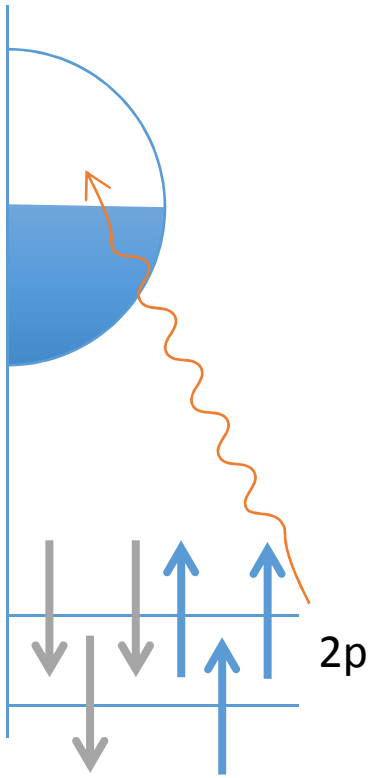
Introduction to crystal field multiplet calculations

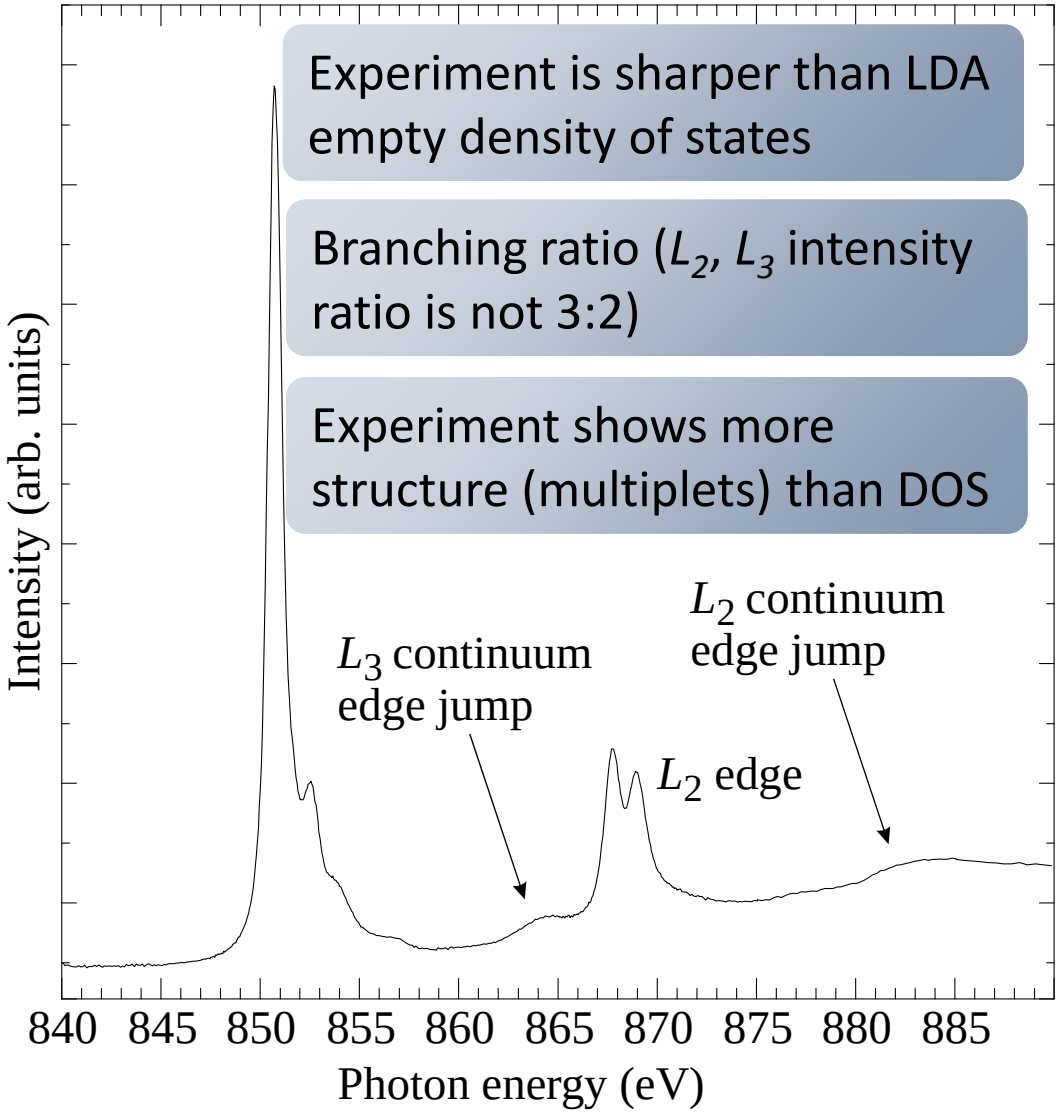
Introduction

Multiplets (atomic physics)

Multiplets (crystal field)

2p XAS


2p


Experiment is sharper than LDA empty density of states
Branching ratio (L_2, L_3 intensity ratio is not 3:2)
Experiment shows more structure (multiplets) than DOS
L_3 continuum edge jump
L_2 continuum edge jump
L_2 edge
Intensity (arb. units)
840 845 850 855 860 865 870 875 880 885
Photon energy (eV)

2p XAS (core level spectroscopy)

- Excitons and multiplets dominate the spectral line-shape.
- It is not sufficient to assume independent electrons interacting with an average potential
- One has to consider the interaction between each pair of electrons explicitly.

Charge Transfer Multiplet program

Quanty, CTM4XAS, Tanaka code (XTLS), etc

Used for the analysis of XAS, EELS,

PES, IPES, Auger, RIXS, NIXS, etc

ATOMIC PHYSICS

⇓

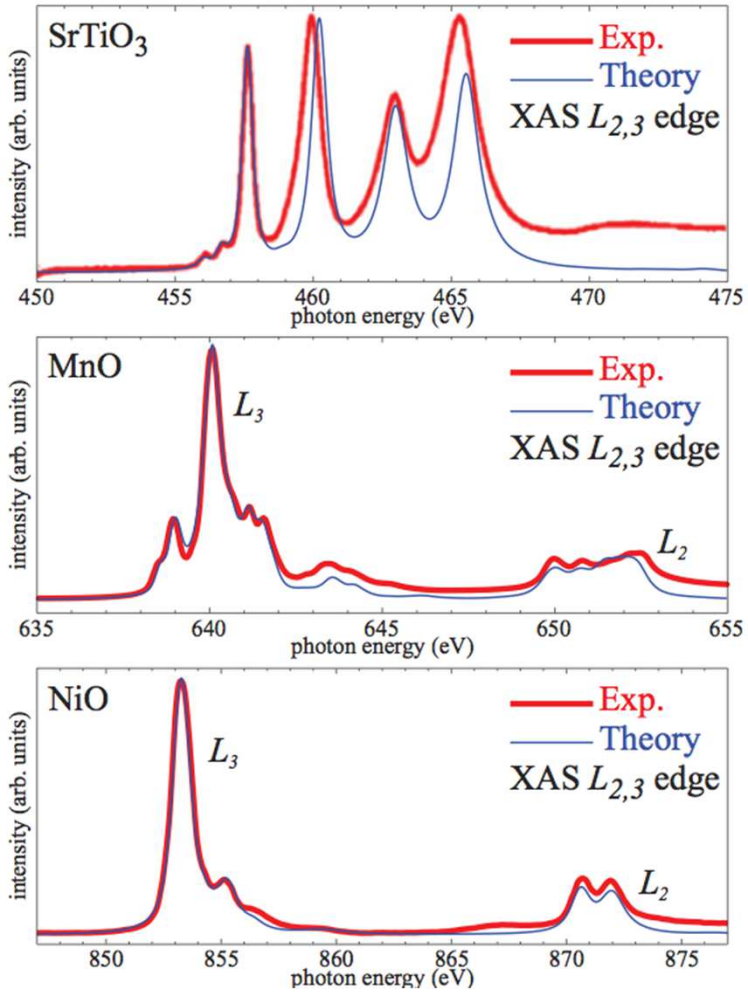
CRYSTAL FIELD THEORY

⇓

CHARGE TRANSFER

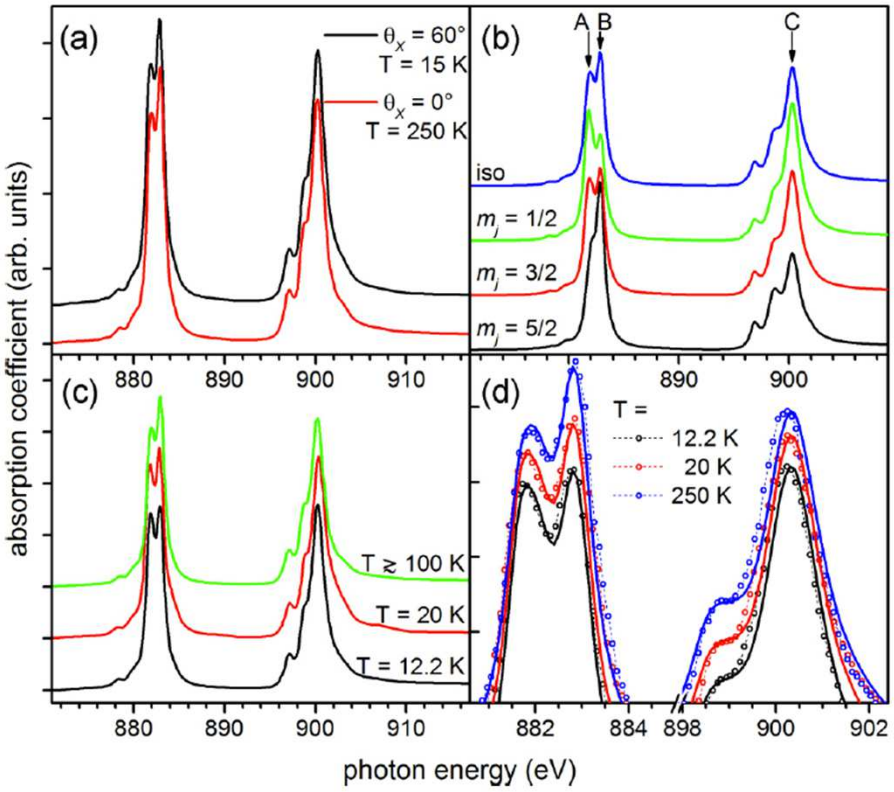
Quanty - XAS

L_{23} edges transition metals



PRB **85**, 165113 (2012)

M_{45} edges rare-earth

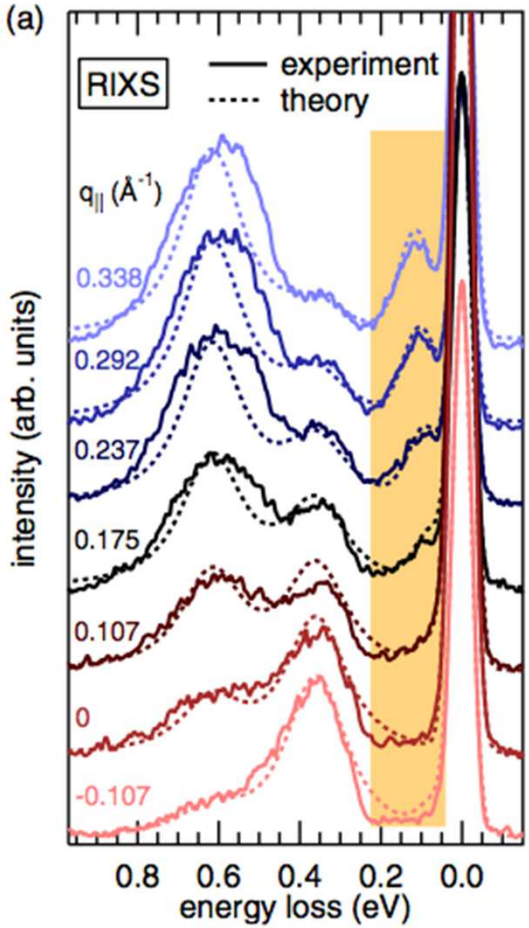


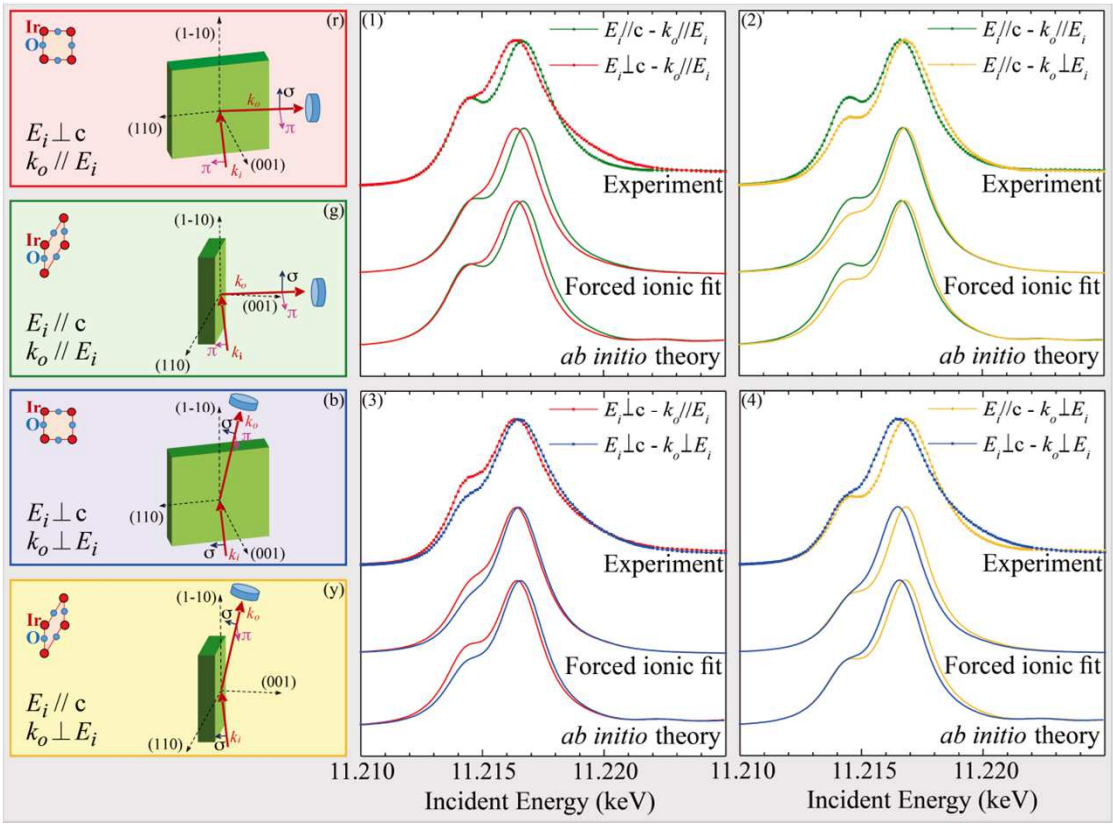
PRB **93**, 165107 (2016)

Quanty – RIXS

Orbital and dispersing magnetic transitions in TiOCl

Linear Dichroism in Sr_2IrO_4

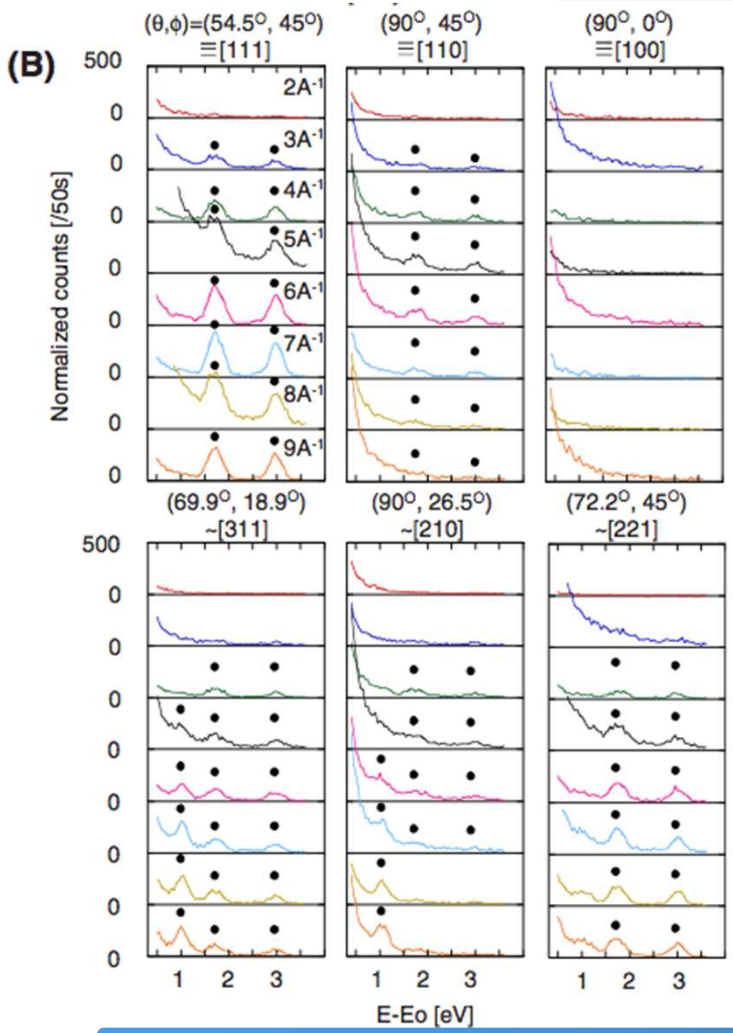


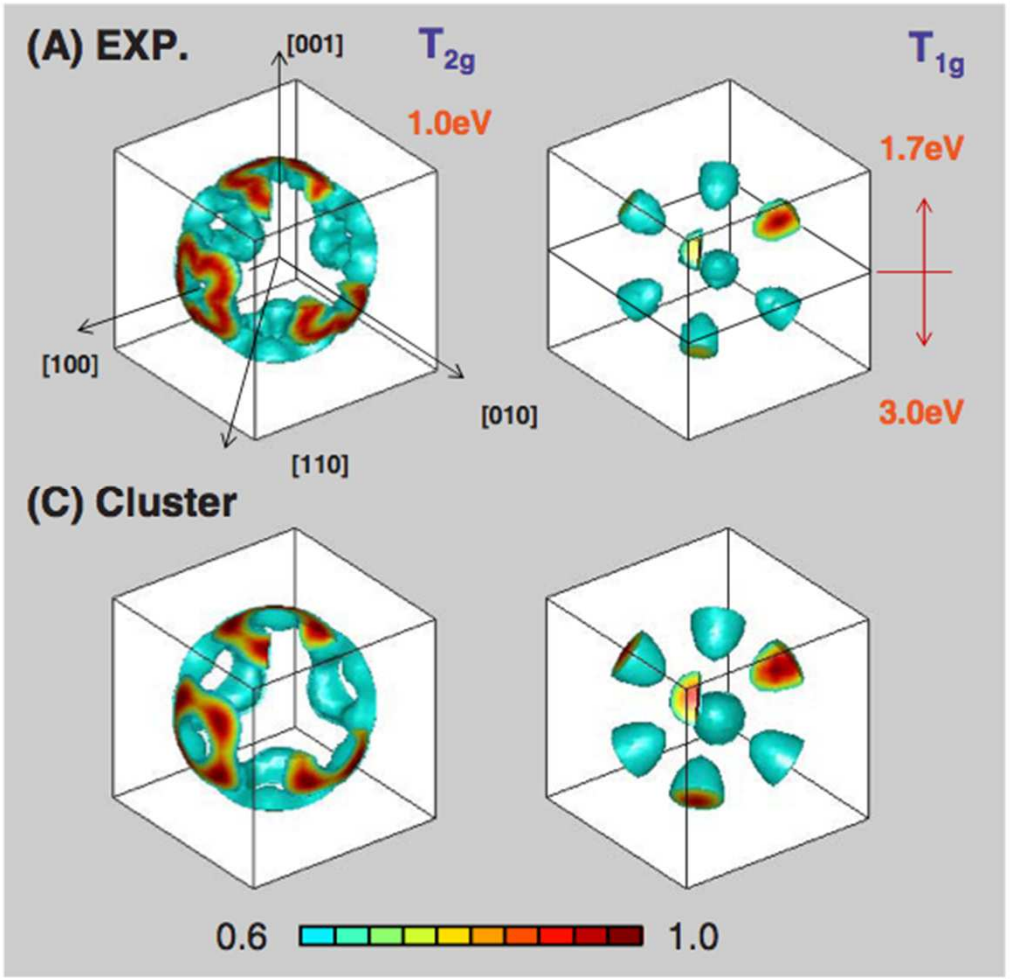


PRL **107**, 107402 (2011).

Quanty – non-resonant IXS

Angular dependence of d-d excitations in NiO





EPL **96**, 37007 (2011)

Charge Transfer Multiplet program input

- Initial State configuration ($3d^8$ for Ni^{2+})
- Final state configuration ($2p^5 3d^9$ for Ni^{2+} 2p XAS)
- Transition operator (dipole for XAS)
- Experimental geometry (polarization of the light, sample orientation, magnetic field, temperature, etc.)
- H_i Hamiltonian of the initial state
- $H_f = H_i + H_{cd} + H^{SOC}_{\text{core}}$ Hamiltonian of the final state

Charge Transfer Multiplet program
What information we can get ?

- Ground state symmetry, important quantum numbers, magnetic moment, etc.
- Orbital occupation and orbital level splitting
- Many body energy level diagram
- Physical properties (magnetic anisotropy, susceptibility, magnetization, g factors, etc.)

Hamiltonian

$$H_i = \sum_{i<j} \frac{e^2}{r_{ij}} + \xi \sum_i l_i \cdot s_i + H_{CF} + H_{hyb} + B_z \cdot (L_z + 2S_z)$$

Hamiltonian (atomic physics)

$$H_i = \sum_{i<j} \frac{e^2}{r_{ij}} + \xi \sum_i l_i \cdot s_i$$

Coulomb interaction

$$\left\langle \phi_{\tau_1}(\vec{r}_1)\phi_{\tau_2}(\vec{r}_2) \left| \frac{e^2}{|\vec{r}_1-\vec{r}_2|} \right| \phi_{\tau_3}(\vec{r}_1)\phi_{\tau_4}(\vec{r}_2) \right\rangle$$

Expand the operator on Spherical Harmonics and split the operator and the wave functions into an angular and a radial part.

$$\sum_{i<j}^{n-1,n} \frac{1}{|r_i - r_j|} =$$

$$\sum_{i<j}^{n-1,n} \sum_{k=0}^{\infty} \sum_{m=-k}^{m=k} \frac{\mathrm{Min}[r_i, r_j]^k}{\mathrm{Max}[r_i, r_j]^{k+1}} C_m^{(k)}(\theta_i, \phi_i) C_m^{(k)}(\theta_j, \phi_j)^*$$

with

$$C_m^{(k)}(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}} Y_m^{(k)}(\theta, \phi)$$

Coulomb interaction

$$\left\langle \phi_{\tau_1}(\vec{r}_1)\phi_{\tau_2}(\vec{r}_2) \left| \frac{e^2}{|\vec{r}_1-\vec{r}_2|} \right| \phi_{\tau_3}(\vec{r}_1)\phi_{\tau_4}(\vec{r}_2) \right\rangle$$

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with

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Coulomb interaction – Slater Integrals

Integral to calculate

$$\left\langle \phi_{\tau_1}(\vec{r}_1)\phi_{\tau_2}(\vec{r}_2) \left| \frac{e^2}{|\vec{r}_1-\vec{r}_2|} \right| \phi_{\tau_3}(\vec{r}_1)\phi_{\tau_4}(\vec{r}_2) \right\rangle$$

$$\phi_\tau(\vec{r}) = \chi_\tau R_{n_\tau}^{(l_\tau)}(r) Y_{m_\tau}^{(l_\tau)}(\theta,\phi)$$

Expansion on renormalized Spherical Harmonics

$$\sum_{k=0}^{\infty} \sum_{m=-k}^{m=k} \left\langle R_{n_{\tau_1}}^{(l_{\tau_1})}(r_1) R_{n_{\tau_2}}^{(l_{\tau_2})}(r_2) \left| \frac{\mathrm{Min}[r_1,r_2]^k}{\mathrm{Max}[r_1,r_2]^{k+1}} \right| R_{n_{\tau_3}}^{(l_{\tau_3})}(r_1) R_{n_{\tau_4}}^{(l_{\tau_4})}(r_2) \right\rangle$$

$$\times \left\langle Y_{m_{\tau_1}}^{(l_{\tau_1})}(\theta_1,\phi_1) \left| C_m^{(k)}(\theta_1,\phi_1) \right| Y_{m_{\tau_3}}^{(l_{\tau_3})}(\theta_1,\phi_1) \right\rangle$$

$$\times \left\langle Y_{m_{\tau_2}}^{(l_{\tau_2})}(\theta_2,\phi_2) \left| C_m^{(k)}(\theta_2,\phi_2)^* \right| Y_{m_{\tau_4}}^{(l_{\tau_4})}(\theta_2,\phi_2) \right\rangle$$

$$\times \left\langle \chi_{\sigma_{\tau_1}} || \chi_{\sigma_{\tau_3}} \right\rangle \left\langle \chi_{\sigma_{\tau_2}} || \chi_{\sigma_{\tau_4}} \right\rangle$$

Coulomb interaction – Slater Integrals

Radial part: Slater integrals

$$R^{(k)}_{\tau_1,\tau_2,\tau_3,\tau_4} =$$

$$\left\langle R^{(l_{\tau_1})}_{n_{\tau_1}}(r_1) R^{(l_{\tau_2})}_{n_{\tau_2}}(r_2) \left| \frac{\mathrm{Min}[r_1,r_2]^k}{\mathrm{Max}[r_1,r_2]^{k+1}} \right| R^{(l_{\tau_3})}_{n_{\tau_3}}(r_1) R^{(l_{\tau_4})}_{n_{\tau_4}}(r_2) \right\rangle$$

Angular part: Analytical solution

$$\left\langle Y^{(l_{\tau_1})}_{m_{\tau_1}}(\theta_1,\phi_1) \left| C^{(k)}_m(\theta_1,\phi_1) \right| Y^{(l_{\tau_3})}_{m_{\tau_3}}(\theta_1,\phi_1) \right\rangle$$

$$\times \left\langle Y^{(l_{\tau_2})}_{m_{\tau_2}}(\theta_2,\phi_2) \left| C^{(k)}_m(\theta_2,\phi_2)^* \right| Y^{(l_{\tau_4})}_{m_{\tau_4}}(\theta_2,\phi_2) \right\rangle$$

$$\times \left\langle \chi_{\sigma_{\tau_1}} \,||\, \chi_{\sigma_{\tau_3}} \right\rangle \left\langle \chi_{\sigma_{\tau_2}} \,||\, \chi_{\sigma_{\tau_4}} \right\rangle$$

Coulomb interaction – Slater Integrals

$$|l_2 - l_4| \leq k \leq |l_2 + l_4|$$
$$|l_1 - l_3| \leq k \leq |l_1 + l_3|$$

d electrons

$$l_1 = l_2 = l_3 = l_4 = 2 \qquad k = 0, 2, 4$$

$$R^{(0,2,4)}_{2,2,2,2} = F^{(0,2,4)}$$

f - electrons

$$l_1 = l_2 = l_3 = l_4 = 3 \qquad k = 0, 2, 4, 6$$

$$R^{(0,2,4,6)}_{3,3,3,3} = F^{(0,2,4,6)}$$

Coulomb interaction – Slater Integrals

Core (p) valence (d) interaction – direct term

$$l_1 = l_3 = 2, l_2 = l_4 = 1 \qquad k = 0, 2$$

$$R^{(0,2)}_{2,1,2,1} = F^{(0,2)}$$

Core (p) valence (d) interaction – exchange term

$$l_1 = l_4 = 2, l_2 = l_3 = 1 \qquad k = 1, 3$$

$$R^{(1,3)}_{2,1,1,2} = G^{(1,3)}$$

Coulomb interaction – Slater Integrals

Core (p) valence (d) interaction – direct term

$$l_1 = l_3 = 2, l_2 = l_4 = 1 \qquad k = 0, 2$$

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$$l_1 = l_4 = 2, l_2 = l_3 = 1 \qquad k = 1, 3$$

$$R^{(1,3)}_{2,1,1,2} = G^{(1,3)}$$

Initial state Hamiltonian (atomic multiplet theory)

Electron-electron interaction of valence states

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k$$

Valence Spin-orbit coupling

$$\xi \sum_i l_i \cdot s_i$$

Final state Hamiltonian (atomic multiplet theory)

Electron-electron interaction of valence states

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k$$

Valence Spin-orbit coupling

$$\xi \sum_i l_i \cdot s_i$$

Core-valence electron interaction

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

Core Spin-orbit coupling

$$\xi \sum_i l_i \cdot s_i$$

Final state Hamiltonian (atomic multiplet theory)

Electron-electron interaction of valence states

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Core Spin-orbit coupling

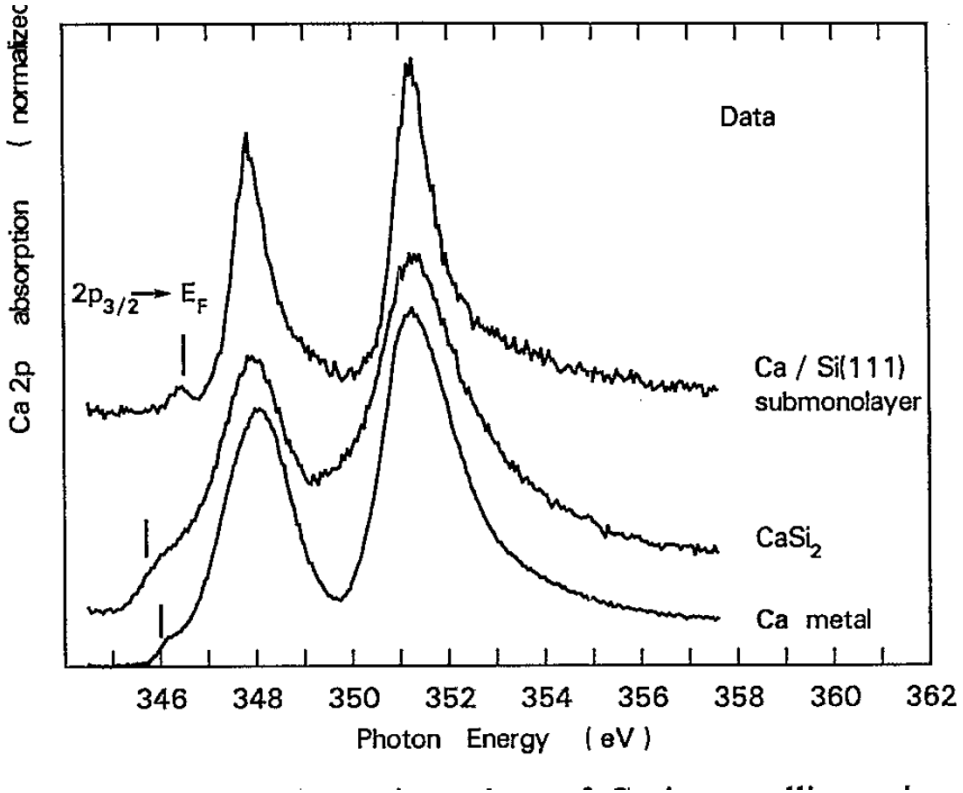
$$\xi \sum_i l_i \cdot s_i$$

Spin-orbit coupling couples L and S quantum numbers

Only the total moment J is a good quantum number

Atomic multiplet theory

Ca 2p XAS



Term symbols

$$^{2S+1}L$$

L =	0	1	2	3	4
Term Symbol	S	P	D	F	G

Term symbols – single electron

Orbital occupation	Angular momentum	Term symbol
s^1	S=1/2, L=0	$\rightarrow$ ^2S
p^1	S=1/2, L=1	$\rightarrow$ ^2P
d^1	S=1/2, L=2	$\rightarrow$ ^2D

Term symbols – two electrons

Orbital occupation	Angular momentum	Term symbol
$1s^1 2s^1$	$S_{1s}=1/2,\ S_{2s}=1/2 \rightarrow S_{tot}=0,1$ $L_{1s}=0,\ L_{2s}=0 \rightarrow L_{tot}=0$	$^1S,\ ^3S$

Term symbols – two electrons

Orbital occupation	Angular momentum	Term symbol
		^{2S+1}L
$2p^1 3d^1$	$S_{2p}=1/2,\ S_{3d}=1/2 \rightarrow S_{tot}=0,1$	$^3P,\ ^3D,\ ^3F$
$(2p^5 3d^1)$	$L_{2p}=1,\ L_{3d}=2 \rightarrow L_{tot}=1,\ 2 \text{ or } 3$	$^1P,\ ^1D,\ ^1F$

Term symbols – two electrons

Orbital occupation	Angular momentum	Term symbol
		$^{2S+1}L_J$
$2p^1 3d^1$ $(2p^5 3d^1)$	$S_{2p}=1/2,\ L_{2p}=1 \rightarrow J_{2p}=1/2,3/2$ $S_{3d}=1/2,\ L_{3d}=2 \rightarrow J_{3d}=3/2,5/2$	$^1P_1,\ ^3P_0,\ ^3P_1,\ ^3P_2$ $^1D_2,\ ^3D_1,\ ^3D_2,\ ^3D_3$ $^1F_3,\ ^3F_2,\ ^3F_3,\ ^3F_4$

For each term symbol

$J_{MAX}= S_1 + L_1$

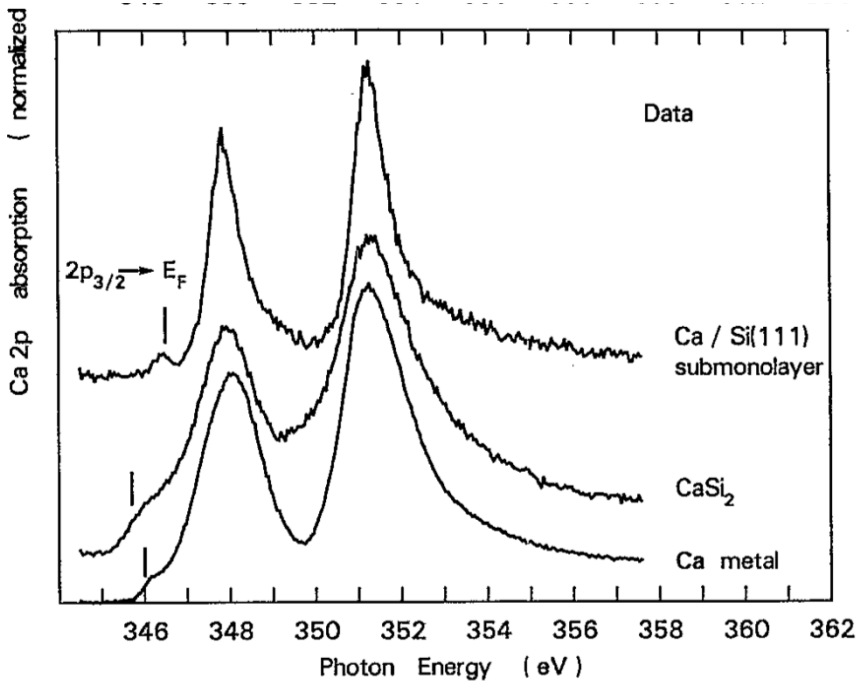
$J_{MIN}= |S_1 - L_1|$

Steps of 1 between J_{MIN} and J_{MAX}

Atomic multiplet theory

Ca 2p XAS

3 peaks in the spectrum. Why?



Atomic multiplet theory

Ca 2p XAS

Dipole transition

$3d^0 \rightarrow 2p^5 3d^1$

Without spin-orbit coupling

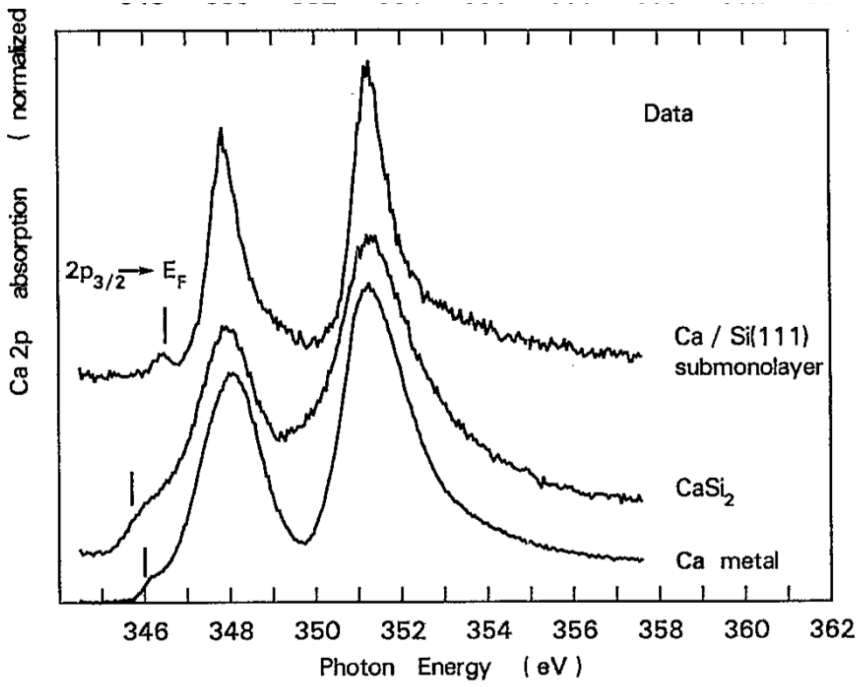
Initial state symmetry :

^1S

Final state symmetry :

^1P, ^1D, ^1F

3 peaks in the spectrum. Why?



Selection rules for dipole transition:

$\Delta L = +1$ or -1

$\Delta S = 0$

Allowed transition

$\langle ^1S | \Delta S=0; \Delta L=+1 | ^1P \rangle \neq 0$

1 peak in the spectrum

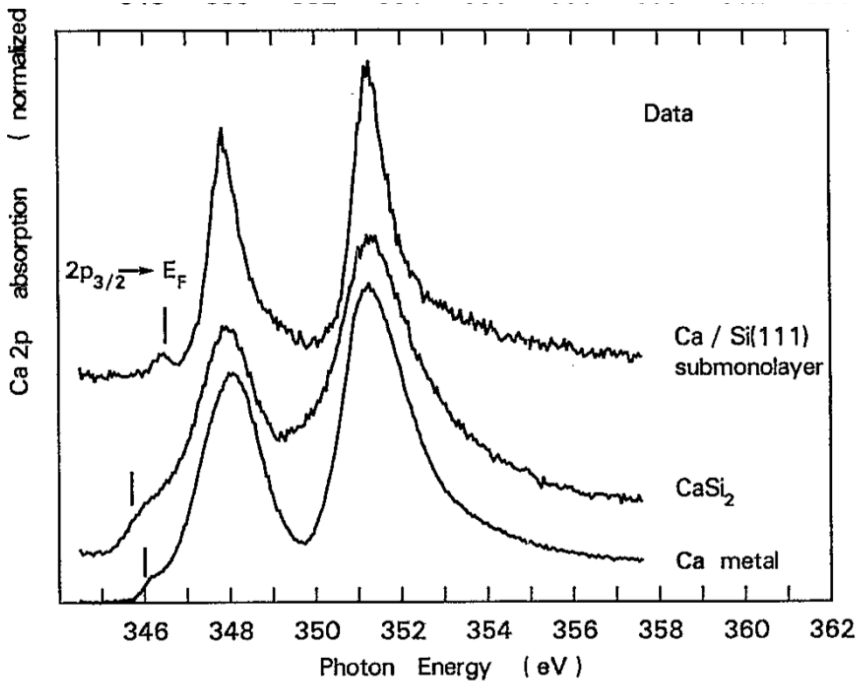
Atomic multiplet theory

Ca 2p XAS

Dipole transition

$3d^0 \rightarrow 2p^5 3d^1$

3 peaks in the spectrum. Why?



With spin-orbit coupling

Initial state symmetry :

$^1S_0$

Final state symmetry :

$^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^3D_1$, $^3D_2$, $^3D_3$

$^1F_3$, $^3F_2$, $^3F_3$, $^3F_4$

Selection rules for dipole transition:

$\Delta J = +1$ or -1 or 0 $\quad J = J' \neq 0$

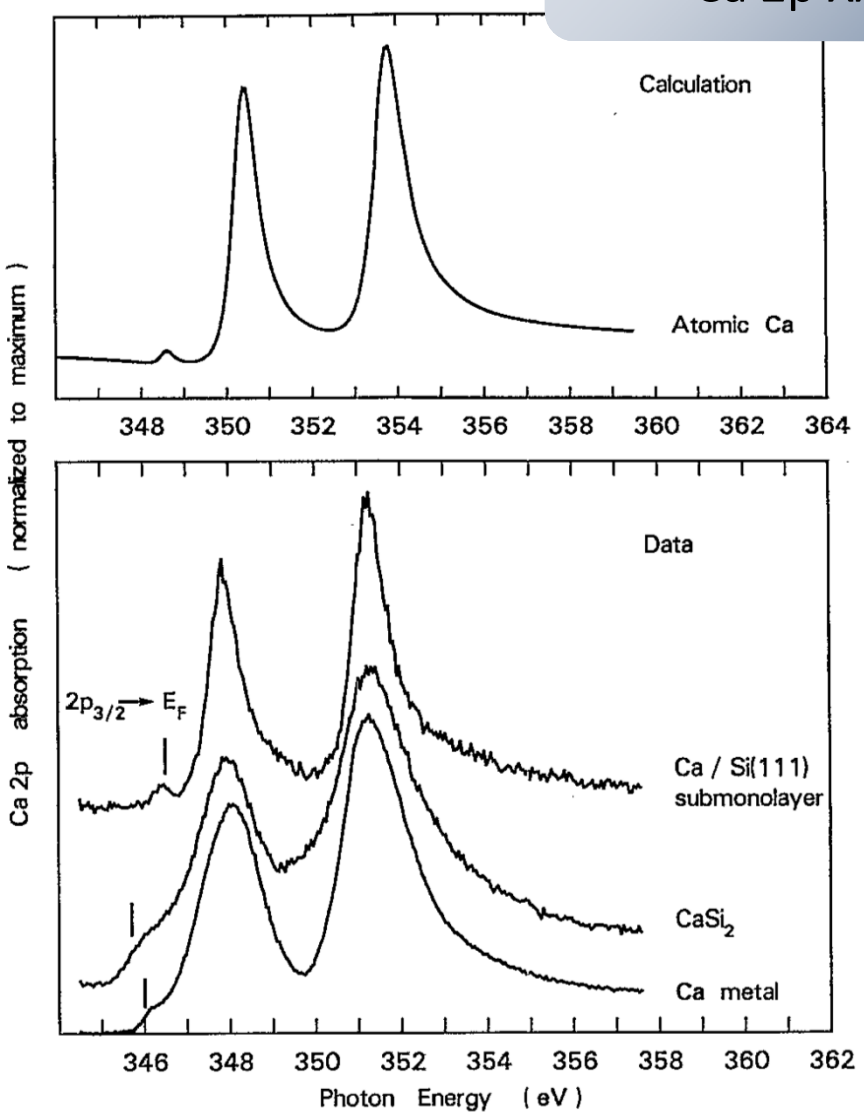
Allowed transitions

$\langle ^1S_0 | \Delta J = +1 | \ ^1P_1, \ ^3P_1, \ ^3D_1 \rangle \neq 0$

3 peaks in the spectrum

Atomic multiplet theory

Ca 2p XAS



Dipole transition

$3d^0 \rightarrow 2p^5 3d^1$

With spin-orbit coupling

Initial state symmetry :

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Final state symmetry :

$^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^3D_1$, $^3D_2$, $^3D_3$

$^1F_3$, $^3F_2$, $^3F_3$, $^3F_4$

Selection rules for dipole transition:

$\Delta J = +1$ or -1 or 0 $\quad J = J' \neq 0$

Allowed transitions

$\langle ^1S_0 | \Delta J = +1 | \ ^1P_1, \ ^3P_1, \ ^3D_1 \rangle \neq 0$

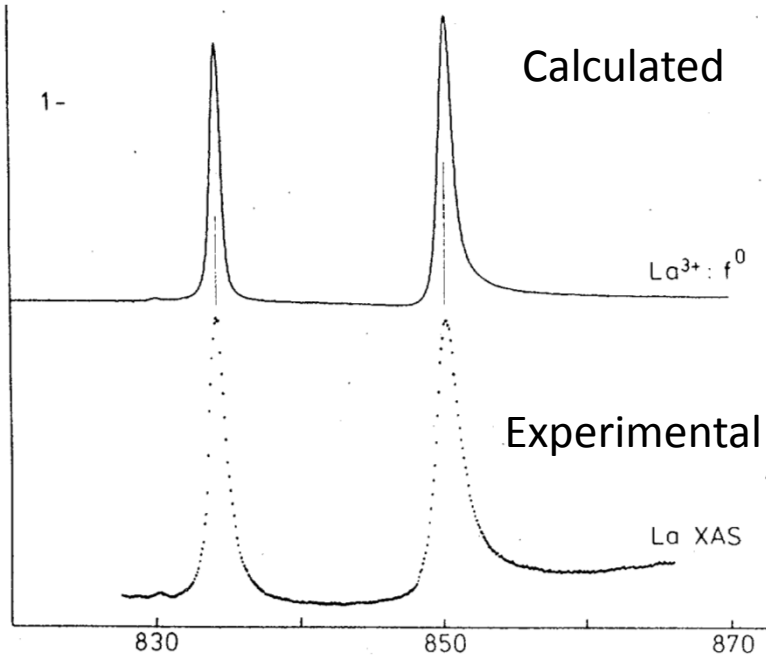
3 peaks in the spectrum

Atomic multiplet theory

La 3d XAS

Dipole transition

$4f^0 \rightarrow 3d^9 4f^1$



With spin-orbit coupling

Initial state symmetry :

$^1S_0$

Final state symmetry :

$^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^3D_1$, $^3D_2$, $^3D_3$, $^1F_3$, $^3F_2$, $^3F_3$, $^3F_4$, $^1G_4$, $^3G_3$, $^3G_4$, $^3G_5$, $^1H_5$, $^3H_4$, $^3H_5$, $^3H_6$

Selection rules for dipole transition:

$\Delta J = +1$ or -1 or 0 $\quad J = J' \neq 0$

Allowed transitions

$\langle ^1S_0 | \Delta J = +1 | \ ^1P_1, \ ^3P_1 , \ ^3D_1 \rangle \neq 0$

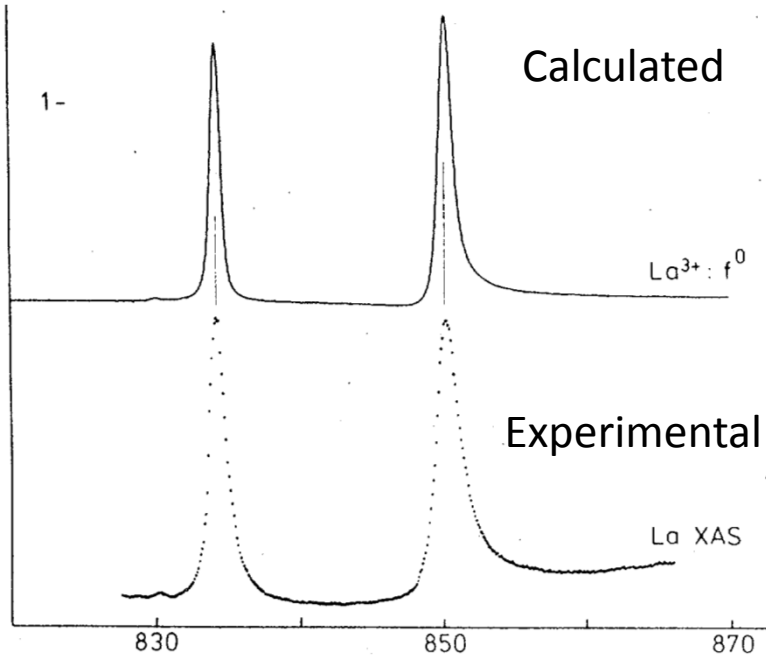
3 peaks in the spectrum

Atomic multiplet theory

La 3d XAS

Dipole transition

$4f^0 \rightarrow 3d^9 4f^1$



With spin-orbit coupling

Initial state symmetry :

$^1S_0$

Final state symmetry :

$^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^3D_1$, $^3D_2$, $^3D_3$, $^1F_3$, $^3F_2$,

$^3F_3$, $^3F_4$, $^1G_4$, $^3G_3$, $^3G_4$, $^3G_5$, $^1H_5$, $^3H_4$, $^3H_5$, $^3H_6$

Selection rules for dipole transition:

$\Delta J = +1$ or -1 or 0 $\quad J = J' \neq 0$

Allowed transitions

$\langle ^1S_0 | \Delta J = +1 | \ ^1P_1, \ ^3P_1 , \ ^3D_1 \rangle \neq 0$

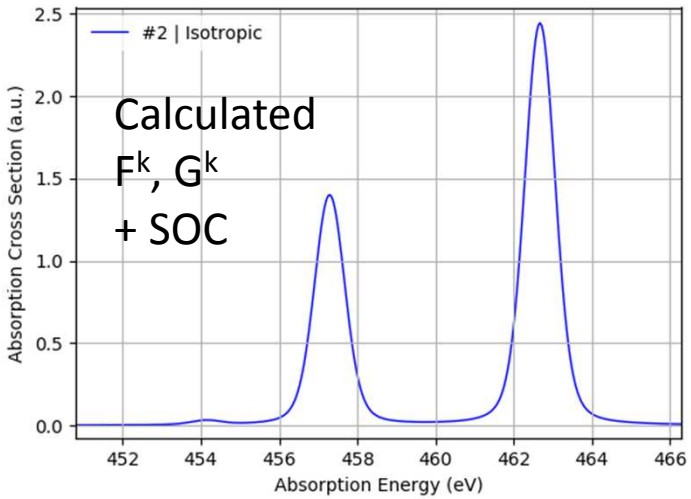
3 peaks in the spectrum

Atomic multiplet theory

Ti^{4+} 2p XAS

Dipole transition

$3d^0 \rightarrow 2p^5 3d^1$



With spin-orbit coupling (SOC)

Selection rules for dipole transition:

$\Delta J = +1$ or -1 or 0 $\quad J = J' \neq 0$

Allowed transitions

$\langle {}^1S_0 | \Delta J = +1 | {}^1P_1, {}^3P_1, {}^3D_1 \rangle \neq 0$

Atomic multiplet theory predicts

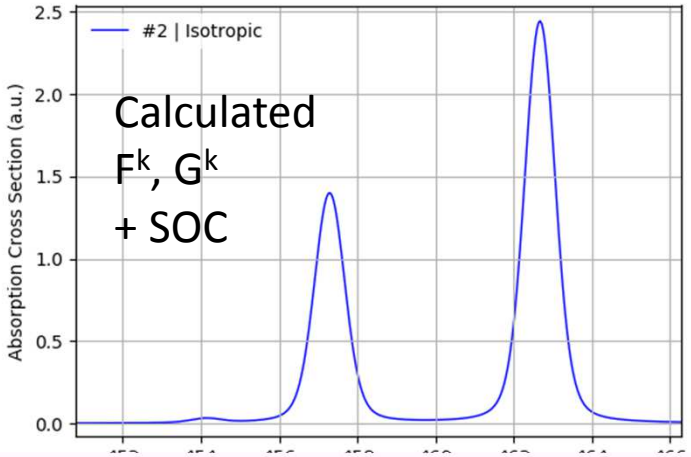
3 peaks in the spectrum

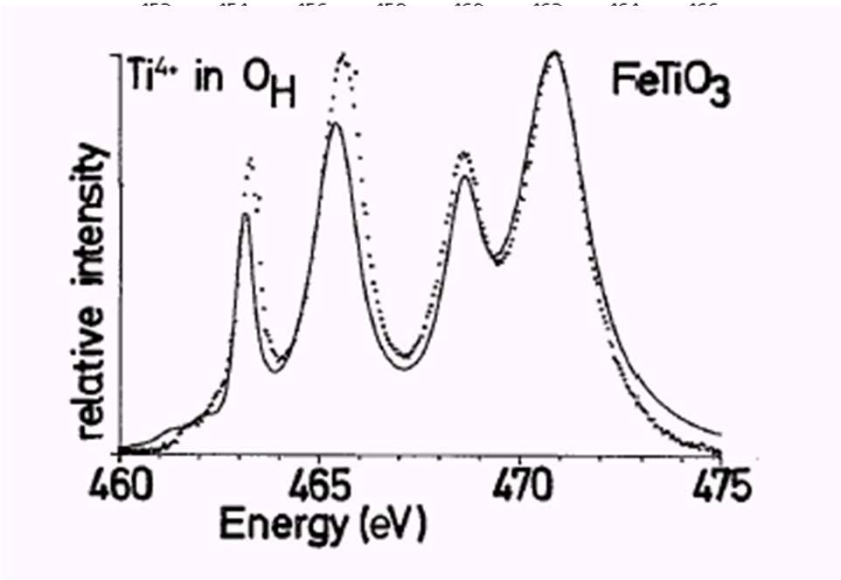
Atomic multiplet theory

Ti^{4+} 2p XAS

Dipole transition

$3d^0 \rightarrow 2p^5 3d^1$





With spin-orbit coupling

Selection rules for dipole transition:

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Allowed transitions

$\langle {}^1S_0 | \Delta J = +1 | {}^1P_1, {}^3P_1, {}^3D_1 \rangle \neq 0$

Atomic multiplet theory predicts

3 peaks in the spectrum

Experimentally 6 peaks

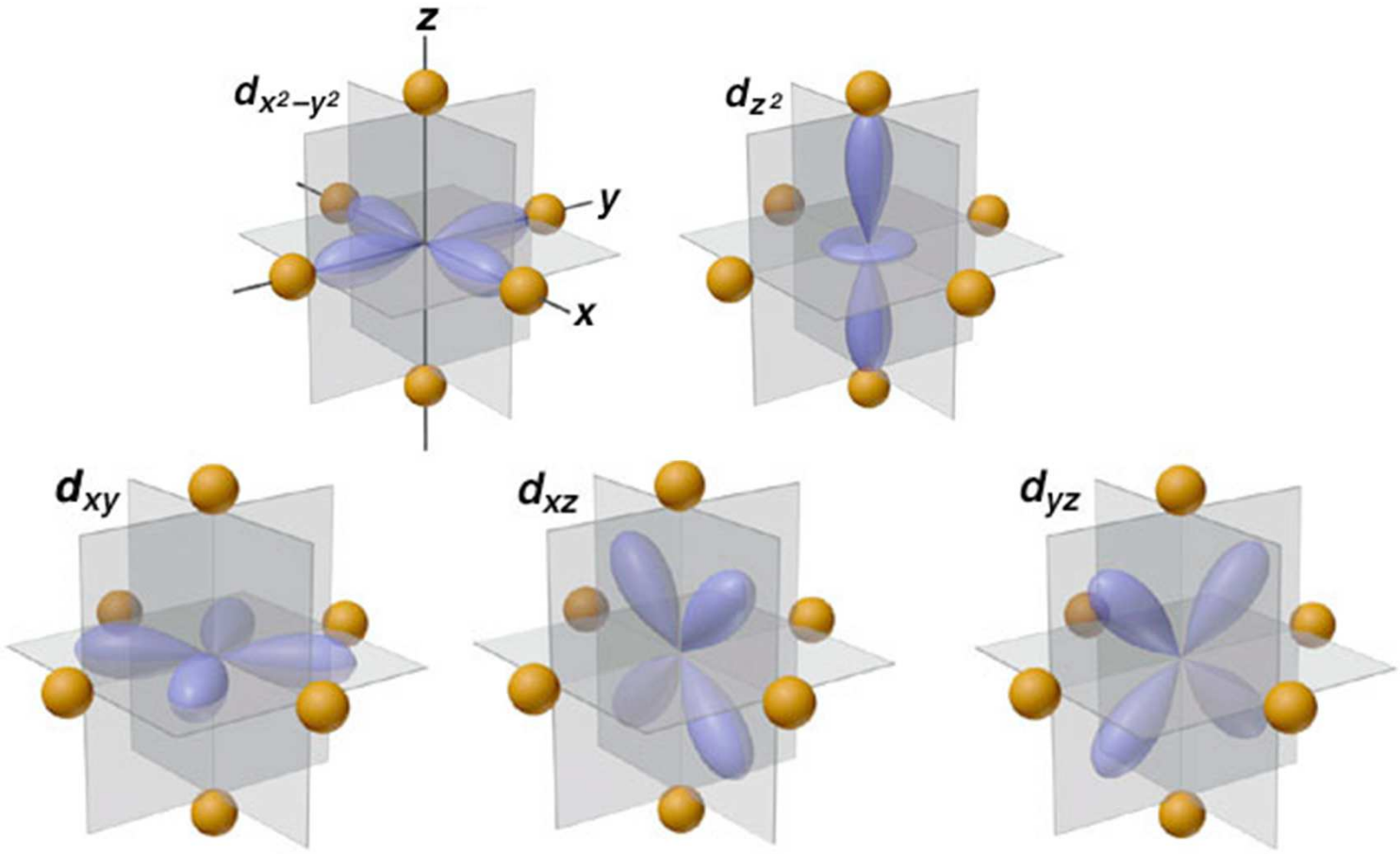
are observed !!!!

Crystal Field theory

d orbitals

e_g states

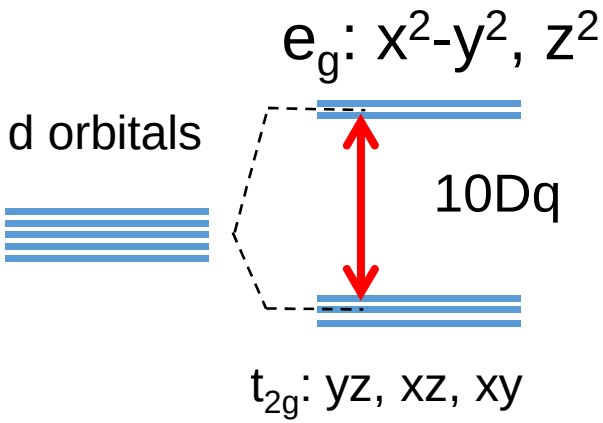
t_{2g} states



Crystal Field theory

Spherical

O_h symmetry (octahedral crystal field)



Crystal field multiplet theory

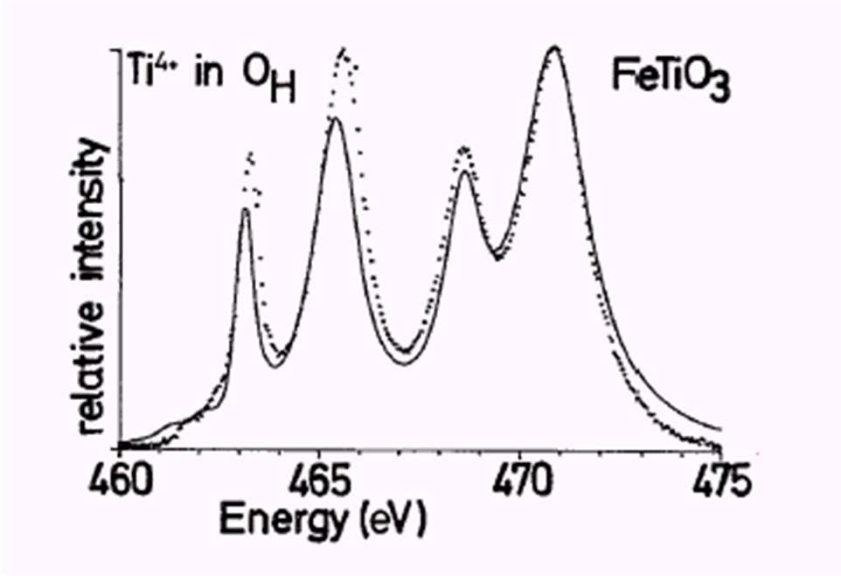
Ti^{4+} 2p XAS

Dipole transition

$3d^0 \rightarrow 2p^5 3d^1$

We need to go beyond the atomic multiplet theory and include the crystal field (CF) in the Hamiltonian

$$\sum_{i<j} \frac{e^2}{r_{ij}} + \xi \sum_i l_i \cdot s_i + H_{CF}$$

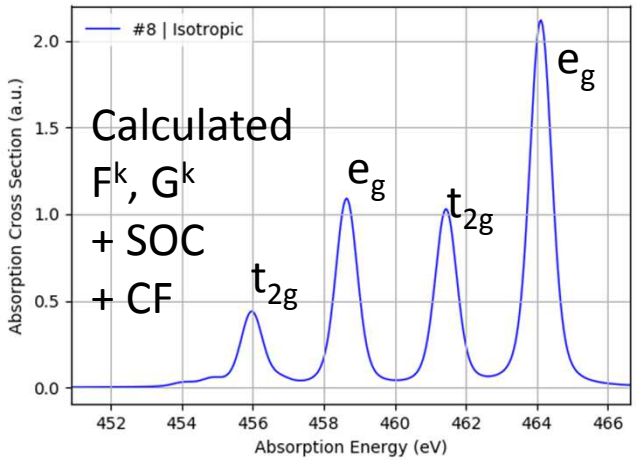


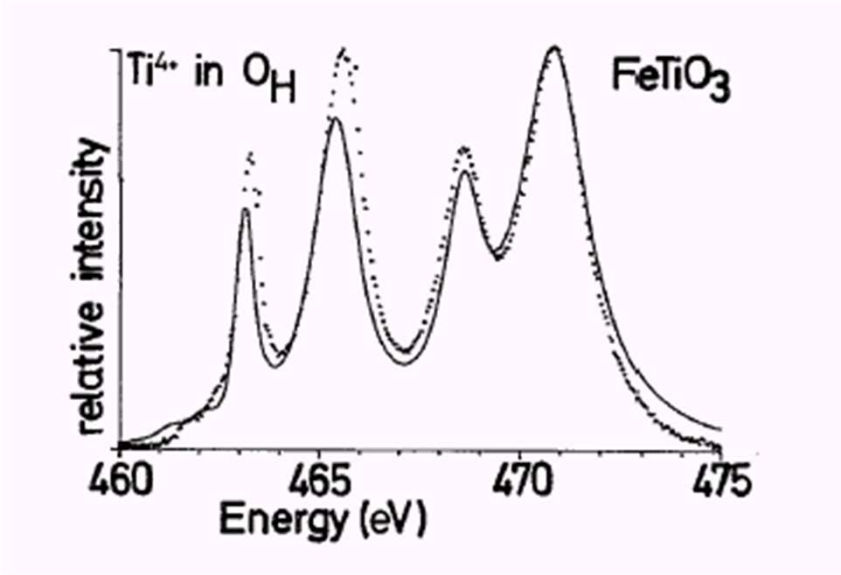
Crystal field multiplet theory

Ti^{4+} 2p XAS

Dipole transition

$3d^0 \rightarrow 2p^5 3d^1$





We need to go beyond the atomic multiplet theory and include the crystal field (CF) in the Hamiltonian

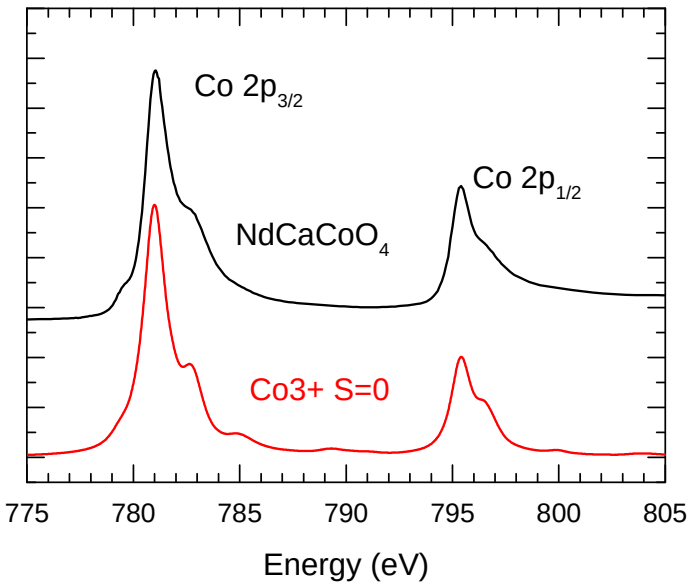
$$\sum_{i<j} \frac{e^2}{r_{ij}} + \xi \sum_i l_i \cdot s_i + H_{CF}$$

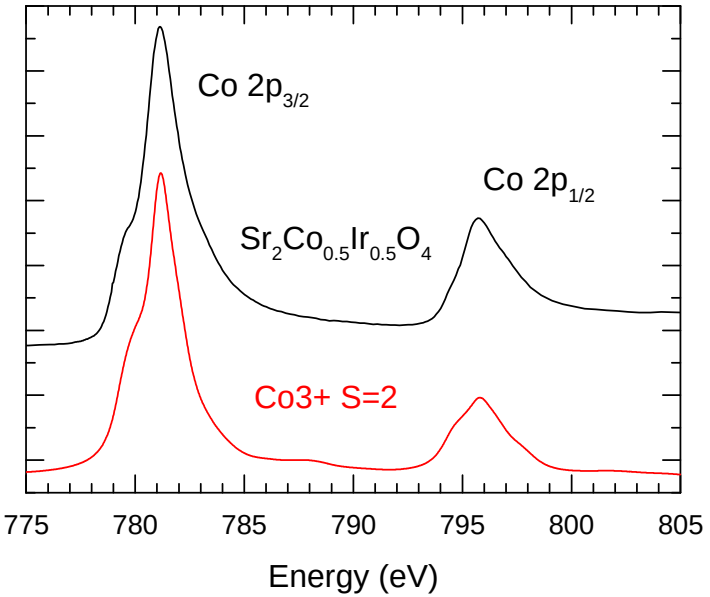
Crystal field multiplet theory

Co^{3+} 2p XAS

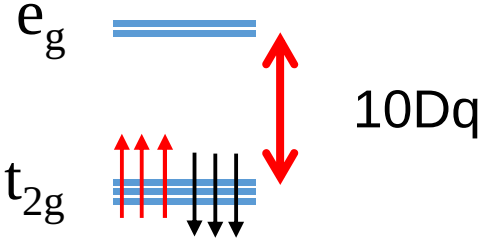
Dipole transition

$3d^6 \rightarrow 2p^5 3d^7$

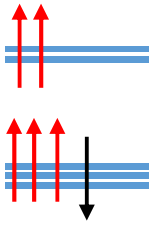




S=0
(low spin)



S=2
(high spin)

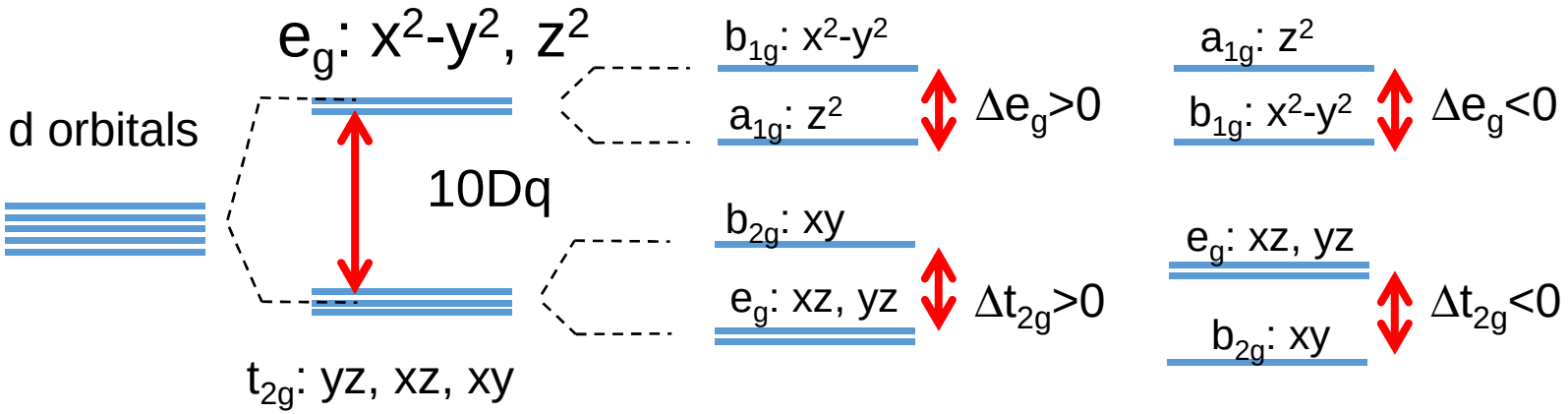


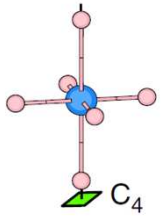
Crystal Field theory

Spherical

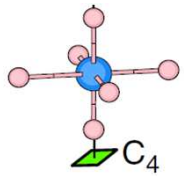
O_h symmetry (octahedral crystal field)

D_{4h} symmetry (tetragonal crystal field)





Elongated

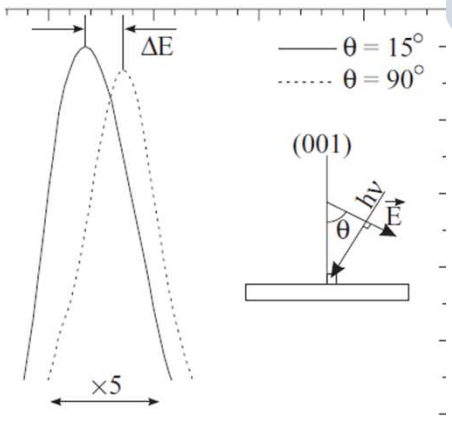


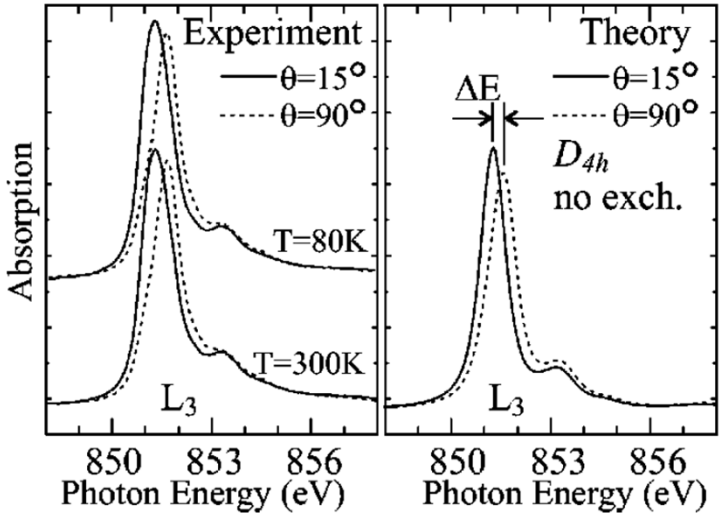
compressed

$$\Delta_{e_g} = 4Ds + 5Dt \text{ and } \Delta_{t_{2g}} = 3Ds - 5Dt$$

Crystal Field theory

Ni 2p XAS of NiO film





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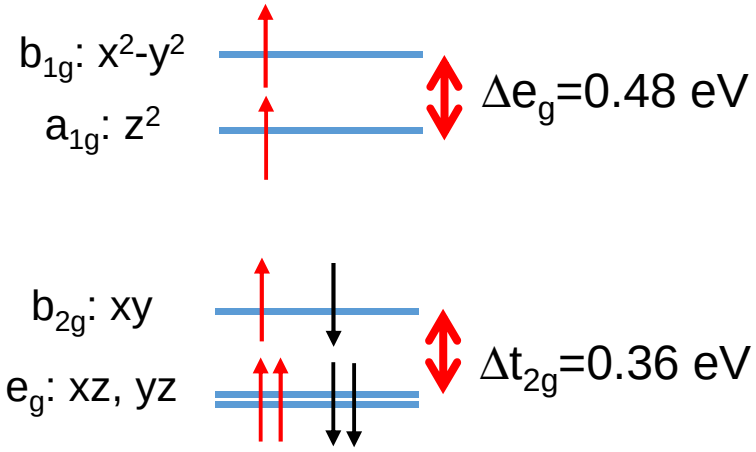
$3d^8$ in D_{4h} symmetry (tetragonal crystal field)



$$\Delta_{e_g} = 4Ds + 5Dt \text{ and } \Delta_{t_{2g}} = 3Ds - 5Dt$$

Ds=0.12 eV, Dt=0 eV

Crystal Field theory