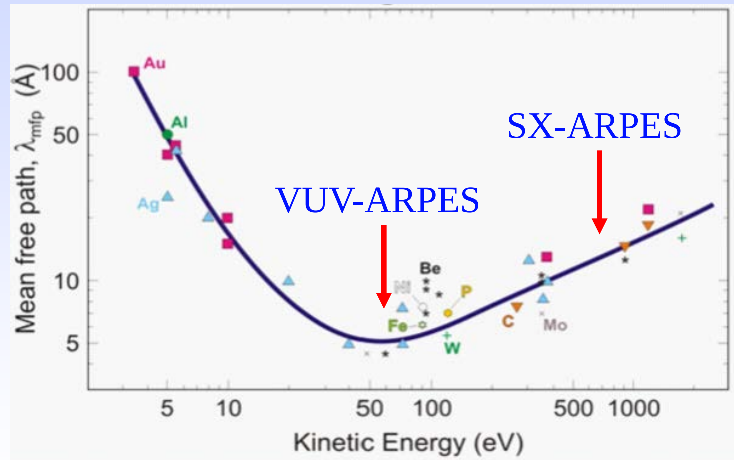
# Soft-X-ray ARPES at Swiss Light Source: k-resolved electronic structure of 3D materials, buried heterostructures and impurities

*V.N. Strocov*, *M. Kobayashi*, *C. Cancellieri*, *M. Reinle-Schmitt*, *P. Willmott* (Swiss Light Sorce, Paul Scherrer Institute, Switzerland), J.-M. Triscone (University of Geneva), *M. Oshima*, *A. Fujimori*, *M. Tanaka* (University of Tokyo, Japan), *P. Blaha* (TU Vienna, Austria)

## 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 ($h\nu$ ~ 300-2000 eV)?

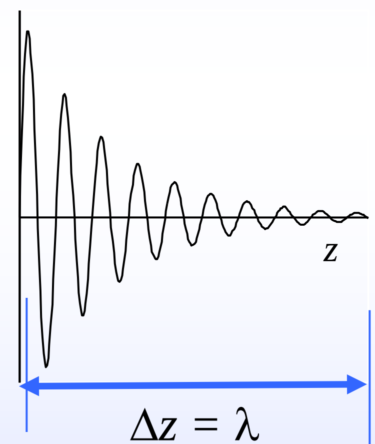



## Virtue 1: Increasing $\lambda$

- increasing bulk sensitivity
- buried impurities, interfaces and heterostructures

## ⇒Virtue 2: Intrinsic resolution $\Delta k_\perp = \lambda^{-1}$

- reducing $\Delta k_\perp$ ⇒ sharply defined 3D **k**-vector
- + free-electron final states ⇒ 3D materials




## Virtue 3: Regular atomic-like matrix elements

- experimental $I(E,\theta)$ ~ 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 $\lambda$ ⇒ buried interfaces, heterostructures and impurities

# Challenges of SX-ARPES

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

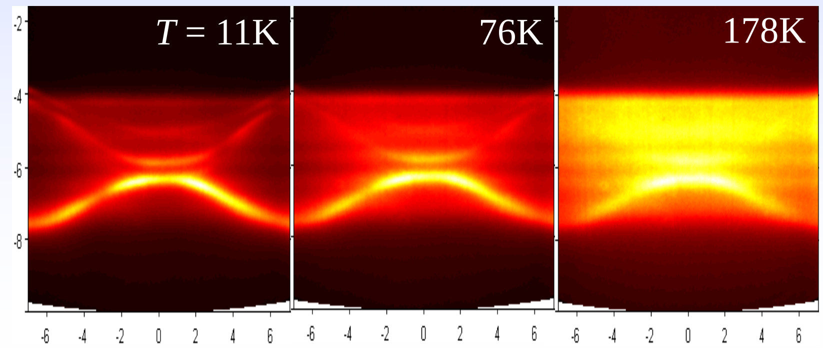
- *e-ph* scattering destructive for **k**-resolution (photo-*e* wavelength ~ thermal motion) ⇒ coherent signal transfers to **k**-integrated DOS:

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

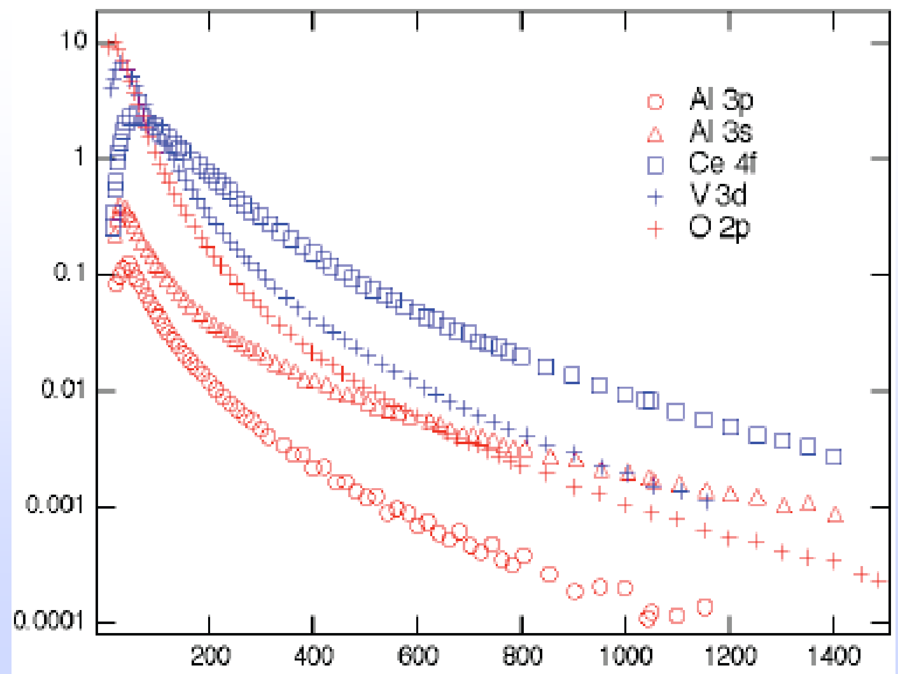
$$W(T) = e^{-\Delta G^2 U_0^2(T)}, \Delta G^2 \propto E \text{ and } U_0^2 \propto T / M_a$$

(full theory - talk of J. Braun)

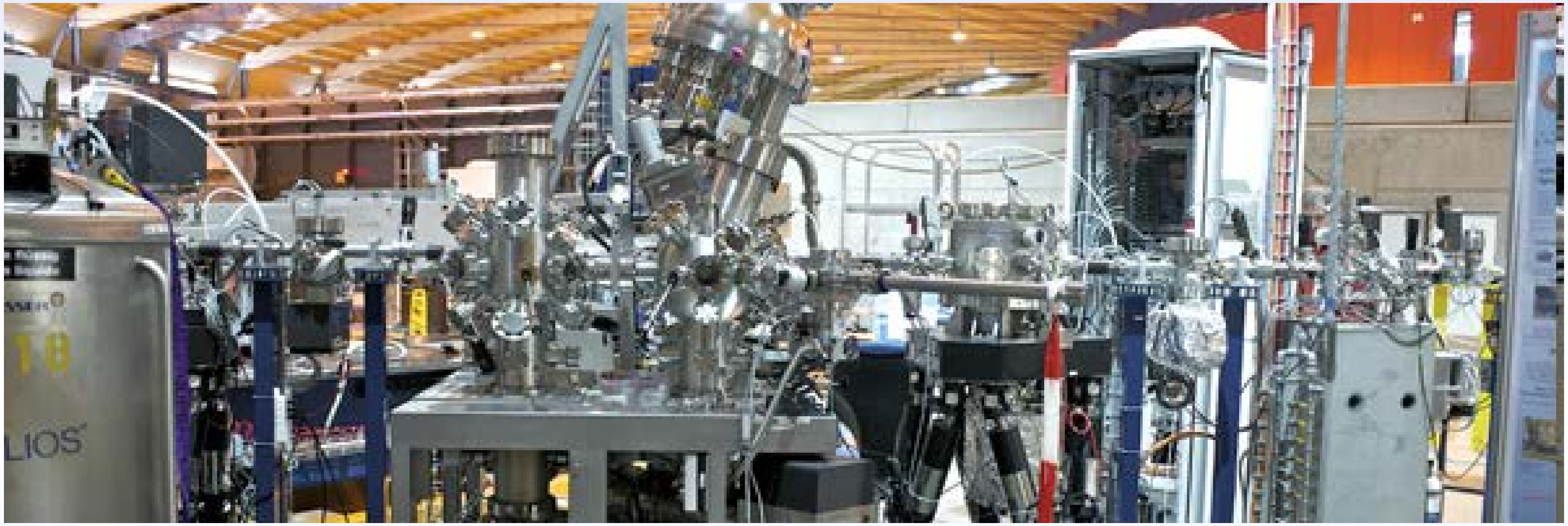
Ag(100), $h\nu$ = 572 eV, *s*-pol




- loss of photoexcitation cross-section by 2-3 orders of magnitude
- efficient detectors and high photon flux instrumentation



# ADRESS (*ADvanced RESonant Spectroscopies*) Beamline at SLS

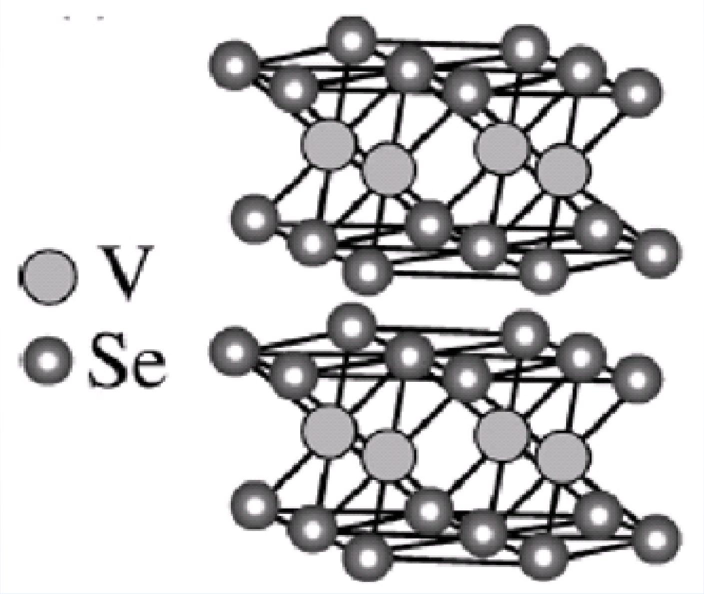



- soft-X-ray radiation in the energy range 300 – 1600 eV
- circular and 0-180° variable linear polarizations
- collimated-light PGM optical scheme
- **flux up to $1.5 \times 10^{13}$ ph/s/0.01%BW:** breakthrough of the cross-section problem
- routine $\Delta E$ around 1 keV from 100 meV (acquisition ~ few min) to 50 meV (~ tens of min)

V.S. *et al*, J. Synchr. Rad **17** (2010) 631

# 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 3*d* and Se 4$p_z$ orbitals

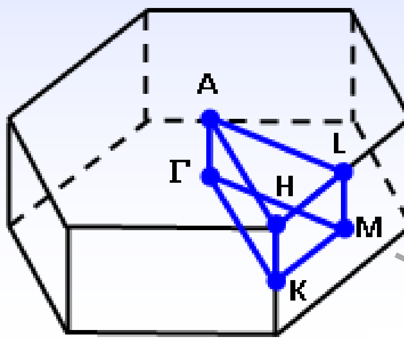


## - Experimental $E$(k)

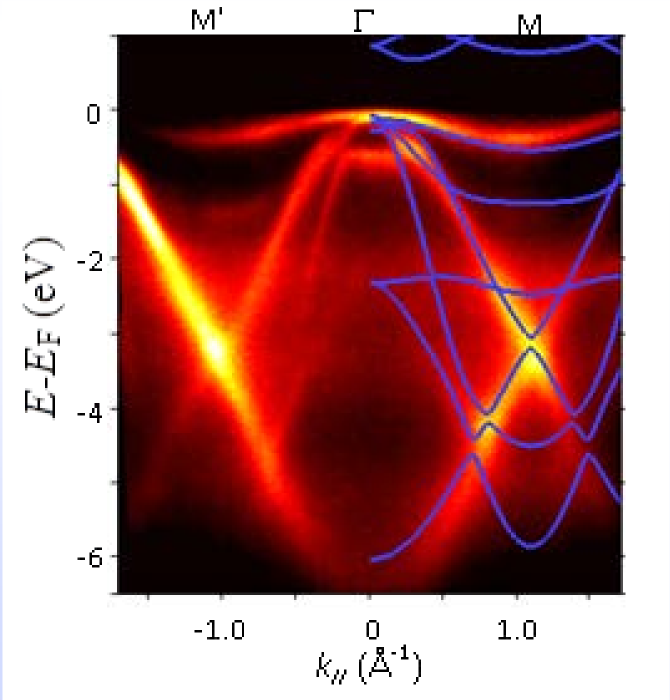
- $k_{\perp}$ by varying $h\nu$ around 900 eV
- $\Delta E$~110 meV

⇓

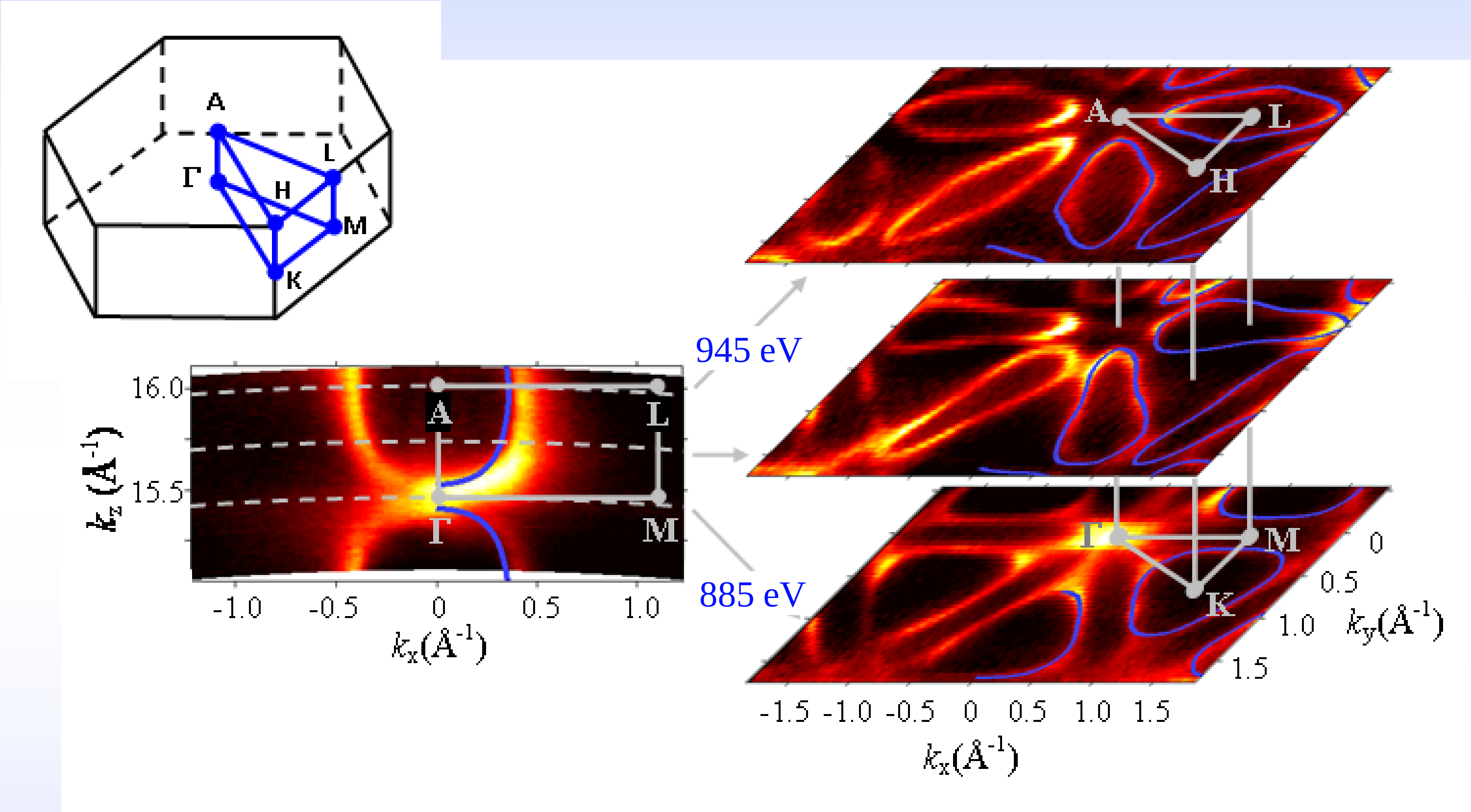
- excellent statistics in a few min despite the cross-section loss (~1800  for V3*d* and 35 for Se 4*p* vs *hv*=50eV)
- *e-ph* scattering effects (spectral weight transfer to 3D-DOS and **k**-broadening) are weak at $T$ = 11K despite low $T_D$ = 220 K
- agreement with GGA-DFT (*P. Blaha, TU Wien*)




***hv* = 885 eV**

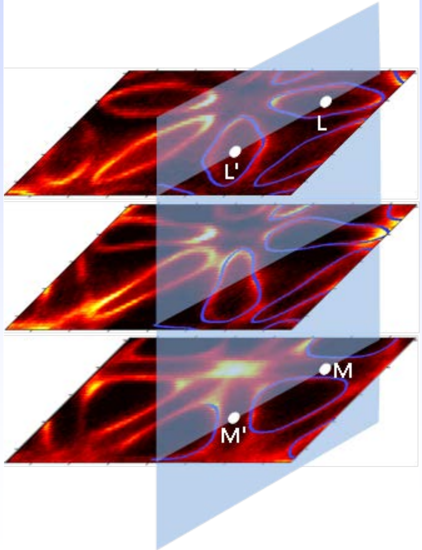


## - Experimental Fermi surface




- significant 3D-lity of the V 3*d* and Se 4$p_z$ 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

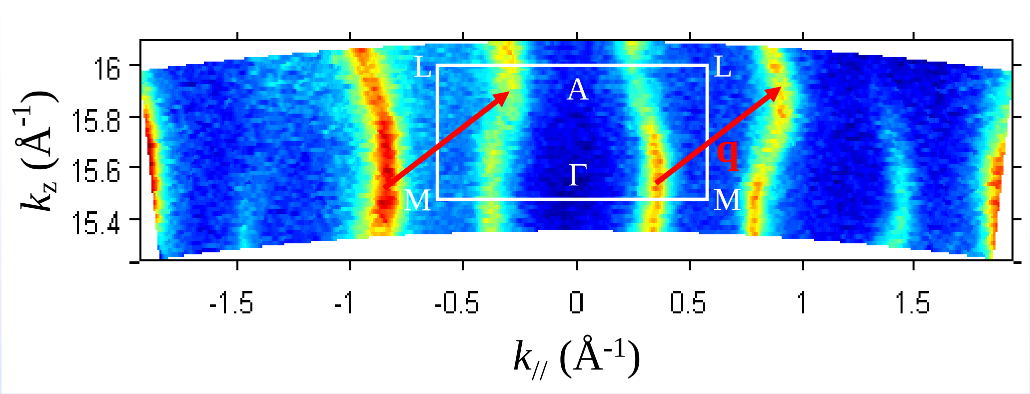
## - Origin of 3-dimensional CDWs

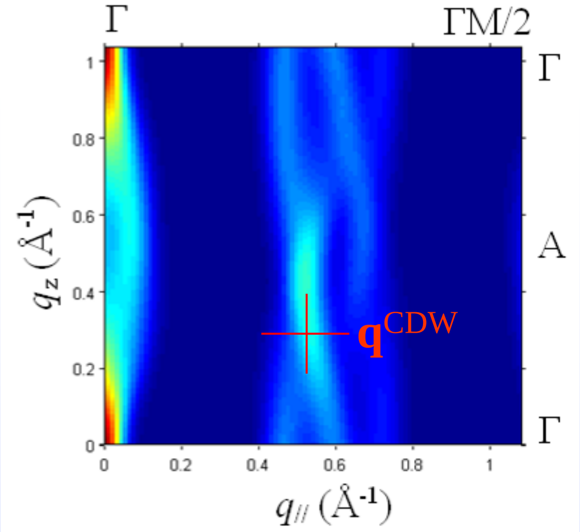



- Unusual 3-dimensionality of CDWs:

$$\mathbf{q}^{CDW}=\mathbf{q}_{//}+\mathbf{q}_{\perp}\ (q_{\perp} \sim k_{\perp}^{BZ}/3)$$

- Perpendicular FS cut in MLL'M' plane




- 3D warping to support nesting near $q_{\perp}^{CDW}$

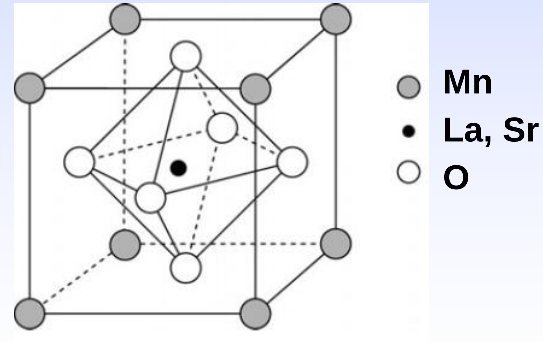
- Autocorrelation peak exactly at $\mathbf{q}^{CDW}$ (slightly shifted by commensurization)

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

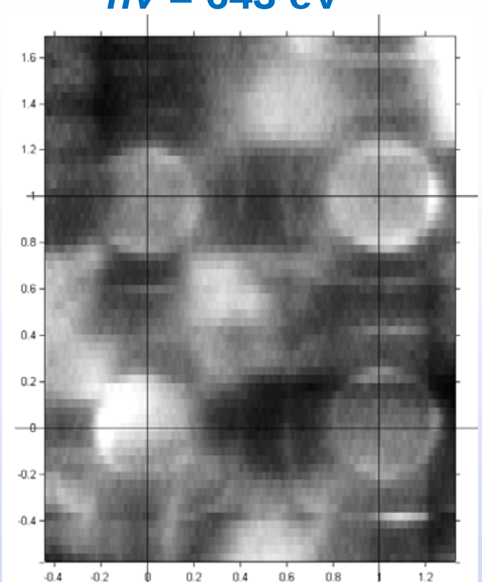
# 3D Fermi surface of the perovskite $La_{0.33}Sr_{0.67}MnO_3$

*L. Lev et al (PSI/Kurchatov Inst/LMU Muenich)*

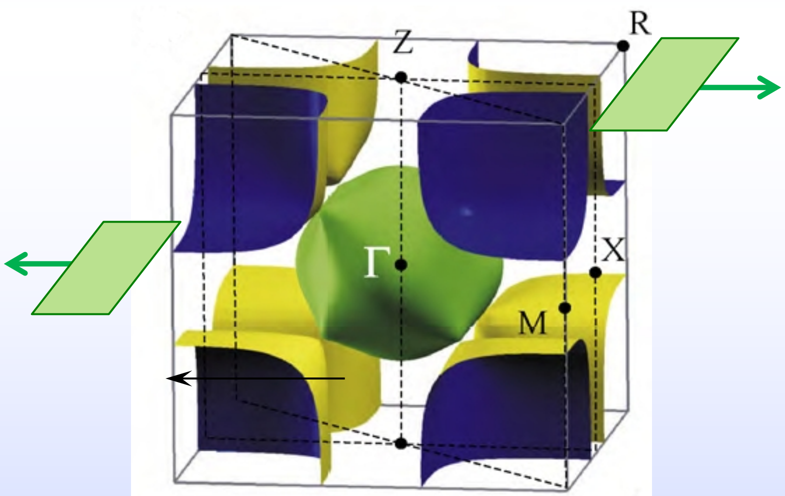
- CMR properties due to interplay of spin, charge and lattice degrees of freedom
- 3D perovskite structure



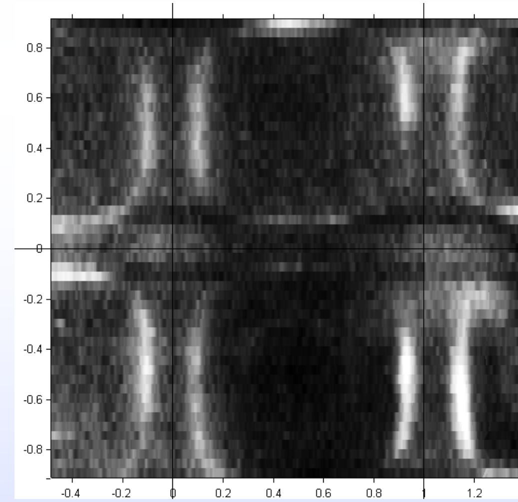

**$h\nu$ = 643 eV**



GGA+U calculations (P. Blaha)

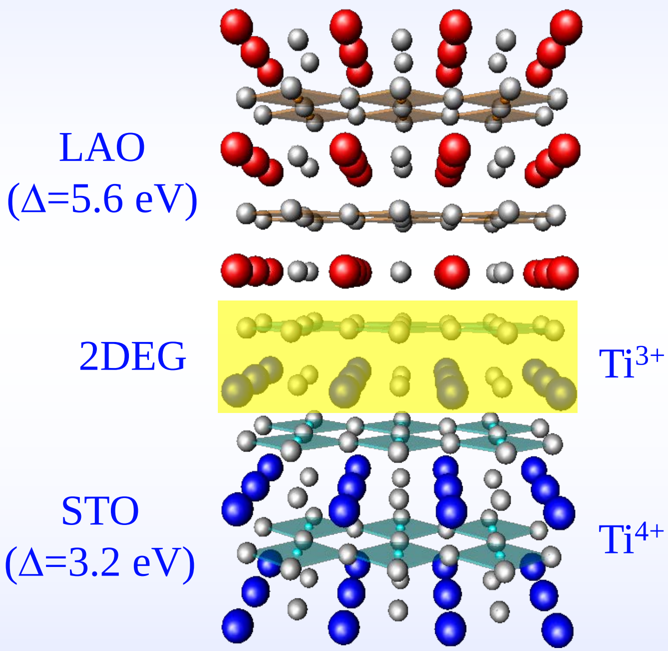



**$h\nu$ = 722 eV**



- first resolution of the FS of LSMO in 3D
- no spectral weight depletion at $E_F$ in contrast to bilayer LSMO
- "shadow" FS shifted by $(^{\pi}/_{a}\,^{\pi}/_{a}\,^{\pi}/_{a})$: Magnetic order or rhombohedral lattice distortion?

# SX-ARPES of buried interfaces: Interface states in $LaAlO_3/SrTiO_3$




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

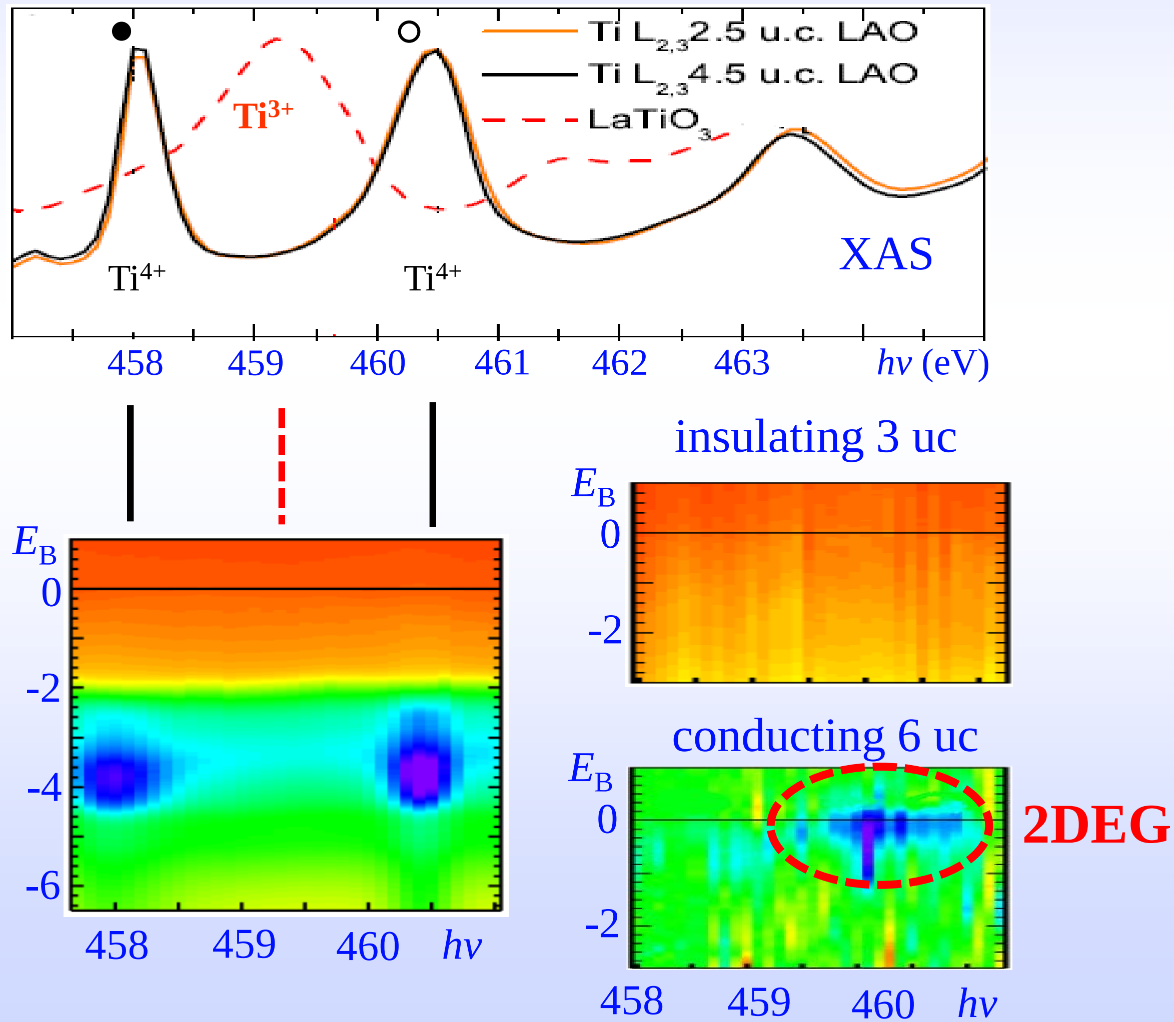
- electrons delivered by $Ti^{3+}$ ions
- Critical LAO thickness of 4 u.c.

⇒ SX-ARPES required

- Idea: $Ti^{3+}$ **resonant** SX-ARPES to enhance the 2DEG signal

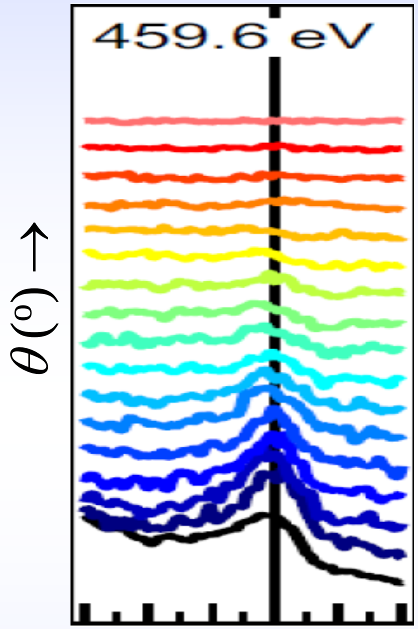
# Resonant XPS depth profiling of the interface state

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



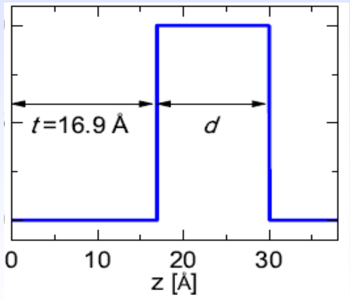

- measurements @ RT ⇒ averaging in **k**-space
- insulating (3 uc LAO) vs conducting (6 uc LAO)

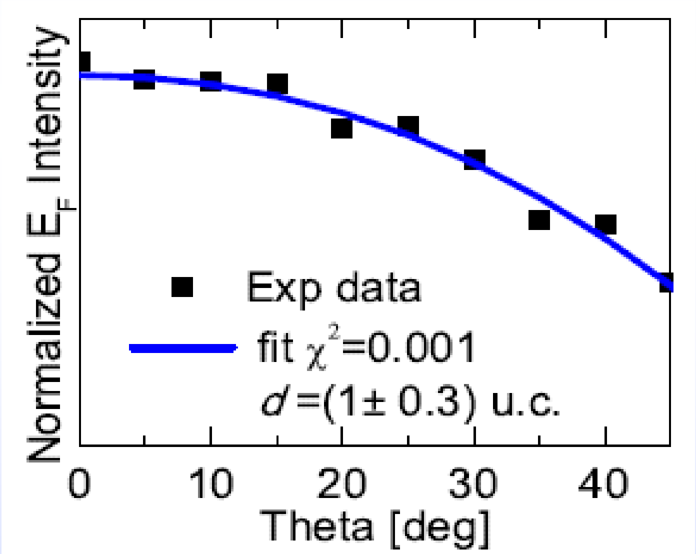
- Angle-dependent XPS to resolve the 2DEG depth profile




- **k**-integration due to RT

$$I(\vartheta) = G(\alpha, \vartheta)\int_0^\infty R(z)e^{-z/\lambda\cos\vartheta}dz$$



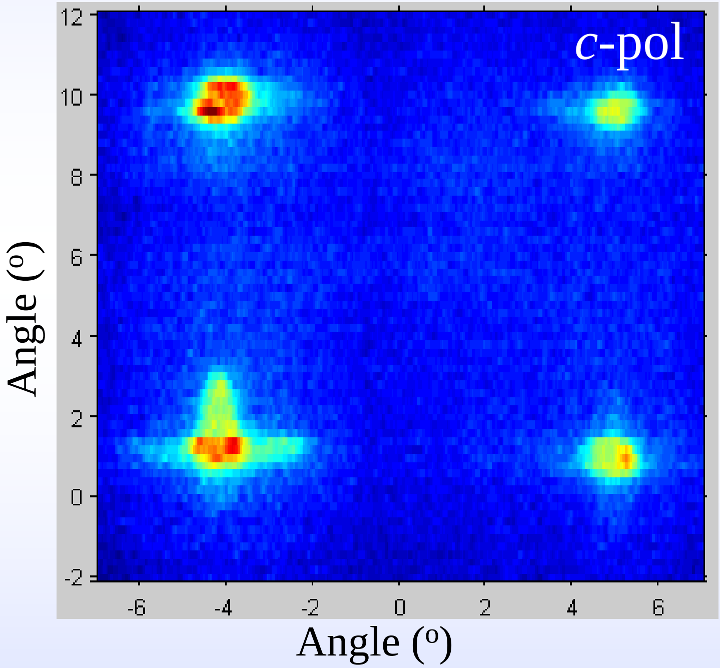



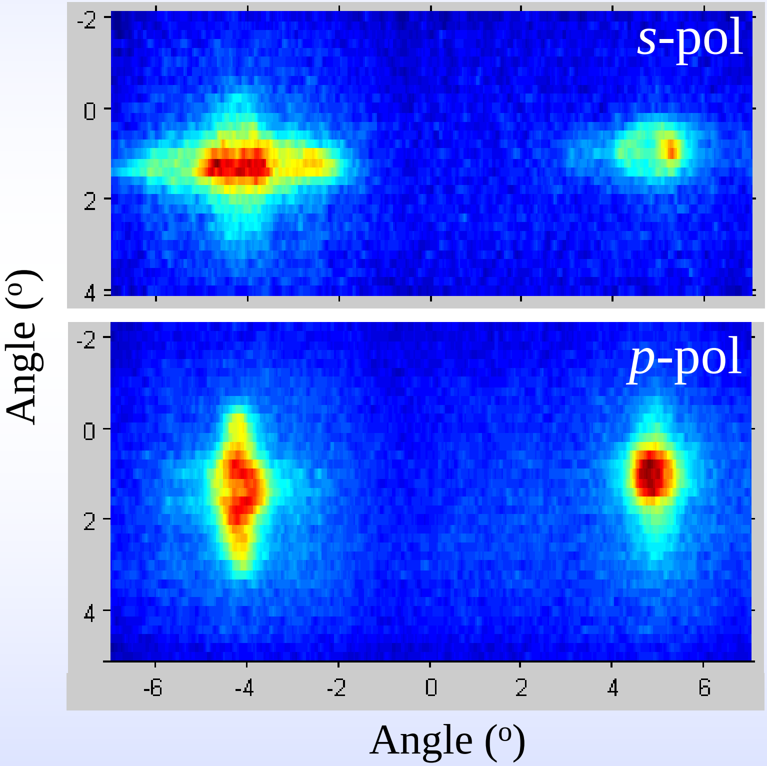

- 2DEG located within **1.0±0.3 u.c.** at the STO side of the interface

- C. Cancellieri *et al.*, PRL **110** (2013) 137601

# Fermi surface and bandstructure of the interface states

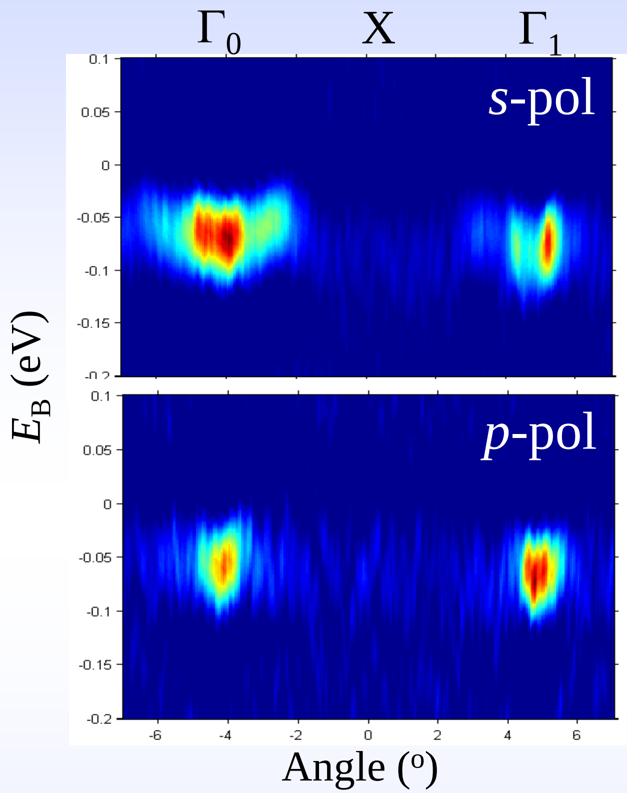
- T = 11 K to suppress *e-ph* scattering
- FS mapping at 2*p* resonance of $Ti^{3+}$ at $h\nu$ = 460.2 eV
- Experimental $\Delta E$ ~ 80 meV

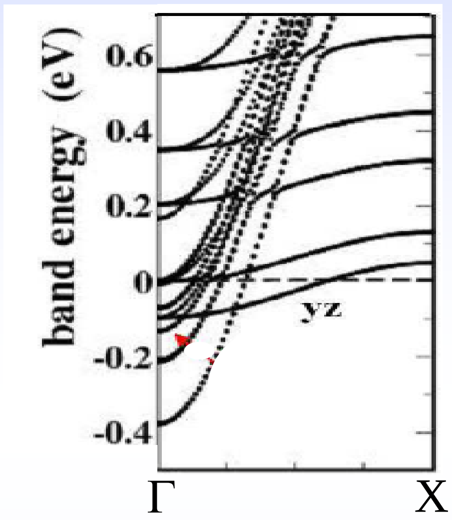



- FS shape of crossed $3d_{xy}$-like cigars (G. Berner *et al*, Phys. Rev. Lett. **110** (2013) 247601 - talk of M. Sing; N. Plumb *et al*, arXiv:1304.5948)
- different FS sheets depending on $\mathbf{K}_{//}$ and polarization

## - Subband structure of the interface state



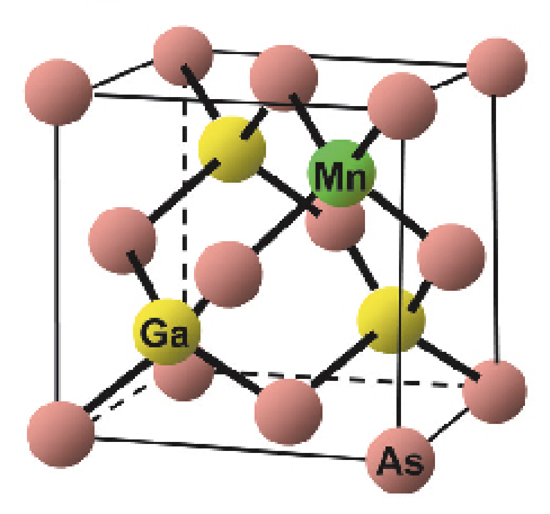

A. Filippetti, P. Ghosez & D. Fontaine

- composite interface state with subbands of different symmetries
- different sample preparations:

- Luttinger count of the FS area follows $n_e$ from transport properties ⇒ 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)

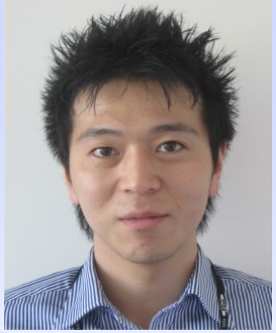
- C. Cancellieri *et al.*, arXiv:1307.6943 (2013)

# SX-ARPES of Impurities: Diluted magnetic semiconductor GaMnAs



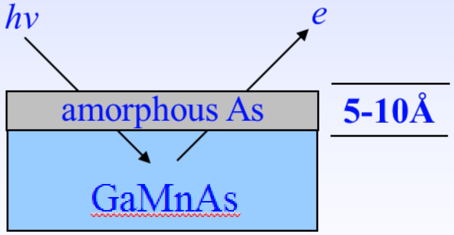

- Impurity vs band states in the ferromagnetism:
  – energy alignment of the Mn impurity band?
  – hybridization with the host GaAs bands?

- HAXPES studies by A.X. Gray *et al* (Nature Mat. **11** (2012) 957) and J. Fujii (PRL **107** (2011) 187203) ⇒ Mn weight below $E_F$

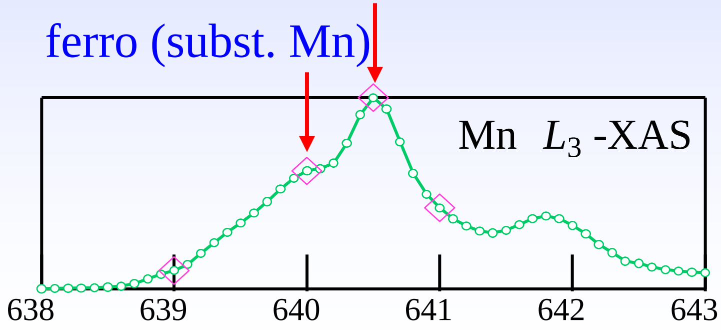


# Resonant SX-ARPES of the impurity state in GaMnAs

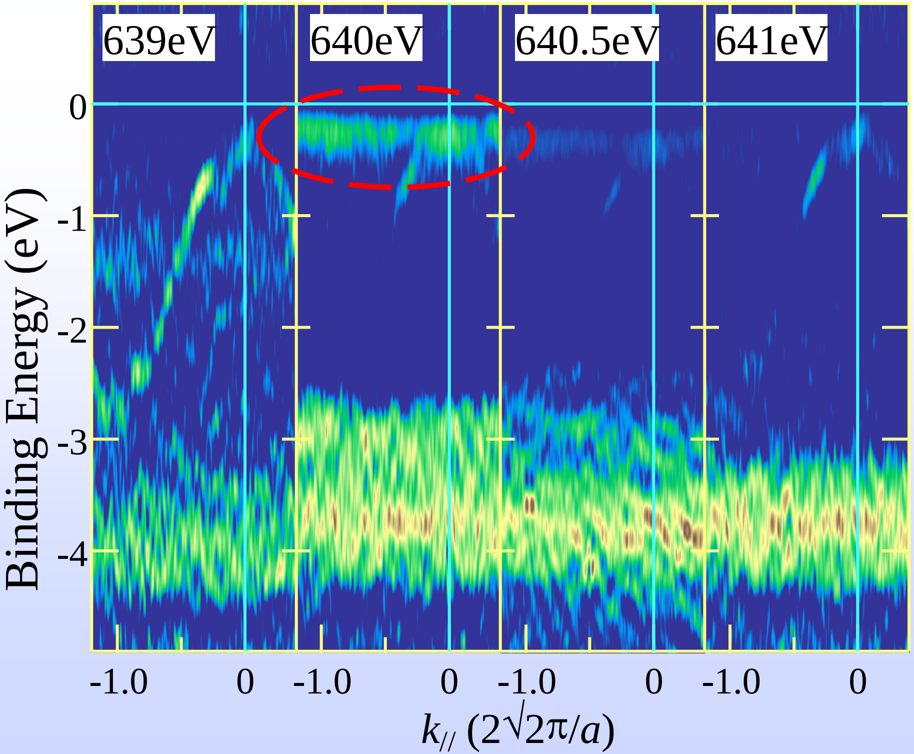
*M. Kobayashi et al (SLS); samples: Uni Tokyo*




- Measurements through amorphous capping As layer: native electronic structure




- Mn concentration only 2.5% of Ga
⇒ hard to see unless **resonantly** enhance Mn 3*d* weight



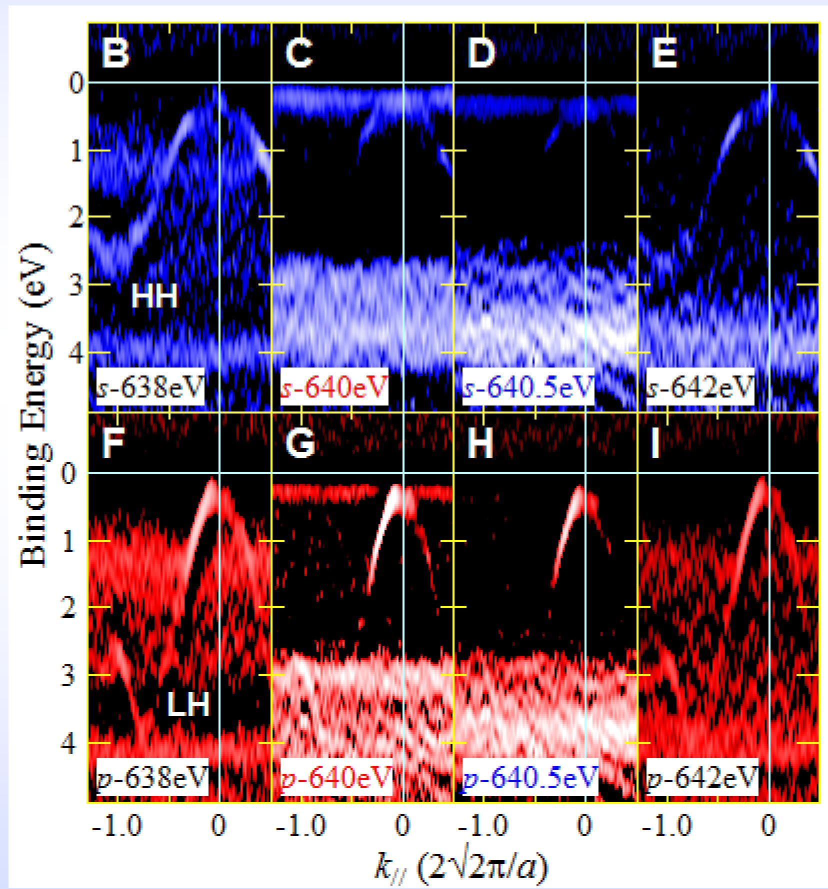

- Resonance on ferromagnetic XAS peak ⇒ **ferromagnetic non-dispersive Mn 3*d* impurity band** just below VBM

## - Linear dichroism: Hybridization of the impurity and host states

ferro ↓ para ↓

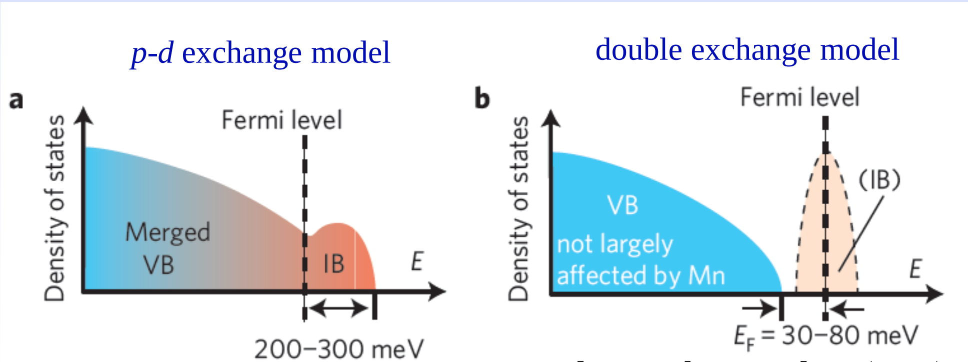
*s*-pol: HH-band

*p*-pol: LH-band

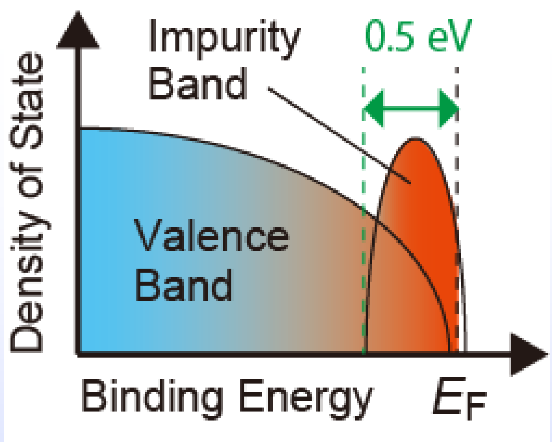


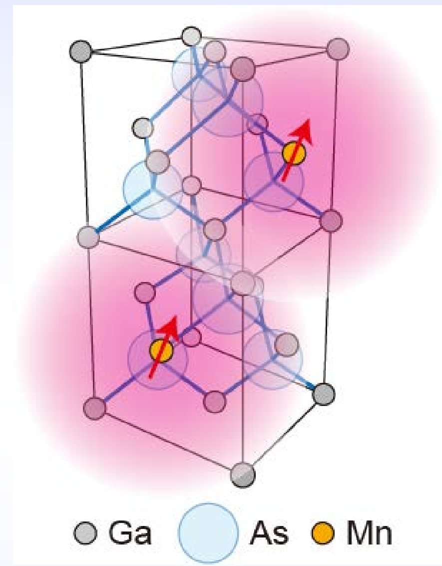

• Intensity at the ferromagnetic resonance ⇒ Mn 3*d* impurity band hybridizes with LH but only weakly with HH band (different wavefunction localization)

# Picture of ferromagnetism in GaMnAs




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




- Occupied Mn 3*d* impurity band hybridizing with GaAs host band

- Ferromagnetism induced by GaAs mediated exchange between Mn atoms
- Description starting from the Anderson impurity model

- M. Kobayashi *et al*., http://arxiv.org/abs/1302.0063 (with Phys. Rev. Lett.)

# Summary

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

- **Bulk materials** resolved in 3-dim **k** (increase of λ 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 λ 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 photoemisson, buried heterostructures and impurities, depth profiling with X-ray standing waves

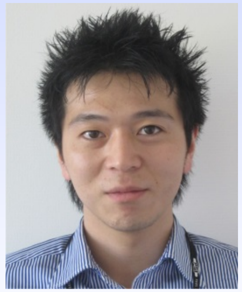
ADRESS

PAUL SCHERRER INSTITUT PSI

SWISS LIGHT SOURCE SLS

## SX-ARPES team

V.N.S.
(BL Scientist)



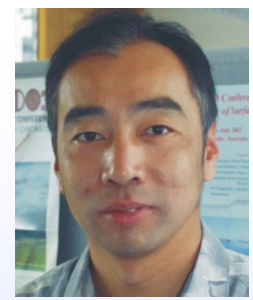
M. Kobayashi
(PostDoc)

L. Lev
(PostDoc)

C. Hess
(BL Technician)

## Collaborators at SLS

T. Schmitt
(RIXS)



M. Shi
(SIS beamline)

L. Patthey
(now SwissFEL)

## External collaborators

C. Cancellieri
(MS group)

J. Minar
(LMU Münich)

C. Fadley
(UC Davis)

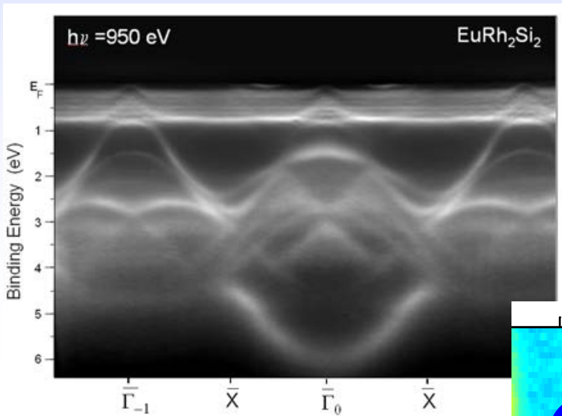
…

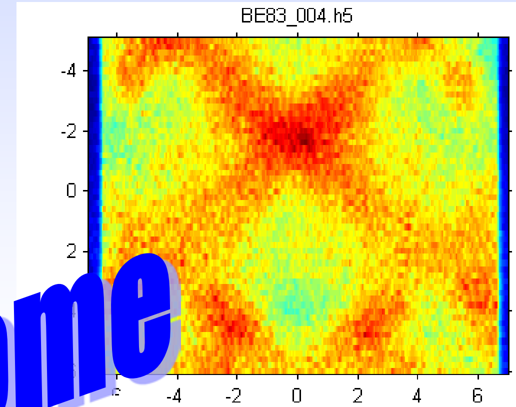
## Support from PSI

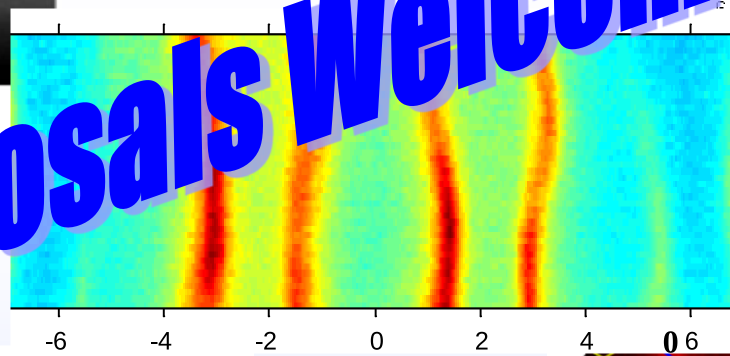
Optics (group of U. Flechsig), ID (group of T. Schmidt), Controls (X. Wang, J. Krempasky) *et al*

# www.psi.ch/sls/adress/

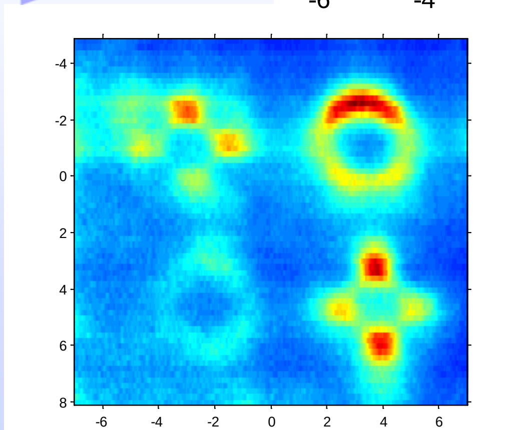
- Postdoc position available

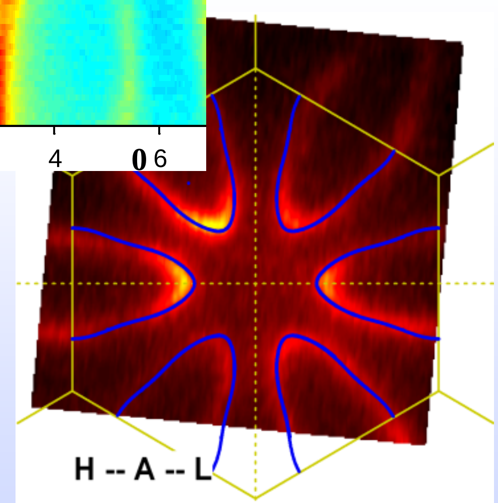


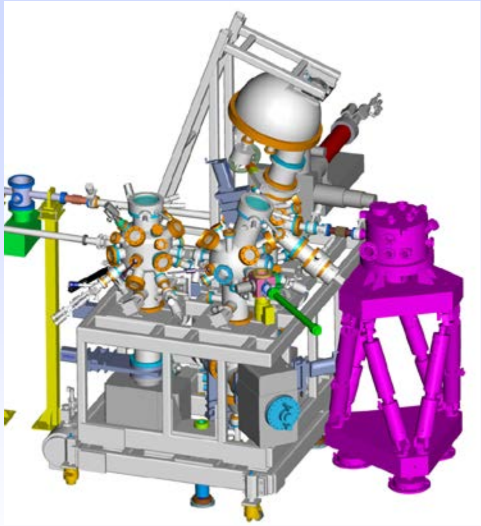
## Proposals Welcome



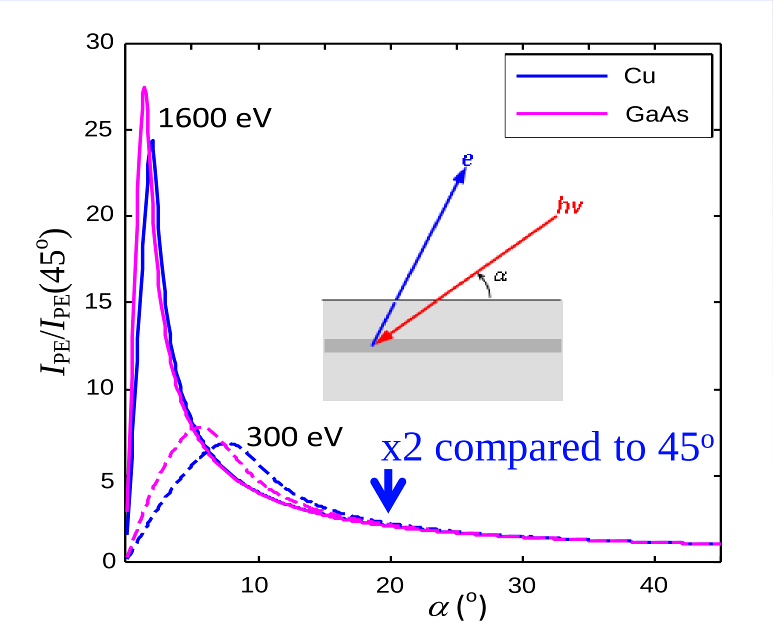



## Next call: September 15

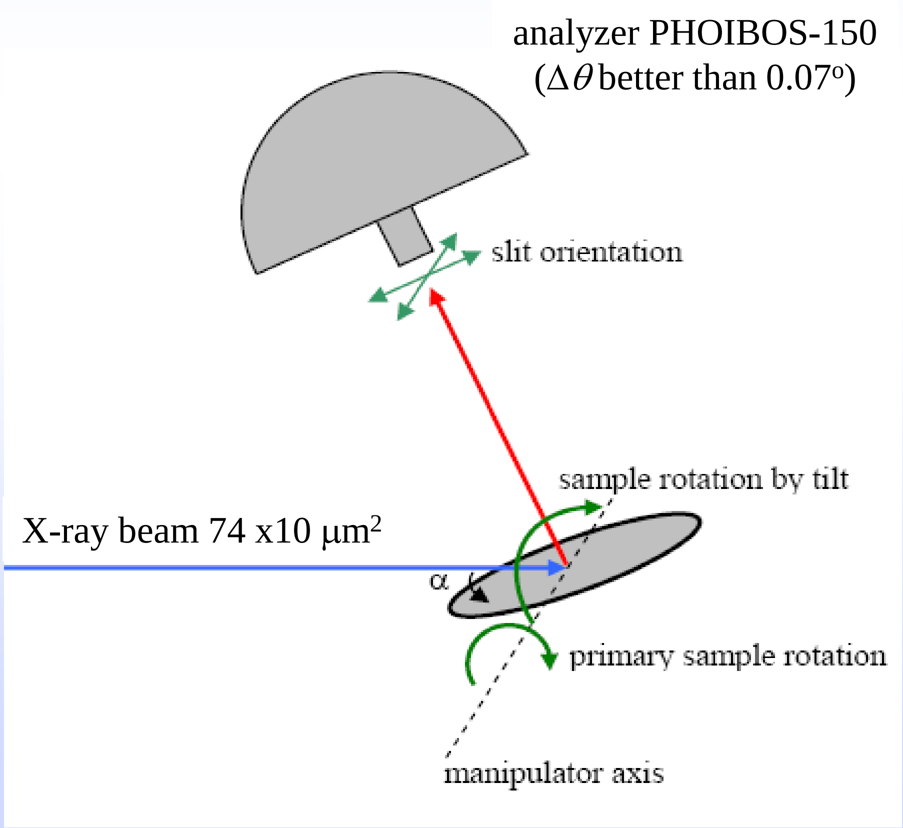
# SX-ARPES Endstation @ ADRESS: Geometry



• **grazing incidence** to increase photoyield




V.S., J. Synchr. Rad **20** (2013) 517




• **horizontal rotation axis** to balance the vertical/ horizontal X-ray footprint

• **vertical measurement plane**

• rotatable analyzer: **parallel slit orientation** ⇒ symmetry analysis of the valence states

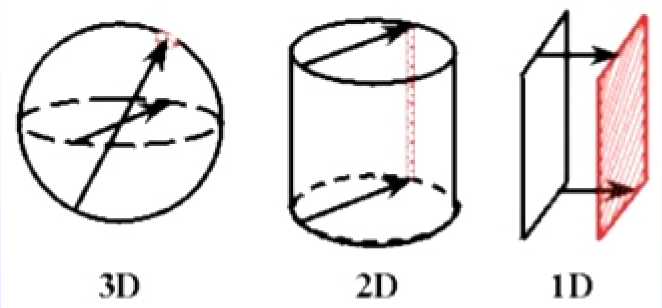
## - CDWs: Principles

**q**-CDW instability condition: $$\frac{4\bar{\eta}_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} \geq \frac{1}{\chi_{\mathbf{q}}} + 2\bar{U}_{\mathbf{q}} - \bar{V}_{\mathbf{q}}$$

"Phonon" scenario:
soft phonon mode

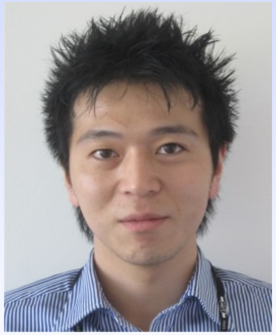
- not likely for $VSe_2$

"Electronic" scenario: singularity of susceptibility $\chi_{\mathbf{q}} = \sum_{\mathbf{k}} \frac{n_F(\varepsilon_{\mathbf{k}}) - n_F(\varepsilon_{\mathbf{k+q}})}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k+q}}}$ associated with FS nesting



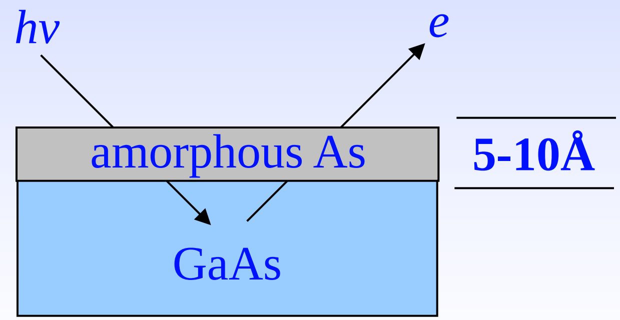

- nesting automatic in 1D (Peierls transition) but most restrictive in 3D

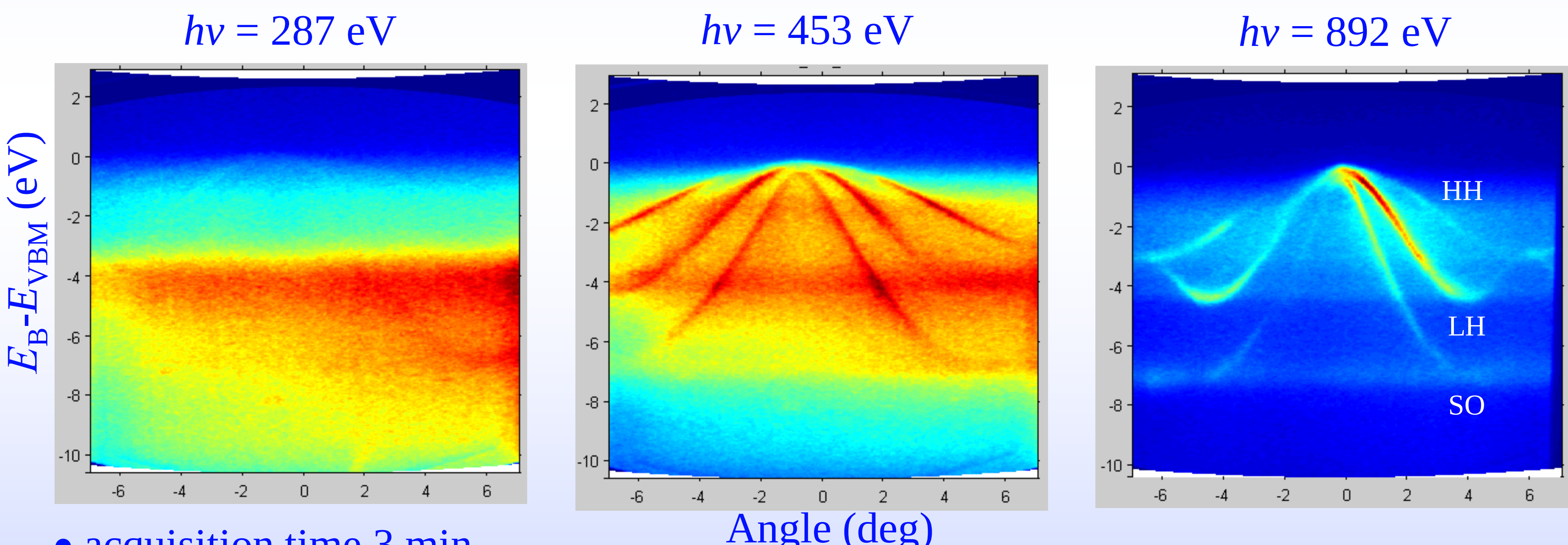
# Penetrating ability of SX-ARPES: Band structure of GaAs through amorphous As layer



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

• large λ required: Soft-X-ray ARPES



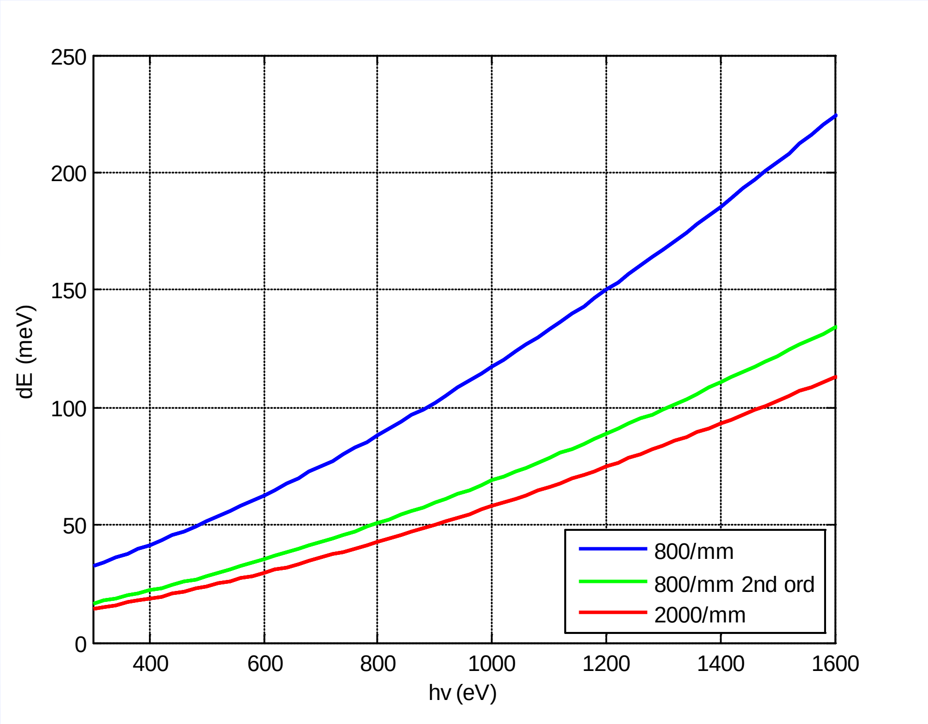



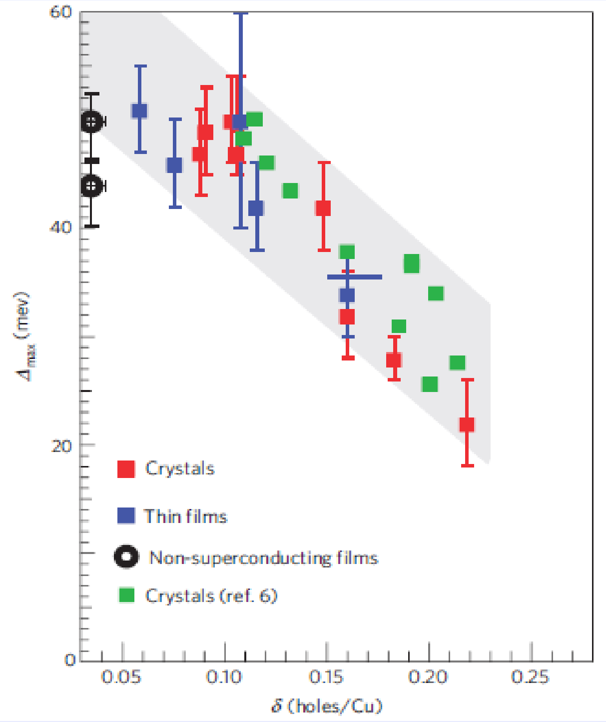

• acquisition time 3 min
• GaAs signal piles up with *hv*
• New diagnostics tool for MBE grown films: Applications in microelectronics

- M. Kobayashi *et al.*, Appl. Phys. Lett. **101** (2012) 242103

# Coming upgrade: Hi-res grating

U. Chatterjee, M. Shi *et al*,
Nature Physics Lett. **6** (2010) 99




- $\Delta E$ down to 25 meV at $h\nu$=500 eV

- **Bulk SC gap in cuprates**