Advanced Light Source Users' Meeting
October 9–11, 2006

Interpretation of X-ray absorption spectra using multiplet calculations: What physical information does it bring?

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BERKELEY LAB

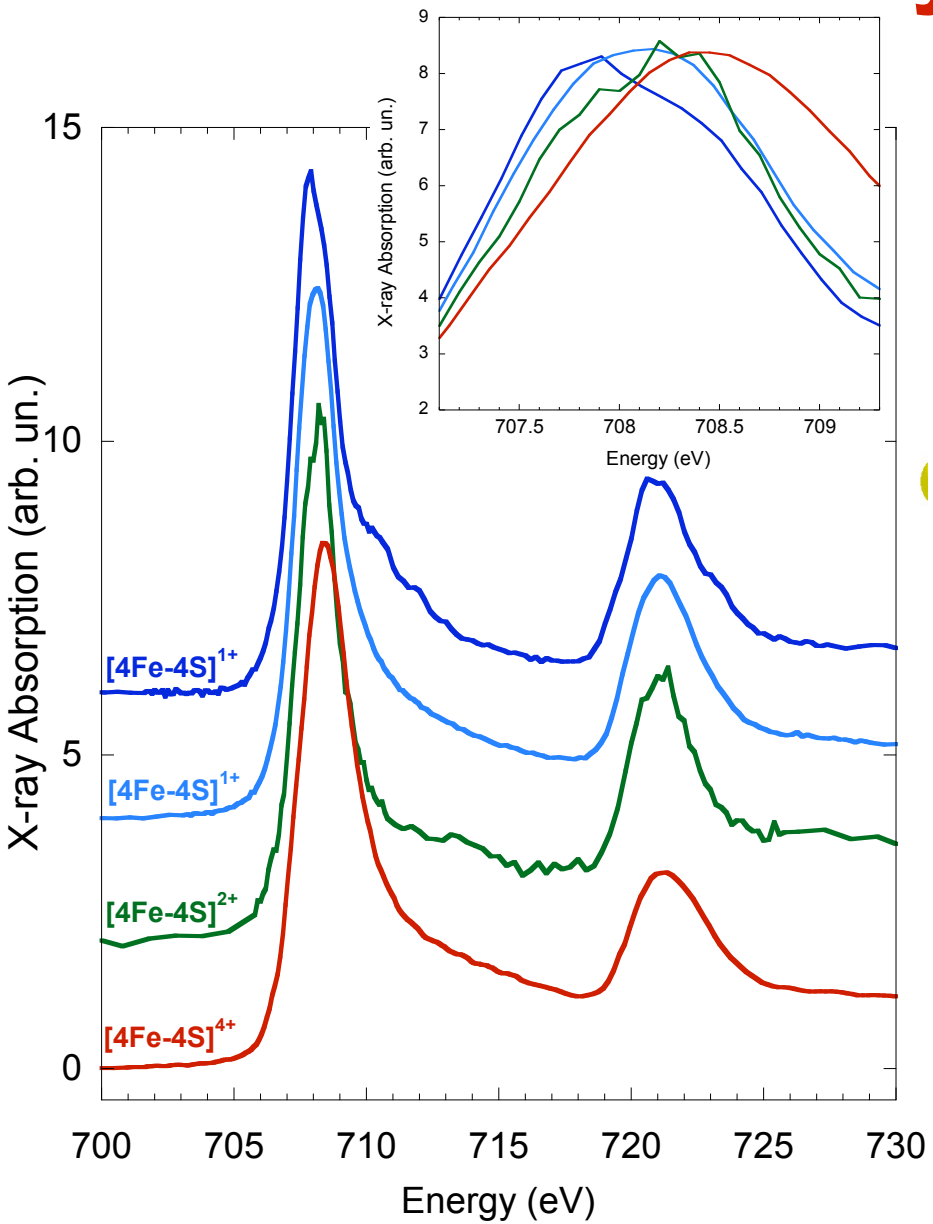
OUTLINE

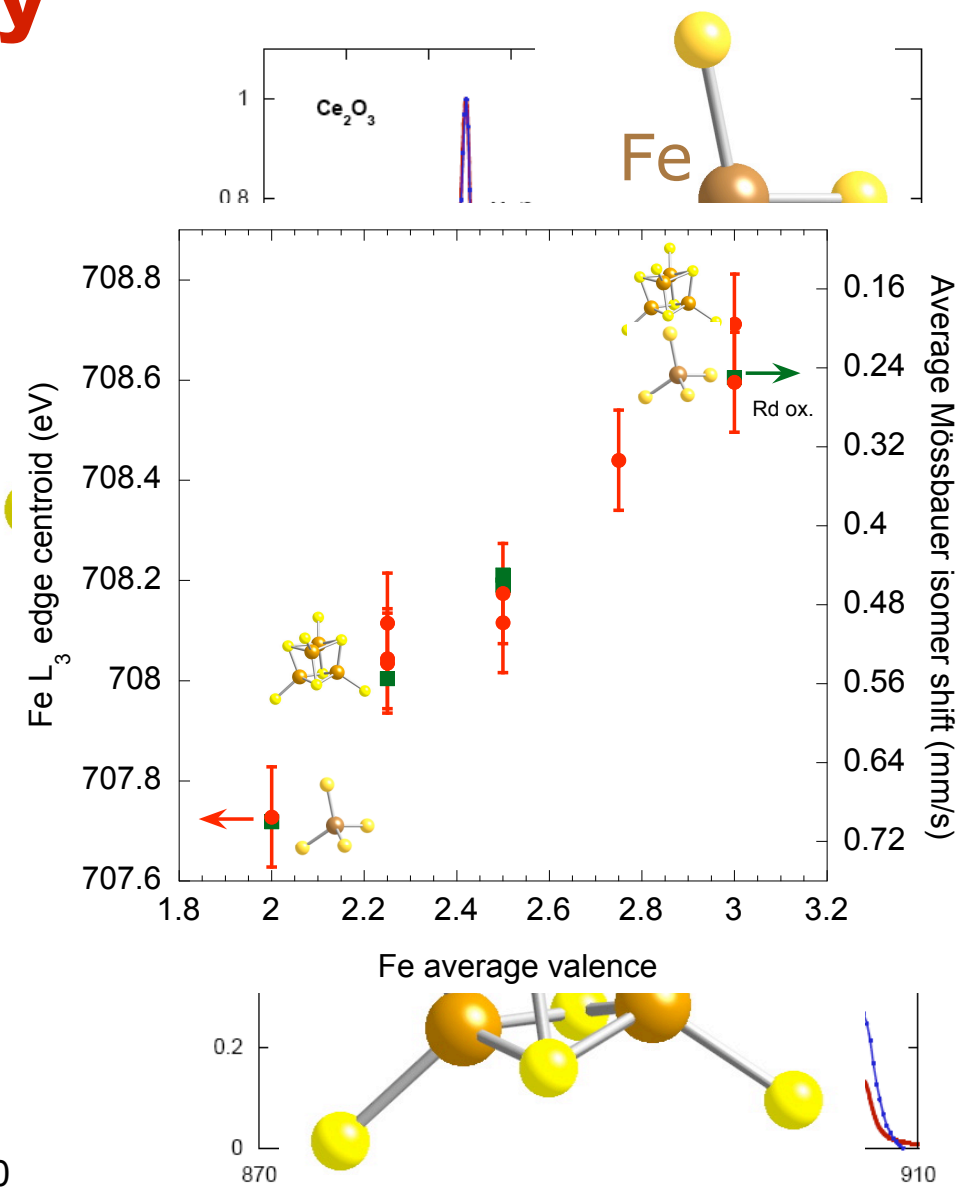
- General characteristics of X-ray Absorption Spectroscopy
  - Need for a theoretical simulation
- Multiplet Simulations
  - Which systems can be applied
  - Which are the input parameters
- Application to *R*NiO_3 systems
  - Extensive application of Multiplet calculations to Ni^{3+}

X-ray Absorption Spectroscopy at transition metal L-edges

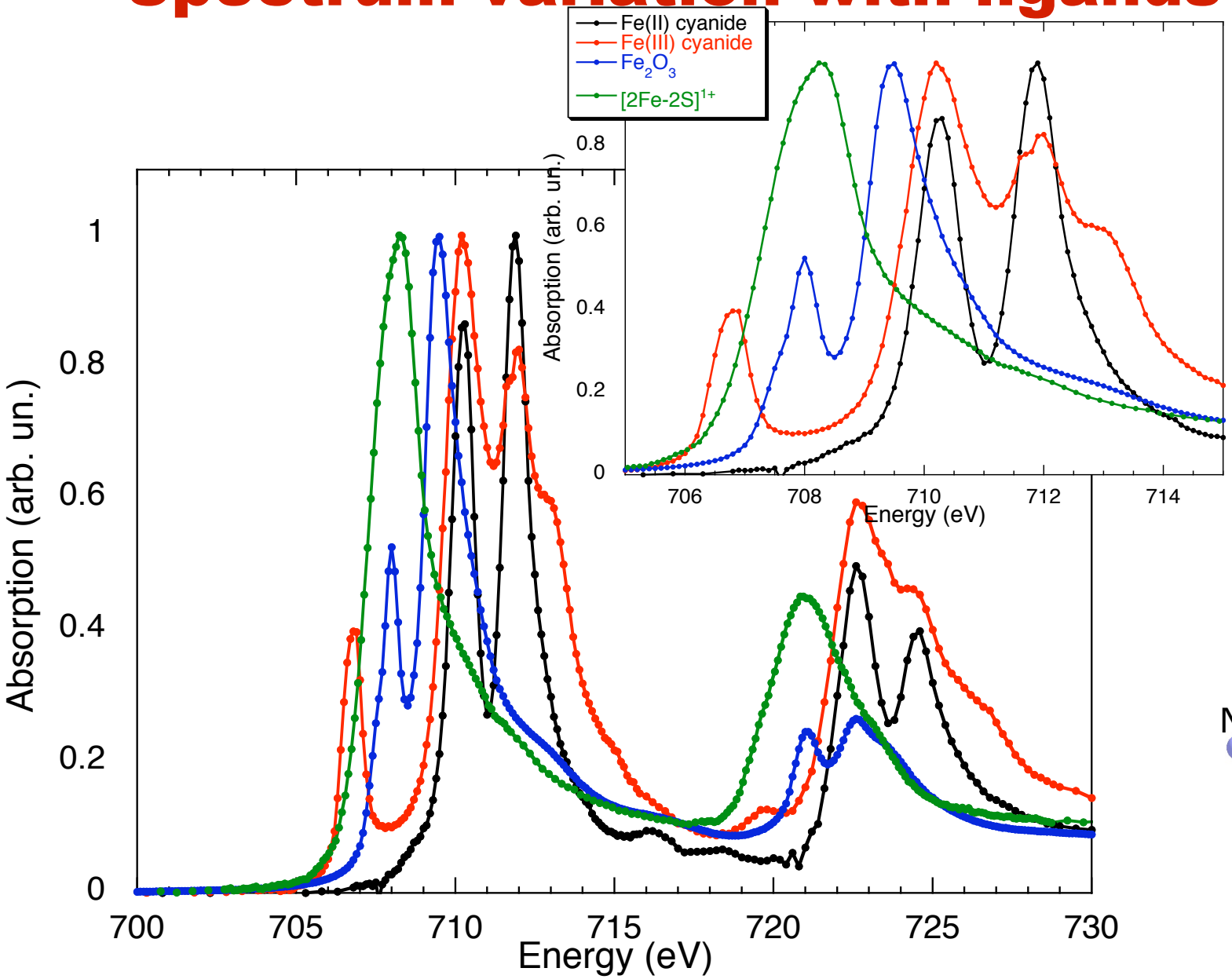
- Valence
- Spin
- Ligands
- Site environment/symmetry

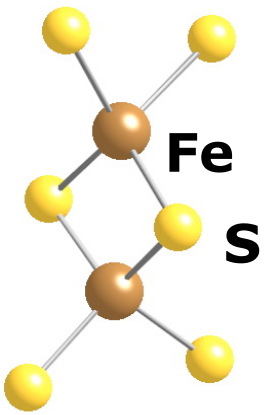
Valence sensitivity

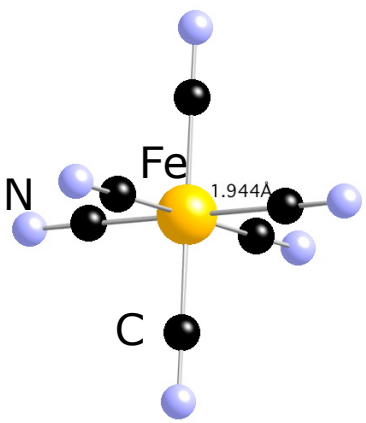




Spectrum variation with ligands

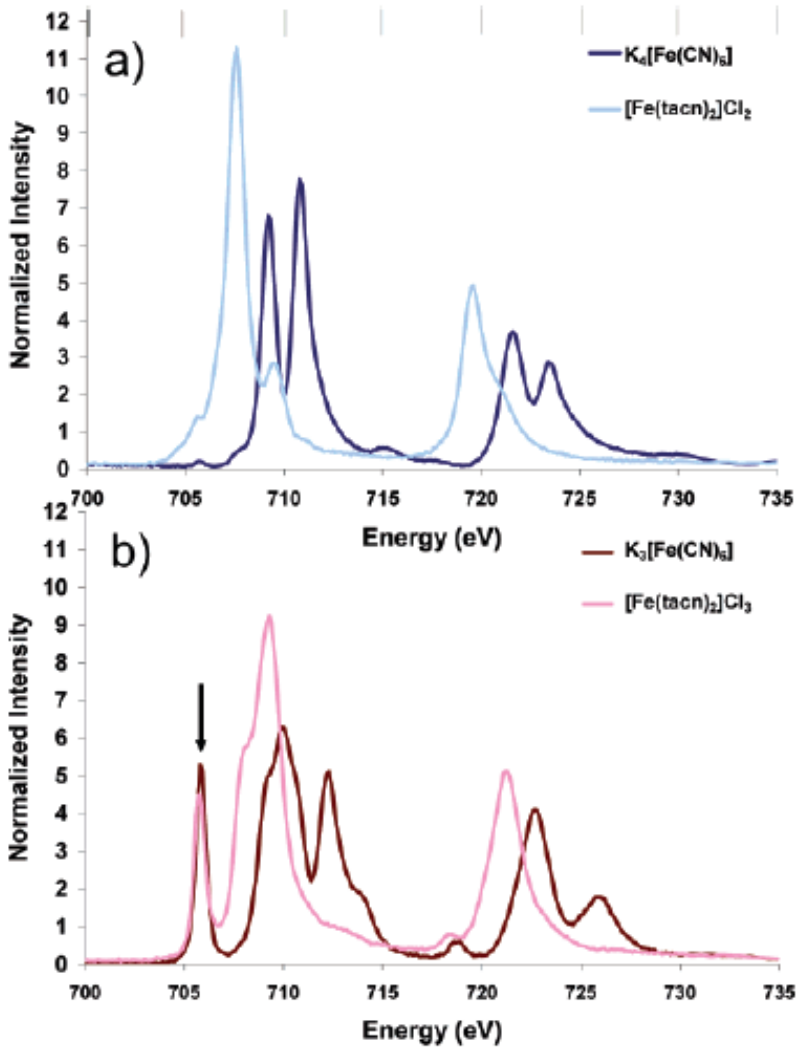




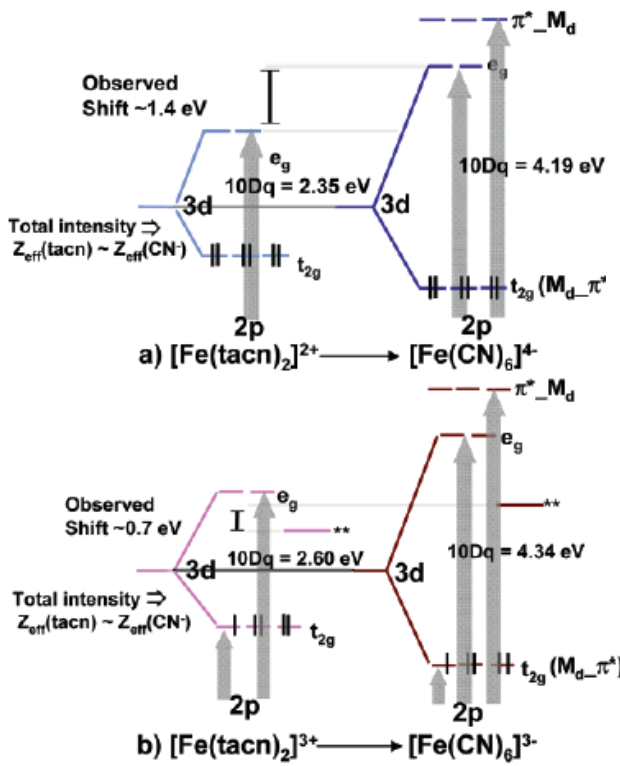


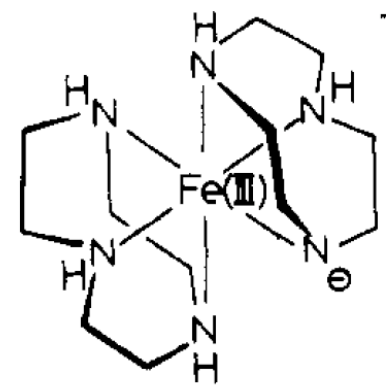
Site Symmetry sensitivity

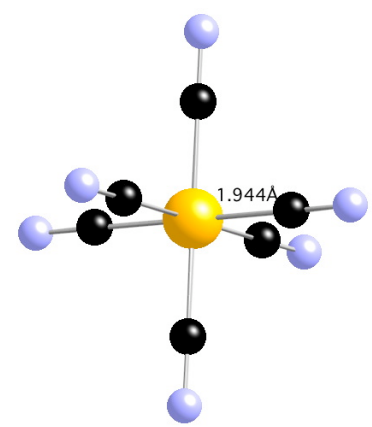
R. Hocking et al. JACS **128** (2006) 10442



Energy shift of 1.4eV between spectra with same valence, but very different crystal field splitting





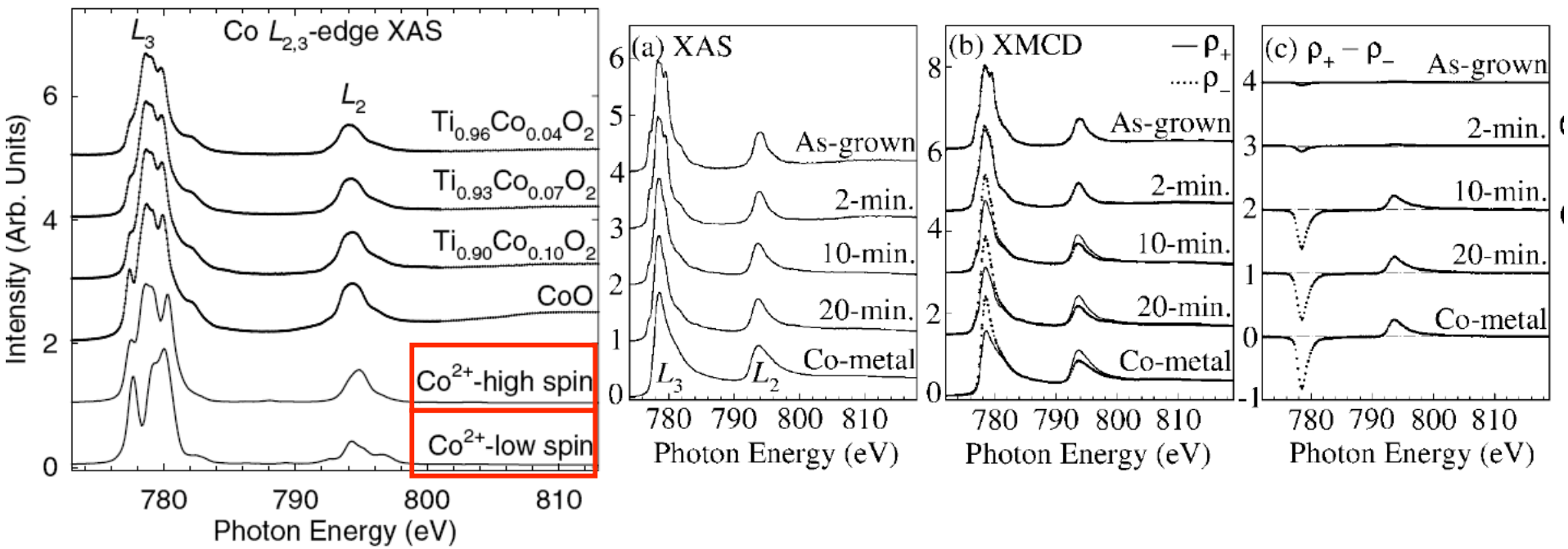


Spin State determination

VOLUME 90, NUMBER 1 PHYSICAL REVIEW LETTERS week ending 10 JANUARY 2003

Ferromagnetism Induced by Clustered Co in Co-Doped Anatase TiO_2 Thin Films

J.-Y. Kim,[1,2] J.-H. Park,[1,*] B.-G. Park,[1] H.-J. Noh,[3] S.-J. Oh,[3] J. S. Yang,[4] D.-H. Kim,[4] S. D. Bu,[4] T.-W. Noh,[4] H.-J. Lin,[5] H.-H. Hsieh,[5] and C. T. Chen[5]



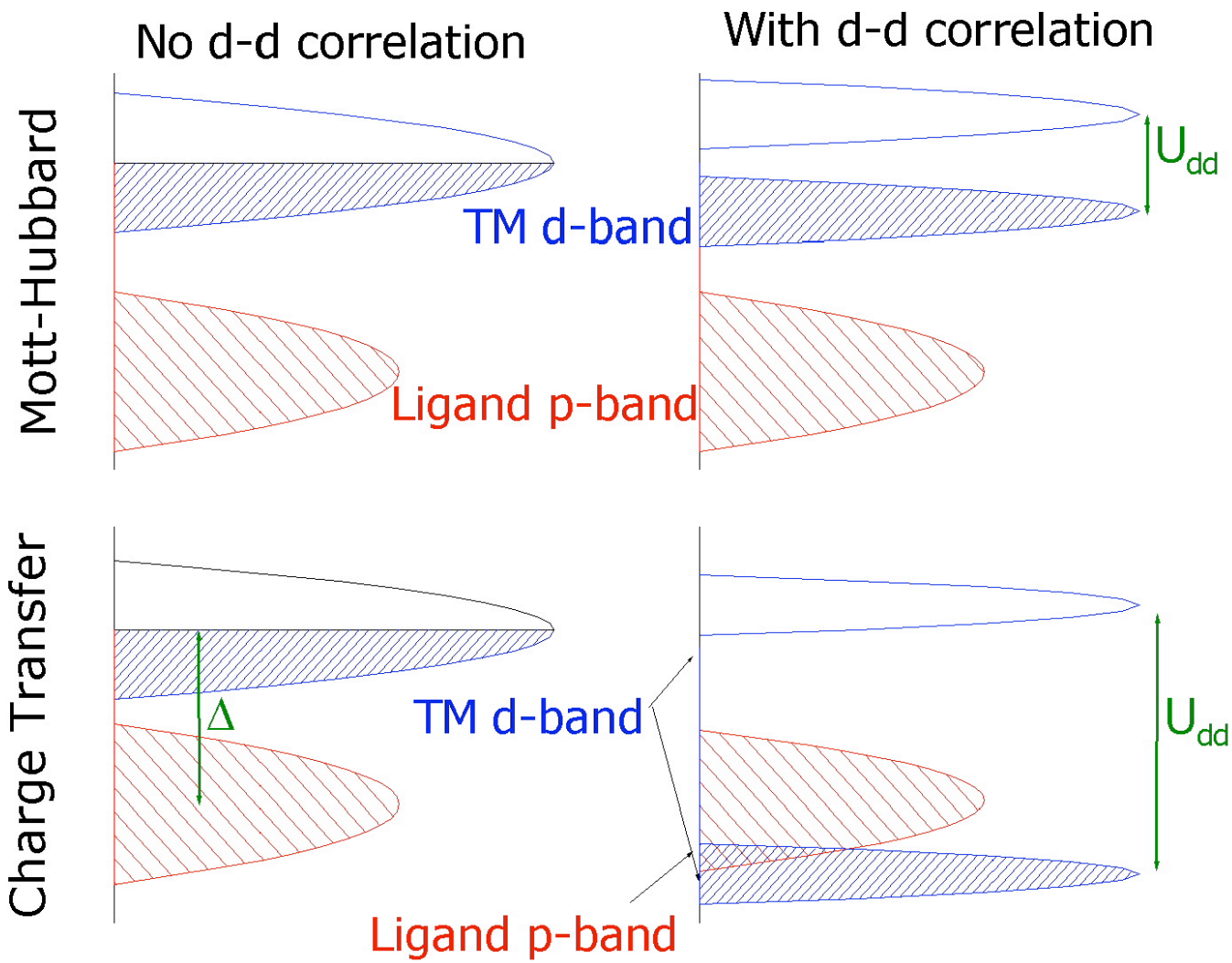
With help of simulations could decide between high-spin and low-spin state

The Multiplet Simulations

Multiplet Simulations

- TT-MULT download: google for **FrankdeGroot**
- Starts from atomic theory
- Includes ligand effects through input parameters
  - Site symmetry, crystal field parameter
  - Hybridization
- **When is the Multiplet description a good approximation?**
  - Systems where **electronic correlation** is important and **states are localized** enough so that an atomic theory is a good approximation:
    - **4f-levels in rare-earths ($M_{4,5}$ edges)**
    - **3d-levels in transition metals ($L_{2,3}$ edges)**

Electronic correlation



Multiplet theory

$H = H_{kinetic} + H_{electron\text{-}nucleus}$

$+ H_{electron\text{-}electron} + H_{spin\text{-}orbit} +$

$+ H_{zeeman}$

$+ H_{crystal\ field} + H_{charge\ transfer}$

Average Energy E_{av}

Multiplets

Zeeman, applied field

Atomic

Calculated by the program

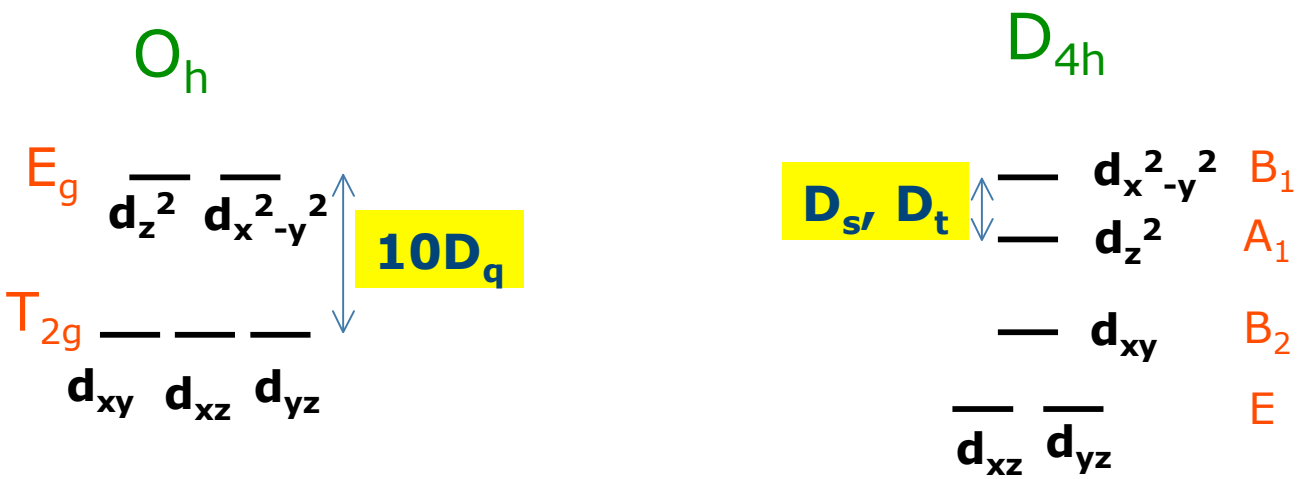
Ligand Effects: ***Input parameters***

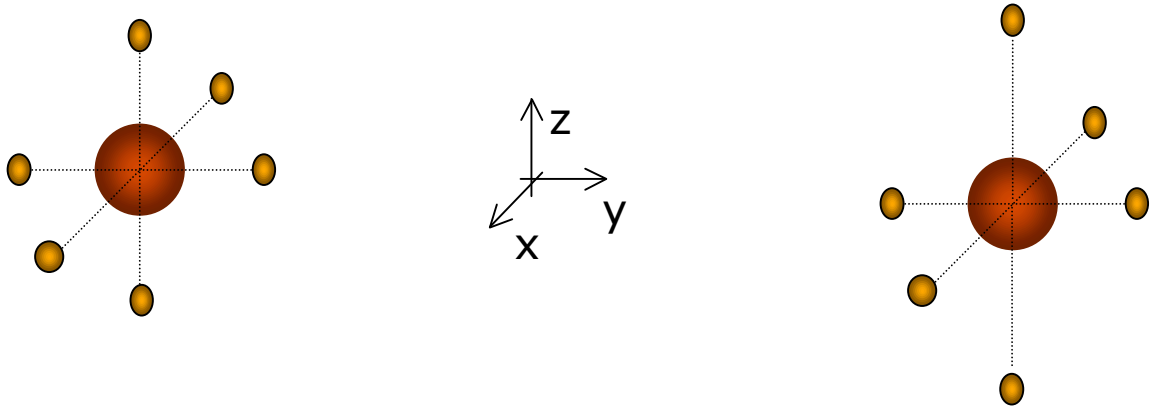
Only partially filled shells are considered, the rest contributes only to E_{av}

XAS L-edge 3d TM: initial state $3d^n$

final state $2p^5\ 3d^{n+1}$

Ligand Field

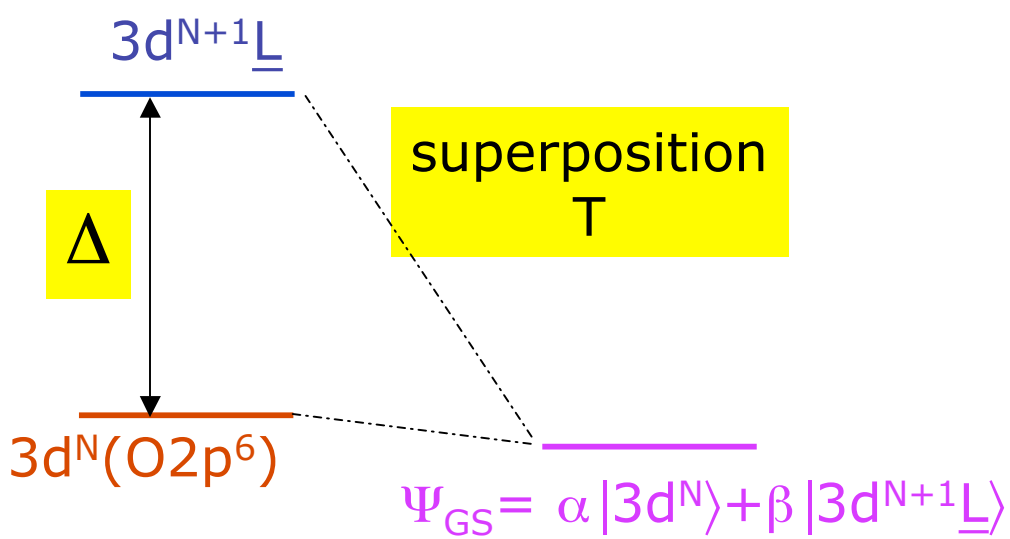




Octahedral **Tetragonal**

In yellow: input parameters for the multiplet program

Charge Transfer - Hybridization

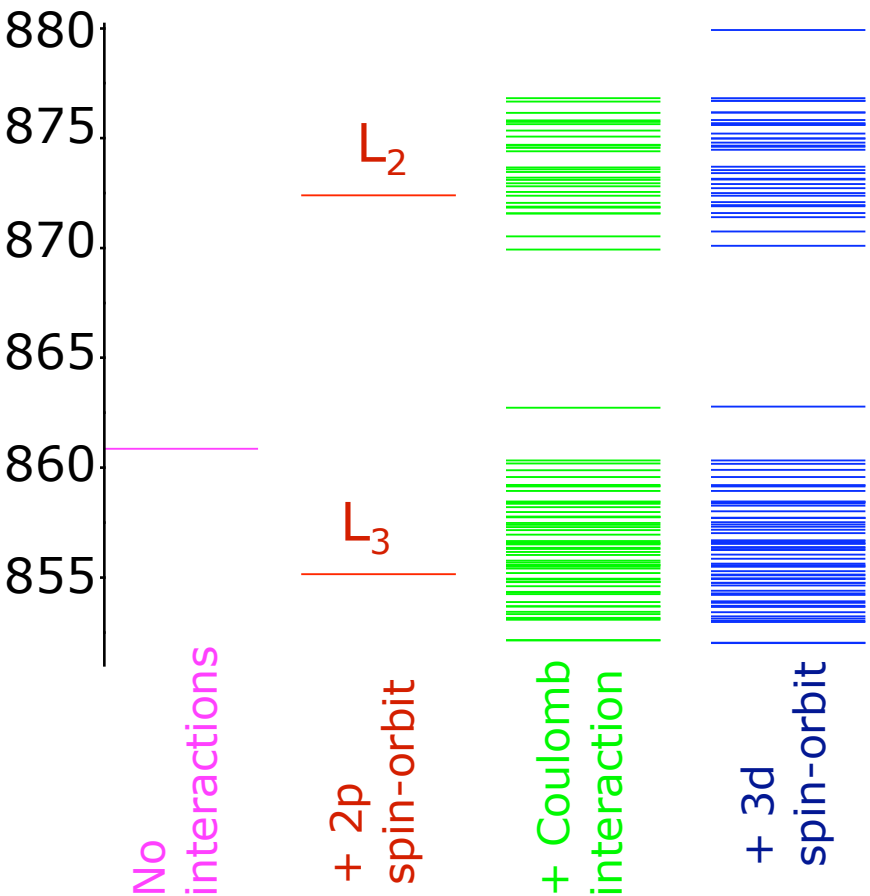


- Ground state described by ionic configuration ($3d^N$) plus contribution of a charge transfer configuration ($3d^{N+1}\underline{\boldsymbol{L}}$)
- $\underline{\boldsymbol{L}}$ denotes a hole in the ligand (ex: oxygen) *p* band
- β: degree of hybridization

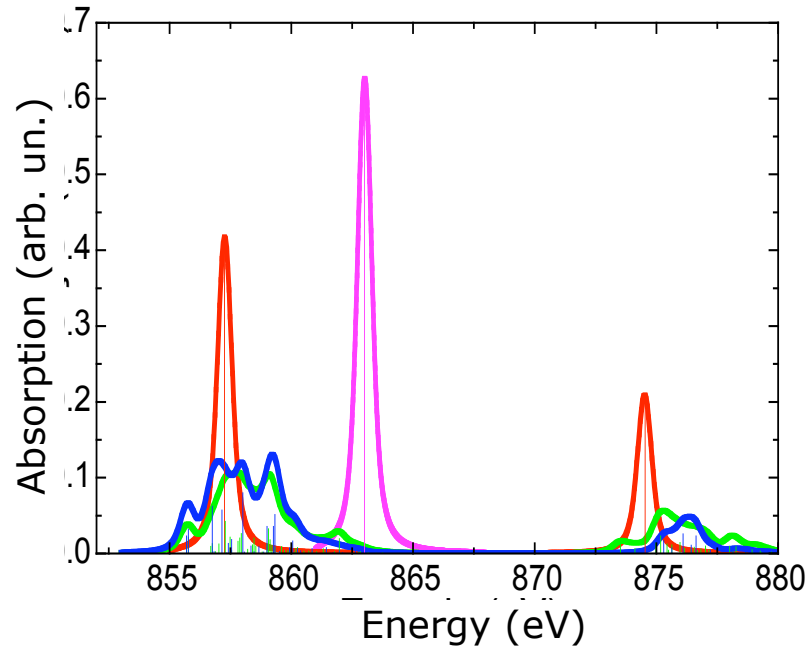
Multitplets

Multiplet effects in XAS final state for Co^{2+}

$2p^5 3d^8$



Correspondent simulated spectrum including different interactions



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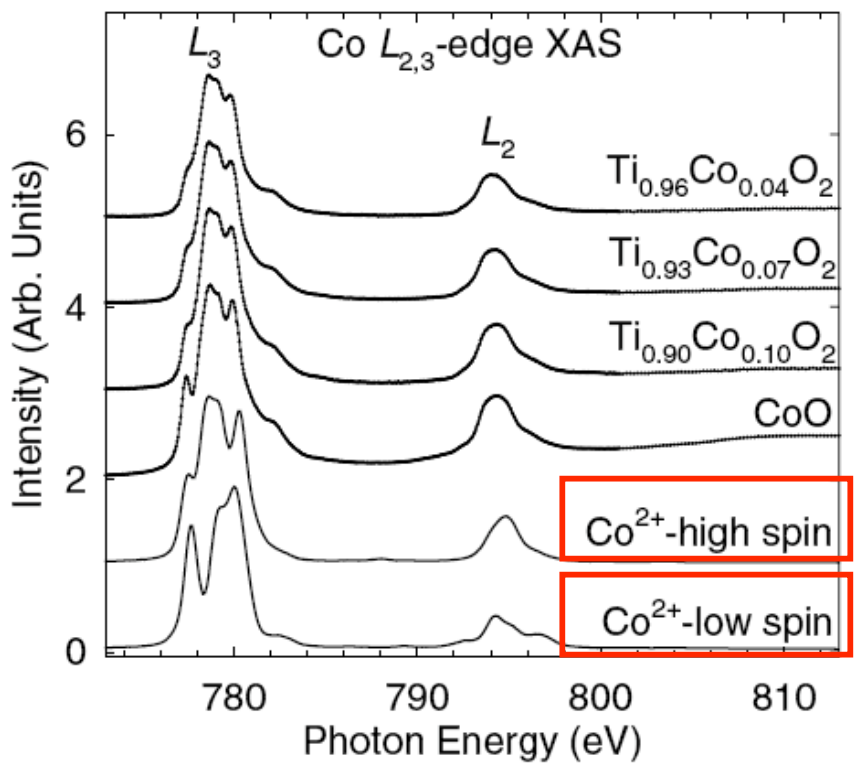
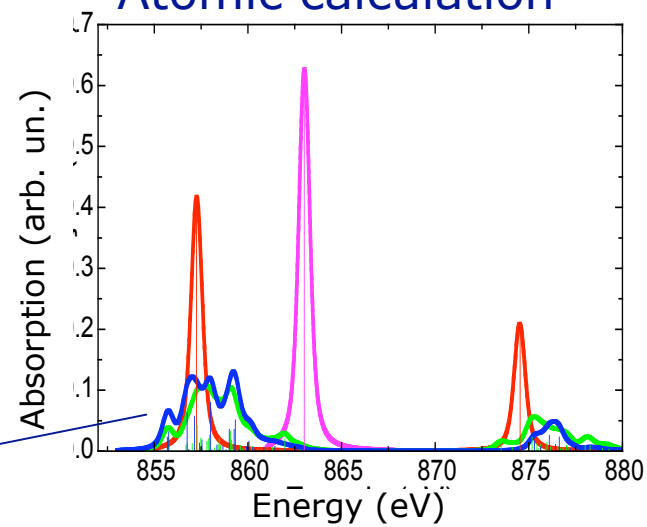


FIG. 2. Co $L_{2,3}$-edge XAS spectra of $Ti_{1-x}Co_xO_2$ ($x = 0.04$, 0.07, 0.10) in comparison with those of CoO and theoretical calculation spectra for high spin Co^{2+} ($3d^7$; $S = 3/2$) and low spin Co^{2+} ($3d^7$; $S = 1/2$) states under O_h symmetry.

Atomic calculation



With help of simulations could decide between high-spin and low-spin state

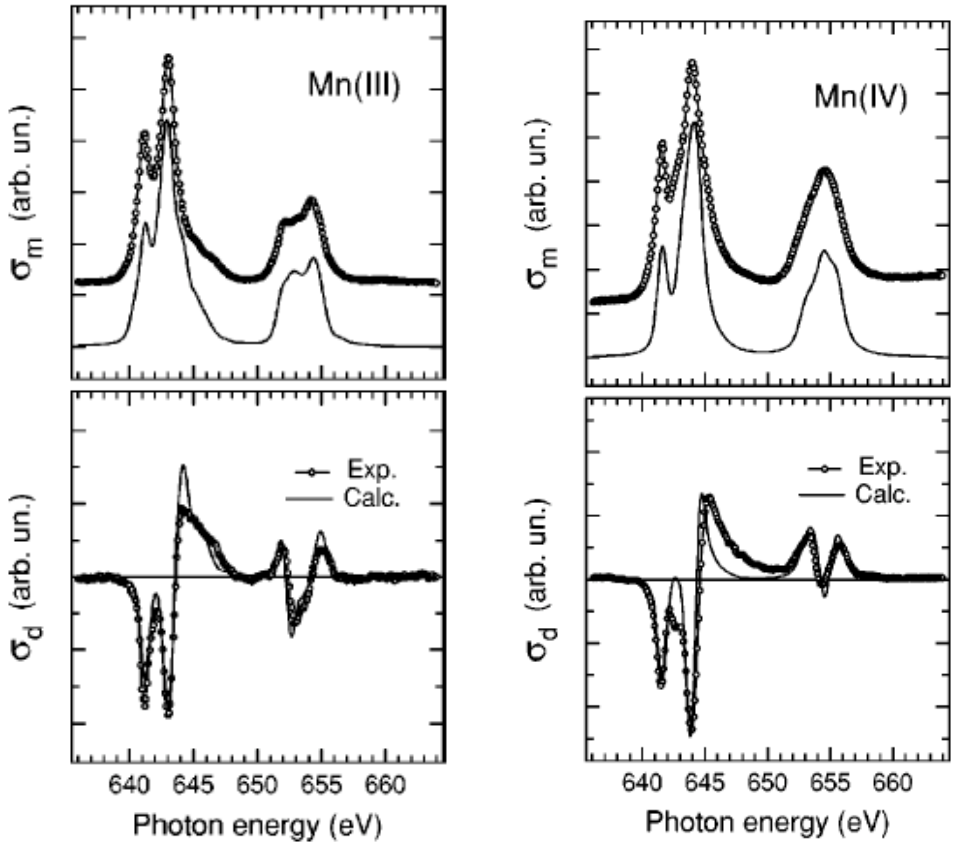
XMCD

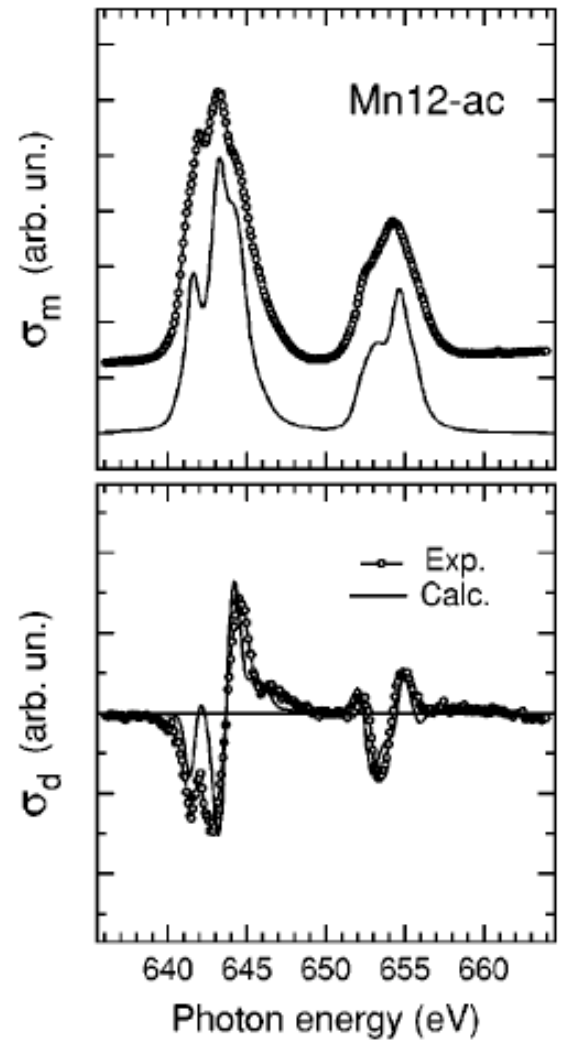
PHYSICAL REVIEW B 68, 064407 (2003)

X-ray magnetic circular dichroism investigation of magnetic contributions from Mn(III) and Mn(IV) ions in Mn12-ac

R. Moroni,[1,*] Ch. Cartier dit Moulin,[1,2] G. Champion,[1,2] M.-A. Arrio,[3] Ph. Sainctavit,[2,3] M. Verdaguer,[1] and D. Gatteschi[4]

- Molecular magnet Mn12-ac
  - 8 Mn(III) ions in distorted octahedra
  - 4 Mn(IV) ions in Oh symmetry
  - Ferrimagnetic alignment



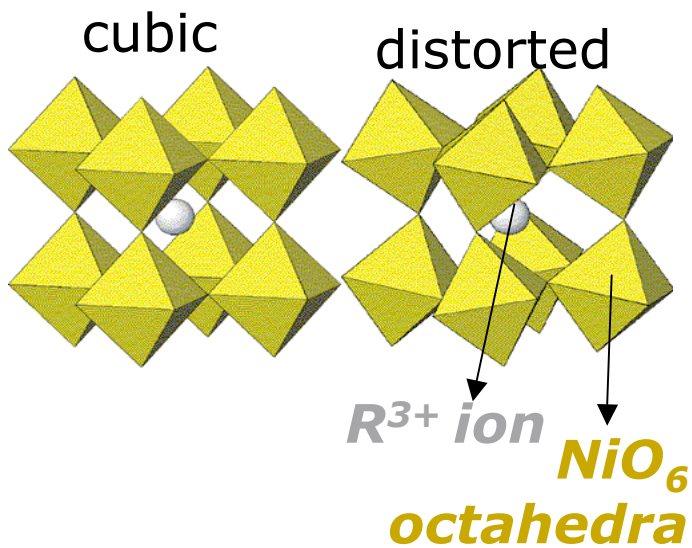


An example: *R*NiO_3 systems

*R*NiO$_3$ systems (*R* = rare earth)

Distorted Perovskite structure

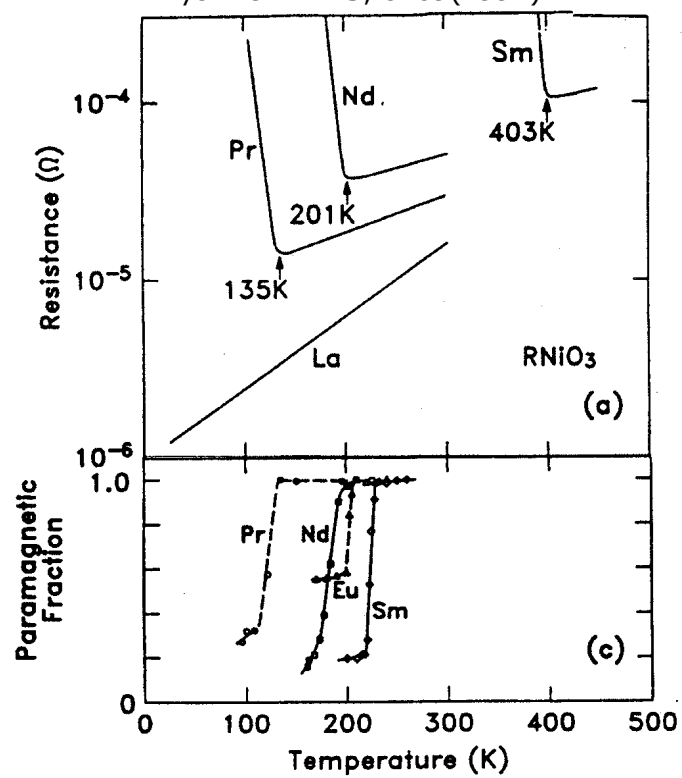
→ structural distortion correlated to *R* size



Metal-insulator (MI) transition

→T_{MI} depends on *R* size

J. B. Torrance et al., Phys. Rev. B **45**, 8209(1992)



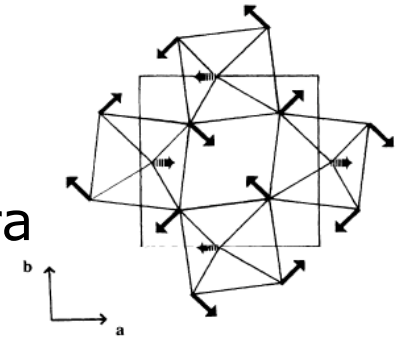
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

← ***Ionic Radius***

*R*NiO$_3$ systems (*R* = rare earth)

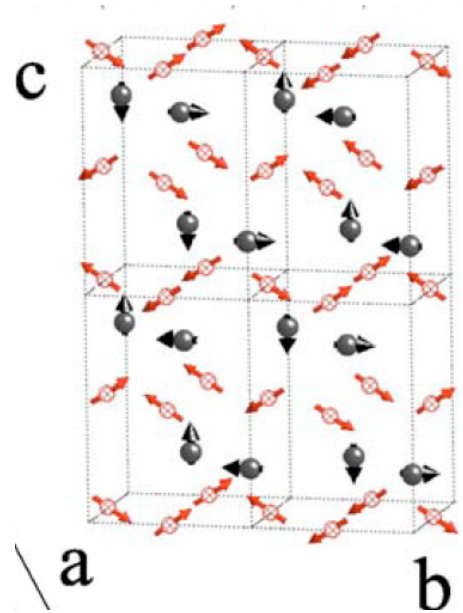
Crystallographic Structure

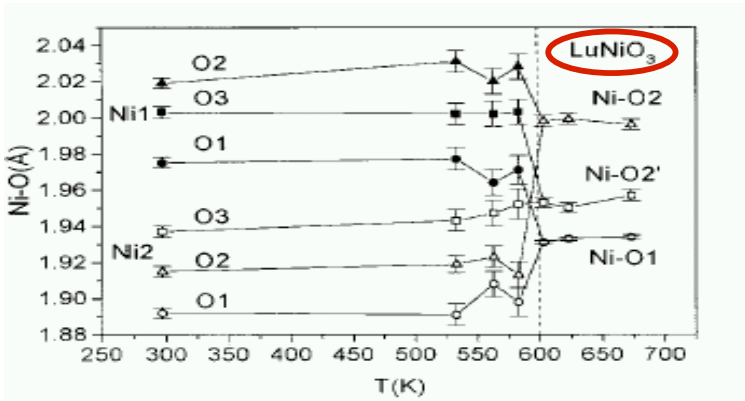
- for **R=Pr-Gd**: orthorhombic with a symmetric NiO$_6$ octahedra
- for **Y, Ho-Lu**: monoclinic with two Ni sites in the insulating phase



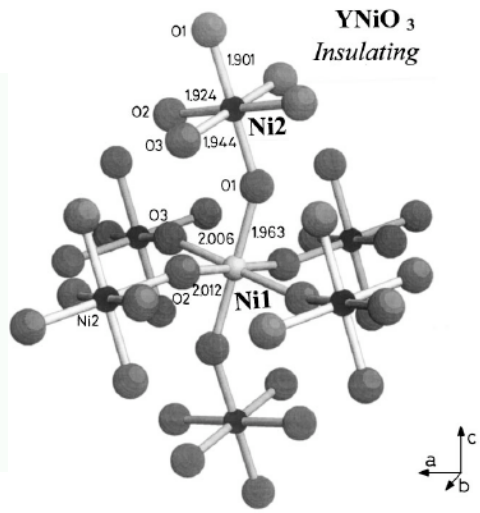
AF structure:

- 2 Ni sites?
- Ni^{3+} low spin





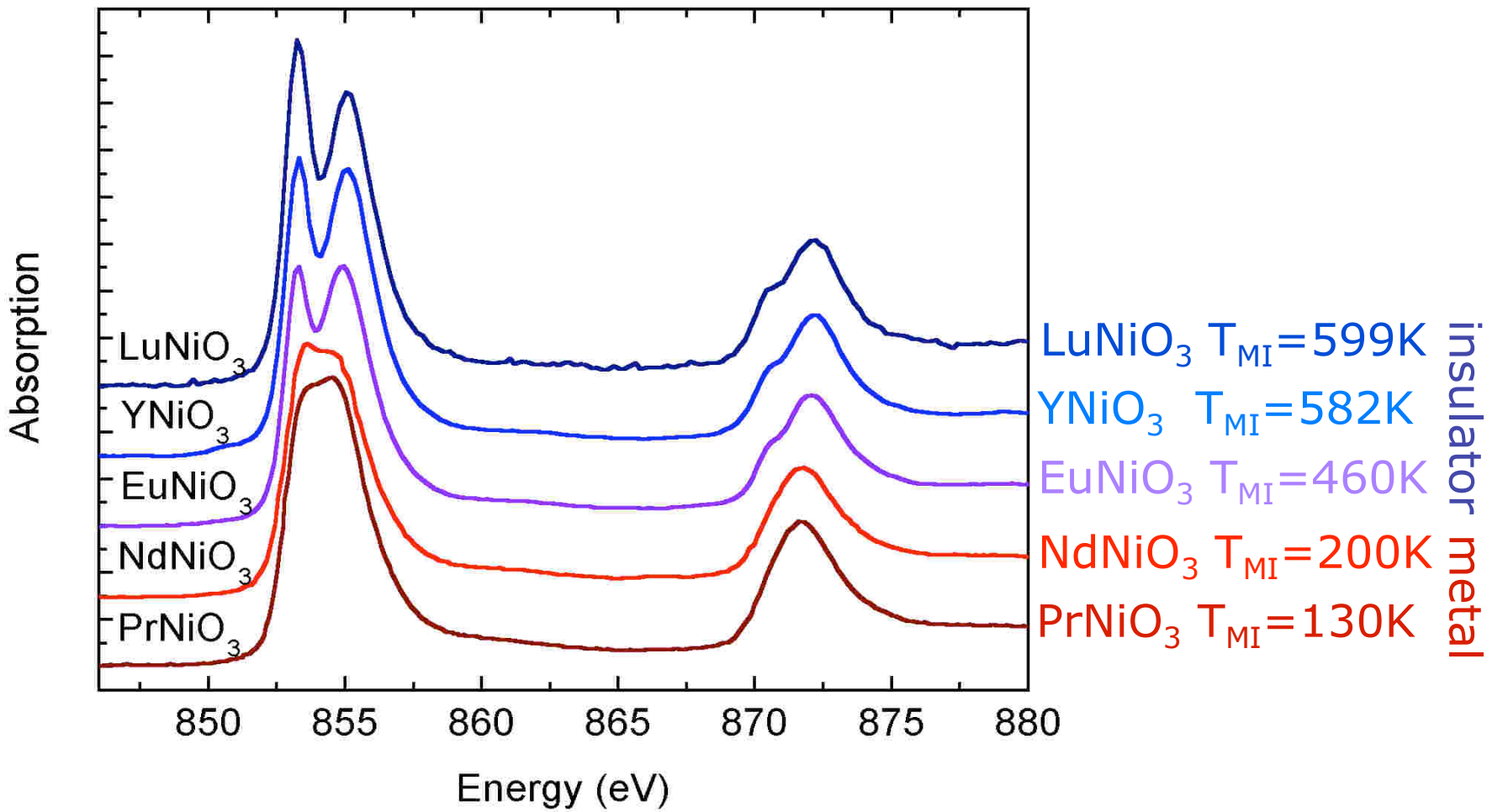
J. A. Alonso et al., Phys. Rev. B **64**, 94102 (2001)



57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

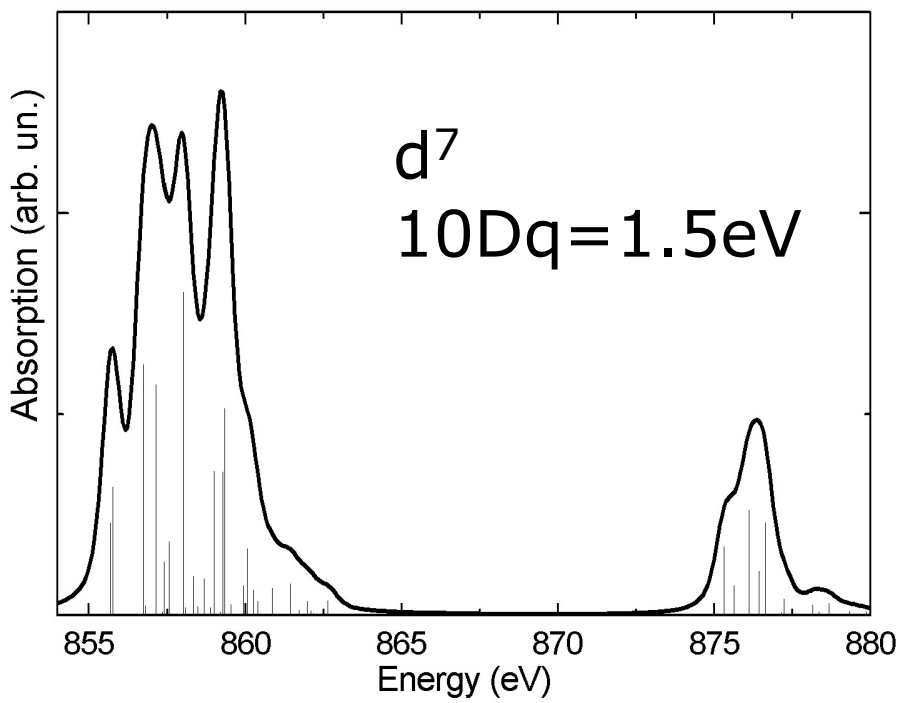
← ***Ionic Radius***

XAS at Ni $L_{2,3}$ edges in *R*NiO_3

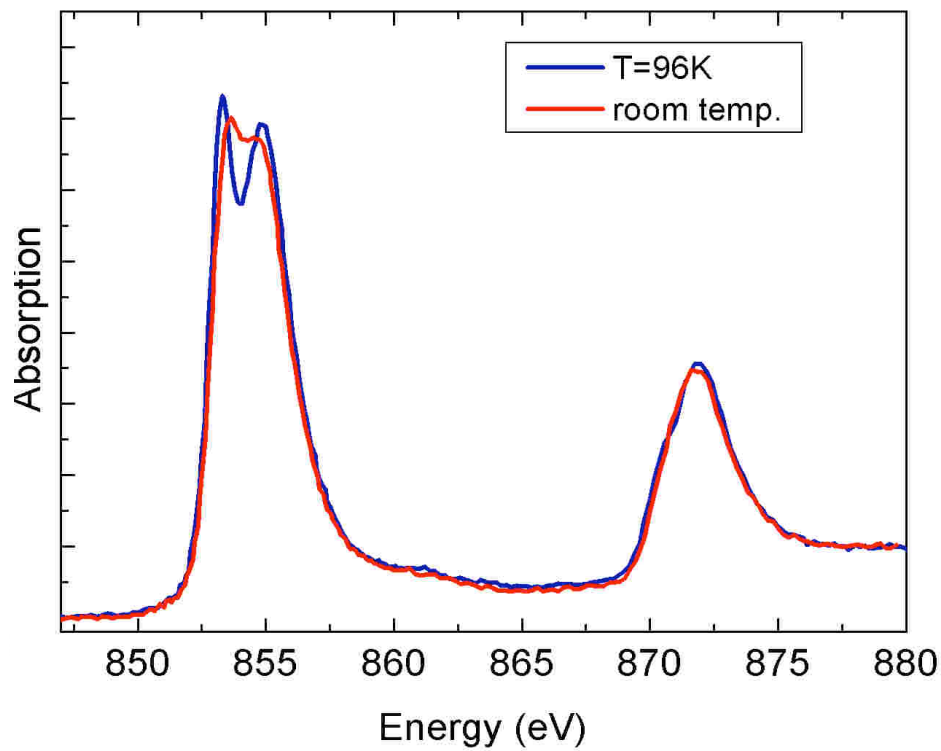


Splitting at L_3 edge for samples at insulating state

XAS at Ni $L_{2,3}$ edges in $RNiO_3$



$NdNiO_3$ T_{MI}=200K



Splitting at L_3 edge is characteristic of insulating state

Simulations

D_{4h} symmetry:

D_s=0.1 D_t=0.2eV

Charge Transfer:

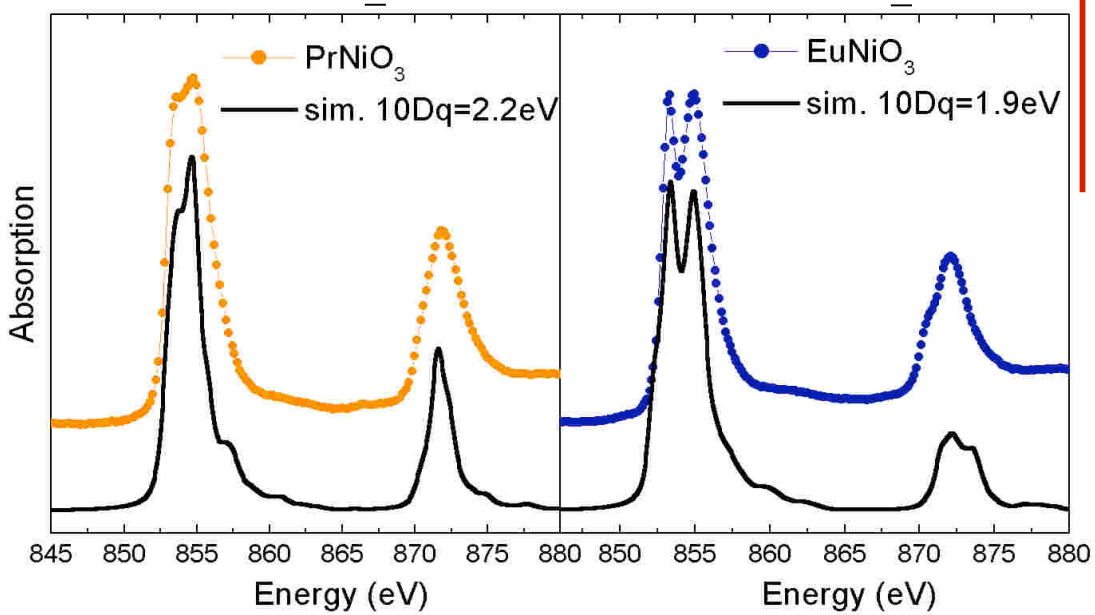
Δ=0.5eV

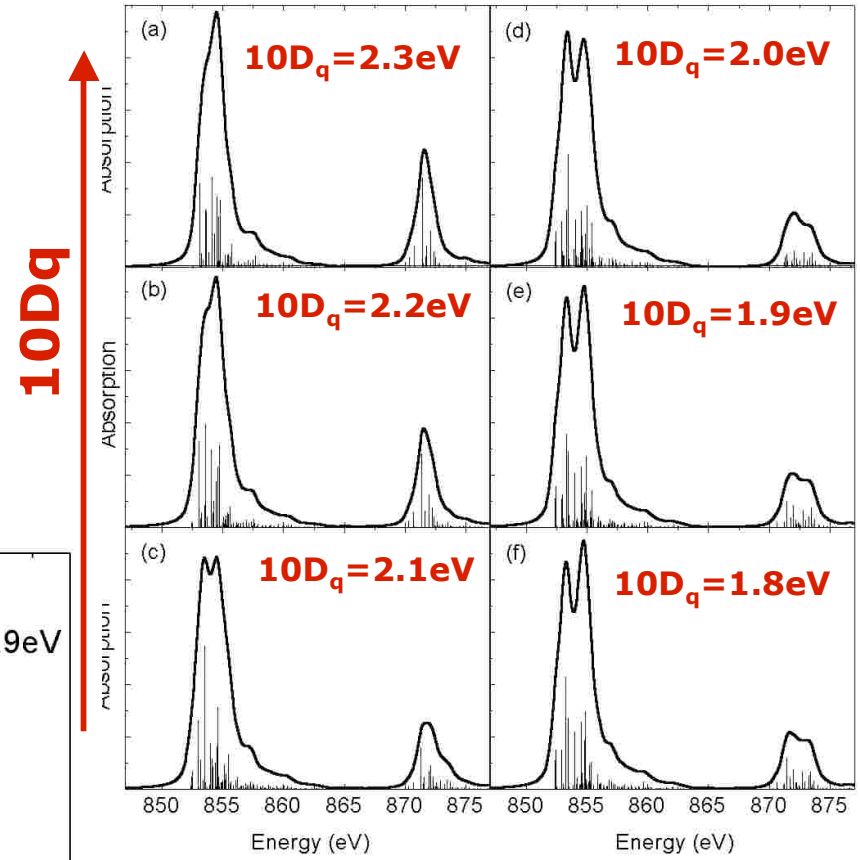
Metal phase simulation

60%$3d^7$ 40%$3d^8\underline{L}$

Insulating phase simulation

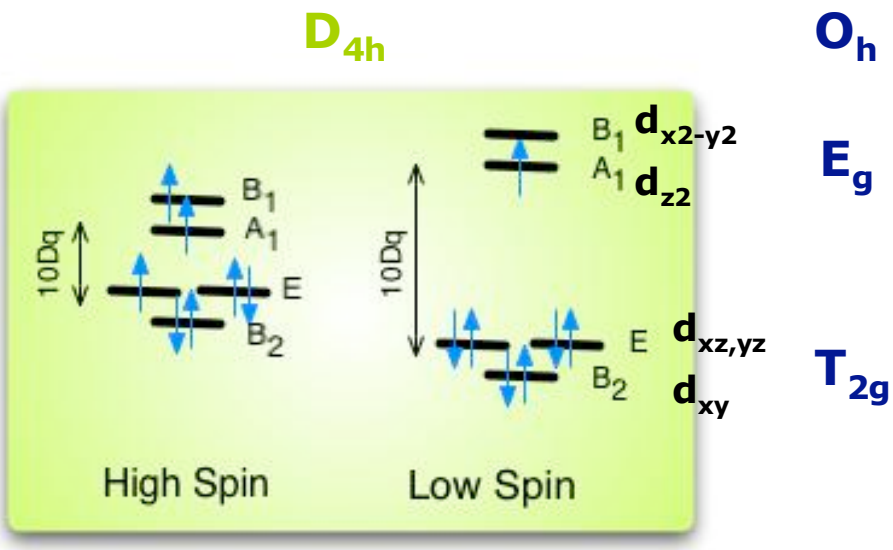
68%$3d^7$ 32%$3d^8\underline{L}$



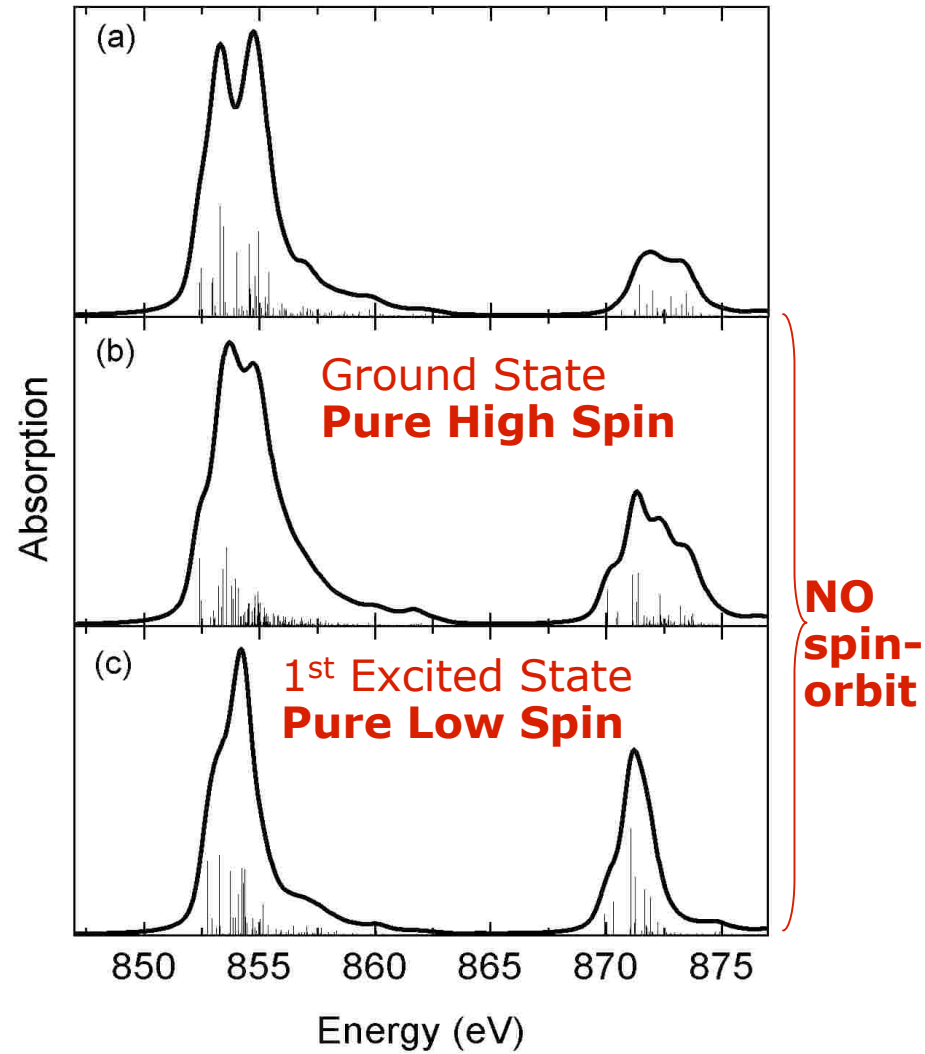


Simulations for different values of $10D_q$

Transition interpretation

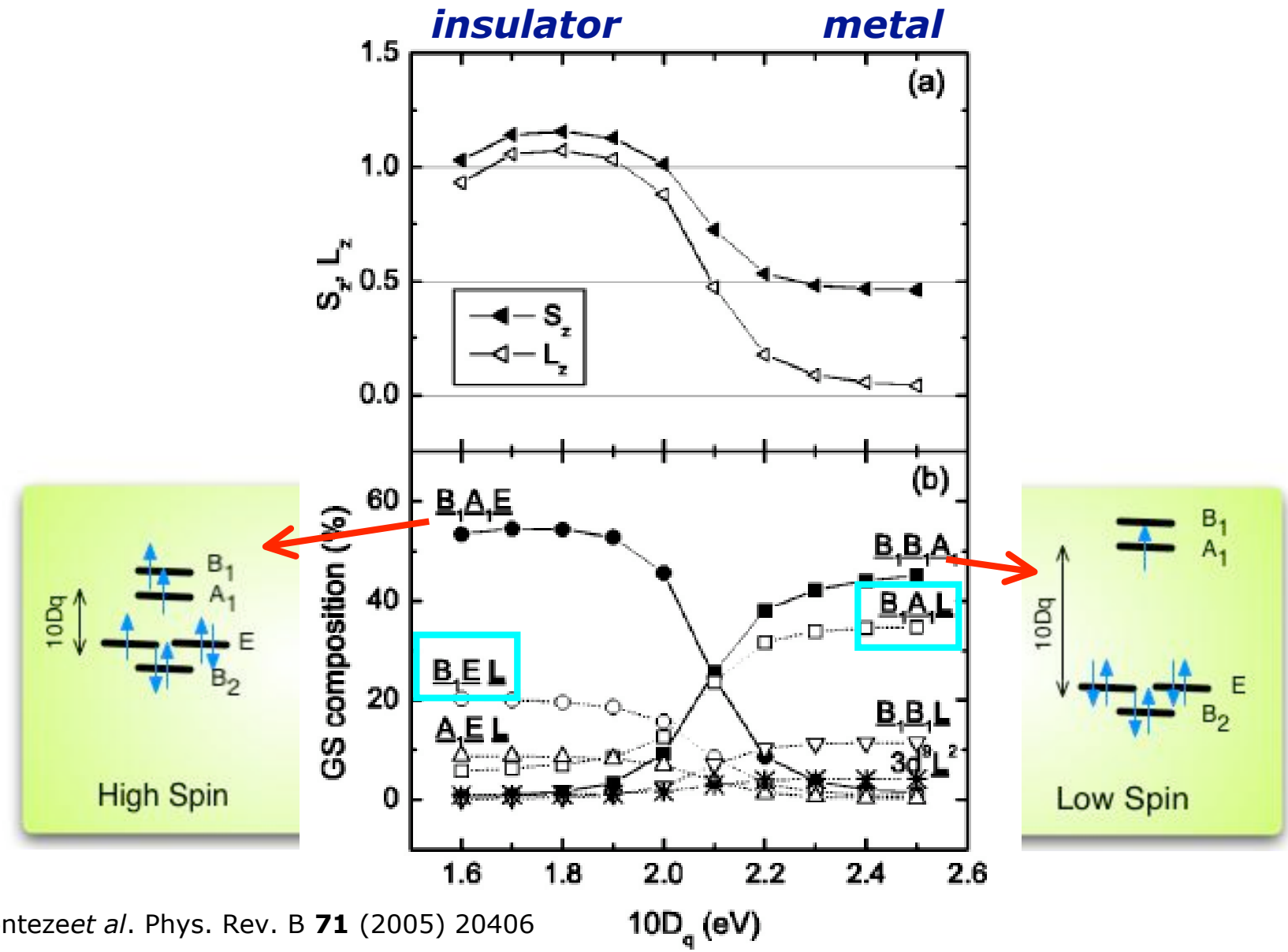


Simulation 10Dq=1.9eV



C. Piamontezeet *al*. Phys. Rev. B **71** (2005) 20406

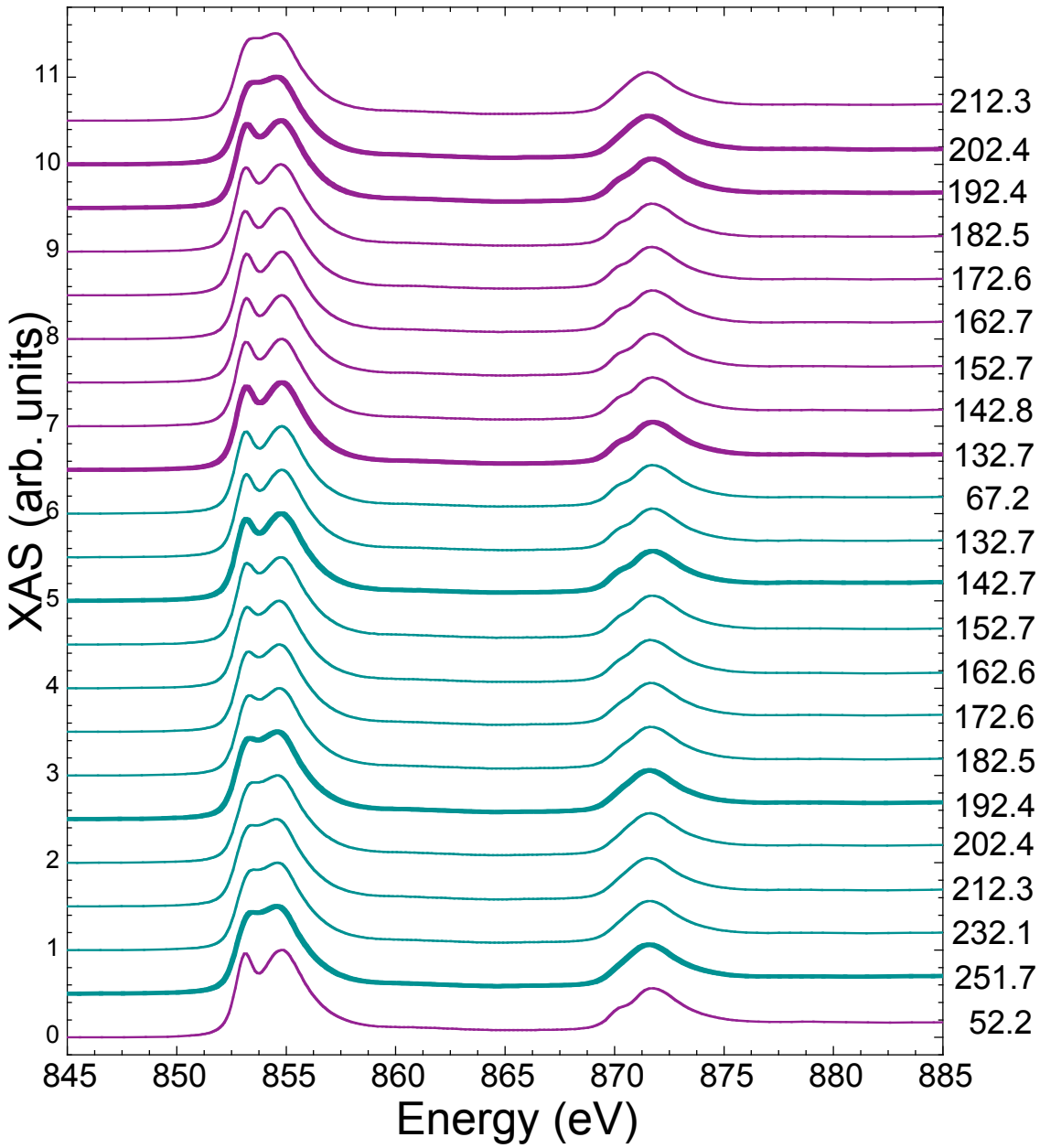
Ground state composition



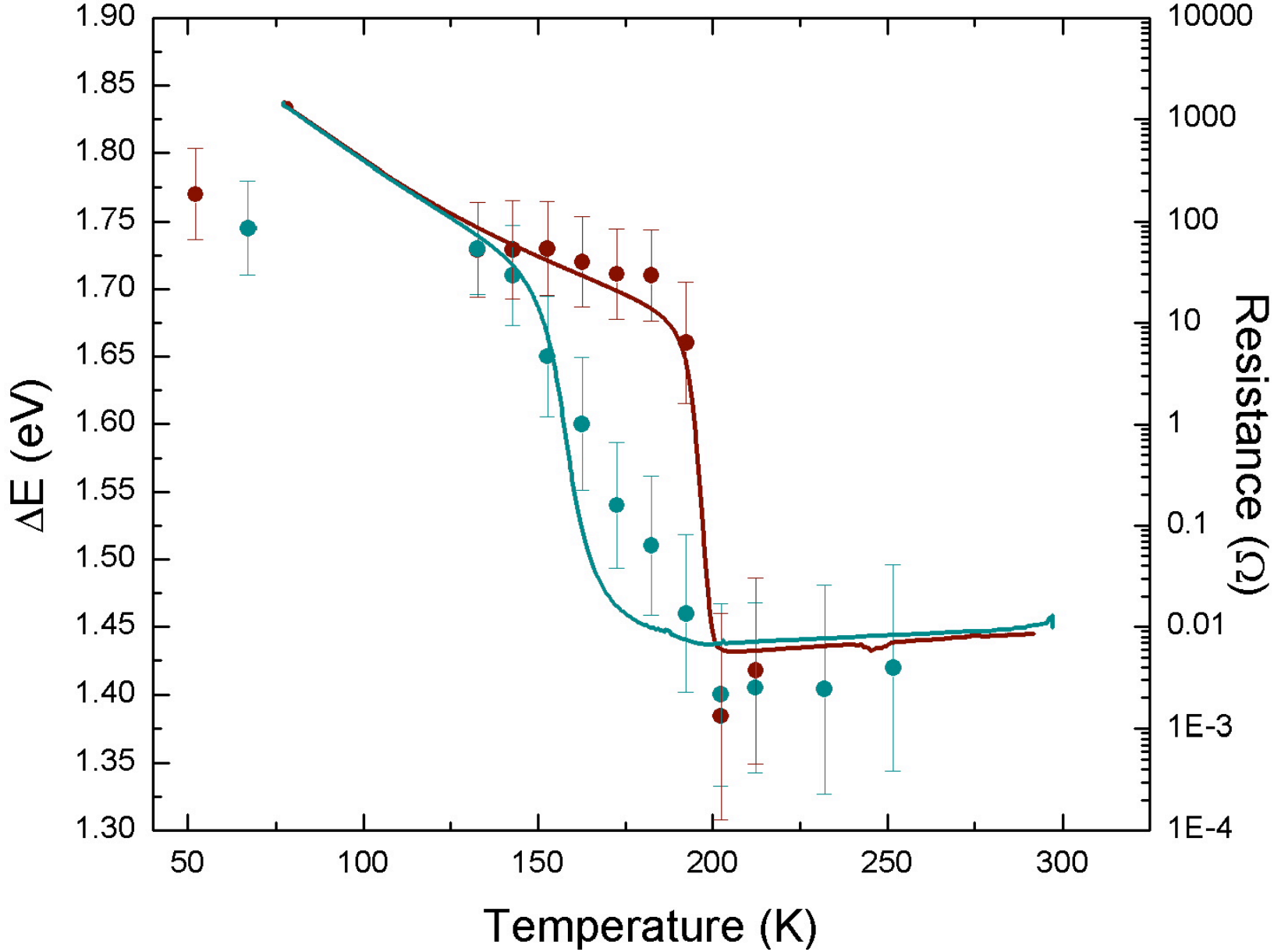
C. Piamontezeet *al*. Phys. Rev. B **71** (2005) 20406

Detailed Temperature Dependence

$NdNiO_3$
T_{MI}=200K



L_3-edge splitting



Summary/Conclusions

- Multiplet simulations:
  - Describes well transition metal $L_{2,3}$-edges and rare earth $M_{4,5}$ edges
  - Includes electronic correlation
  - Neighboring environment described by crystal field splitting
  - Charge transfer can be included for highly hybridized systems
  - Brings new insight in understanding of macroscopic properties

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