Soft-X-ray ARPES at Swiss Light Source: k-resolved electronic structure of 3D materials, buried heterostructures and impurities

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Outline

1. Why ARPES in the soft-X-ray range?
   - probing depth, 3D momentum resolution and resonant photoemission
2. Instrumentation
3. Spectroscopic abilities of SX-ARPES and results
   - from 3D electronic structure to buried heterostructures and impurities
Why Soft-X-Ray ARPES \((h\nu \sim 300-2000 \text{ eV})\)?

**Virtue 1: Increasing \(\lambda\)**
- increasing bulk sensitivity
- buried impurities, interfaces and heterostructures

\(\Rightarrow \text{Virtue 2: Intrinsic resolution } \Delta k_\perp = \lambda^{-1}\)
- reducing \(\Delta k_\perp \Rightarrow\) sharply defined 3D \(k\)-vector
- + free-electron final states \(\Rightarrow\) 3D materials

**Virtue 3: Regular atomic-like matrix elements**
- experimental \(I(E,\theta) \sim\) pure spectral function \(A(\omega,\mathbf{k})\)

**Virtue 4: Elemental specificity through resonant photoemission**
- \(L\)-edges of TMs and \(M\)-edges of REs
- combination with increasing \(\lambda \Rightarrow\) buried interfaces, heterostructures and impurities
Challenges of SX-ARPES

- $\Delta E$ of a few tens meV (vs a few meV in VUV-ARPES)

- $e-ph$ scattering destructive for $k$-resolution (photo-$e$ wavelength $\sim$ thermal motion) $\Rightarrow$ coherent signal transfers to $k$-integrated DOS:

$$I^{coh} = W(T)I^{coh}_{T=0}$$

$$W(T) = e^{-\Delta G^2 U_0^2(T)}, \Delta G^2 \propto E \text{ and } U_0^2 \propto T / M_a$$

(full theory - talk of J. Braun)

- loss of photoexcitation cross-section by 2-3 orders of magnitude
  - efficient detectors and high photon flux instrumentation
• soft-X-ray radiation in the energy range 300 – 1600 eV
• circular and 0-180° variable linear polarizations
• collimated-light PGM optical scheme
• **flux up to 1.5x10^{13} ph/s/0.01\%BW:** breakthrough of the cross-section problem
• routine $\Delta E$ around 1 keV from 100 meV (acquisition ~ few min) to 50 meV (~ tens of min)

SX-ARPES of bulk materials: 3D bandstructure and Fermi surface of VSe$_2$

- quasi-2D structure with weaker interlayer interaction
- significant 3D-lity due to V $3d$ and Se $4p_z$ orbitals
**SX-ARPES of bulk materials: VSe₂**

- **Experimental $E(k)$**
  - $k_\perp$ by varying $hv$ around 900 eV
  - $\Delta E \sim 110$ meV

  ↓

  - excellent statistics in a few min despite the cross-section loss ($\sim 1800$ for V3$d$ and 35 for Se 4$p$ vs $hv=50$eV)
  - *e-ph* scattering effects (spectral weight transfer to 3D-DOS and $k$-broadening) are weak at $T = 11$K despite low $T_D = 220$ K
  - agreement with GGA-DFT (*P. Blaha, TU Wien*)

$h_v = 885$ eV
- Experimental Fermi surface

- significant 3D-lity of the V 3d and Se 4p_z orbitals
- agreement with GGA-DFT (P. Blaha, TU Wien)
- clarity of the experimental data: sharp definition of 3D wavevector + regular matrix elements at soft-X-ray energies
- **Origin of 3-dimensional CDWs**

  - Unusual 3-dimensionality of CDWs:
    
    \[
    \mathbf{q}_{\text{CDW}} = \mathbf{q}_{//} + \mathbf{q}_{\perp} \quad (q_{\perp} \sim k_{\perp} \text{BZ}/3)
    \]

- **Perpendicular FS cut in MLL'M' plane**

  - 3D warping to support nesting near \( q_{\perp}^{\text{CDW}} \)

- **V.S. et al., PRL 109 (2012) 086401**

- Autocorrelation peak exactly at \( \mathbf{q}_{\text{CDW}} \)
  (slightly shifted by commensurization)
SX-ARPES of buried interfaces: Interface states in LaAlO$_3$/SrTiO$_3$

2DEG at the LAO/STO interface (talk of F. Baumberger):

- electrons delivered by Ti$^{3+}$ ions
- Critical LAO thickness of 4 u.c. ⇒ SX-ARPES required

- Idea: Ti$^{3+}$ **resonant** SX-ARPES to enhance the 2DEG signal
Resonant XPS depth profiling of the interface state

C. Cancellieri, M. Reinle-Schmitt et al; samples: Uni Geneve

- measurements @ RT ⇒ averaging in k-space
- insulating (3 uc LAO) vs conducting (6 uc LAO)
- C. Cancellieri et al., PRL 110 (2013) 137601
Fermi surface and bandstructure of the interface states

- \( T = 11 \text{ K} \) to suppress \( e-ph \) scattering
- FS mapping at \( 2p \) resonance of \( \text{Ti}^{3+} \) at \( h\nu = 460.2 \text{ eV} \)
- Experimental \( \Delta E \sim 80 \text{ meV} \)

- different FS sheets depending on \( \mathbf{K}_{\parallel} \) and polarization
- Subband structure of the interface state

- composite interface state with subbands of different symmetries
- different sample preparations:
  - Luttinger count of the FS area follows $n_e$ from transport properties $\Rightarrow$ coherent interface conductivity with insignificant contribution of ox-vacancies
  - interface charge varies and differs from 0.5 $e$/u.c. (deviations from both structural deformation and polar catastrophe model)

- A. Filippetti, P. Ghosez & D. Fontaine

SX-ARPES of Impurities:
Diluted magnetic semiconductor GaMnAs

• Impurity vs band states in the ferromagnetism:
  – energy alignment of the Mn impurity band?
  – hybridization with the host GaAs bands?

• HAXPES studies by A.X. Gray et al (Nature Mat. 11 (2012) 957)
  and J. Fujii (PRL 107 (2011) 187203) \( \Rightarrow \) Mn weight below \( E_F \)
Resonant SX-ARPES of the impurity state in GaMnAs

M. Kobayashi et al (SLS); samples: Uni Tokyo

- Measurements through amorphous capping As layer: native electronic structure
- Mn concentration only 2.5% of Ga ⇒ hard to see unless resonantly enhance Mn 3d weight
- Resonance on ferromagnetic XAS peak ⇒ ferromagnetic non-dispersive Mn 3d impurity band just below VBM
- Linear dichroism: Hybridization of the impurity and host states

- Intensity at the ferromagnetic resonance $\Rightarrow$ Mn 3$d$ impurity band hybridizes with LH but only weakly with HH band (different wavefunction localization)
Picture of ferromagnetism in GaMnAs

- Occupied Mn 3d impurity band hybridizing with GaAs host band
- Ferromagnetism induced by GaAs mediated exchange between Mn atoms
- Description starting from the Anderson impurity model


S. Ohya et al., Nat. Phys. (2011)
Summary

- **Spectroscopic abilities** of SX-ARPES with advanced instrumentation:

  - **Bulk materials** resolved in 3-dim $k$ (increase of $\lambda$ resulting in $k_\perp$ definition): FS and CDWs in VSe$_2$; shadow FS in perovskite CMR-La$_{0.33}$Sr$_{0.67}$MnO$_3$; intra-cell interference effects in pnictide HTSCs; bulk Rashba splitting in non-centrosymmetric BiTeI (talk by G. Landolt); $sp$- and $f$-states hybridization in heavy-fermions (talk by D. Vyalikh); bulk band renormalization and correlation effects in '122' pnictides (talk by E. Razzoli) …

  - **Buried interfaces** (increase of $\lambda$ combined with elemental specificity through resonant PE): Depth localization and FS of LaAlO$_3$/SrTiO$_3$; FS of LaAlO$_3$/LaNiO$_3$ …

  - **Buried impurities**: Ferromagnetic impurity band in GaMnAs; magnetic impurities in pnictides; InFeAs …

- **SX-ARPES keywords**: global VB energy scale, large probing depth, 3D electronic structure, elemental specificity through resonant photoemission, buried heterostructures and impurities, depth profiling with X-ray standing waves
SX-ARPES team

V.N.S. (BL Scientist)  M. Kobayashi (PostDoc)  L. Lev (PostDoc)  C. Hess (BL Technician)

Collaborators at SLS

External collaborators

C. Cancellieri (MS group)  J. Minar (LMU Münich)  C. Fadley (UC Davis)

T. Schmitt (RIXS)  M. Shi (SIS beamline)  L. Patthey (now SwissFEL)

Support from PSI

Optics (group of U. Flechsig), ID (group of T. Schmidt), Controls (X. Wang, J. Krempasky) et al
Postdoc position available

www.psi.ch/sls/adress/

Next call: September 15
SX-ARPES Endstation @ ADDRESS: Geometry

- **grazing incidence** to increase photoyield
- **analyzer PHOIBOS-150** ($\Delta \theta$ better than $0.07^\circ$)
- **slit orientation**
- **sample rotation by tilt**
- **primary sample rotation**
- **manipulator axis**
- **X-ray beam 74 x 10 μm²**

- **horizontal rotation axis** to balance the vertical/horizontal X-ray footprint
- **vertical measurement plane**
- **rotatable analyzer: parallel slit orientation** $\Rightarrow$ symmetry analysis of the valence states


![Graph showing Iₚₑ/Iₚₑ(45°) for Cu and GaAs](image-url)
Penetrating ability of SX-ARPES: Band structure of GaAs through amorphous As layer

M. Kobayashi et al (SLS); samples: Uni Tokyo

- large $\lambda$ required: Soft-X-ray ARPES

$hv = 287$ eV

$hv = 453$ eV

$hv = 892$ eV

- acquisition time 3 min
- GaAs signal piles up with $hv$
- New diagnostics tool for MBE grown films: Applications in microelectronics