

“X-ray Spectroscopy and Electronic Structure of Transition Metal Compounds: Correlation vs. Covalence Effects

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Group of Electronic Structure of Highly Correlated Systems

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Outline

- Introduction/Motivation
- Basic Concepts:
  1. Electronic structure
  2. Transition metal compounds
  3. X-ray spectroscopy (XPS/XAS)
- Examples:
  1. $Sr_{n+1}Fe_nO_{3n+1}$
  2. Resonant Photoemission
  3. $SrRuO_3$
- Conclusions

Group of Electronic Structure of Highly Correlated Systems

- What I do?

I study the electronic structure of transition metal compounds via x-ray spectroscopy.

- Electronic structure: microscopic origin of all physical properties.
- Transition metal compounds – highly correlated systems: rich variety of physical properties.
- X-ray spectroscopy: direct access to the electronic structure.

Group of Electronic Structure of Highly Correlated Systems

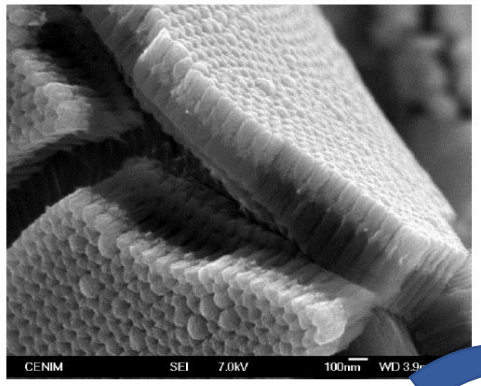
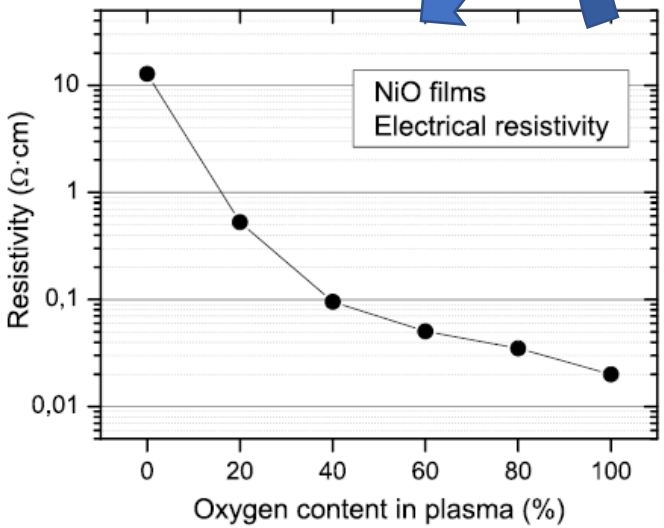
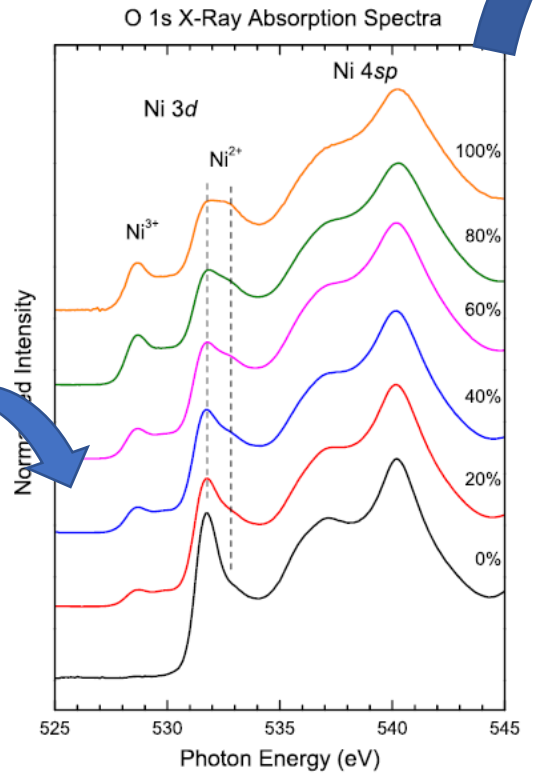
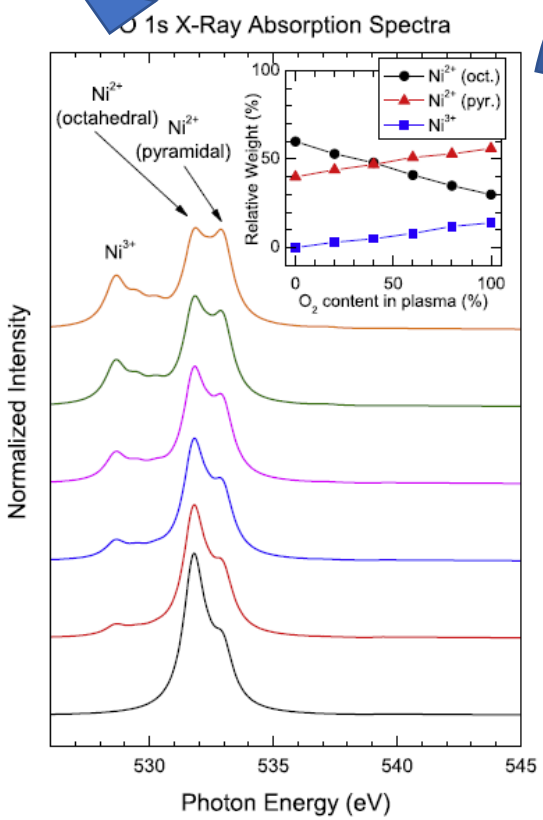
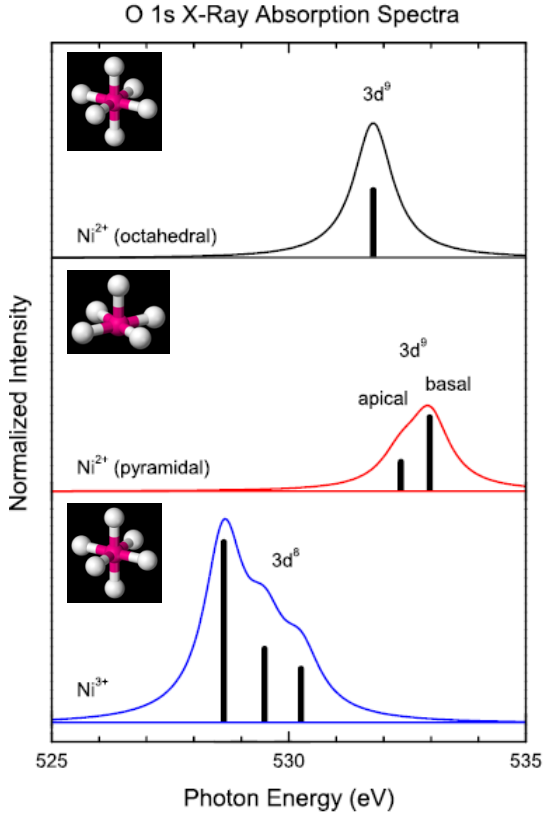


Figure 1: SEM micrograph of NiO thin film growth on nanoporous alumina membrane



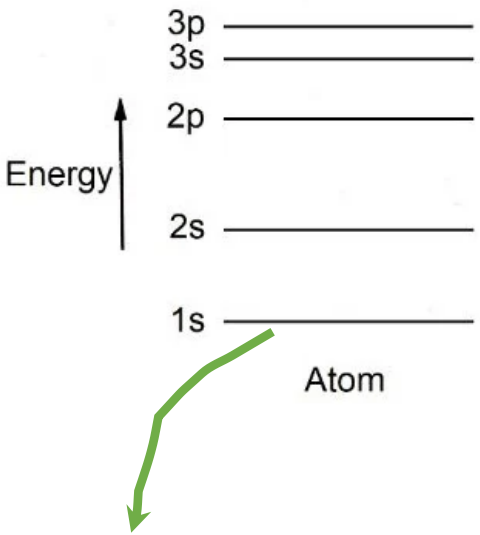


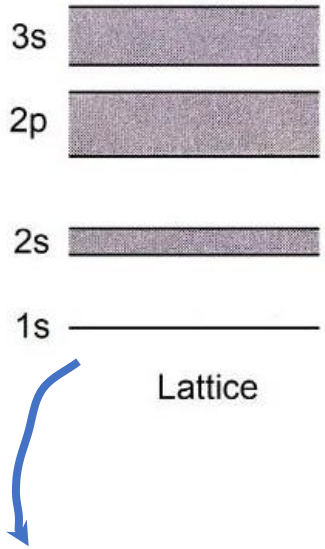




1. Electronic Structure (of solids)

- Bottom-up approach: from atoms to solids



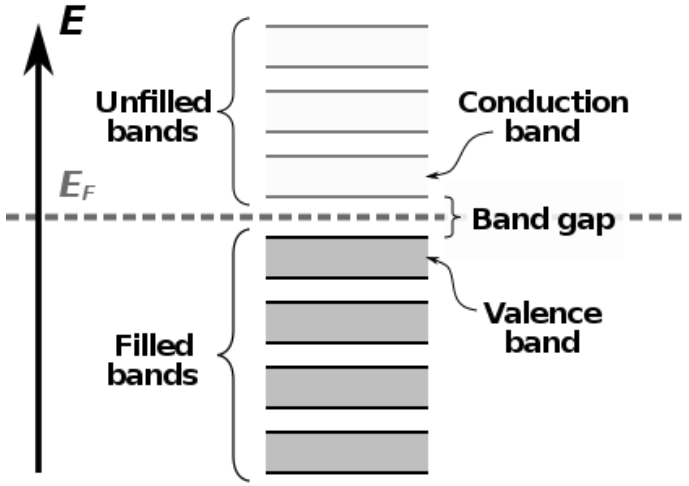


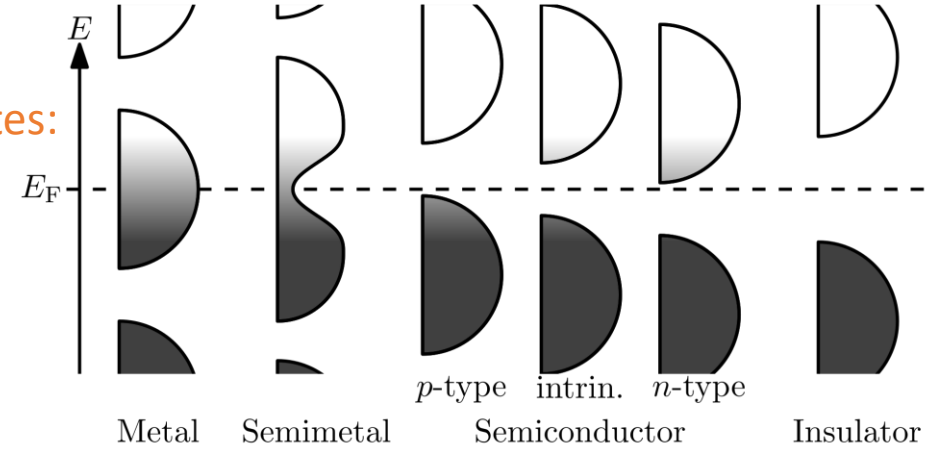
discrete energy levels
quantum numbers (n, l, j, m_j)

core states: tightly bound
(nuclei interaction)

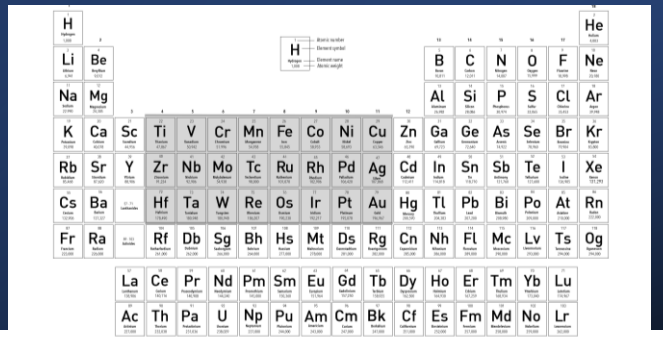
Valence/conduction states:
neighboring interaction

ENERGY BANDS!!!

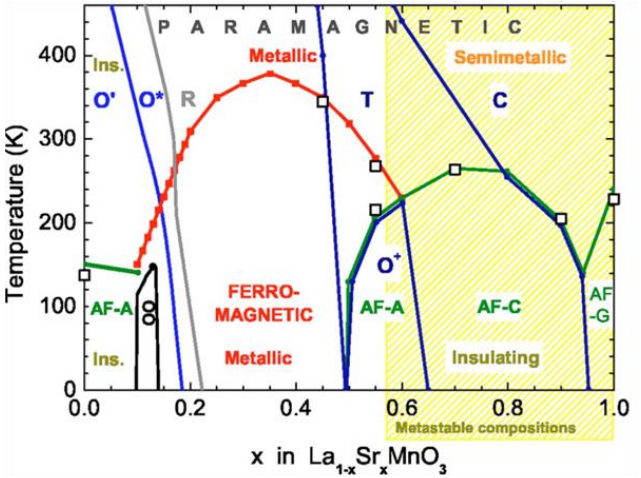




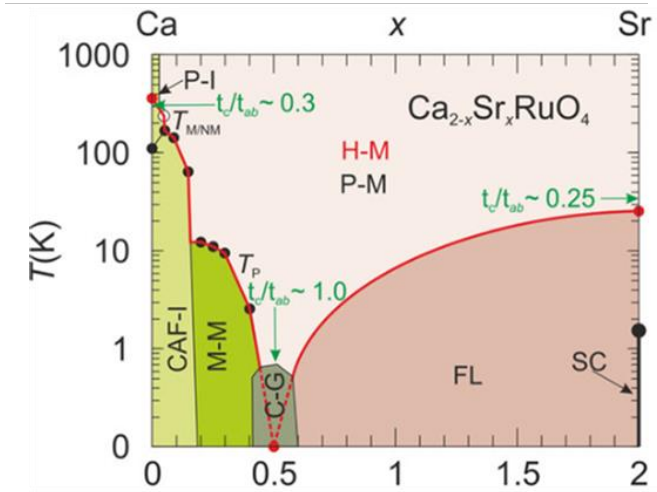
2. Transition metal compounds



- Rich variety of physical properties:
  - metals, insulators, semiconductors;
  - para-, ferro-, antiferro-, diamagnetism;
  - HTC superconductors, magnetorresistance;
  - phase transitions;
  - etc.



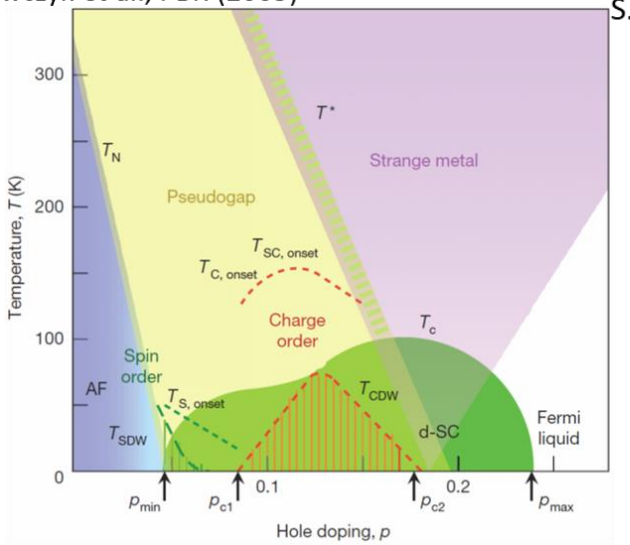
A. Szewczyk et al., PBR (2005)



S. Acharya et al., J. Phys. Comm (2018)

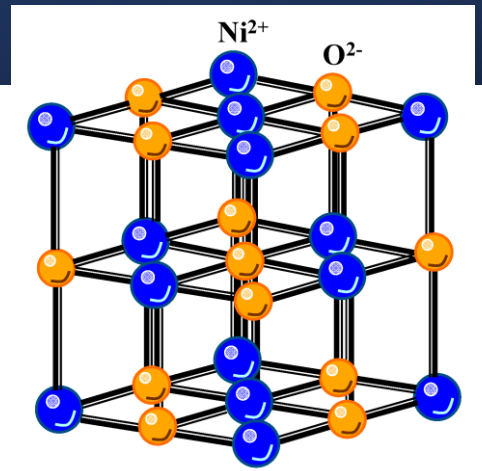
- "Active" states: TM d electrons – correlated electrons

- But also: ligand electrons – covalence effects

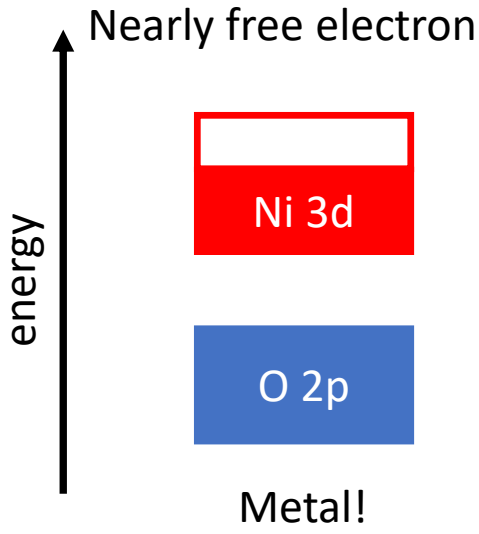


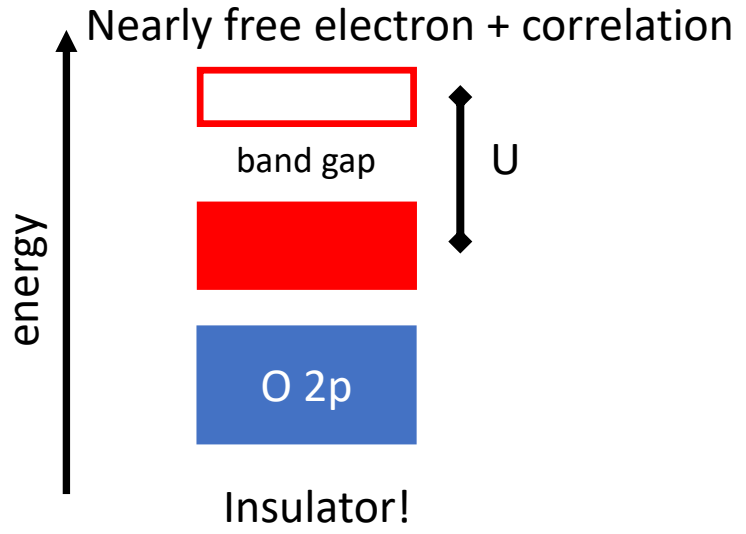
YBCO
B. Keimer et al., Nature (2015)

2. Transition metal compounds – correlation vs. covalence



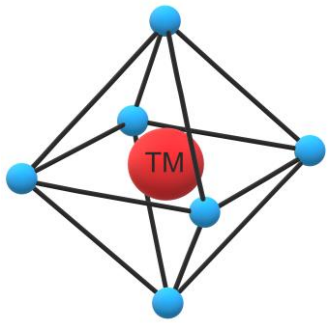
- ELECTRON CORRELATION: e-e interaction
  - Typical case: NiO (Ni^{2+} O^{2-}) → filled O 2p and empty Ni 3d states
  - Electron localization!

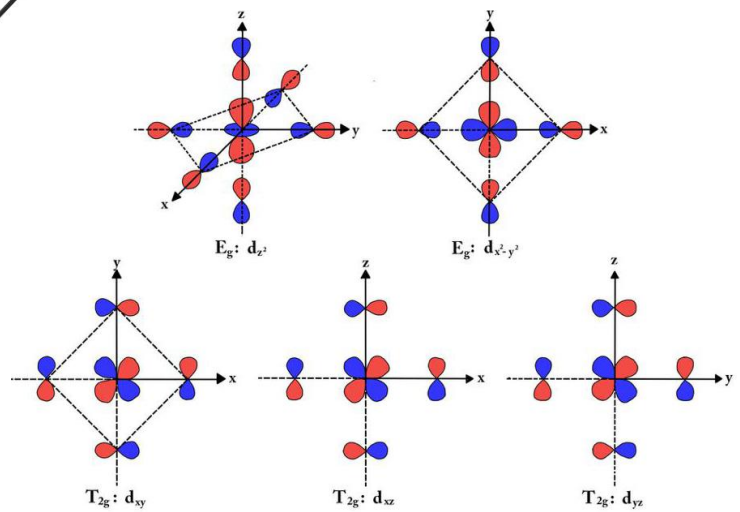


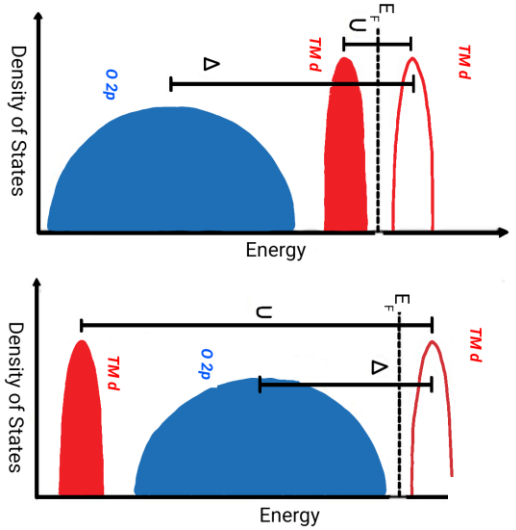


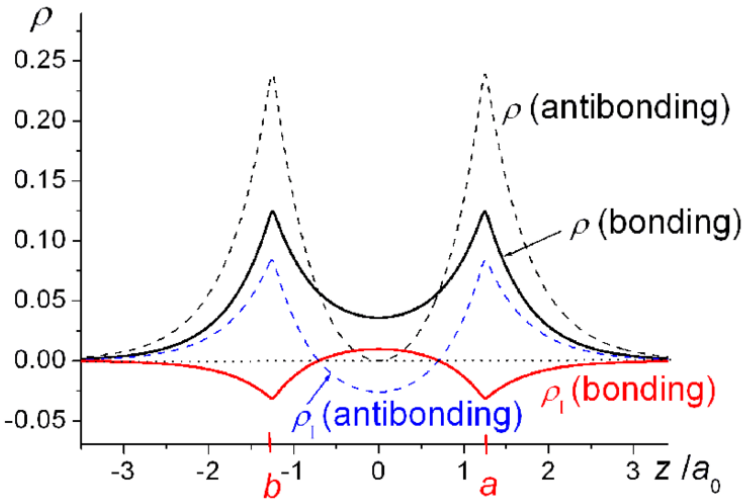
2. Transition metal compounds – correlation vs. covalence

- COVALENCE EFFECTS: TM – ligand interaction





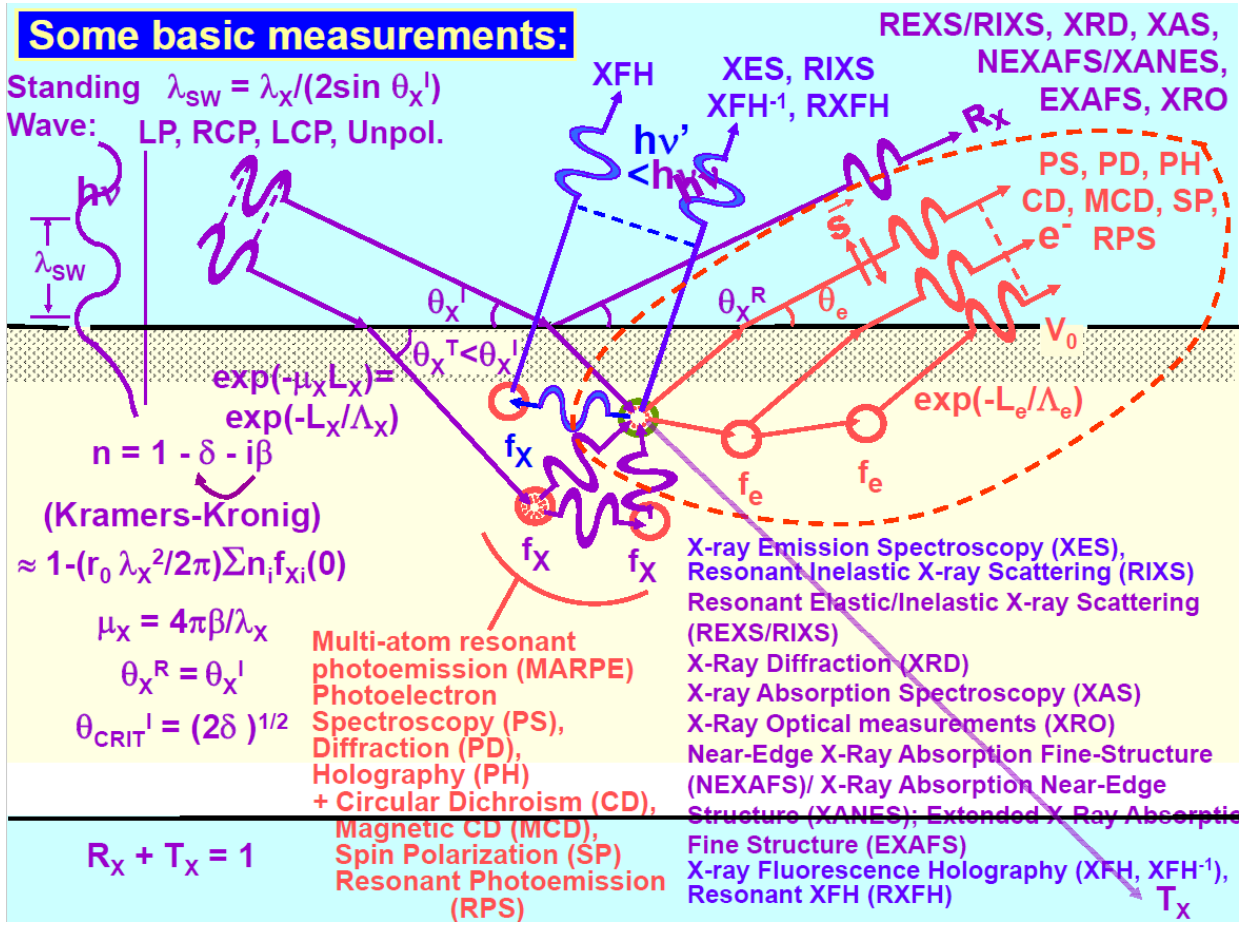




- Wave function superposition → Electron delocalization!

3. X-ray spectroscopy

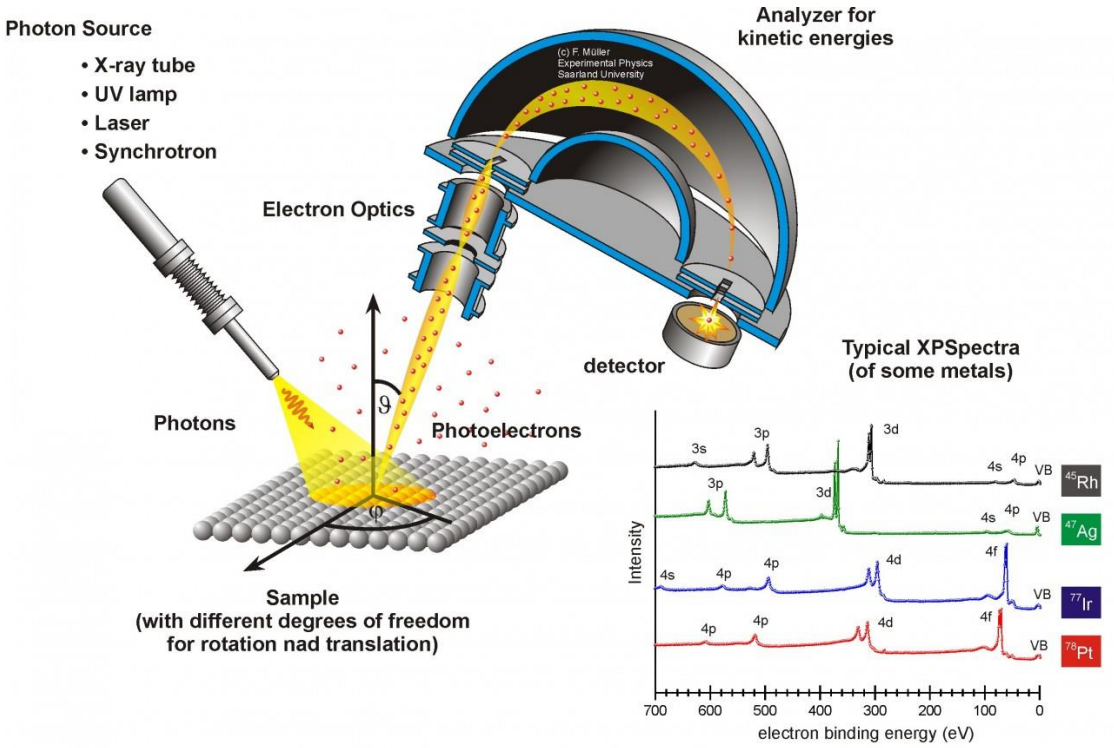
- Interaction of x-rays with matter:



C. Fadley, UFPR Lecture (2016)

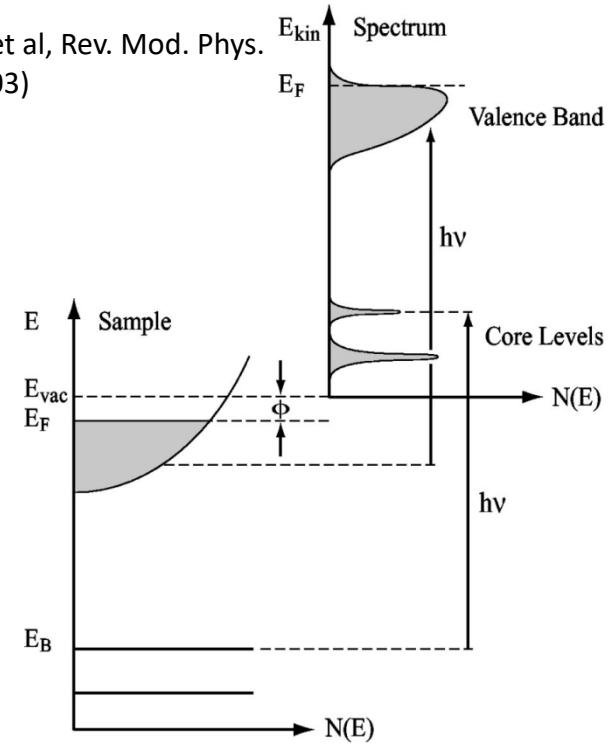
3. X-ray spectroscopy

- X-ray photoemission (XPS,PES):



AG Jacobs, Un. Des Saarlanders

Damascelli et al, Rev. Mod. Phys. 75, 473 (2003)

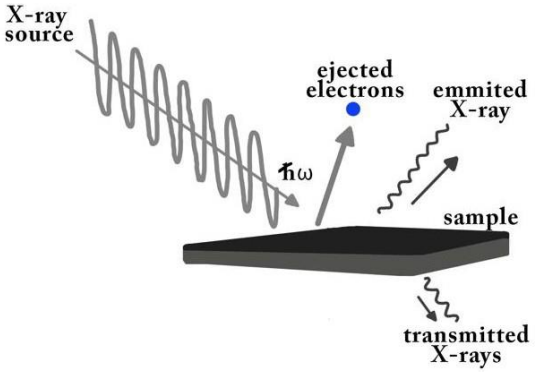


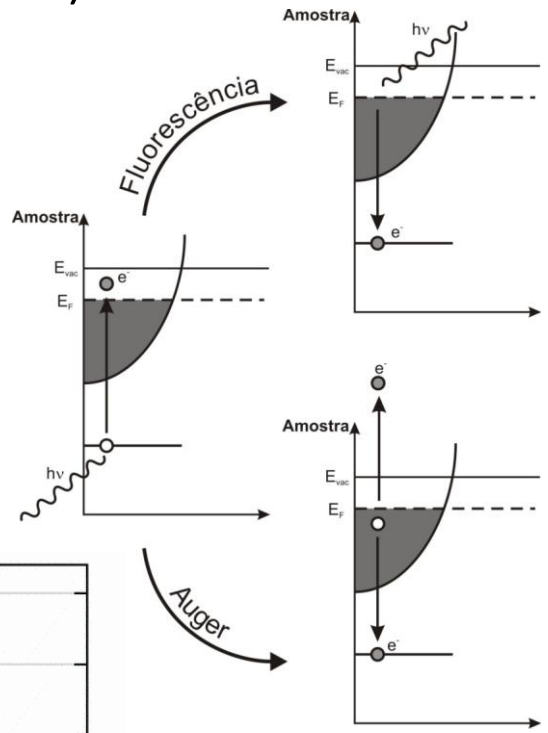
OCCUPIED ELECTRONIC STATES!!!

- Qualitative (what?) analysis
- Quantitative (how much) analysis
- Chemical (interaction) analysis

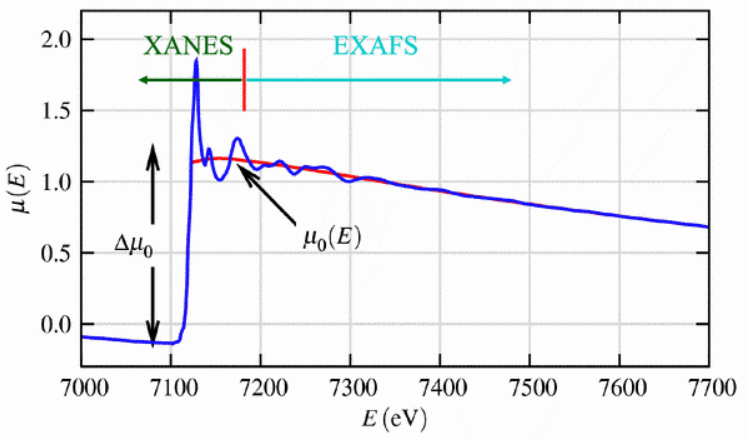
3. X-ray spectroscopy

- X-ray absorption (XAS):





- Absorption edge



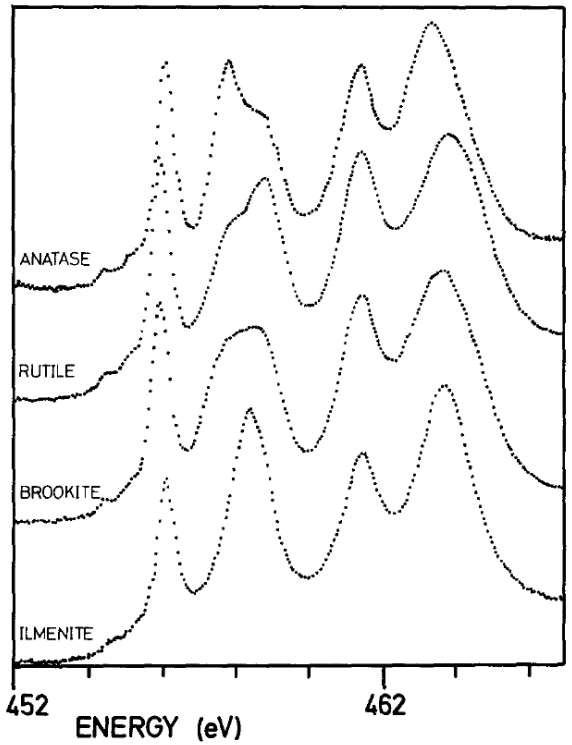
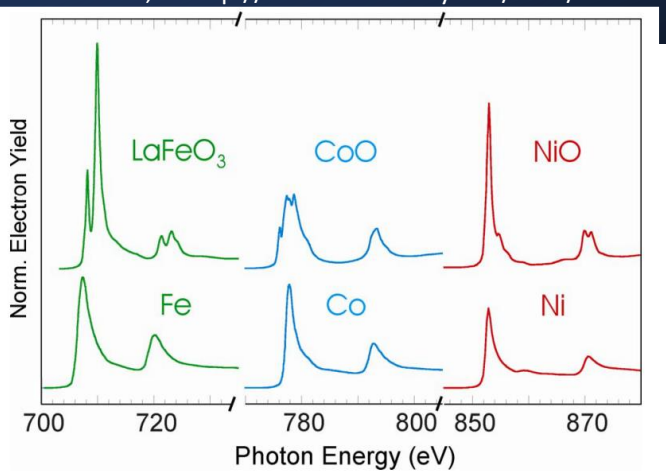


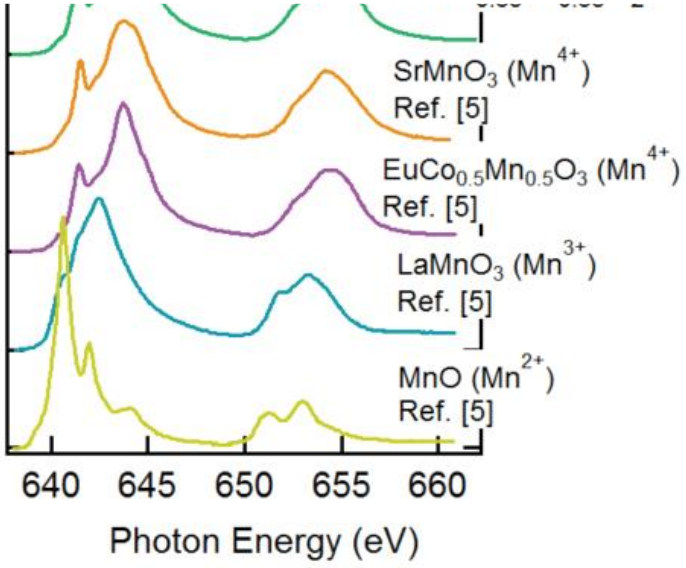
Fig. 3. 2*p* X-ray absorption spectra of the minerals Rutile, Anatase, Brookite and Ilmenite

F.M.F. de Groot et al., Phys Chem Minerals (1992) 19:140-147

J. Stohr, at http://ast.coe.berkeley.edu/srms/



H. Wadati et al. CHEMICAL & MATERIALS SCIENCE, CANADIAN LIGHT SOURCE



UNOCCUPIED ELECTRONIC STATES!!!

- Atom/ion specific
- Chemical environment (valence, symmetry, spin state, etc.)

Examples

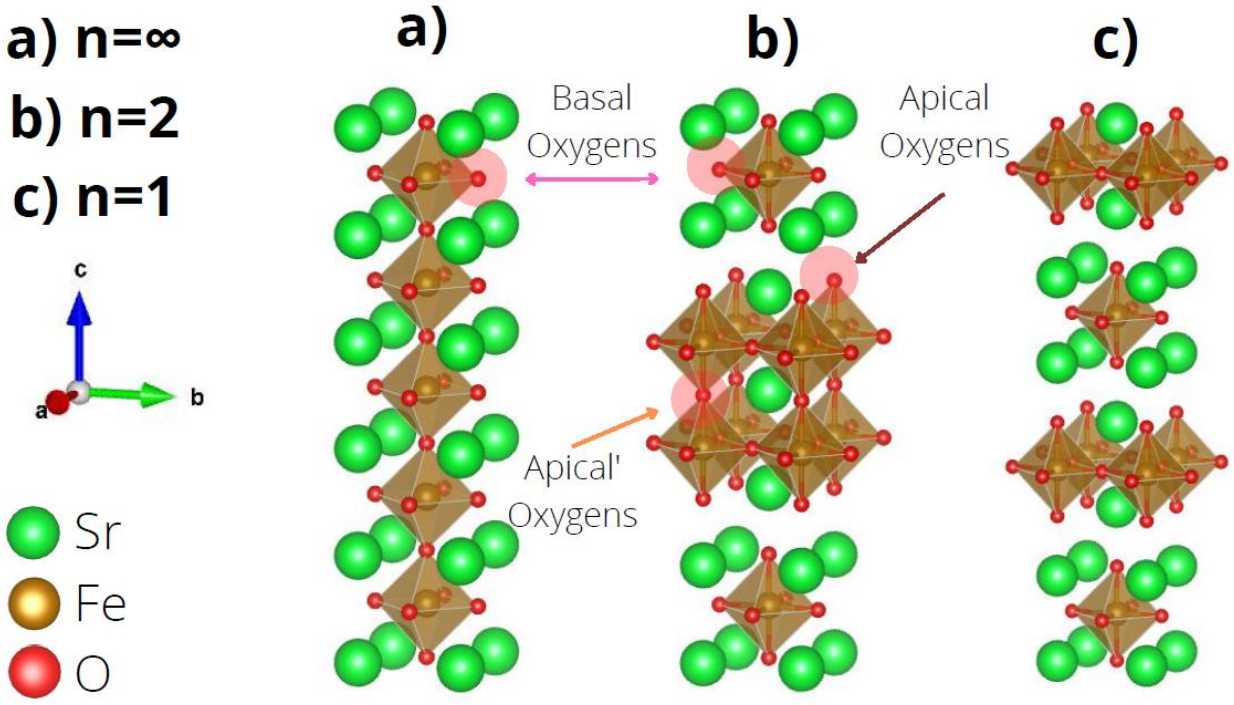
- $Sr_{n+1}Fe_nO_{3n+1}$
- Resonant Photoemisison
- $SrRuO_3$

1. $Sr_{n+1}Fe_nO_{3n+1}$ – Matheus F. Ribeiro (MSc.)

- Ruddlesden-Poppen series:
- n × ($SrFeO_3$) + (SrO)

perovskite insulating oxide

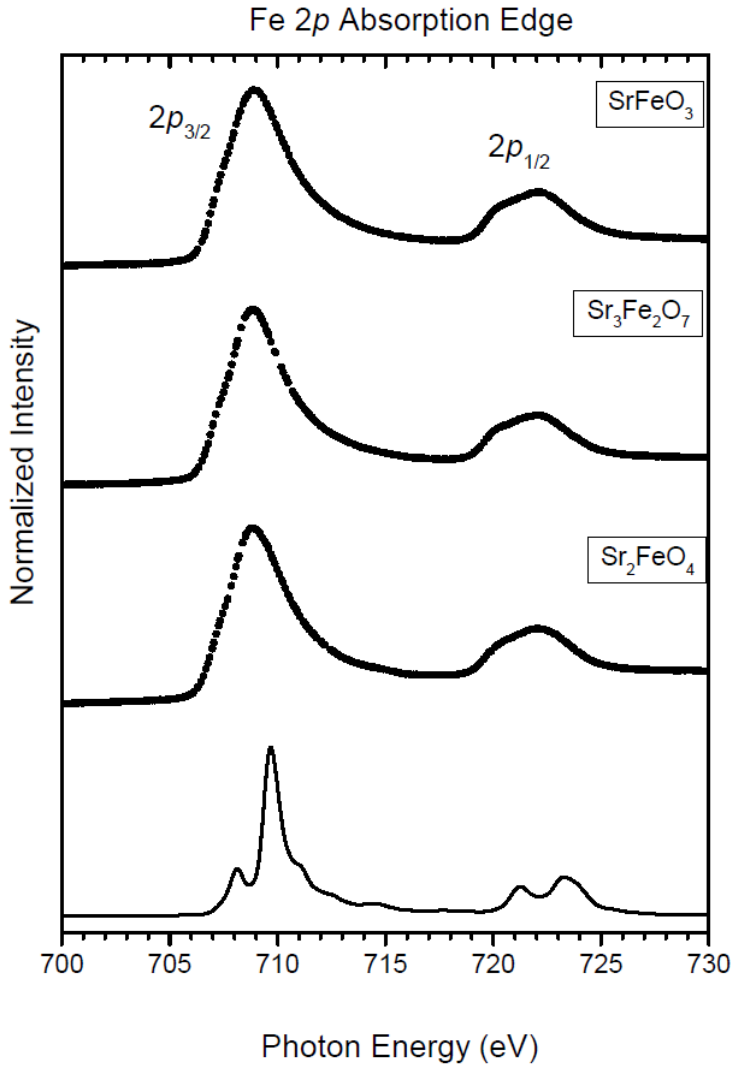
- n controls the dimensionality: 3D to 2D!

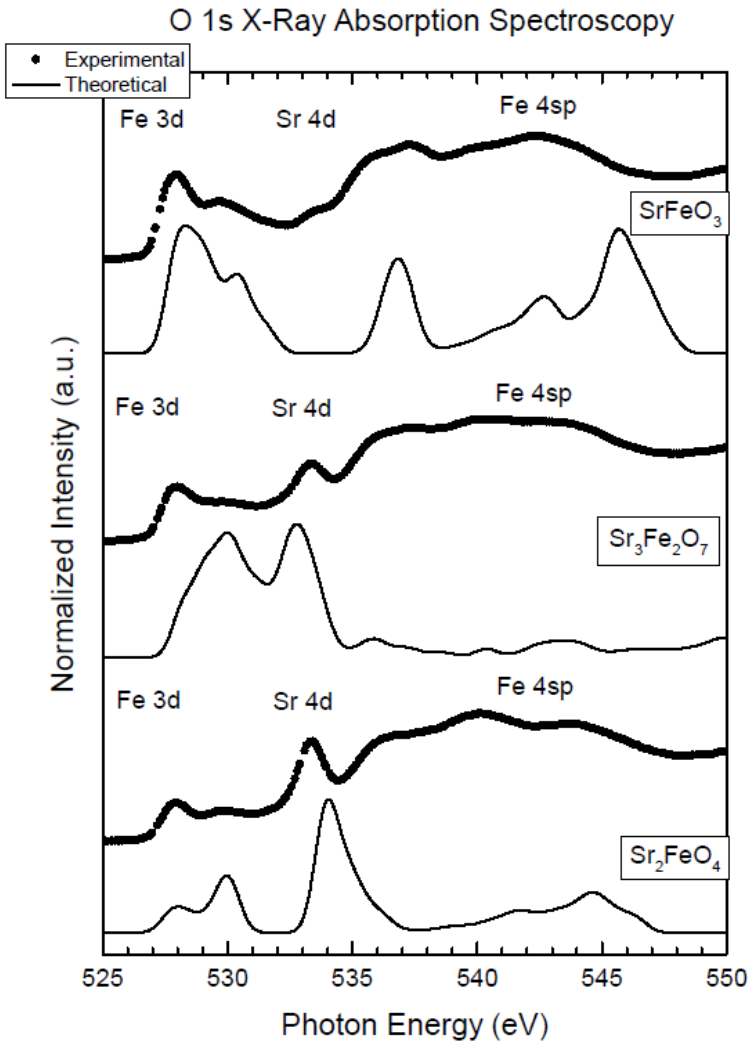


Material	Conductivity	Magnetic Ordering	Special Characteristics
$SrFeO_3$ [1,2]	metallic	cycloidal antiferromagnetic ($T_N \approx 134K$)	half-metal
$Sr_3Fe_2O_7$ [3,4]	p-semiconductor	G-type antiferromagnet ($T_N \approx 110K$)	covalence quenched Jahn-Teller
Sr_3FeNiO_7 [5]	p-semiconductor	paramagnetic	spin-glass ($T < 40K$)
Sr_2FeO_4 [4,6]	insulator	elliptical cycloidal spin ($T_N \approx 56K$)	hidden distortion to stabilize ground state

1. $Sr_{n+1}Fe_nO_{3n+1}$ – Matheus F. Ribeiro (MSc.)

- Fe 2p and O 1s XAS:
  - Iron states: “Fe3+” without change!!!
  - Oxygen states: relative intensity evolution!!!

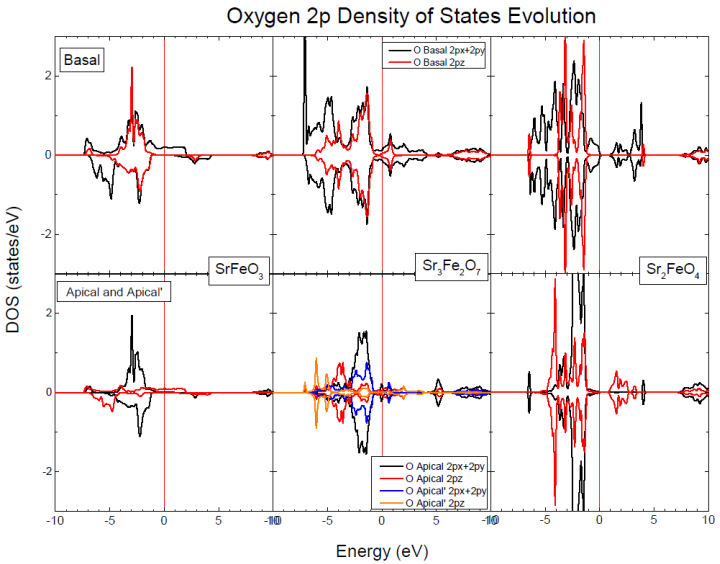


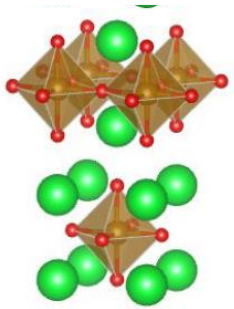


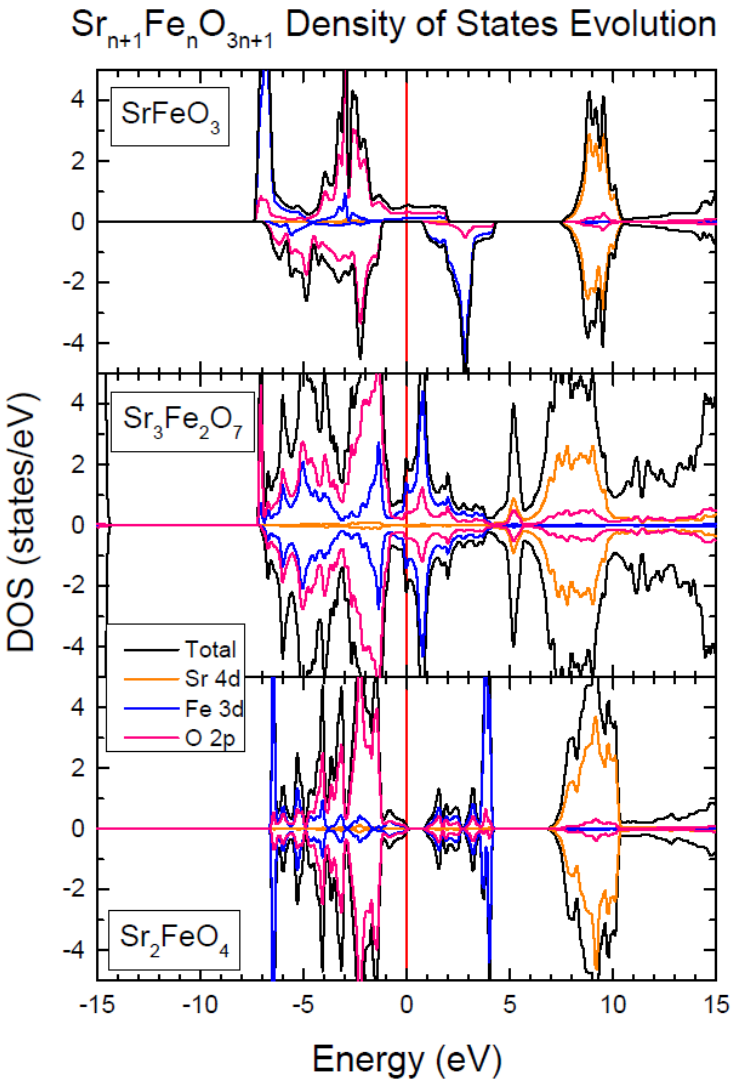
1. $Sr_{n+1}Fe_nO_{3n+1}$ – Matheus F. Ribeiro (MSc.)

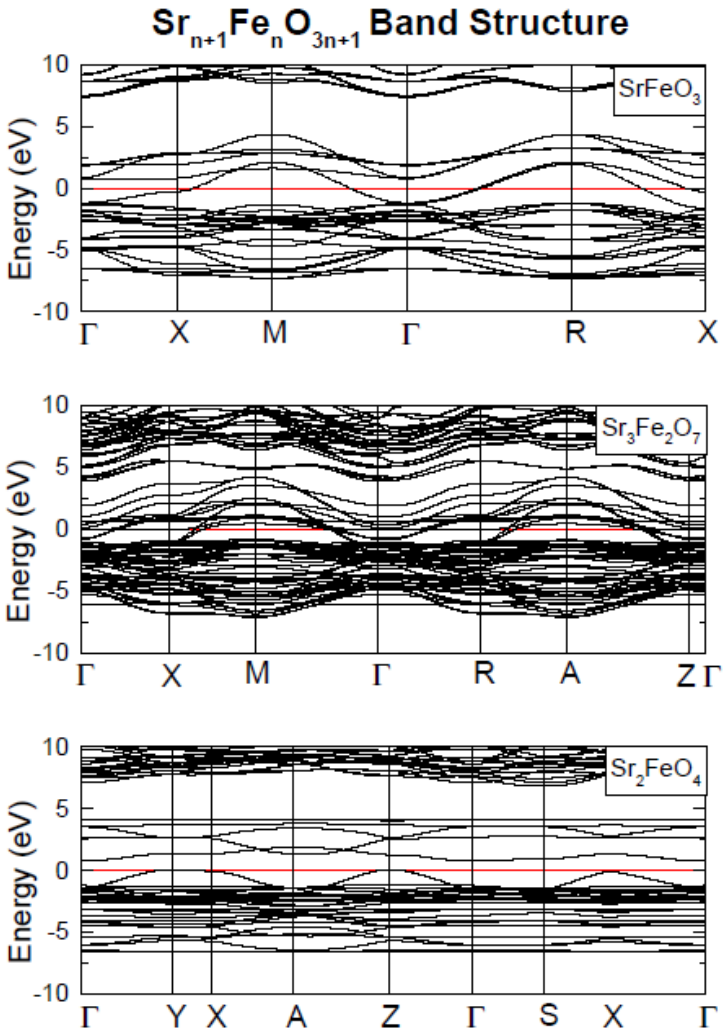
- SFO density of states:
  - metal to insulator transition
  - Competition between Fe – O and Sr – O covalence.

- SFO band structure:
  - Localization of bands due to dimensionality effects.



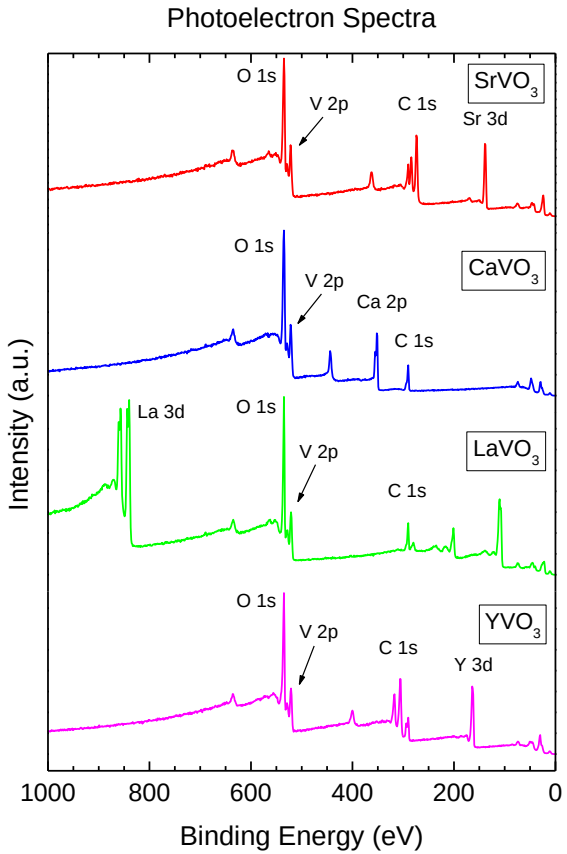


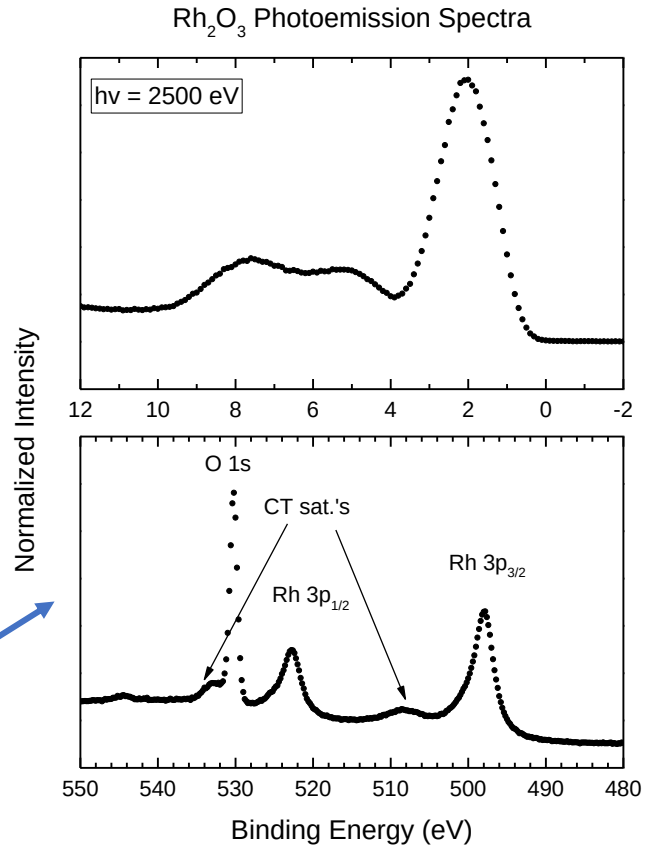




2. Resonant Photoemission – Viviane Stoeberl et al. PRB 102, 155112 (2021)

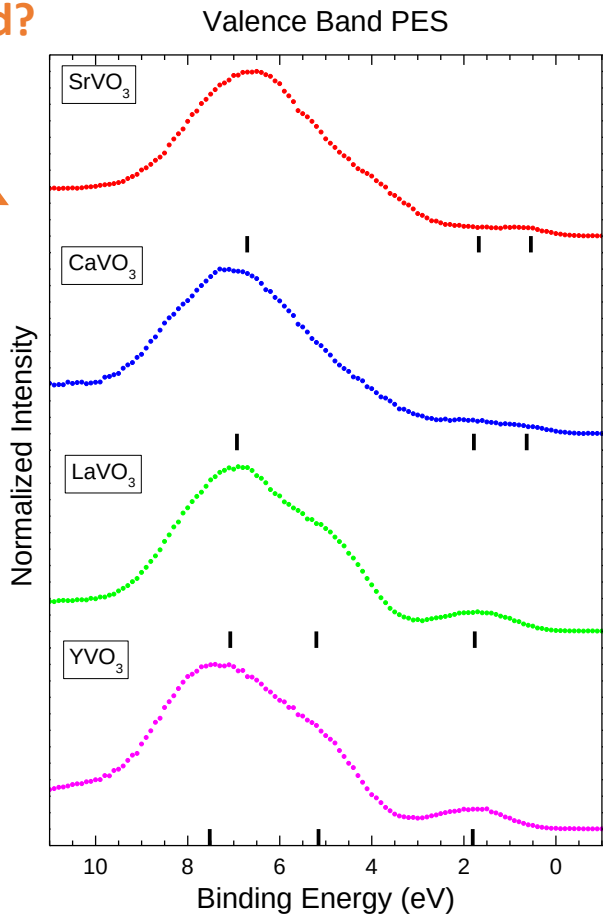
- How can one distinguish different contributions in the valence band?





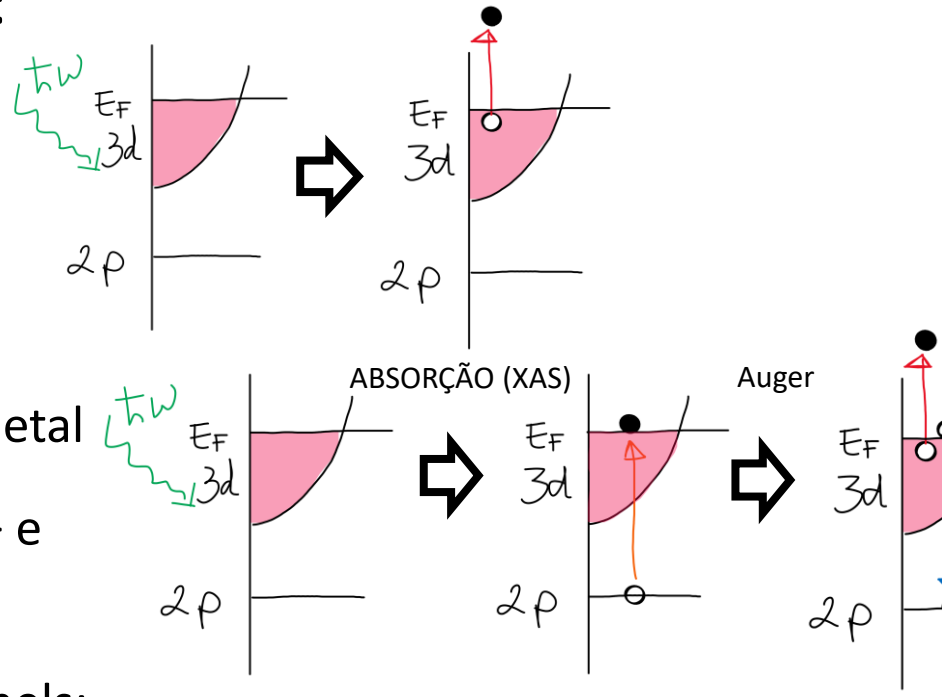
core level, OK!

valence band?

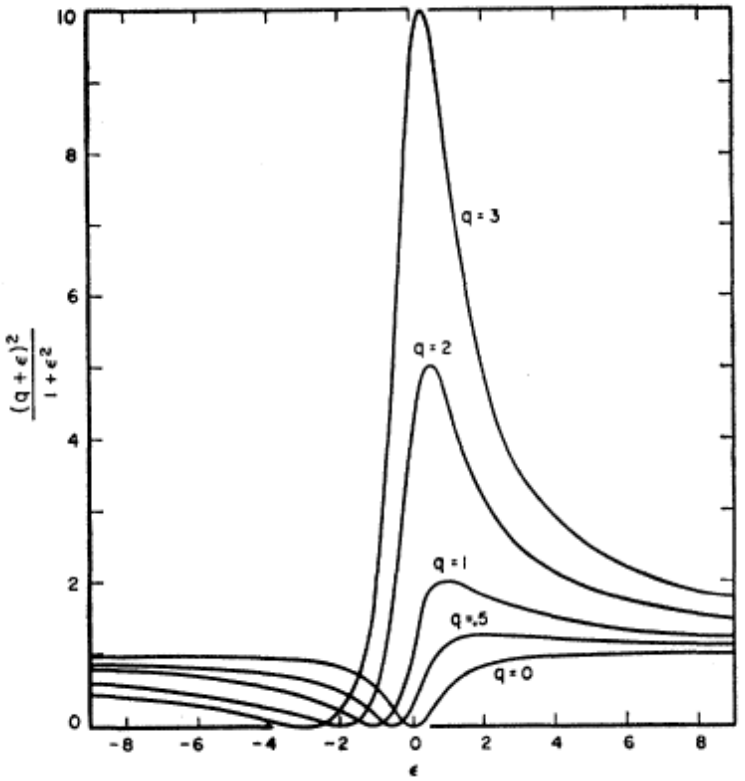


2. Resonant Photoemission – Viviane Stoeberl et al. PRB 102, 155112 (2021)

- Resonant Photoemission:
  - "regular" valence band photoemission:
  - $d^n + \hbar\omega \rightarrow d^{n-1} + e$
  - photon energy within a metal absorption edge:
  - $d^n + \hbar\omega \rightarrow \underline{c}4d^{n+1} \rightarrow d^{n-1} + e$
  - Interference of both channels:
    - (anti)resonance → changes in the relative intensity
    - **"Fano lineshape"**



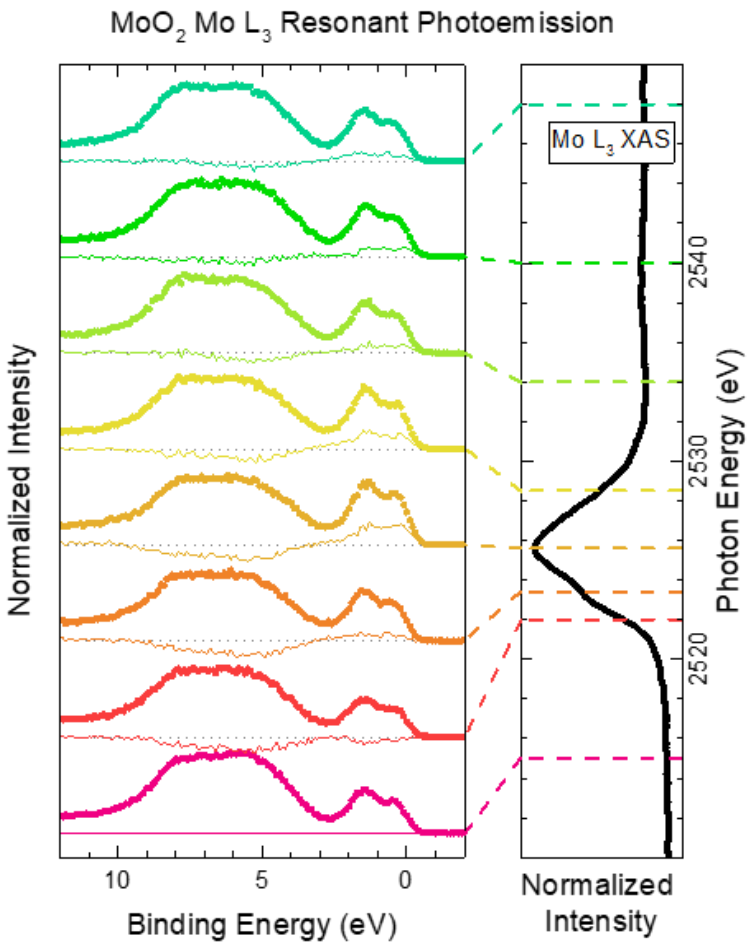
$$\frac{|(\Psi_E|T|i)|^2}{|(\psi_E|T|i)|^2} = \frac{(q+\epsilon)^2}{1+\epsilon^2}$$

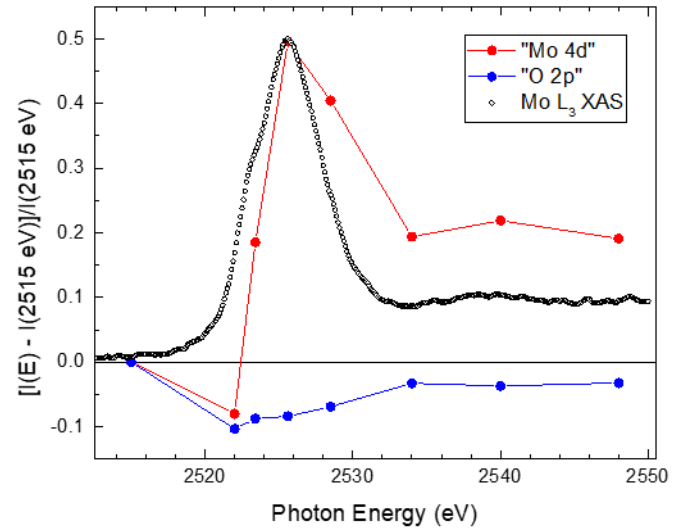


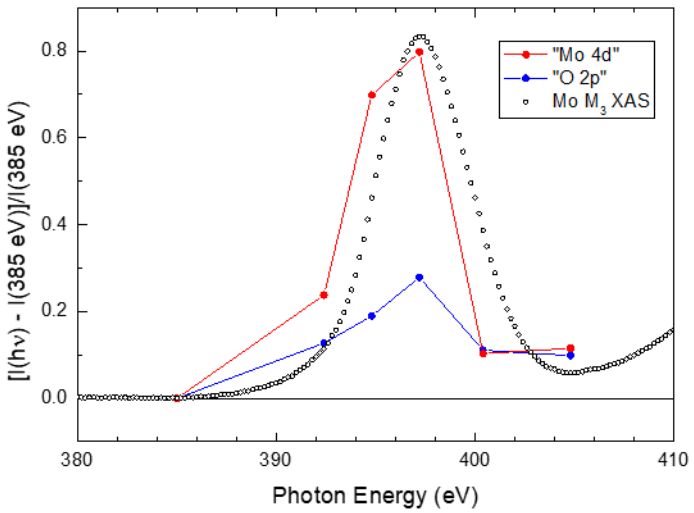
U. Fano, PR **124**, 1866 (1961)

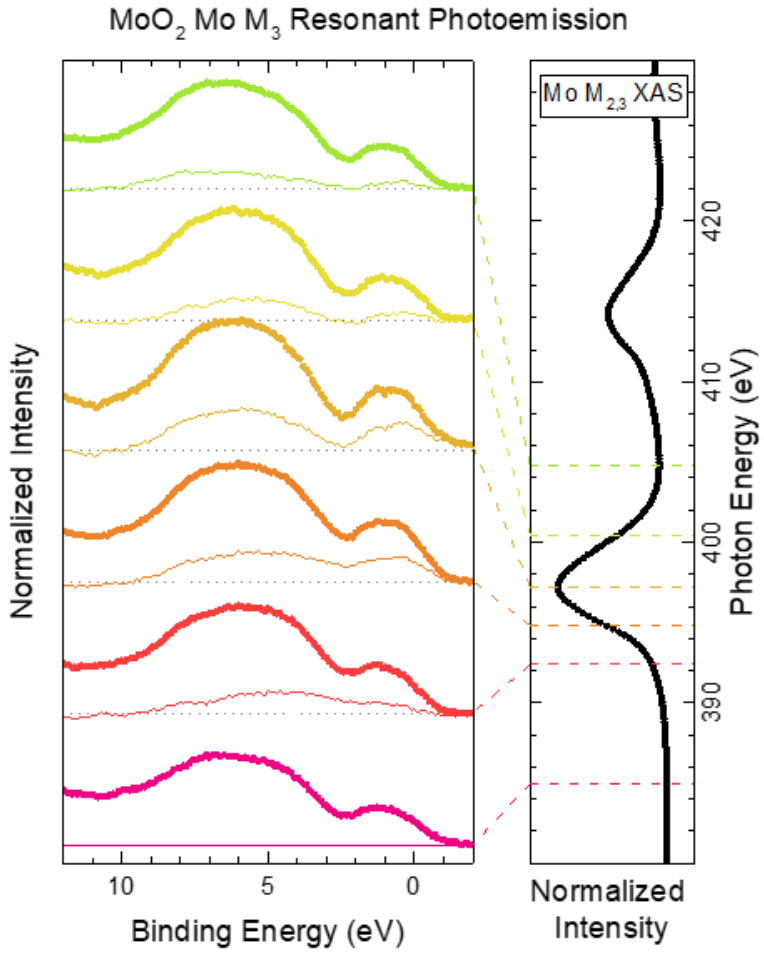
2. Resonant Photoemission – Viviane Stoeberl et al. PRB 102, 155112 (2021)

- MoO_2 L_3 and M_3 RPES:
  - SXS and PGM beamlines @ LNLS, Brazil



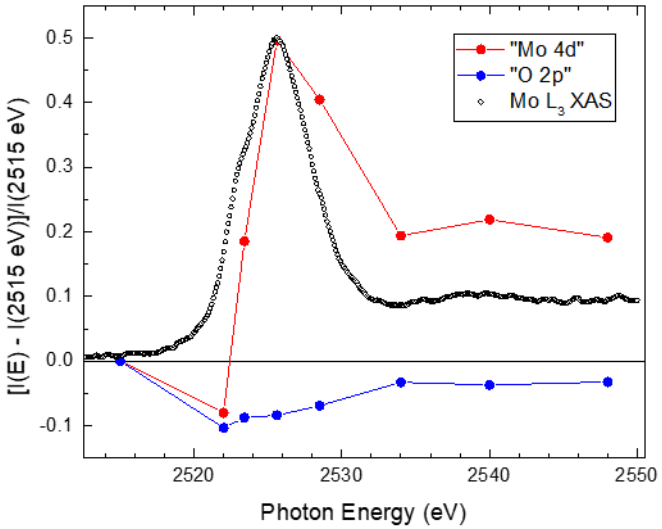




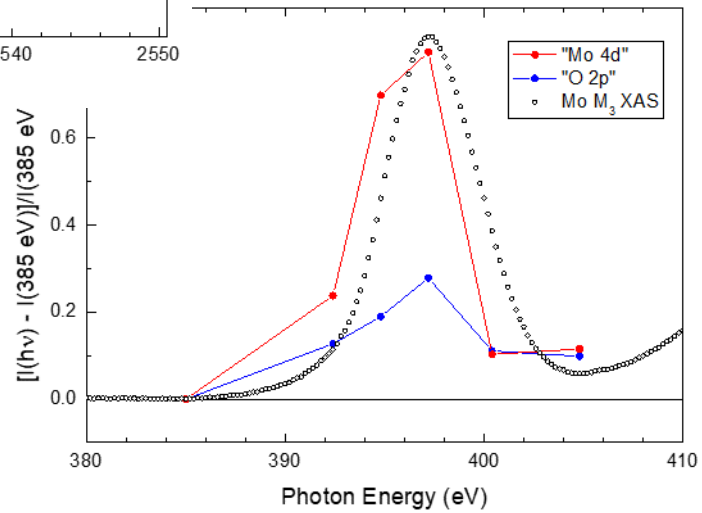


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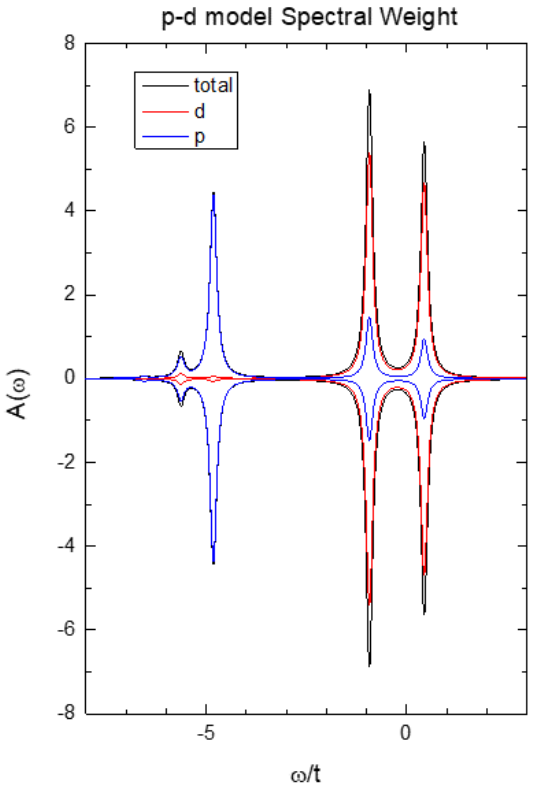
- MoO_2 L_3 and M_3 RPES:
  - SXS and PGM beamlines @ LNLS, Brazil

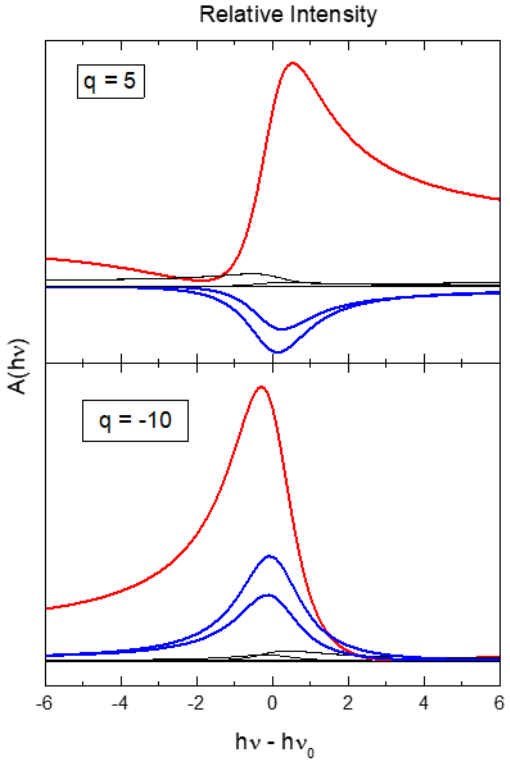


$$\frac{|(\Psi_E|T|i)|^2}{|(\psi_E|T|i)|^2} = \frac{(q+\epsilon)^2}{1+\epsilon^2}$$



- A p-d model which includes q...
  - The resonance depends on the chosen absorption edge (q)
  - **The resonance depends on the character (screening) of the final state!!!**



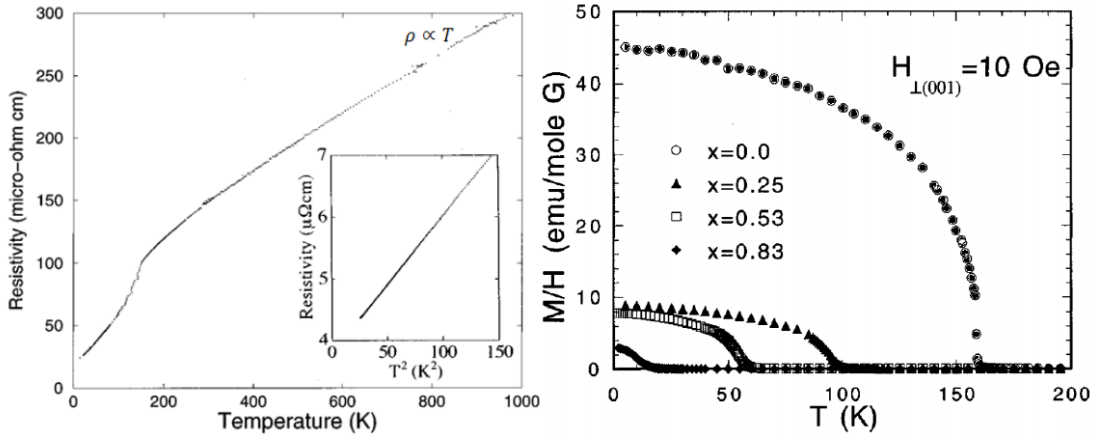


END

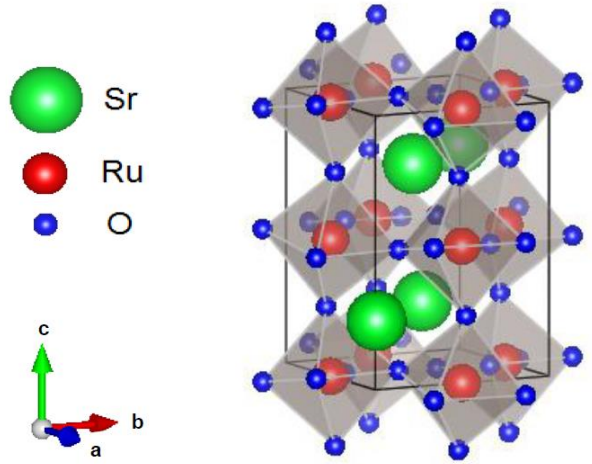
3. $SrRuO_3$ - E.B. Guedes et al., PRB 86, 235127 (2012)

- $SrRuO_3$ – perovskite structure

The complex oxide perovskite $SrRuO_3$ has fascinated researchers for over 40 years. The first property to draw attention was its surprising itinerant ferromagnetism (Randall and Ward, 1959). More recently, interest in $SrRuO_3$ has broadened to include its unusual transport properties and the degree and consequences of correlation. For example, while at low temperatures $SrRuO_3$ is a Fermi liquid (Mackenzie *et al.*, 1998), at high temperatures it exhibits bad metal behavior (Klein, Dodge, Ahn, Snyder *et al.*, 1996). In



G. Koster et al., RMP **84**, 253 (2012)



- what influences the most in the electronic structure/physical properties?
  - electronic correlation?
  - Ru – O covalence?

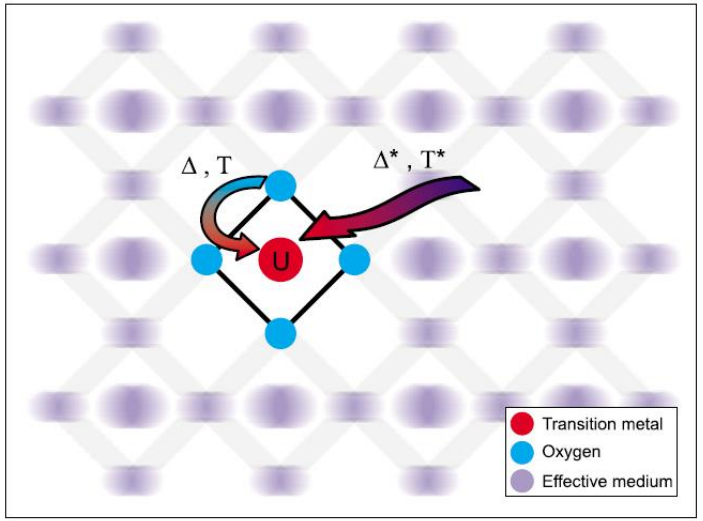
3. $SrRuO_3$ - E.B. Guedes et al., PRB 86, 235127 (2012)

- Experimental: core level and valence band XPS, O1s XAS
  - SXS, SGM beamlines @ LNLS, Brazil.



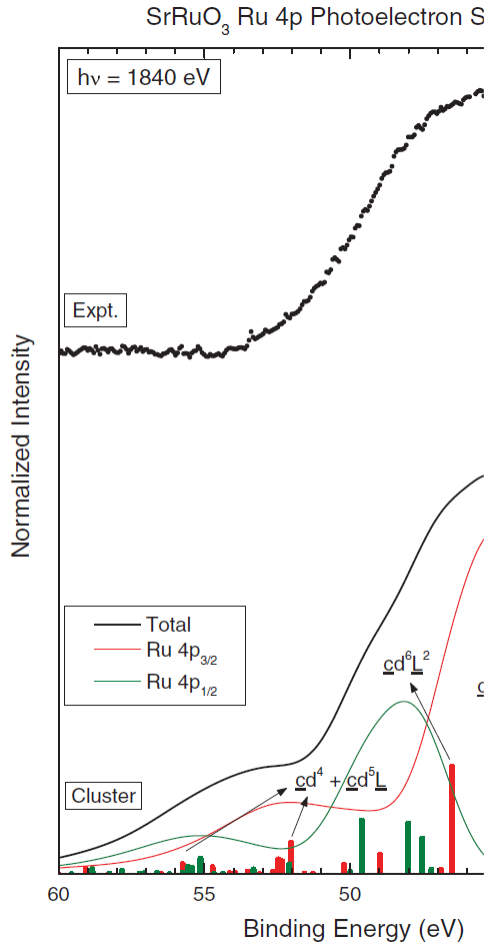
- Theory: extended cluster model.
  - Includes all ingredients to describe the electronic structure.
  - Correlation and charge transfer effects.

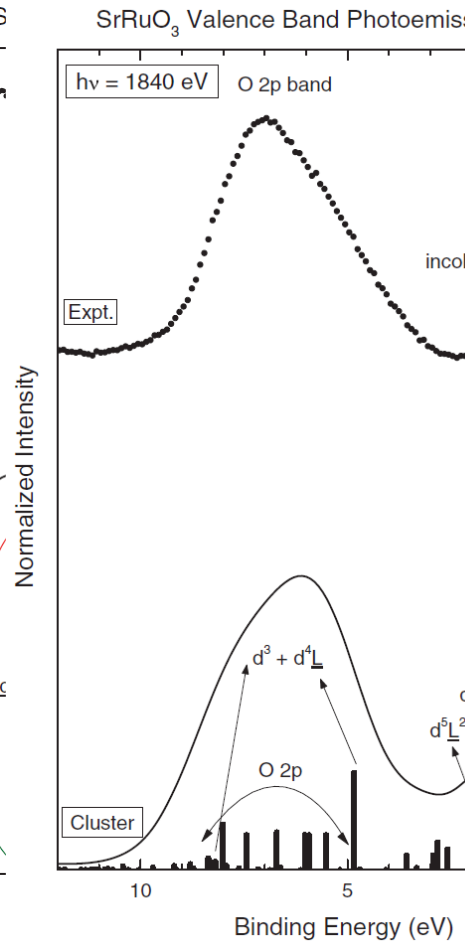
Extended Cluster Model

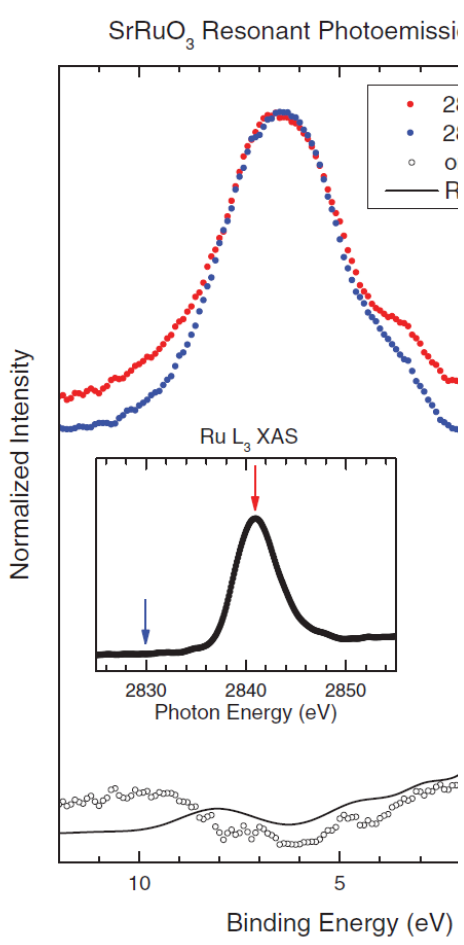


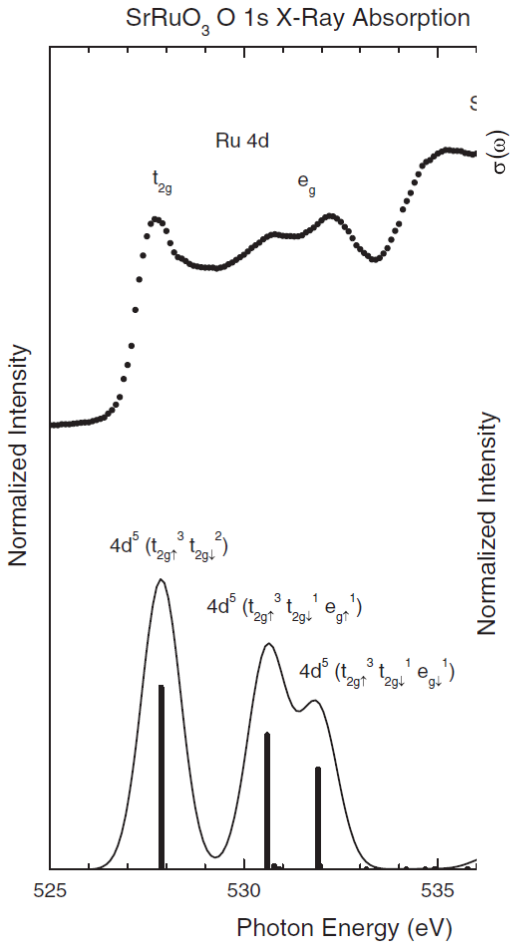
3. $SrRuO_3$ - E.B. Guedes et al., PRB 86, 235127 (2012)

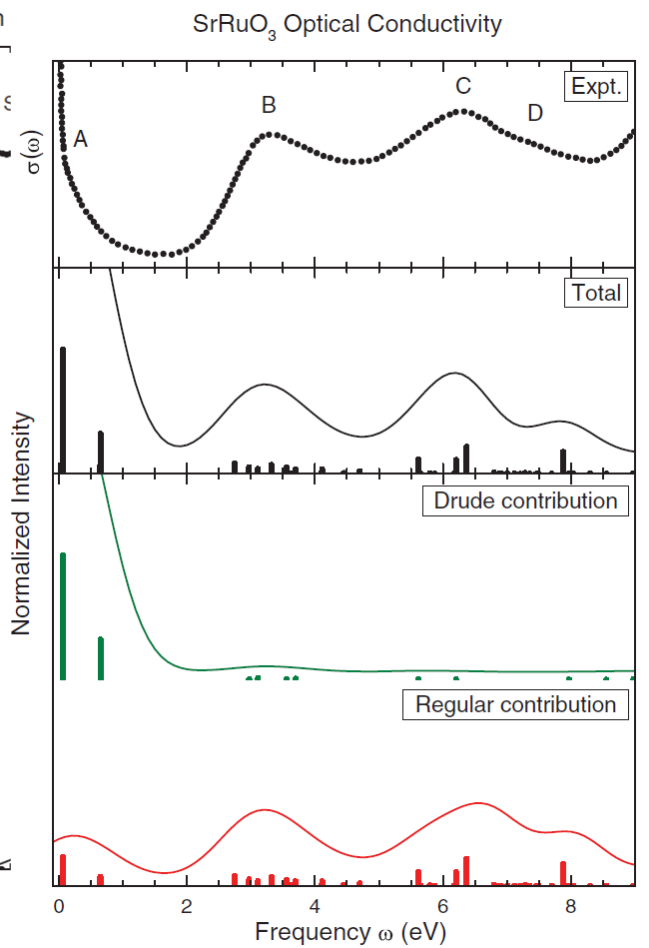
- Results:











3. $SrRuO_3$ - E.B. Guedes et al., PRB 86, 235127 (2012)

- Conclusion:
  - Ground state:

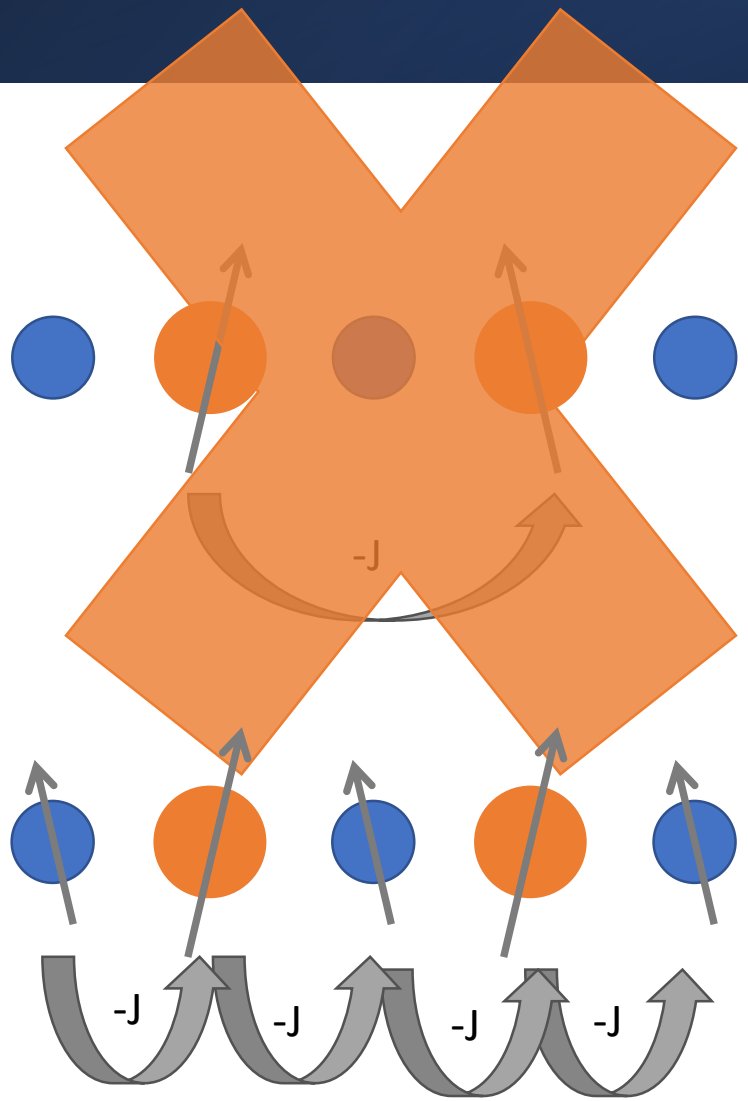
Ru^{4+}: $4d^4$

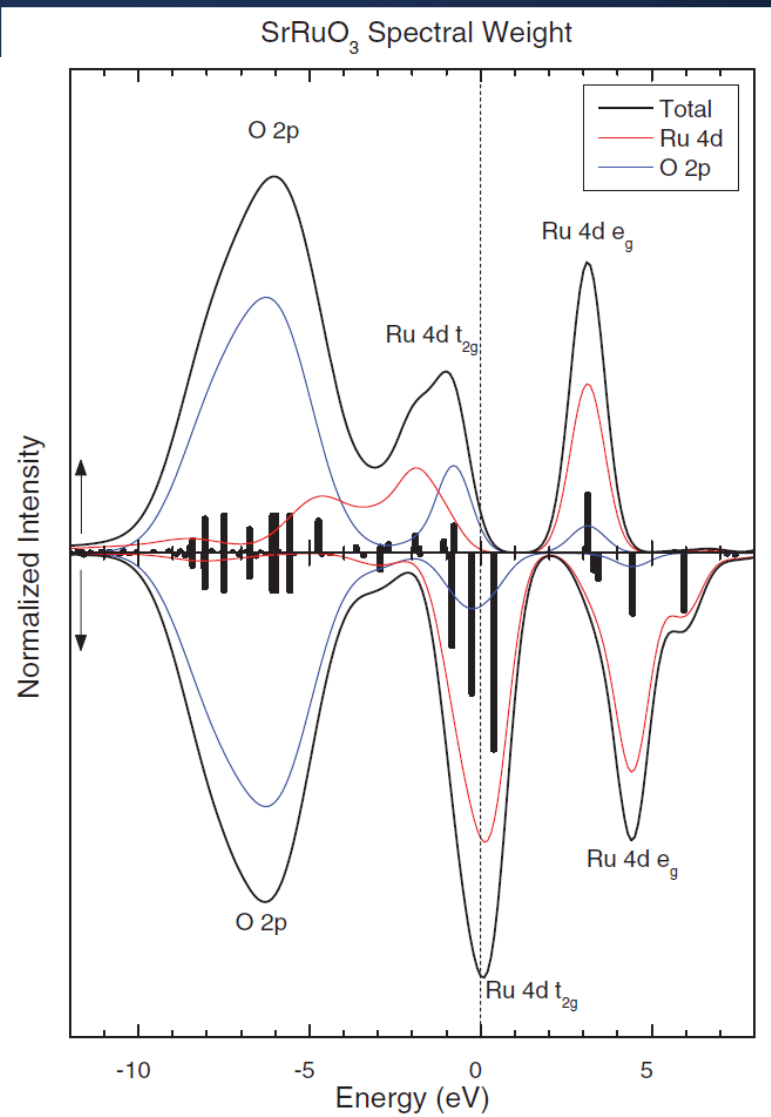
O^{2-}: $2p^6$

  - Ground state:

Ru^{3+}: $4d^5$

O^{1-}: $2p^5$





Conclusions

- Electronic structure: microscopic origin of all physical properties.
- Transition metal compounds – highly correlated systems: rich variety of physical properties.
- X-ray spectroscopy: direct access to the electronic structure.