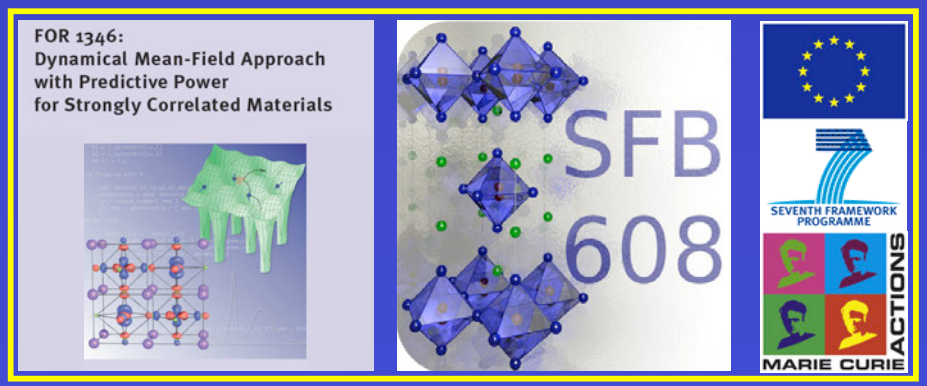
Challenges from experiment

Hao Tjeng

Physics of Correlated Matter

Max-Planck-Institute
Chemical Physics of Solids
Dresden

- Zhiwei Hu, Jonas Weinen, Yi-Ying Chin, Nils Hollmann, Stefano Agrestini – *Dresden*
- Maurits Haverkort – *MPI FKF, Stuttgart*
- Thomas Koethe, Hua Wu, Roger Chang, Tobias Burnus, Christian Zobel, Marco Reuther, Helena Hartmann, Daniel Khomskii, Markus Braden, Thomas Lorenz,– *Cologne*
- Arata Tanaka – *Hiroshima, Japan*
- J. Cezar, N. Brookes – *ESRF, France*
- H.-J. Lin, K.-D. Tsuei, H.-H. Hsieh, C.T. Chen – *NSRRC, Taiwan*



Correlated electron systems:

• how does the spectral weight distribution change as a function of U / W ?

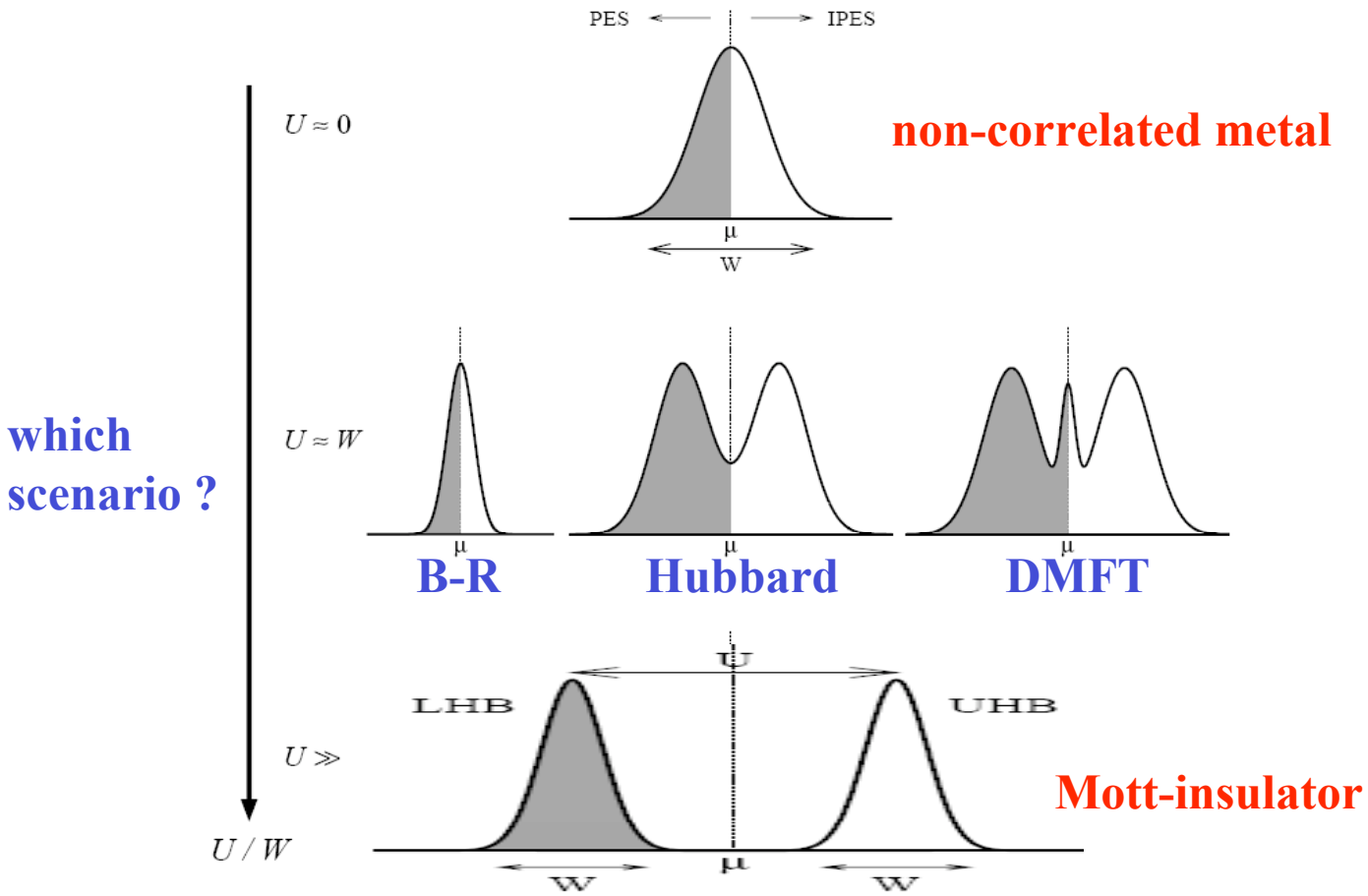


Figure 1.5: Photoemission and inverse photoemission spectra as expected in a Hubbard model for different values of U/W. The grey shading indicates occupied states. Adapted from Morikawa et al. [61]. *Phys. Rev. B 54, 8446 (1996).*

Transition metal oxides: wide range of properties

• d^1:		Ti_2O_3	VO_2	$LaTiO_3$	
• d^2:	TiO	V_2O_3	CrO_2	YVO_3	
• d^3:	VO	Cr_2O_3		$LaCrO_3$	
• d^4:				$LaMnO_3$	Ca_2RuO_4
• d^5:	MnO	Fe_2O_3		$BaCoO_3$	
• d^6:	FeO			$LaCoO_3$	$NaCoO_2$
• d^7:	CoO			$LaNiO_3$	
• d^8:	NiO				La_2NiO_4
• d^9:	CuO				La_2CuO_4

+ doping

- atomic multiplet interactions
- nearest neighbor interactions

→ determine effective U, W

and more !!!

(difficult to make a general scheme – each compound form ist own universe)

I. Importance of atomic multiplet interactions

Example: cobaltates

(a material class with very rich phyiscs)

- Metal-Insulator-Transitions, Colossal-Magneto-Resistance, Thermoelectric power in:

  - layered: $RBaCo_2O_{5+x}$ (R=Eu,Gd)
  - "113": $La_{1-x}A_xCoO_3$ (A=Ca,Sr,Ba)

- Superconductivity: $Na_xCoO_2.yH_2O$
- Unusual magnetic properties: $Ca_3Co_2O_6$ *(Ising/steps)*
- Multiferroicity: Ca_3MnCoO_6 *(Ising)*

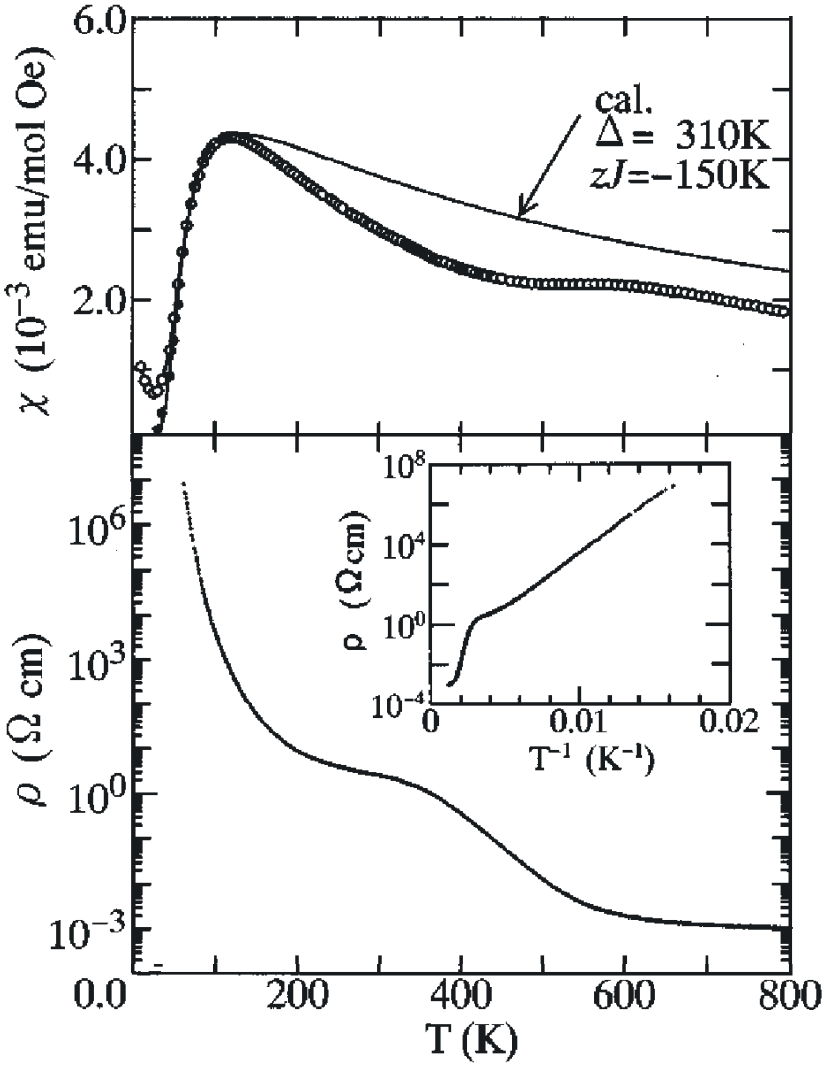
What is special about Co ions ?

- valence state : 2+ 3+ 4+
- spin state: HS HS/IS/LS HS/IS/LS
- spin state transitions and *spin-blockade* mechanism
- local coordination: oct/pyramidal/trig/prismatic-trig
- *spin-orbit interaction*

Confusion in the literature about:

- valence, orbital, and spin state
- all kinds of possible scenarios are proposed from neutron and magnetic susceptibility experiments
- band theories give conflicting results

$LaCoO_3$: a benchmark system Co^{3+}: $3d^6$

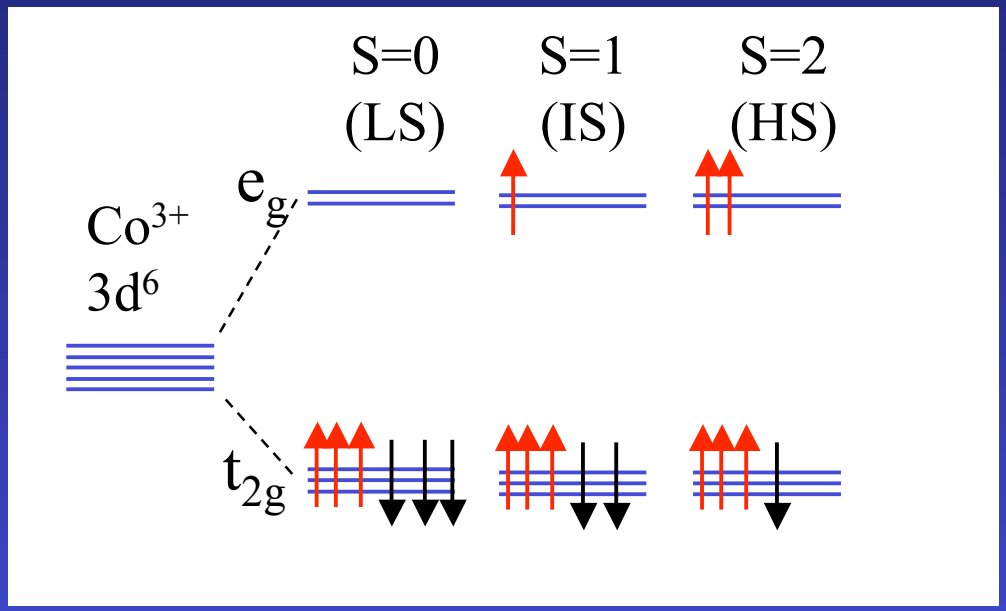


S. Yamaguchi *et al.*, PRB **53**, 2926 (1996)

- non-magnetic insulator at low T
- non-magnetic to paramagnetic transition for T>25K, with max. in magn. susceptibility at 100K
- resistivity drop T = 350K -550K, "metal-insulator transition"

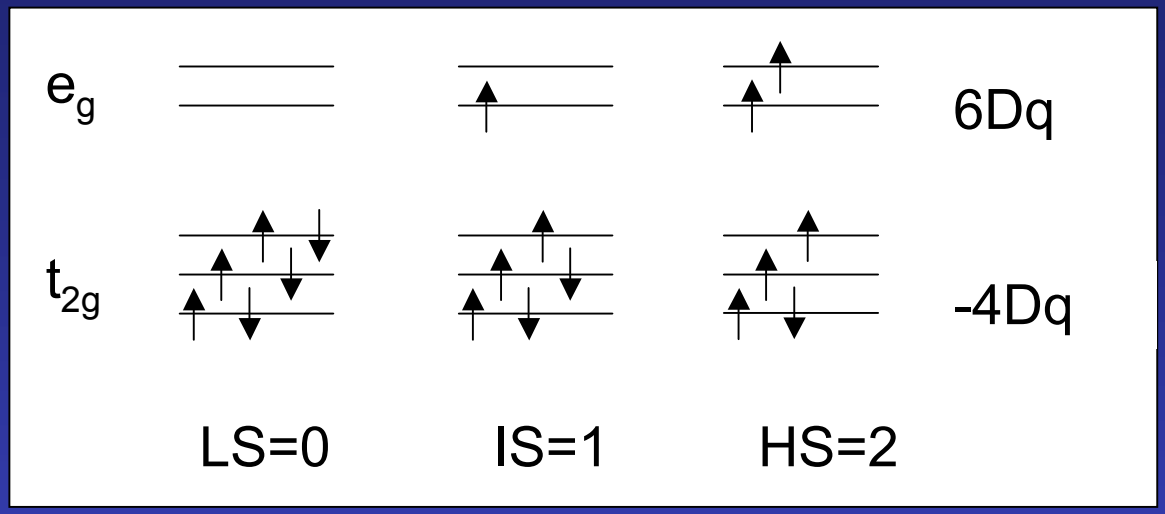
Spin-state transitions ?
Low – Intermediate – High spin ?

Puzzle: what is the spin state of Co^{3+} ??



competition:
crystal field - band formation - Hund‘s exchange

Energetics of $3d^6$ spin states: ionic picture



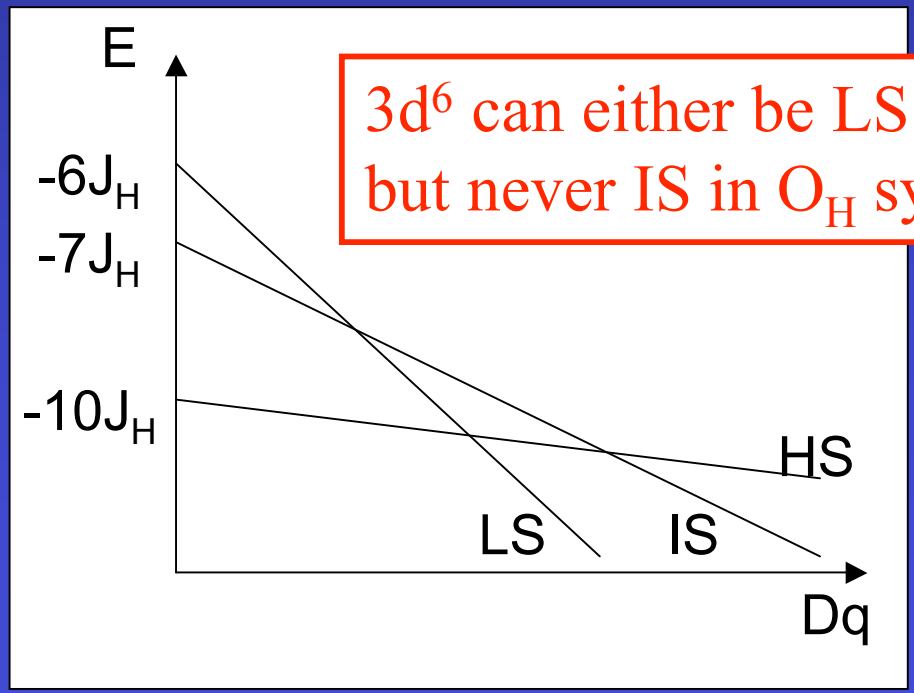
Simplest scheme:

E_{LS}= -24Dq - $6J_H$

E_{IS}= -14Dq - $7J_H$

E_{HS}= -4Dq - $10J_H$

LS-HS crossing occurs at 10Dq = 2 J_H ≈1.6 eV



$3d^6$ can either be LS or HS but never IS in O_H symmetry

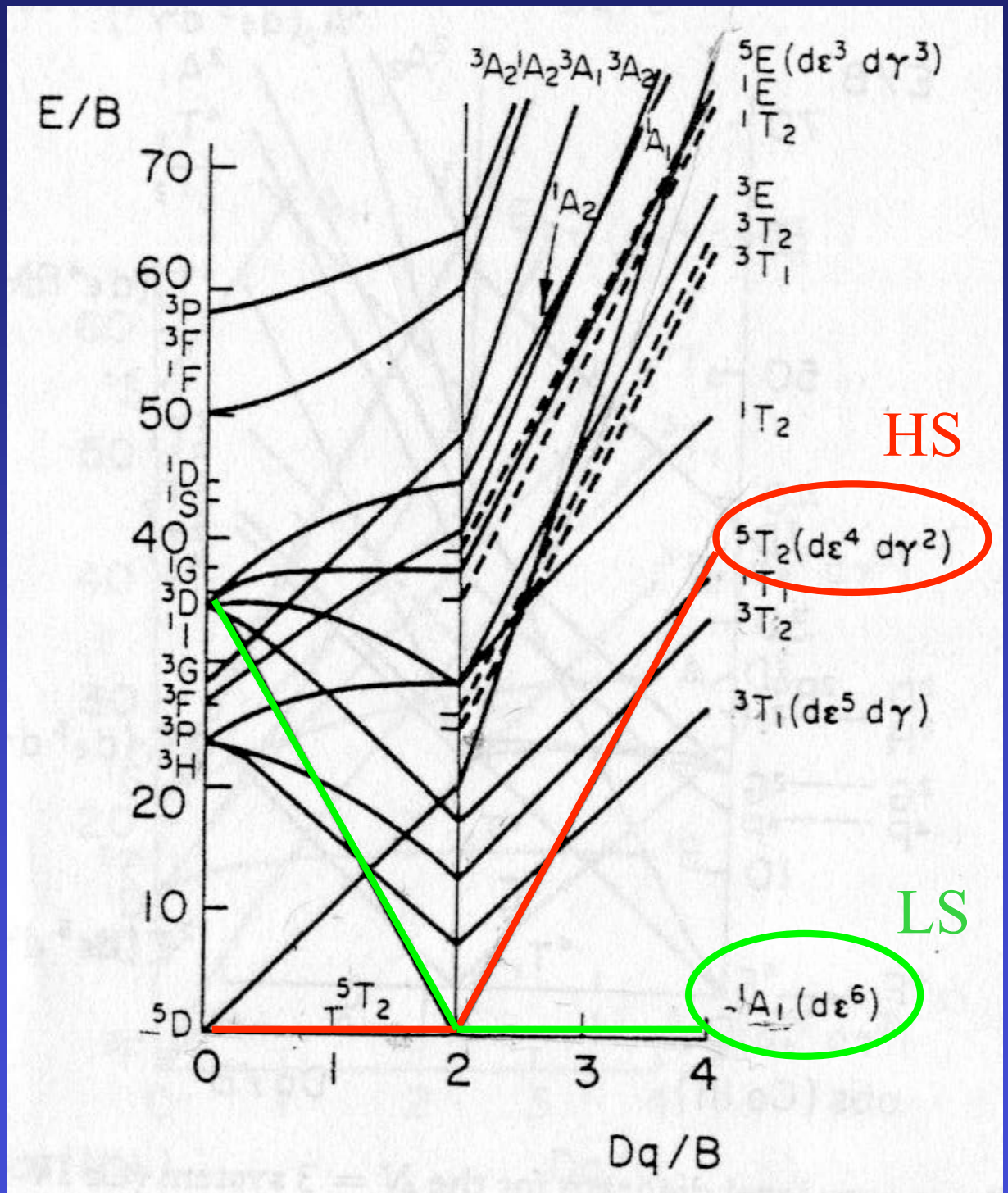
Energetics of $3d^6$ spin states: an ionic picture

full atomic multiplet theory

Sugano, Tanabe, Kamimura - 1970

$3d^6$ can either be LS or HS but never IS in O_H

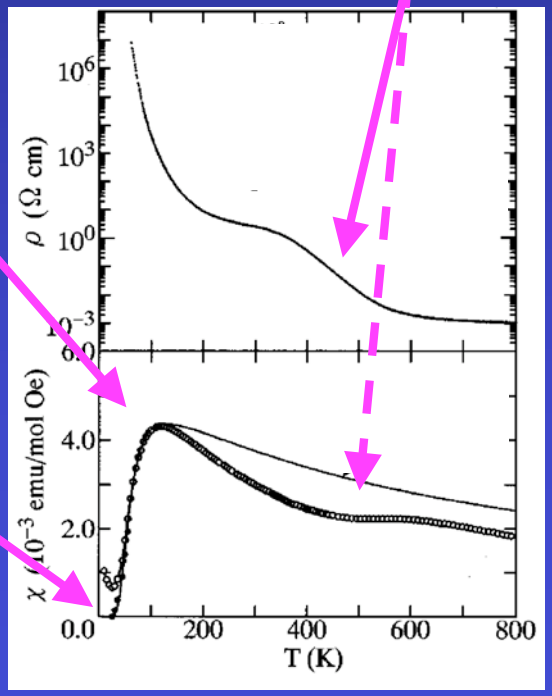
LS-HS crossing at 10Dq=20B≈2.2eV



Classic model: LS-HS scenario

J.B. Goodenough *et al.* (1960s) proposed:

- LS ground state non-magnetic at T = 0K
- increasing paramagnetism through thermal population of HS, $E_{HS} - E_{LS} \leq 80$meV
- reduced resistivity through ordering of LS-HS Co-sites at higher temperatures



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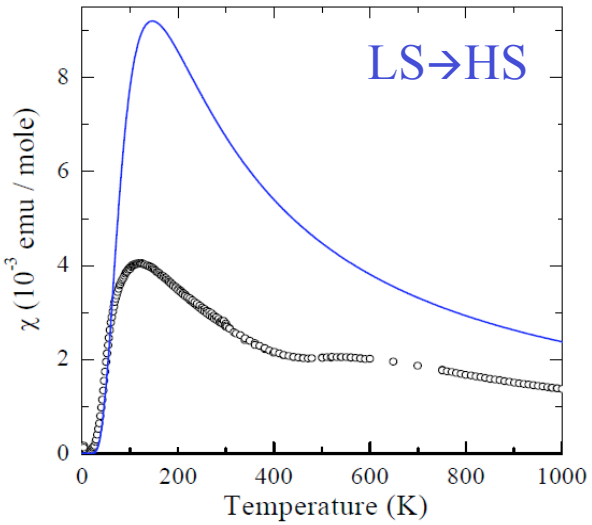
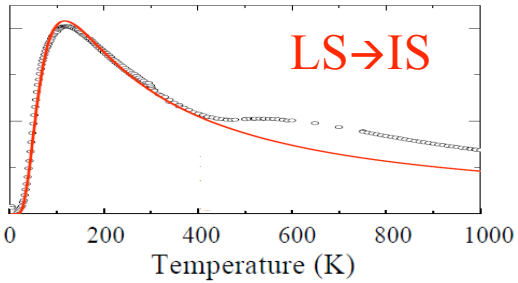
- reduced resistivity through ordering of LS-HS Co-sites at higher temperatures

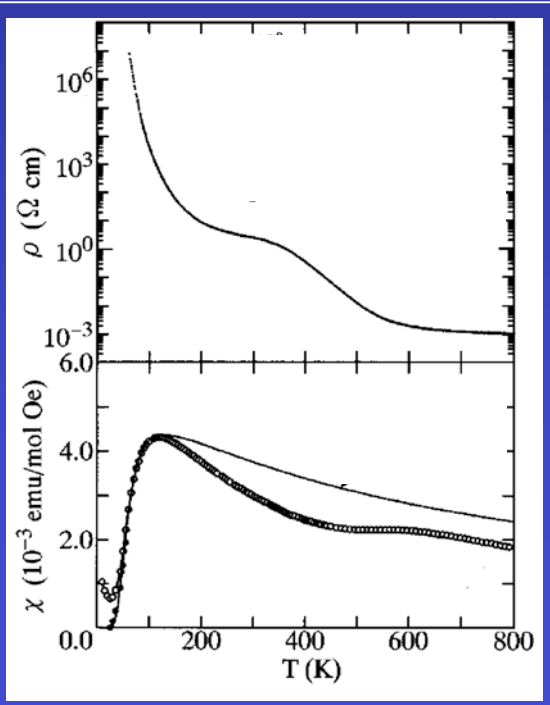
T. Lorenz

But LS→HS does not fit quantitatively !!!



LS→IS better ???



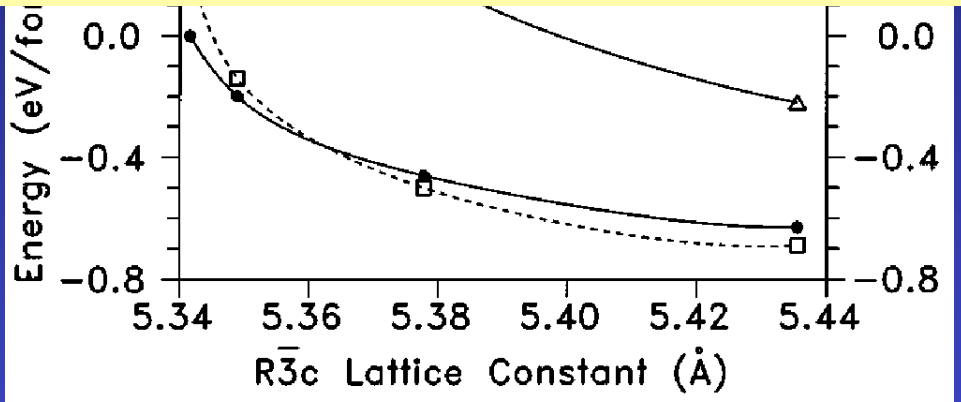


Modern model: LS-IS scenario

Remark:
LDA+U cannot implement full-multiplet effects $U_{ijkl}\mathbf{d}^\dagger_i\mathbf{d}_j\mathbf{d}^\dagger_k\mathbf{d}_l$
LDA+U is a single Slater determinant approach: $U_{ij}\ \mathbf{d}^\dagger_i\mathbf{d}_i\mathbf{d}^\dagger_j\mathbf{d}_j$
→ incorrect energies for especially IS !!

Kor
Saw

- **ba**
- **spin state transition from LS to *orbitally ordered* IS at 150K**
- **metallic *disordered* IS at higher temperatures**



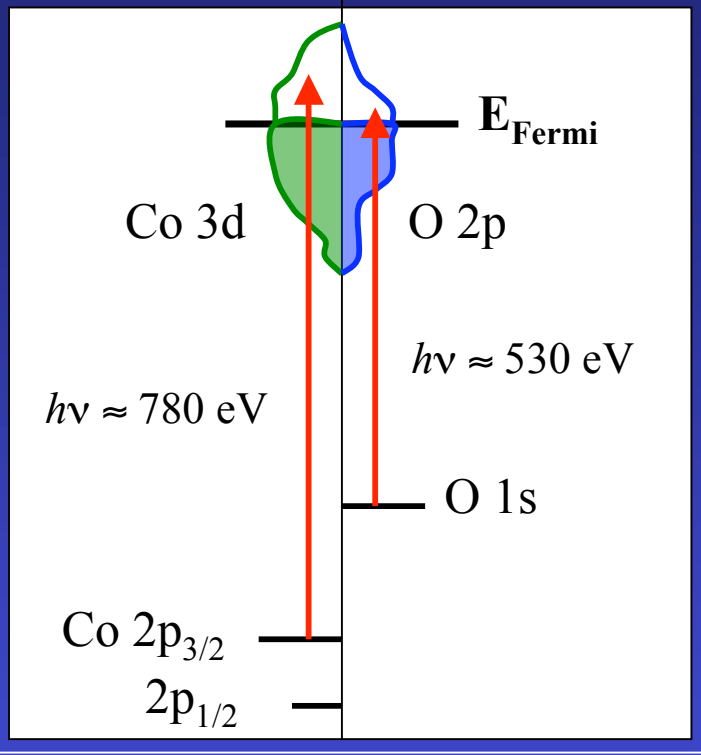
LDA + U: PRB **54**, 5309 (1996)

Remark: results may strongly depend on details of calculations, e.g.
- assumed magnetic ordering
- value of Hubbard U parameter
- coexistence of spin states not considered
- incomplete implementation of multiplet effects

How to determine spin state of Co ions:

Soft-X-Ray Absorption and Magnetic Circular Dichroism

(spectroscopically-resolved magnetic susceptibility measurement)



- use of core levels → local transitions → element and site specific
- involves most relevant orbitals: *2p-3d (TM), 3d-4f (RE), 1s-2p (O,N,C)*
- dipole allowed → very strong intensities
- dipole selection rules + multiplet structure give extreme sensitivity to symmetry of initial state: charge, spin and orbital

Spectrum $(h\nu) = \Sigma_f |\langle i | e.r | f \rangle|^2 \, \delta(h\nu - E_f + E_i)$

$|i\rangle$ = initial state, $|f\rangle$ = final state

e.r = dipole transition.

If experimental spectrum is simulated correctly, then also initial state and final states are known.

theory:

TM 2p-3d: Cluster calculations with full atomic multiplet theory

O 1s-2p : LDA+U calculations

Technique developed in late 1980‘s:

- Fink, Sawatzky, Fuggle
- Thole, van der Laan
- Chen, Sette

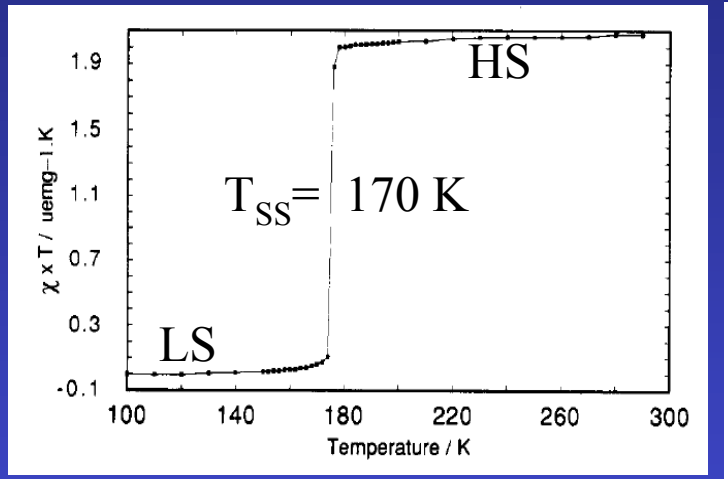
6196 *J. Phys. Chem.* **1992**, *96*, 6196–6198

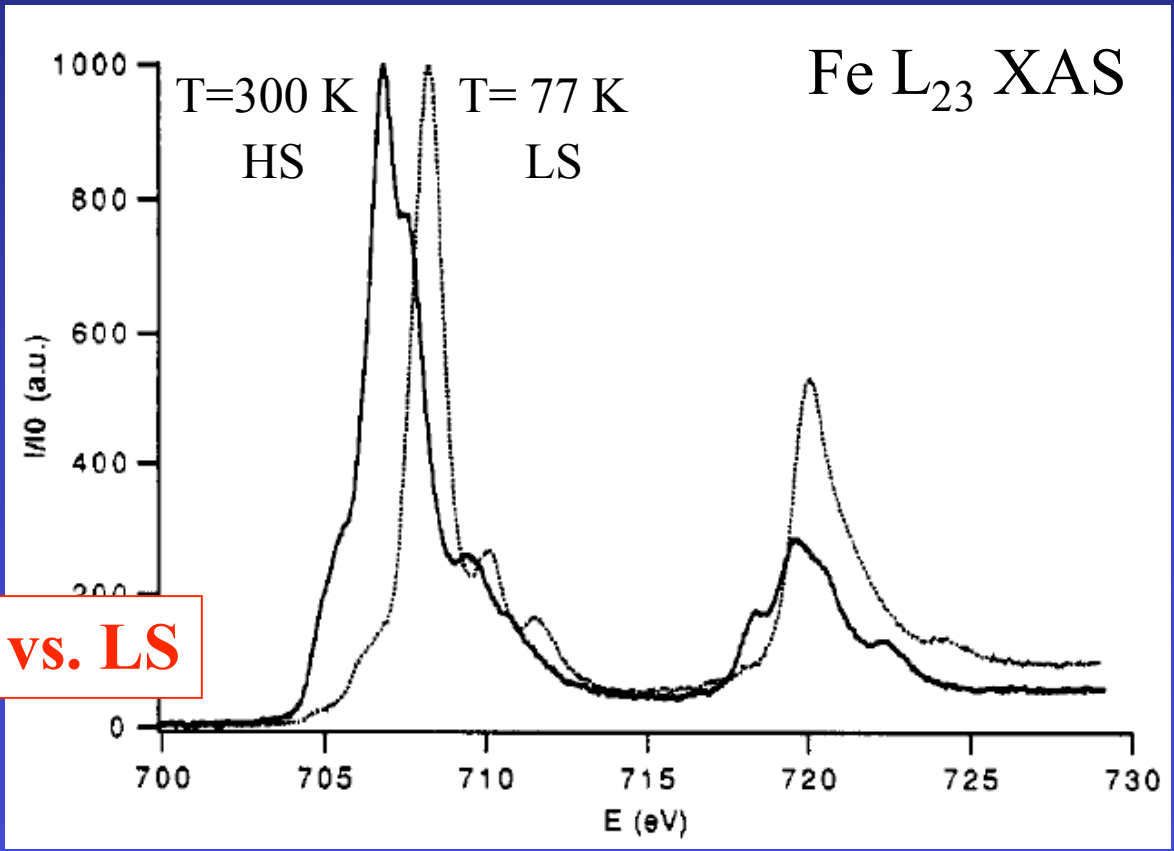
Spin Transition Evidenced by Soft X-ray Absorption Spectroscopy

Christophe Cartier dit Moulin,*,† Petra Rudolf,‡,§ Anne-Marie Flank,† and Chien-Te Chen‡

LURE, Bâtiment 209d, F-91405 Orsay, France, and AT&T Bell Laboratories, Murray Hill, New Jersey 079074 *(Received: January 14, 1992; In Final Form: March 31, 1992)*

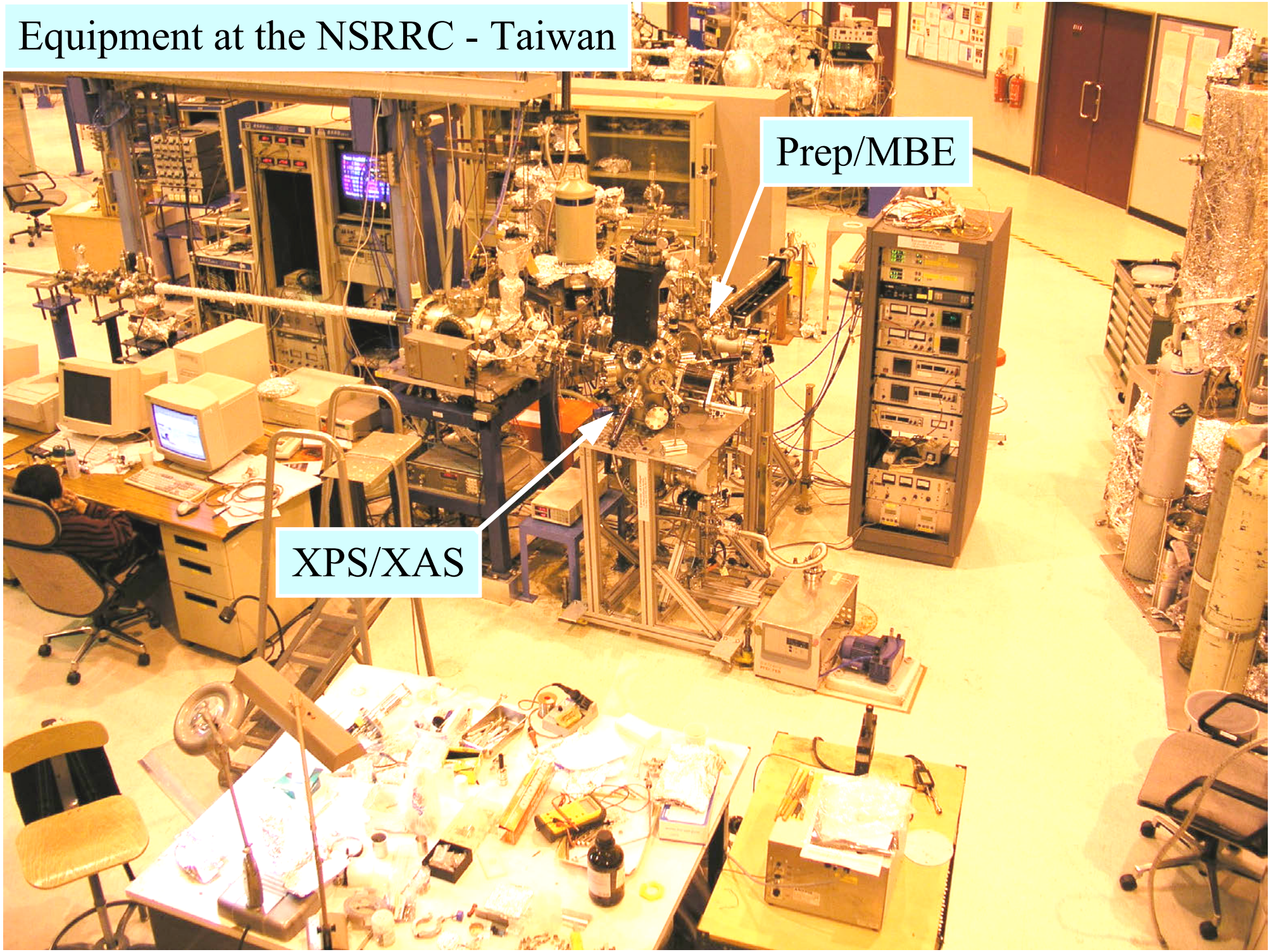
$Fe^{II}(phen)_2(NCS)_2$ Fe $3d^6$



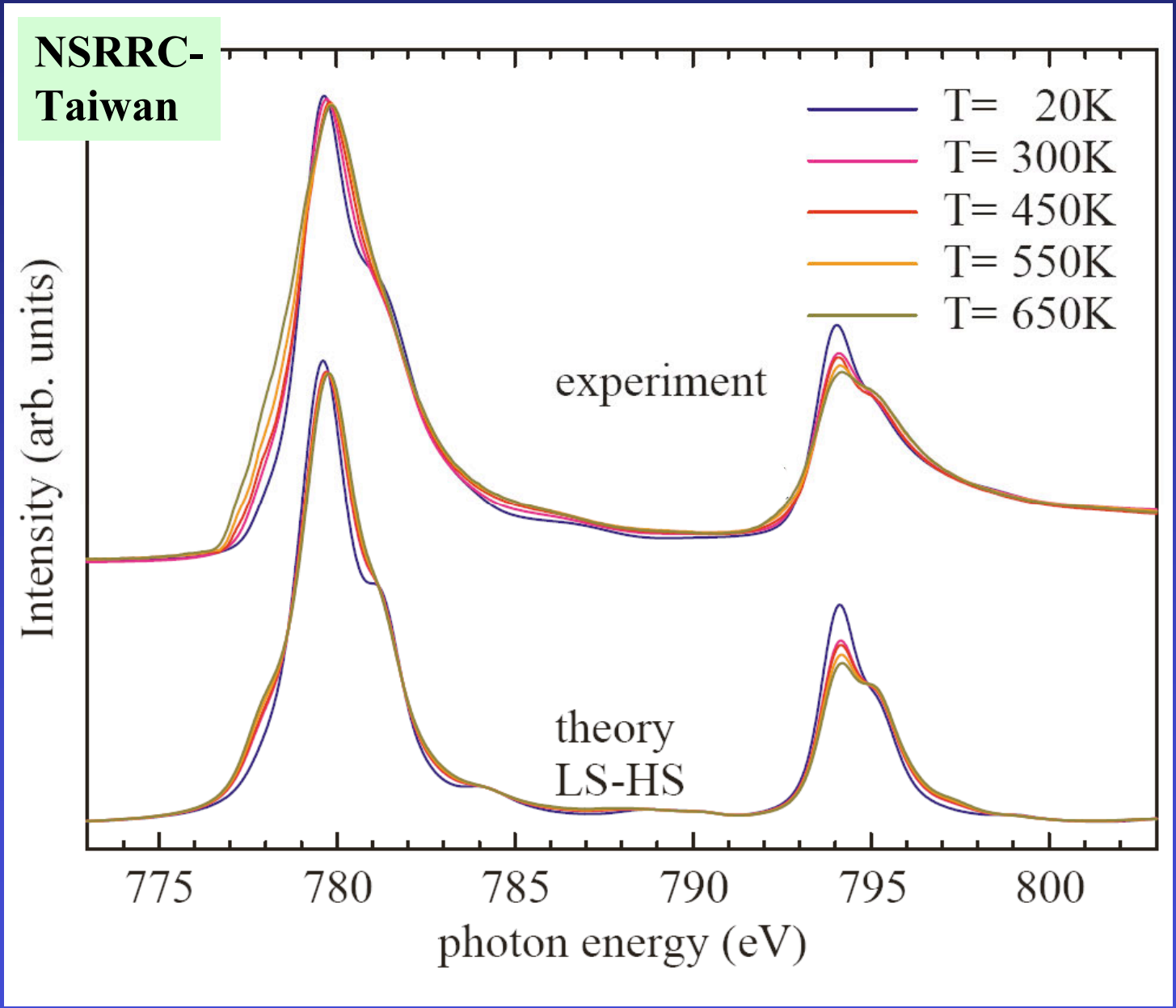


XAS: sensitive to HS vs. LS

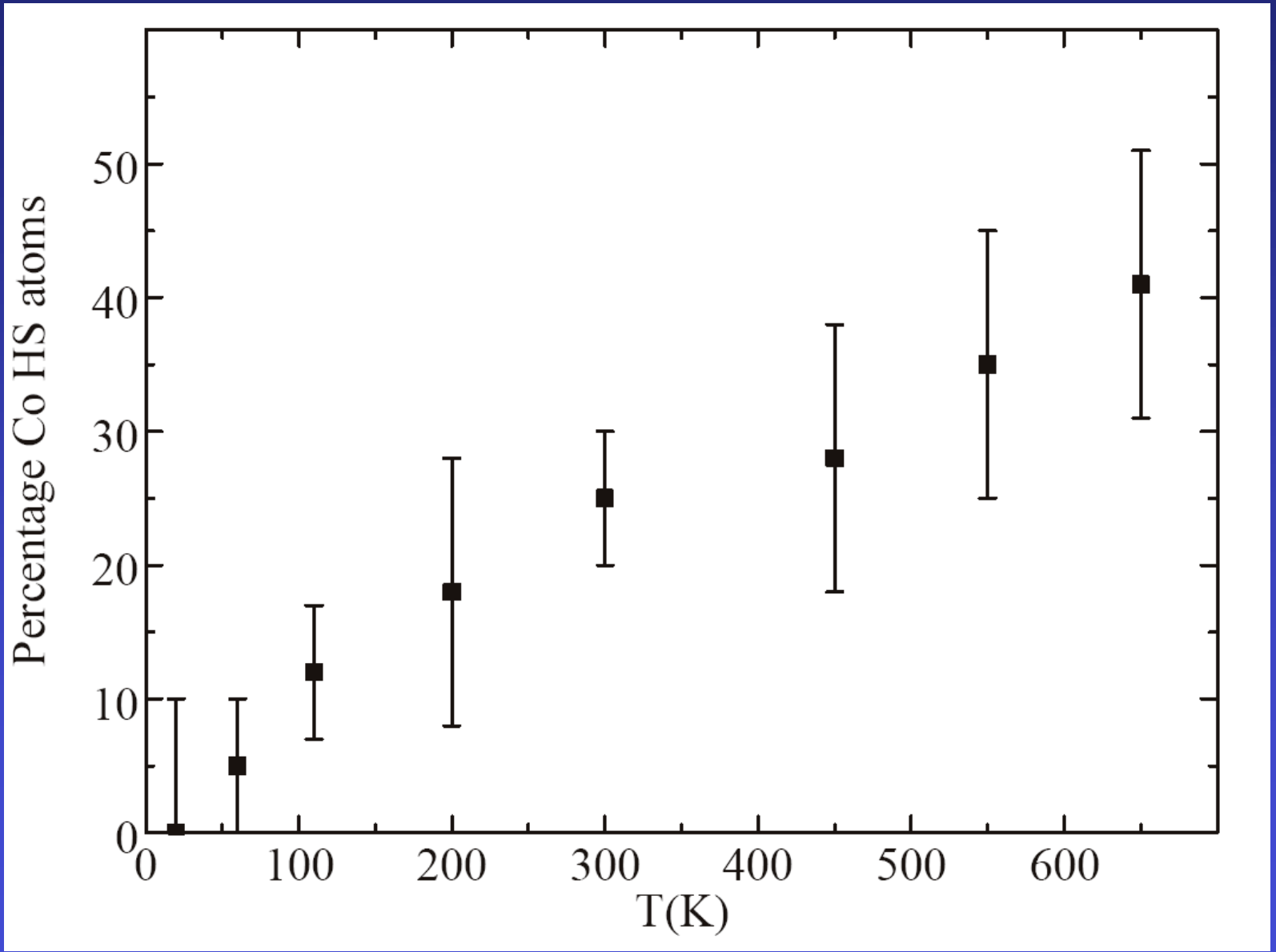
Equipment at the NSRRC - Taiwan



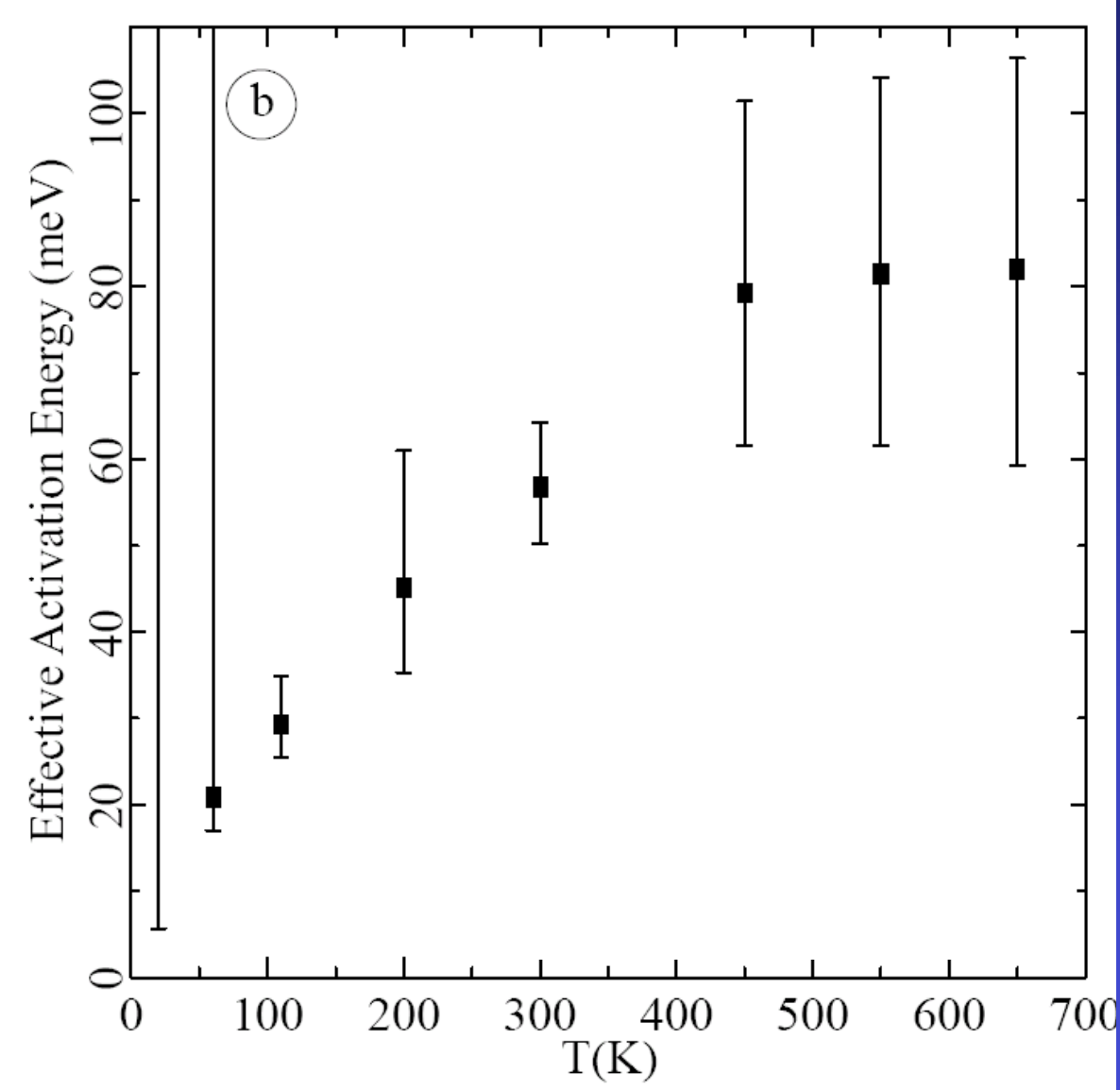
XAS study on the spin state of Co^{3+} ion in $LaCoO_3$



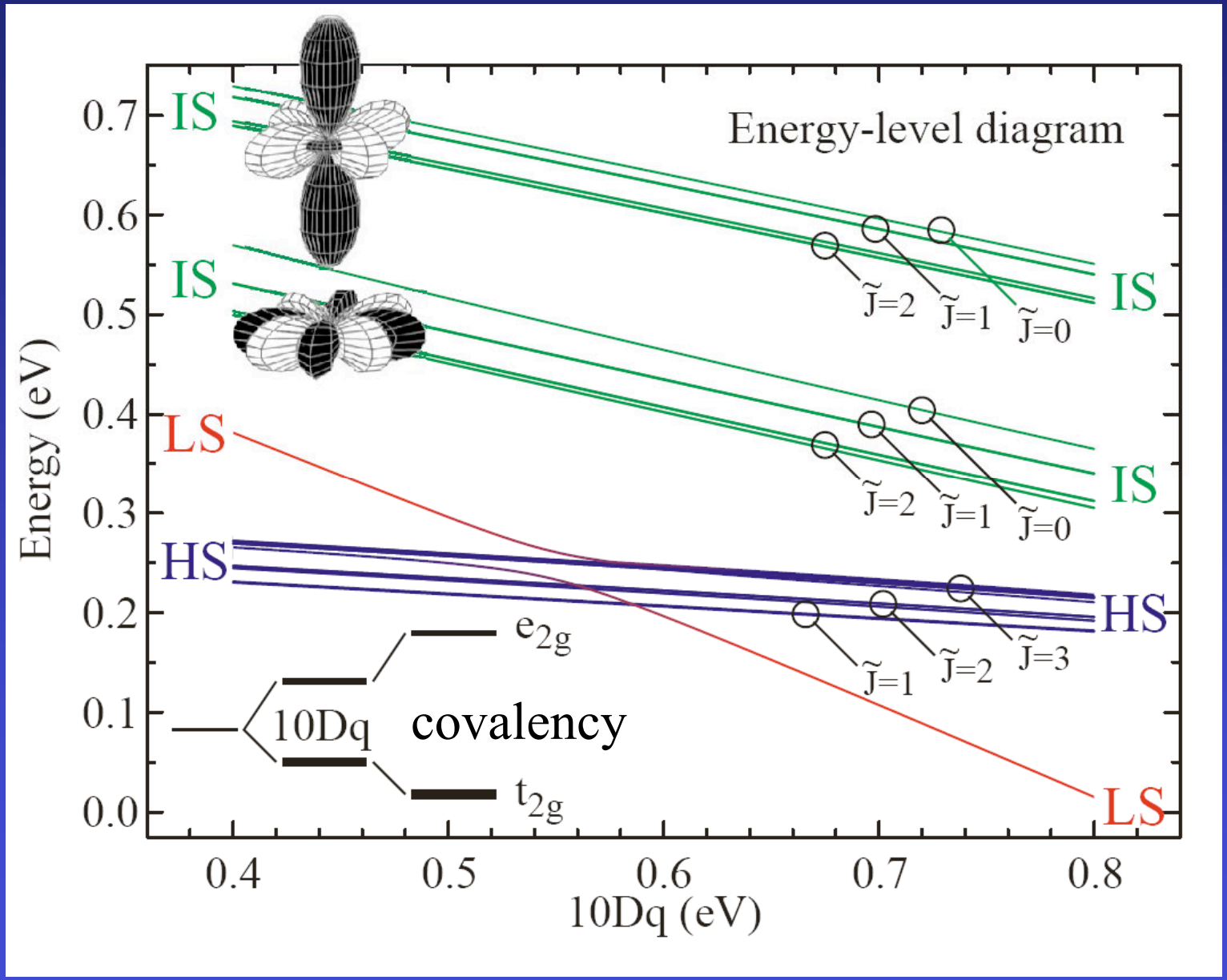
$LaCoO_3$: occupation of HS in the LS-HS scenario



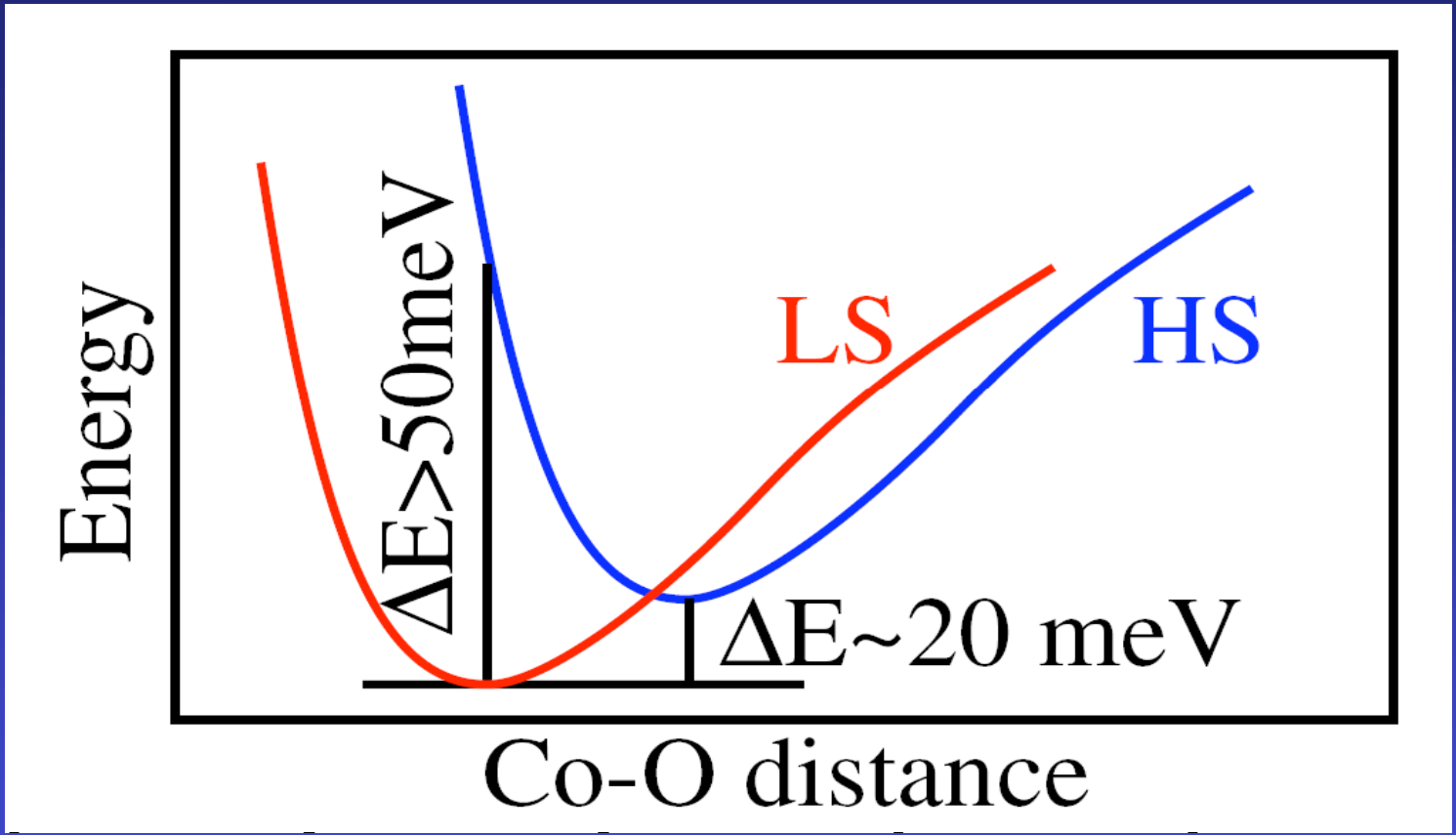
Effective activation energy: temperature dependent !



Energy level diagram: CoO_6 cluster incl. covalency



Spin state transition: local lattice relaxation

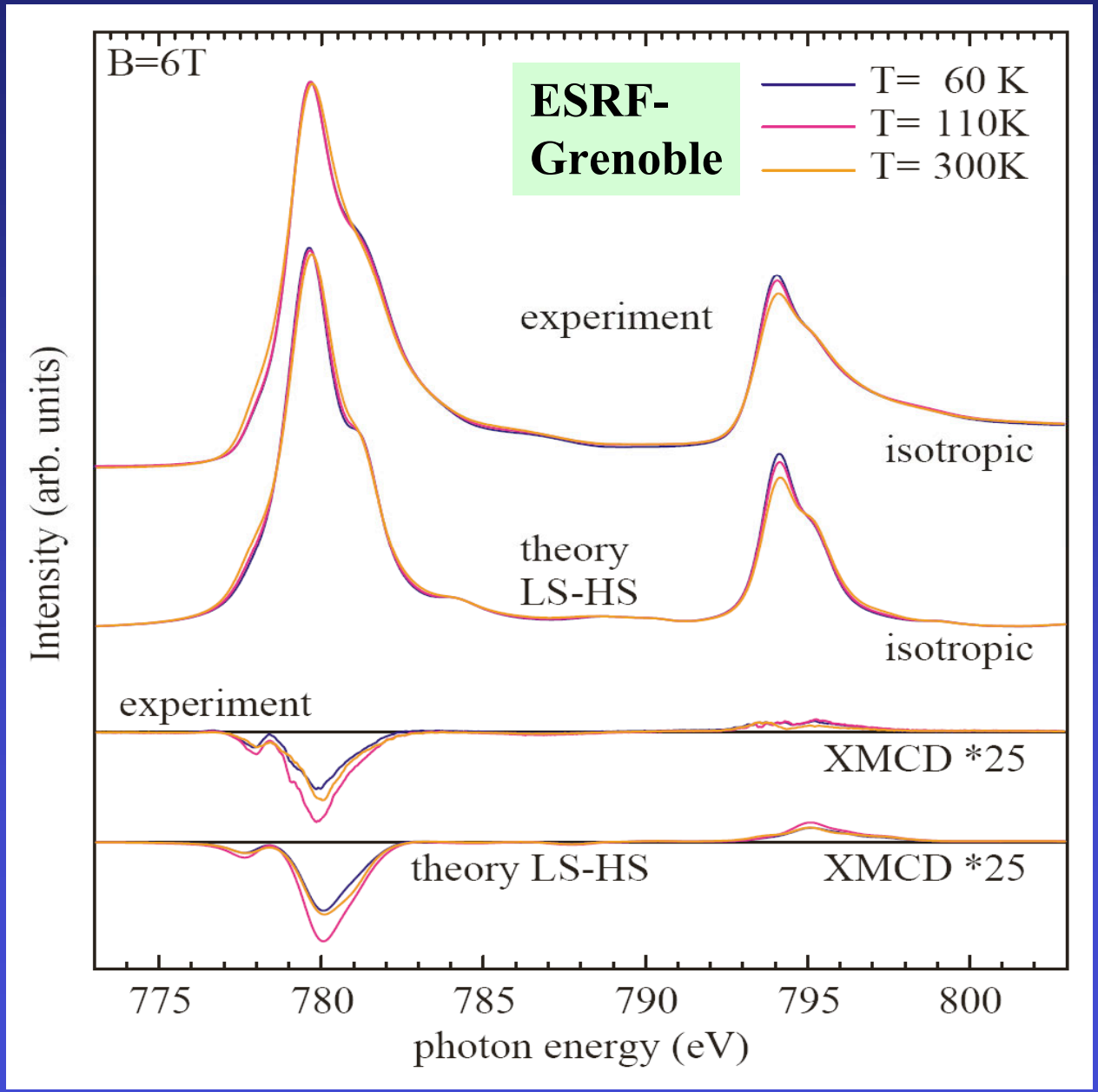


- frozen lattice: $\Delta E >> k_B T$

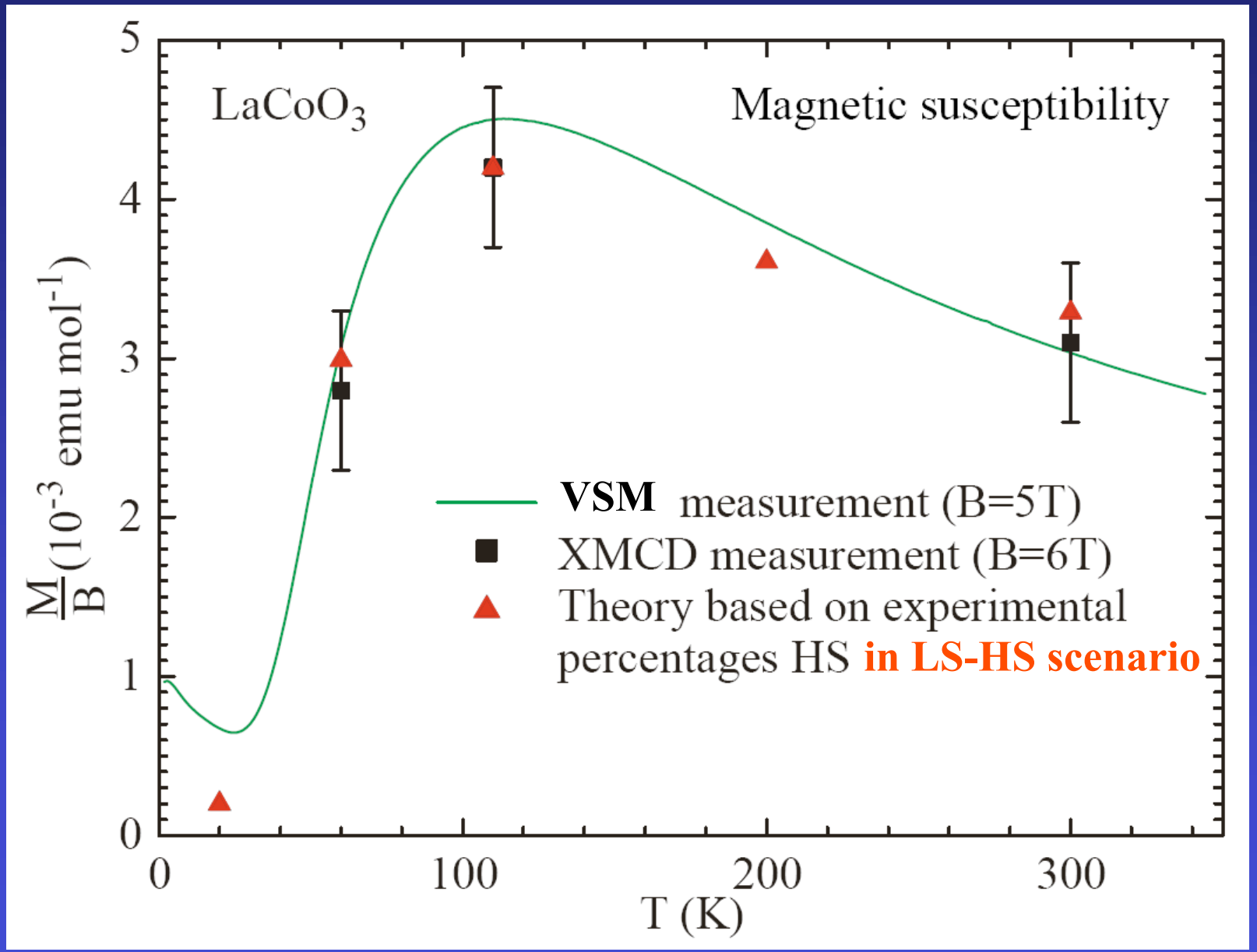
  otherwise too much Van Vleck and incorrect XAS spectra

- inhomogeneous mixed spin-state system

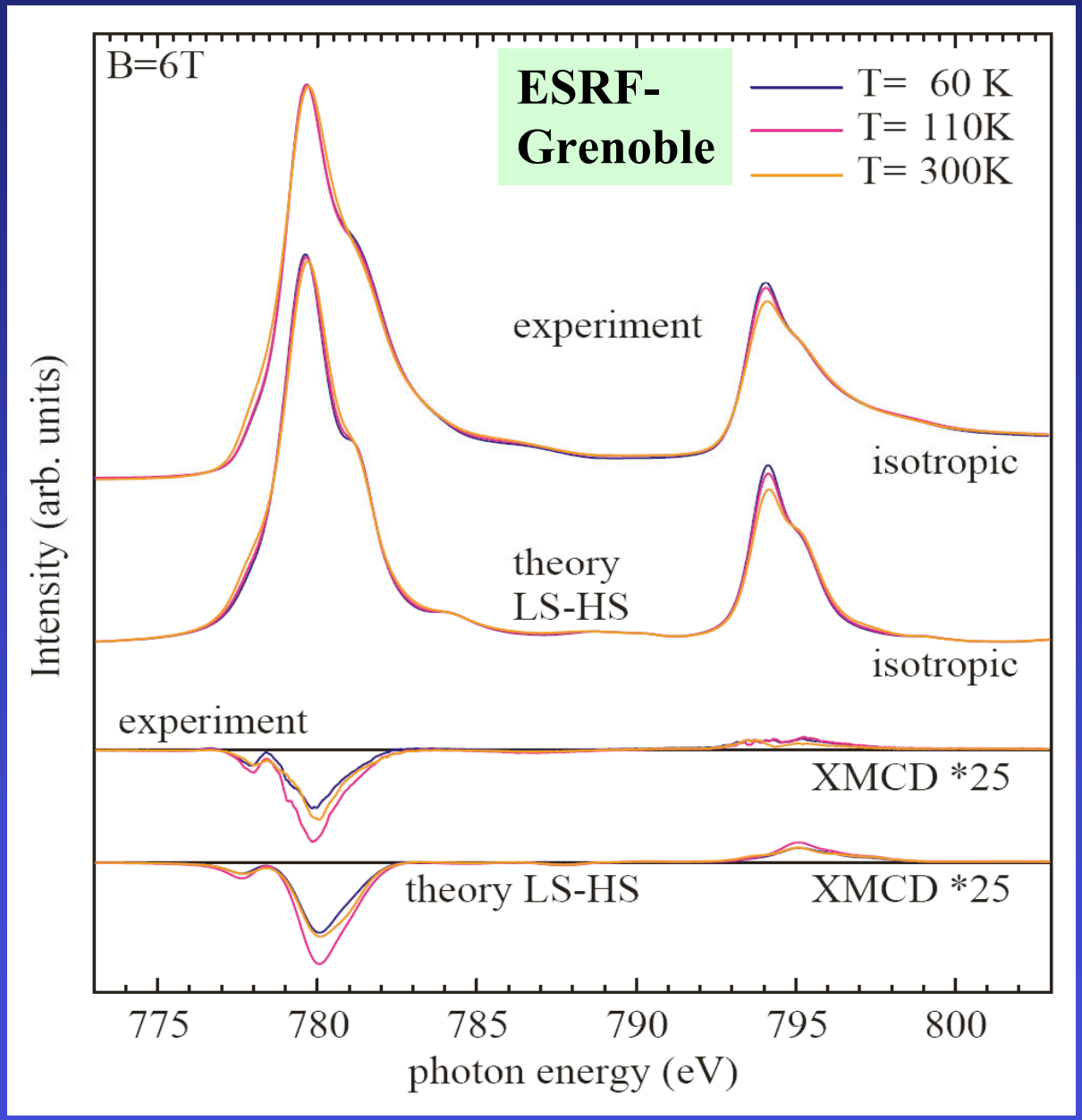
Magnetic Circular Dichroism: *paramagnetic* $LaCoO_3$



Magnetic susceptibility – MCD - XAS



Can we rule out the LS-IS scenario ?!

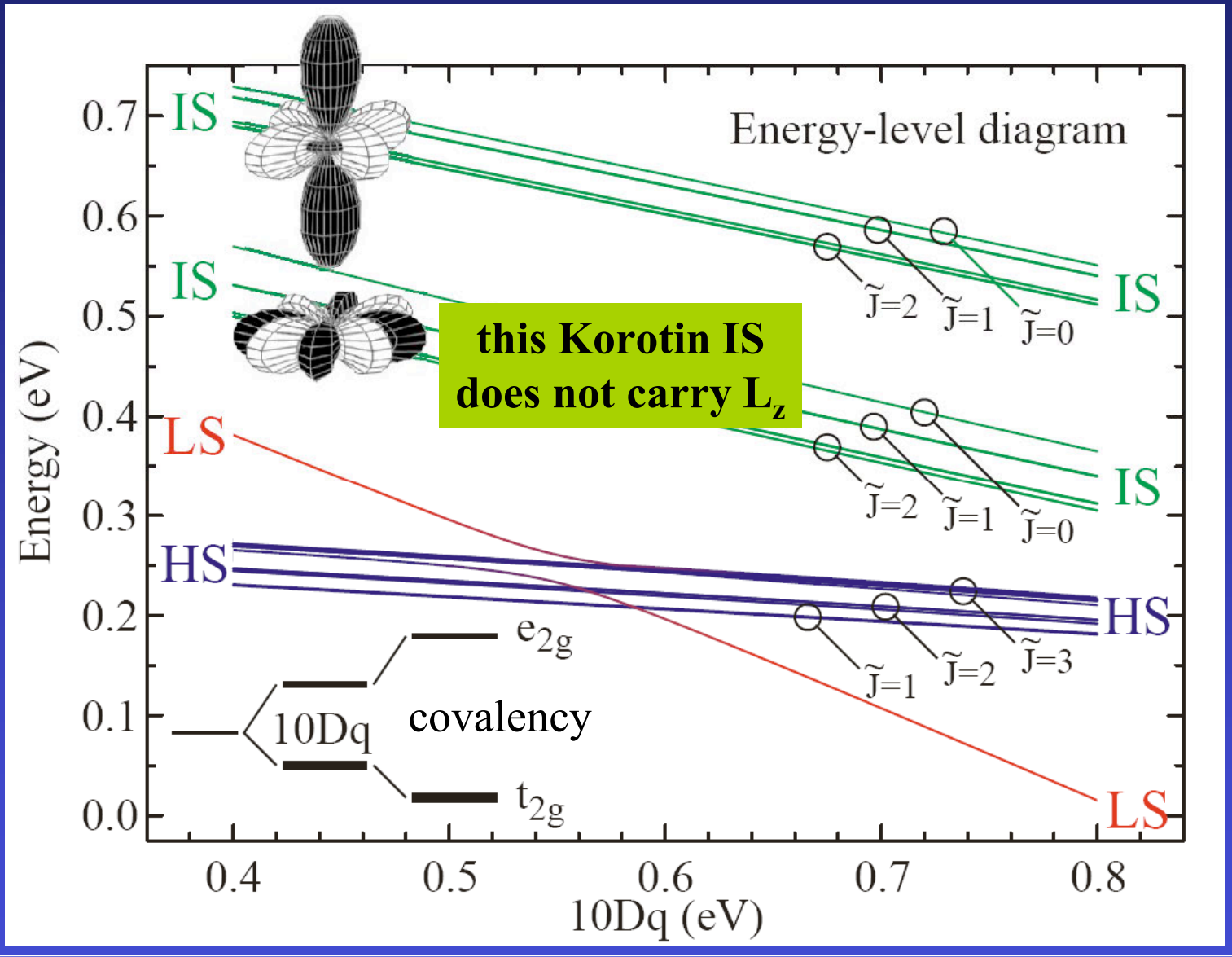


crucial finding:

orbital/spin-moment sum-rules:

$L_z/S_z \approx 1/2$

Energy level diagram: CoO_6 cluster incl. covalency



Very difficult to find an IS state with L_z which also fits the XAS/MCD spectra

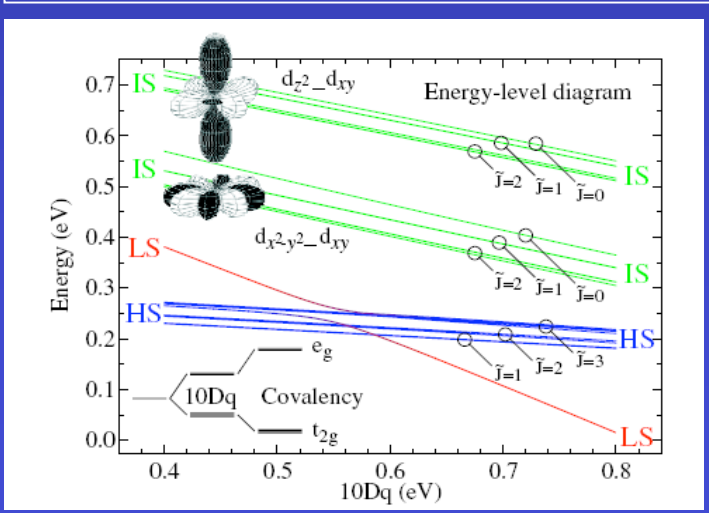
Summary: magnetic properties of $LaCoO_3$

- $LaCoO_3$: non-magnetic at low T [$Co^{3+} = 3d^6$]
  paramagnetic T>25 K
- 1960's : Low-Spin (S=0) → High-Spin (S=2)
- 1996 : Low-Spin (S=0) → Intermediate-Spin (S=1)

Korotin, Ezhov, Solovyev, Anisimov, Khomskii, Sawatzky, PRB 54, 5309 (1996): LS-IS

claimed experimental proof: thermodynamic properties
best explained by ***triply*** degenerate excited state

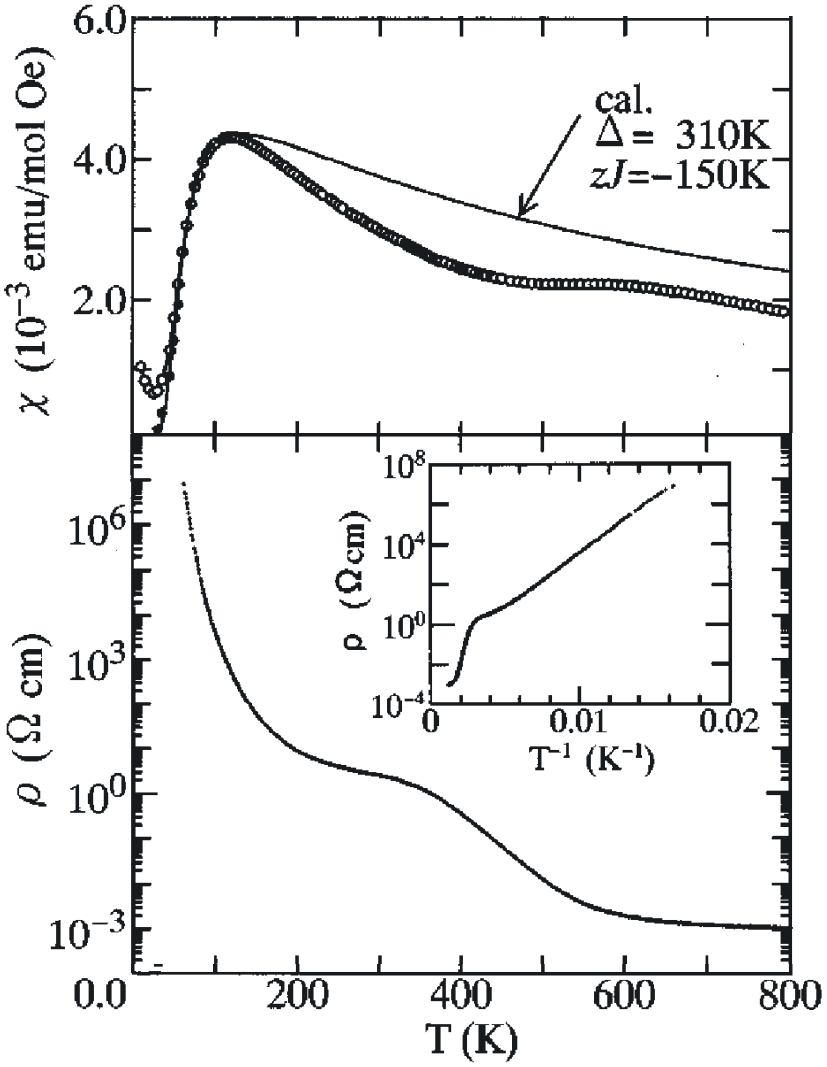
Spectroscopy XAS/MCD



- Low-Spin (S=0) to High-Spin (S=2)
- temperature dependent activation energy

Full multiplet theory:
- High-Spin (S=2) is 3-fold degenerate !!
- Interm.-Spin (S=1) is 5-fold degenerate !!
- due to spin-orbit interaction

Temperature dependence of the resistivity of $LaCoO_3$



S. Yamaguchi *et al.*, PRB **53**, 2926 (1996)

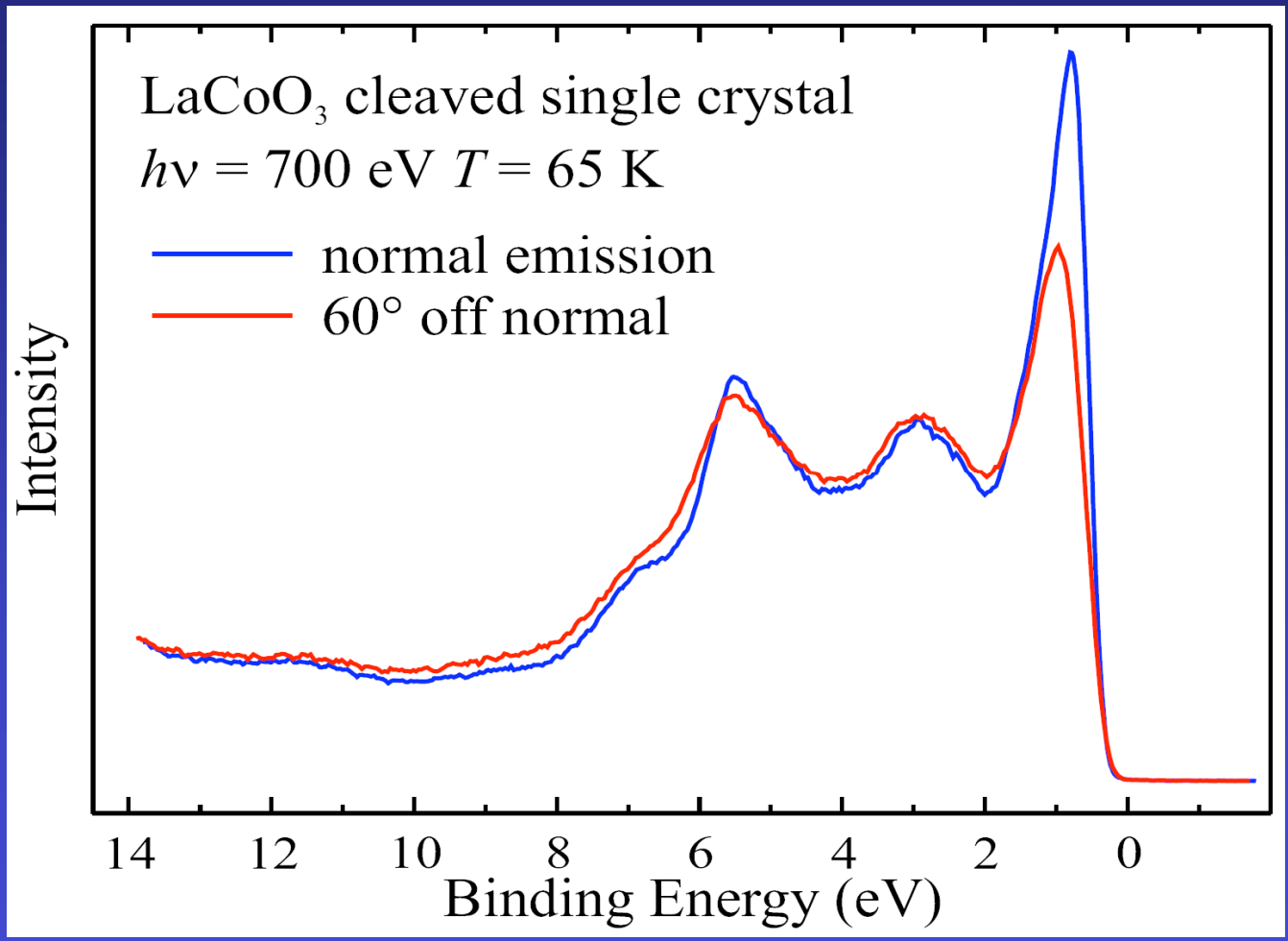
- non-magnetic insulator at low T
- non-magnetic to paramagnetic transition for T>25K, with max. in magn. susceptibility at 100K

- resistivity drop T = 350K -550K, "metal-insulator transition"

What happens with the band gap of $LaCoO_3$?

Photoelectron spectrocopy on $LaCoO_3$

T. Koethe -- PhD thesis



spectrum of **surface** different from spectrum of **bulk** !!

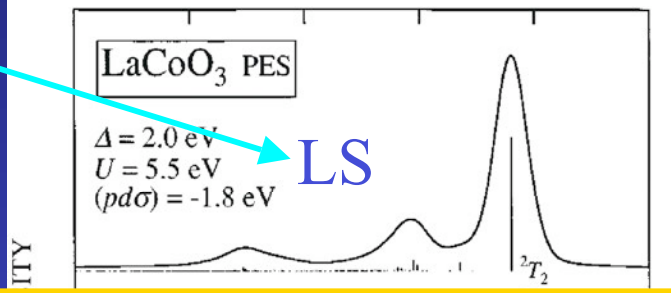
Photoelectron spectrocopy on correlated oxide systems

T. Koethe -- PhD thesis

Spin state transition in $LaCoO_3$

„bulk“

Cluster model calculations:
Saitoh *et al.*, PRB **55**, 4257 (1997)

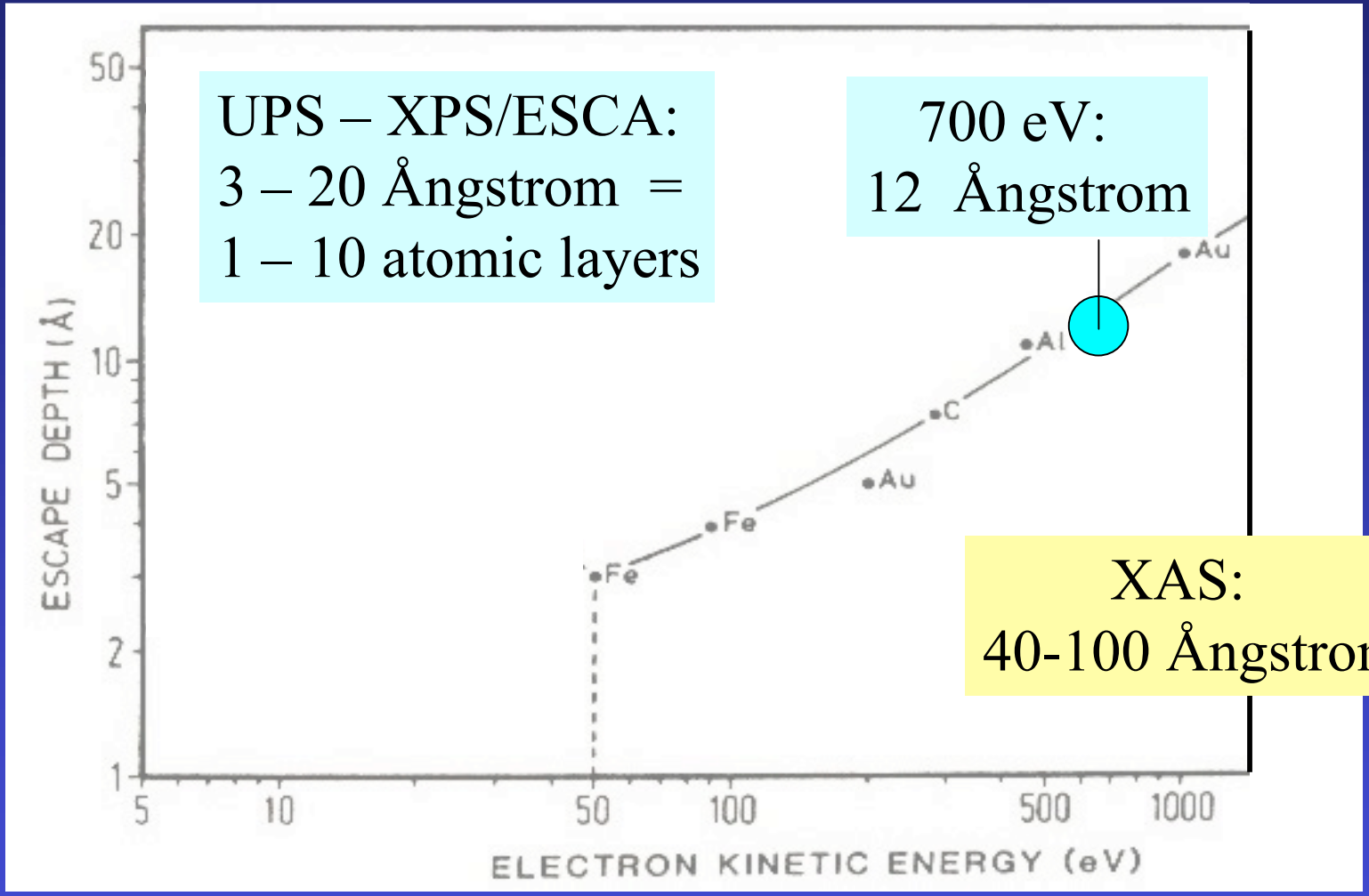


correlated electron systems:
surface tends to have a different electronic structure than **bulk**

this is especially acute for systems close to an instability,
e.g. metal-insulator and spin-state transitions

spin state at the surface
is different from bulk !!

Probing depth of photoelectron spectroscopy



Problematic for obtaining bulk PES electronic structure of $LaCoO_3$

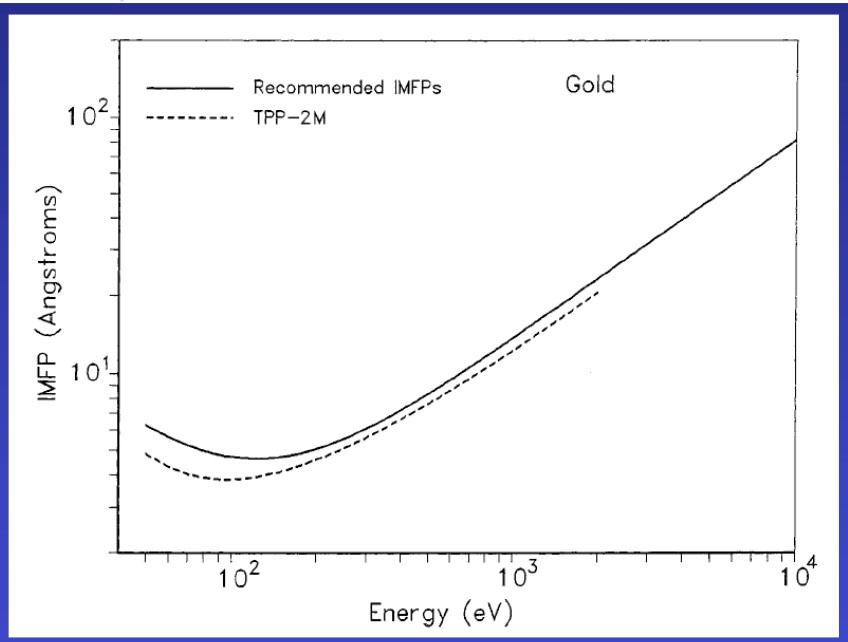
Problematic for high temperature phases: loss of oxygen at surface

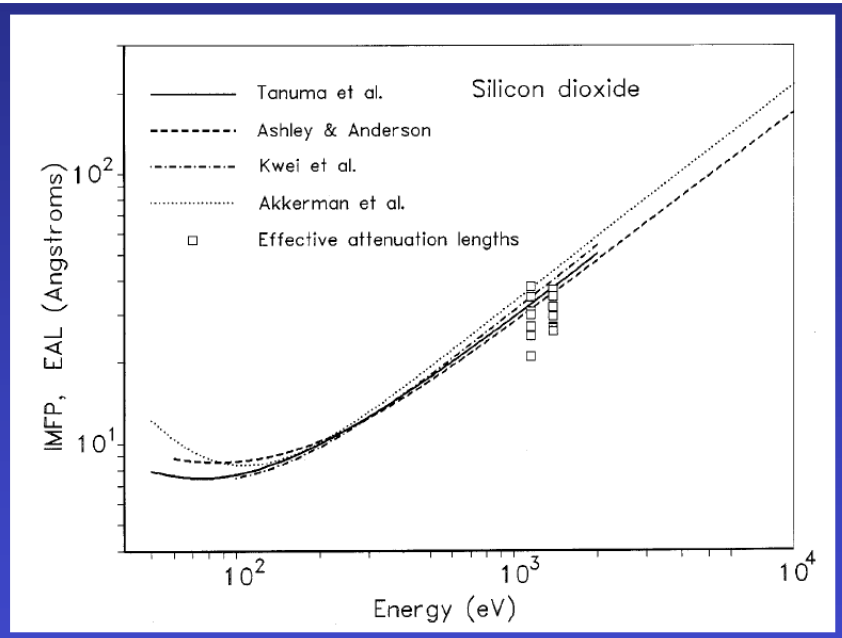
How to increase the probing depth of photoemission ?

SURFACE AND INTERFACE ANALYSIS
Surf. Interface Anal. **29**: 108–114 (2000)

Evaluation of electron inelastic mean free paths for selected elements and compounds†

C. J. Powell[1]* and A. Jablonski[2]

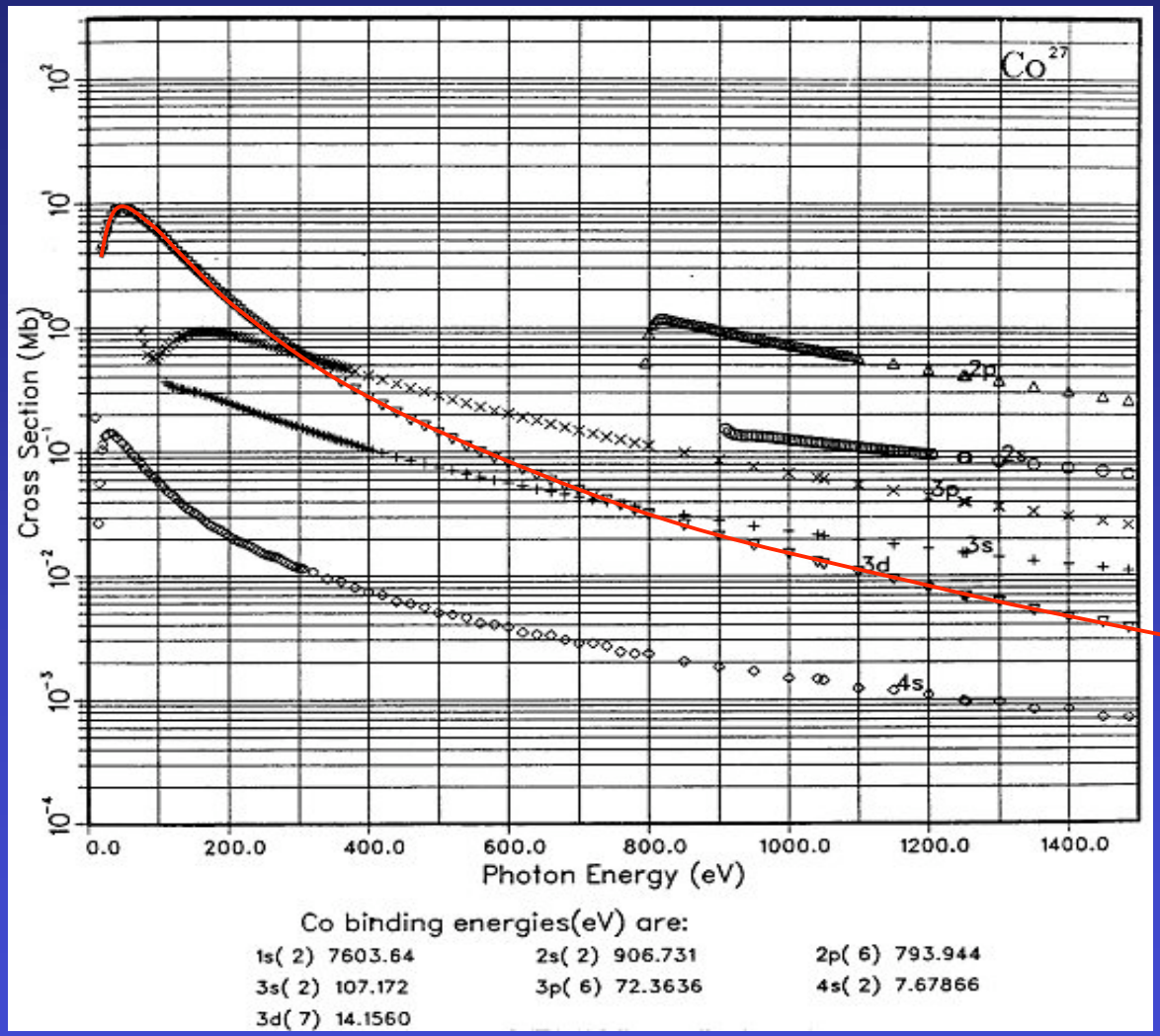




electron energies 10 keV → probing depths 80-200 Ångstrom !!

→ hard-x-ray photoelectron spectroscopy = HAXPES

Photo-ionization cross-section



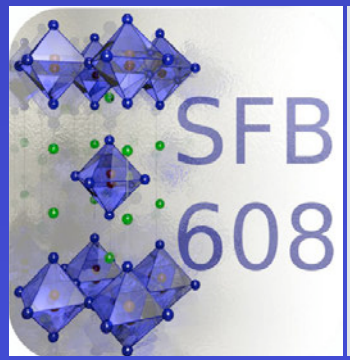
- cross-sections go down with increasing hν
- transition metal 3d 20 eV→10 keV : 10^{-6}
- needs bright sources !!

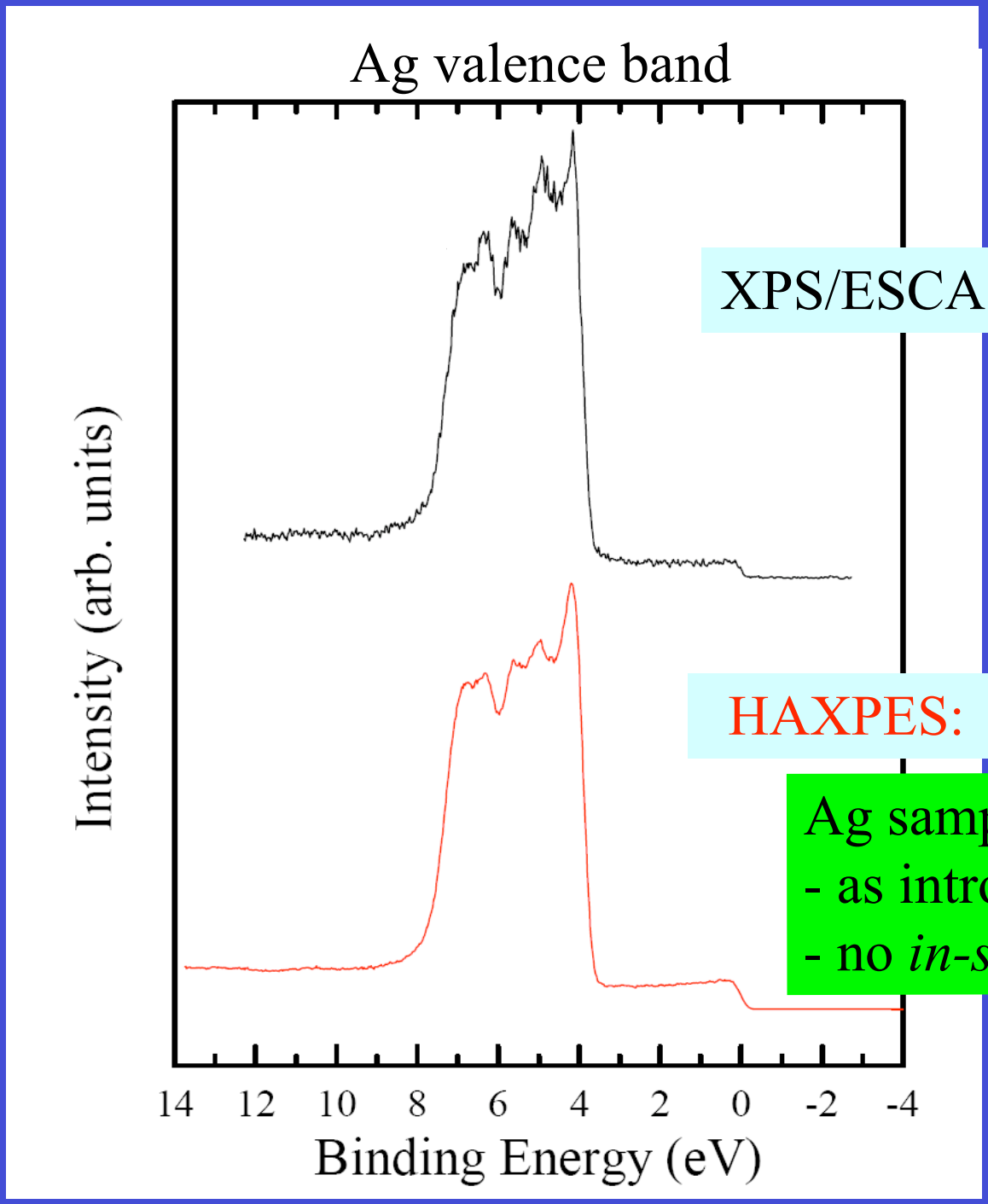
Hard-x ray photoelectron spectroscopy (HAXPES):

MPI-CPfS-Dresden
Univ. Cologne

NSRRC-Taiwan

- PhD project Jonas Weinen

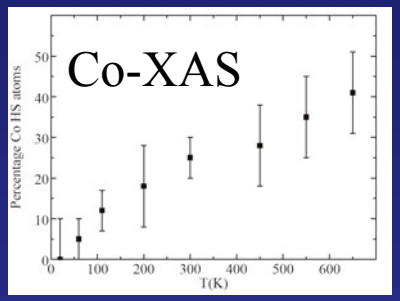




XPS/ESCA: hv = 1486 eV

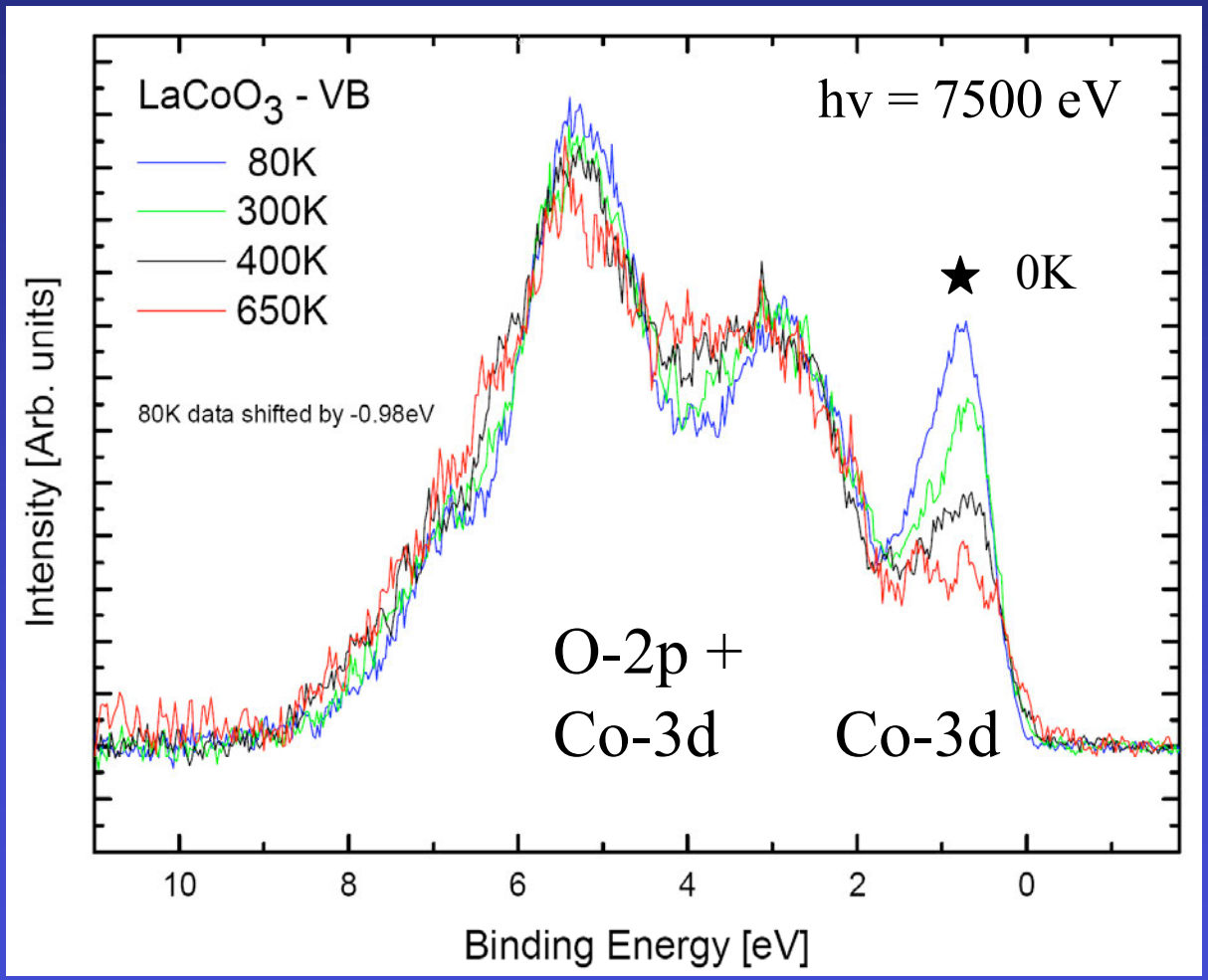
HAXPES: hv = 7600 eV

Ag sample
- as introduced from air
- no *in-situ* treatments



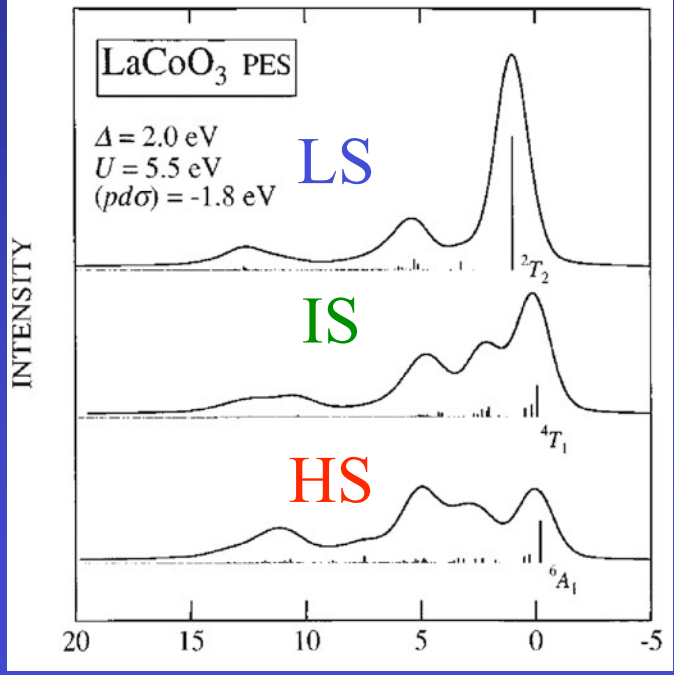
HAXPES: valence band $LaCoO_3$

Stefano Agrestini, Jonas Weinen



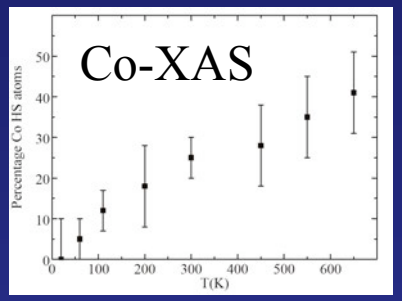
Cluster model calculations:

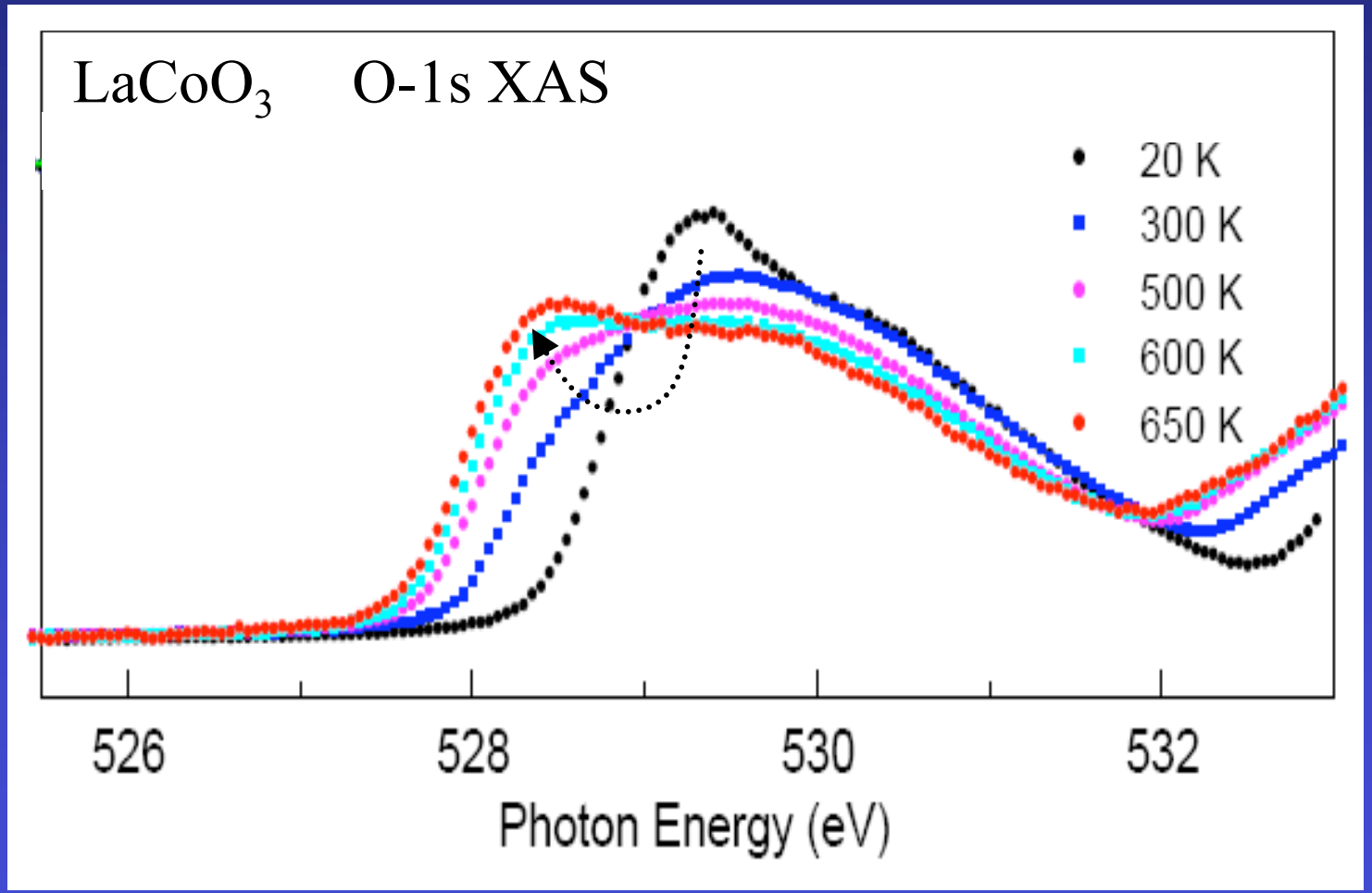
Saitoh *et al.*, PRB **55**, 4257 (1997)

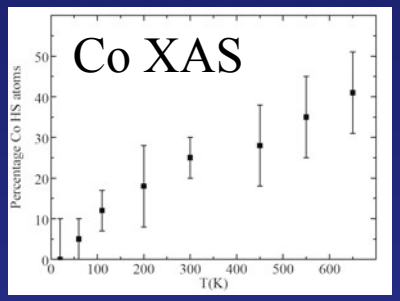


conduction band $LaCoO_3$: O-1s XAS

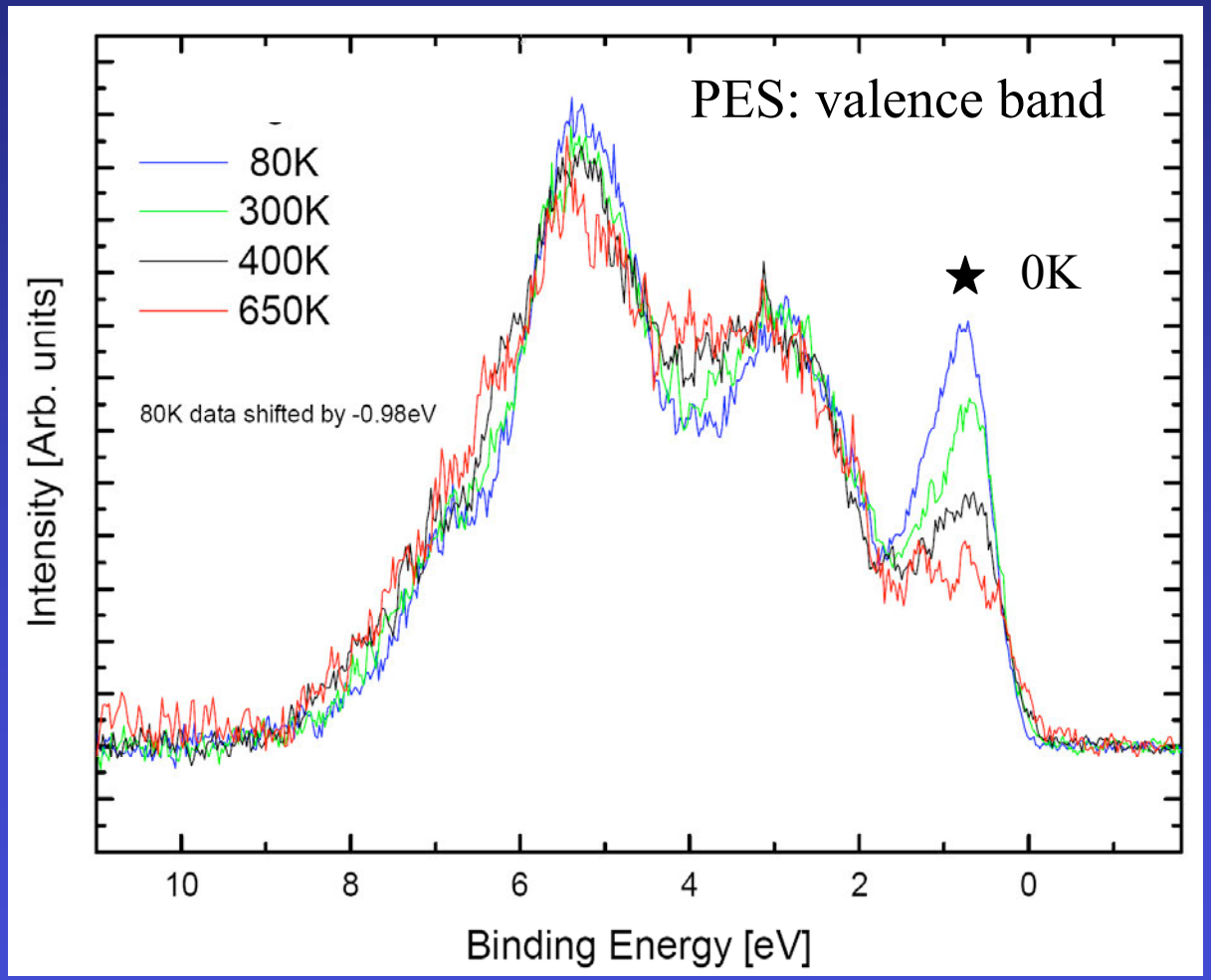
(IPES would have been better)

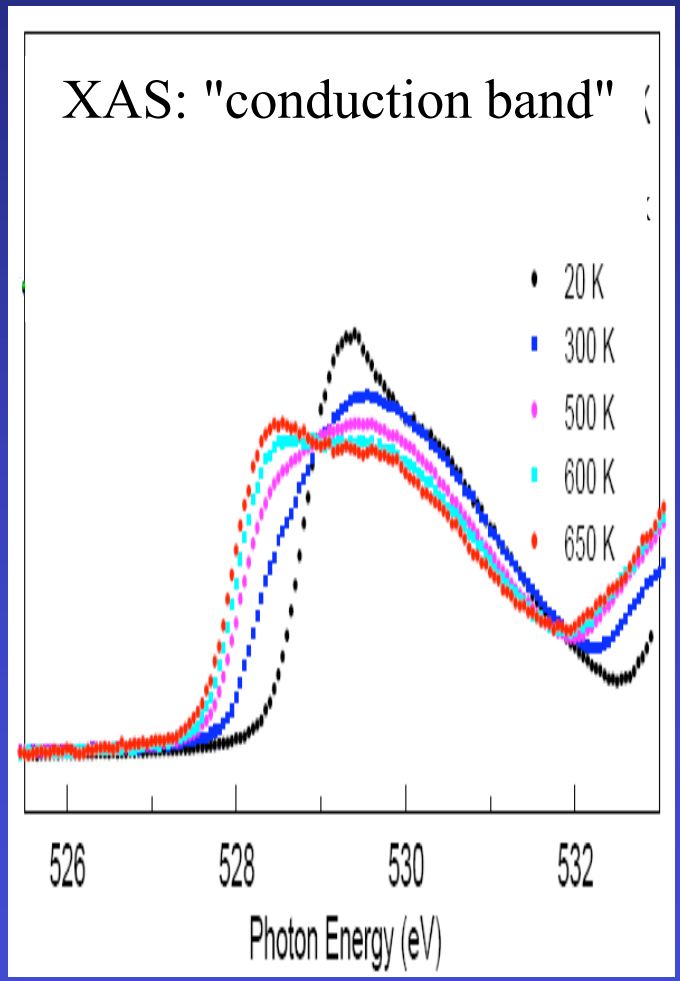


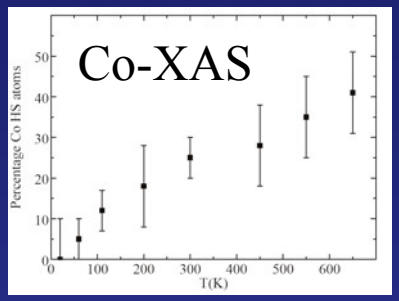




- Band gap reduces by 1 eV from 0 to 650 K
- $LaCoO_3$ is still a bad metal across the "MIT"

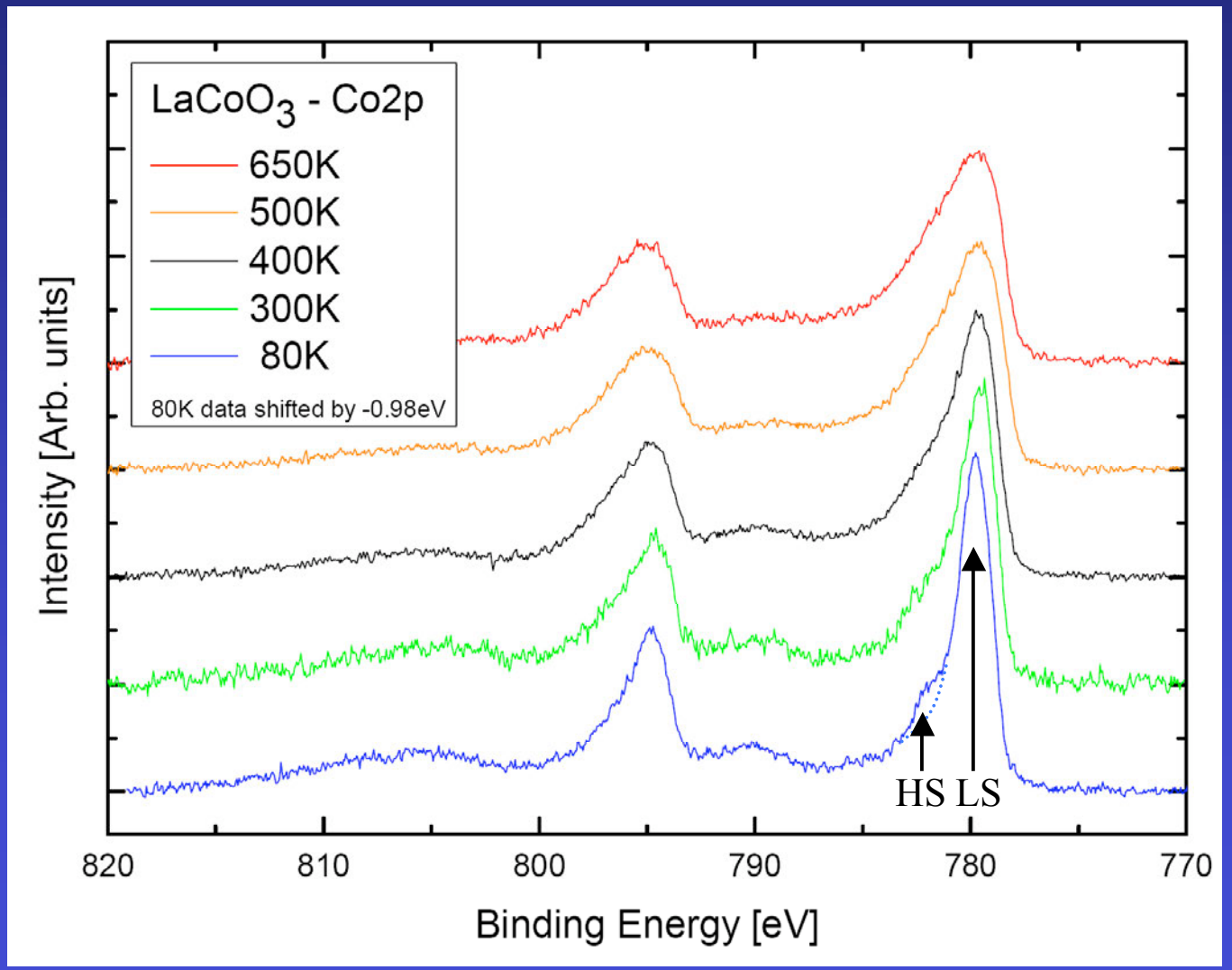


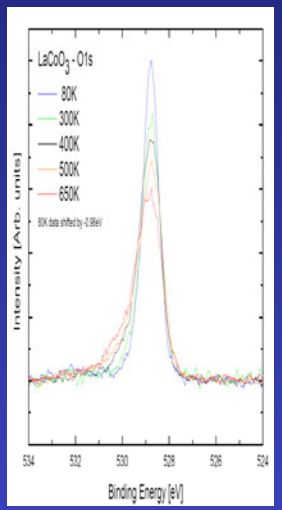


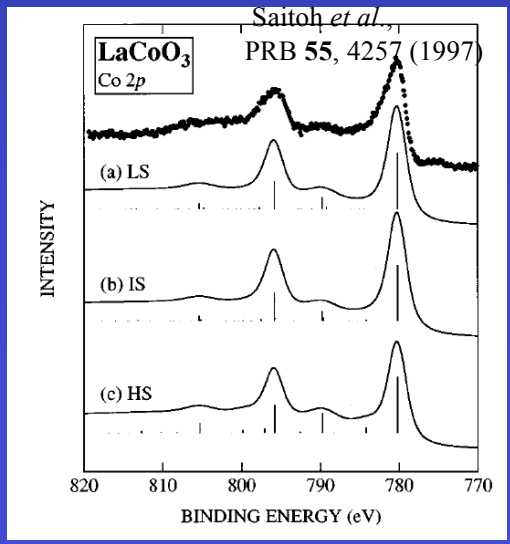


HAXPES: core levels $LaCoO_3$

- $LaCoO_3$ is an inhomogeneous spin-state system







Saitoh *et al.*, PRB **55**, 4257 (1997)

- Cobaltates: a material class with very rich physics
  metal-insulator-transitions, colossal-magneto-resistance, thermoelectric power, superconductivity, multiferroicity, unusual magnetic properties.

• valence state :	2+	3+	4+
• spin state:	HS	HS/IS/LS	HS/IS/LS

- spin state transitions and spin-blockade mechanism
- local coordination: oct/pyramidal/trig/prismatic-trig

113 cobaltates:

$LaCoO_3$	Co: 3+	LS/HS		
$LaMn_{0.5}Co_{0.5}O_3$	Co: 2+	HS	Mn: 4+	HS
$EuMn_{0.5}Co_{0.5}O_3$	Co: 2+	HS	Mn: 4+	HS

one-dimensional cobaltates:

$Ca_3Co_2O_3$	Co: trig. 3+	HS	Co: oct. 3+	LS
Ca_3CoRhO_6	Co: trig. 2+	HS	Rh: oct. 4+	LS
Ca_3FeRhO_6	Fe : trig. 3+	HS	Rh: oct. 3+	LS
Ca_3CoMnO_6	Co: trig. 2+	HS	Mn: oct. 4+	HS

layered cobaltates:

$GdBaCo_2O_{5.5}$	Co: 3+	HS/LS	Co_{pyr}: 3+	HS
$La_{1.5}Sr_{0.5}CoO_4$	Co: 3+	LS	Co: 2+	HS

Na_xCoO_2	Co: 3+	LS	Co: 4+	LS
$Na_xCoO_2{\cdot}nH_2O$	Co: 3+	LS	Co: 4+	LS

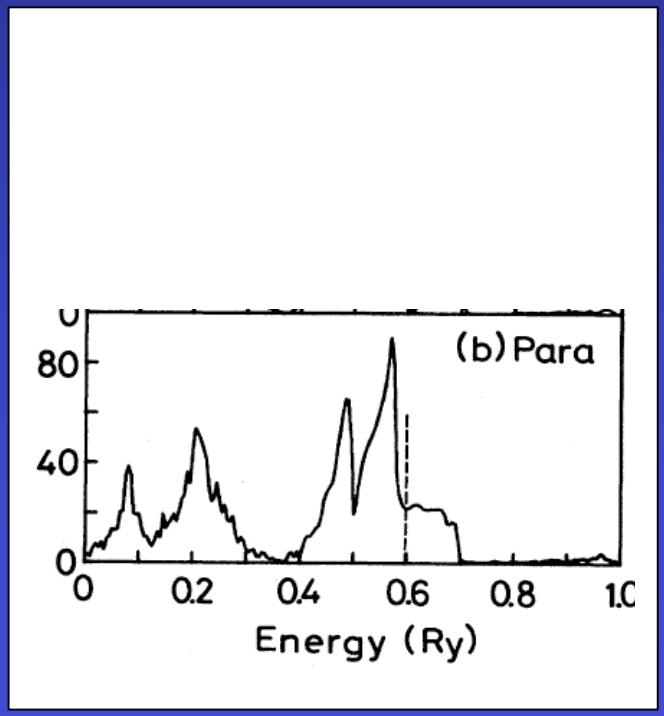
II. Multiplet interactions and band formation

Example : NiO

Benchmark system in solid state physics

- partially field 3d-shell
- antiferromagnetic insulator

Standard band theory: NiO metallic



Example : NiO

Benchmark system in solid state physics

- partially field 3d-shell
- antiferromagnetic insulator

Standard band theory: NiO metallic

PHYSICAL REVIEW B VOLUME 28, NUMBER 11 1 DECEMBER 1983

Band theory of the magnetic interaction in MnO, MnS, and NiO

VOLUME 52, NUMBER 20 PHYSICAL REVIEW LETTERS 14 MAY 1984

Transition-Metal Monoxides: Band or Mott Insulators

PHYSICAL REVIEW B VOLUME 30, NUMBER 8 15 OCTOBER 1984

Band theory of insulating transition-metal monoxides: Band-structure calculations

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A. R. Williams
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

J. Kübler
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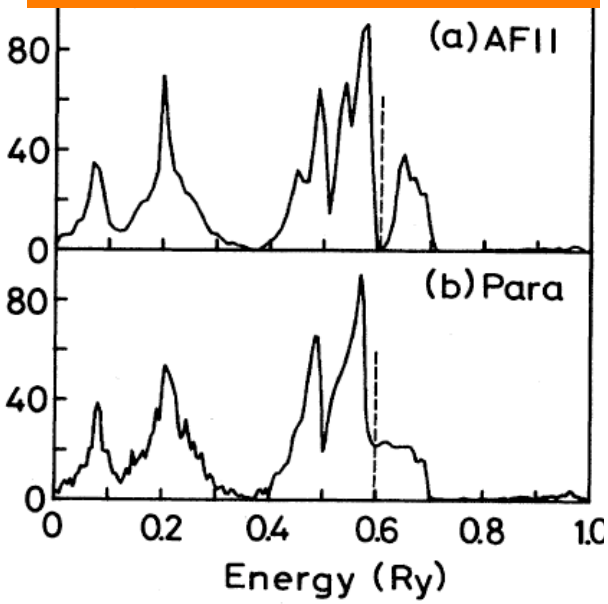
(Received 11 April 1984)

Early attempt to fix: Slater insulator

Gap is very small: 0.2 eV



Example : NiO

Benchmark system in solid state physics

- partially field 3d-shell
- antiferromagnetic insulator

PHYSICAL REVIEW B VOLUME 30, NUMBER 2 15 JULY 1984

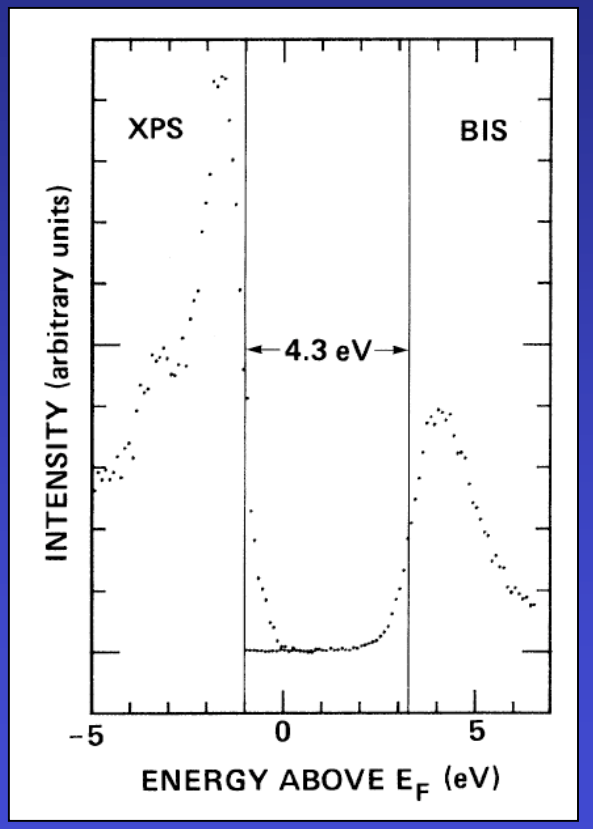
Valence-band photoemission and optical absorption in nickel compounds

Atsushi Fujimori* and Fujio Minami
National Institute for Research in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 305, Japan
(Received 21 February 1984)

VOLUME 53, NUMBER 24 PHYSICAL REVIEW LETTERS 10 DECEMBER 1984

Magnitude and Origin of the Band Gap in NiO

G. A. Sawatzky[(a)] and J. W. Allen
Xerox Palo Alto Research Center, Palo Alto, California 94304
(Received 5 July 1984)



PES- IPES experiment: gap is large → 4.3 eV

importance of Hubbard U

Example : NiO

Benchmark system in solid state physics

- partially field 3d-shell
- antiferromagnetic insulator

VOLUME 65, NUMBER 9 PHYSICAL REVIEW LETTERS 27 AUGUST 1990

Transition-Metal Oxides in the Self-Interaction–Corrected Density-Functional Formalism

A. Svane
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

O. Gunnarsson
Max-Planck Institut für Festokörperforschung, D-7000 Stuttgart 80, West Germany
(Received 14 May 1990)

Ab-initio:
SIC fixes the gap

TABLE I. The LSD, SIC-LSD, and experimental energy band gaps (in eV) and spin magnetic moments (in μ_B) for VO, CrO, MnO, FeO, CoO, NiO, and CuO. The moments in parenthesis include the orbital contribution. The last column shows the energy difference ΔE (in eV) between the LSD and the SIC-LSD calculation.

	Band gap			Magnetic moment			
Compound	LSD	SIC-LSD	Expt.	LSD	SIC-LSD	Expt.	ΔE
VO	0.0	0.0	0.0	0.0	0.0	0.0	
CrO	0.0	1.01		2.99	3.49 (3.44)		1.0
MnO	0.8	3.98	3.6–3.8 [a]	4.39	4.49 (4.49)	4.79,[b] 4.58[c]	3.9
FeO	0.0	3.07		3.42	3.54 (4.55)	3.32[d]	4.6
CoO	0.0	2.81	2.4[e]	2.33	2.53 (3.72)	3.35,[f] 3.8,[d] 3.8[g]	6.6
NiO	0.2	2.54	4.3,[h] 4.0[i]	1.04	1.53 (1.80)	1.77,[b] 1.64,[j] 1.90[c]	9.5
CuO	0.0	1.43	1.37[k]	0	0.65 (0.78)	0.65[l]	14.7

Example : NiO

Benchmark system in solid state physics

- partially field 3d-shell
- antiferromagnetic insulator

PHYSICAL REVIEW B VOLUME 44, NUMBER 3 15 JULY 1991-I

Band theory and Mott insulators: Hubbard *U* instead of Stoner *I*

Vladimir I. Anisimov,* Jan Zaanen,† and Ole K. Andersen

PHYSICAL REVIEW B VOLUME 48, NUMBER 23 15 DECEMBER 1993-I

Density-functional theory and NiO photoemission spectra

V. I. Anisimov, I. V. Solovyev, and M. A. Korotin
M. T. Czyżyk and G. A. Sawatzky

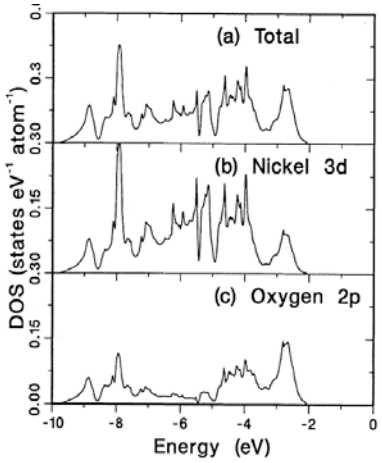


FIG. 1. The density of states (DOS) for the NiO valence band in the LDA + *U* calculation ("unmodified"). (a) The total DOS, (b) the Ni 3*d* partial DOS, and (c) the O 2*p* partial DOS.

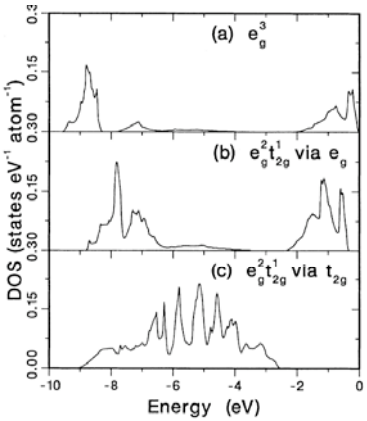


FIG. 2. The partial Ni 3*d* DOS from the LDA + *U* ca tion with "modified" hopping parameters for (a configuration e_g^3; (b) the configuration $e_g^2t_{2g}^1$, hybridizati the e_g channel; and (c) the configuration $e_g^2t_{2g}^1$, hybridizati the t_{2g} channel.

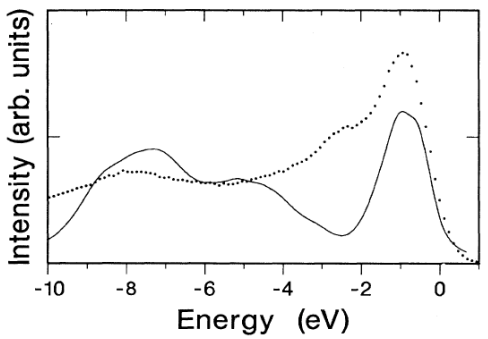


FIG. 3. The experimental (dots) and the calculated (solid line) photoemission spectra for NiO.

LDA+U not "dynamic" enough for excitation spectra

VOLUME 64, NUMBER 20 PHYSICAL REVIEW LETTERS 14 MAY 1990

Aspects of the Correlation Effects, Antiferromagnetic Order, and Translational Symmetry of the Electronic Structure of NiO and CoO

Z.-X. Shen,[1] C. K. Shih,[2] O. Jepsen,[3] W. E. Spicer,[1] I. Lindau,[1] and J. W. Allen[4]

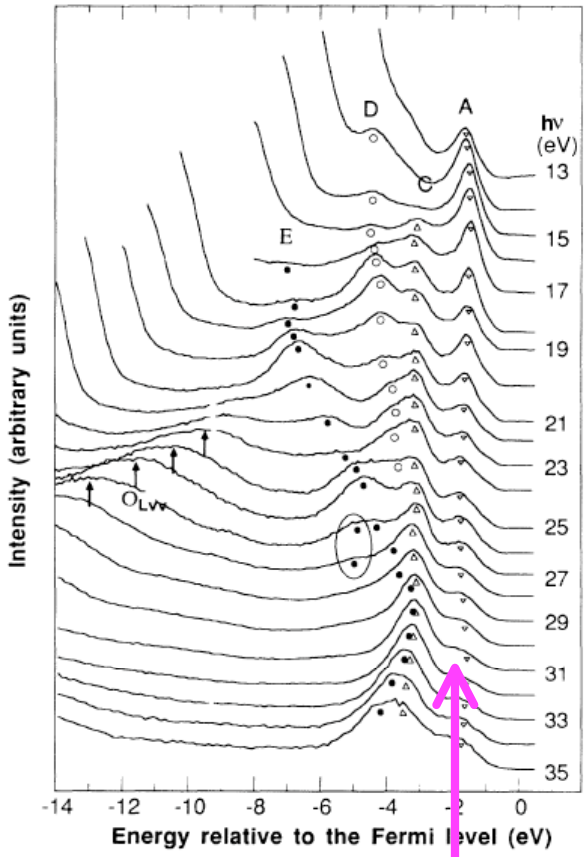
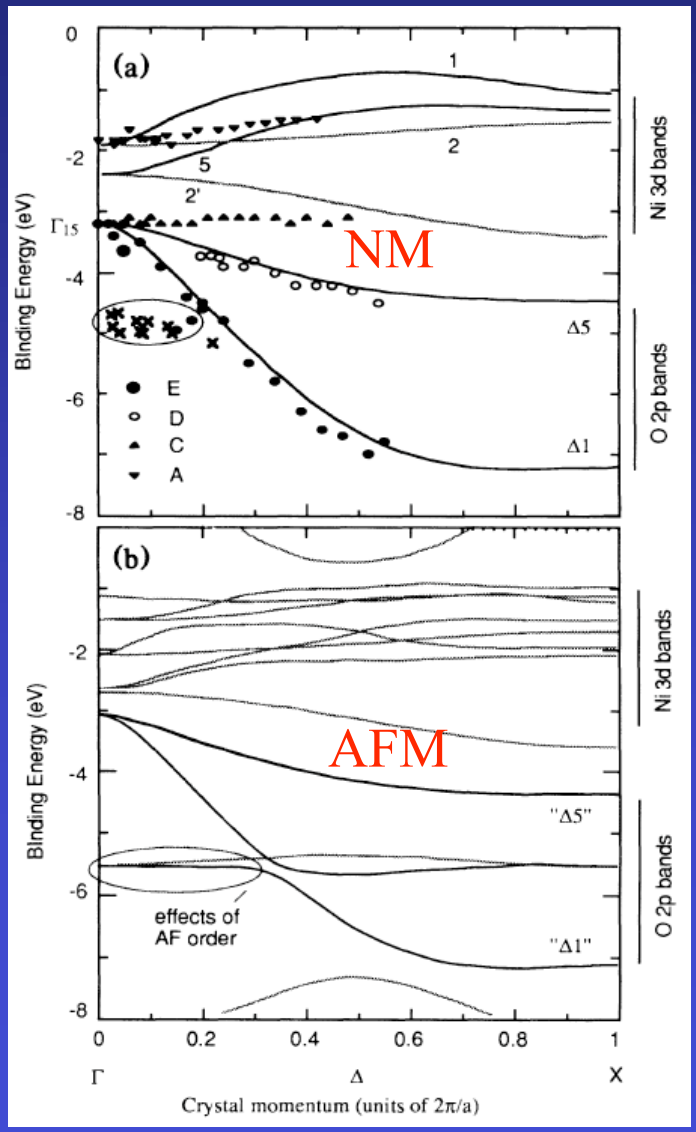
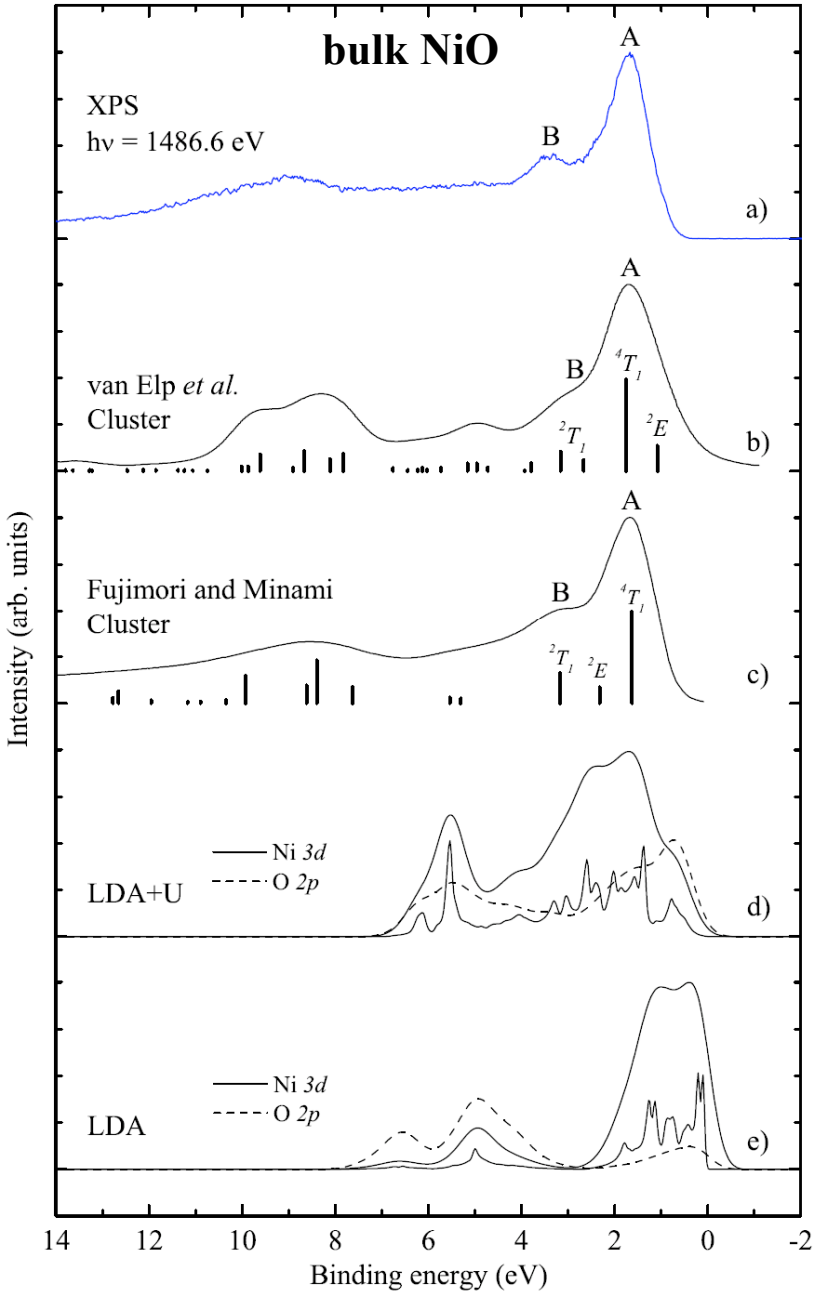


FIG. 1. Normal-emission data from the NiO [001] surface recorded at photon energies between 13 and 35 eV.



hardly any dispersion in the 3d band

Haupricht, Weinen *et al.*



peak B due to surface effects ??

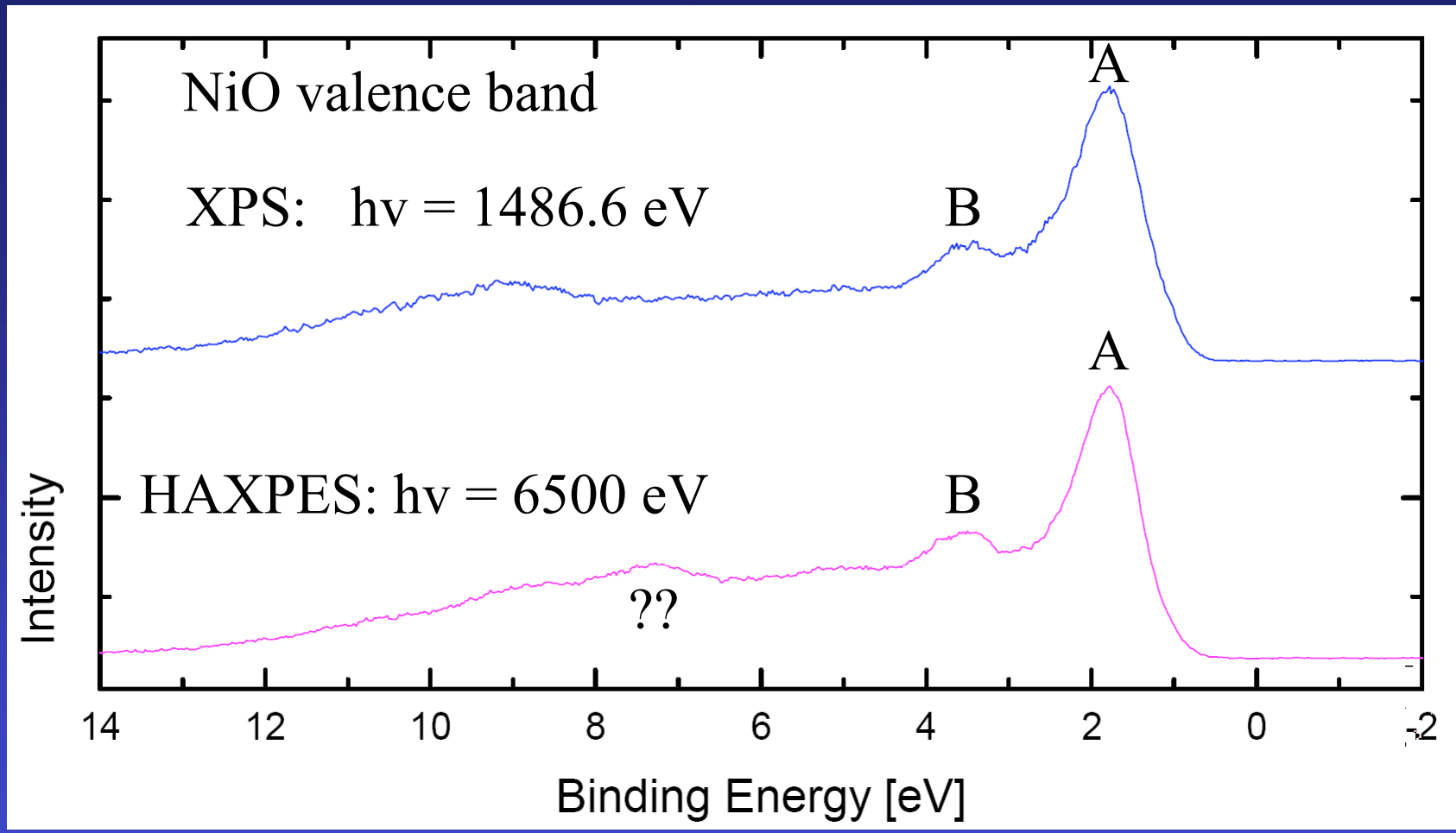
experimental spectrum

cluster: even smaller peak B

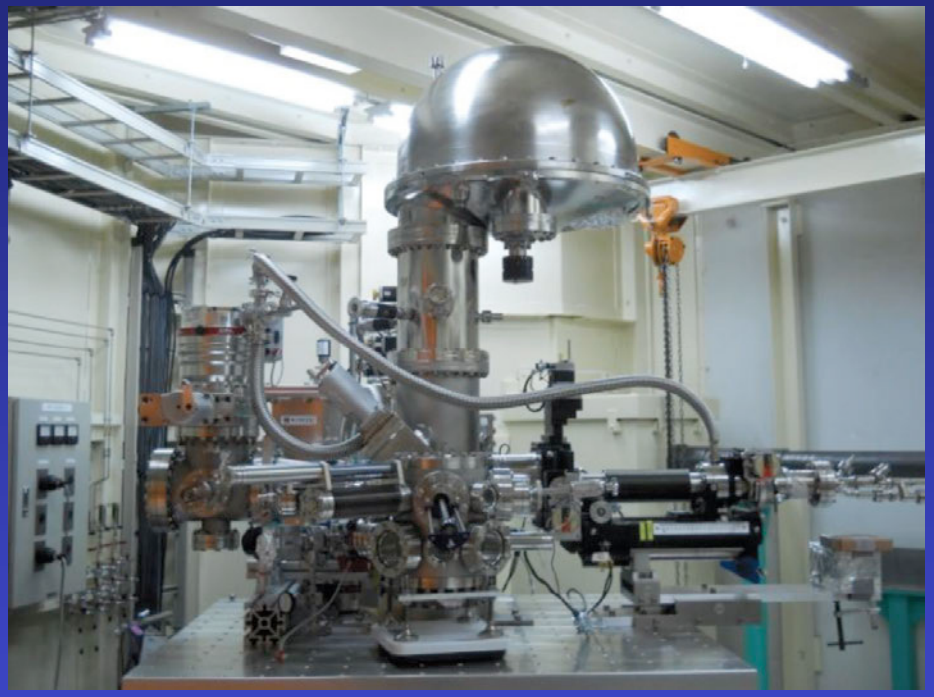
cluster: small peak B

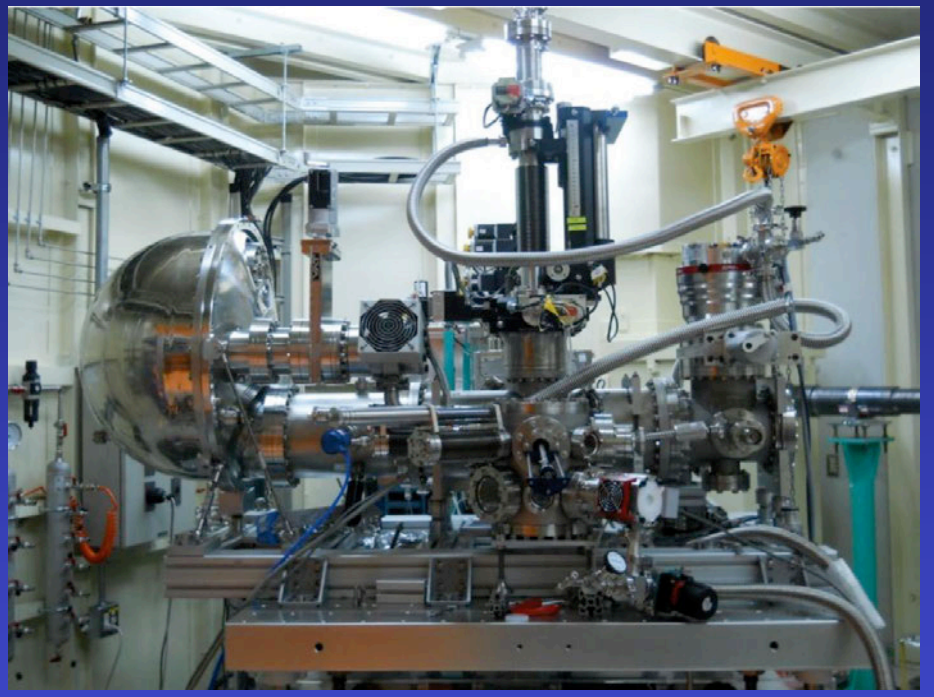
LDA+U: wrong lineshape

LDA: metal


NiO valence band
XPS: hv = 1486.6 eV
A
B
A
HAXPES: hv = 6500 eV
B
??
Intensity
14
12
10
8
6
4
2
0
-2
Binding Energy [eV]

"vertical" set-up ⟷ light polarization ⟷ „horizontal" set-up

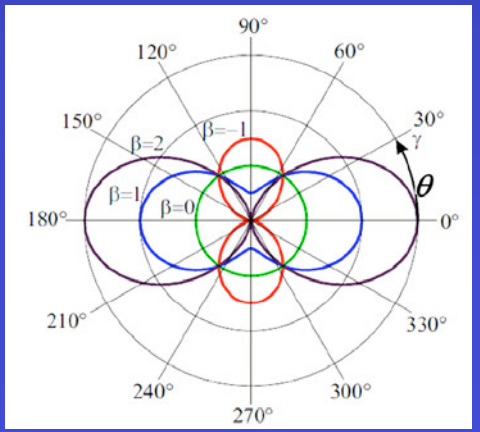


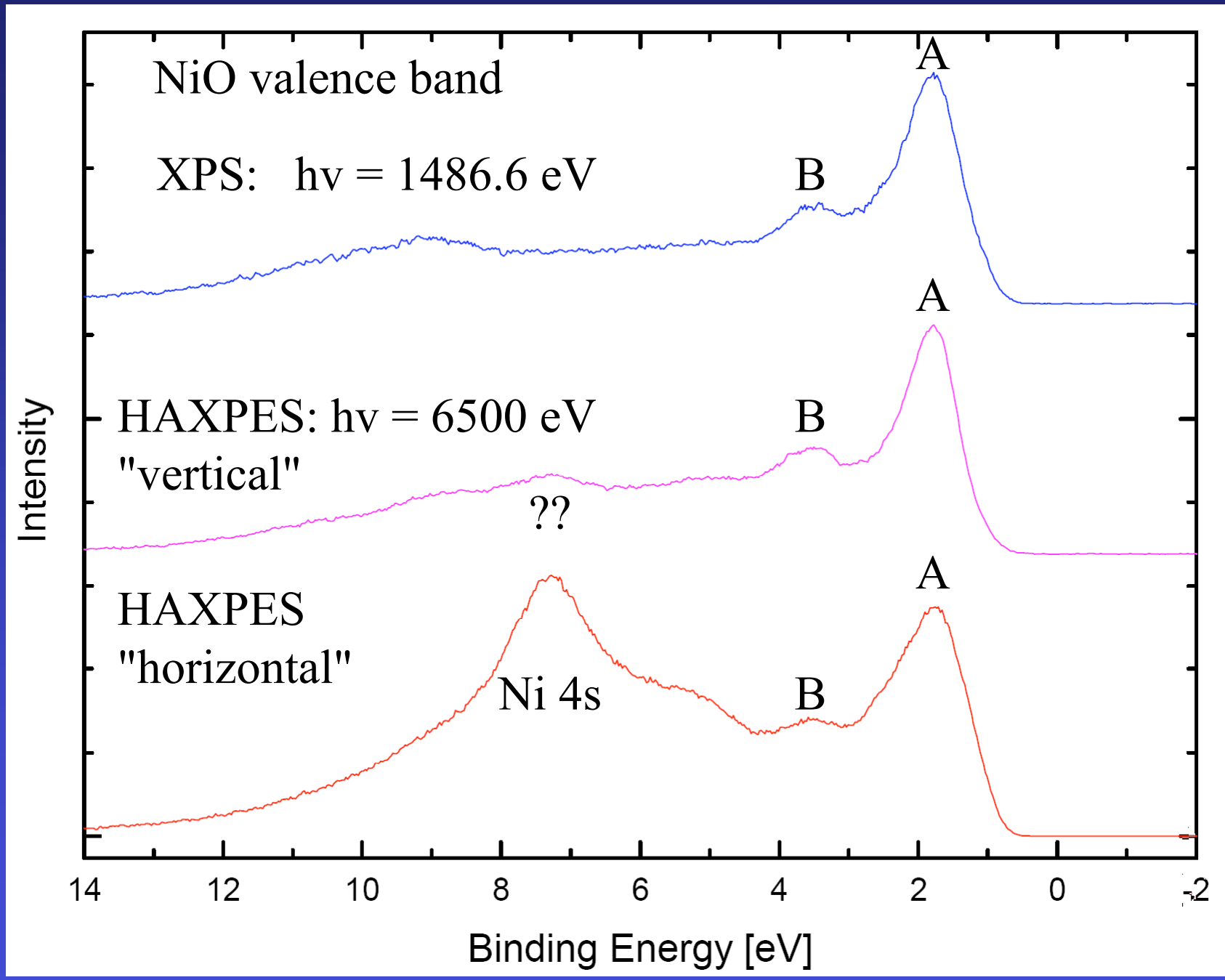


$$\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi}[1 + \beta P_2(\cos\theta) + \ldots]$$

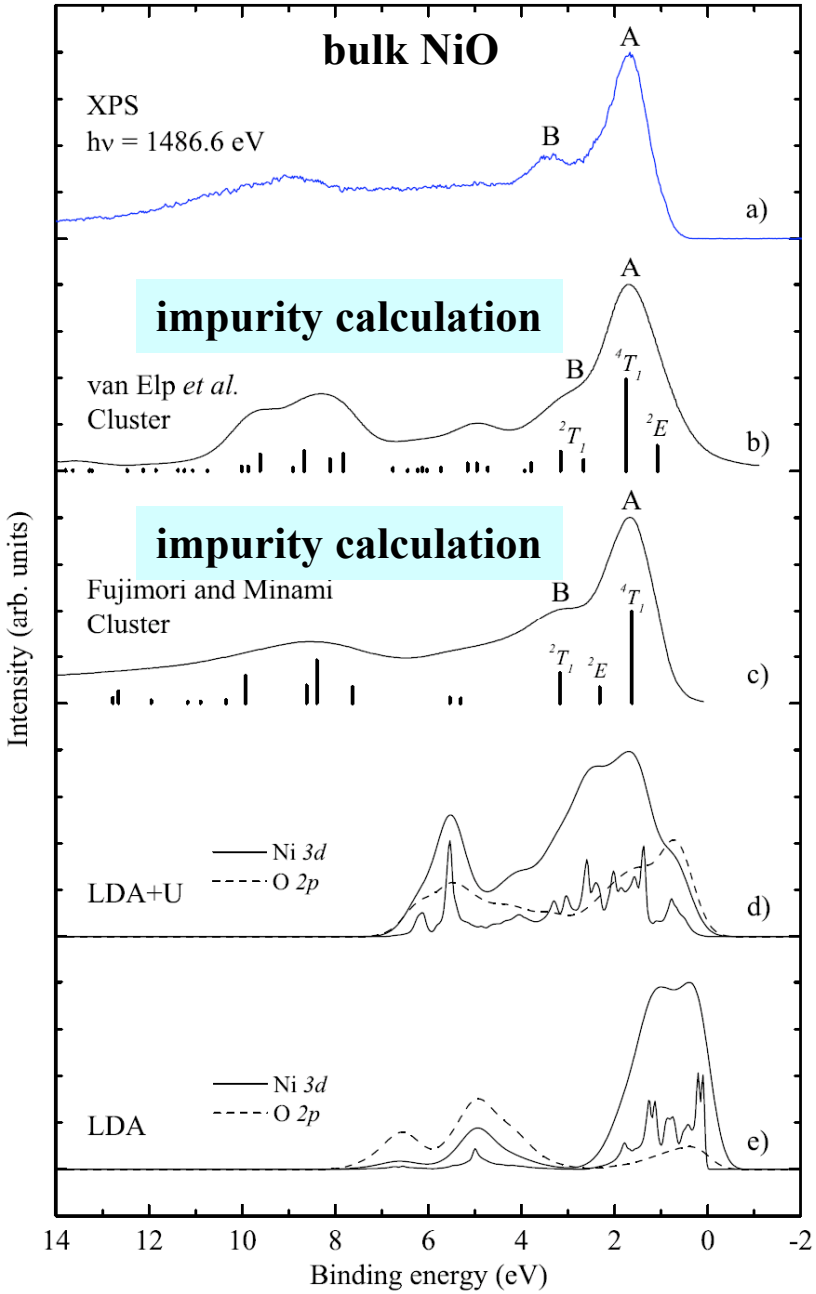
β-parameters @ hν= 5-10 keV

Cu 3*d*	0.48 - 0.32
Cu 4*s*	1.985
Zn 3*d*	0.50 - 0.33
Zn 4*s*	1.987 - 1.986

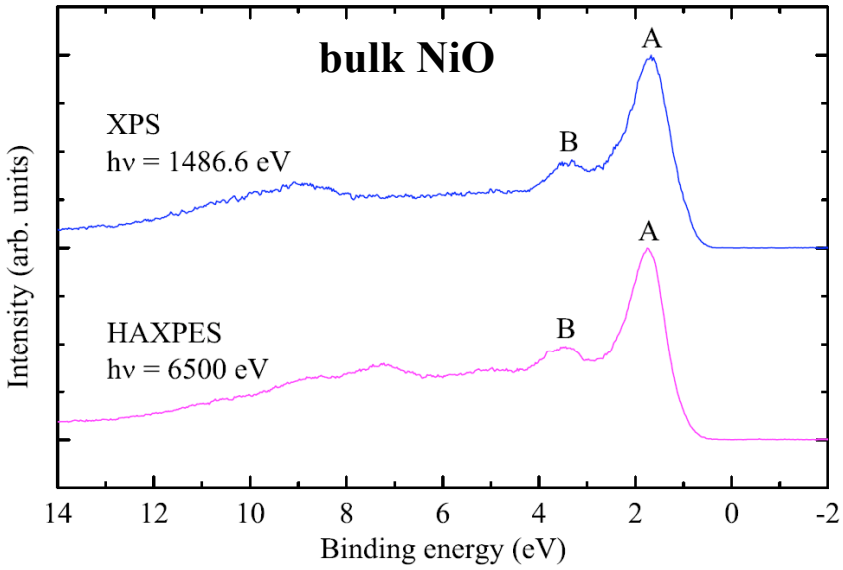



NiO valence band
XPS: hv = 1486.6 eV
A
B
HAXPES: hv = 6500 eV
"vertical"
??
A
B
HAXPES
"horizontal"
Ni 4s
A
B
Intensity
14
12
10
8
6
4
2
0
-2
Binding Energy [eV]

Haupricht, Weinen *et al.*



Haupricht, Weinen *et al.*



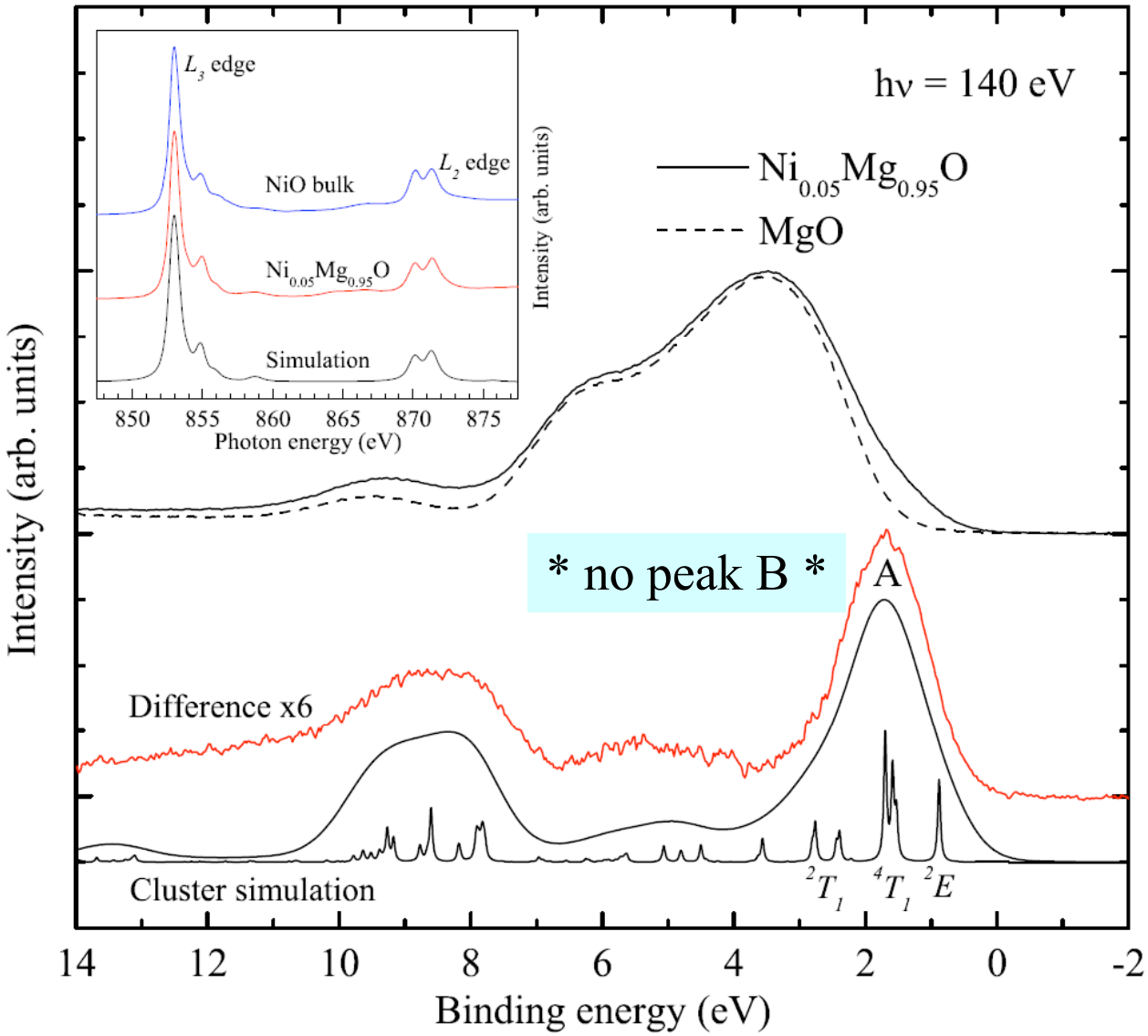
HAXPES is more bulk sensitive than XPS
80 Angstrom - probing depth - 20 Angstrom

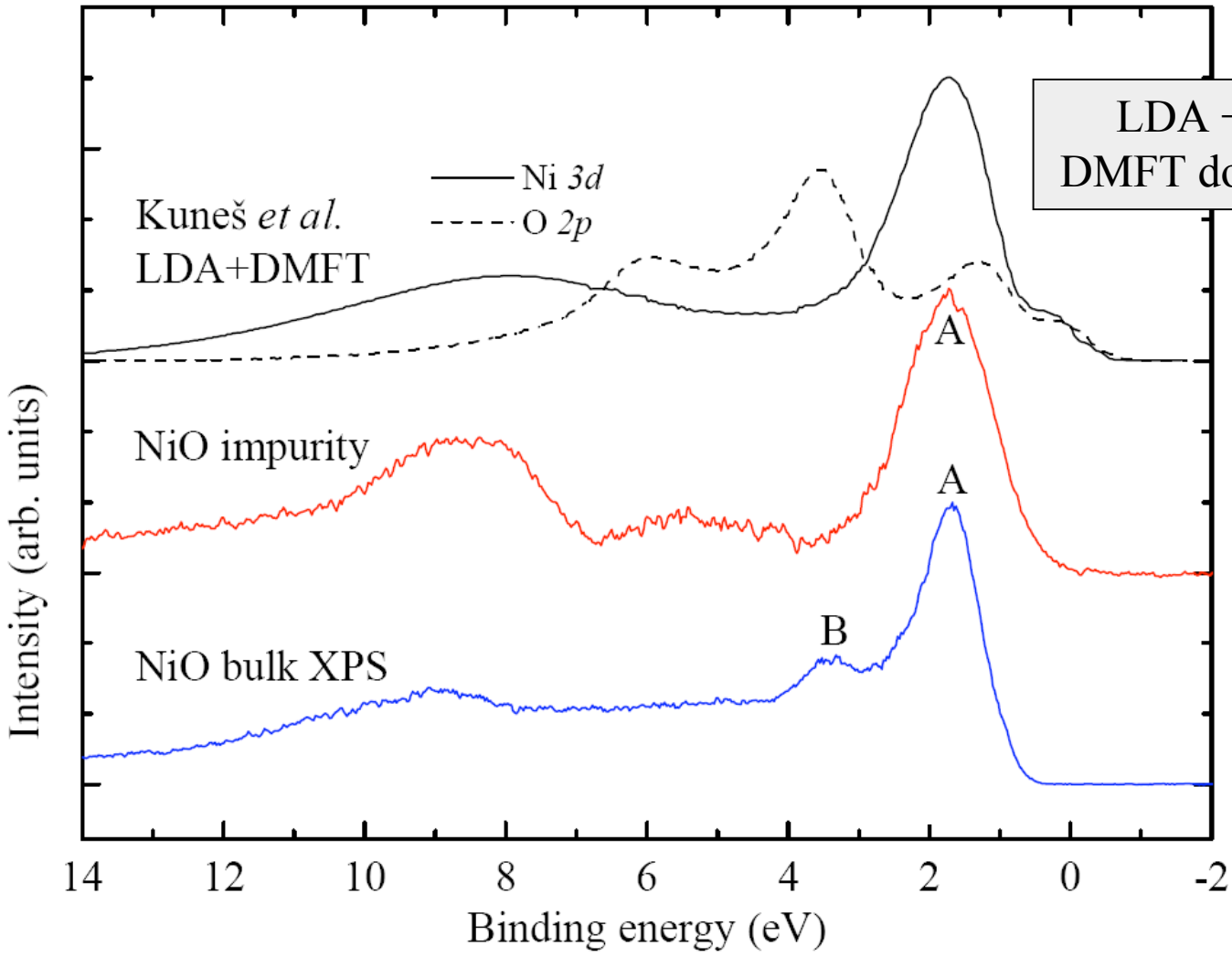
peak B belongs to bulk spectrum !!

How does the NiO impurity spectrum looks like ?? → Ni:MgO

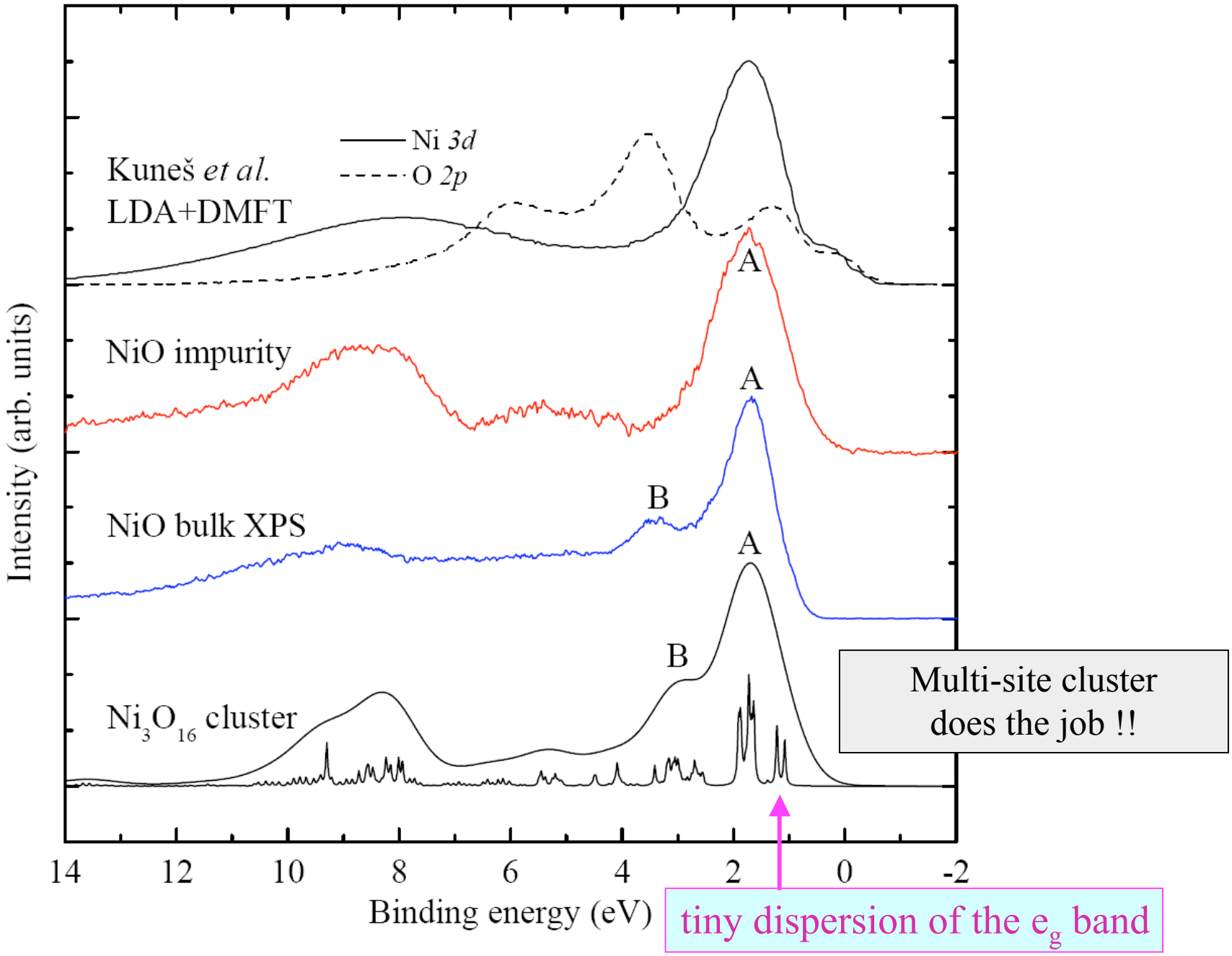
NiO impurity spectrum → Ni:MgO

Haupricht, Weinen *et al*.



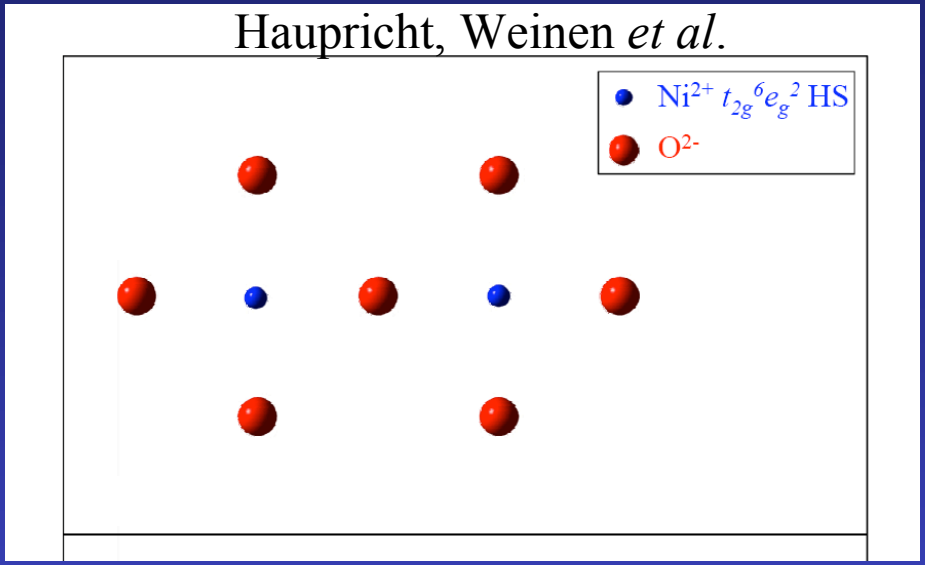


LDA + single site
DMFT does not work !!


Ni 3d
O 2p
Kuneš et al.
LDA+DMFT
NiO impurity
NiO bulk XPS
Ni3O16 cluster
A
A
B
A
B
Intensity (arb. units)
14
12
10
8
6
4
2
0
-2
Binding energy (eV)
Multi-site cluster
does the job !!
tiny dispersion of the eg band

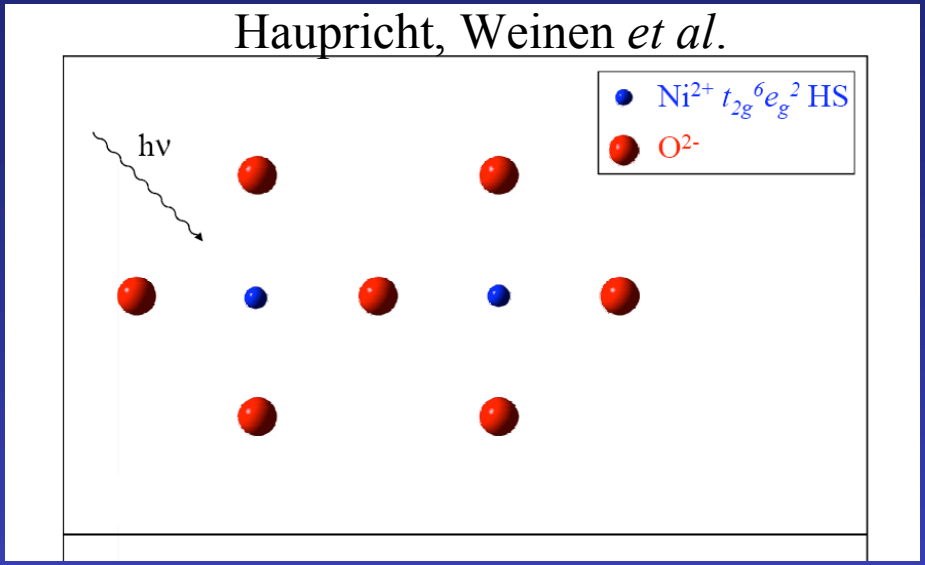
What is the origin of peak B ??

before PES



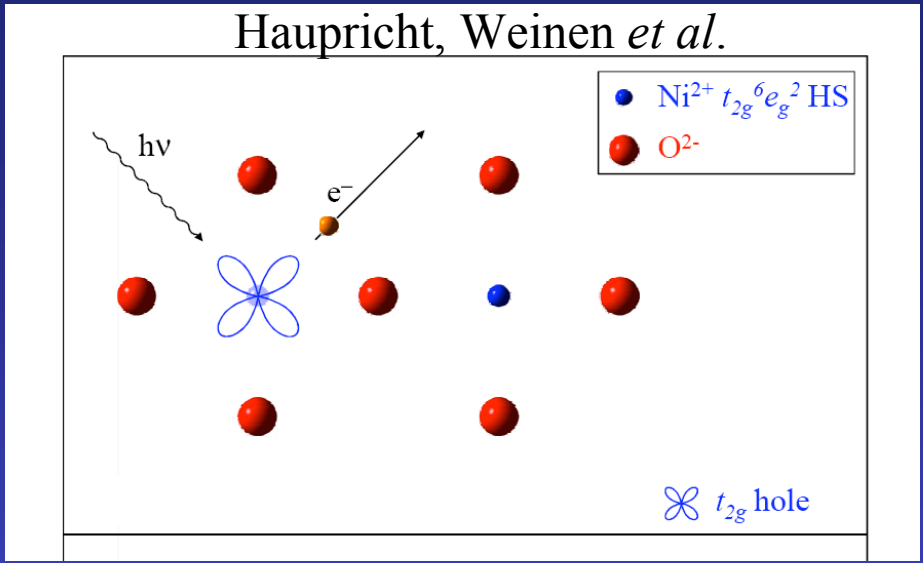
What is the origin of peak B ??

PES



What is the origin of peak B ??

PES

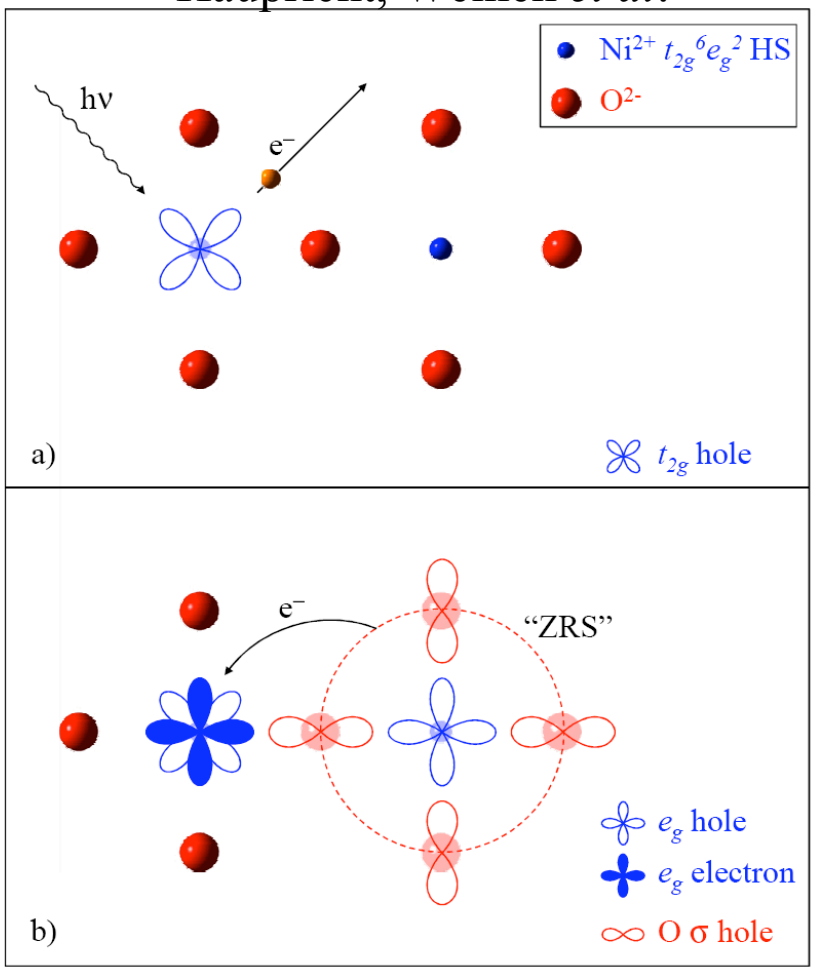


What is the origin of peak B ??

PES

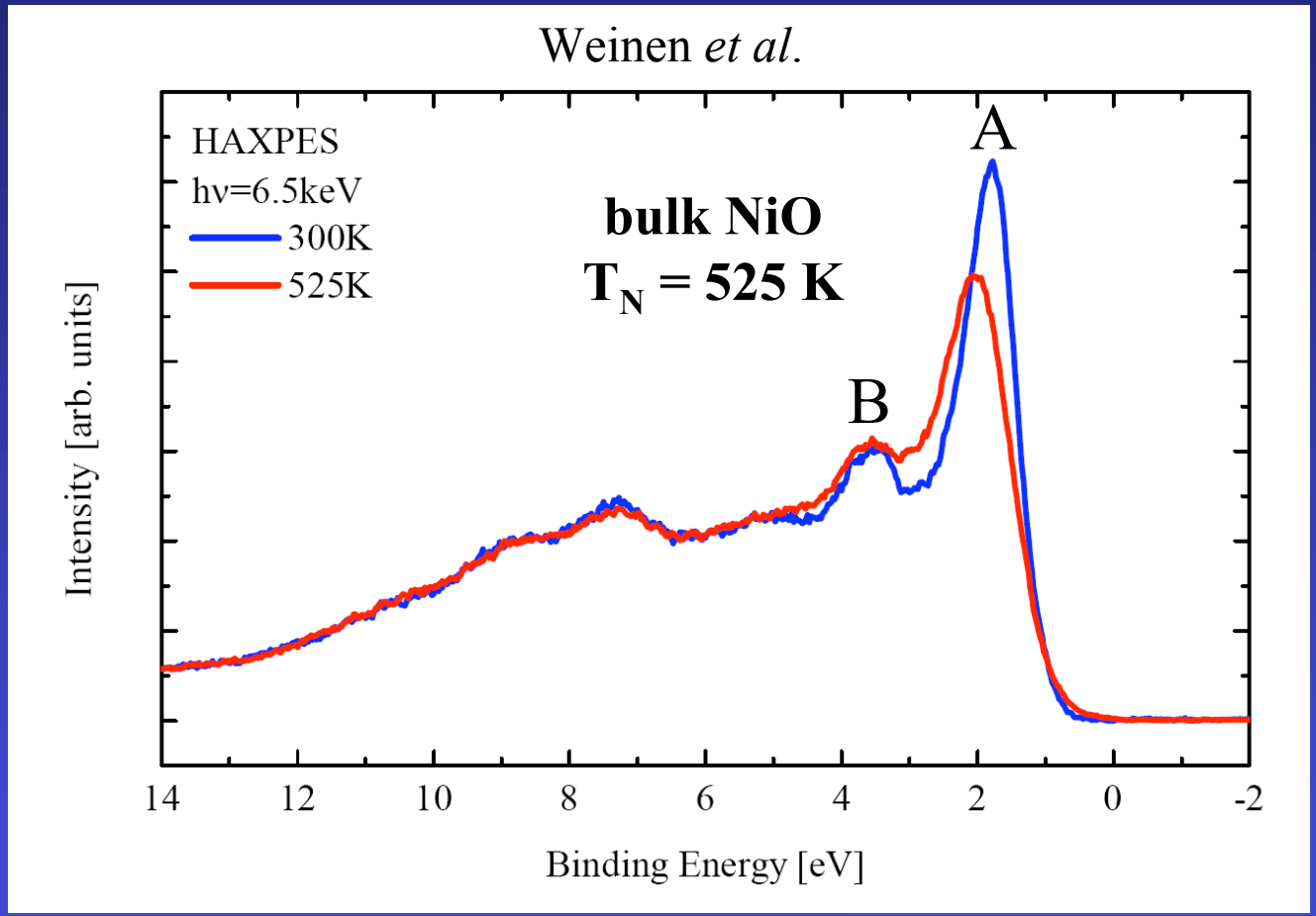
“ after“ PES

Haupricht, Weinen *et al.*



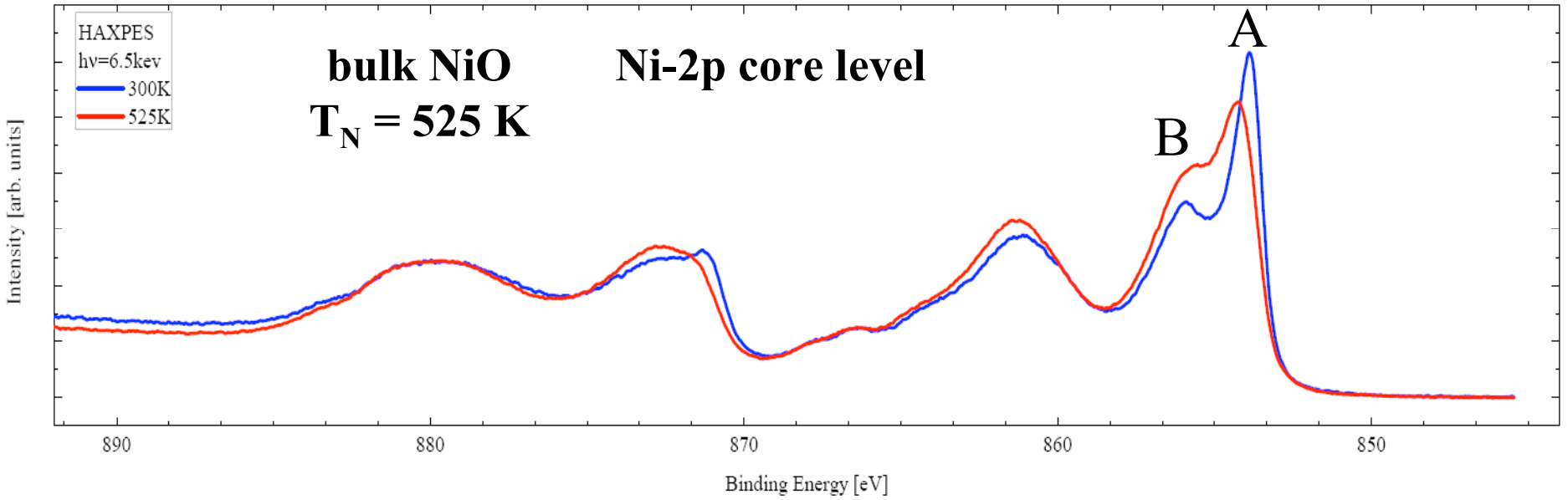
Screening from a neighboring Ni cluster,
creating a *many-body* hole state (‘ZRS‘)

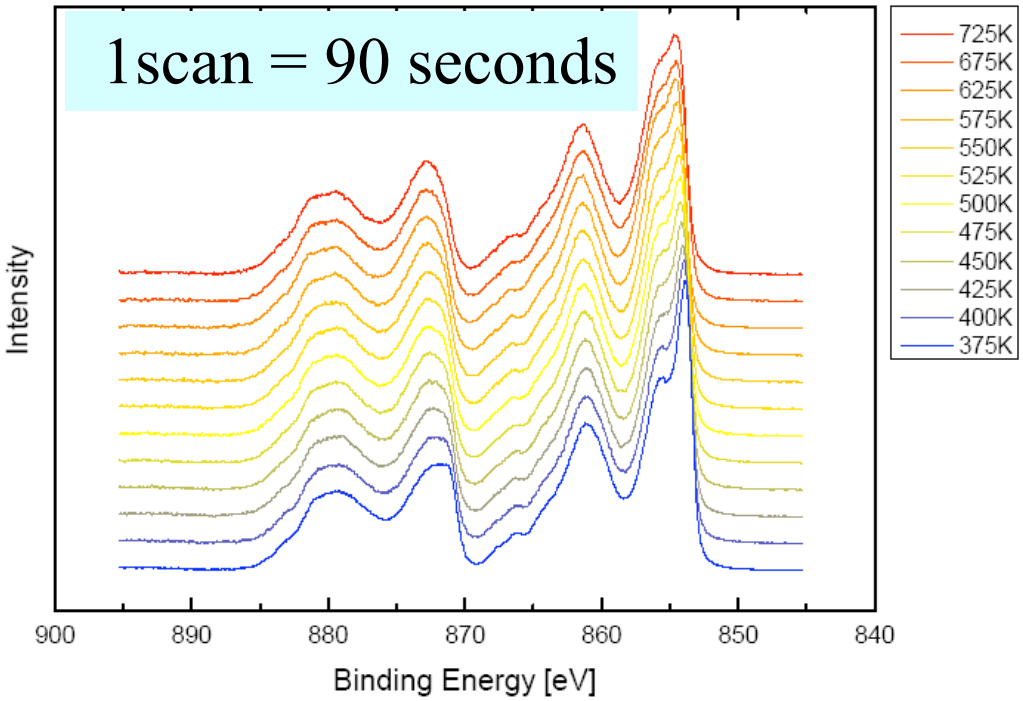
Testing non-local screening model: temperature dependence ?

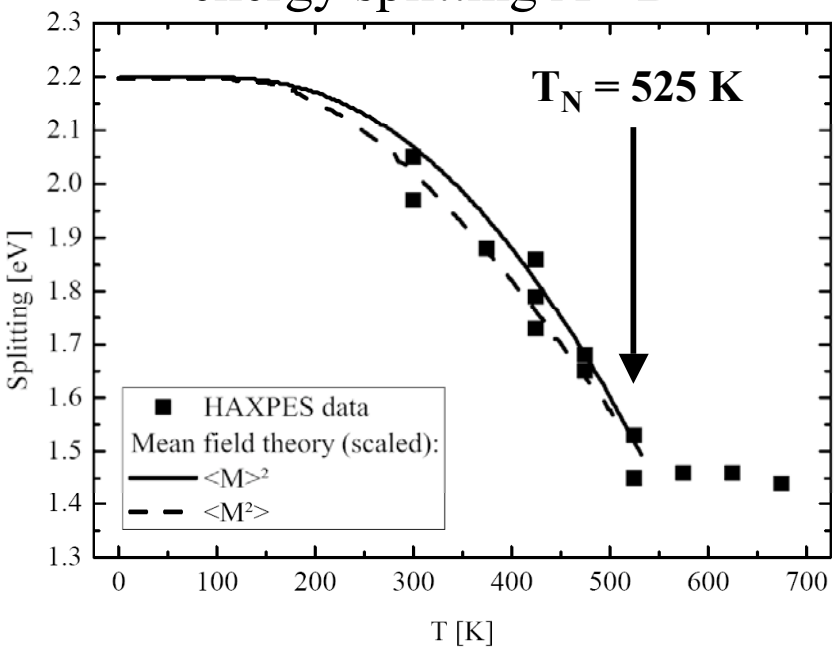


Screening is reduced above T_N :
indeed, screening needs AF nearest neighbor spin alignment !

Weinen *et al.*


HAXPES
hν=6.5kev
300K
525K
bulk NiO
T_N = 525 K
Ni-2p core level
A
B
Intensity [arb. units]
890
880
870
860
850
Binding Energy [eV]


1scan = 90 seconds
725K
675K
625K
575K
550K
525K
500K
475K
450K
425K
400K
375K
Intensity
900
890
880
870
860
850
840
Binding Energy [eV]


energy splitting A - B
T_N = 525 K
Splitting [eV]
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
HAXPES data
Mean field theory (scaled):
<M>²
<M²>
0
100
200
300
400
500
600
700
T [K]

Concluding remarks:

$LaCoO_3$: a prototype spin state transition material
- full atomic multiplet theory is necessary
- influence of lattice is important

NiO: simple AFI system but very complex electronic structure
- correlations, multiplets, band formation, screening
- charge transfer insulator, compensated-spin 1st ionization state

Soft-x-ray absorption spectroscopy (XAS/MCD):
- extremely sensitive to valence, spin and orbital state

Photoelectron spectroscopy:
- very sensitive to short-range spin-spin correlations