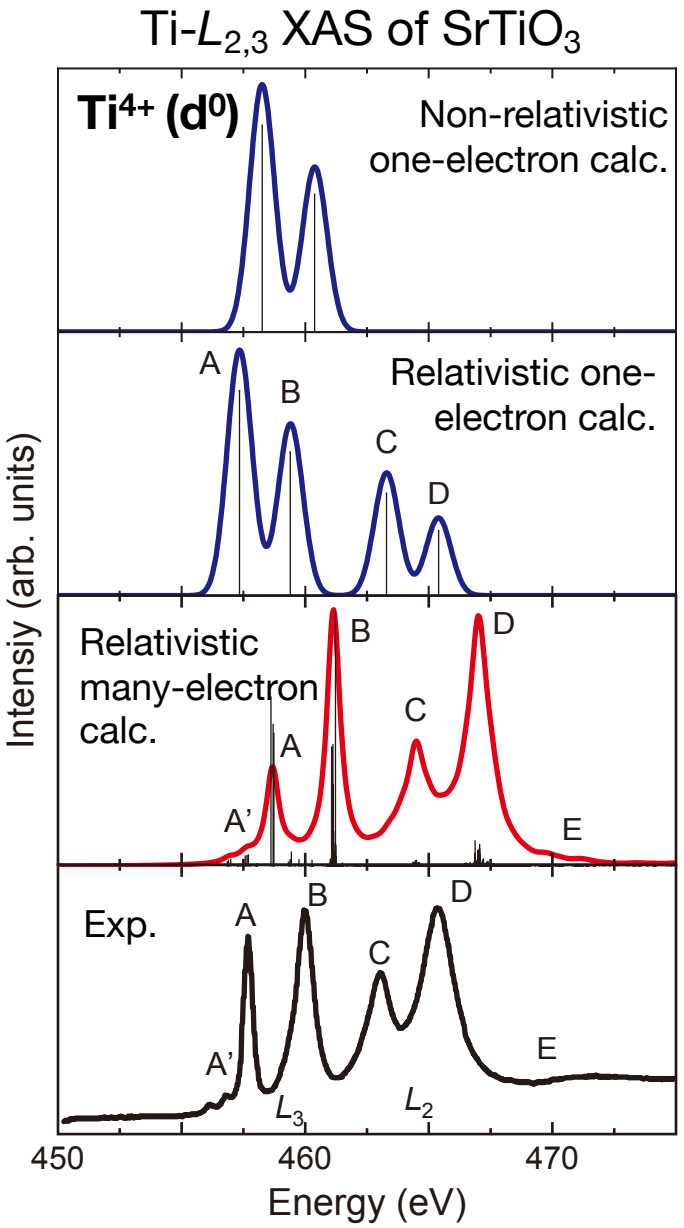


Strong correlations
core-hole & 3*d* electrons

Modifies spectral shape
Multiplet Effect

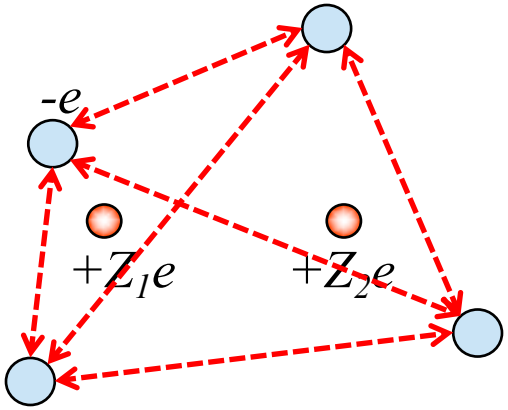
Relativistic effects
e.g. spin-orbit coupling





Ikeno *et al.*, J. Phys.: Condens. Matter **21** (2009) 104208.

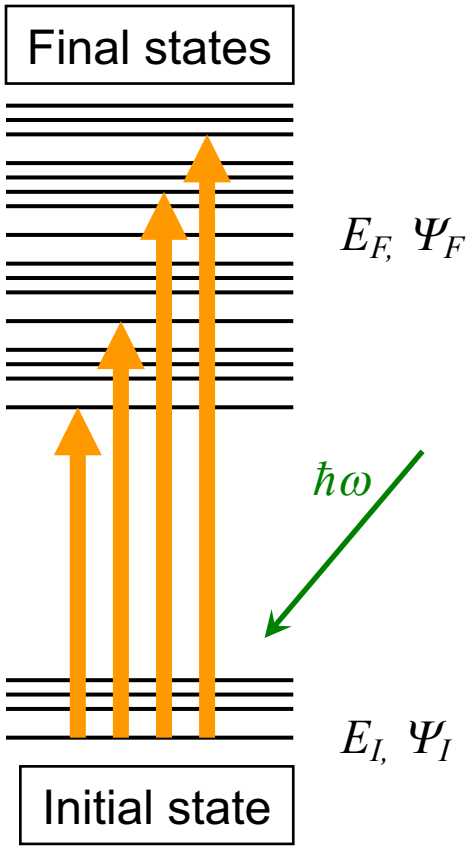
Go Beyond DFT!



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

Difficulties in calculations

- Many-body problem
- relativistic effect (core-levels)
- explicit inter-electron interactions



Calculations for XAS using Model Hamiltonian

Charge Transfer Multiplet method

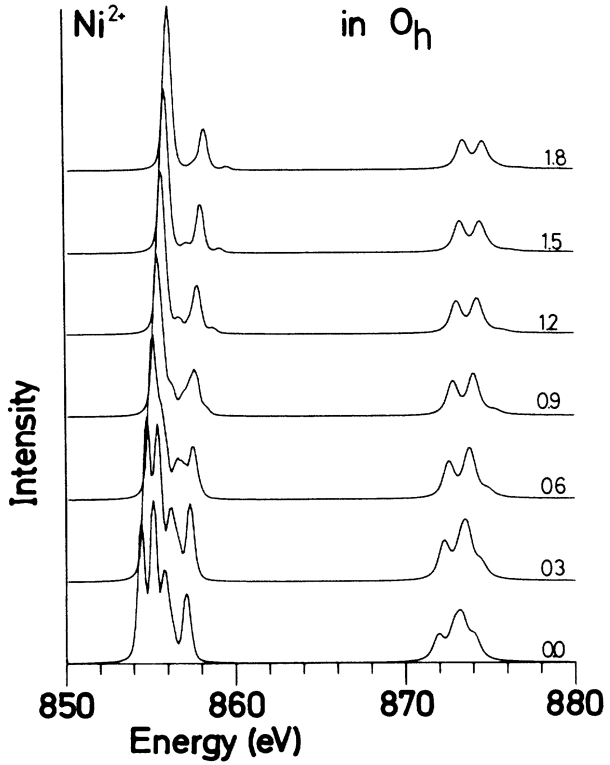
- Model Hamiltonian
- Fit spectra with adjustable parameters

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

☹ Little predictive performance

☹ Only for highly symmetric systems

the lower the symmetry, more adjustable parameters are required



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

Development of a *ab-initio* approach has been strongly desired

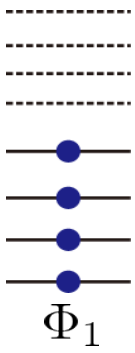
- ❖ No adjustable parameter
- ❖ Applicable to arbitrary atomic structures

Ab-Initio Multiplet Approach

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

Independent particle approximation (Hartree-Fock, DFT)

$$\Psi_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) =$$



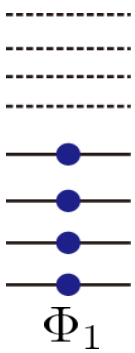
Φ_1

$$\Phi_p = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{p1}(\boldsymbol{r}_1) & \phi_{p2}(\boldsymbol{r}_1) & \cdots & \phi_{pN}(\boldsymbol{r}_1) \\ \phi_{p1}(\boldsymbol{r}_2) & \phi_{p2}(\boldsymbol{r}_2) & \cdots & \phi_{pN}(\boldsymbol{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{p1}(\boldsymbol{r}_N) & \phi_{p2}(\boldsymbol{r}_N) & \cdots & \phi_{pN}(\boldsymbol{r}_N) \end{vmatrix}$$

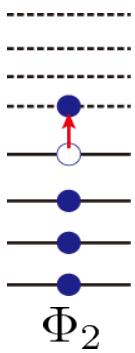
$\{\phi_i(\boldsymbol{r})\}$: one-electron states

CI wavefunction – Linear combinations of Slater determinants

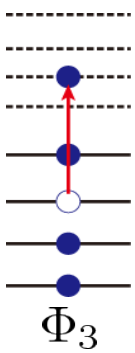
$$\Psi_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = C_{1k}$$



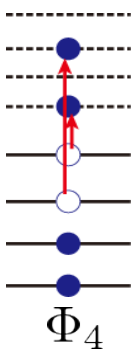
Φ_1 $+C_{2k}$



Φ_2 $+C_{3k}$



Φ_3 $+C_{4k}$



Φ_4 $\cdots$

Dynamical correlations between 2p and 3d electrons

Many-Electron Hamiltonian

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

One-electron integrals

$$\langle \phi_i | \hat{h} | \phi_k \rangle = \int \phi_i^\dagger(\boldsymbol{r}) \hat{h}(\boldsymbol{r}) \phi_j(\boldsymbol{r}) d\boldsymbol{r}$$

Kinetic energy, spin-orbit coupling, potentials from nuclei

CTM: adjustable parameters

Crystal field splitting (10*Dq*)
hopping integral (*t*)
Charge transfer energy (Δ)

Two-electron integrals

$$\langle \phi_i \phi_j | \hat{g} | \phi_k \phi_l \rangle = \int \phi_i^\dagger(\boldsymbol{r}_1) \phi_j^\dagger(\boldsymbol{r}_2) \hat{g}(\boldsymbol{r}_1, \boldsymbol{r}_2) \phi_k(\boldsymbol{r}_1) \phi_l(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

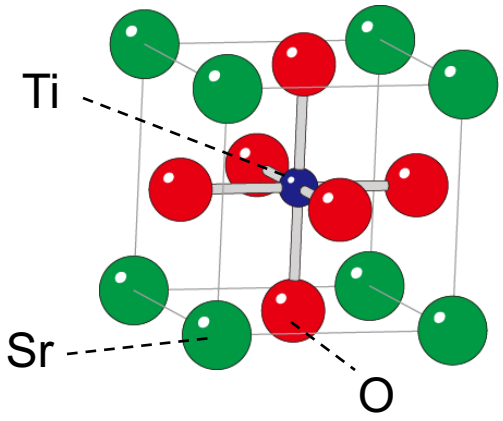
Inter-electron interactions

CTM: Atomic value (HF)

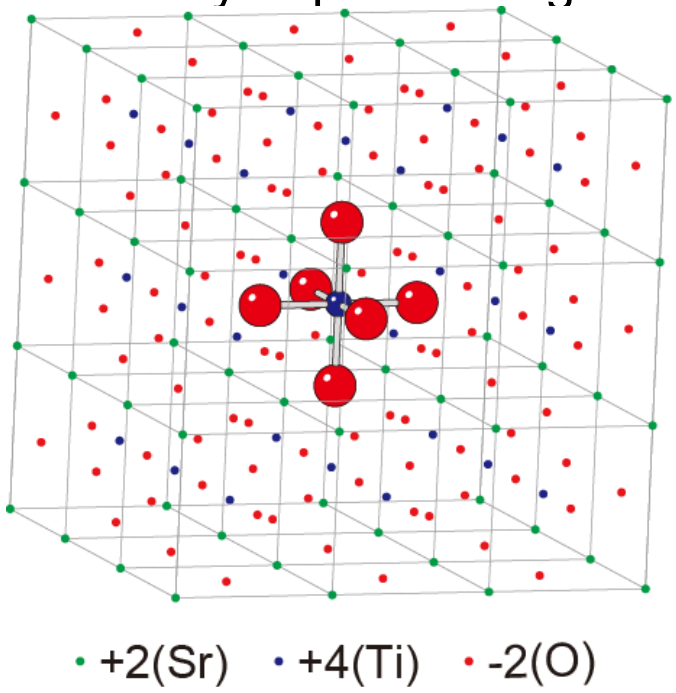
Details of Calculations

- Solving Dirac equation with Local Density Approximation (LDA)
  $[c\boldsymbol{\alpha}\cdot\boldsymbol{p} + mc^2\beta + v_{\mathrm{ext}}(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r})]\phi_i(\boldsymbol{r}) = \epsilon_i\phi_i(\boldsymbol{r})$
- Model cluster (one TM ion and coordinating ligand ions)
- Madelung potential

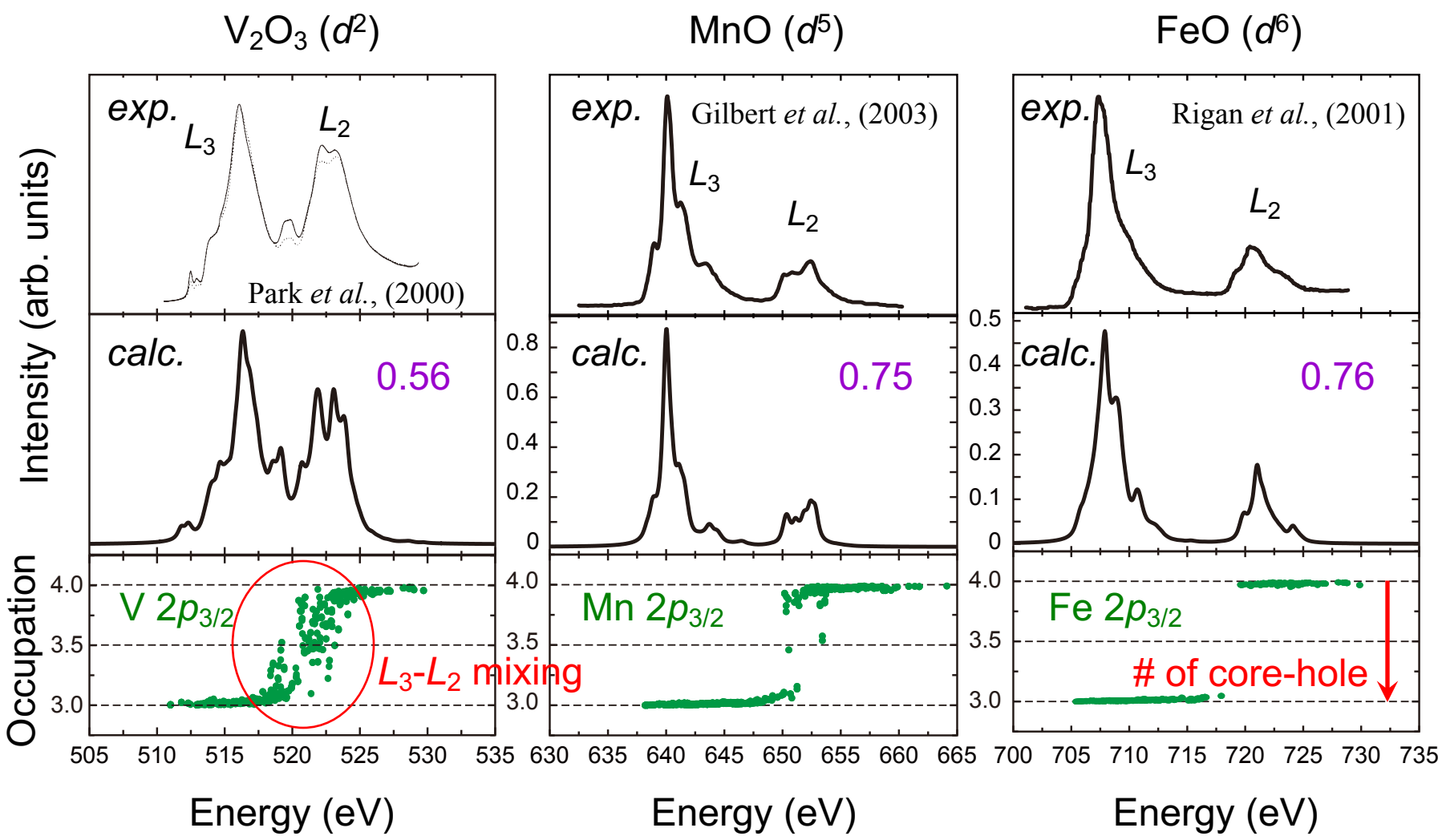
$SrTiO_3$ unit cell



TiO_6^{8-} cluster embedded in the array of point charges



TM-$L_{2,3}$ XAS of V_2O_3, MnO, and FeO



Branching ratio: $L_3/(L_3+L_2)$

Theoretical Fingerprints of TM-$L_{2,3}$ XAS

THE JOURNAL OF PHYSICAL CHEMISTRY C

ARTICLE

pubs.acs.org/JPCC

JPCC **115,** 11871 (2011).

Theoretical Fingerprints of Transition Metal $L_{2,3}$ XANES and ELNES for Lithium Transition Metal Oxides by ab Initio Multiplet Calculations

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ABSTRACT: With the ab initio multiplet method, transition metal (M) $L_{2,3}$-edge X-ray absorption near-edge structures (XANES) and electron energy loss near-edge structures (ELNES) can be predicted in detail. In this study, theoretical fingerprints, their orientation dependences, and theoretical branching ratios of M L_3- and L_2-edges for $LiMO_2$ and Li-extracted MO_2 (M = Mn, Fe, Co, Ni) are obtained. The spectra are found to be strongly dependent on the oxidation state and spin state of M ions in all compounds, which proves that they can be unambiguously determined by matching the experimental spectra with the theoretical fingerprints. The variation of the spectra with the crystal structure is small in $LiMO_2$, whereas it is sensibly large in Li-extracted MO_2. This can be as represented by the fraction of the O-2p in the molecular orbitals t oxides. The $L_3/(L_3 + L_2)$ branching ratio is also computed systemat spin states of M ions but is insensitive to crystal structure. The effects Mn^{3+} and Fe^{4+} (d^4 high-spin state). The presence and orientation c the orientation dependence of the spectra, although the orientation

PHYSICAL REVIEW B **83**, 155107 (2011)

Ab initio charge transfer multiplet calculations on the $L_{2,3}$ XANES and ELNES of 3*d* transition metal oxides

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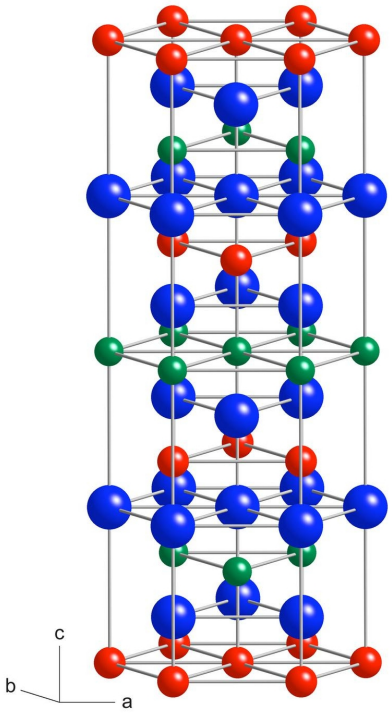
The $L_{2,3}$ x-ray absorption near-edge structures (XANES) and electron energy loss near-edge structures (ELNES) of 3*d* transition metal (TM) oxides are systematically calculated by the *ab initio* charge transfer multiplet (CTM) method using fully relativistic molecular spinors on the basis of density-functional theory. The electronic excitation from molecular spinors mainly composed of O-2*p* to those of TM-3*d*, that is, charge transfer, is included by considering additional electronic configurations in the configuration interactions. The effects of the covalency and charge transfer on the TM-$L_{2,3}$ XANES are investigated in detail. The power of the *ab initio* CTM method to quantitatively reproduce the spectra is demonstrated. Meanwhile, limitations of the application of the method are discussed.

PRB **83,** 155107 (2011).

DOI: 10.1103/PhysRevB.83.155107 PACS number(s): 78.70.Dm, 31.15.am, 71.15.Qe

Ni-$L_{2,3}$ ELNES of $LiNiO_2$ and Related Compounds

$LiNiO_2$: Model cathode material with layered rocksalt structure



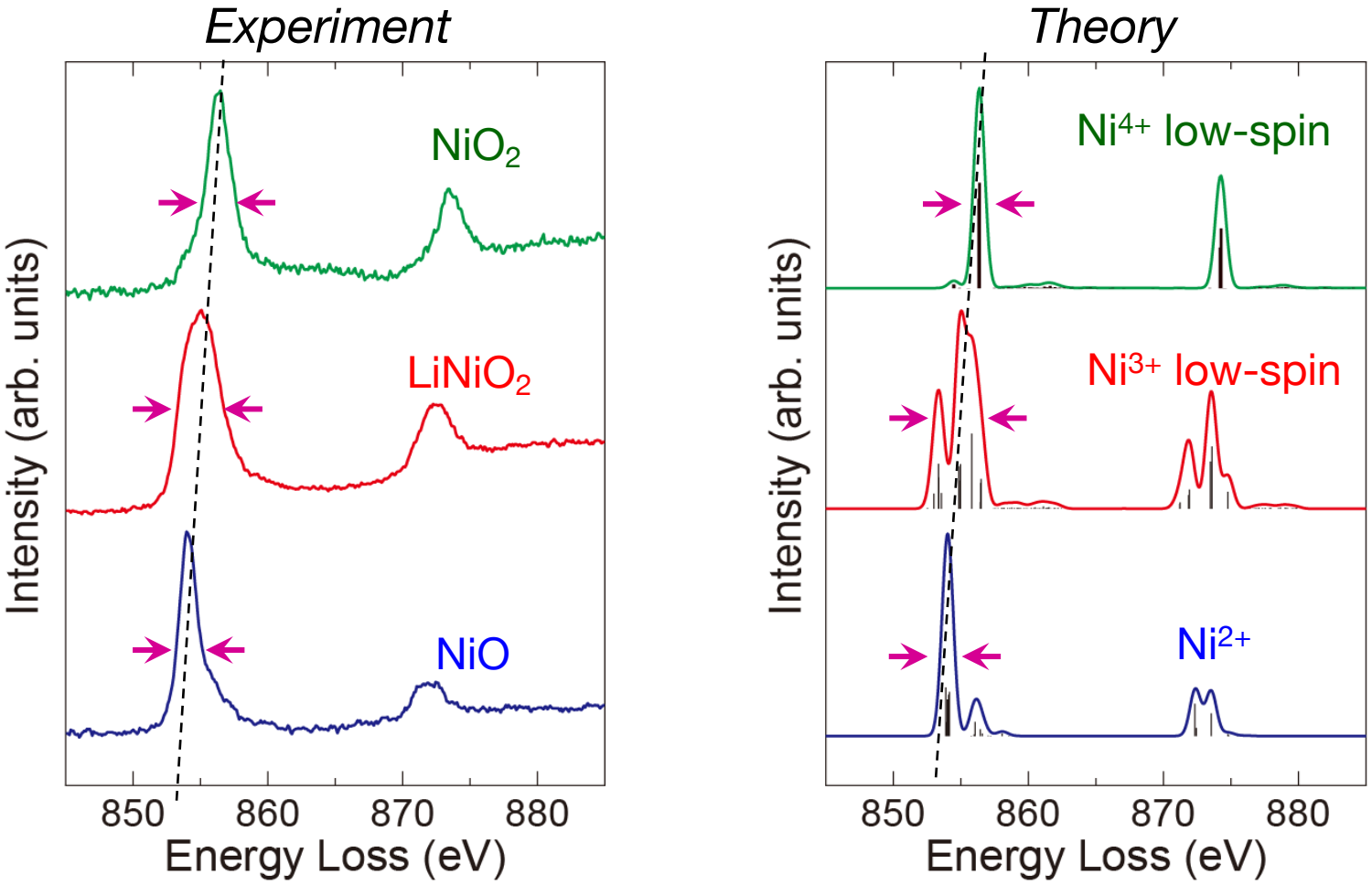
T. Ohzuku *et al.*, Electrochimica Acta **38** (1993) 1159.
Ni-O bond length, magnetic susceptibility
Ni^{3+}, low-spin

L. A. Montoro *et al.*, Chem. Phys. Lett. **309** (1999) 14.
Ni $L_{2,3}$-XAS
Ni^{2+}, charge transfer from oxygen to Ni

- TEM-ELNES measurements of Ni $L_{2,3}$-edges in $LiNiO_2$ and related compounds ***(bulk sensitive)***
- *Ab-initio* multiplet calculations Ni $L_{2,3}$-edges

H. Ikeno, I. Tanaka, Y. Koyama, T. Mizoguchi, *Phys. Rev. B* **72,** 075123 (2005).
Y. Koyama, T. Mizoguchi, H. Ikeno, I. Tanaka, *J. Phys. Chem. B* **109,** 10749 (2005).

Ni-$L_{2,3}$ ELNES of $LiNiO_2$ and Related Compounds



Theory: Ikeno *et al.*, Phys. Rev. B **72**, 075123 (2005).
Experiments: Y. Koyama *et al.,* J. Phys. Chem. B **109**, 10749 (2005).

Redox on Li_2MnO_3 Cathode Material

Li_2MnO_3: reference compound for Li-excess cathode material

Mn-redox mechanism

$$Li_2Mn^{4+}O_3 \rightarrow Li^+ + e^- + LiMn^{5+}O_3^{2-}$$

Mn-*K* (1*s*→**4*p***) XAS

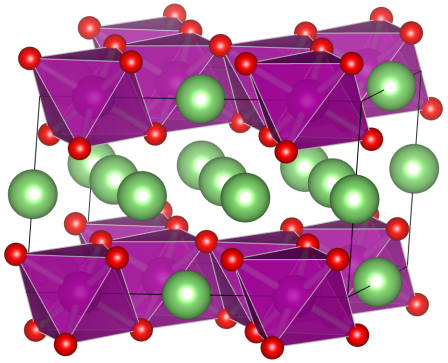
[Yu *et al.,* J. Electrochem. Soc. **156,** A417 (2009).]

O-redox mechanism

$$Li_2Mn^{4+}O_3 \rightarrow Li^+ + e^- + LiMn^{4+}O_3^{1.67-}$$

DFT calculations

[Koyama *et al.,* J. Power Sources **189,** 798 (2009).]



monoclinic
(C2/m)

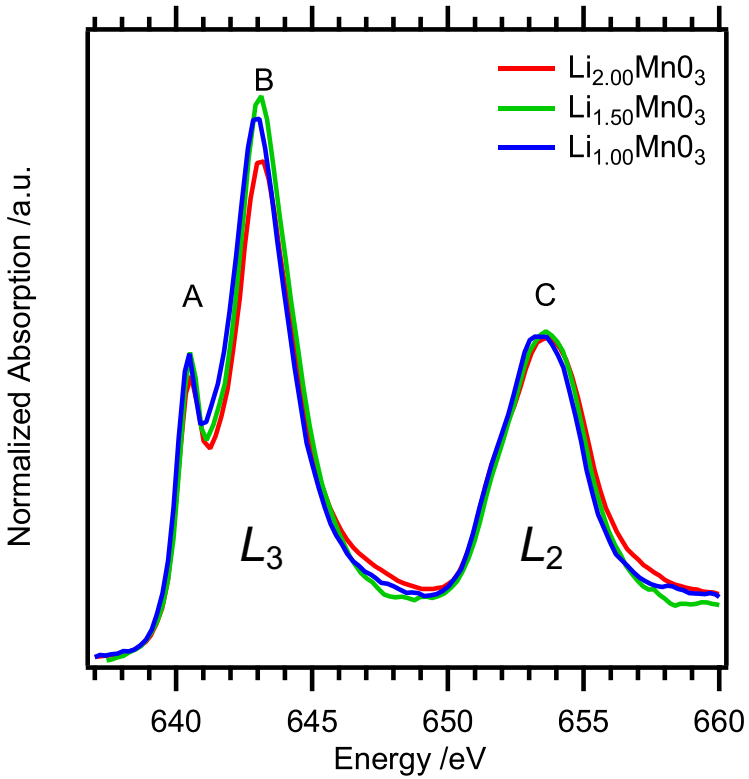
Mn-$L_{2,3}$ XAS + *Ab-initio* calculations
*direct information of Mn-**3d** states*

Kubobuchi, Ikeno, Mizoguchi *et al.,* Appl. Phys. Lett. **104,** 053906 (2014).

Mn-$L_{2,3}$ XAS of Li_xMnO_3

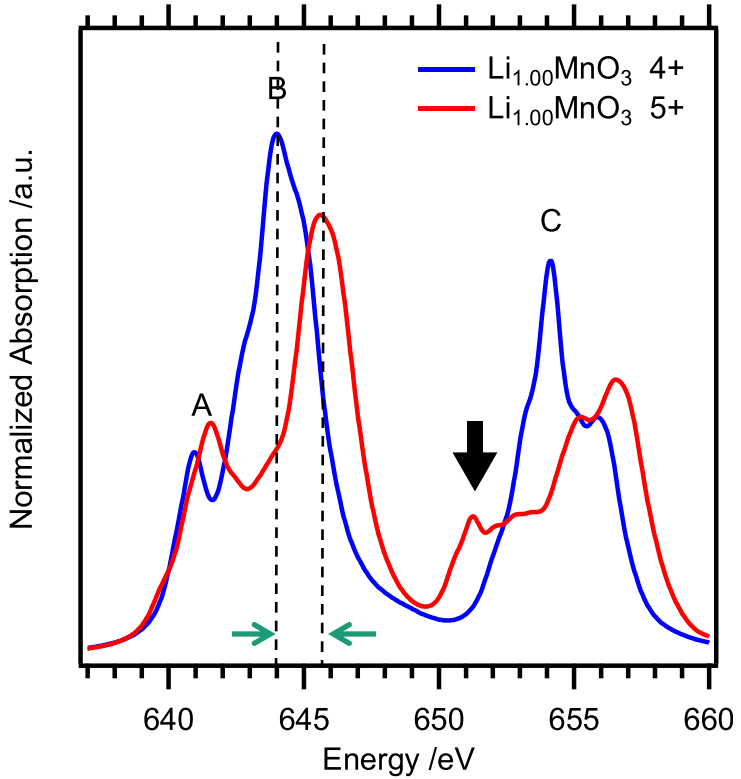
Experiment

BL2@Ritsumeikan SR



Ab-initio calculations

$Li_{1.00}MnO_3$ (Mn^{4+} and Mn^{5+})



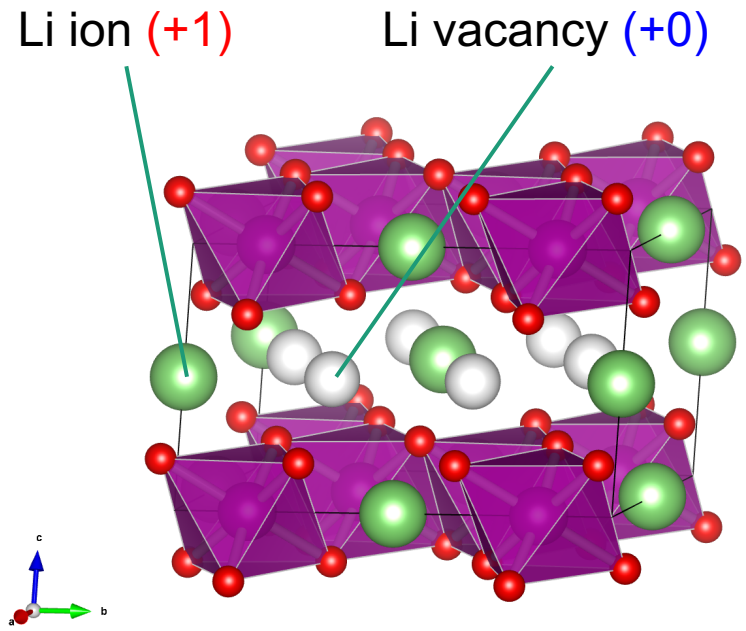
Mn ions are 4+ states in $Li_{1.00}MnO_3$

Mn^{4+}/Mn^{5+}-redox mechanism cannot explain the results

Kubobuchi, Ikeno, Mizoguchi *et al.*, Appl. Phys. Lett. **104,** 053906 (2014).

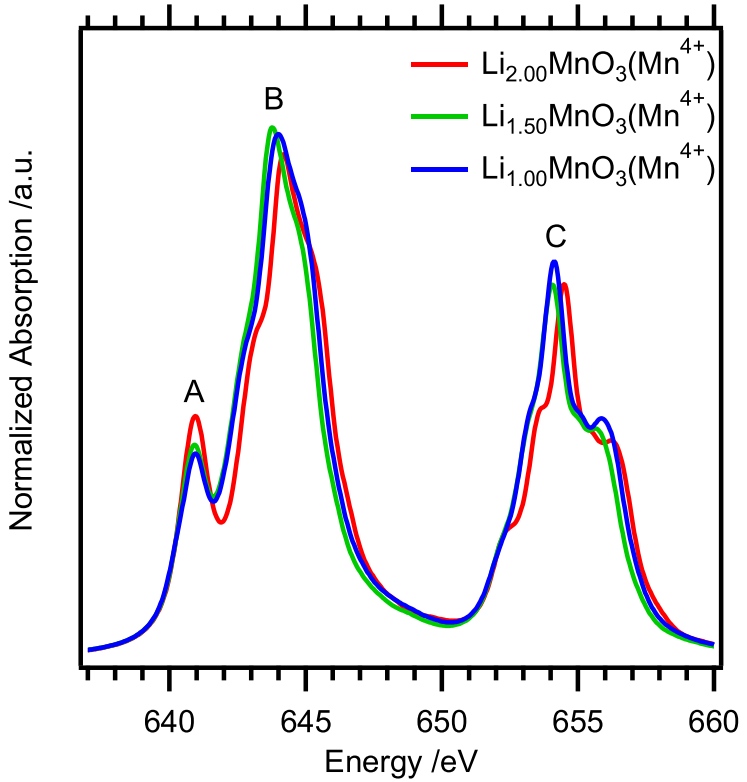
Mn-$L_{2,3}$ XAS of Li_xMnO_3

$Li_{1.00}MnO_3$



Ab-initio calculations

Li_xMnO_3, x = 1.0,1.5,2.0 (Mn^{4+})



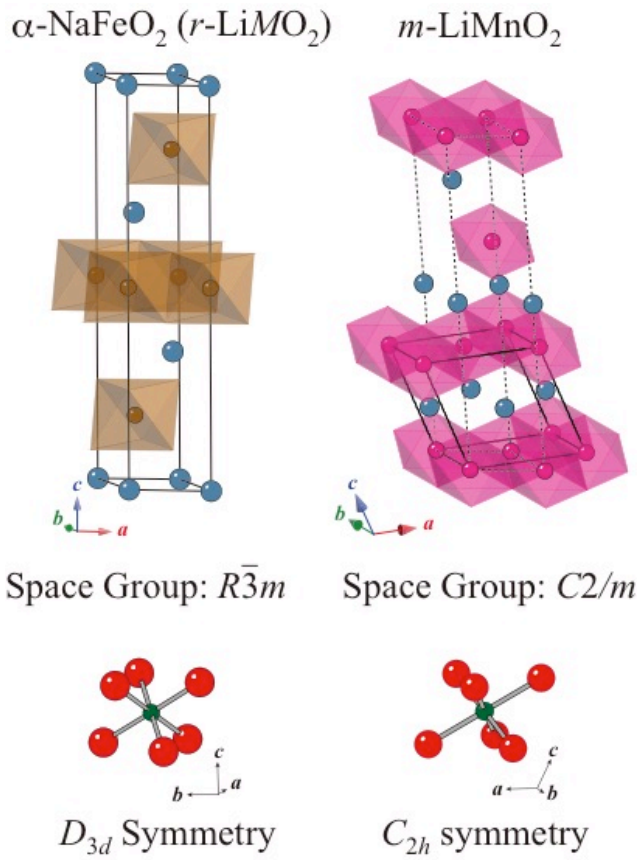
The changes of spectral shapes are due to

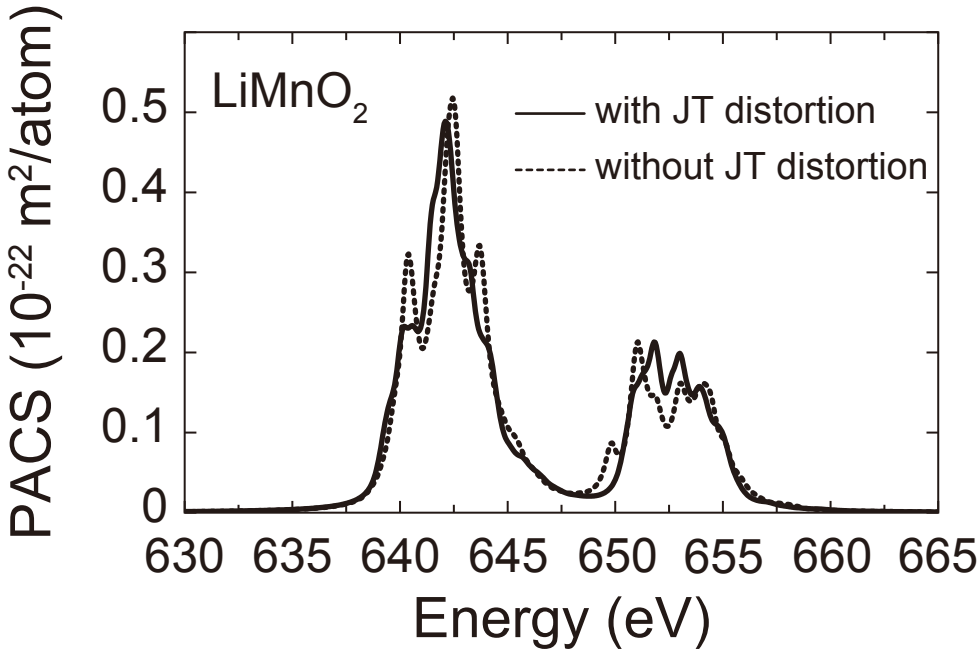
- Changes of electrostatic potential
- Local distortion around Mn ions

Kubobuchi, Ikeno, Mizoguchi *et al.*, Appl. Phys. Lett. **104,** 053906 (2014).

Effects of the Jahn-Teller Distortion

Mn-$L_{2,3}$ XAS of $LiMnO_2$ (Mn^{3+}, d^4)

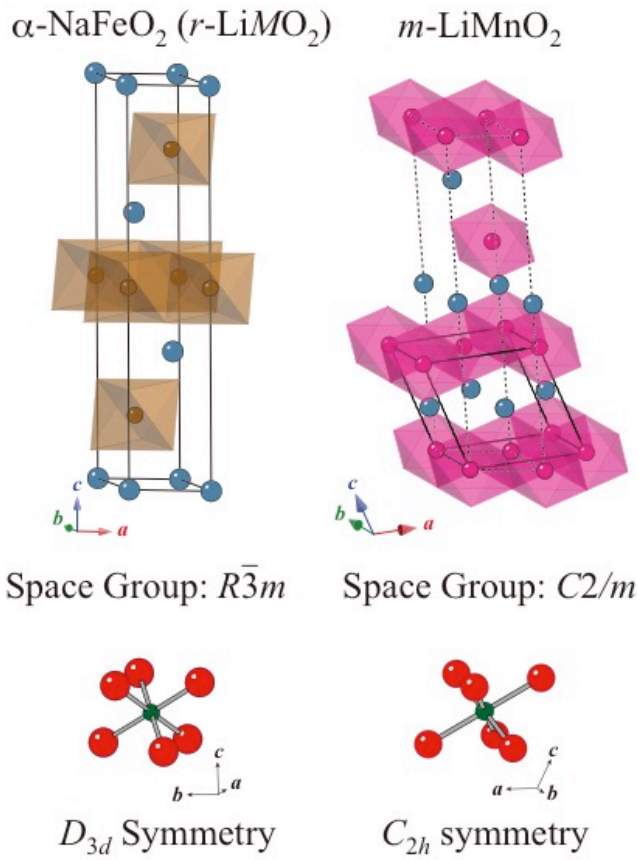


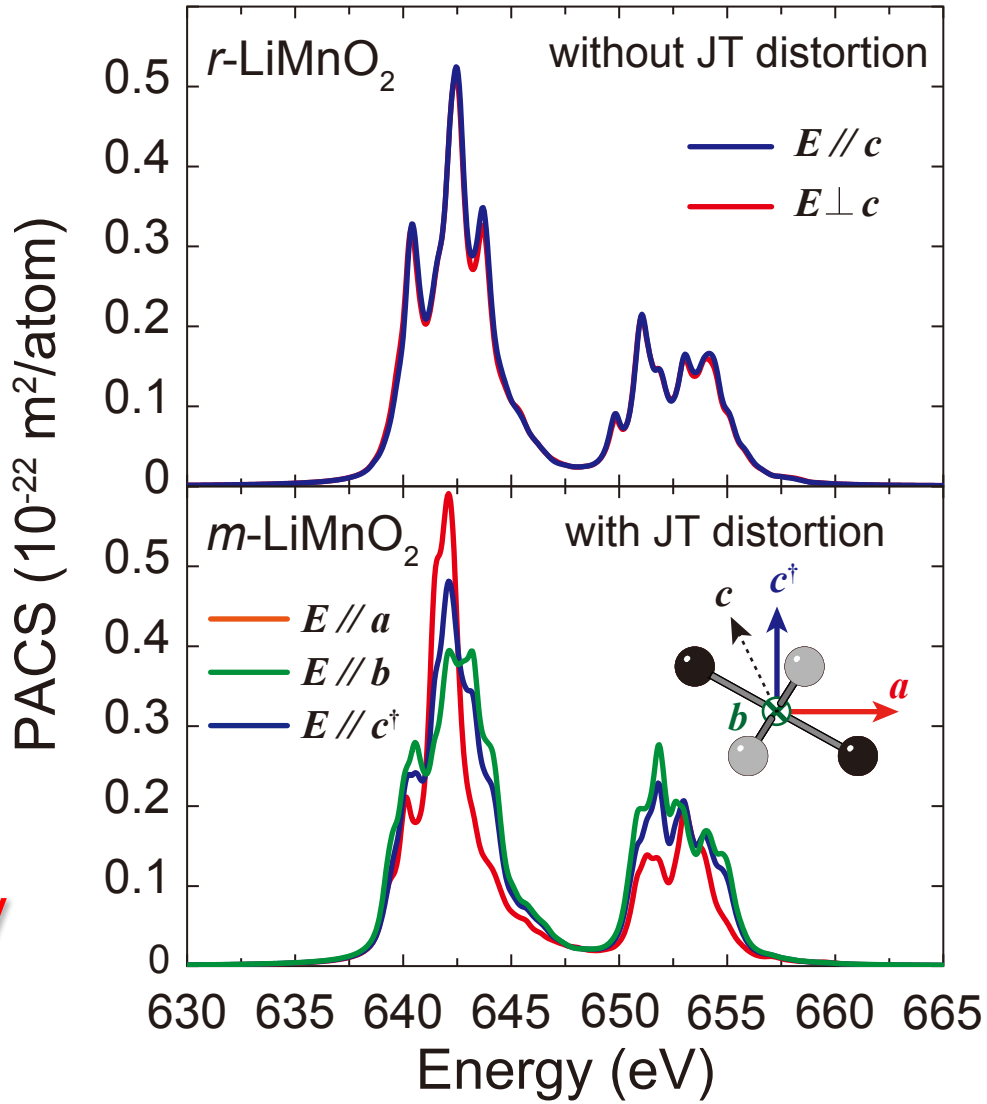


H. Ikeno, *et al.,* J. Phys. Chem. C **115,** 11871 (2011).

Effects of the Jahn-Teller Distortion

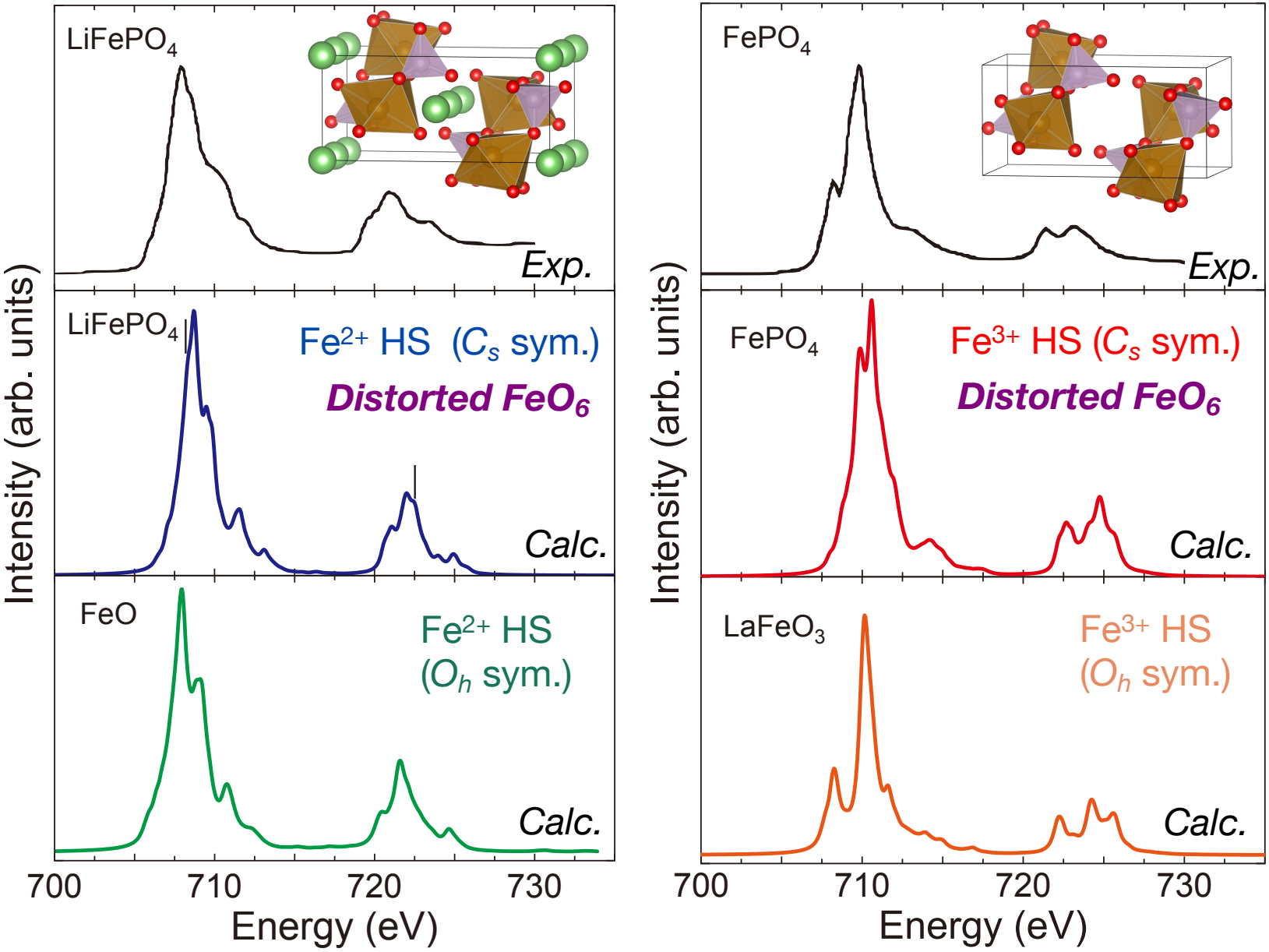
Mn-$L_{2,3}$ XAS of $LiMnO_2$ (Mn^{3+}, d^4)





JT distortion can be clearly detected by measuring orientation dependence

Fe-$L_{2,3}$ XAS in Olivine



Summary

Development of an *ab-initio* method for transition metals $L_{2,3}$ XAS

- Full-relativistic MO calculation using cluster models
- Configuration interaction calculations for multiplet levels
- Applicable to arbitrary atomic & spin arrangements
- Quantitatively *reproduce* & ***predict*** experimental spectra

High quality XAS measurements

+ *Ab-initio* multiplet calculations

= Unique & powerful technique for the characterization of TM in cathode materials

Identify chemical states, spin states, local symmetries etc.

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