Synchrotron Radiation Spectroscopy of Colossal Magnetoresistive Oxides and Buried Magnetic Interfaces— Some Recent Results and Some New Directions Relevant to the APS (0.5-10 keV)

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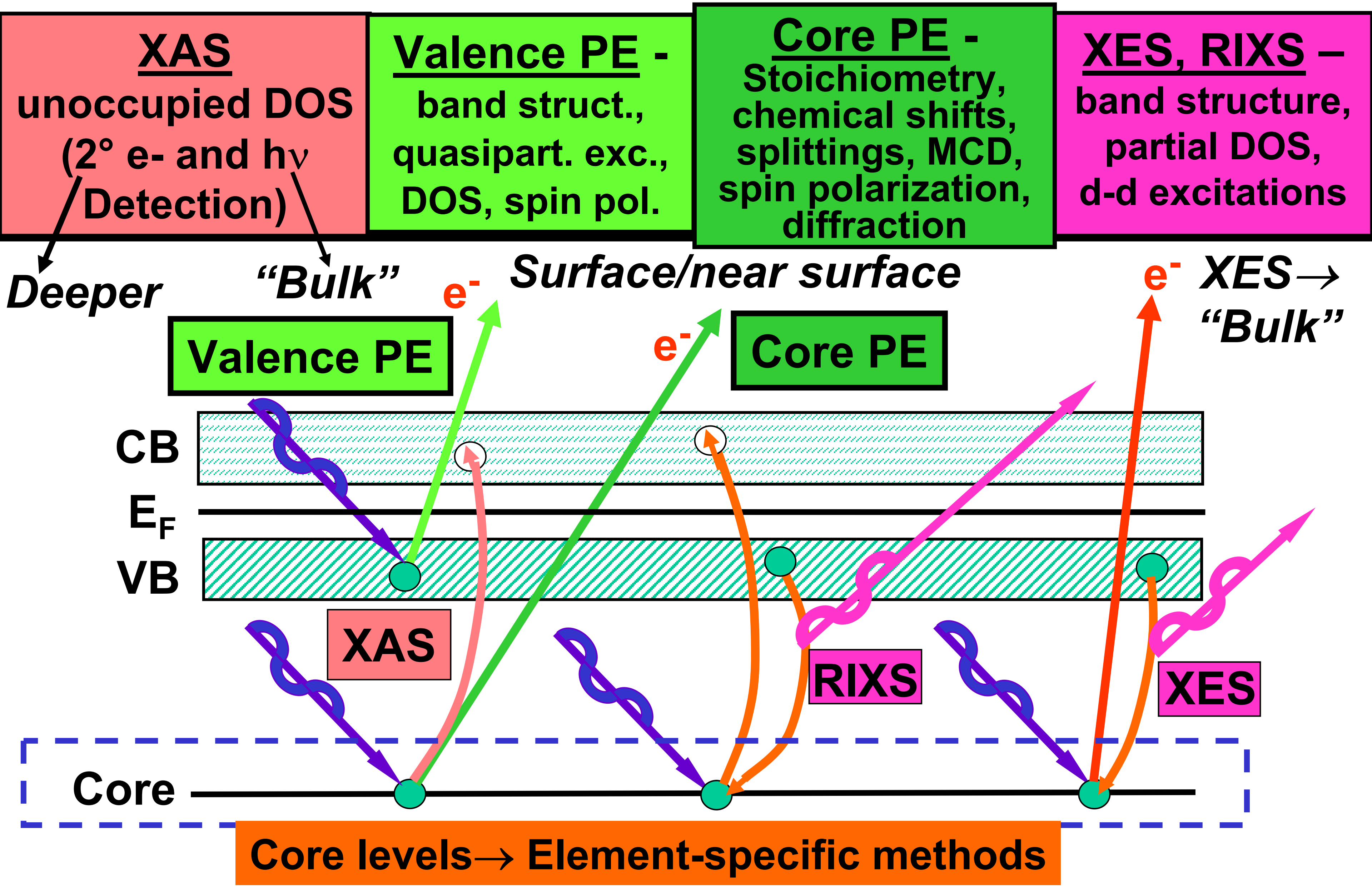
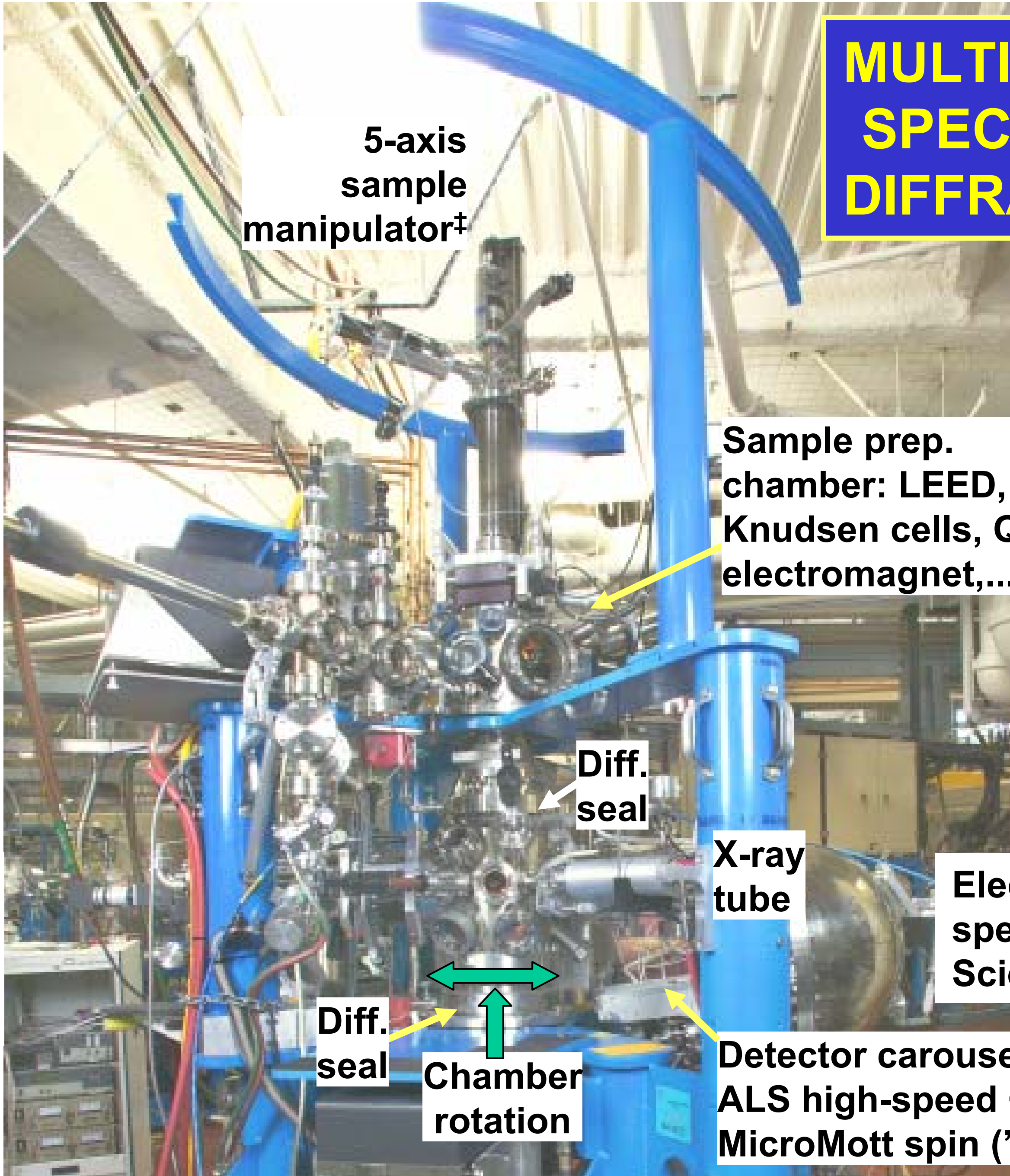
- Instrumentation and detectors
- Multiple spectroscopies applied to CMR manganites
- X-ray standing wave studies of buried interfaces
- Summary and some thoughts for a future APS

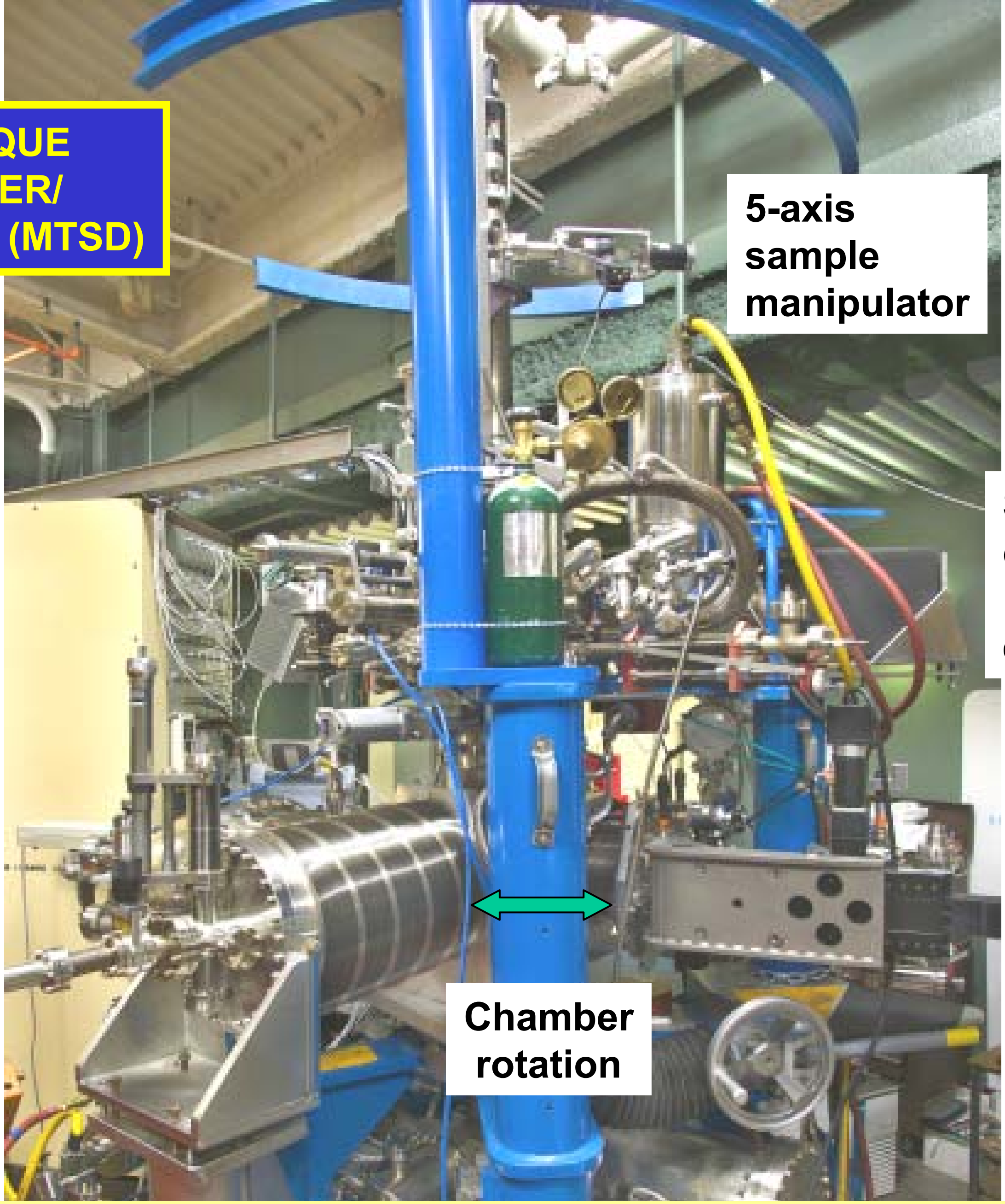
The Soft (and Hard) X-Ray Spectroscopies



MULTI-TECHNIQUE SPECTROMETER/ DIFFRACTOMETER

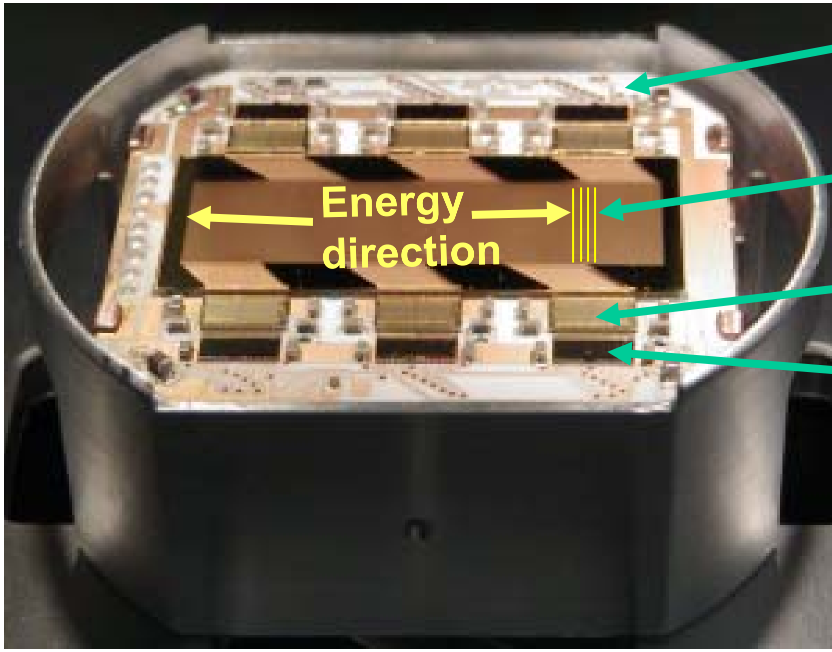


MULTI-TECHNIQUE SPECTROMETER/ DIFFRACTOMETER (MTSD)



Permits using all relevant soft x-ray spectroscopies on a single sample: PS, PD, PH; XAS (e^- or photon detection), XES/RIXS in MCD, MLD

Next Generation Detection: ALS High-Speed Detector



Ceramic substrate

768 collector strips

Amplifier/discriminator chip (CAFE-M) from HEP

Buffered multichannel counter chip (BMC)

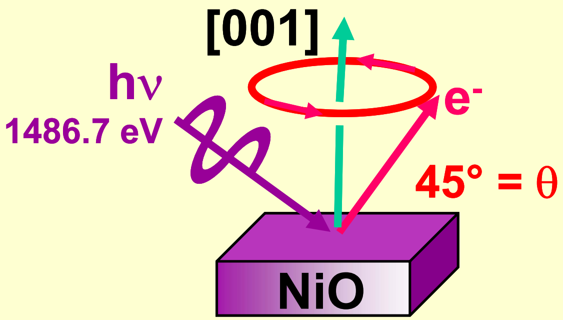
Microchannel plates

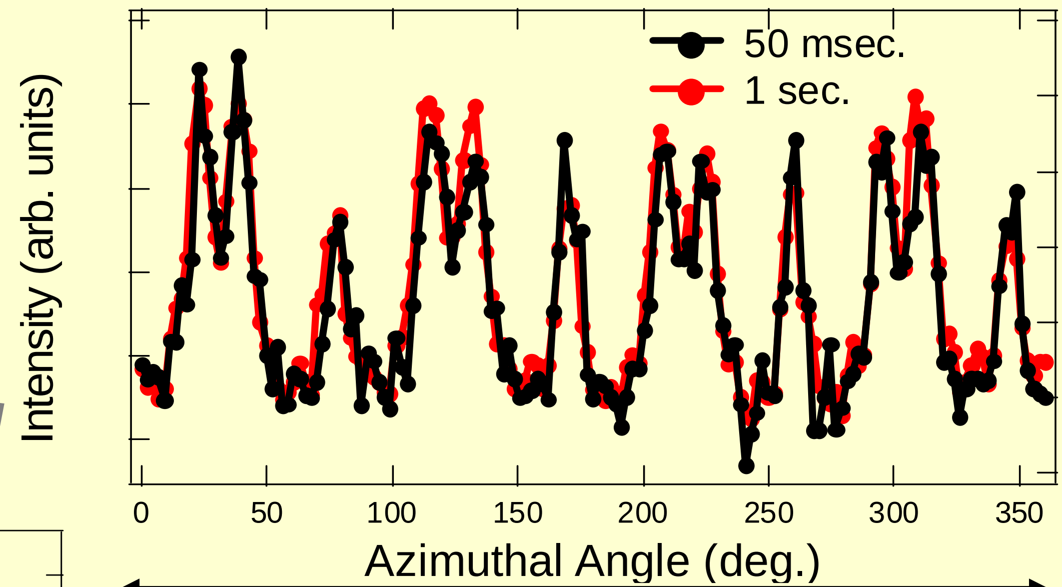
e^-, $h\nu$

- **Basic specifications:**
  - 768 channels along one dimension
  - ~75 micron spatial resolution
  - >2 GHz overall linear count-rate→ 100-1000x faster than present
  - spectral readout in as little as 200 μs→ time-resolved measurements
  - programmable, robust
- **Operating since July, 2003, improvements underway: HV insulation, memory buffering**

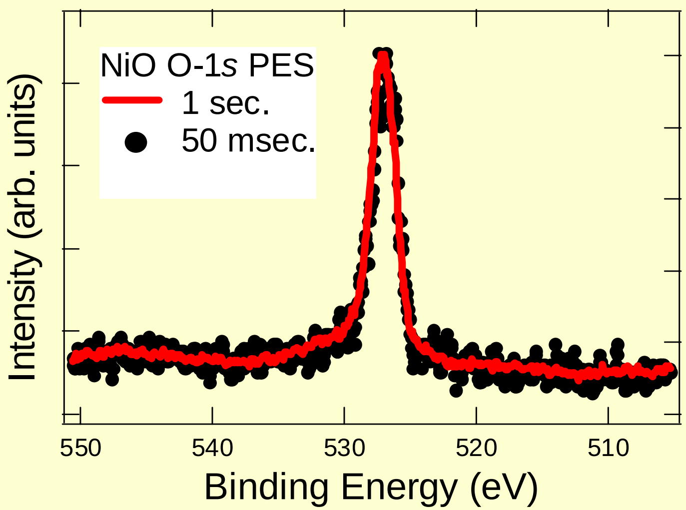
ALS High-Speed Detector: Some First Data

Photoelectron Diffraction from NiO(001)





O 1s Spectrum



~150 spectra

Total 2 min. @ 50 msec/spectrum
→7 sec. without CPU process time.
With future data buffering:
→ 30 ms total @ 200 μs/spectrum

→Time-resolved PS studies of magnetic nanostructures?

Direct Observation of Electronic Structure Changes and Polaron Formation on Going Above the Curie Temperature in $La_{1-x}Sr_xMnO_3$ Colossal Magnetoresistive Oxides

Norman Mannella[1,2], A. Rosenhahn[2], C. H. Booth[3], S. Marchesini[2], B.S. Mun[1,2,4], S.-H. Yang[2], J. Guo[4], M. W. West[2], A. Mei[2], Y. Tomioka[5], Y. Tokura[5], K. Ibrahim[6], E. Arenholz[4], A. Young[4], B. Sell[1,2] A. Nambu[4,7], M. Watanabe[8], S. Ritchey[1,2], J. Chen[9], A. Navrotsky[9], M. A. Van Hove[2], Z. Hussain[4], and C.S. Fadley[1,2]

Temperature-dependent study of the electronic structure of cleaved/fractured single crystals of $La_{1-x}Sr_xMnO_3$ (x = 0.3, 0.4) using core and valence photoemission, x-ray absorption, x-ray emission and x-ray extended fine structure spectroscopies

Mannella et al.,
Phys. Rev. Lett. 92,
166401 (2004)

Some key questions

Changes in the electronic structure on passing T_C?

Jahn-Teller instabilities $\rightarrow$ electron localization effects via polarons?

Short-range magnetic order vs. long-range magnetic order?

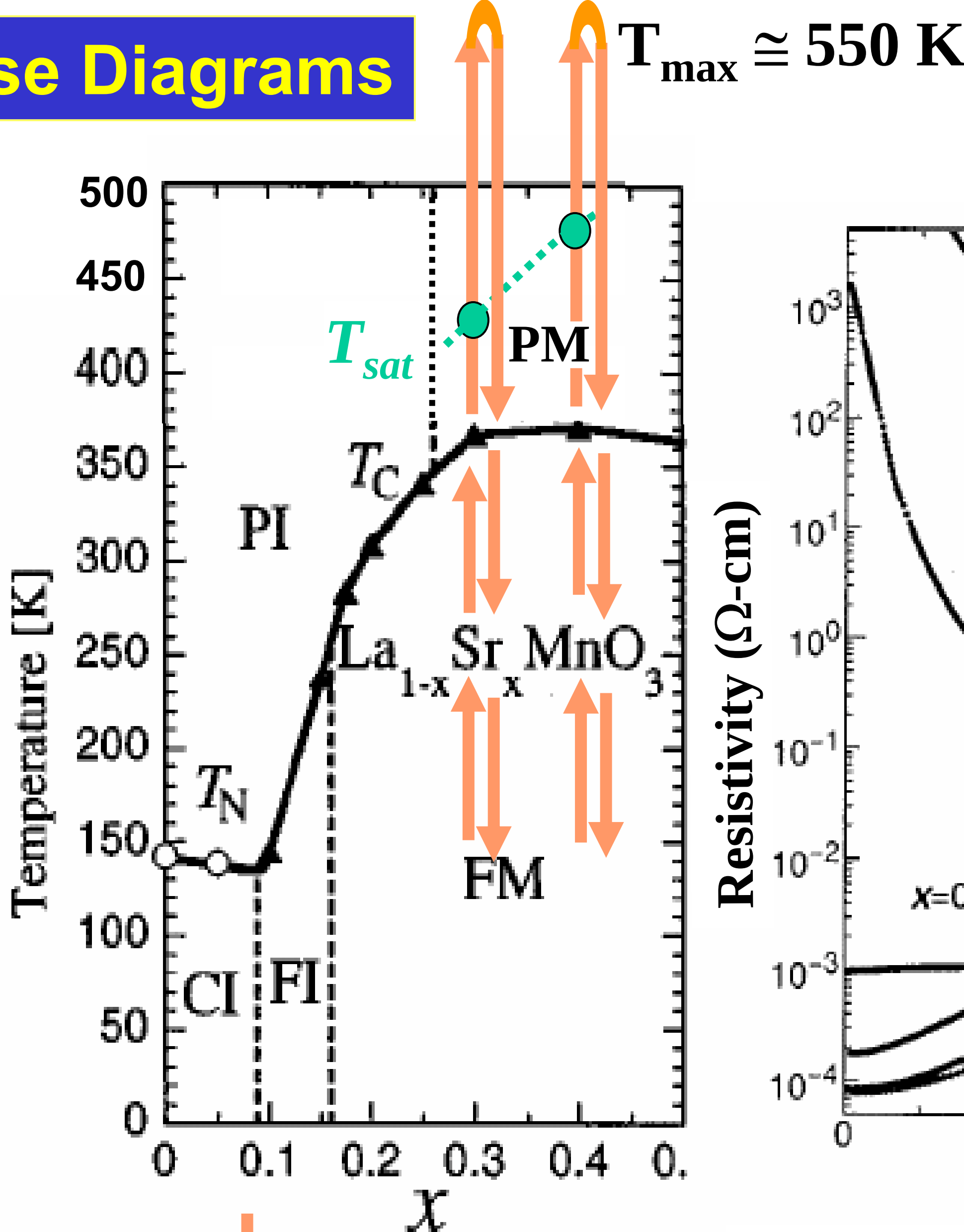
Phase separation/Griffiths phases?

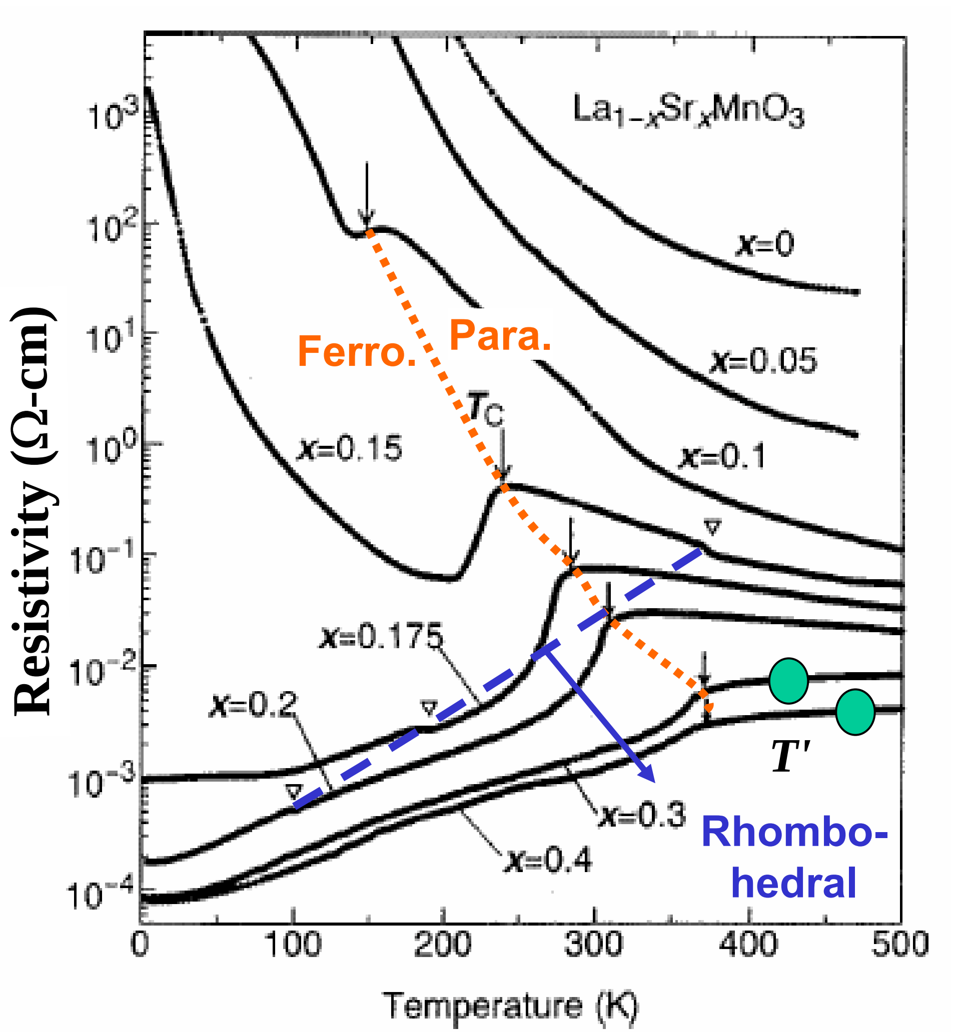
Coupling of charge, spin, orbital occupation, lattice (Jahn-Teller, strain),?

Effects on conductivity, heat capacity, …?

Properties of interfaces in multilayers, other nanostructures?

Phase Diagrams



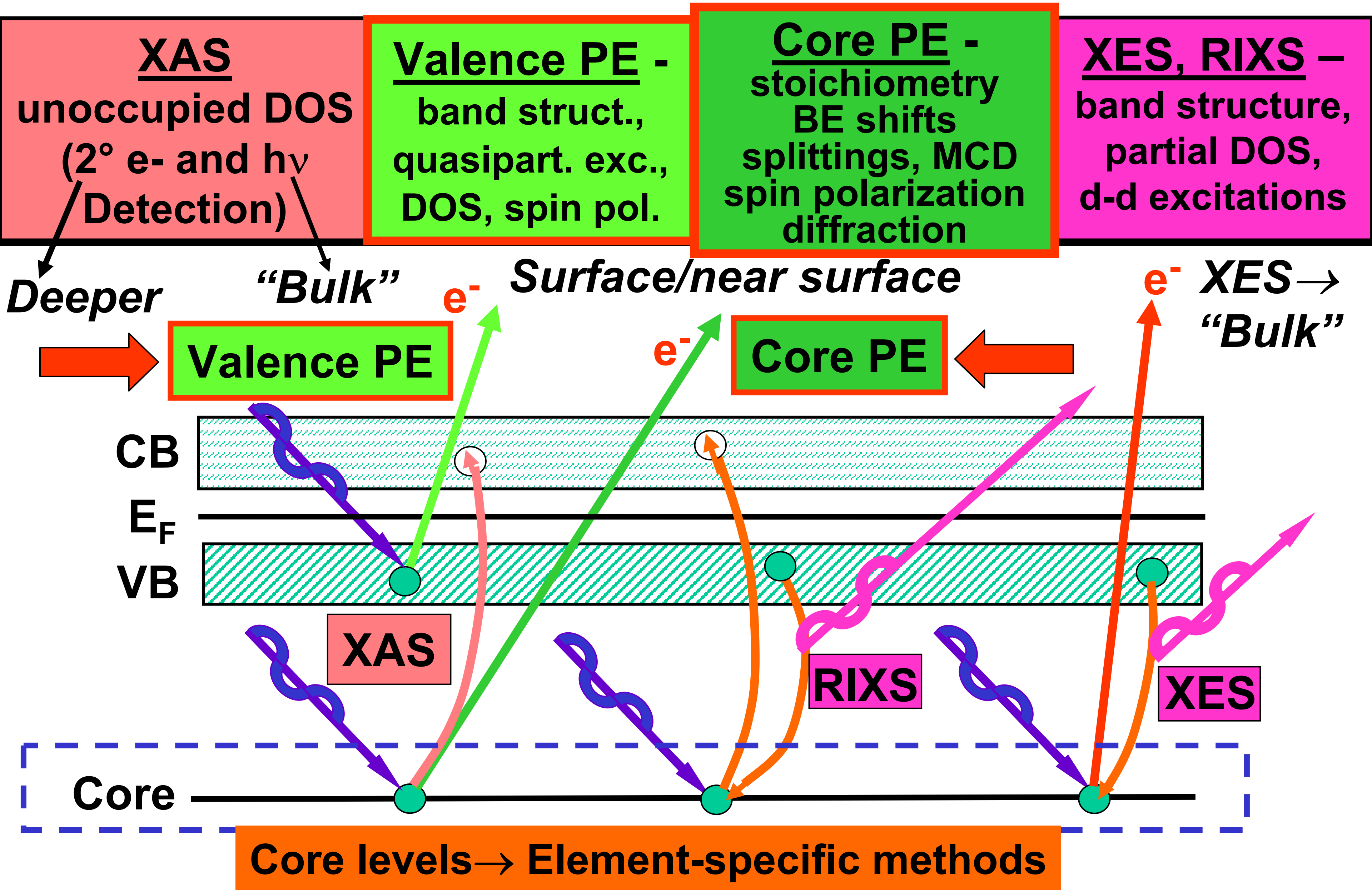


= lines measured in this work

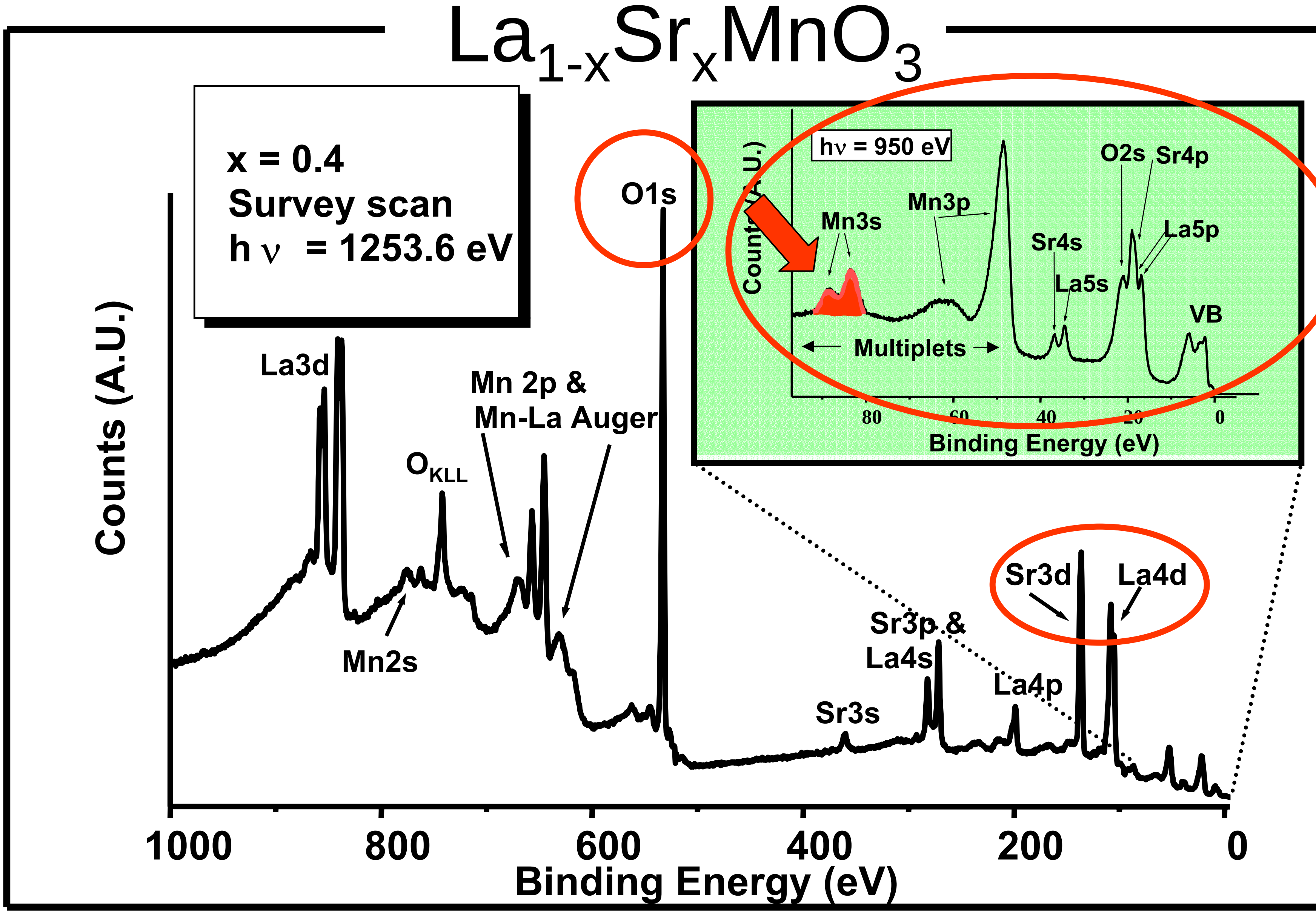
Urushibara *et al.*, PRB 51 14103, 1995

Surfaces fractured in UHV:
Very stable via XPS

The Soft X-Ray Spectroscopies



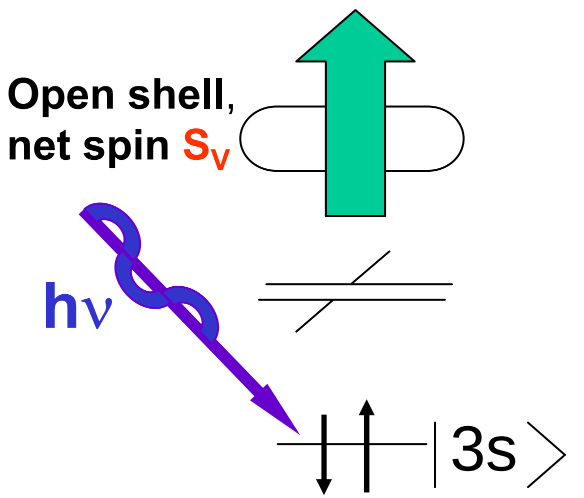
Core and valence photoemission

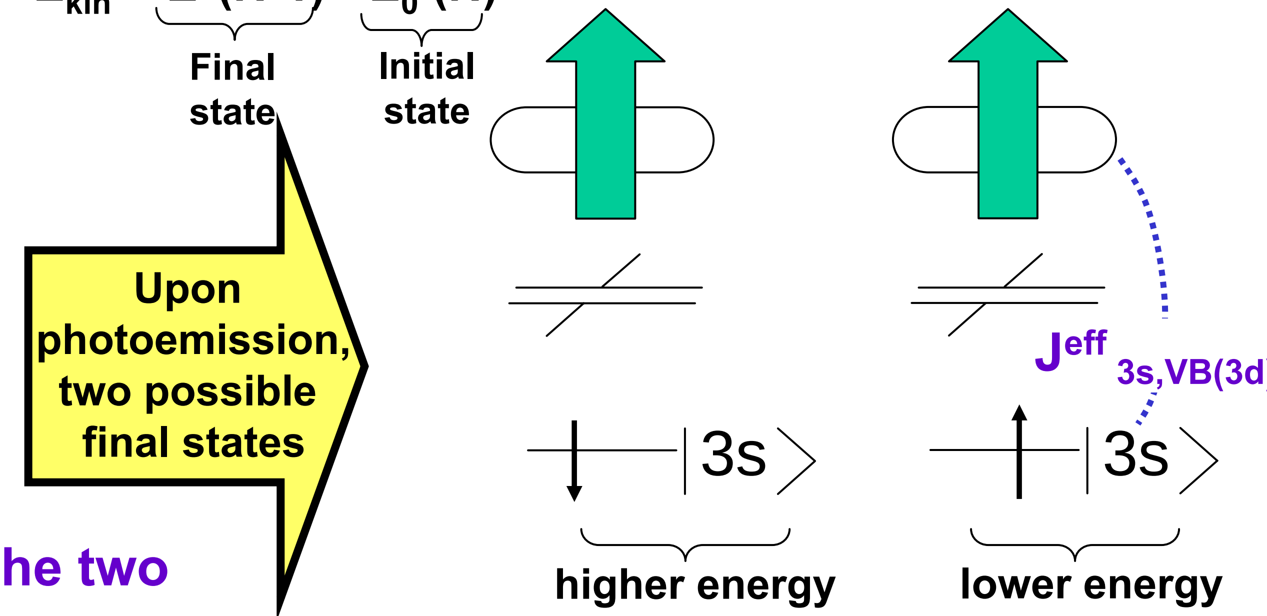


= Spectra recorded during temperature-dependent measurements

Multiplet splitting in core levels of transition metal oxides

$$BE = h\nu - E_{kin} = \underbrace{E^*(N-1)}_{\text{Final state}} - \underbrace{E_0\,(N)}_{\text{Initial state}}$$





The splitting between the two peaks is given by

$$\Delta E_{3s} \approx (2S_V + 1)\, J^{eff}_{3s,VB(3d)}$$

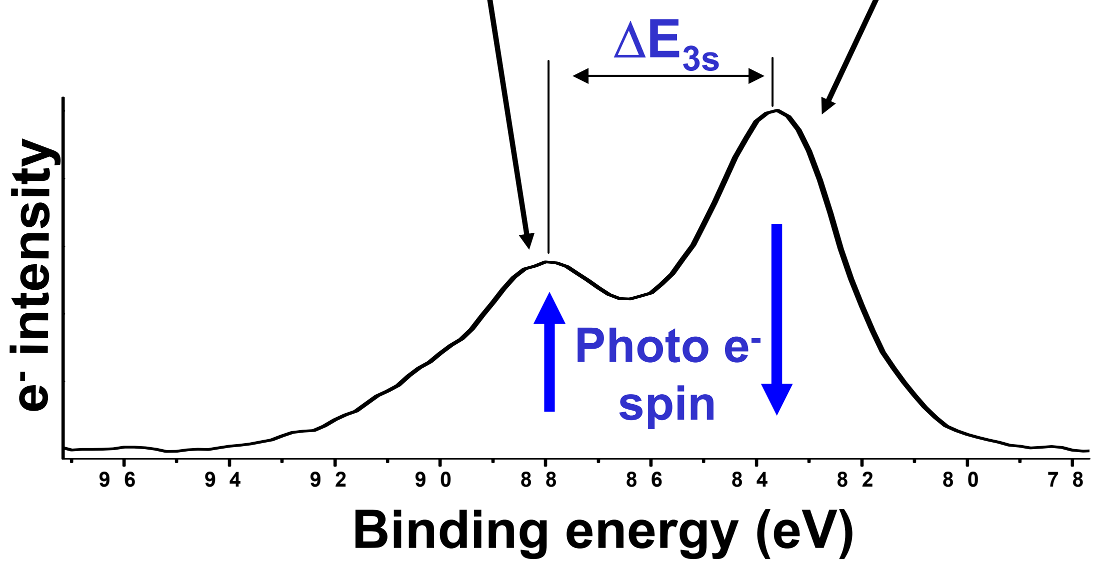
(Van Vleck Theorem)

For the cubic manganites in simplest doping model,

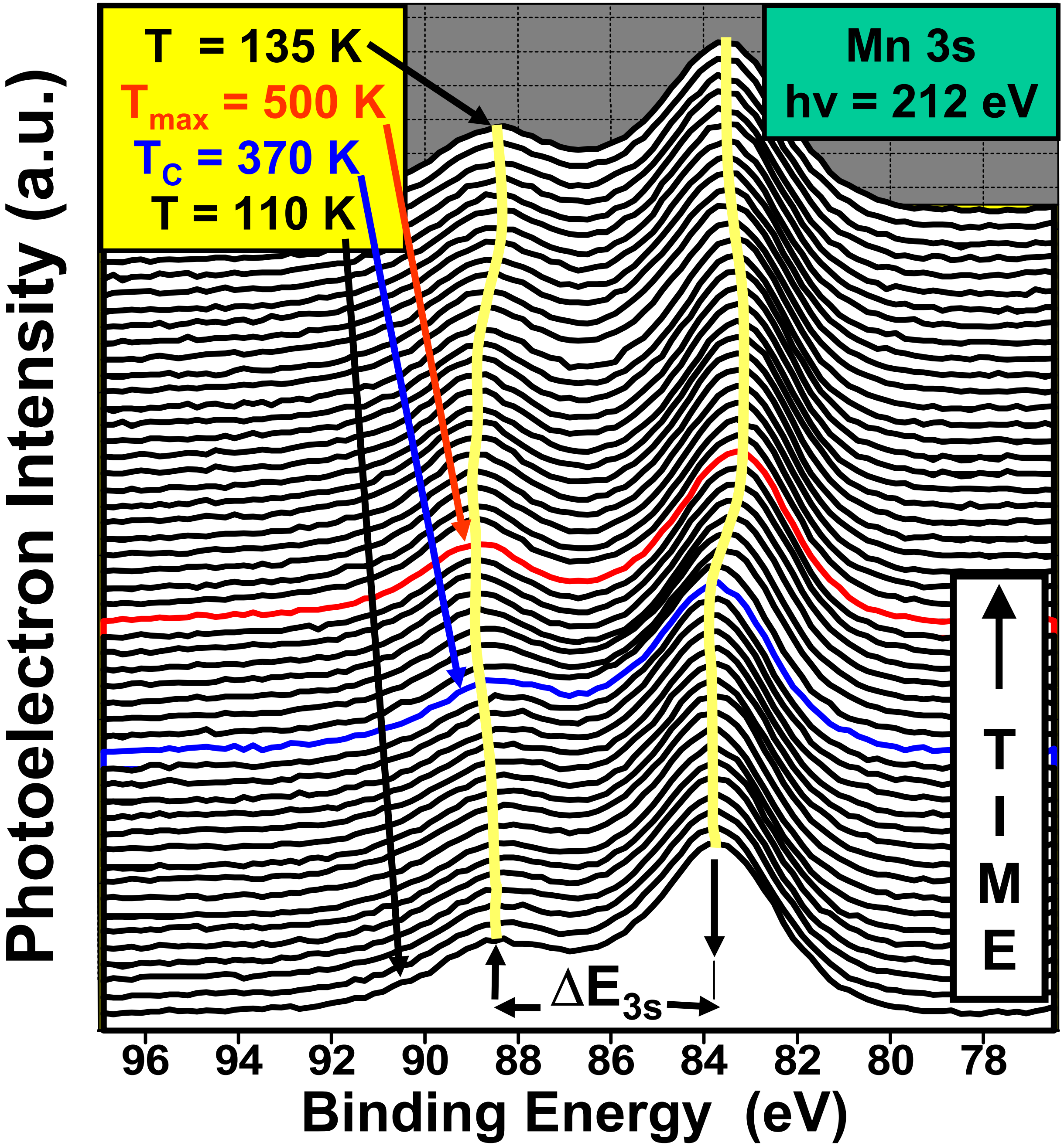
$S_V = 1/2(4-x) \rightarrow$

$\Delta E_{3s} \approx [5-x]\, J^{eff}_{3s,\, VB)3d)}$

with $J^{eff}_{3s,\, VB} \approx 1.1$ eV



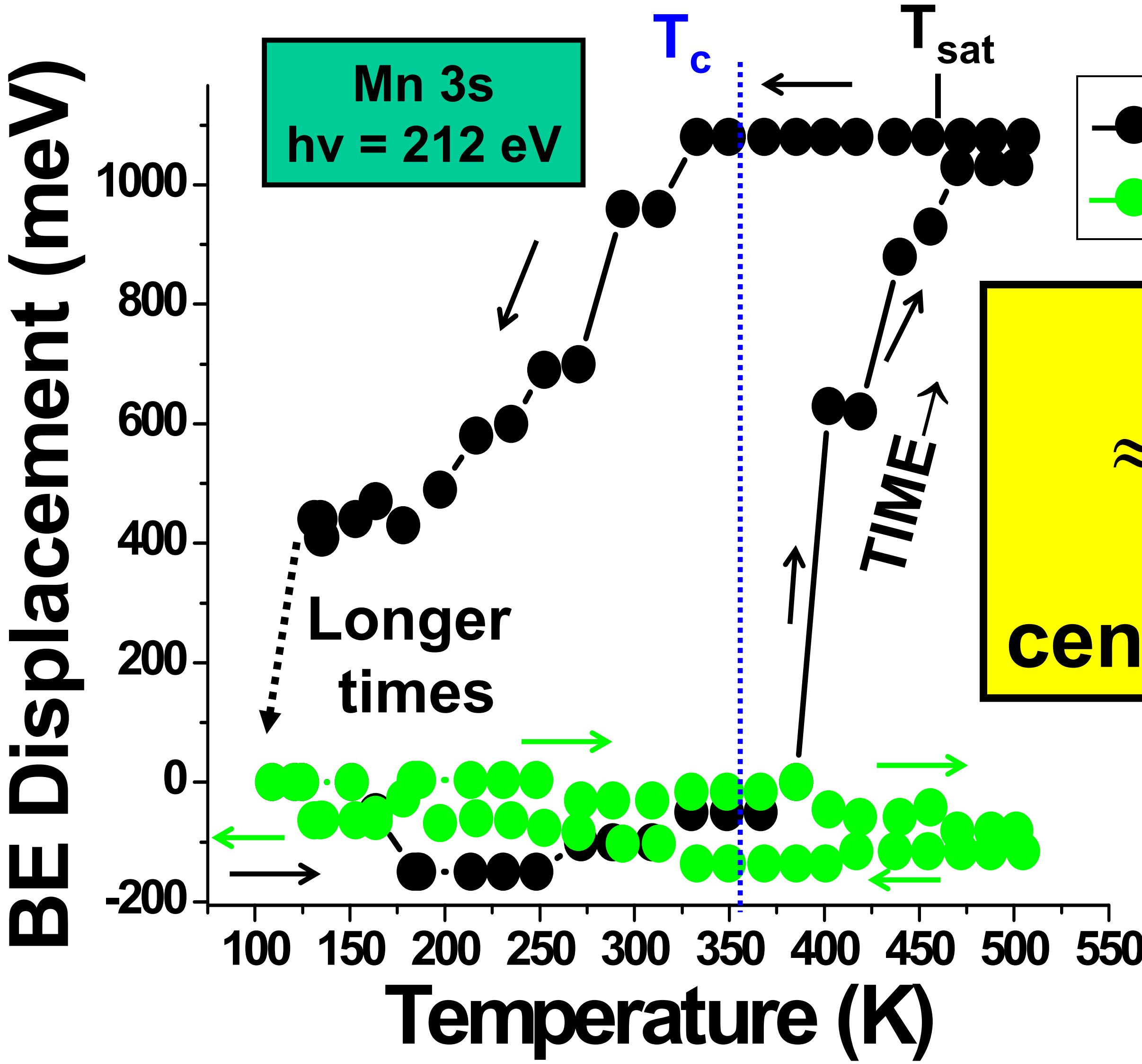
Temperature dependence of Mn3s spectra



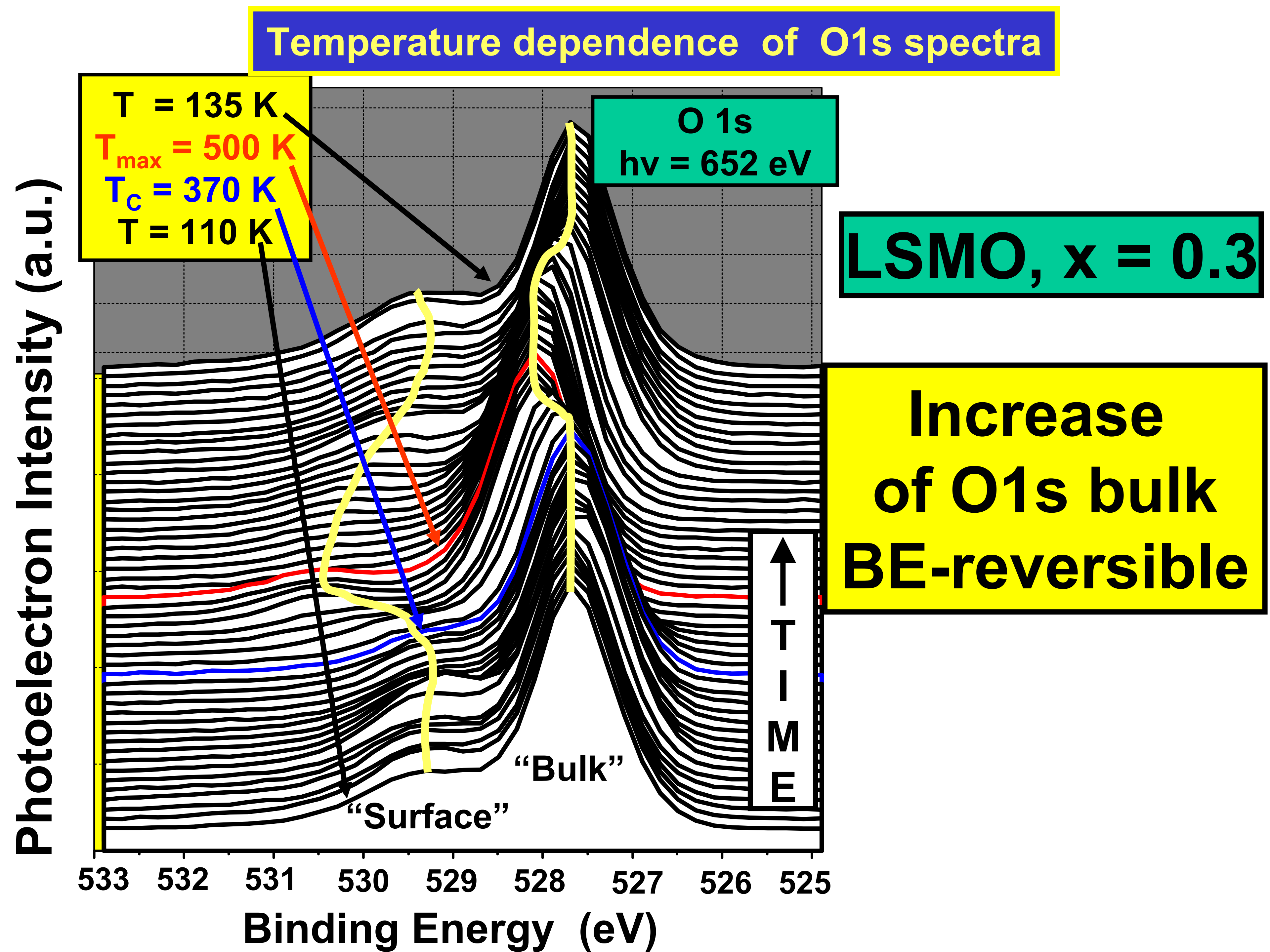
LSMO, x = 0.3

Increase of the Mn3s splitting- reversible

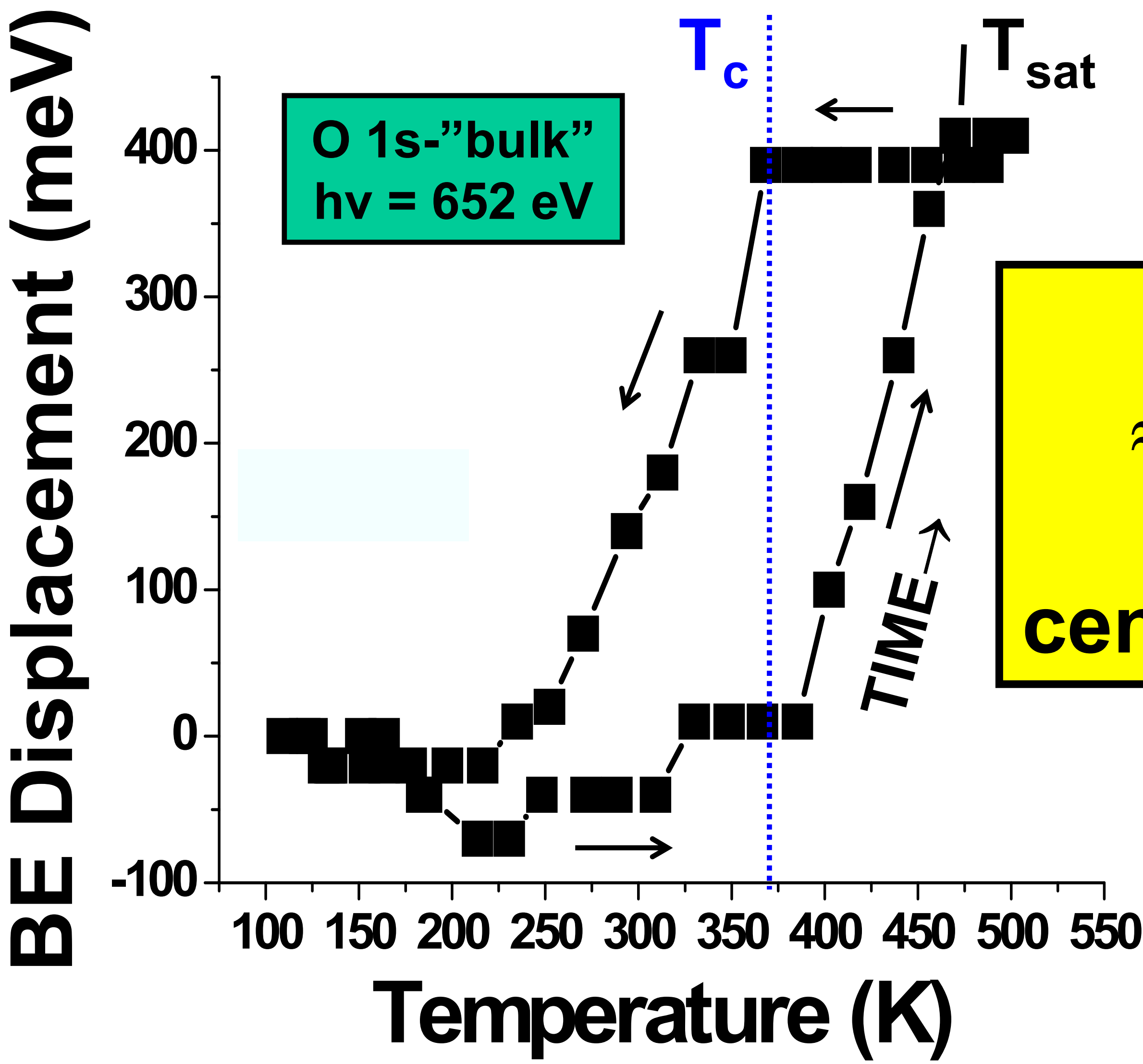
Mn 3s--Average binding energy displacement and multiplet separation vs. Temperature: Hysteresis cycle for LSMO, x = 0.3



Reversible ≈ 200 K – wide hysteresis centered around T_C


Temperature dependence of O1s spectra
T = 135 K
T_max = 500 K
T_C = 370 K
T = 110 K
O 1s
hv = 652 eV
LSMO, x = 0.3
Increase of O1s bulk BE-reversible
TIME
"Bulk"
"Surface"
Photoelectron Intensity (a.u.)
533 532 531 530 529 528 527 526 525
Binding Energy (eV)

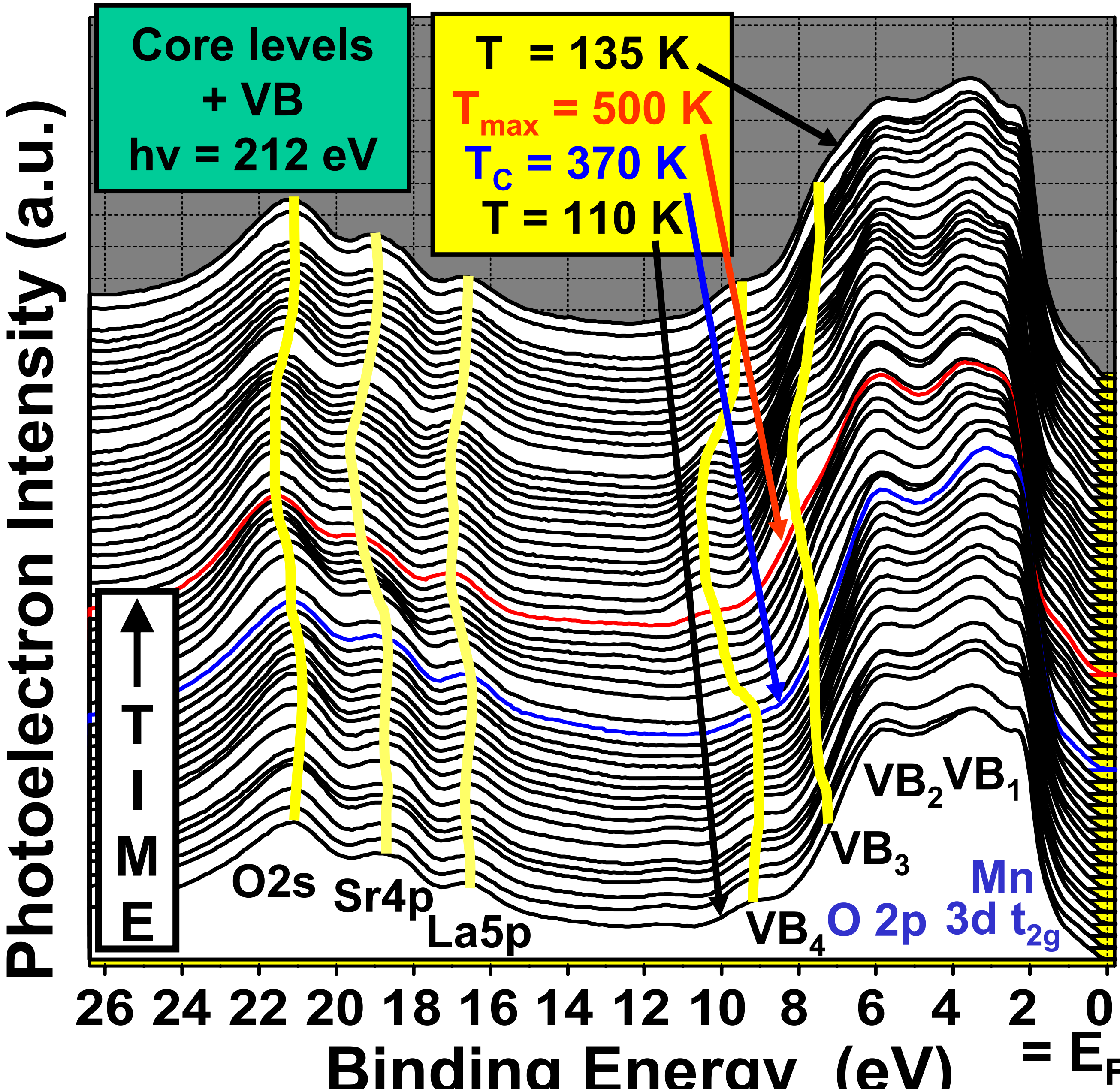
O 1s--Binding Energy Displacement vs. Temperature: Hysteresis cycle for LSMO, x = 0.3



Reversible ≈ 200 K – wide hysteresis centered around T_C

Temp. dependence of core and VB spectra

LSMO, x = 0.3



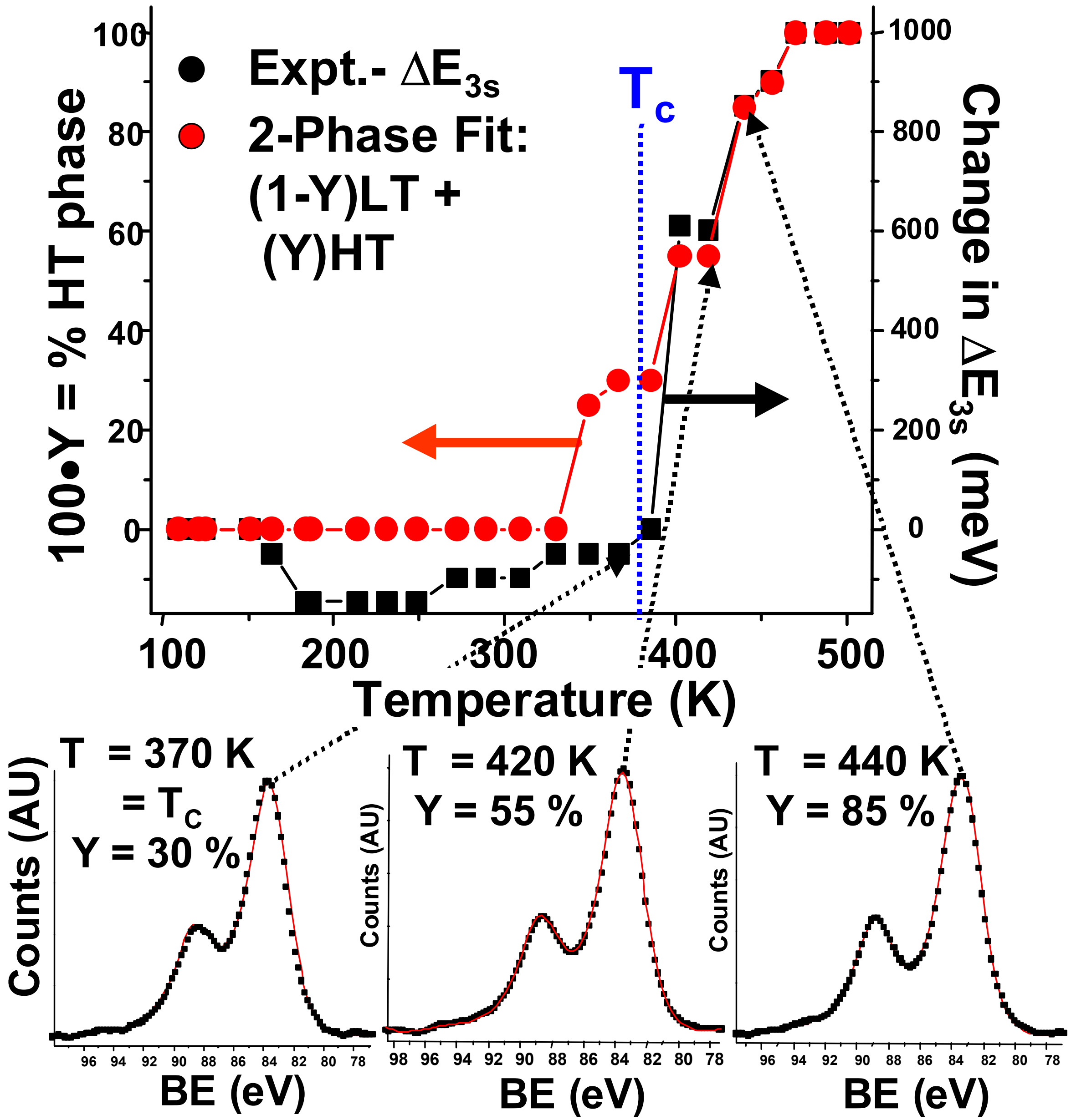
On passing $T_C \rightarrow T_{sat}$:

- Large increase (≈1 eV) of the Mn3s splitting
- Significant increases (.45-.65 eV) in BEs of other core levels
- Broadening in VB
- Slow hysteresis (hours)
- No shift in E_F → no charging

⬇

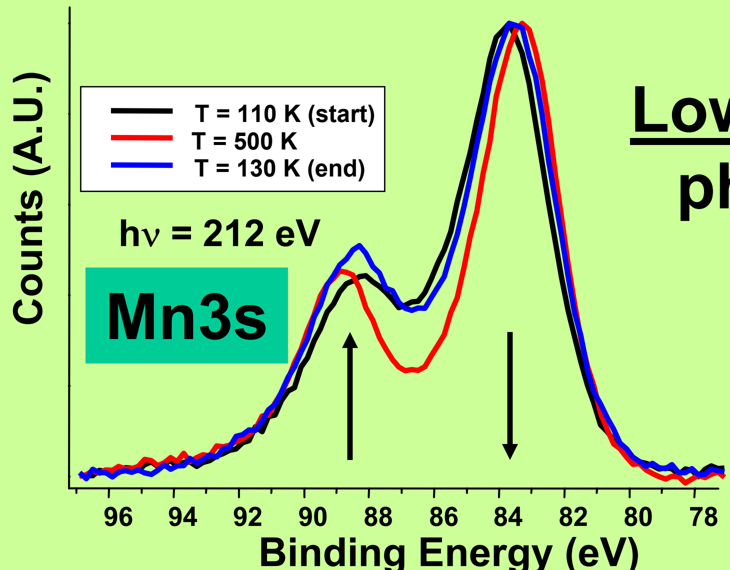
- Increase of effective Mn spin moment (~ 1.2 μ_B)
- Charge transferred to Mn (~ 1.2 e^-)

Can spectra be described as mix of two-phases?



Same for O 1s, other core peaks, consistent with two-phase model, but no info. on length scale

Is this a near-surface or a bulk effect ?

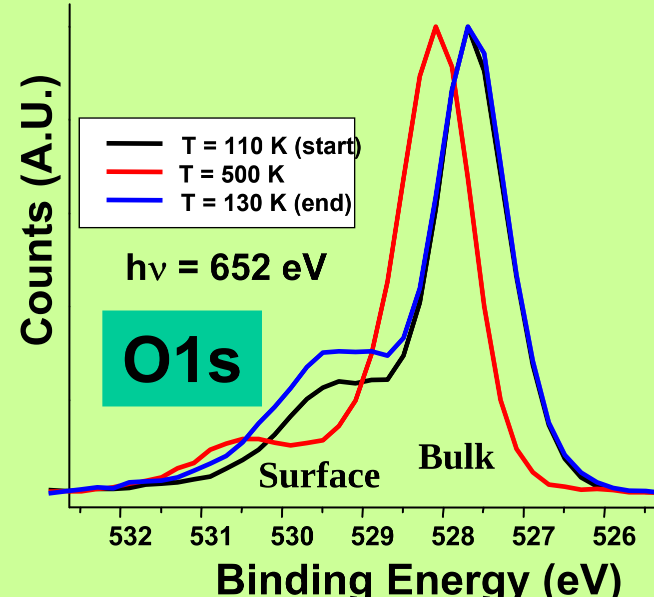


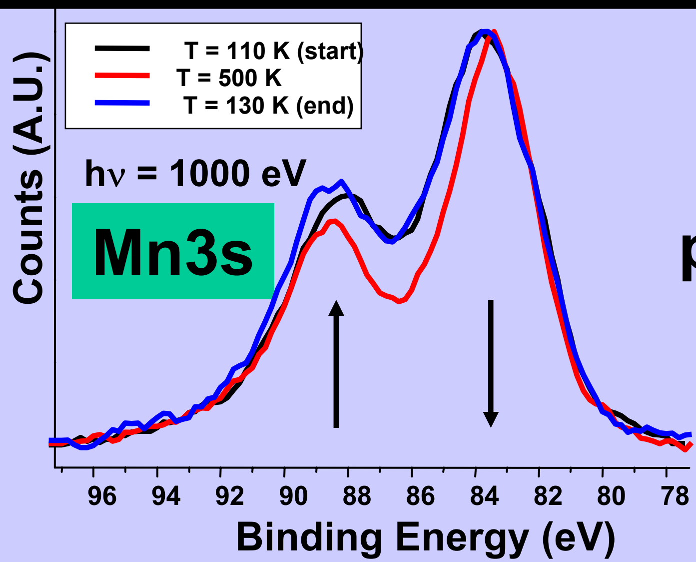
Low kinetic energy photoelectrons:

KE ≈ 130 eV

$\Lambda_e \approx 5$ Å

≈ 1 cell



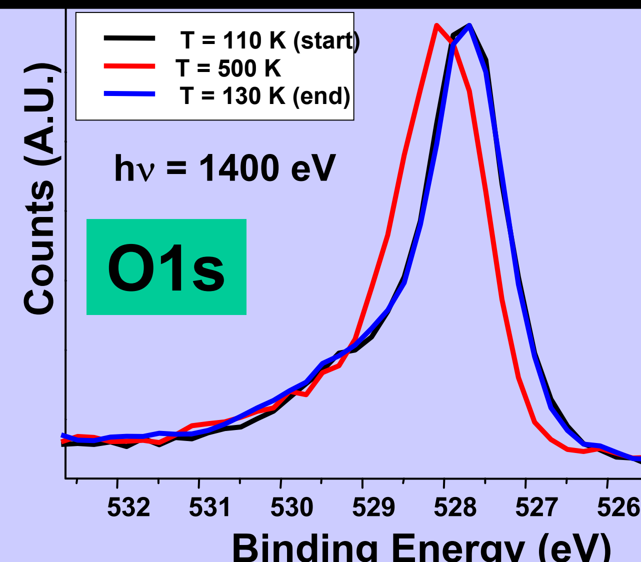


High kinetic energy photoelectrons:

KE ≈ 900 eV

$\Lambda_e \approx 15$ Å

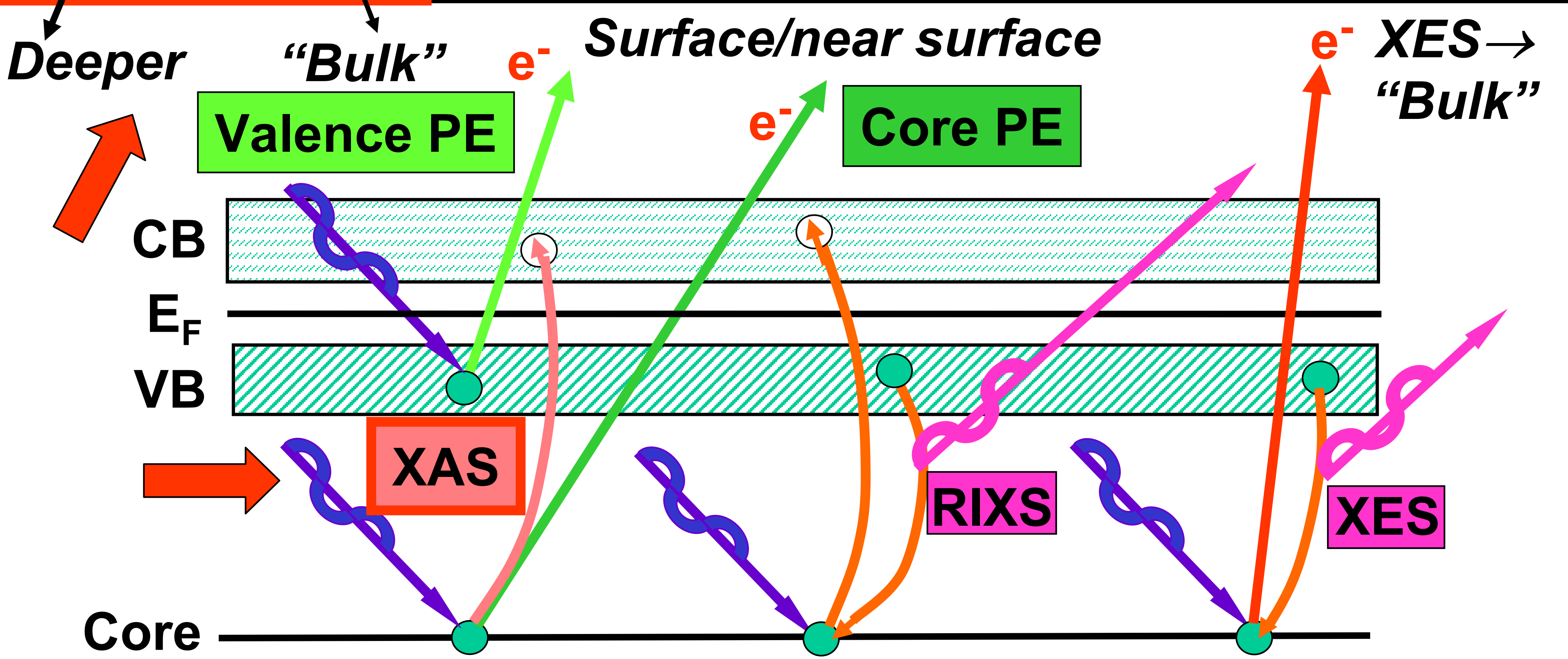
≈ 3 cells



Similar effects at high energy: effect down to at least 30 Å

The Soft X-Ray Spectroscopies

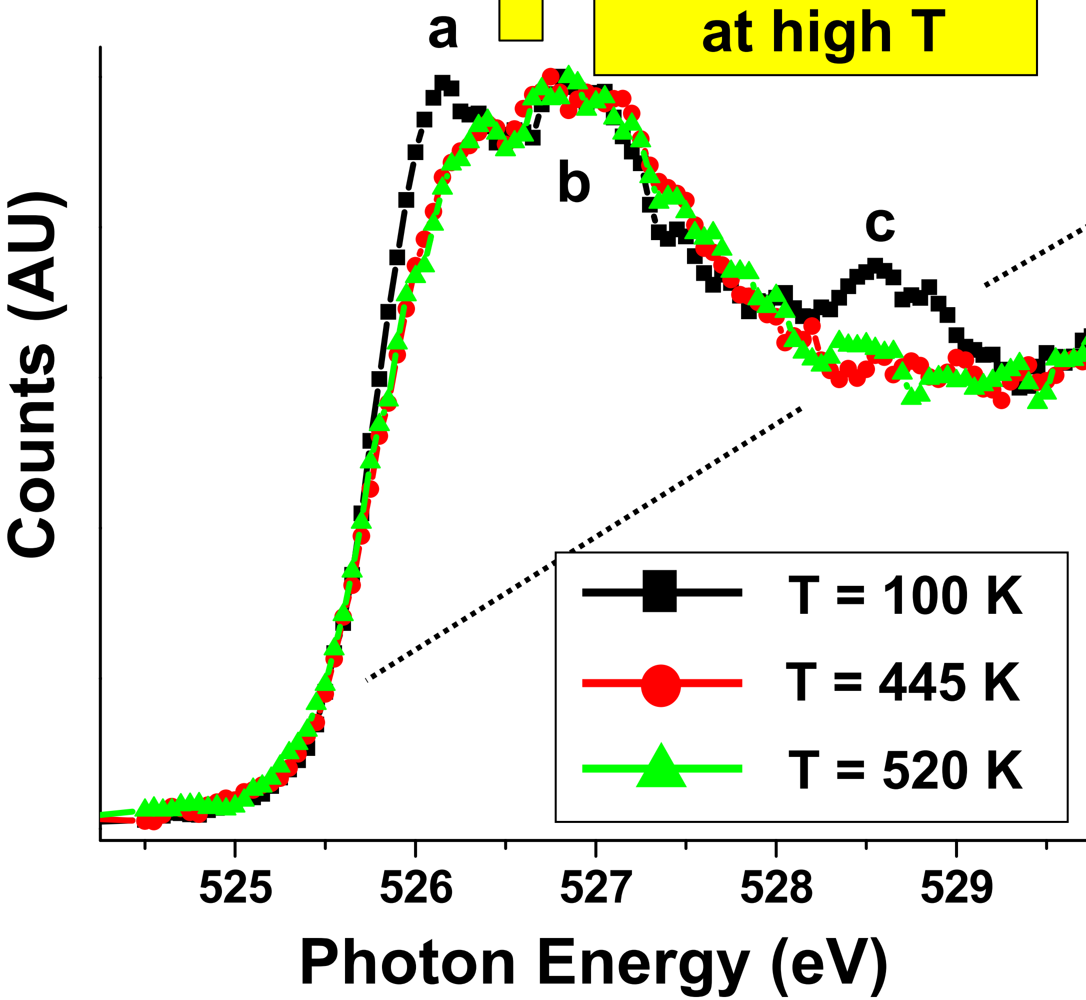
XAS	**Valence PE** -	**Core PE** -	**XES, RIXS** –
unoccupied DOS (2° e- and hν Detection)	band struct., quasipart. exc., DOS, spin pol.	stoichiometry, BE shifts, splittings, MCD, spin pol.	Band structure, PDOS, d-d excitations

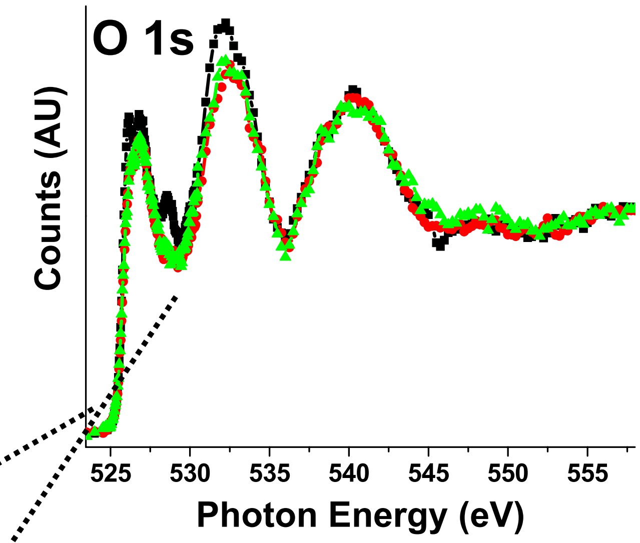


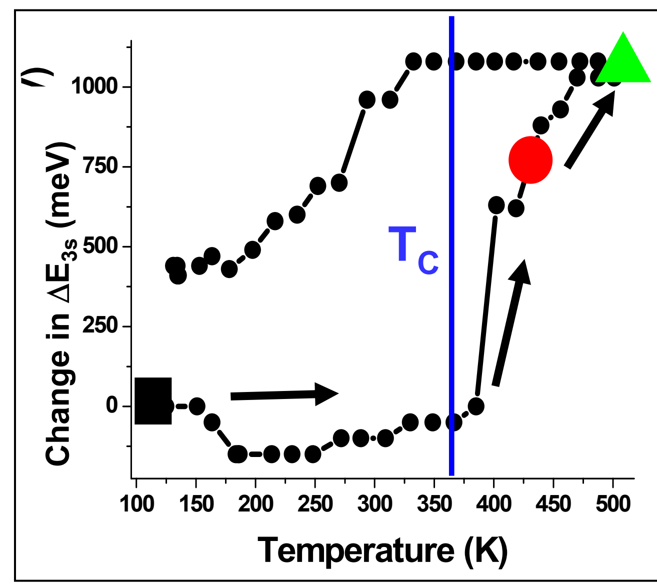
O K edge XAS
Photon detection

LSMO, x = 0.3

Also suggests Jahn-Teller at high T



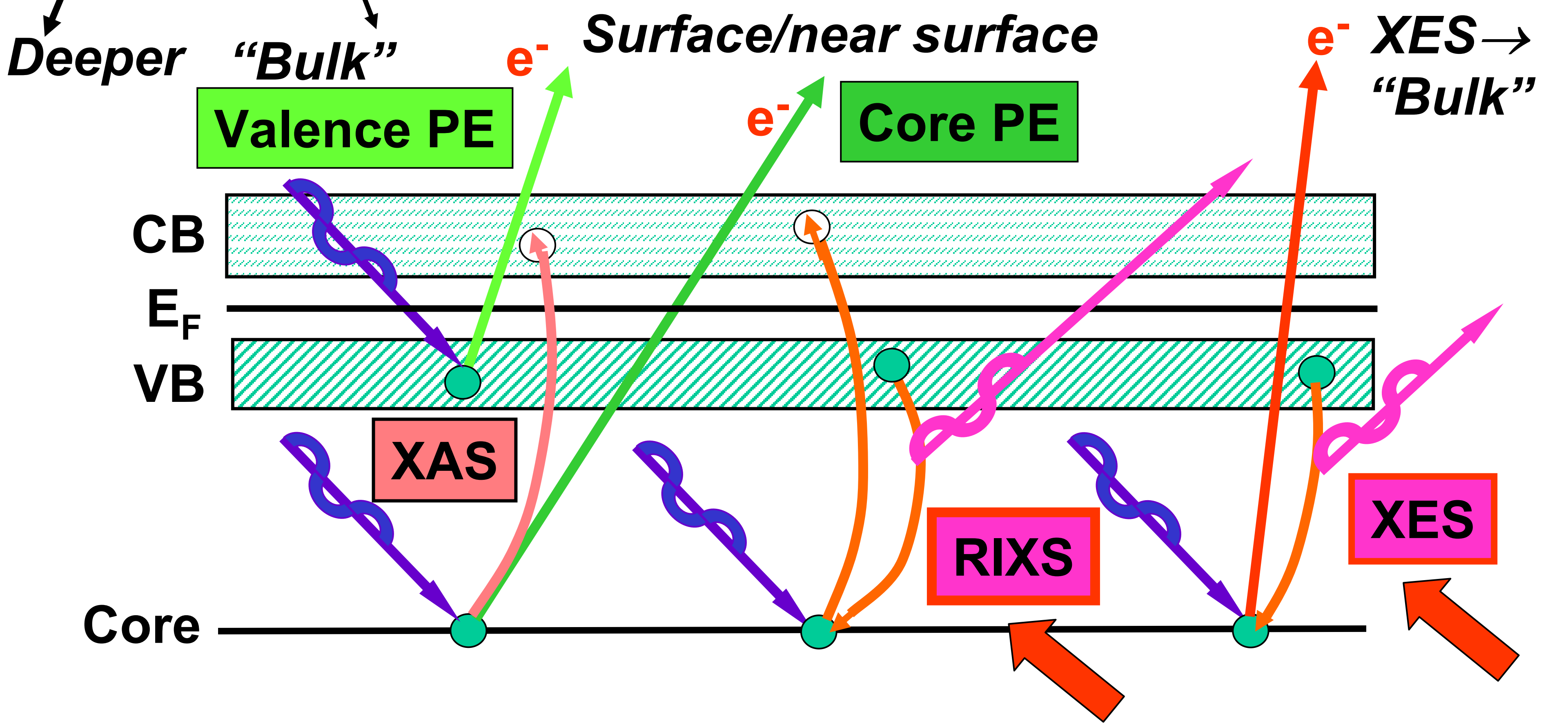




Large change on passing $T_C \rightarrow \approx 400$ Å $\approx$ bulk

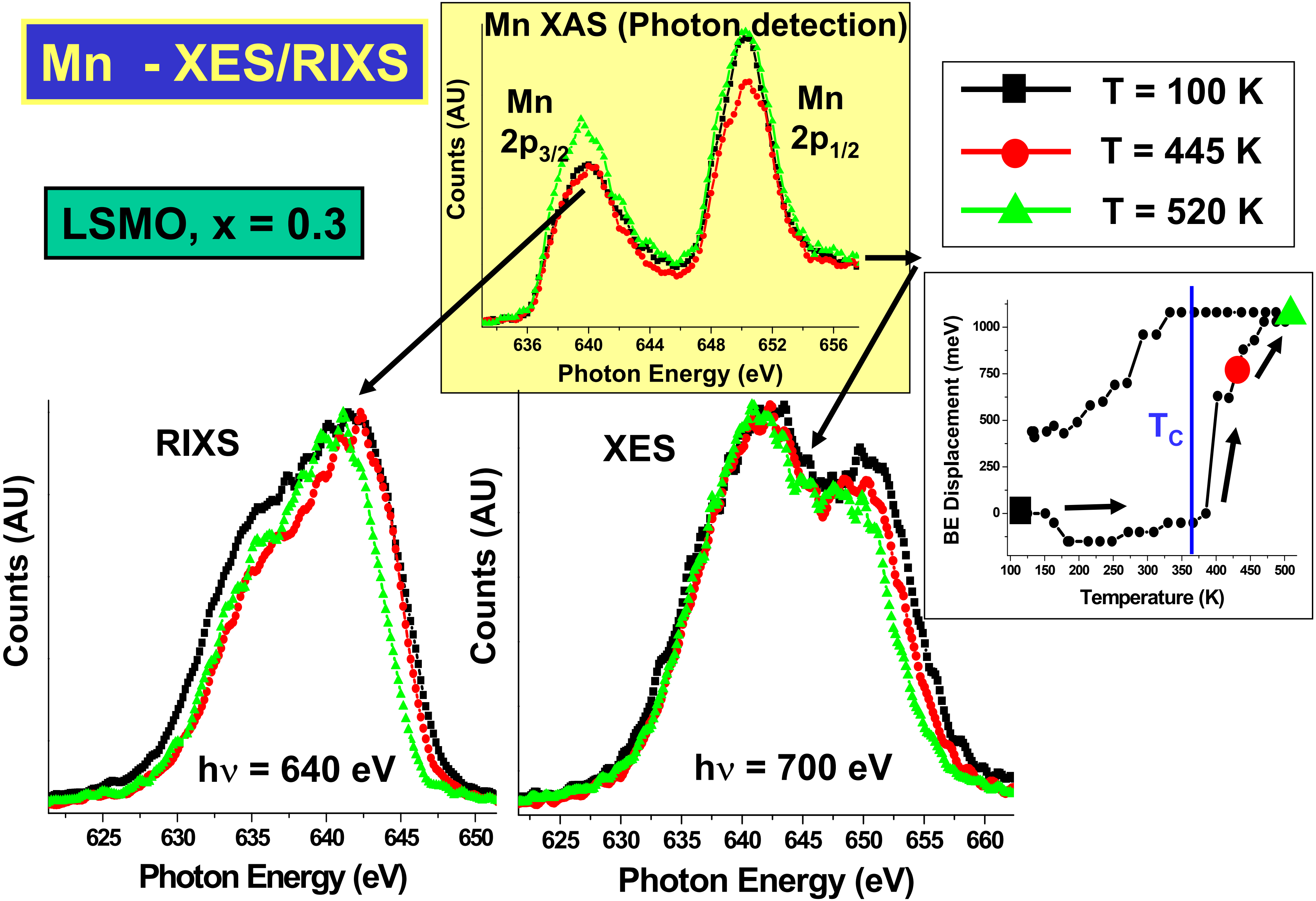
The Soft X-Ray Spectroscopies

XAS	**Valence PE** -	**Core PE** -	**XES, RIXS** –
unoccupied DOS (2° e- and hν Detection)	band struct., quasipart. exc., DOS, spin pol.	stoichiometry, BE shifts, splittings, MCD, spin pol.	Band structure, PDOS, d-d excitations



Mn - XES/RIXS

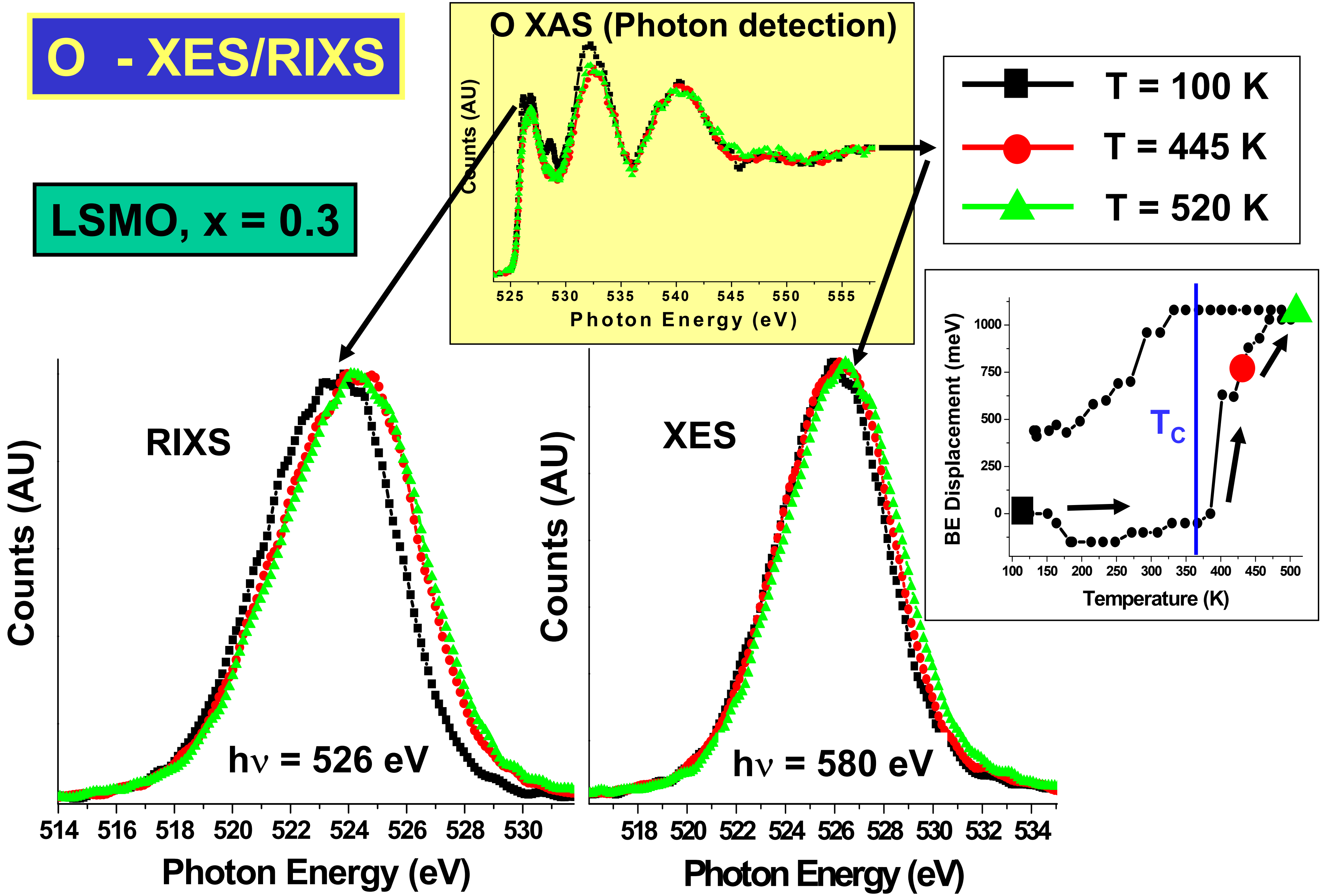
LSMO, x = 0.3



Changes on passing $T_C \rightarrow T_{sat} \rightarrow$ XES $\rightarrow$ 1,300 Å ≈ bulk

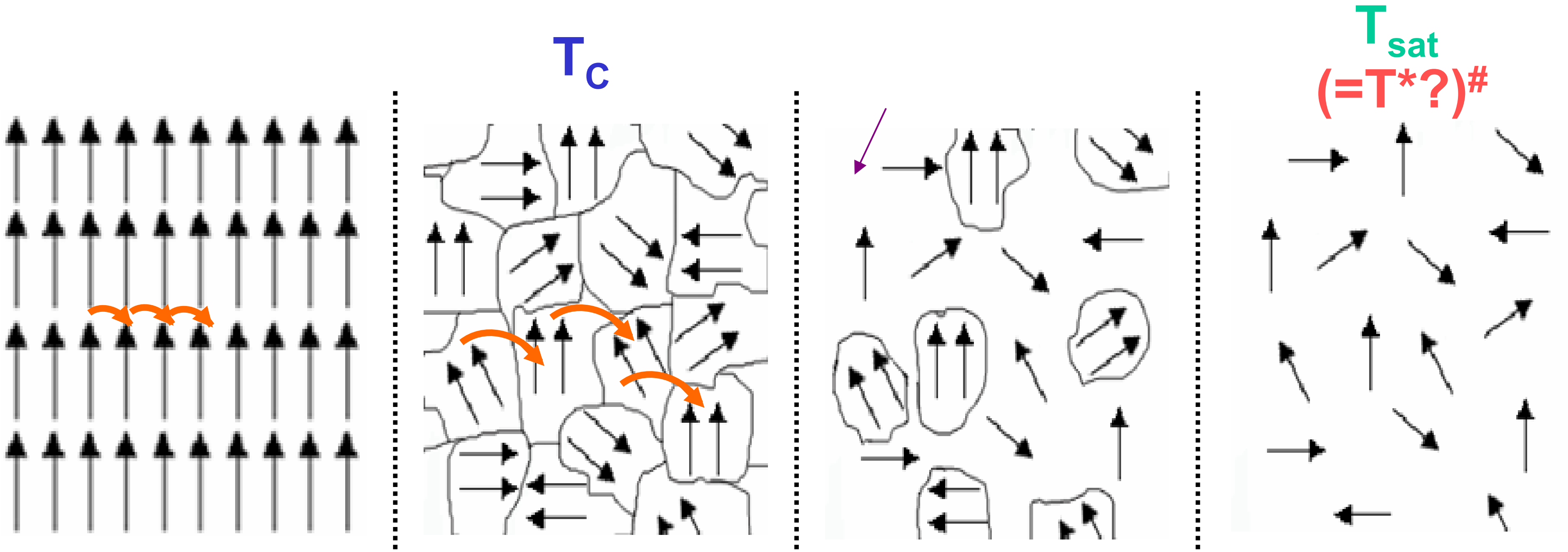
O - XES/RIXS

LSMO, x = 0.3



Changes on passing T_C → XES→1,500 Å ≈ bulk

Possible scenario



Loss of long - range order at T_C: some percolation

Short - range order above T_C up to T_{sat}

T^* : e.g. see Dagotto et al. Phys. Rev. Lett. 87, 277202 (2001)

Mannella et al., Phys. Rev. Lett. 92, 166401 (2004)

CMR Spectroscopy--Summary

$La_{1-x}Sr_xMnO_3$ (x = 0.3, 0.4) single crystals

Dramatic change of the electronic structure on crossing $T_C \rightarrow T_{sat}$

Direct evidence for charge localization - polarons in the metallic paramagnetic state: ~1 e^- added to Mn

Multiple spectroscopies of varying depth sensitivity indicate a "bulk" effect, but hard x-ray photoemission desirable to clarify

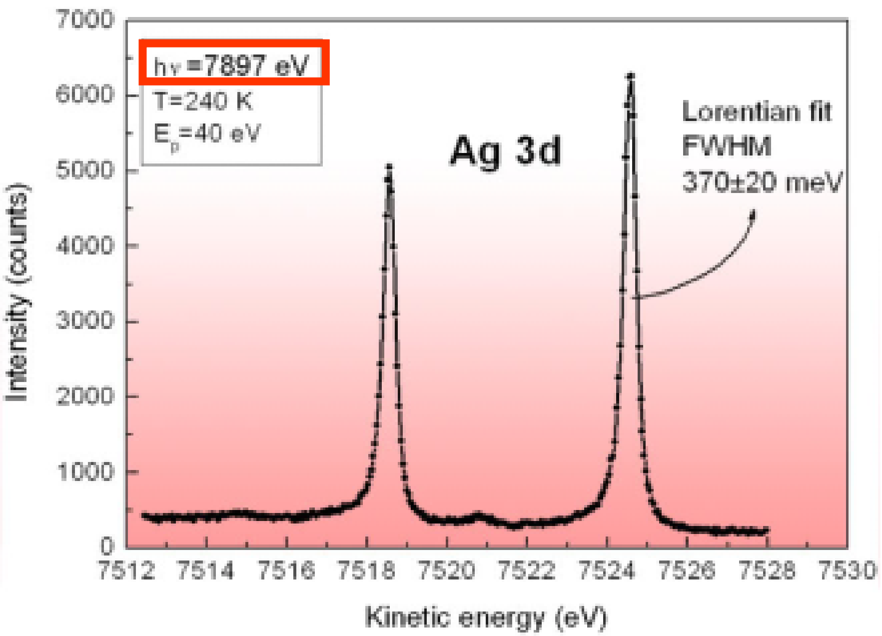
Structural evidence for polarons also from EXAFS

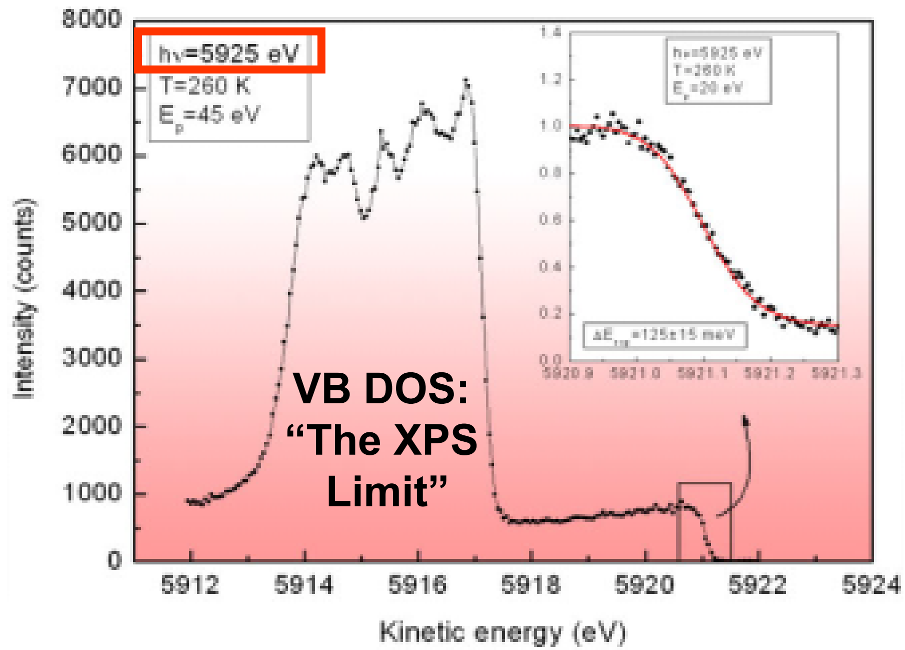
Future experiments on multilayer structures of CMRs, other transition metal oxides, other oxide nanostructures

Mannella et al., Phys. Rev. Lett. 92, 166401 (2004)

Photoemission at 5-10 keV to Probe Bulk Properties and DOSs (Suga et al., Kunz et al., Panaccione et al.,…)

E.g.--First Test of the VOLPE Project at the ESRF: VOLume Sensitive PhotoEmission from Solids using Synchrotron Radiation



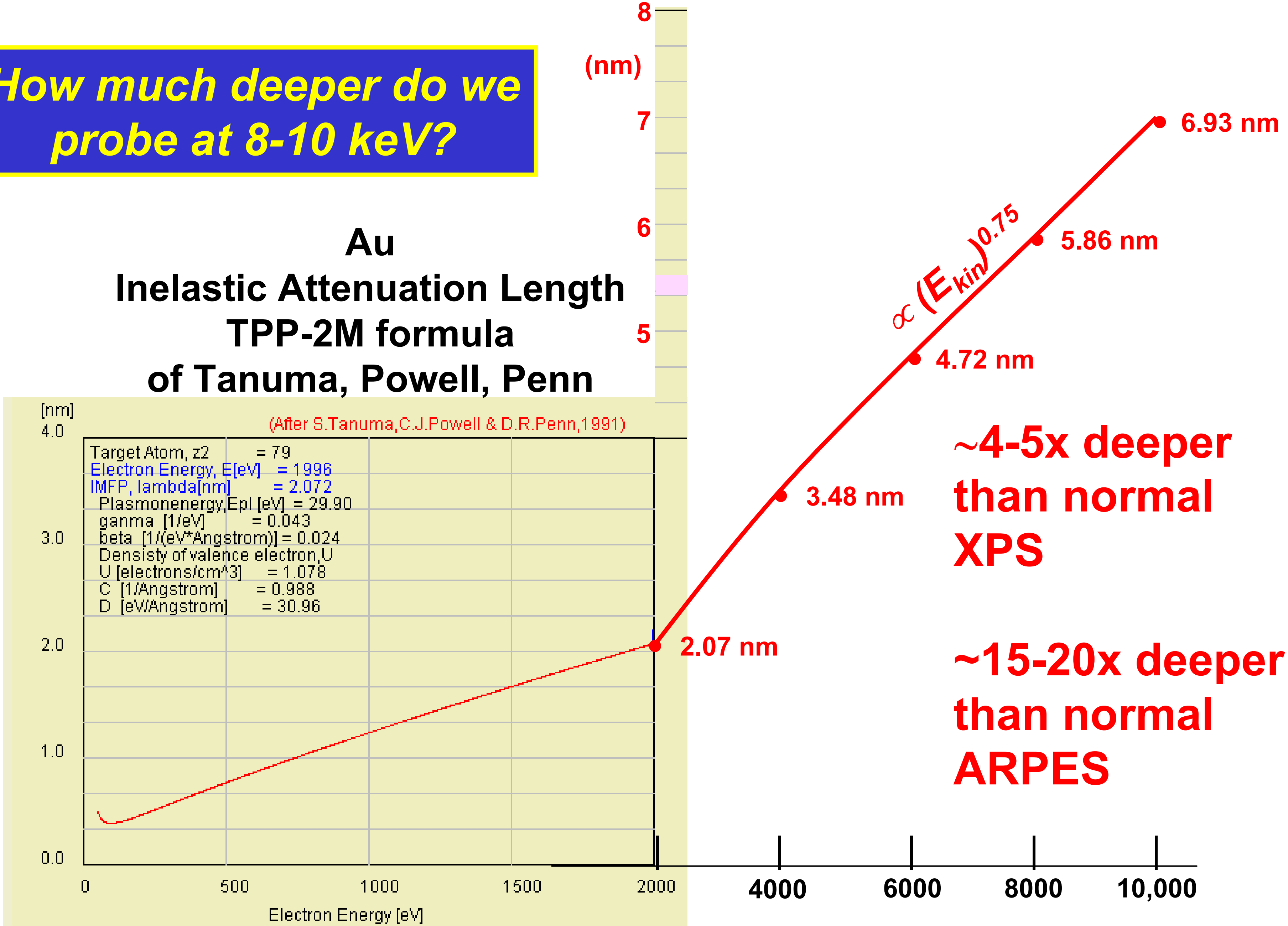


Current best energy resolution: 70 meV

Panaccione et al.,
http://www.esrf.fr/UsersAndScience/Publications/Spotlight/2004_05_14VOLPE/

How much deeper do we probe at 8-10 keV?

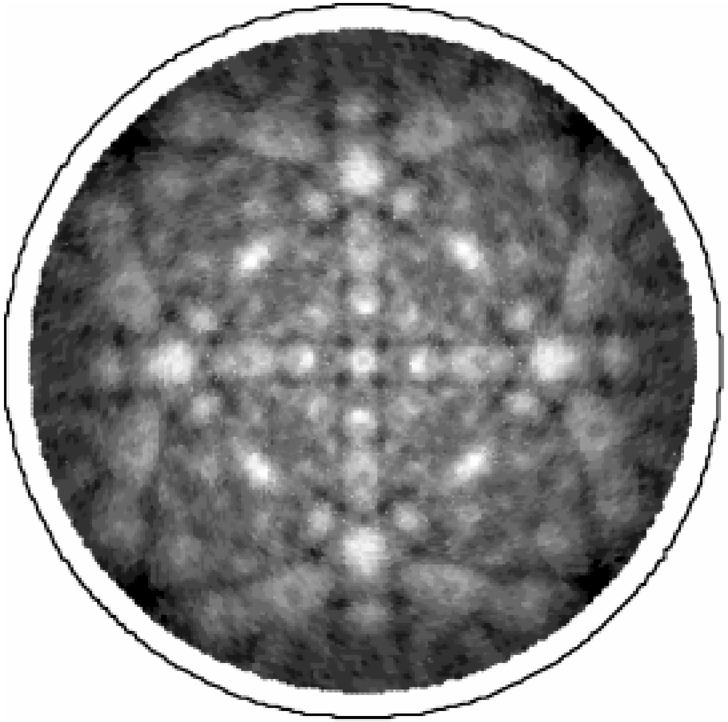
Au
Inelastic Attenuation Length
TPP-2M formula
of Tanuma, Powell, Penn



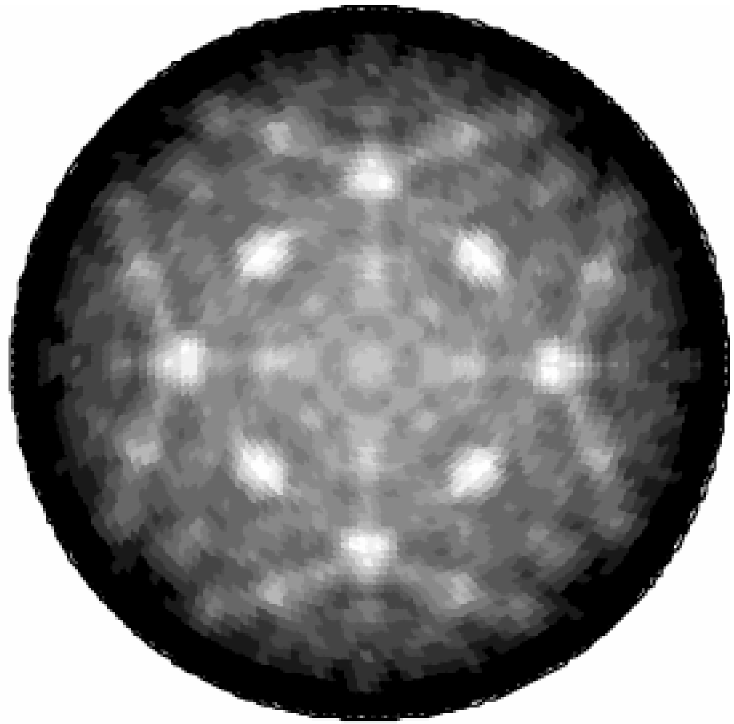
http://www.ss.teen.setsunan.ac.jp/e-imfp.html

Element-specific local atomic structure in epitaxial/single crystal systems with ≥ short-range order

High-resolution XPD from Si(001)-(2x1): Local atomic structure



Expt. Si 2p XPD
(1154 eV)

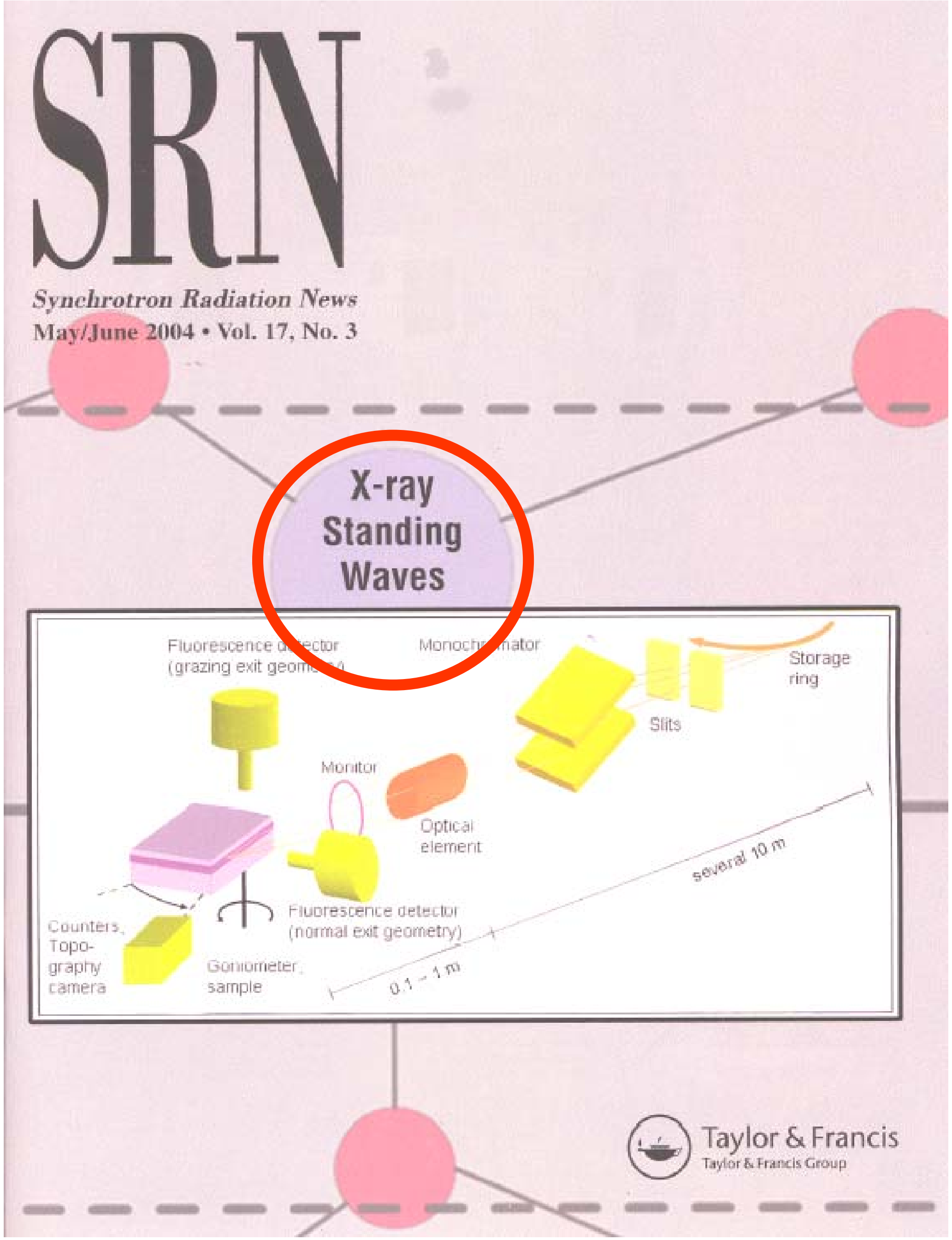


Multiple Scattering
Calculations (Kaduwela Code)

Kikuchi-
Band like:
Much sharper
At 5-10 keV

J. A. Martin-Gago, M. C. Asensio, P. Aebi, R. Fasel,
D. Naumovic, J. Osterwalder, unpublished

Buried interfaces: The ubiquitous challenge



Probing Buried Magnetic Interfaces with Standing-Wave Excited Photoemission

S.-H. Yang, B. S. Mun, N. Mannella, L. Zhao, A.W. Kay, S.B. Ritchey, B.C. Sell, A. Nambu, M. Watanabe, M. West, L. Pham and C. S. Fadley

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Advanced Light Source, LBNL

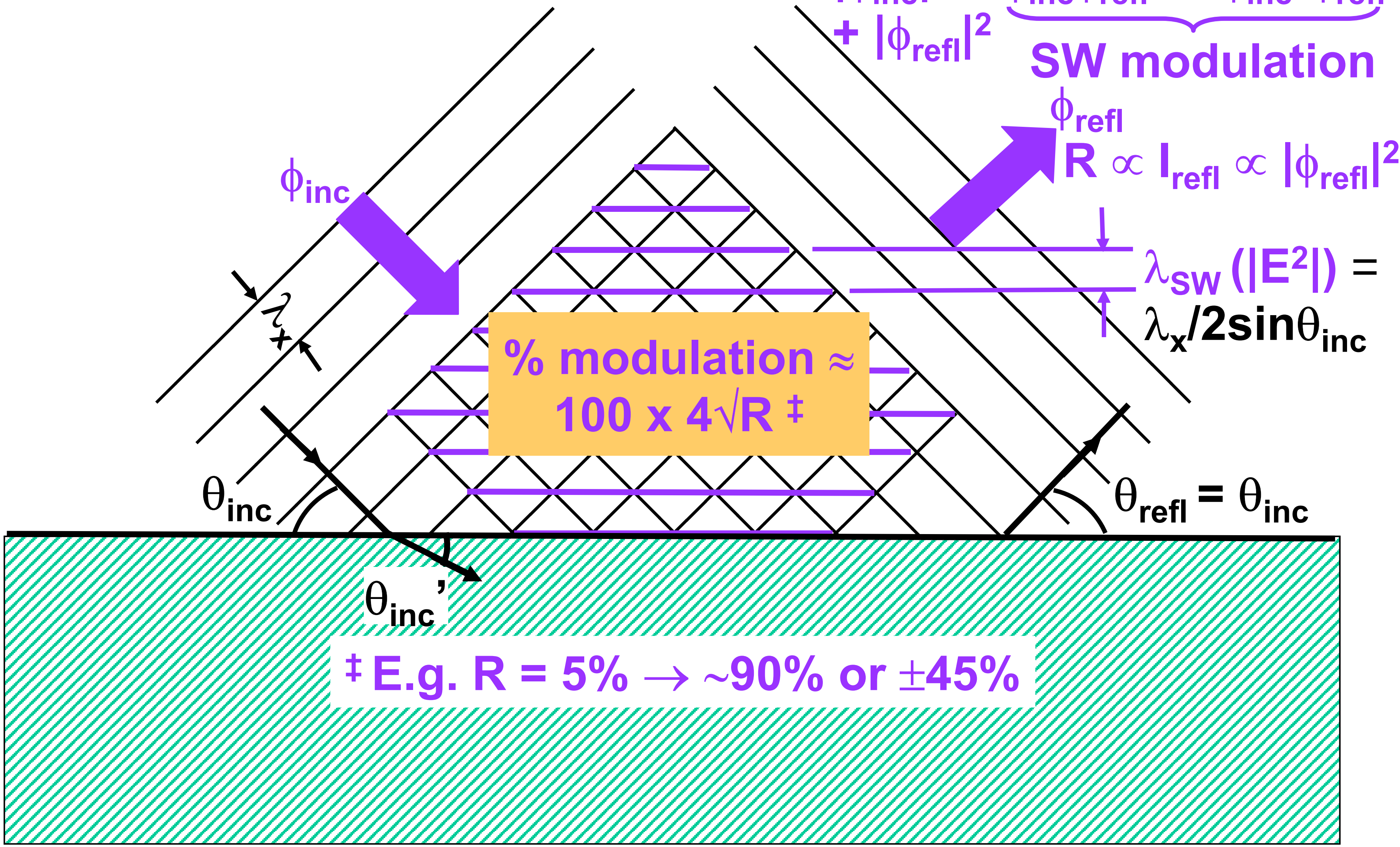
The Advanced Light Source

S.S.P. Parkin and S.-H. Yang

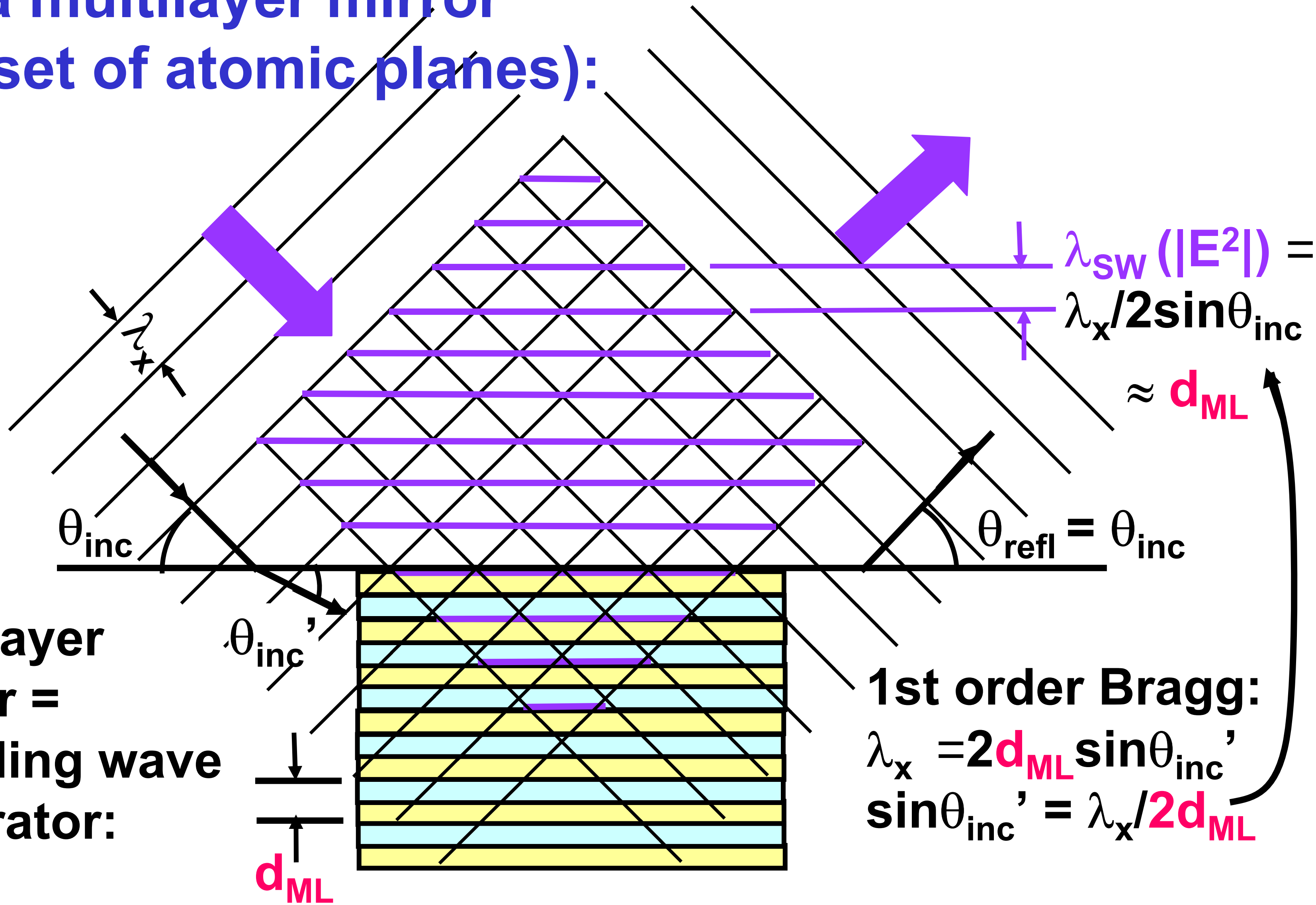
IBM Almaden

Standing wave formation:

$$I_{SW}(|E^2|) \propto |\phi_{inc} + \phi_{refl}|^2 = |\phi_{inc}|^2 + \underbrace{\phi_{inc}\phi_{refl}^* + \phi_{inc}^*\phi_{refl}}_{\text{SW modulation}} + |\phi_{refl}|^2$$



Standing wave formation with a multilayer mirror (or a set of atomic planes):



Multilayer mirror = Standing wave generator:

1st order Bragg:
$\lambda_x = 2d_{ML}\sin\theta_{inc}'$
$\sin\theta_{inc}' = \lambda_x/2d_{ML}$

X-ray Optical Calculations :

Calculating XRO effects on spectroscopy

- *$n(h\nu) = 1 - \delta(h\nu) + i\beta(h\nu)$*
- *variable polarization*
- *multiple reflection/ refraction*
- *exact treatment of interlayer intermixing a/o roughness*
- *electric field at i-th layer:*

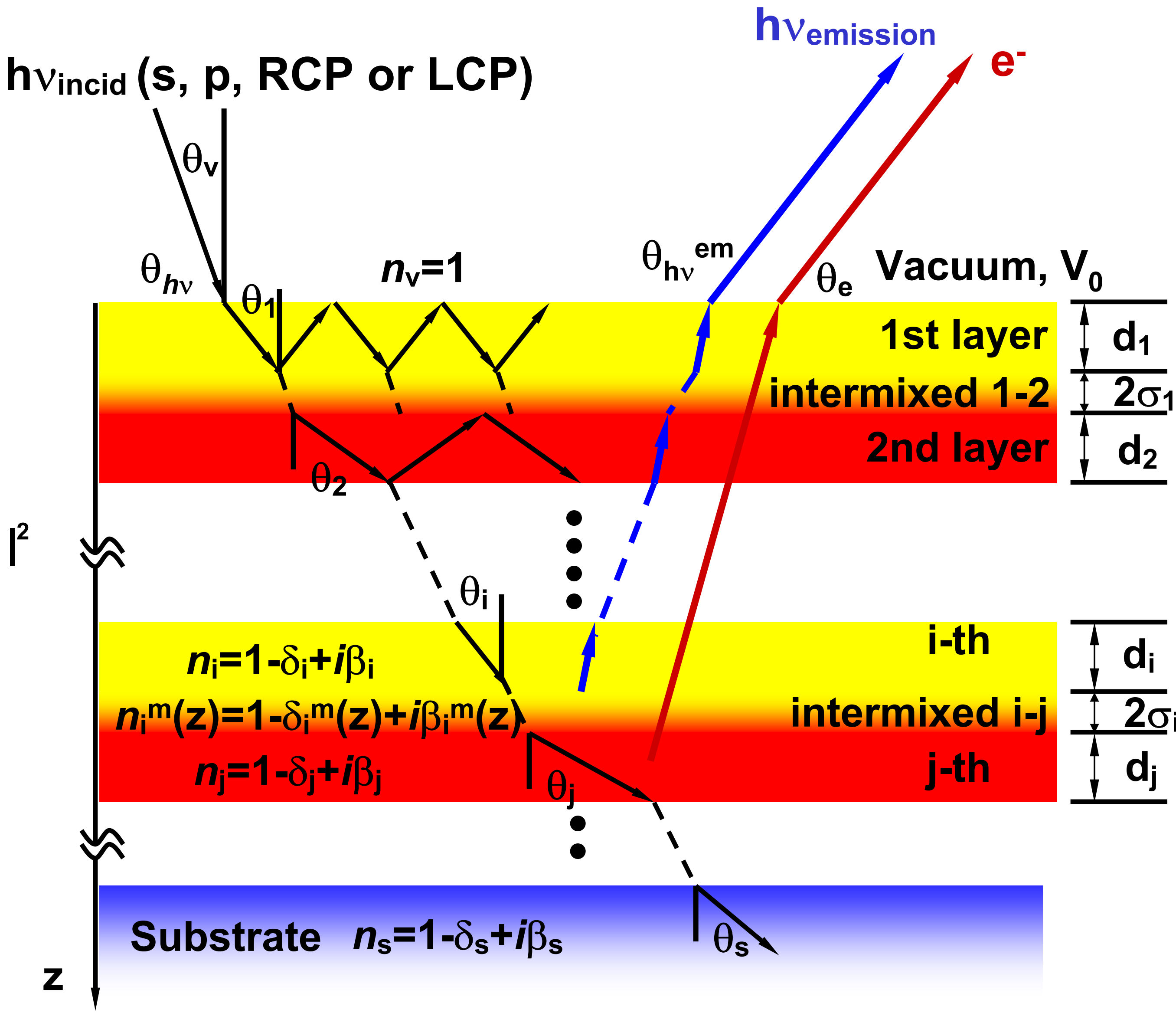
$$I_i(z) = |E_i^+(z) + E_i^-(z)|^2$$

Photoemission:

- differential cross section
- inelastic attenuation
- surface refraction

X-ray emission:

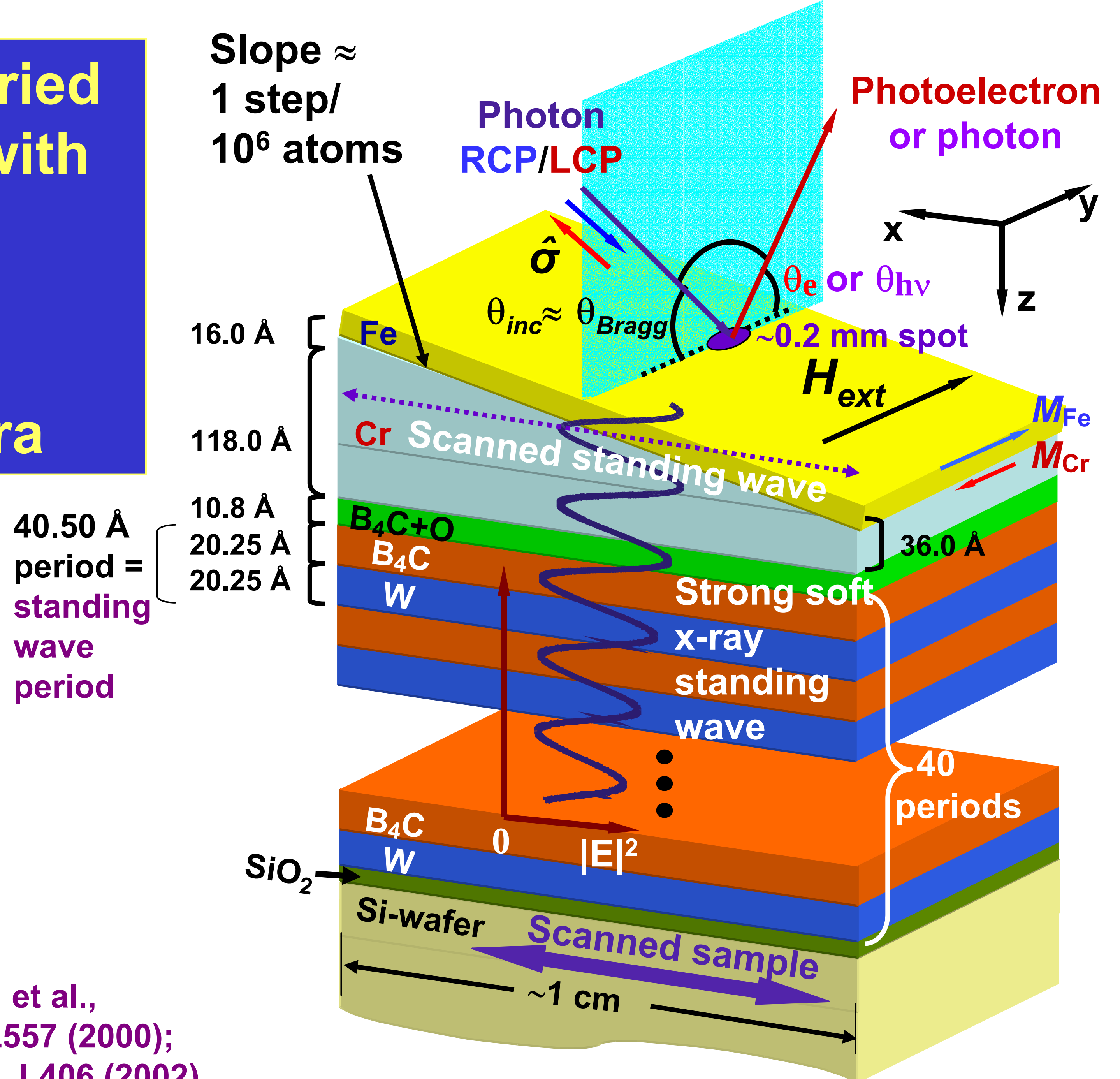
- fluorescence yield



Multilayer PS, XES--S.-H. Yang et al., Surf.Sci.Lett. 461, L557 ('00); J.Phys.C.M. 14, L406 ('02)

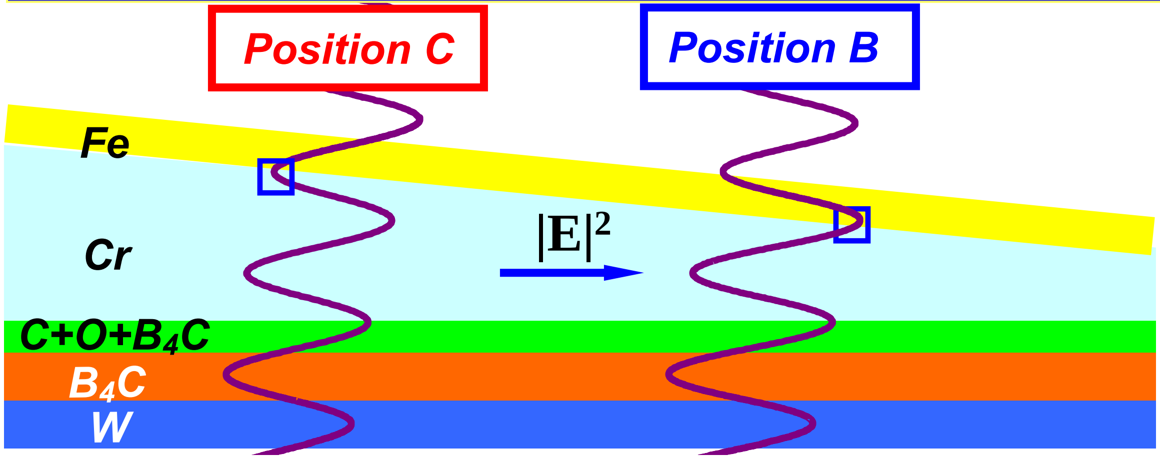
Probing Buried Interfaces with Soft X-ray Standing Waves: Core Spectra

Fe/Cr: a prototypical system for giant magneto-resistance



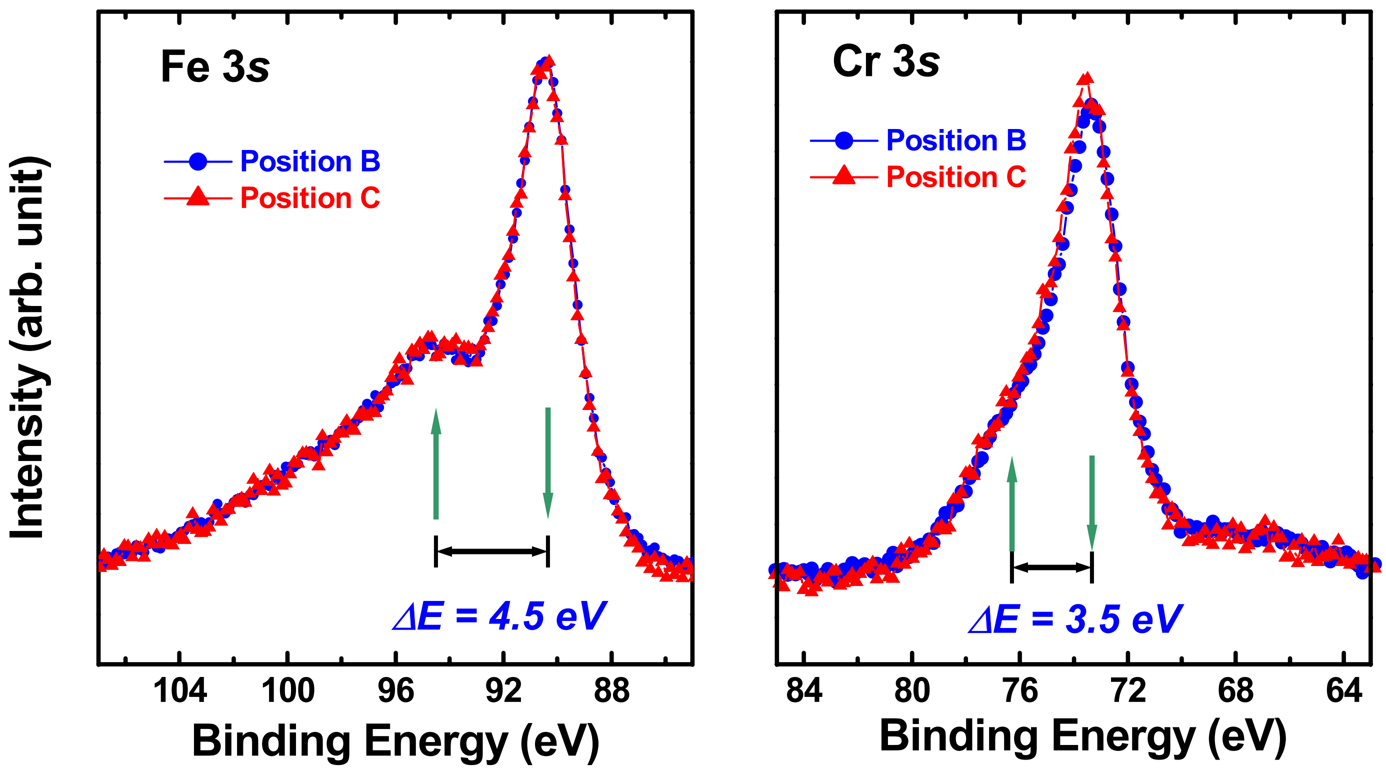
S.-H. Yang. B.S. Mun et al., Surf. Sci. Lett. 461, L557 (2000); Phys. Cond. Matt. 14, L406 (2002)

Fe and Cr 3s multiplets--probe of on-site spin moments



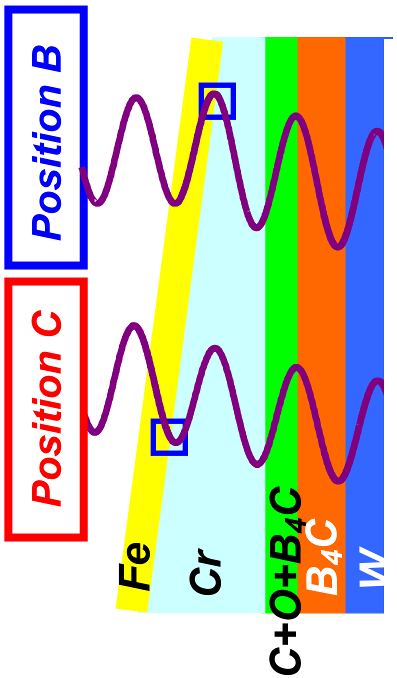
No change in magnitude of local spin magnetic moment thru interface

Fe and Cr 3s Photoemission from wedge (Fe/Cr)+SWG

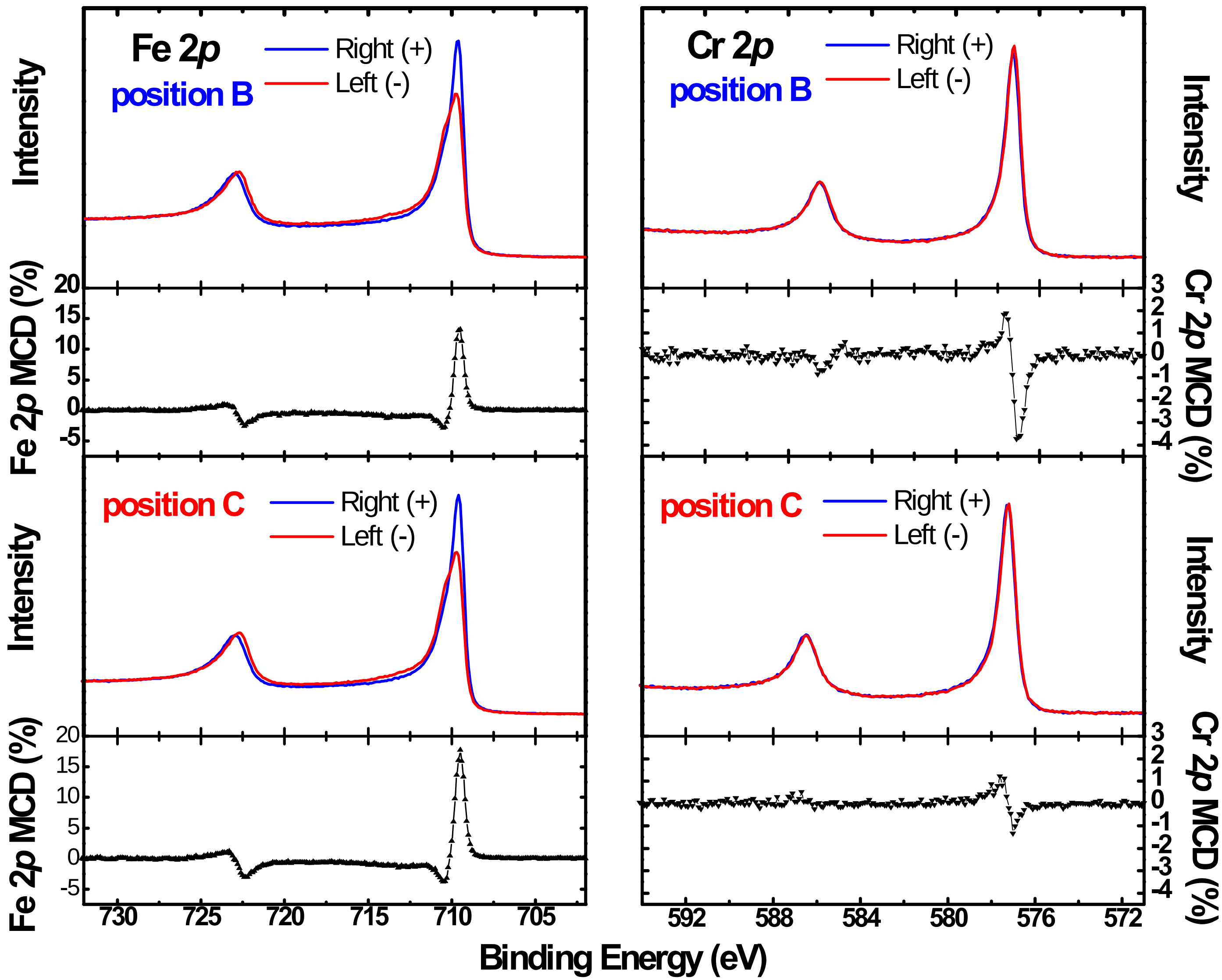


Fe and Cr 2p magnetic circular dichroism--probe of y-axis magnetization

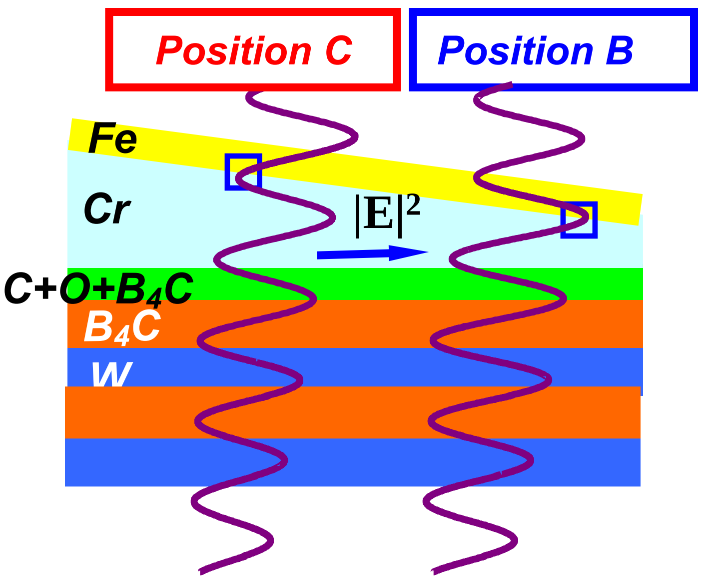
Cr magnetization Is antiparallel to Fe; systematic variation of MCD strengths vs d_{cr}

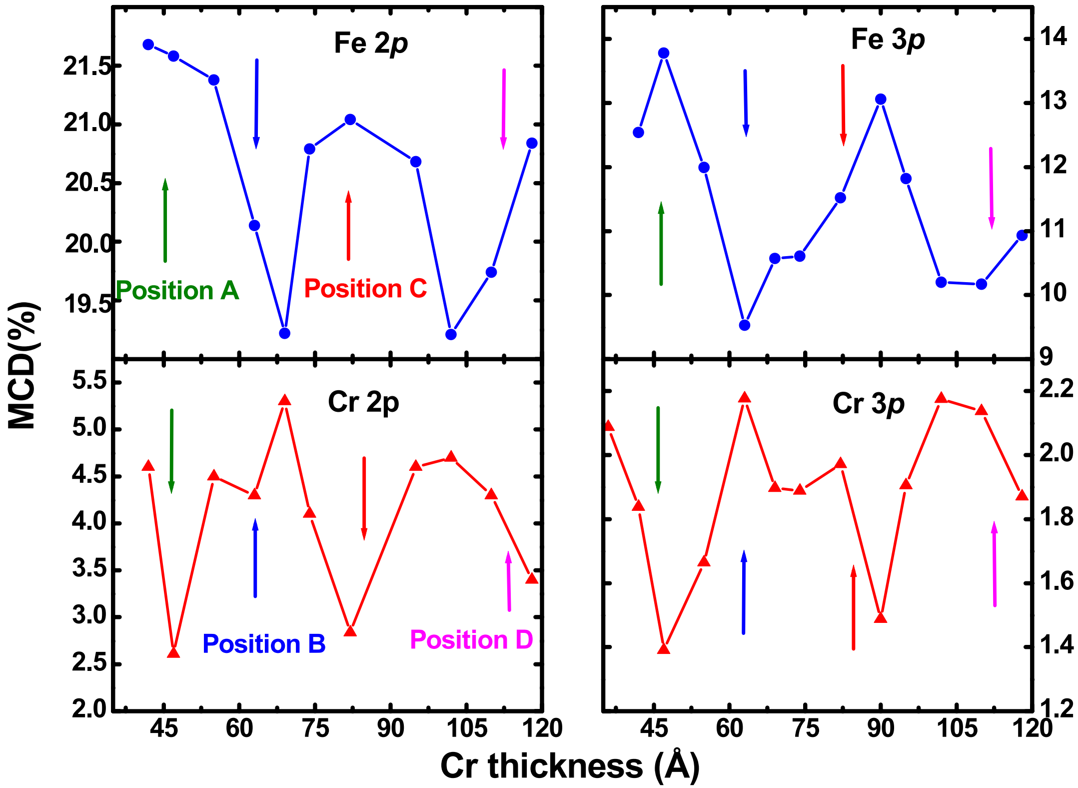


Fe & Cr 2p MCD Data from wedge (Fe/Cr)+SWG

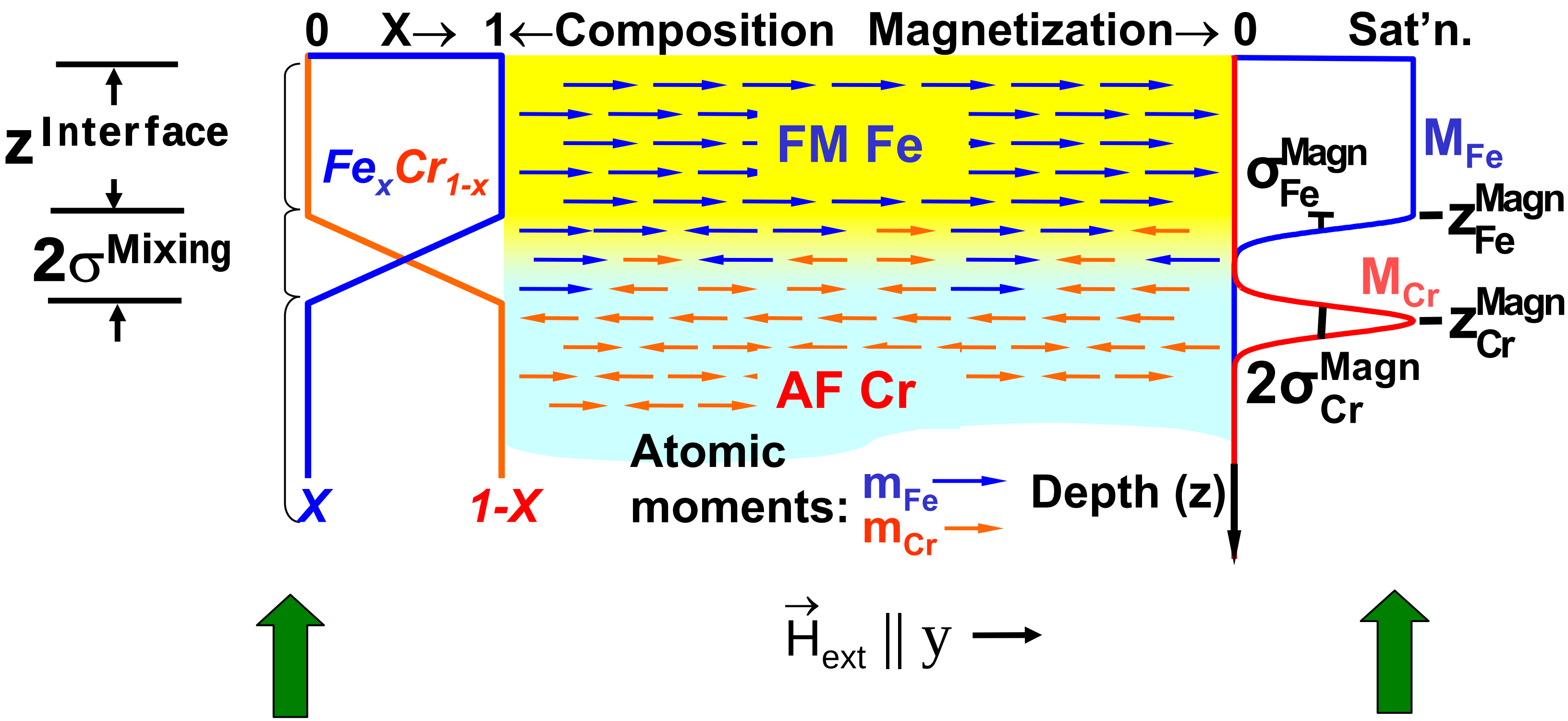


Experimental thickness dependence of Fe and Cr 2p and 3p MCD signals--Standing wave scanned ~2 times through the interface



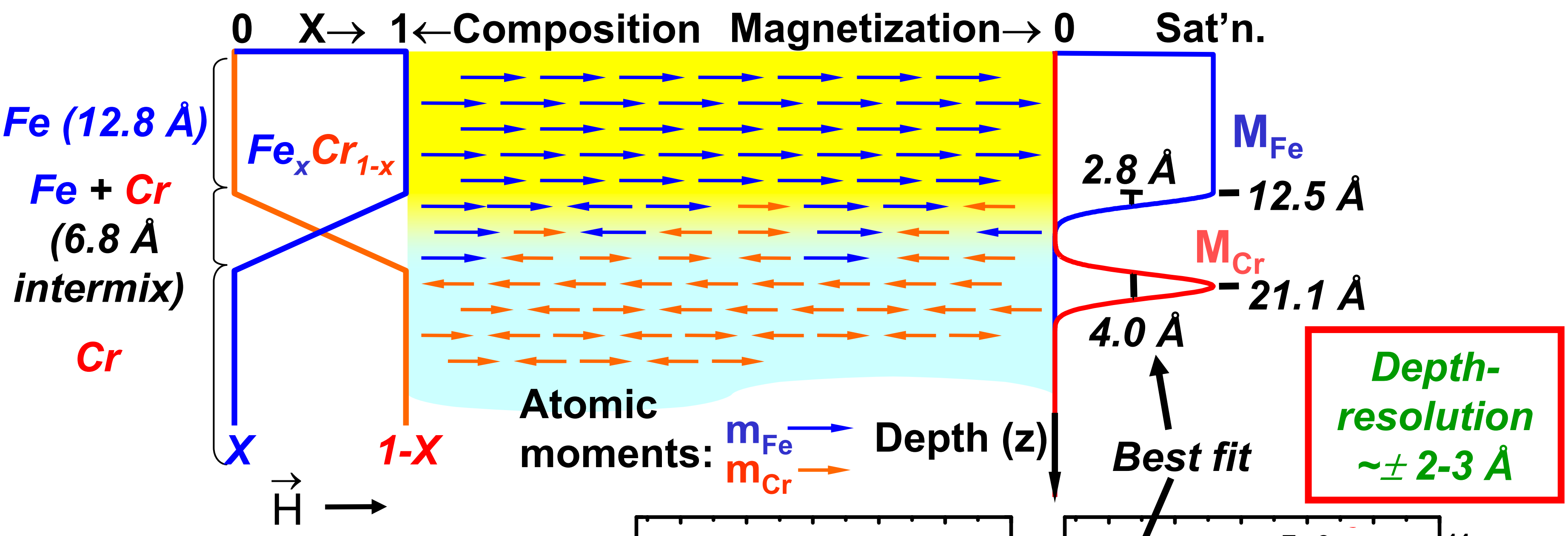


Models used to fit SW photoemission results

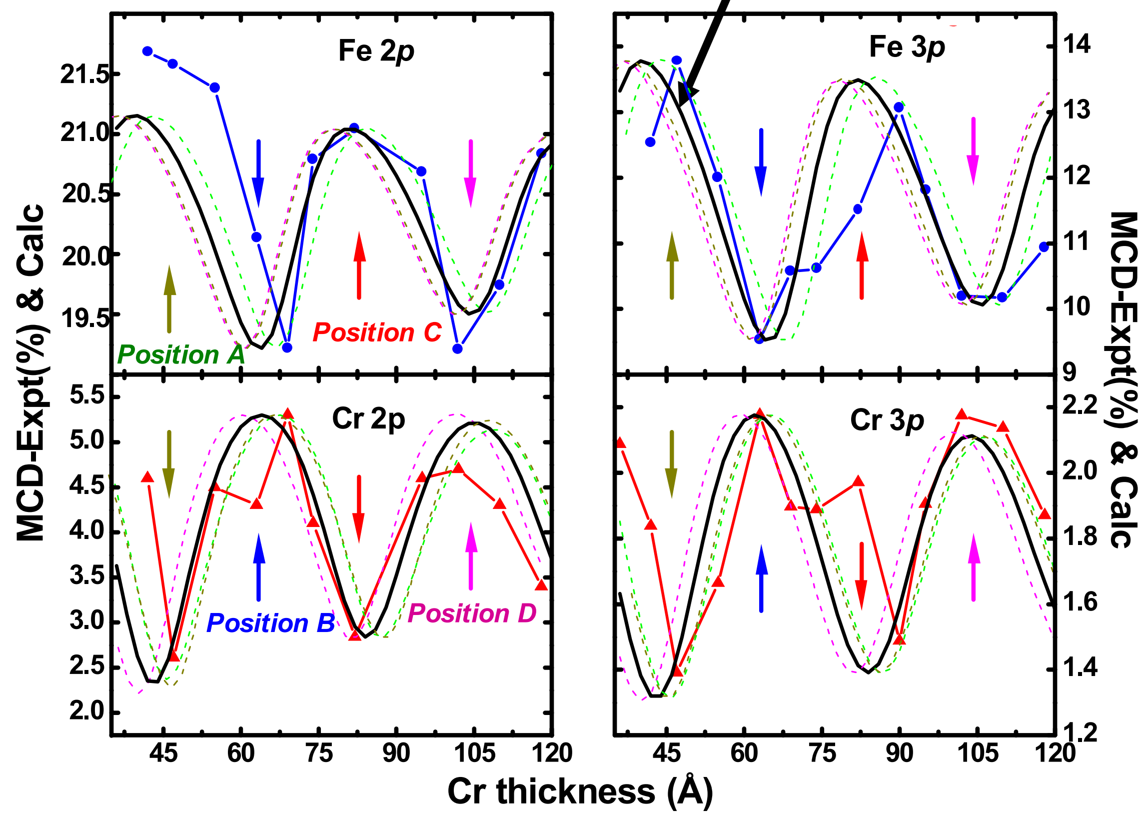


I(Fe 3p)/I(Cr 3p) ratio data

Fe 2p,3p and Cr 2p,3p MCD data



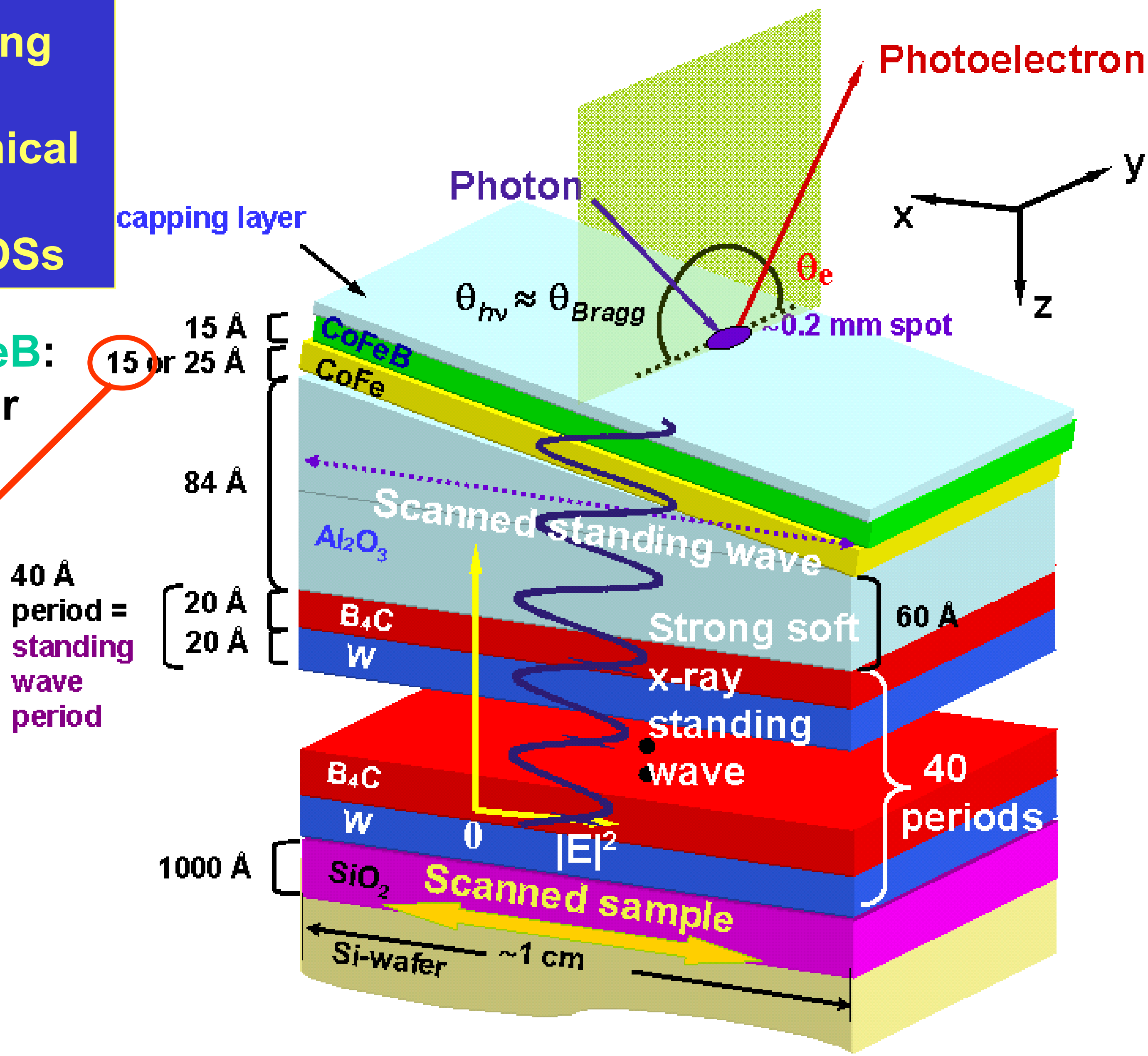
Non-destructive, depth-resolved determination of composition and magnetization profiles from standing-wave excited photoemission (& now also x-ray emission)



Probing Buried Interfaces with Soft X-ray Standing Waves: Core-Level Chemical Shifts and Valence Band DOSs

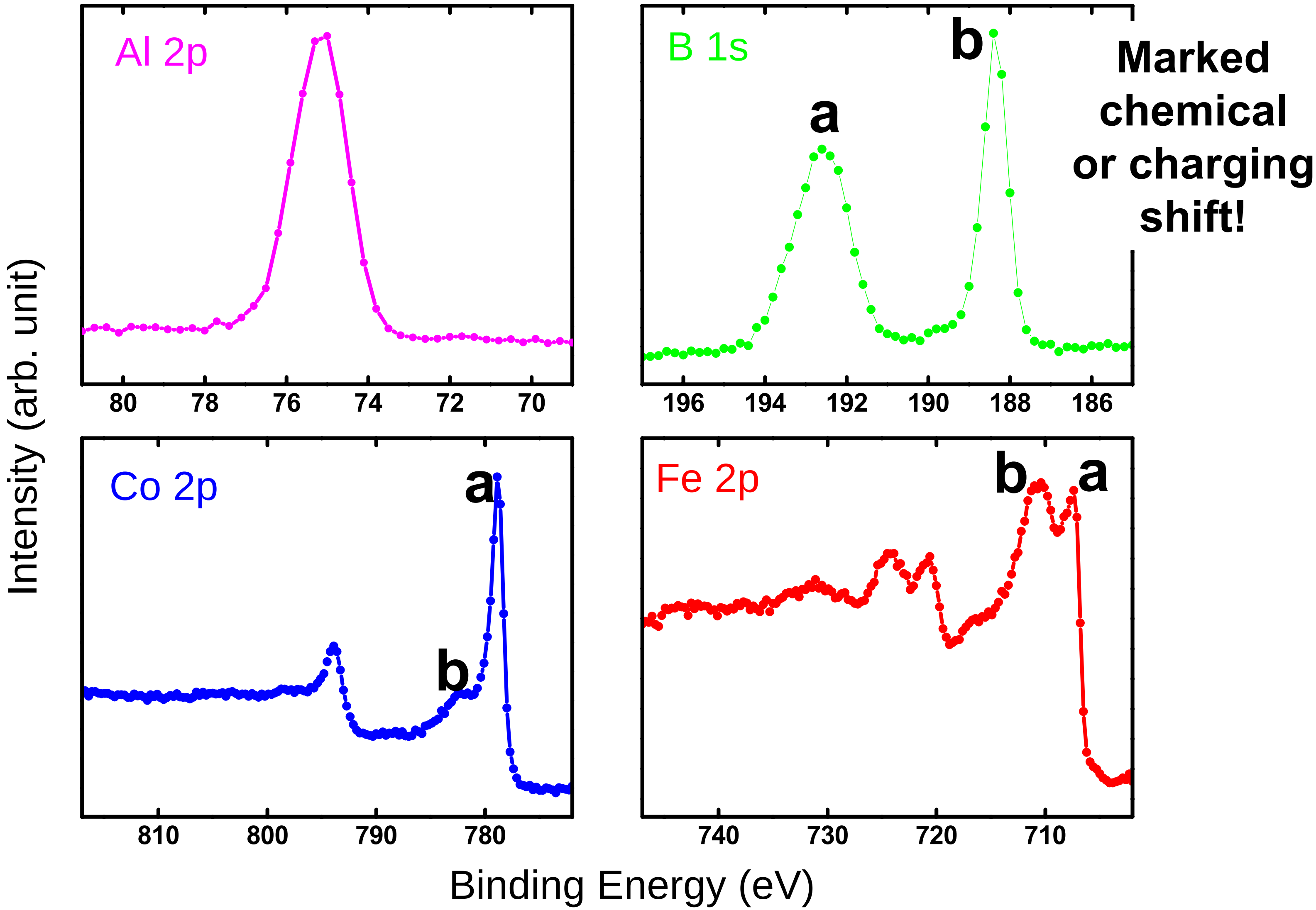
Al_2O_3/CoFe/CoFeB: model system for magnetic tunnel resistance

Higher Tunnel Resistance



With S.-H. Yang And S. Parkin

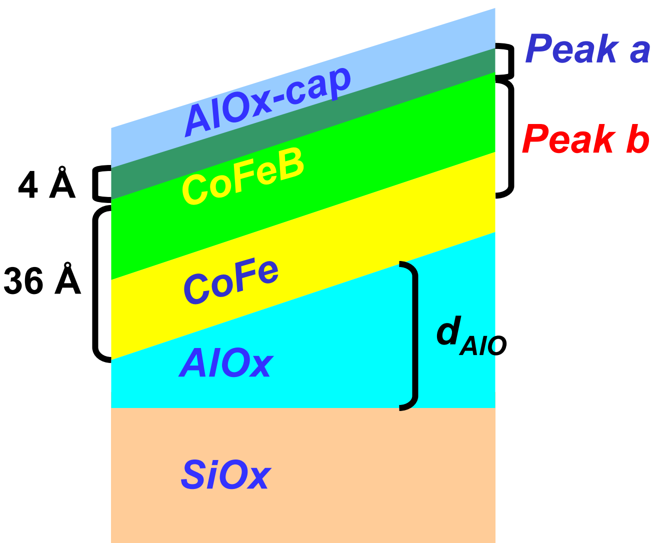
Core-level photoemission spectra

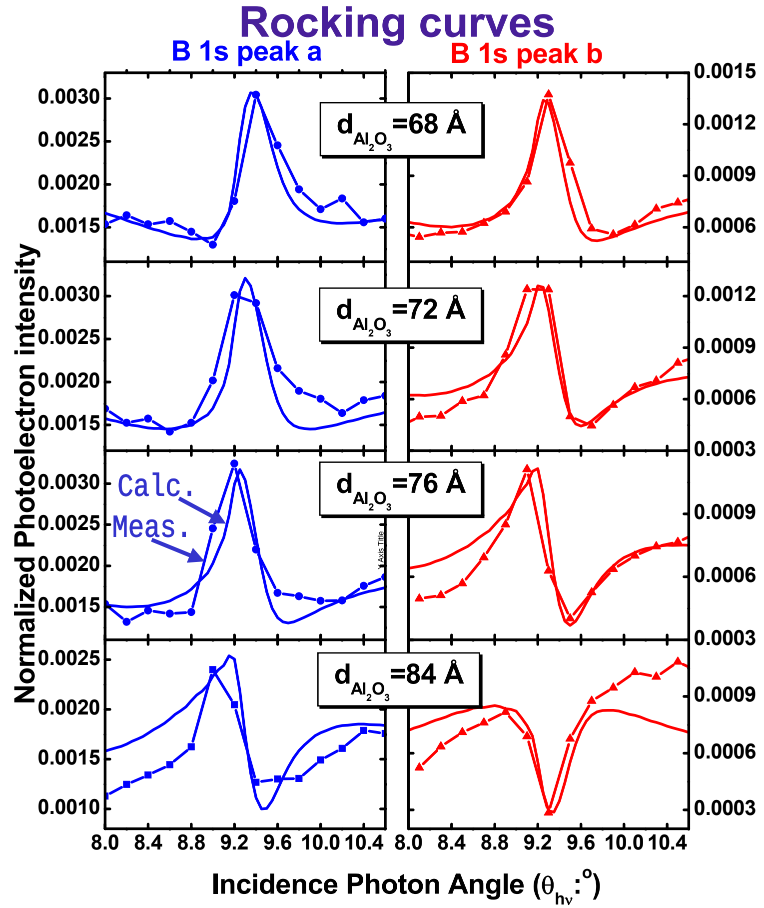


Rocking curve and sample scan analysis: B 1s data

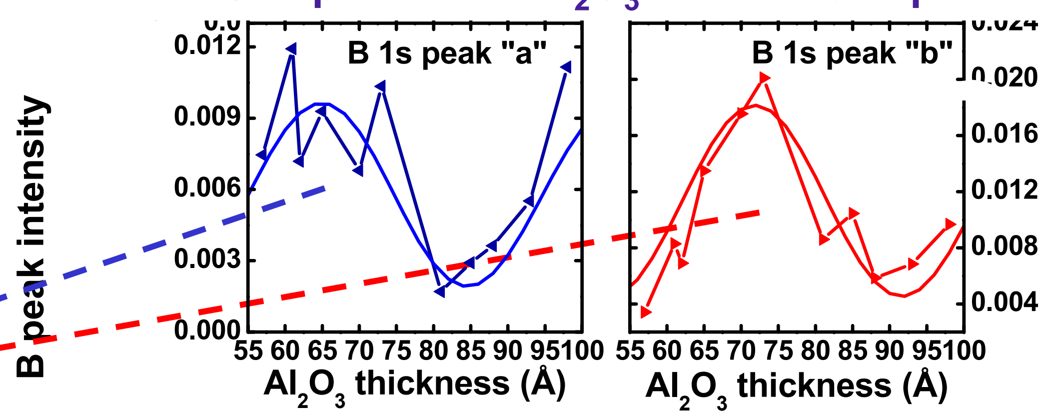
Peak a : B 1s from CoFeB amorphous layer + CoFe alloy

Peak b : B 1s from few topmost CoFeB layers



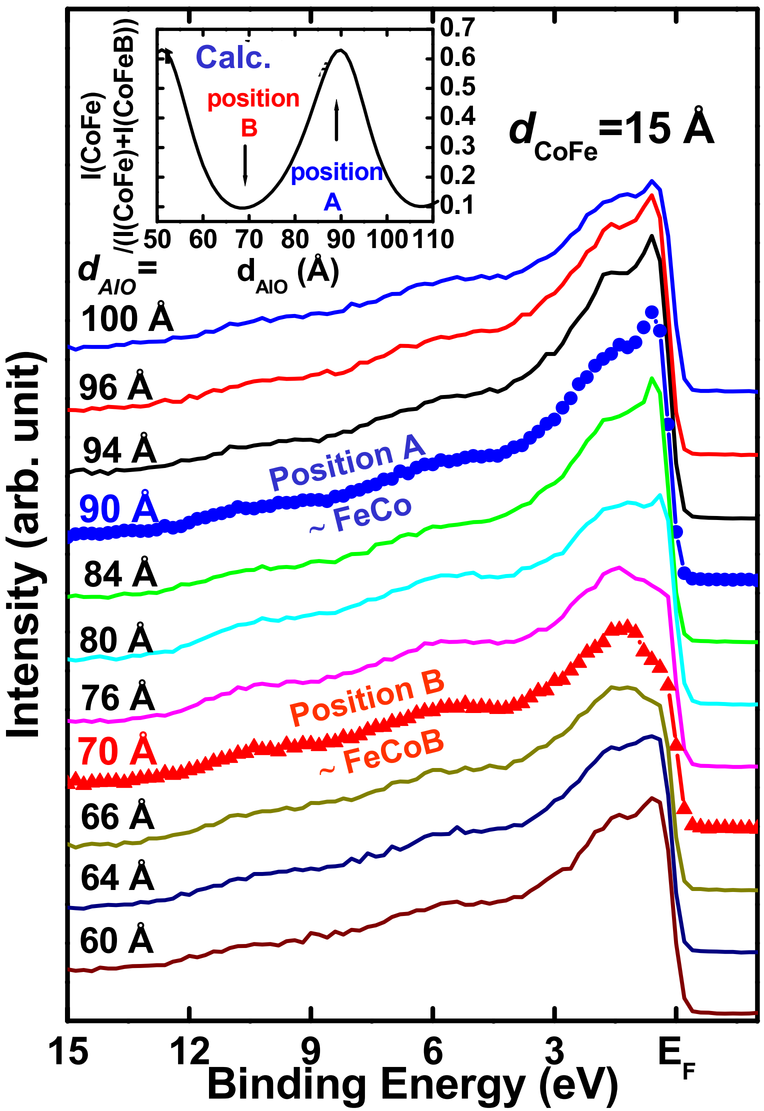


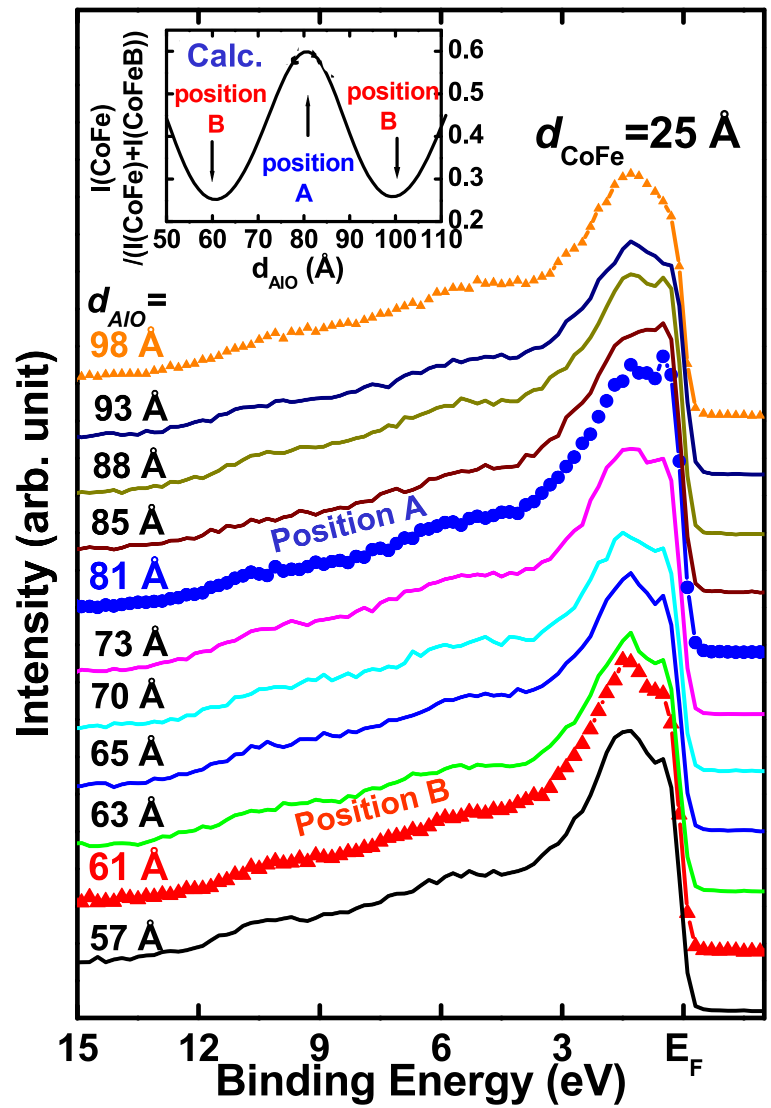
Sample scan = Al_2O_3 thickness depend.



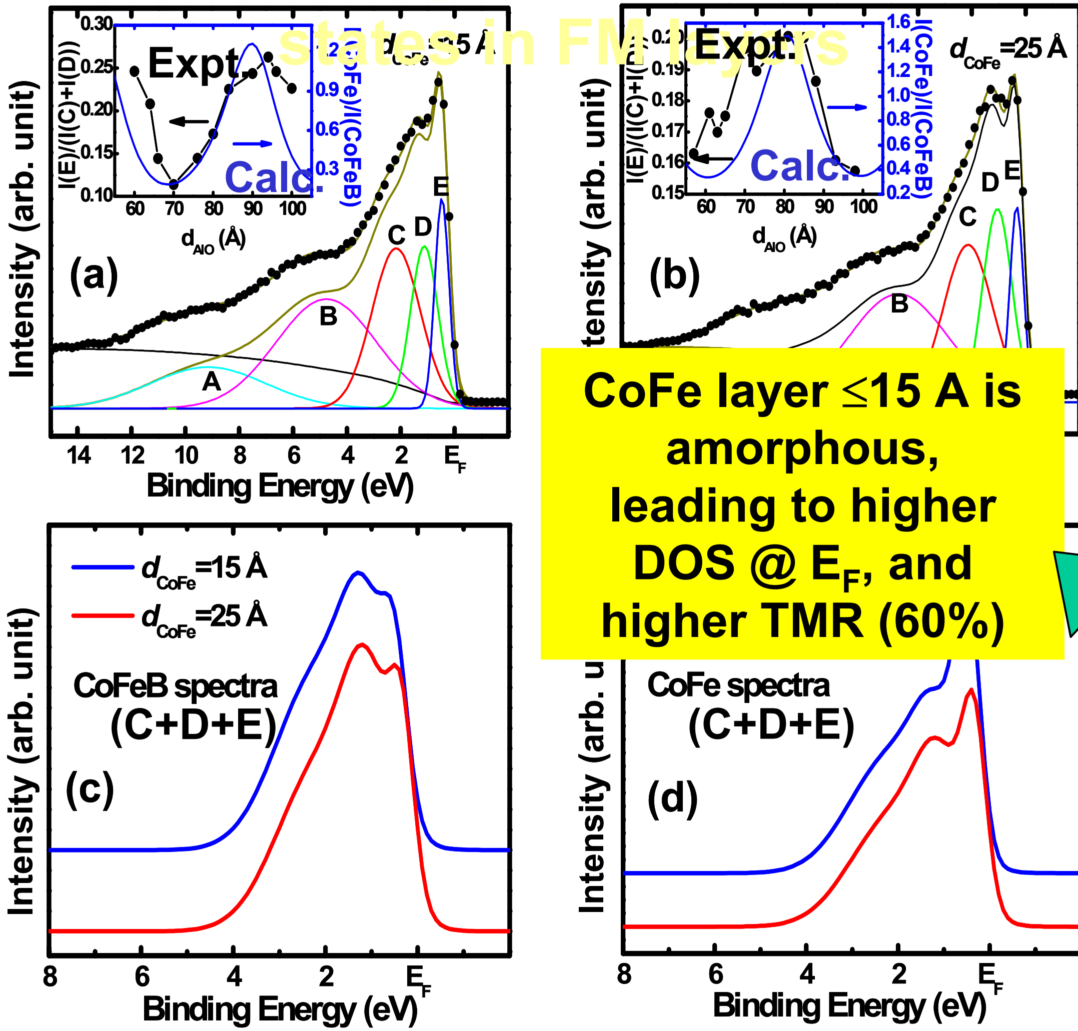
6.5 Å difference

Variation of valence band DOSs with standing wave position





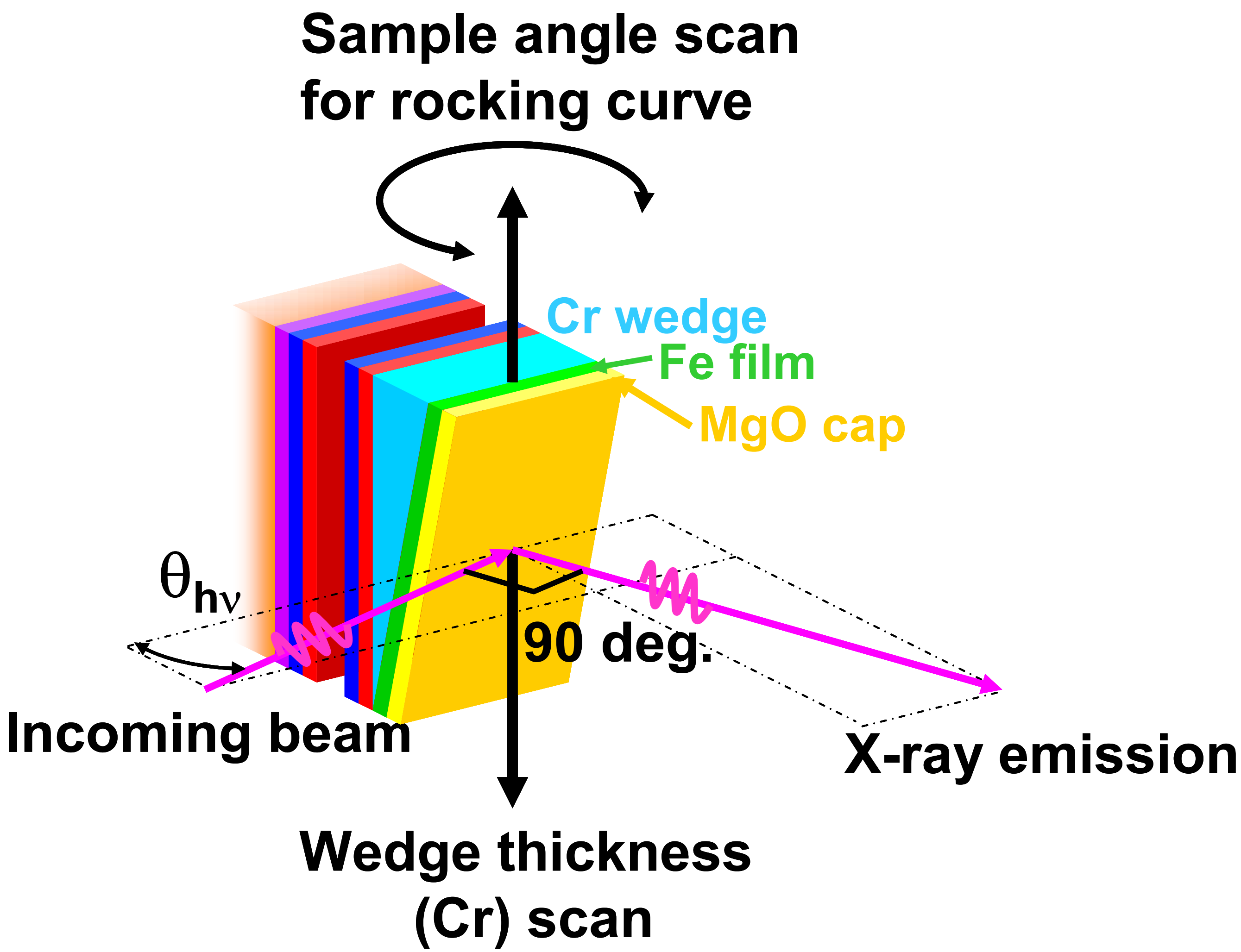
Extraction of depth-resolved densities of states in FM layers



CoFe layer ≤15 A is amorphous, leading to higher DOS @ E_F, and higher TMR (60%)

Decon-voluted CoFeB and CoFe DOSs

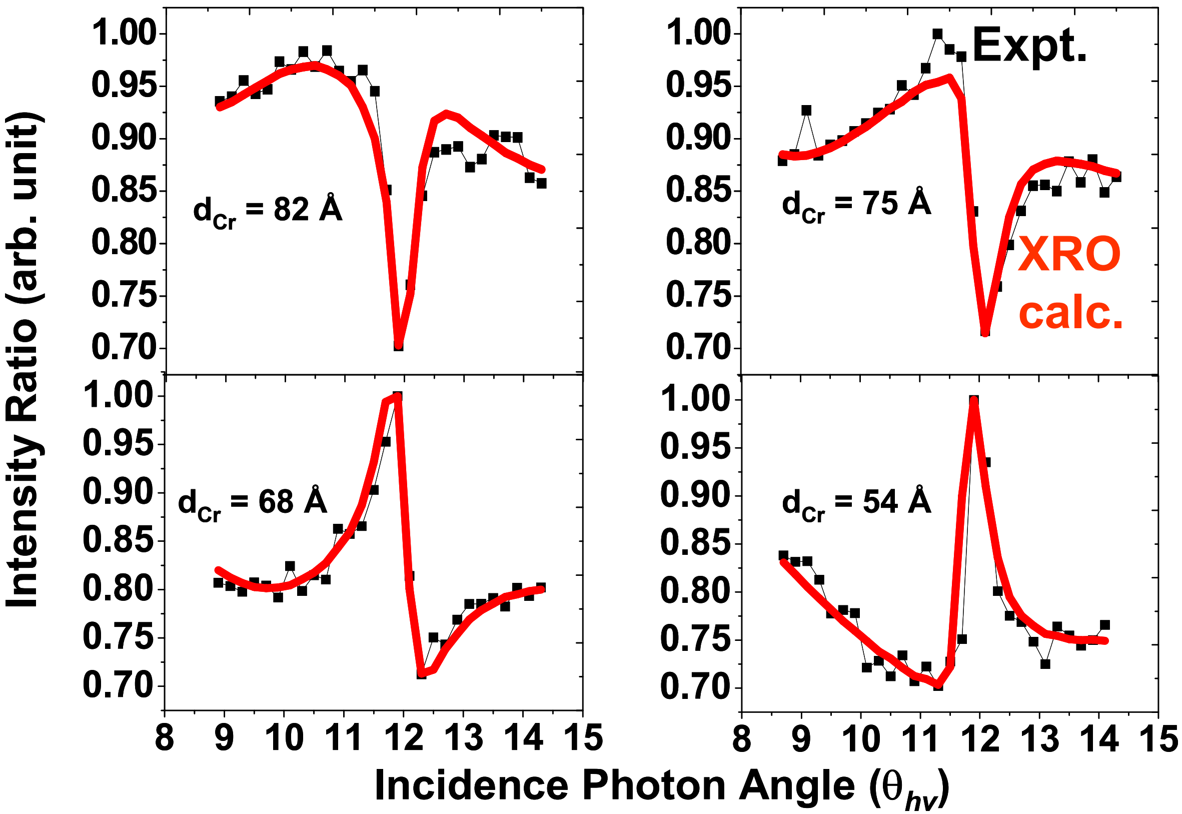
Standing wave excitation of x-ray emission in a multilayer magnetic structure

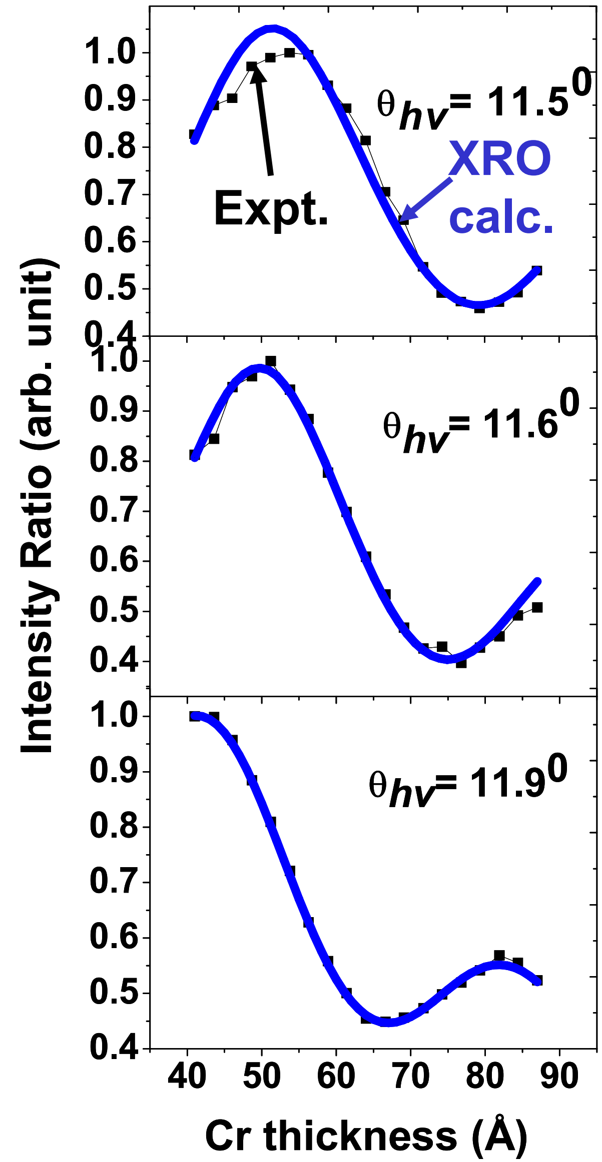


Experimental + Calculated
X-Ray Emission Yield Ratio
I(Fe Lαβ)/I(Cr Lαβ) from Fe/Cr wedge
on standing-wave multilayer

Cr thickness depend.
→ ≈ standing-wave profile

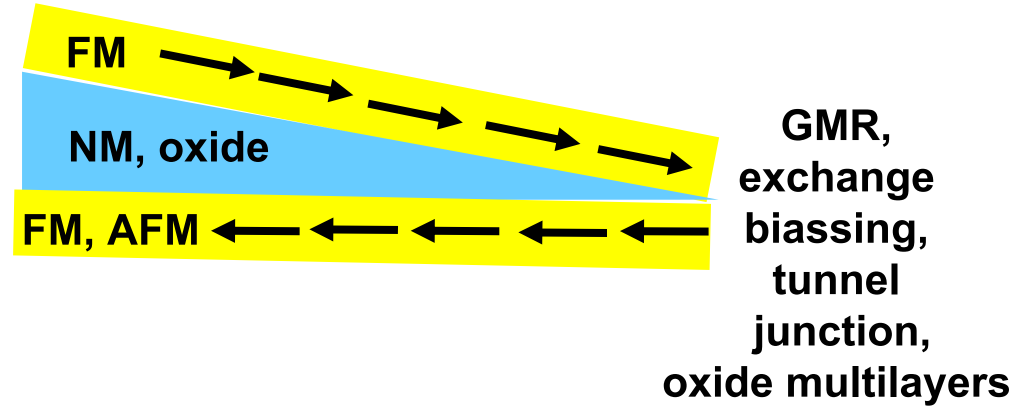
Rocking curves

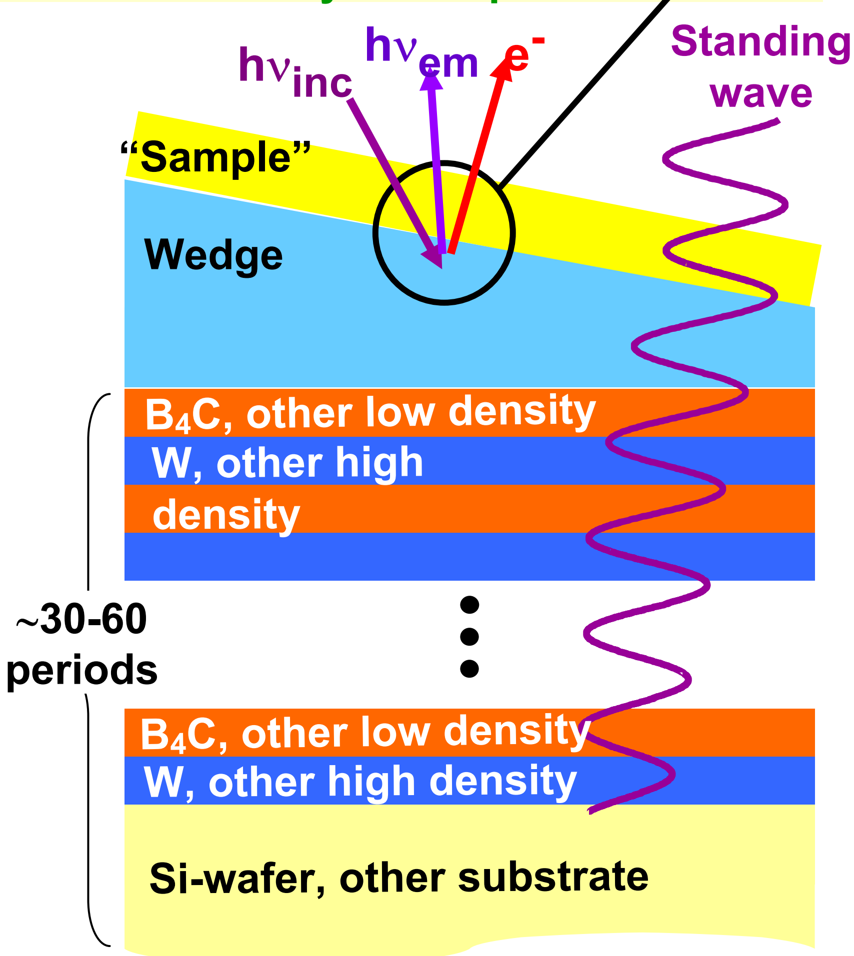




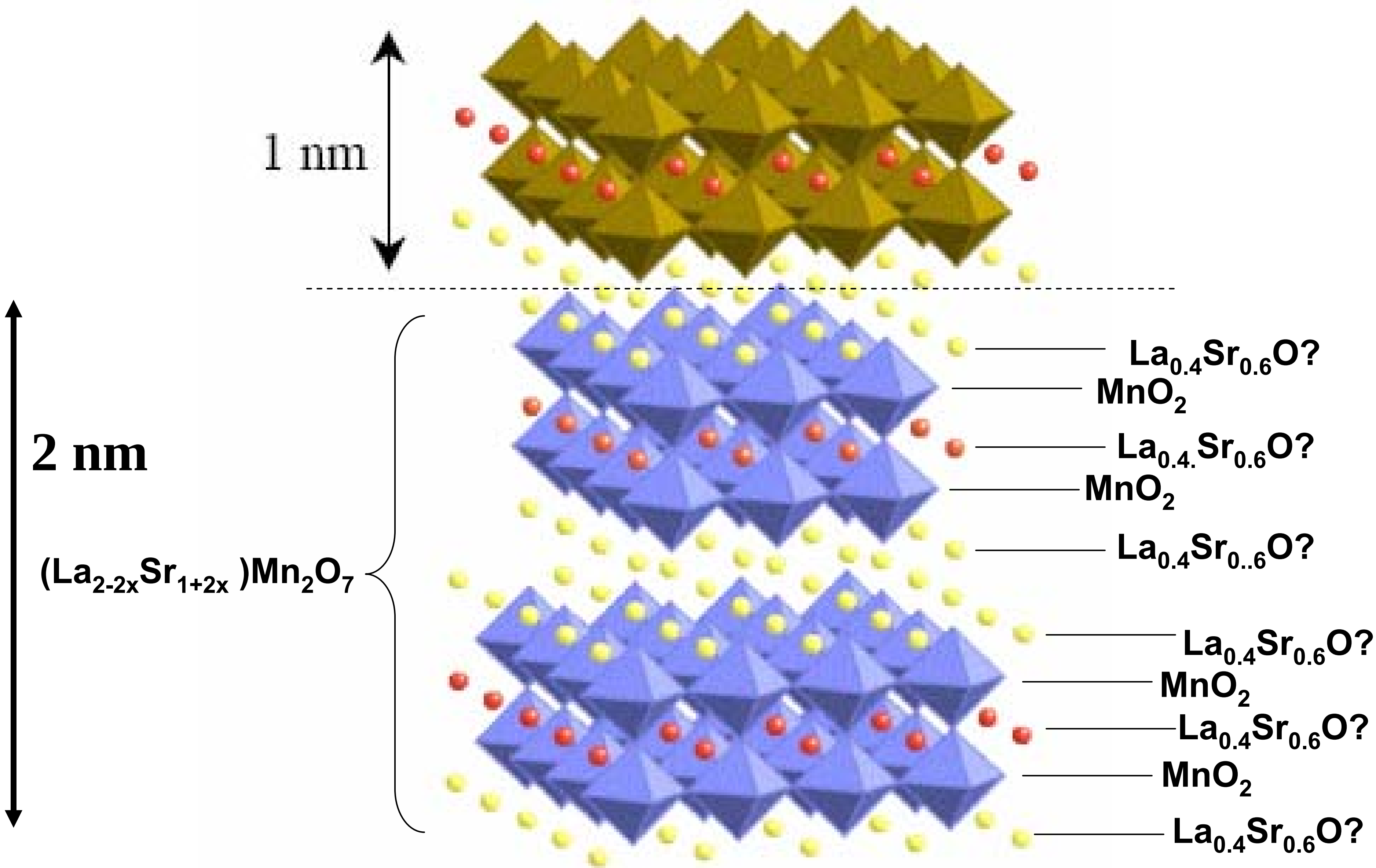
STANDING-WAVE EXCITED SPECTROSCOPY--FUTURE POSSIBILITIES

- Other material pairs in multilayer (B_4C/W, Al_2O_3/Pt,…) + epitaxial multilayers → epitaxial samples
- Smaller periods (to ~25-30 Å) → smaller SW period, better resolution
- Lower $h\nu_{inc}$ →higher Bragg angles→perpend. component of M
- X-ray emission→ deeper layers, more sensitivity to SW position

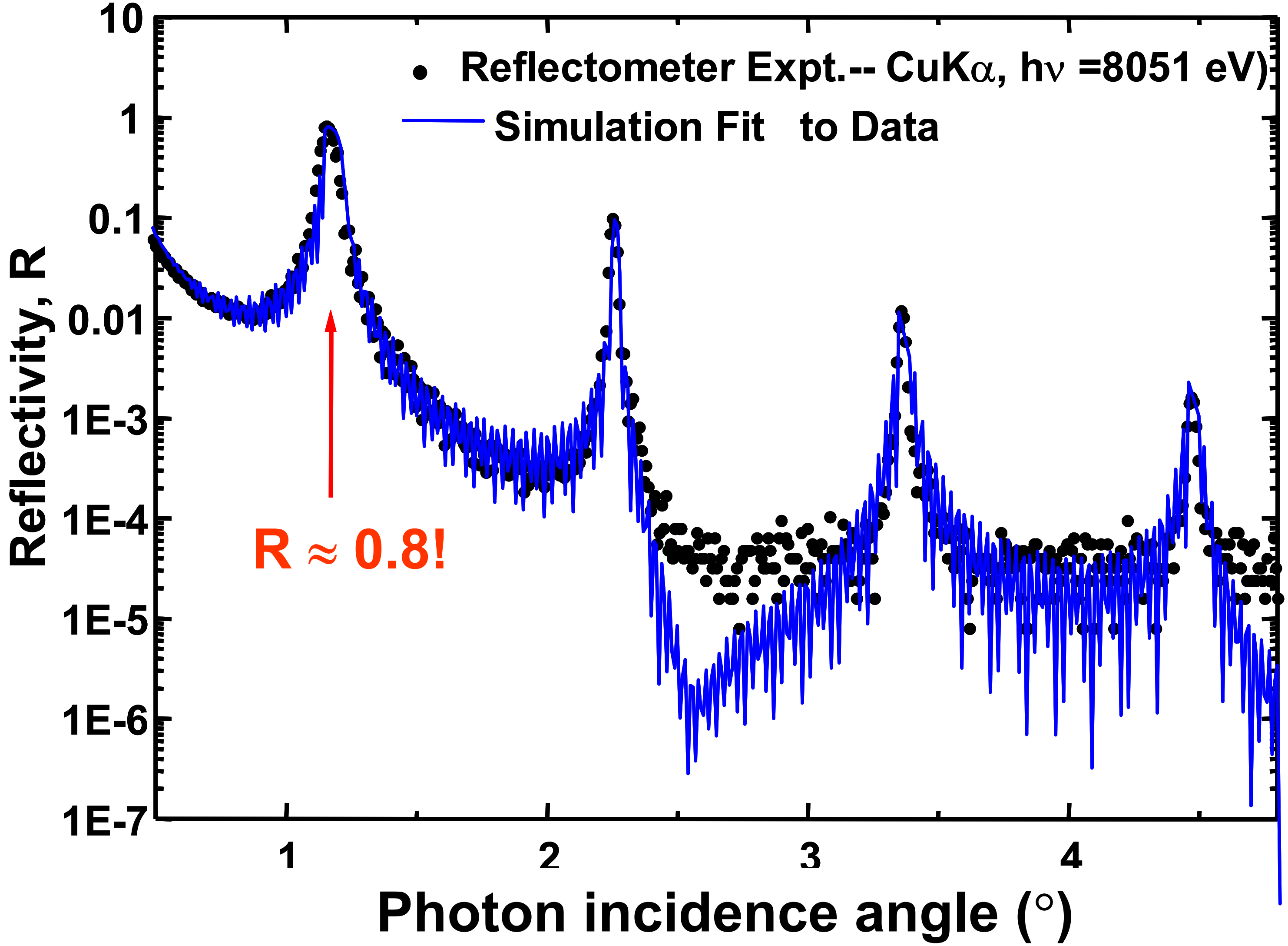




STANDING-WAVE EXCITED SPECTROSCOPY—BILAYERED MANGANITE



Standing waves with hard x-rays: reflectivity from a B_4C/W multilayer: ~ 8.0 keV



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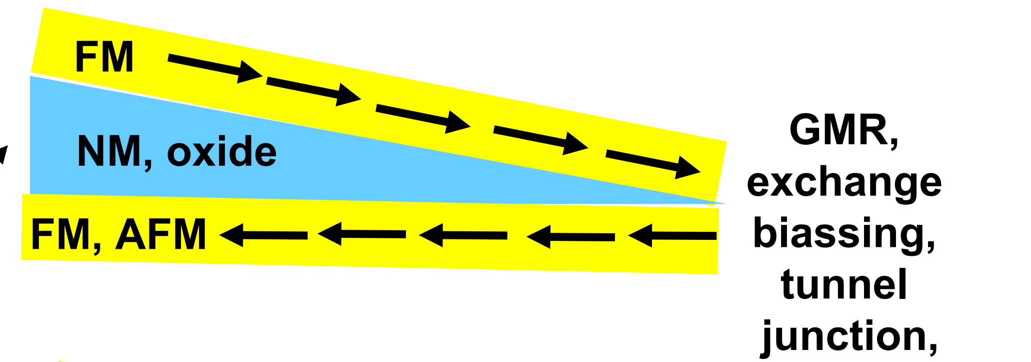
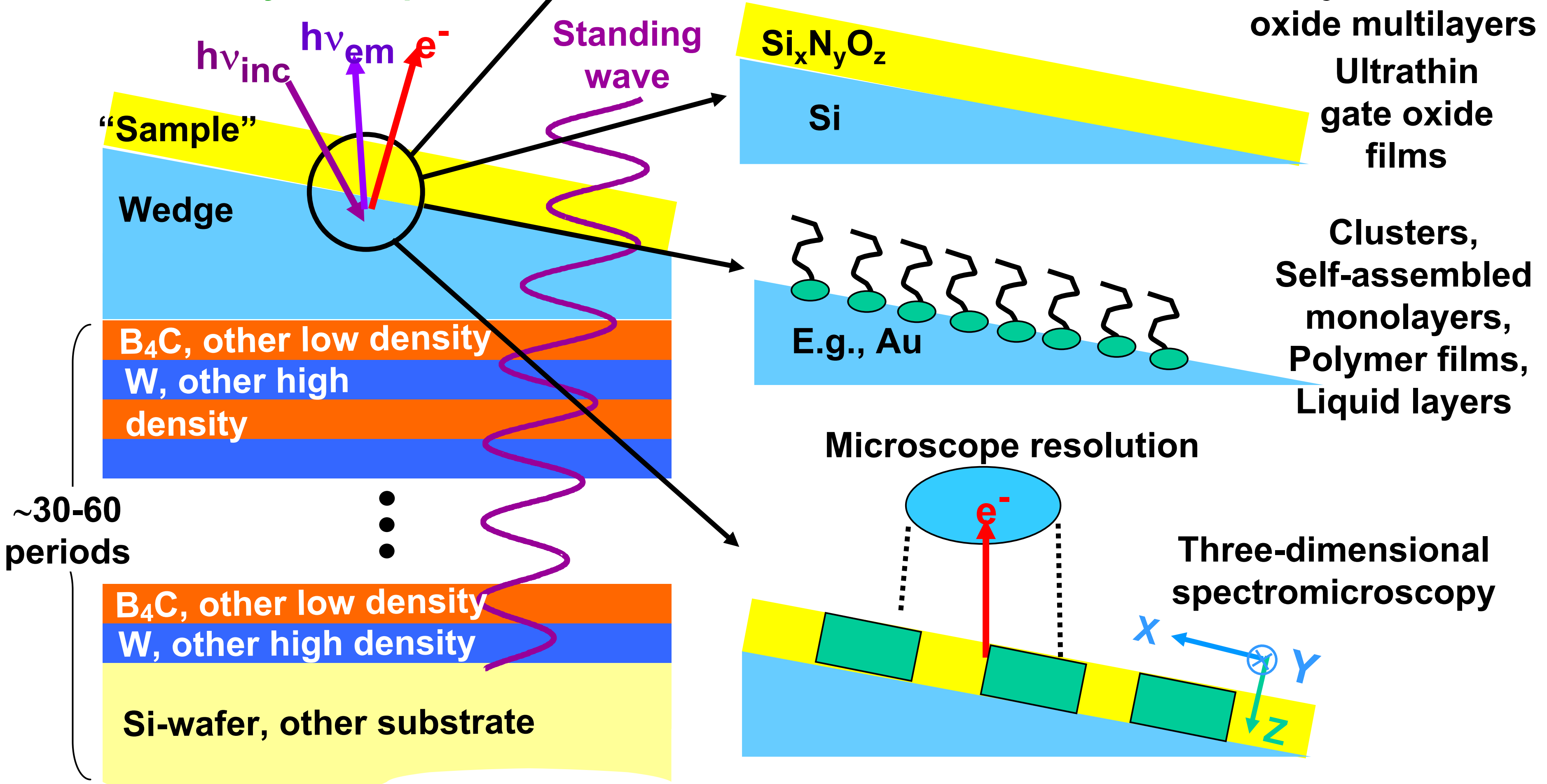
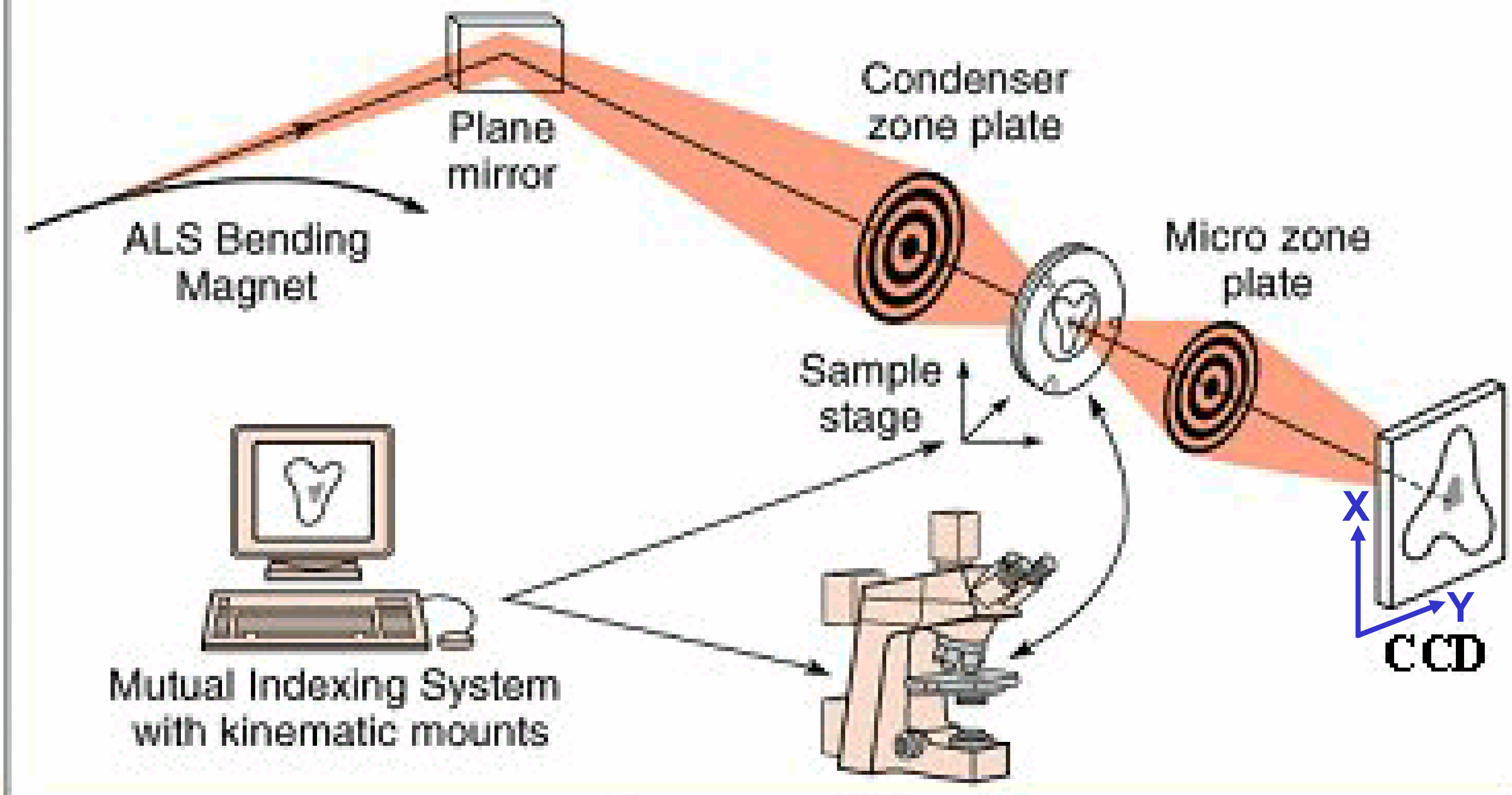
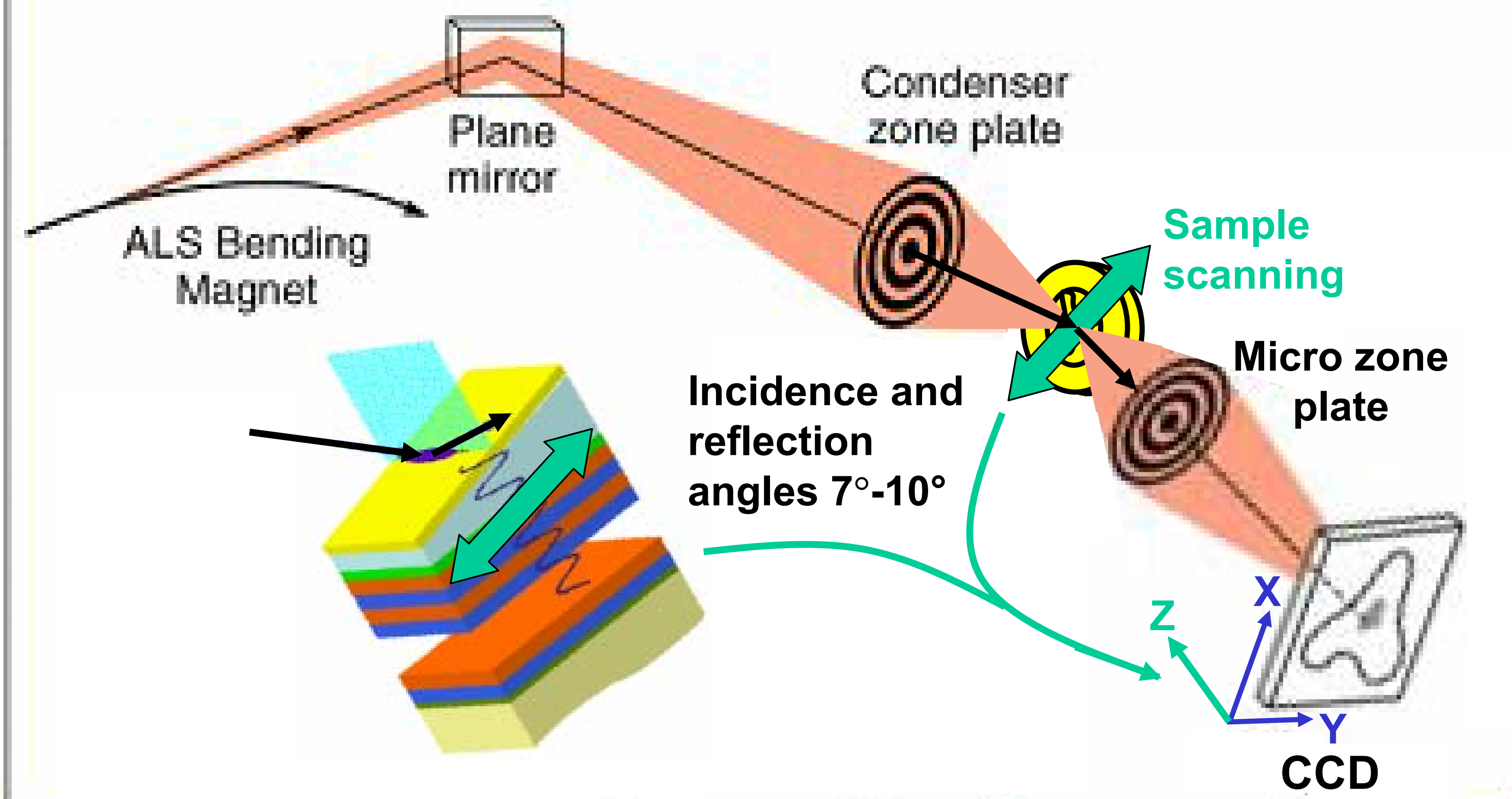




ALS X-ray microscope XM-1--Normal Transmission Configuration



ALS X-ray microscope XM-1--Proposed Reflection Configuration



G. Denbeaux, P. Fischer, C.F. et al.

Standing-wave spectroscopy also in:

- PEEMs if incidence angle can be tuned sufficiently
- Focussed beam scanning microscopes—APS nanobeamline @ 50 nm

Summary and Future Prospects at the APS

→***INSTRUMENTATION:*** **Multi-technique experimental system for studying samples, plus much faster detection system for the future**

→***MULTIPLE SPECTROSCOPIC MEASUREMENTS (PS, XAS, XES/RIXS) ON A CMR OXIDE: $La_{1-x}Sr_xMnO_3$ (x = 0.3, 0.4):*** **High-temperature electron localization onto Mn (polaron), connection with T*→desirable with hard x-ray photoemission as well**

→***BURIED INTERFACES STUDIED WITH X-RAY STANDING WAVES:***

GMR--Fe (ferromagnet)/Cr(non-magnetic):

- **Core photoelectron multiplets—**
  No change in Fe or Cr local moments through interface
- **Core intensities and MCD, standing wave wedge scan and rocking curves--**
  ~ 2-3 Å resolution in depth, induced ferromagnetism in Cr just below the interface

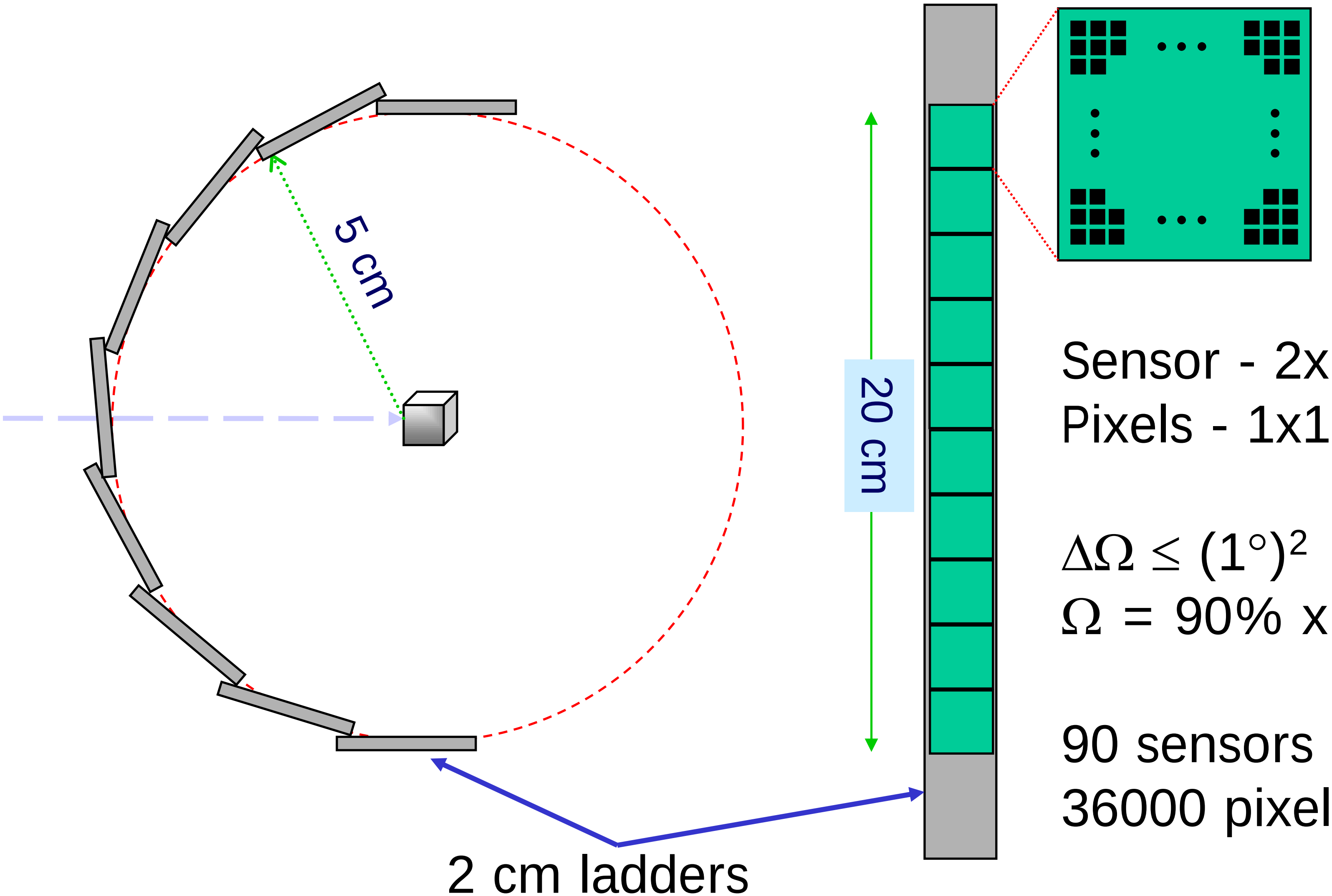
MTJ--Al_2O_3/CoFe/CoFeB:

- **Core binding energies--Two states of B identified and localized in depth**
- **Valence spectra--density of states enhancement @ E_F vs CoFe thickness,**
  explains higher magnetic tunnel resistance

→***AT THE APS OF THE FUTURE:***

- **High-energy photoemission/diffraction in the 5-10 keV range:**
  variable bulk sensitivity, MCD/MLD, focussed beam to ≤50 nm
- **Standing wave studies of buried interfaces in the 0.5-10 keV range:**
  photoelectron and fluorescent x-ray detection
- **Next-generation detection systems, time-resolved pump-probe studies,**
  spin detector for photoelectrons

Next Generation Detection for EXAFS/X-ray Fluorescence Holography (P. Denes et al., LBNL, proposed)



Sensor - 2x2 cm^2
Pixels - 1x1 mm^2

$\Delta\Omega \leq (1°)^2$
$\Omega = 90\% \times 2\pi$

90 sensors
36000 pixels

Applications: Ultrahigh-speed EXAFS, Holograms in seconds or single XFEL pulse