

# Applications of XAFS to materials and nano – science

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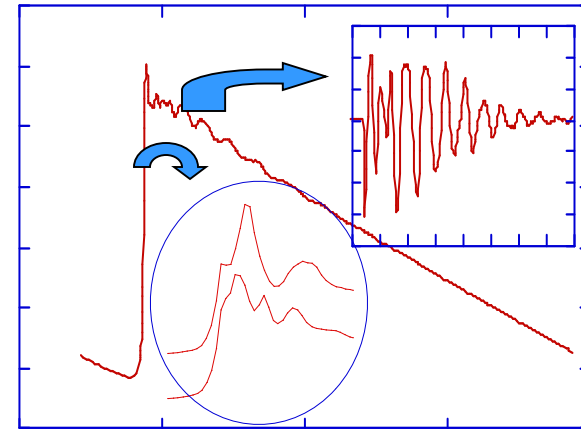
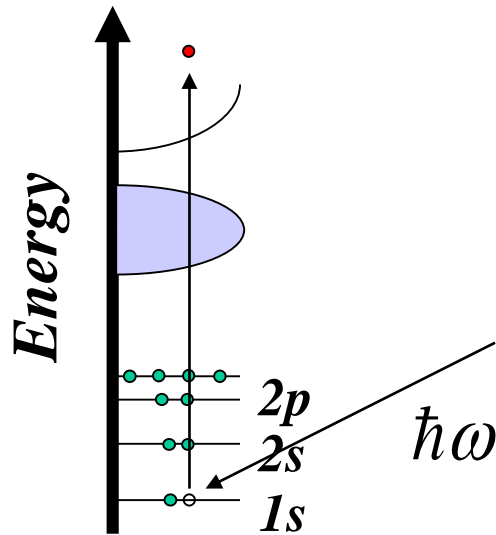


# Plan

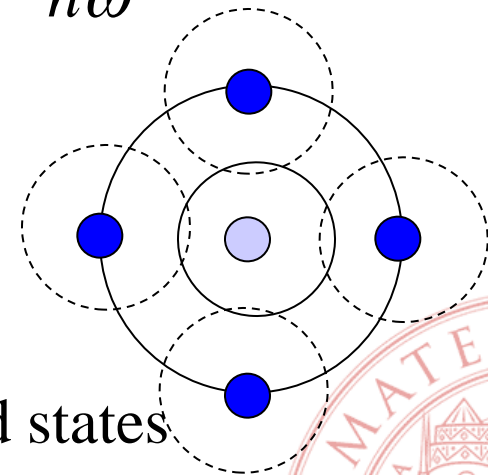
- Introduction
  - Review basics of XAFS
  - Characteristics of the technique
  - Role of XAFS
- Examples of applications, using both
  - results which have “stood the test of time”
    - Why? Because we tend to **forget** work done by others some time ago (or don't bother searching the literature) and **do the measurements again!**
      - It will get published in the end,  
but **not a good use of time & money!**
  - recent results



# X-Ray Absorption Fine Structure



$\hbar\omega$



- “EXAFS”: Coordination numbers  
Interatomic distances  
Disorder of distances
- “XANES”: Absorber symmetry and valence/oxidation state  
Electronic structure of unoccupied states  
Medium range structure



# EXAFS

- Extended X-ray Absorption Fine Structure
- When applicable, fit with the “standard” EXAFS equation

From *ab-initio* calculations or from reference compounds

$$\chi(k) = S_0^2 \sum_{j=\text{shells}} N_j A_j(k) \sin[2kr_j + \overbrace{\varphi_j + 2\delta_1}] e^{-2k^2\sigma_j^2}$$

$$k = \frac{\sqrt{2m(\hbar\omega - E_B)}}{\hbar}$$

**Measure:**

Coordination  
number

Interatomic  
distance

Debye Waller factor  
- thermal vibration  
- static disorder



# XANES

- X-ray Absorption Near Edge Structure  
(also NEXAFS)

$$\sigma(\hbar\omega) = 4\pi^2 \alpha \hbar\omega \left| \langle i | \hat{\epsilon} \cdot \vec{r} | f \rangle \right|^2 \rho(E_f) \quad \Delta l = \pm 1, \Delta m_l = 0$$

(lin. pol. light)

- “Molecular orbital” approach: 1 electron approximation, constant matrix element: probe **site** and **symmetry** projected density of states of final electronic states
- “Multiple scattering” approach: structural interpretation through simulation



# Characteristics of XAFS

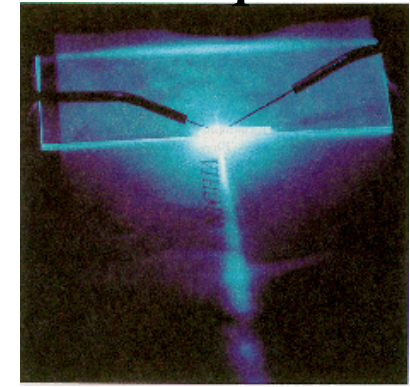
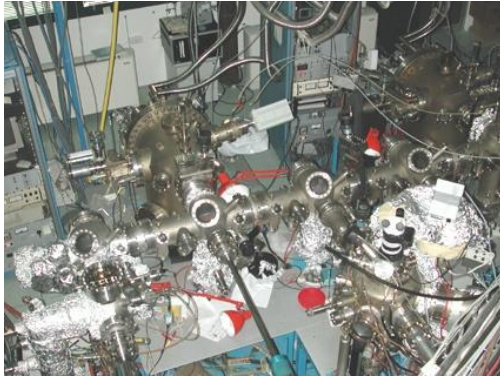
- Atomic selectivity (choose  $Z$  via photon energy)
- Equally applicable to ordered or disordered matter
- A core level technique: a local probe
- Interesting underlying physics
- Sensitive to high dilutions
- EXAFS: high distance resolution
- XANES: 3D structural sensitivity
- Recent developments:
  - Sub  $\mu\text{m}$  spot size
  - ns, ps and ...fs time resolution
  - Combined use of XES / RIXS



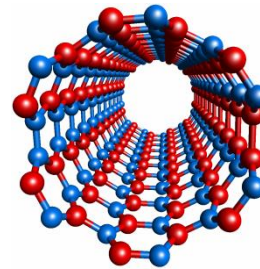
# Role of XAFS in Materials Science

Growth

Physical Properties



Structure

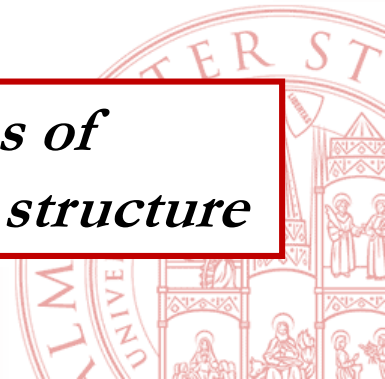


MBE@TASC

*Nakamura et al., Jpn. J. Appl. Phys. 35, L217, 1996*

XAFS

***Objective: an understanding of physical properties of novel materials based on knowledge of their local structure***



# Today's topics

- Dopants, defects
- Alloys
- Phase transitions
- Thin films, interfaces, surfaces
- Nanostructures
  - Semiconductor dots
  - Metallic clusters





# XAFS and dopants/dilute elements

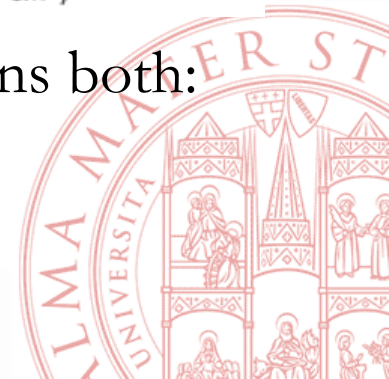
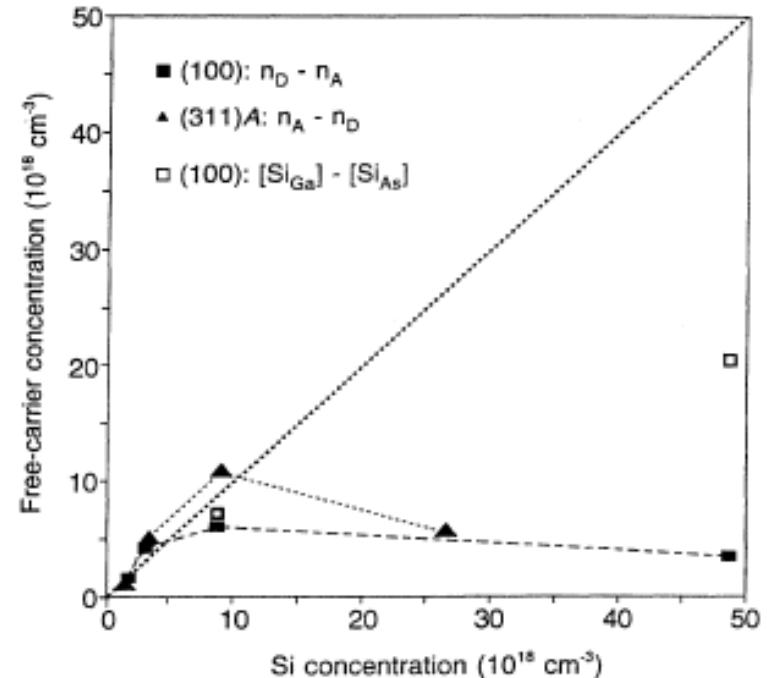
- Only the structure around the photo-excited atom is probed
- Fluorescence detection greatly enhances sensitivity
- Present sensitivity limit (depends on sample)
  - dopants in the bulk
    - EXAFS  $\sim 10^{18}$  at/cm<sup>3</sup>
    - XANES  $\sim 10^{17}$  at/cm<sup>3</sup>
  - thin films (single layer)  $\sim 10^{14}$  at/cm<sup>2</sup>



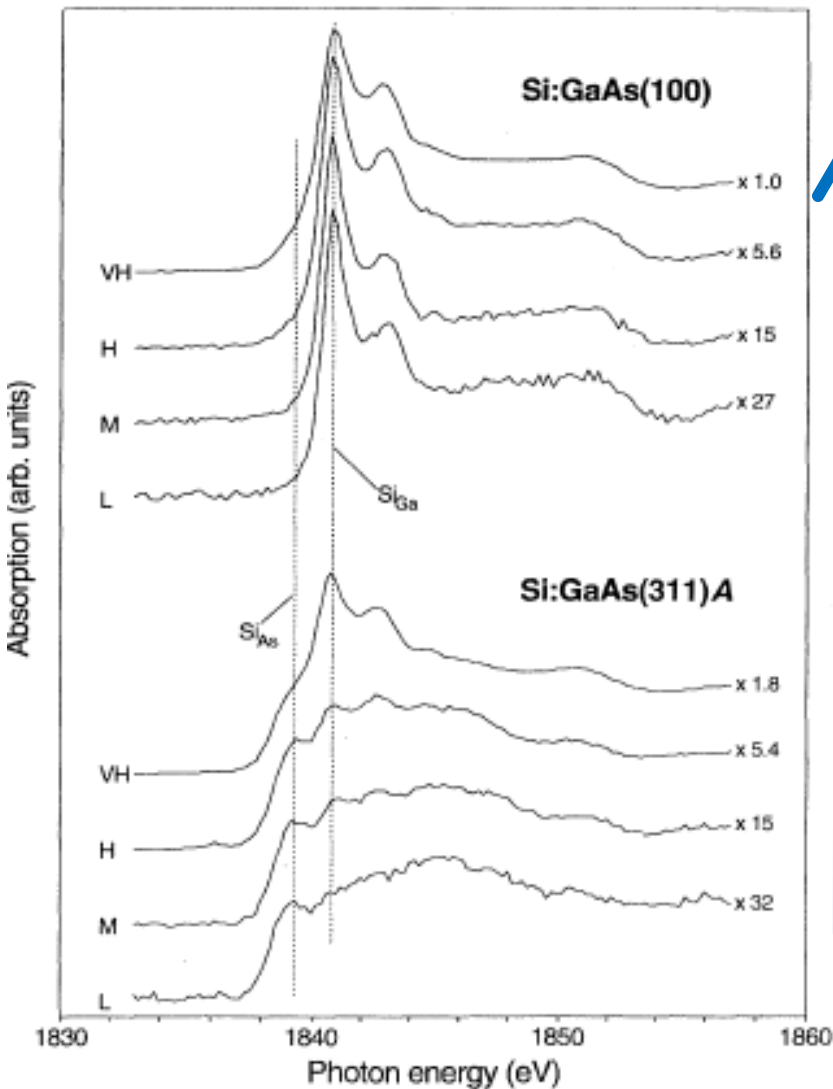
# Si in GaAs

S. Schuppler, D.L. Adler, L.N. Pfeiffer, K.W. West, E.E. Chaban,  
and P.H. Citrin, Appl. Phys. Lett. **63**, 2357 (1993) and Phys. Rev. B **51**, 10527 (1995)

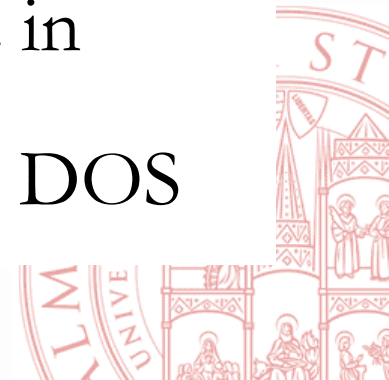
- Si common dopant in GaAs
- Si:GaAs exhibits deactivation
- Accepted explanation : amphoteric nature of Si
  - $\text{Si}_{\text{Ga}}$  (Si in Ga site): donor
  - $\text{Si}_{\text{As}}$ : acceptor
  - At low concentration all  $\text{Si}_{\text{Ga}}$ , at higher concentrations both: autocompensation



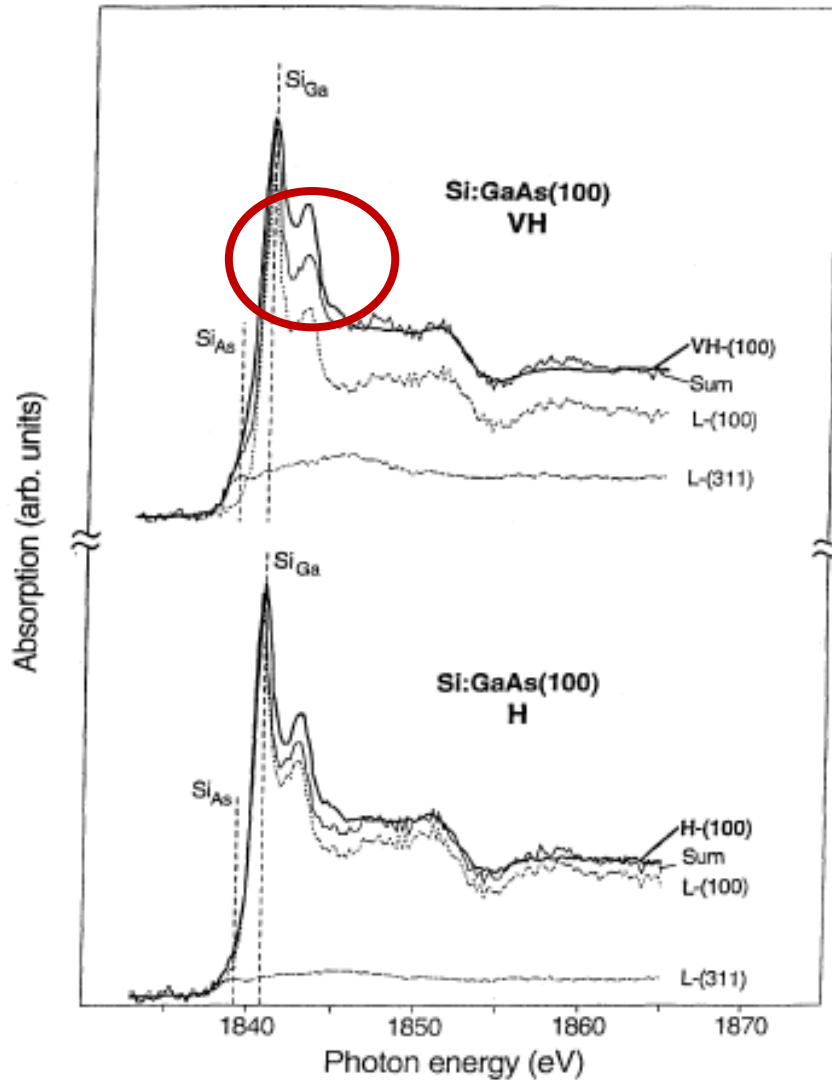
# Si in GaAs: XANES



- Samples studied
  - Si:GaAs(001)
    - at low concentration Si<sub>Ga</sub>
  - Si:GaAs(311)A
    - at low concentration Si<sub>As</sub>
- XANES exhibit reasonable evolution with concentration
- Difference in lineshape between Si<sub>Ga</sub> and Si<sub>As</sub> due to difference in charge on Si and conduction band DOS



# Si in GaAs: XANES

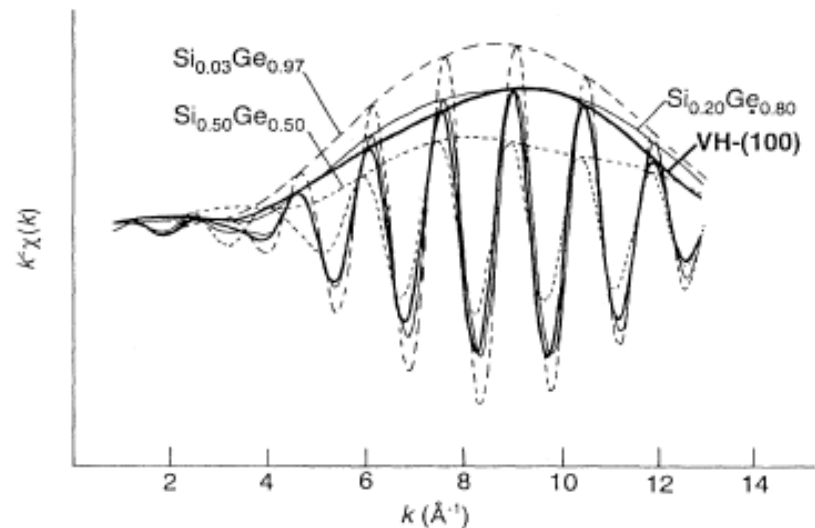
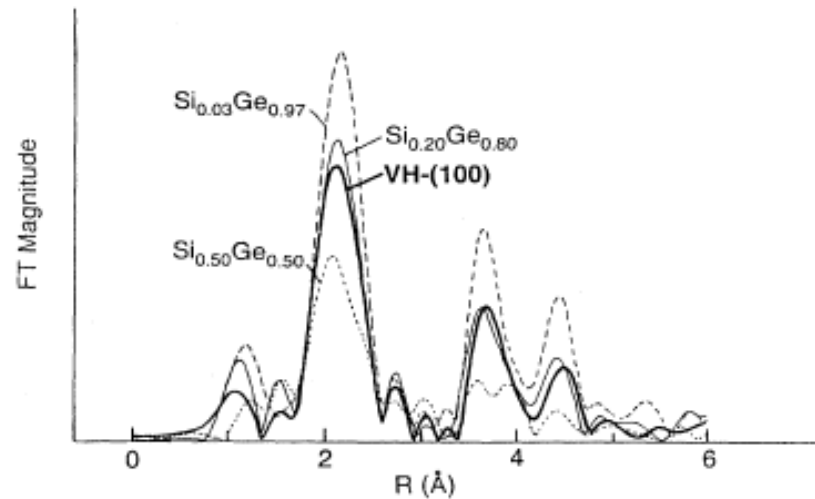


- Fitting of Very High concentration sample indicated that lineshape cannot be explained only on the basis of combination of  $\text{Si}_{\text{Ga}}$  and  $\text{Si}_{\text{As}}$



# Si in GaAs : EXAFS

- Compare EXAFS spectra with those of  $\text{Si}_x\text{Ge}_{1-x}$  random alloys
- Ge has similar scattering amplitude to Ga and As
- VH sample spectrum very similar to  $\text{Si}_{0.2}\text{Ge}_{0.8}$ 
  - 20% of Si is bonded to Si
- Conclusion: deactivation due also to presence of **Si dimers and clusters**



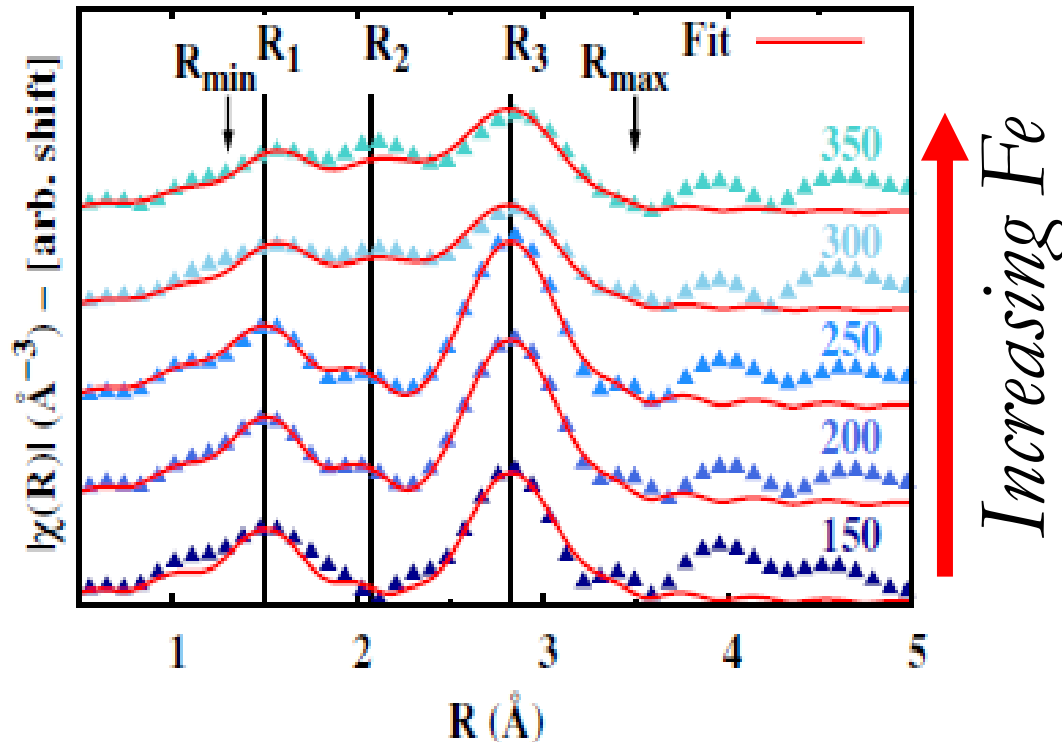
# Fe in GaN

- A. Bonanni, A. Navarro-Quezada, Tian Li, M. Wegscheider, Z. Matěj, V. Holý, R. T. Lechner, G. Bauer, M. Rovezzi, F. D'Acapito, M. Kiecana, M. Sawicki, and T. Dietl, Phys. Rev. Lett. **101**, 135502 (2008)
- M. Rovezzi, F. D'Acapito, A. Navarro-Quezada, B. Faina, T. Li, A. Bonanni, F. Filippone, A. Amore Bonapasta, and T. Dietl, Phys. Rev. B **79**, 195209 (2009)
- A. Navarro-Quezada, W. Stefanowicz, Tian Li, B. Faina, M. Rovezzi, R. T. Lechner, T. Devillers, F. D'Acapito, G. Bauer, M. Kiecana, M. Sawicki, T. Dietl, and A. Bonanni Phys. Rev. **81**, 205206 (2010)

- Candidate material for spintronic applications
- Grown by Metal Organic Vapor Phase Epitaxy
- Fe concentrations  
 $4 \times 10^{19} \text{ cm}^{-3} - 4 \times 10^{20} \text{ cm}^{-3}$
- Aims:
  - Determine the site of Fe in GaN
  - Determine the effect of Si co-dopant
  - Correlate with magnetic properties



# Fe:GaN data



## Low Fe content:

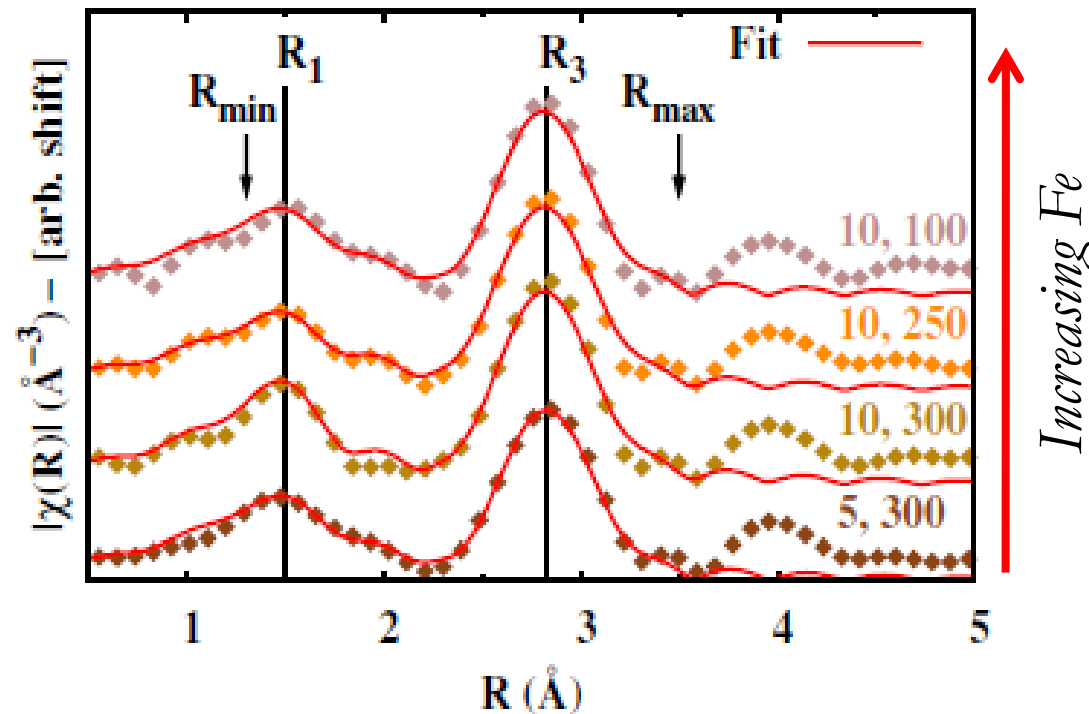
- only two Fe-N ( $R_1$ ) and Fe-Ga ( $R_3$ ) bonds.
- Fe substitutional; bond length in agreement with DFT for  $\text{Fe}^{3+}$

## High Fe content

- Appearance of Fe-Fe ( $R_2$ ) coming from a precipitated  $\text{Fe}_x\text{N}$  phase



# Si,Fe:GaN data

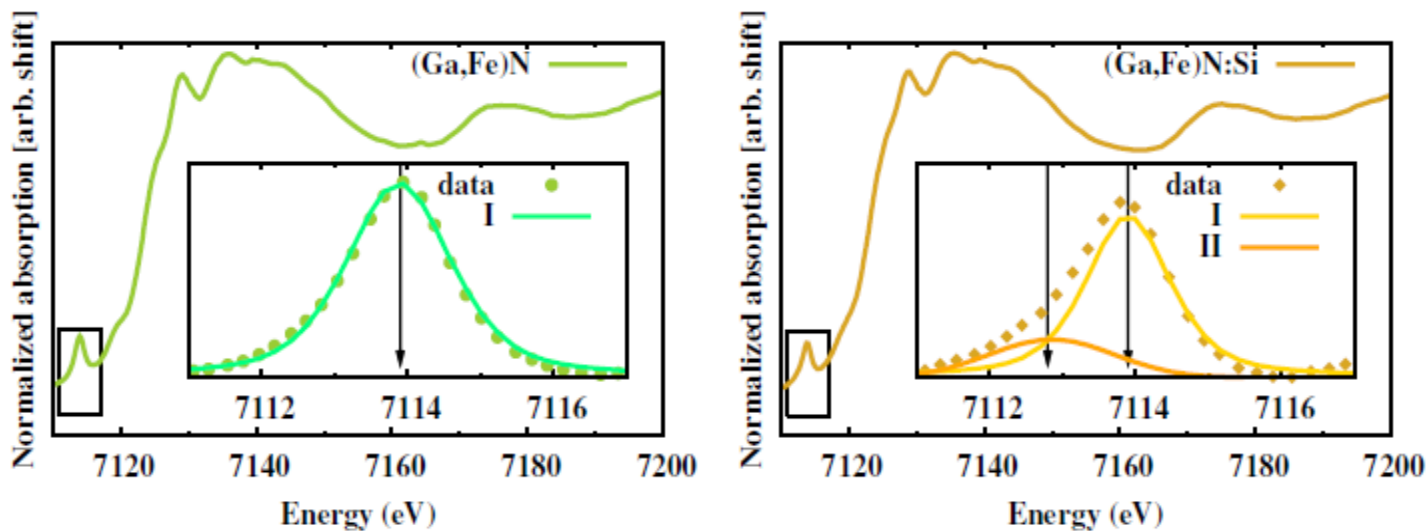


- For the same Fe content Si co-doping prevents the formation of  $\text{Fe}_3\text{N}$
- No evidence of the Fe-Fe bond at  $R_2$





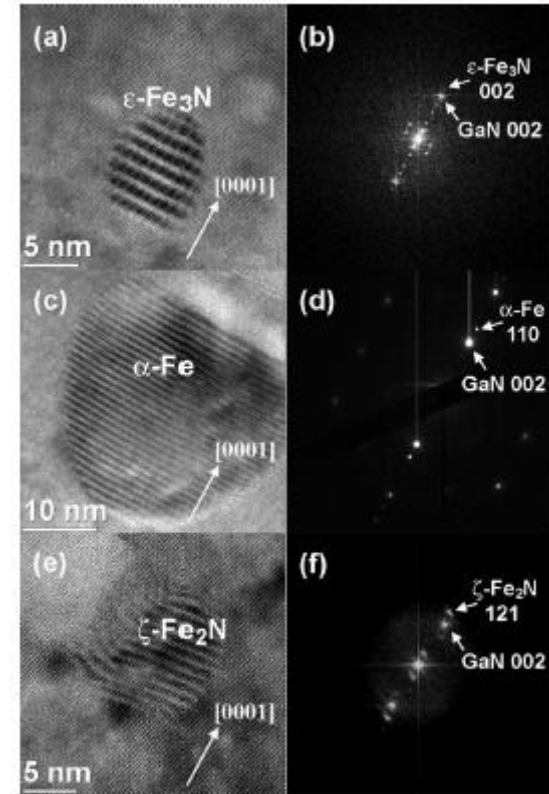
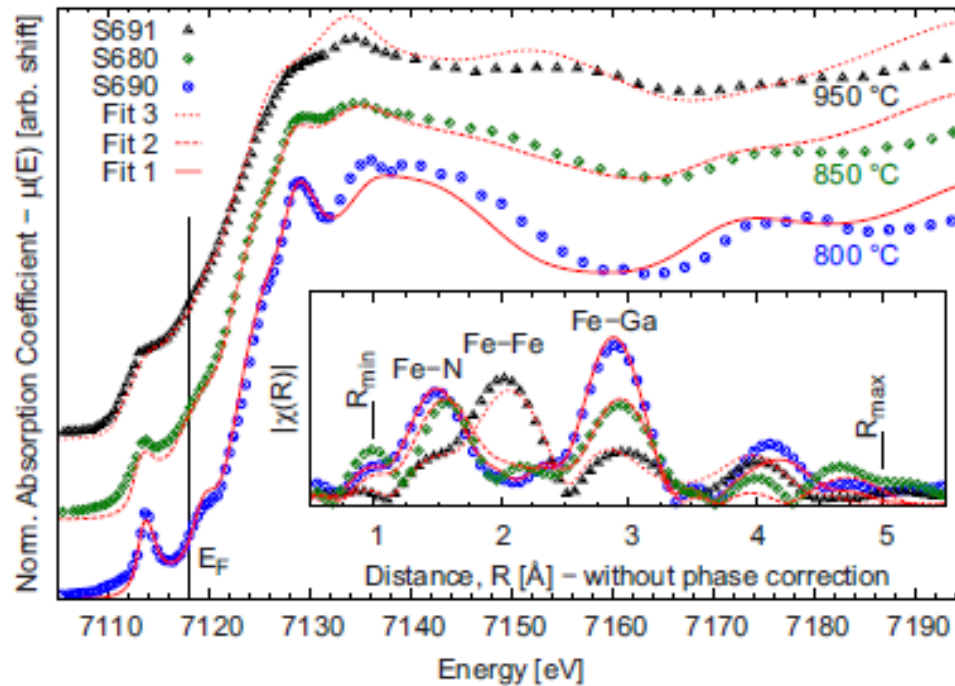
# Si affects the charge state of Fe



- Si addition causes partial reduction of  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$
- Notable ability of XAFS to determine structure and valence



# Role of the growth temperature



- Higher growth temperature favours formation of Fe<sub>x</sub>N and  $\alpha$ -Fe



# Fe:GaN conclusions (2010 paper)

- Magnetization due to various components, including one due to ferromagnetic nanocrystals of  $\epsilon$ -Fe<sub>3</sub>N,  $\alpha$ -Fe,  $\gamma'$ -Fe<sub>4</sub>N,  $\gamma$ -Fe<sub>2</sub>N and  $\gamma$ -Fe
- Si codoping reduces the formation of Fe rich nanocrystals and permits a higher incorporation of Fe.
- Use new term: (Ga,Fe)N nanocomposites, not real doping



# Metal precipitates in Si solar cells

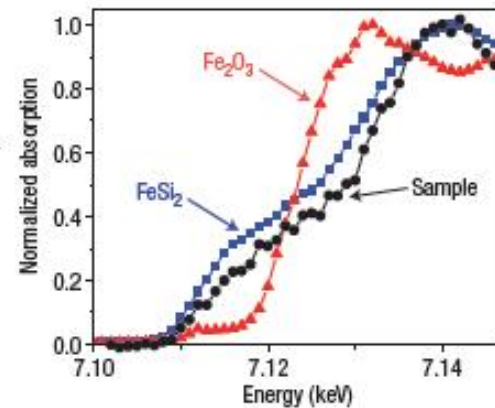
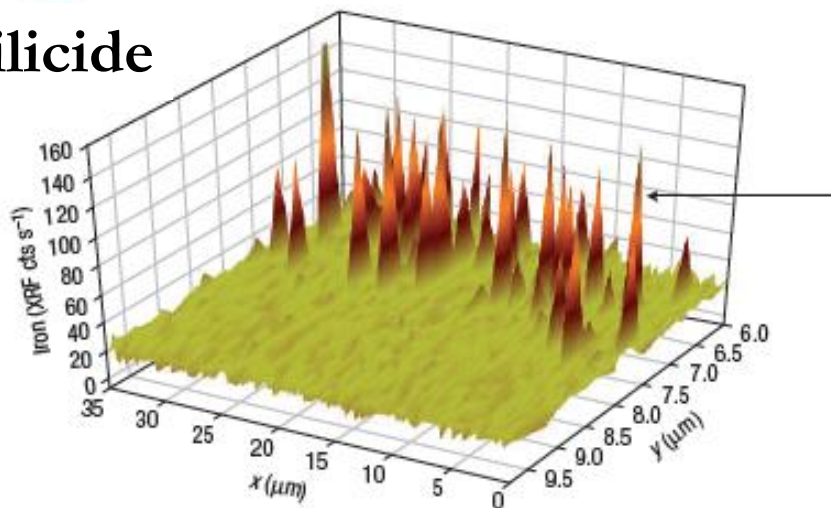
Buonassisi et al, Nature Mat. 4, 676 (2005)

- Supply of high purity Si  $\ll$  demand
- Use of lower purity material
- Problem: impurities decrease efficiency
- $\mu$ -XRF and  $\mu$ -XAFS to characterize metal precipitates and suggest processing to improve efficiency

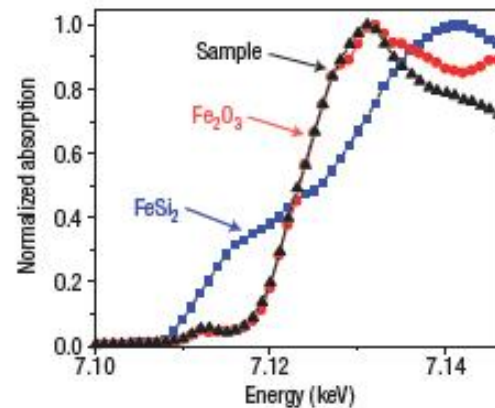
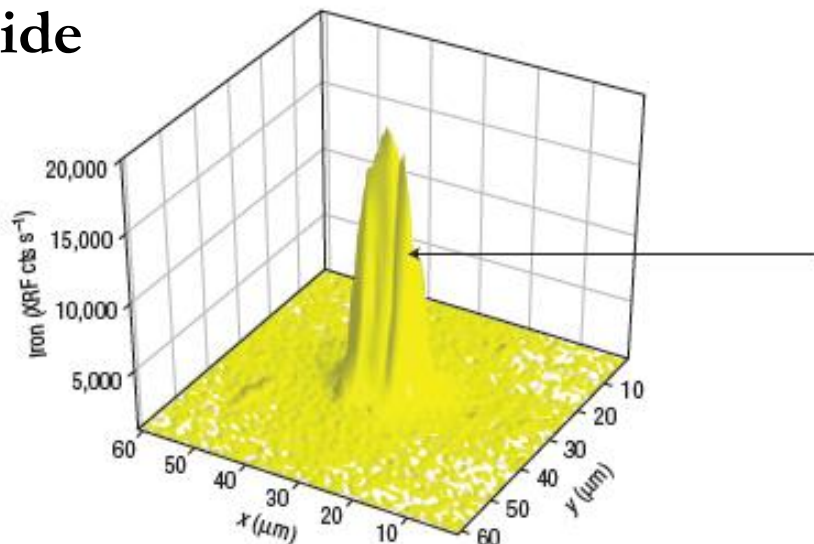


# $\mu$ -XRF & $\mu$ -XAFS: two defects

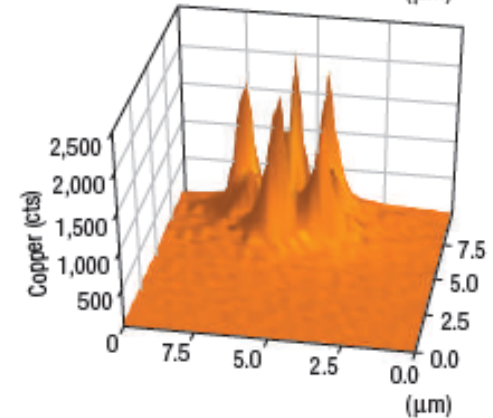
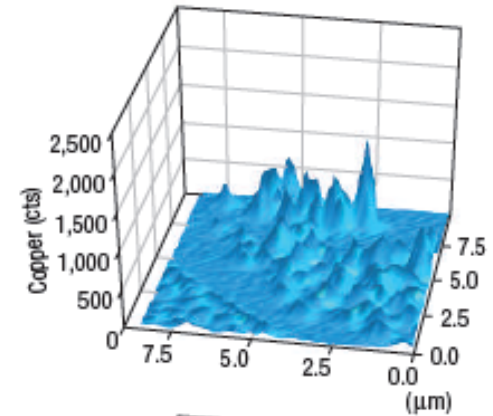
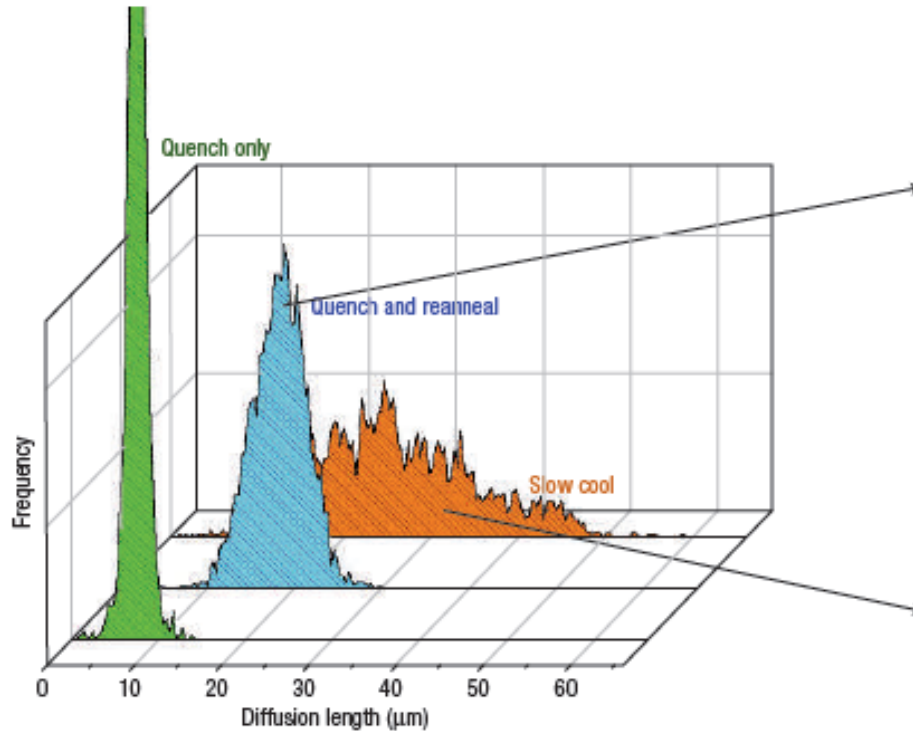
$\sim 20$  nm silicide



$\sim 10$  μm oxide



# Processing & characterization



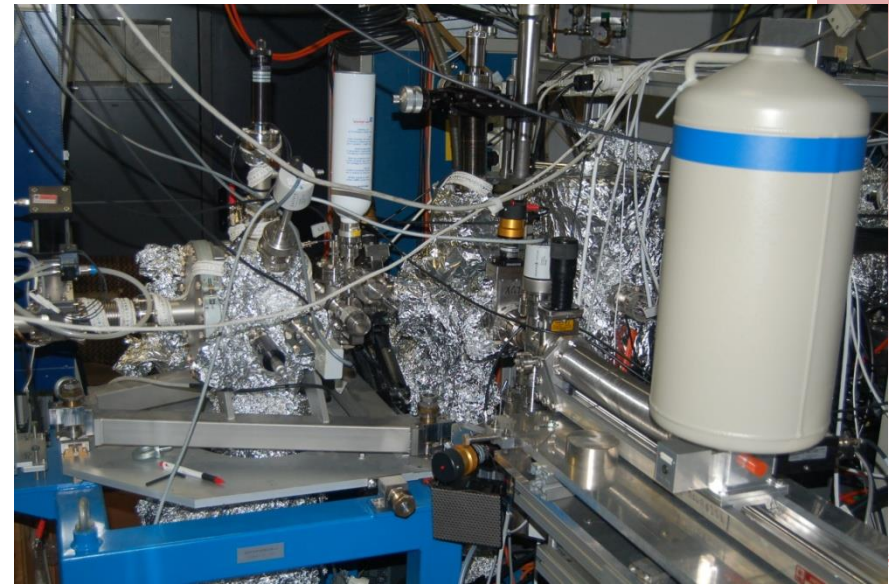
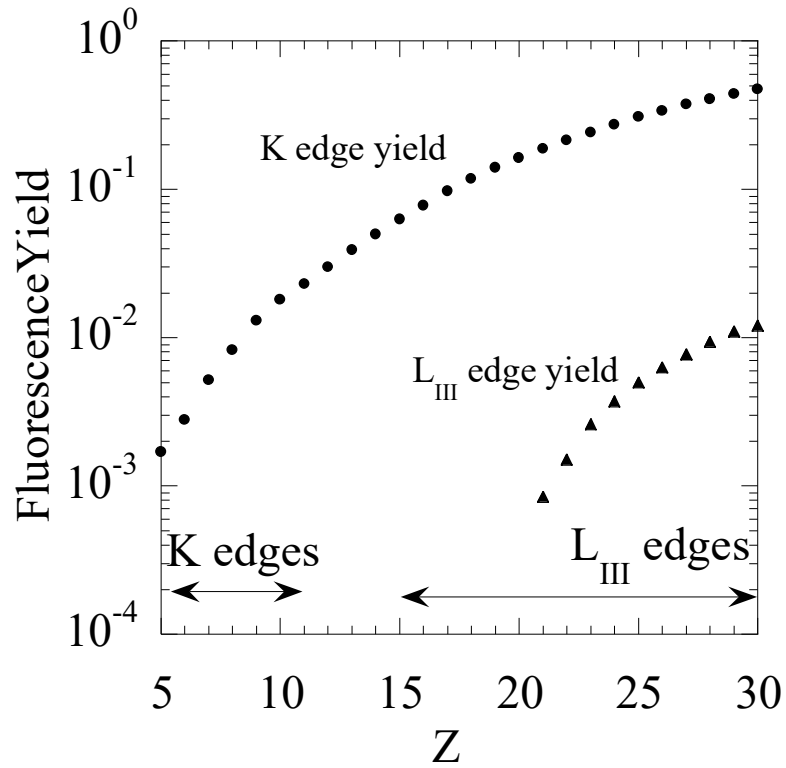
Best process: slow cool ( $5\text{ }^{\circ}\text{C s}^{-1}$ ) from  $1200\text{ }^{\circ}\text{C}$   
 $\mu\text{m}$  sized, low density precipitates lead to  
greater carrier diffusion lengths





# Low Z dopants and XAS

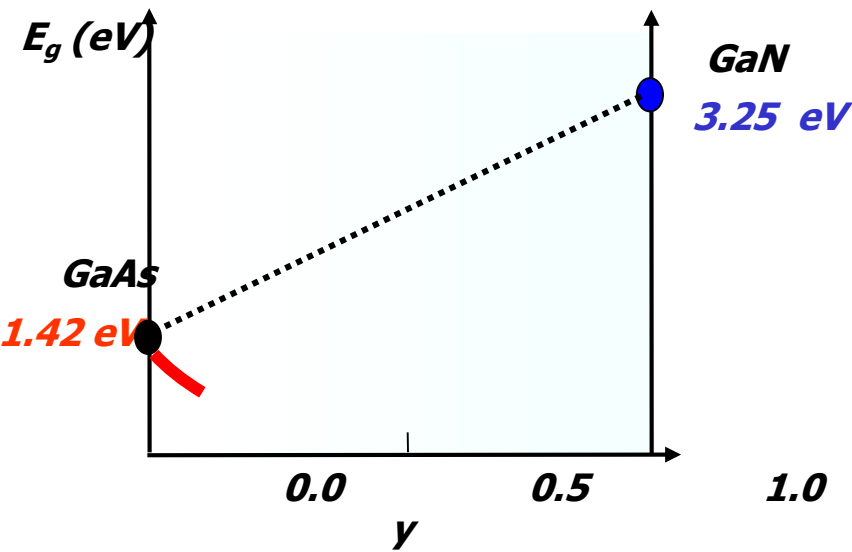
- C, N & O often used as dopants
- Experimentally difficult: low fluorescence yield, soft X-rays, UHV



ALOISA beamline @ ELETTRA



# Dilute nitrides: $\text{GaAs}_{1-y}\text{N}_y$ , $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$



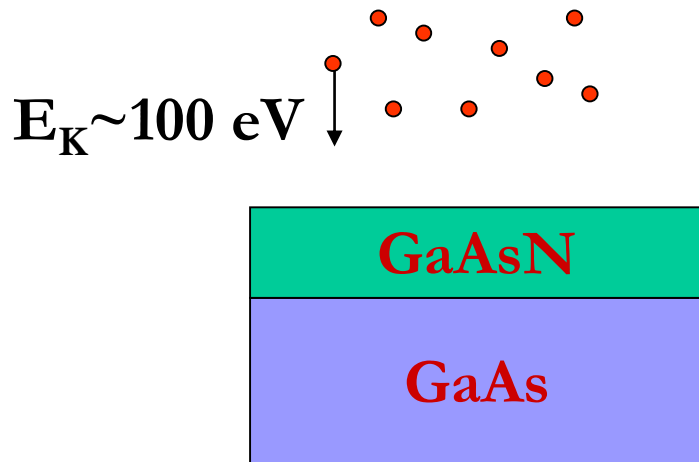
- Anomalous non-linear optical and electronic properties of III-V nitrides
- Red shift of the band gap by adding few % of nitrogen ( $\approx 0.05\text{-}0.1$  eV per N atomic percent in InGaAsN)
- Huge and composition dependent optical bowing



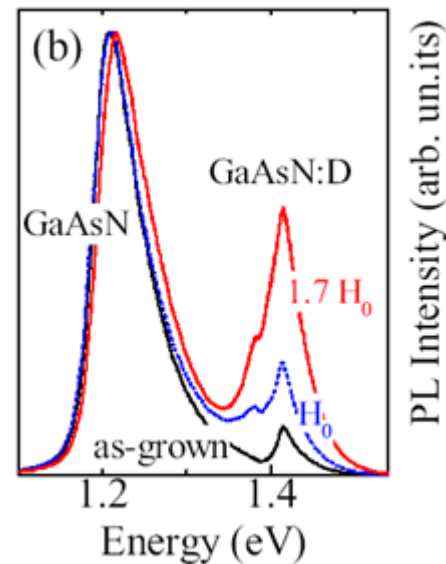


# Hydrogen – nitrogen complexes in dilute nitrides

- Hydrogenation leads to reversible opening of  $E_g$



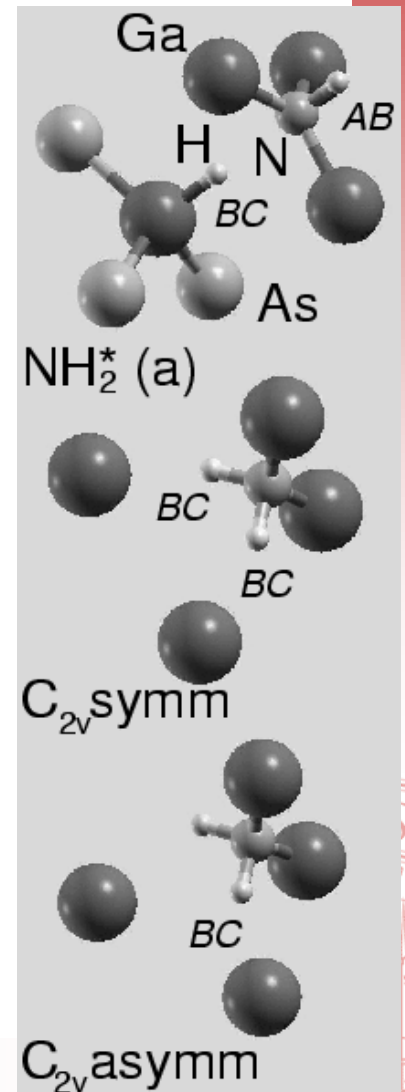
photoluminescence



# Hydrogen – nitrogen complexes in dilute nitrides

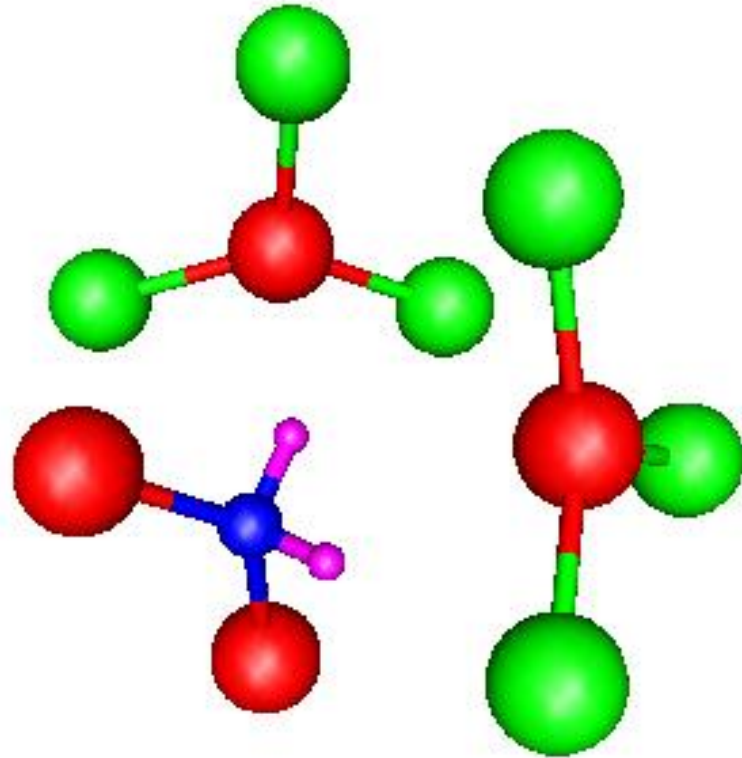
- Which is the hydrogen –nitrogen complex responsible for these changes?

Some candidate  
low energy structures



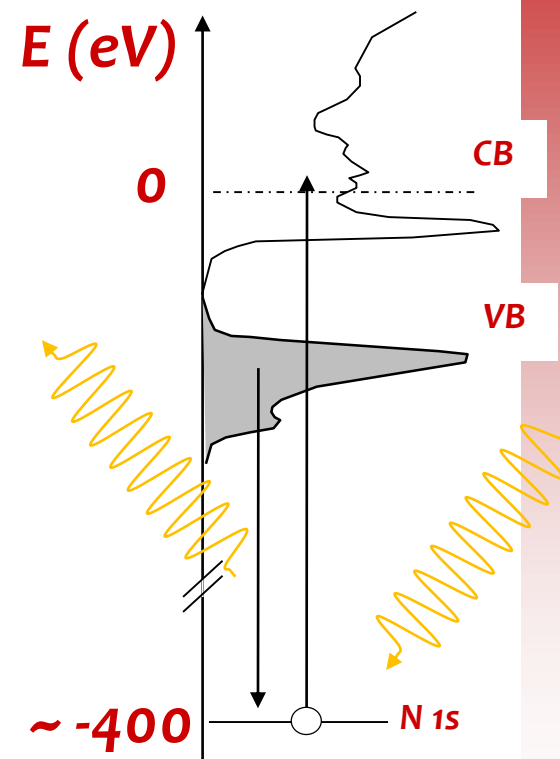
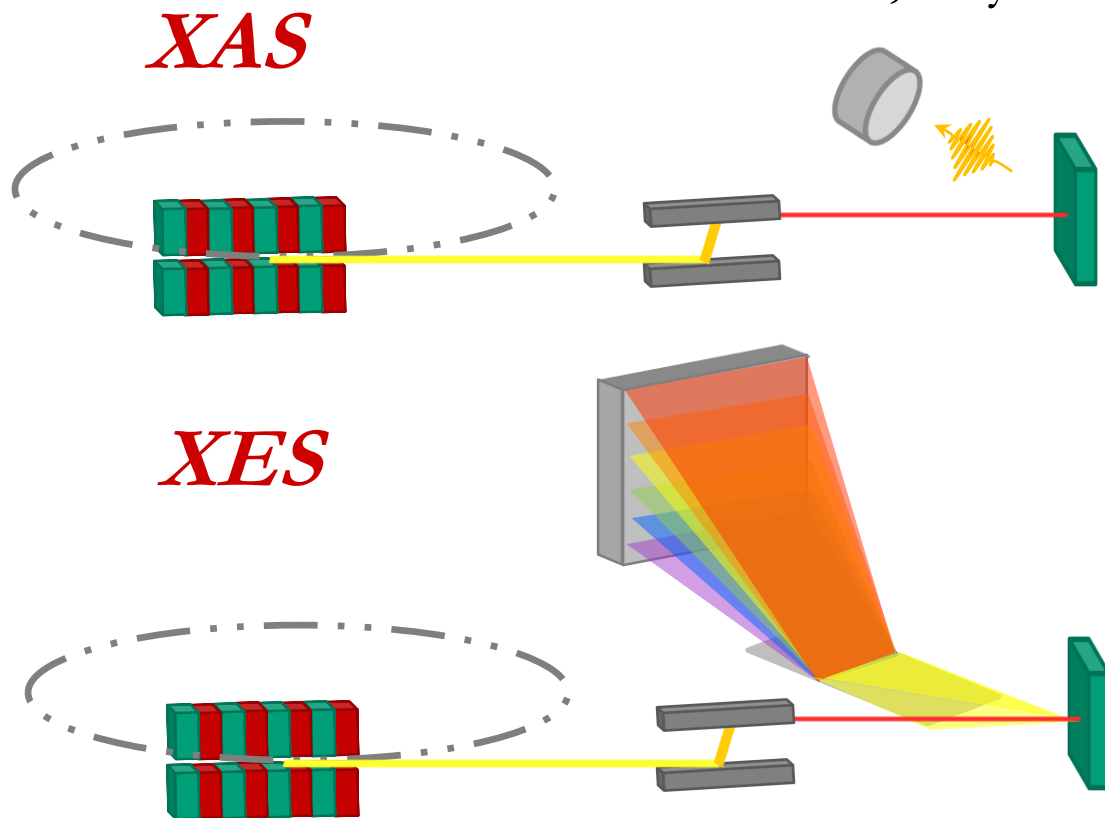
# H–N complexes in dilute nitrides

- G. Ciatto, F. Boscherini, A. Amore Bonapasta, F. Filippone, A. Polimeni and M. Capizzi, Phys. Rev. B **71**, 201301 (2005)
- M. Berti, G. Bisognin, D. De Salvador, E. Napolitani, S. Vangelista, A. Polimeni, M. Capizzi, F. Boscherini, G. Ciatto, S. Rubini, F. Martelli, and A. Franciosi, Phys. Rev. B **76**, 205323 (2007)
- G. Ciatto, F. Boscherini, A. Amore Bonapasta, F. Filippone, A. Polimeni, M. Capizzi, M. Berti, G. Bisognin, D. De Salvador, L. Floreano, F. Martelli, S. Rubini, and L. Grenouillet, Phys. Rev. B **79**, 165205 (2009)
- DFT calculations to determine lowest energy geometries
- Full multiple scattering XANES simulations
- **Answer:**  $C_{2v}$  – like complexes are mostly present
- 3-D sensitivity of XANES!!



# Combined XAFS and XES

Amidani et al., Phys. Rev. B 89, 085301 (2014)



XES now possible, a complementary tool with sensitivity to

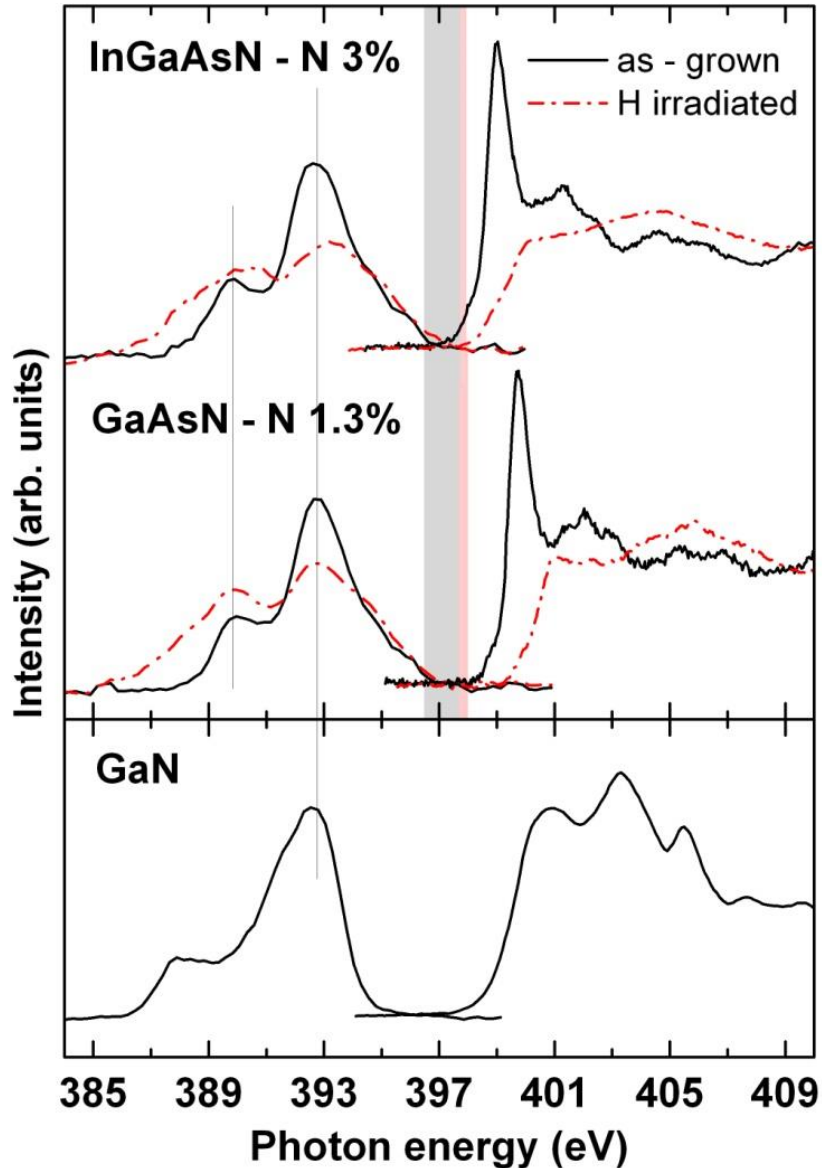
- Valence band electronic structure
- Atomic structure
- New level of refinement in x-ray spectroscopy



# Combined XAFS and XES

## XES

- local VBM unchanged
- decrease of main peak in favor of lower energy states

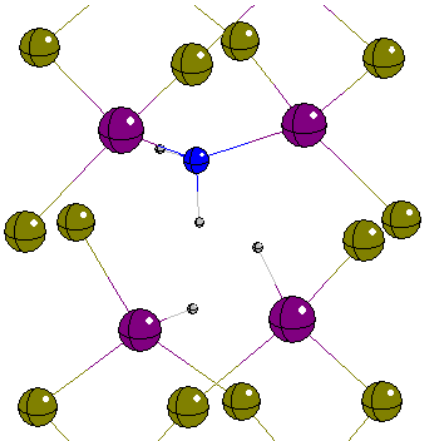


## XAFS

- main peak disappears and local CBM is strongly blue-shifted
- N states move far from the CBM

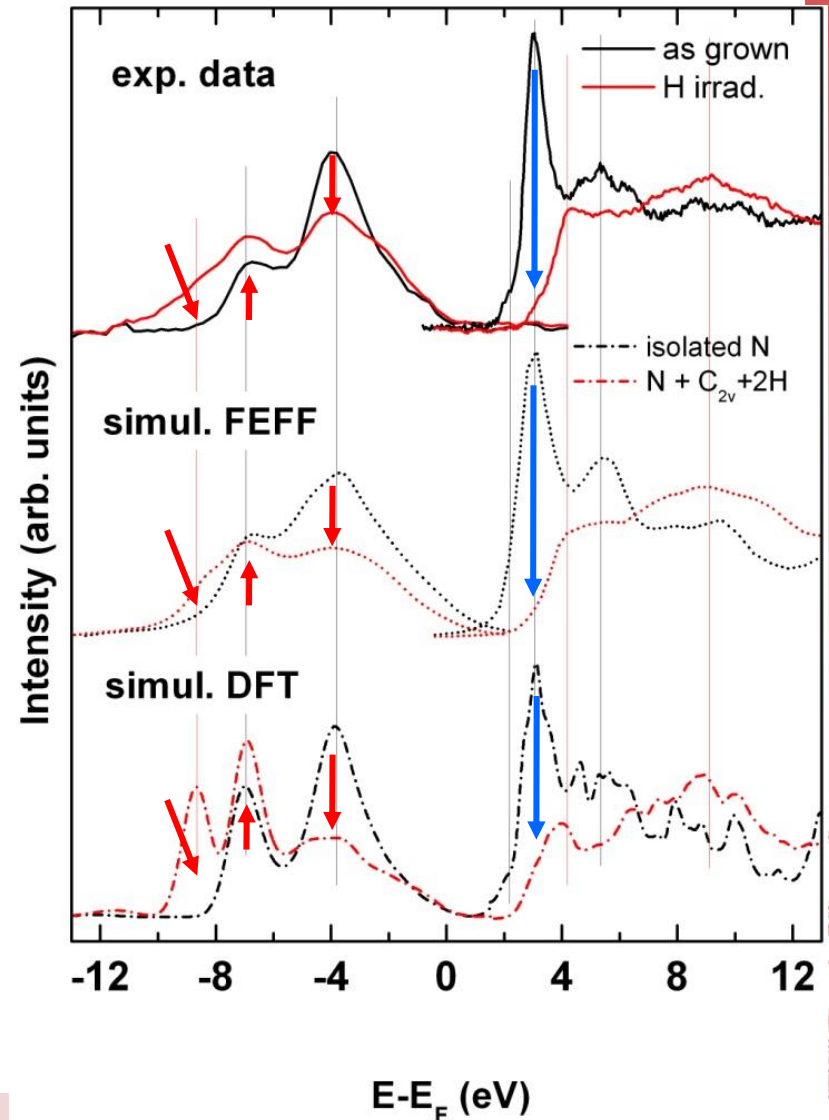


# XAFS and XES simulations



**Good news**: all spectral features are well reproduced by:

- MS spectral simulations based on DFT atomic structure
- ab-initio DFT simulations of electronic and atomic structure



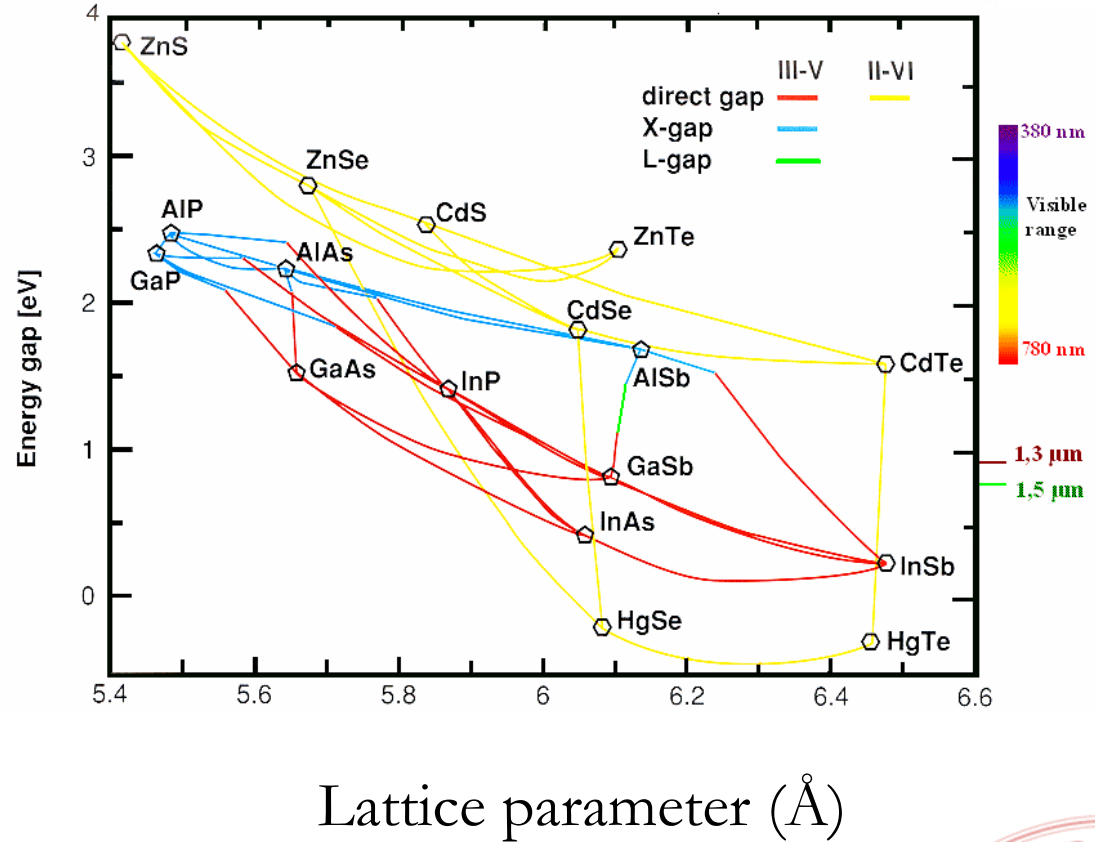
# XAFS and alloys

- High resolution in probing the local coordination in first few coordination shells
- Study, as a function of composition
  - Deviation of local structure from average structure
  - Atomic ordering



# Semiconductor alloys

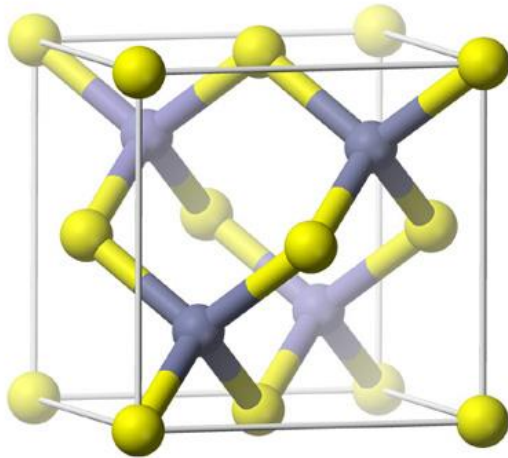
- For example:  
 $\text{In}_x\text{Ga}_{1-x}\text{As}$
- Alloying leads to changes in
  - band-gap
  - lattice parameter



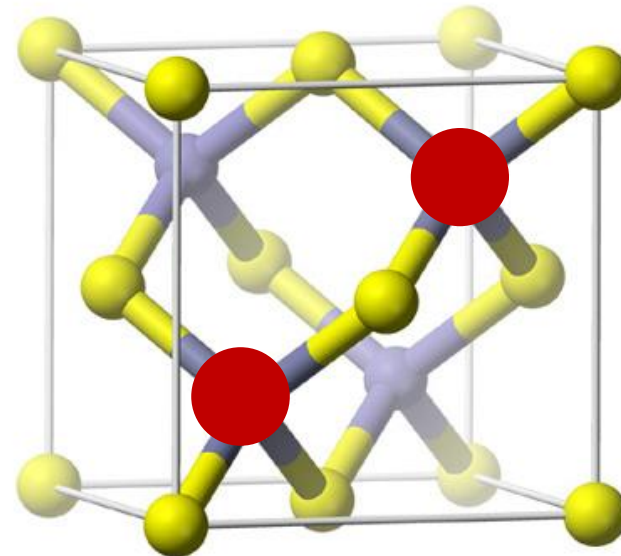


# Vegard's law & Virtual Crystal Approximation

- The lattice parameter depends linearly on concentration: “Vegard's law”
- VCA: a linear and isotropic variation of the local structure with concentration
  - All atoms retain symmetric tetrahedral bonding



GaAs

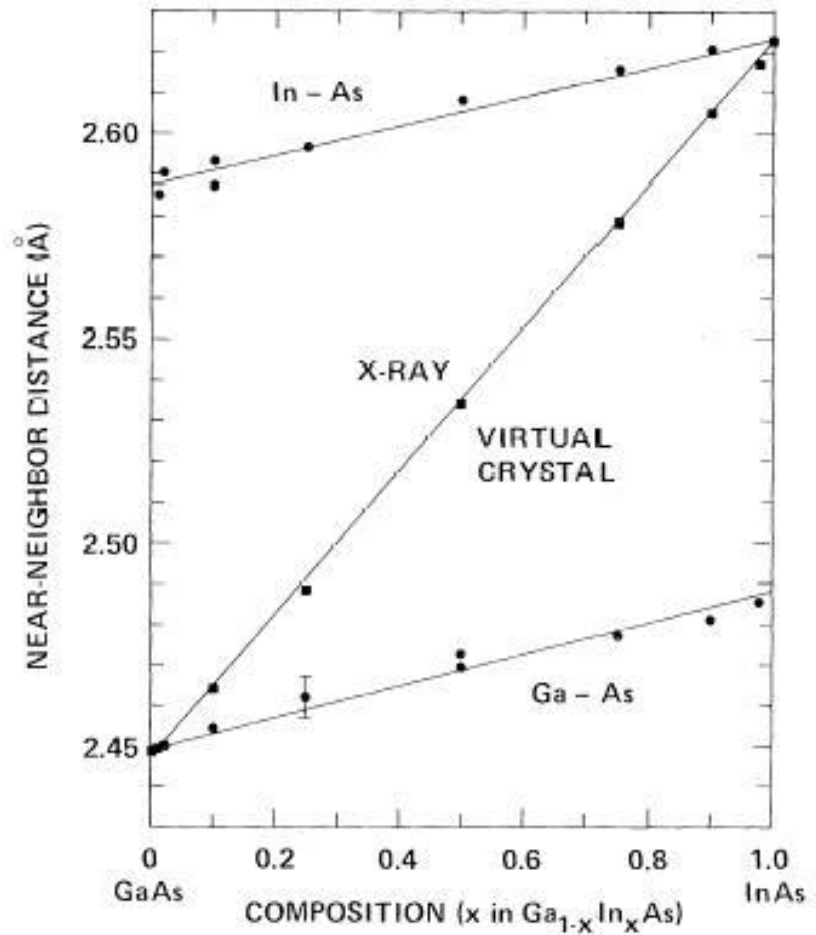


In<sub>0.5</sub>Ga<sub>0.5</sub>As



# Bond lengths in $\text{In}_x\text{Ga}_{1-x}\text{As}$

- The high resolution of EXAFS in determining bond lengths (0.01 Å) has shown that they stay close to sum of covalent radii
- Violation of the VCA
- First evidence of strong local structural distortions
- Mikkelsen Jr. and Boyce, Phys. Rev. Lett. **49**, 1412 (1982)



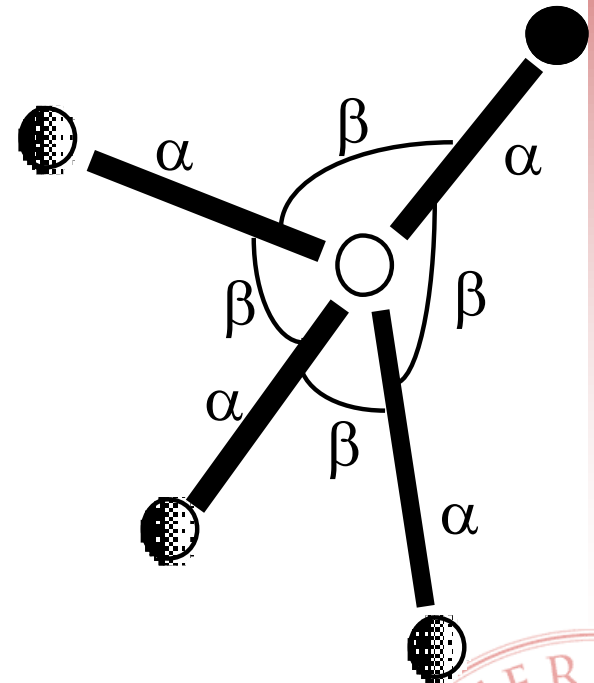
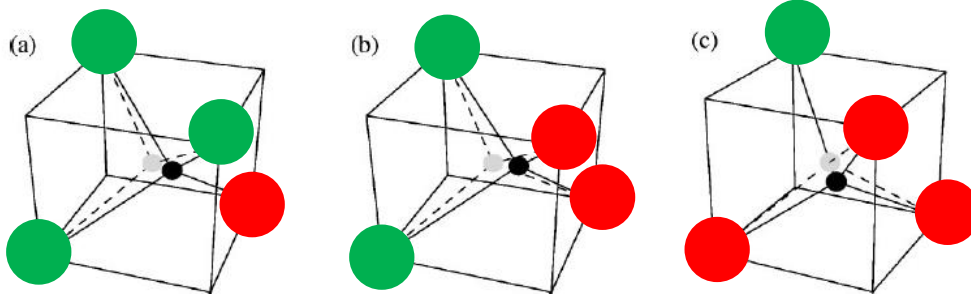
# Origin of local structural distortions

- Local deformation potential:

$$V(\{R_{ij}\}, \{\theta_{ijk}\}) =$$

$$\frac{\alpha}{2} \sum_{ij} (R_{ij} - R_{ij}^0)^2 + \frac{\beta}{8} R_e^2 \sum_{ijk} (\cos \theta_{ijk} + \frac{1}{3})^2$$

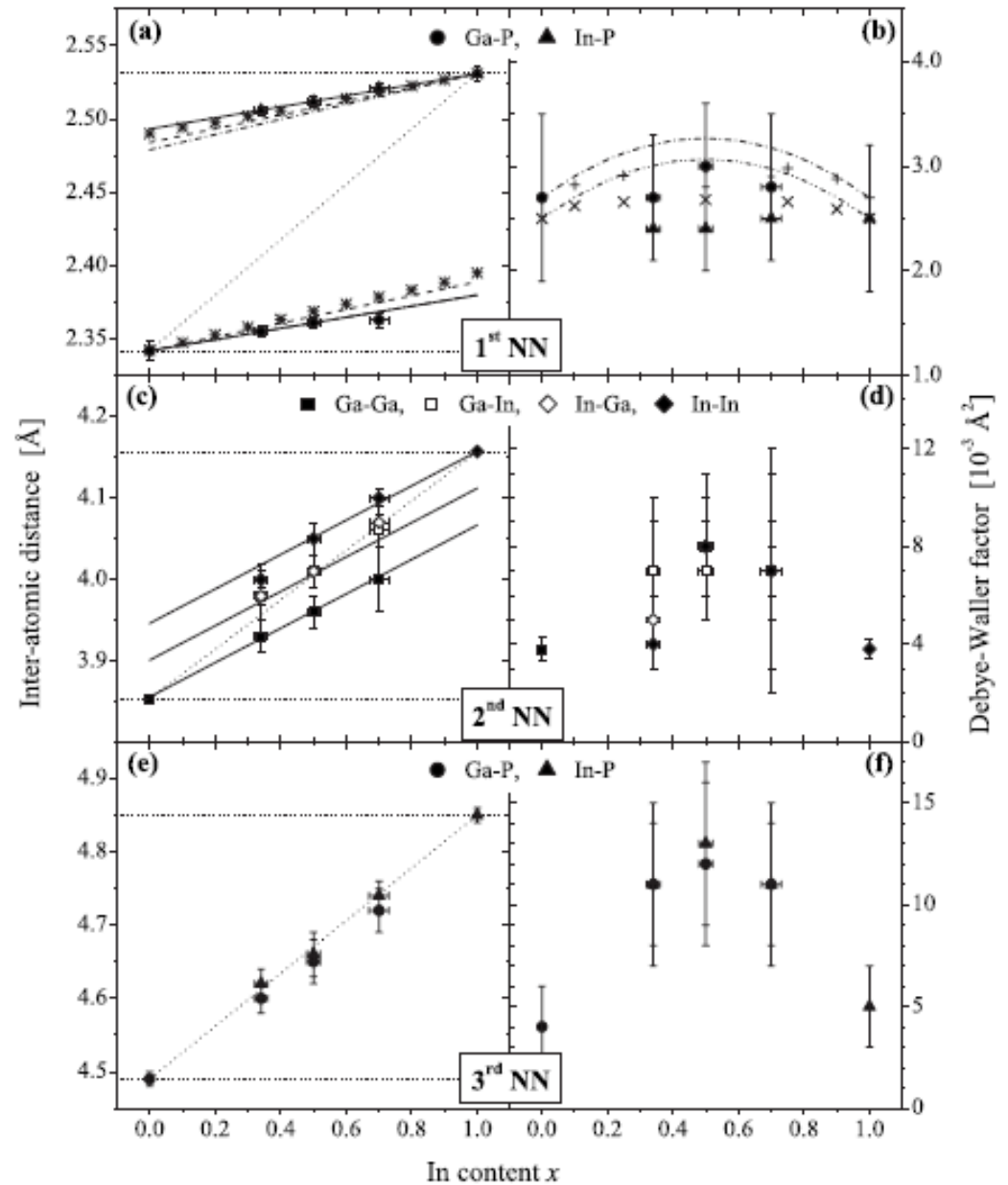
- For most semiconductors  $\alpha \gg \beta$ 
  - The covalent bond is stiff and directional



# Ga<sub>1-x</sub>In<sub>x</sub>P alloys

C. S. Schnohr, L. L. Araujo, P. Kluth,  
D. J. Sprouster, G. J. Foran, and  
M. C. Ridgway, Phys. Rev. **78**, 115201  
(2008)

- 26 years later
  - Much better data
  - More sophisticated analysis
- Same conclusion!



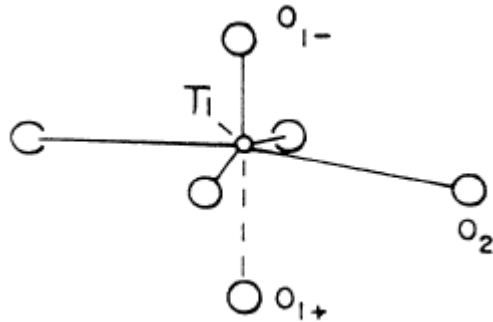
# XAFS and phase transitions

- Measure local structure through the phase transition
- XAFS has highlighted the difference between the real local structure and the average structure



# Ferroelectric Phase transitions in $\text{PbTiO}_3$

Sicron, Ravel, Yacoby, Stern, Dogan and Stern, Phys. Rev. B 50, 13168 (1994)

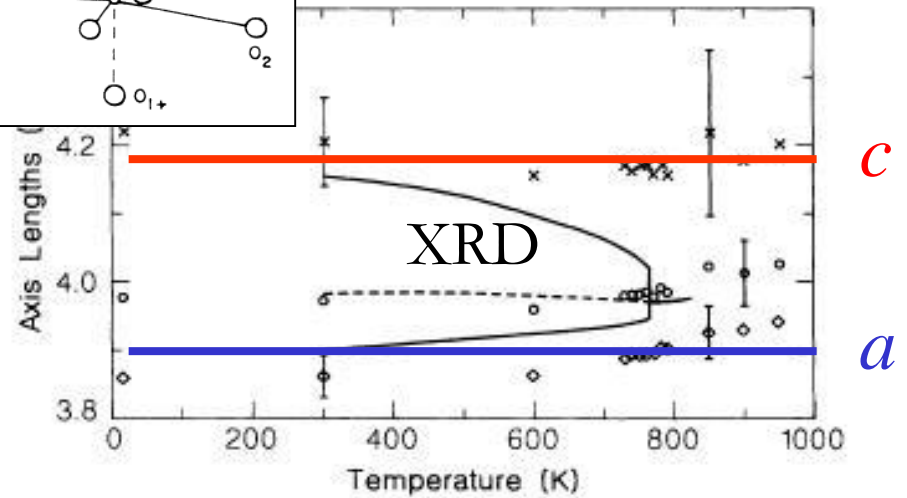
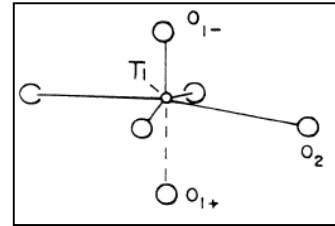


low temp

- At  $T_c = 763 \text{ K}$   $\text{PbTiO}_3$  undergoes tetragonal to cubic phase transition
- $T < T_c$  it is ferroelectric (permanent dipole moment)
- Phase transition believed to be purely displacive (no local distortion for  $T > T_c$ )



# Ferroelectric Phase transitions in $\text{PbTiO}_3$



- Ti and Pb XAFS data
- "Local lattice parameters" and local distortions do not change at  $T_c$ 
  - $c$ : sum of  $R(\text{Ti-O}_1)$
  - $a$ : calculated from  $R(\text{Ti-O}_2)$

## Conclusion

- local distortions survive above  $T_c$
- Above  $T_c$  random orientation of domains with permanent dipole moment





# Phase change mechanism in optical media

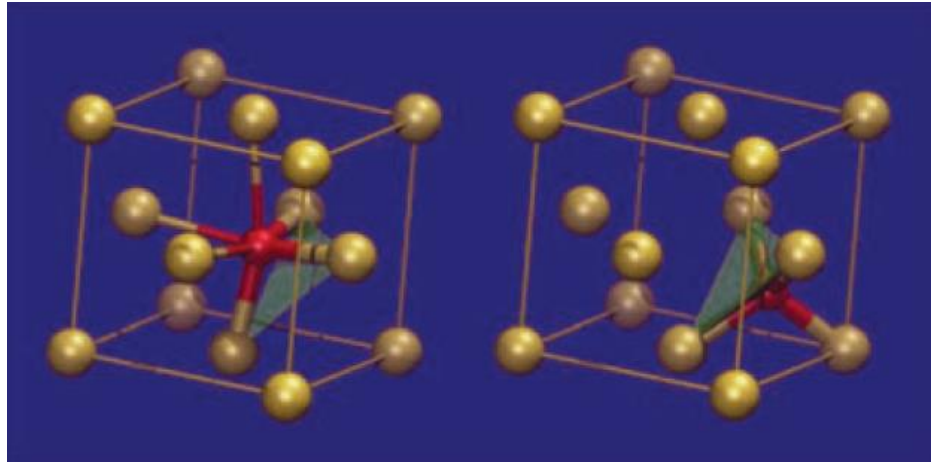
Kolobov et al., Nature Materials **3**, 703 (2004)

- Phase change optical discs used in DVD-RAMs are based on  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST)
- Writing: appropriate laser pulses induce reversible phase changes from amorphous to crystalline
- Reading: the reflectivity of the two phases is different
- What is associated structural change?

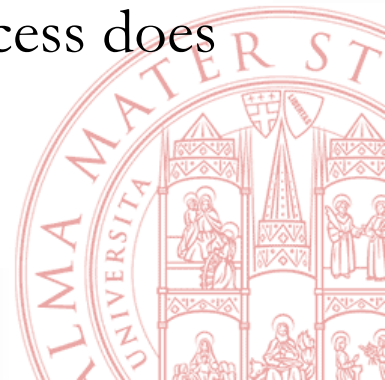




# Phase change mechanism in optical media



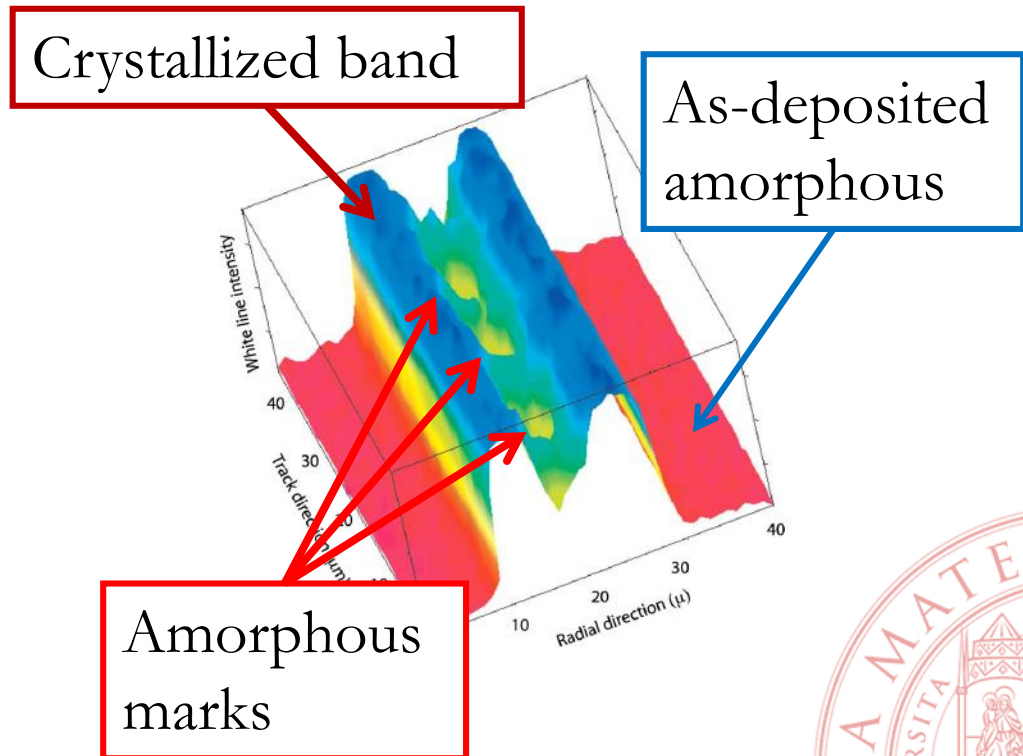
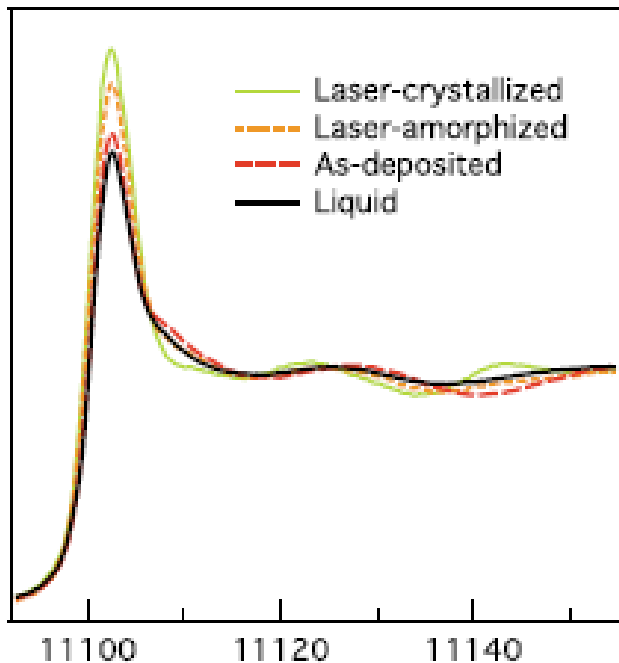
- Phase change is based on “umbrella flip” of Ge, from octahedral to tetrahedral coordination within Te fcc lattice
  - Three strong Ge – Te covalent bonds remain intact
  - Weaker Ge – Te bonds are broken by laser pulse
- Phase change in GST is fast and stable because the process does not require rupture of strong bonds or diffusion



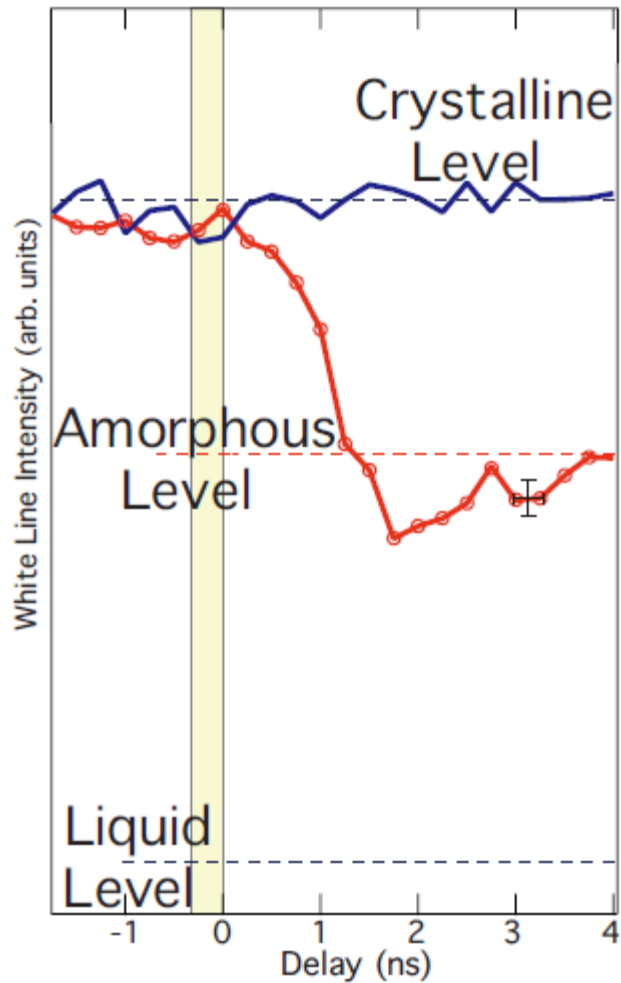
# Time resolved XAFS of phase change

Fons et al., Phys. Rev. B **82**, 041203 (2010)

- Sub nanosecond time resolved XAFS with  $\mu\text{m}$  spot size at SPring-8
- The intensity of the “white line” is different for crystalline, amorphous and liquid phases



# Time resolved XAFS of phase change



- White line intensity versus time
  - 100 ps time resolution
- Phase change does not involve melting



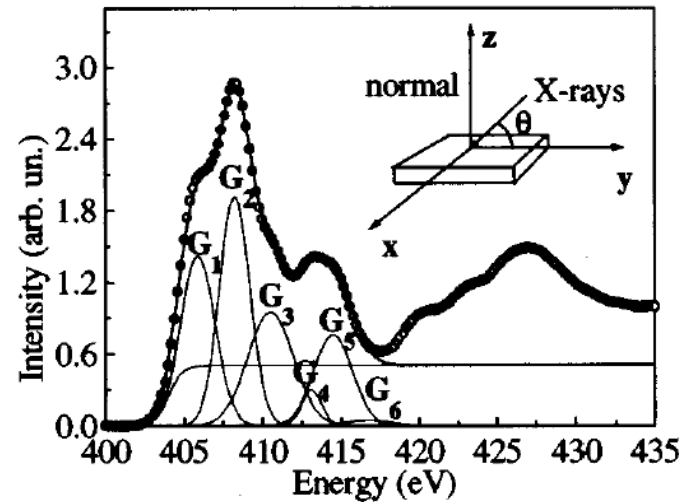
# XAFS and thin films / interfaces

- With specific detection schemes sensitivity to very thin films achievable
  - Grazing incidence
  - Electron / fluo detection
- Exploit linear polarization of SR to obtain information on
  - Orientation
  - Lattice symmetry



# Cubic and hexagonal GaN

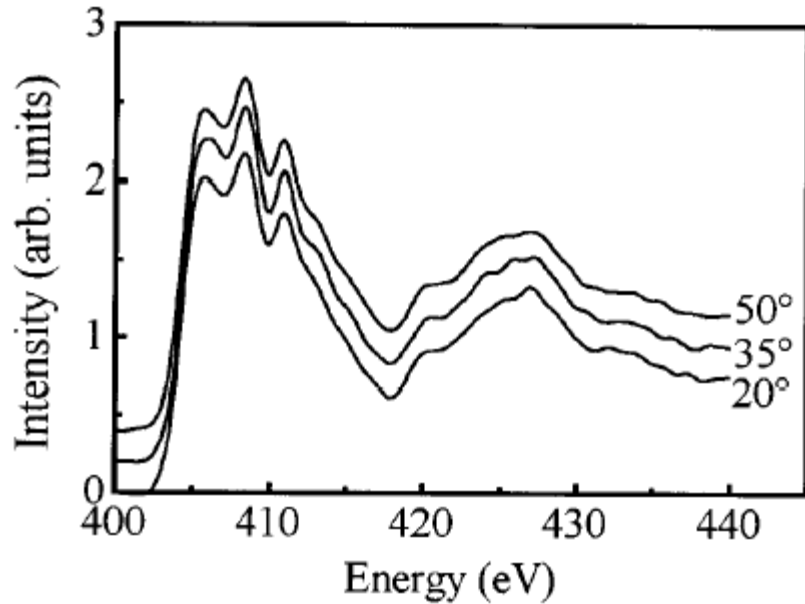
- N K-edge XAS to study relative amounts of cubic and hexagonal GaN
- Exploit
  - linear polarization of SR
  - polarization dependence of cross-section
- XAS signal must exhibit (at least) point group symmetry of the crystal
  - $T_d$ : isotropic signal
  - $C_{6V}$ :



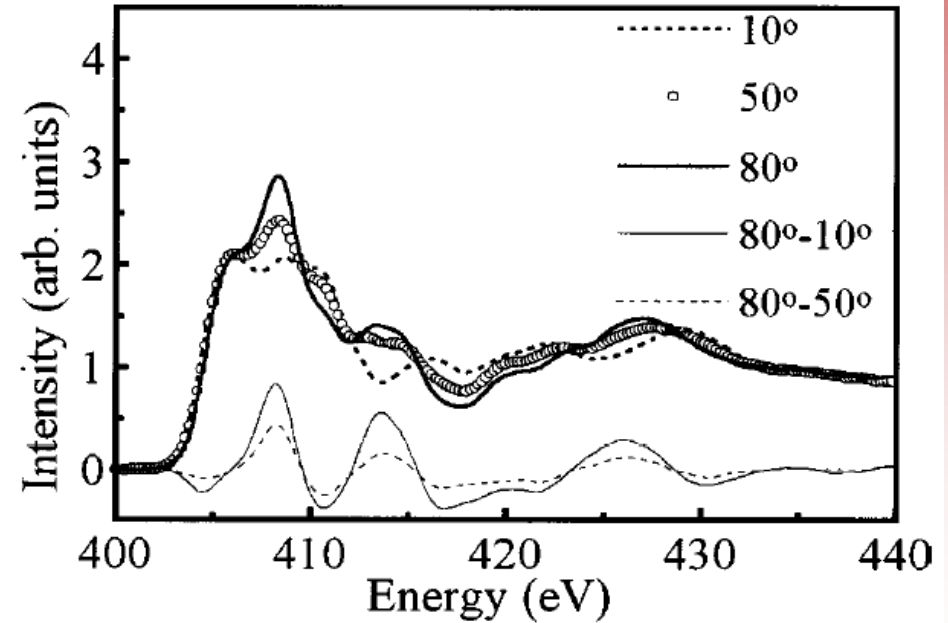
$$\sigma^{tot}(E, \theta) = \sigma^{iso}(E) + (3\cos^2\theta - 1)\sigma^1(E)$$



## CUBIC



## HEXAGONAL

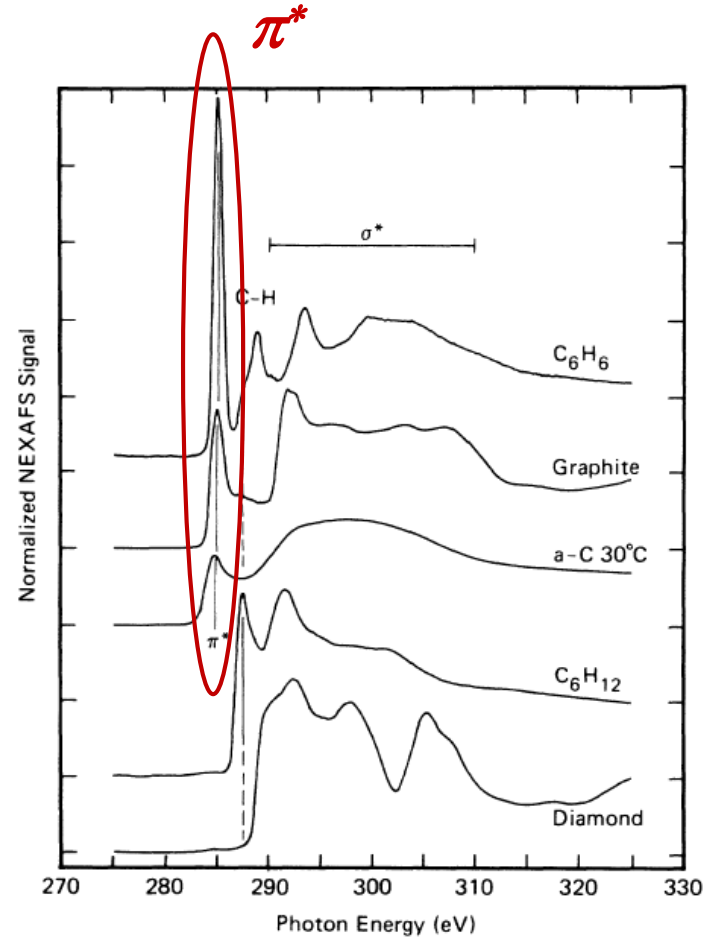


- Katsikini et. al., APL **69**, 4206 (1996); JAP **83**, 1440 (1998)

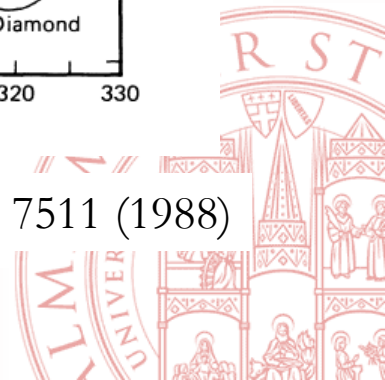


# C K edge XANES

- Transitions to  $\pi^*$  molecular orbitals give rise to strong peak



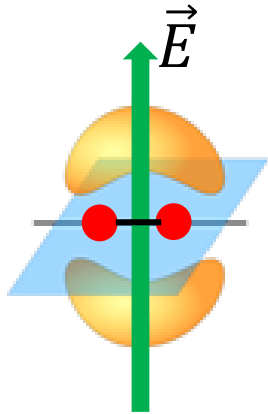
Comelli et al., Phys. Rev. B 38, 7511 (1988)



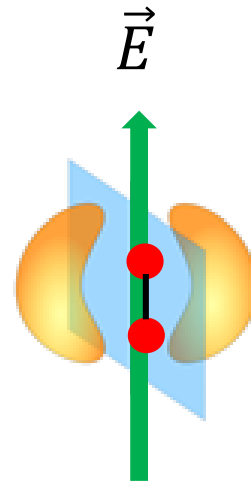


## Use of linear dichroism

- Intensity of peaks related to transitions to  $\pi^*$  orbitals depends on the orientation between the orbital and  $\vec{E}$



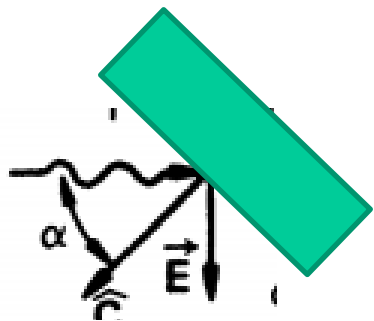
Maximum intensity



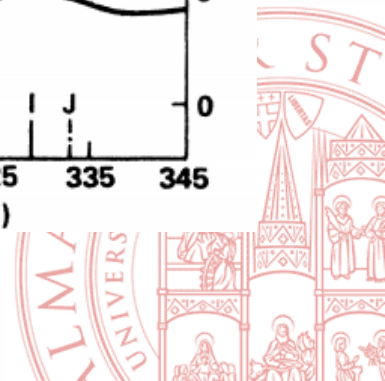
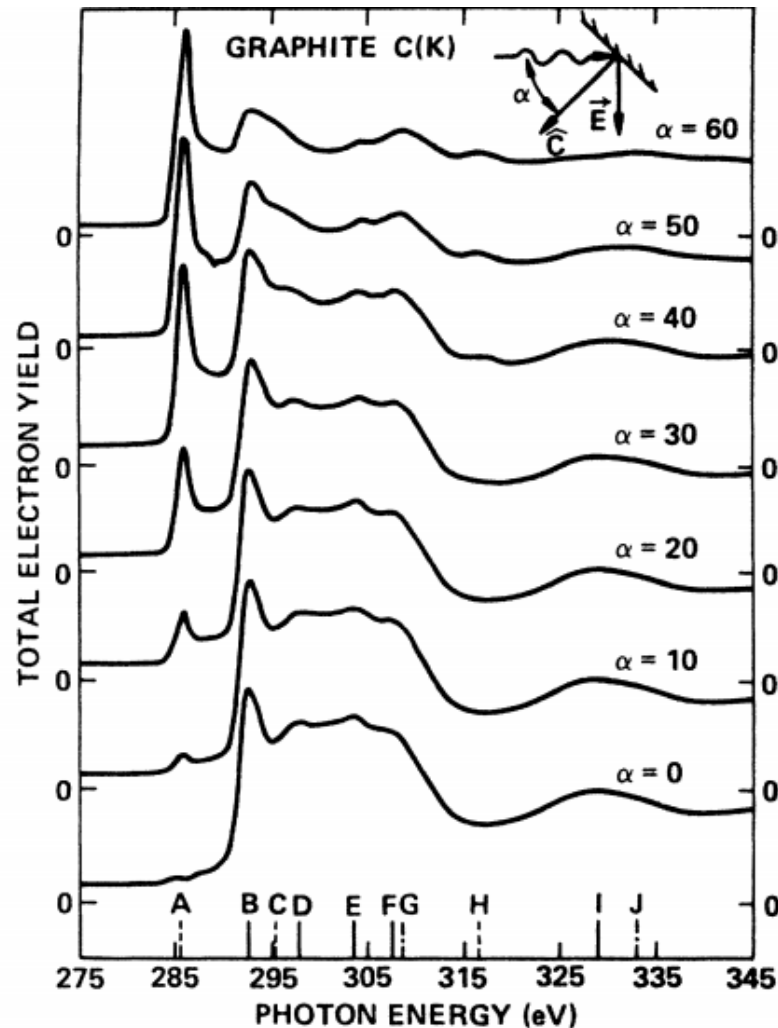
Minimum intensity



# C K edge XANES of graphite

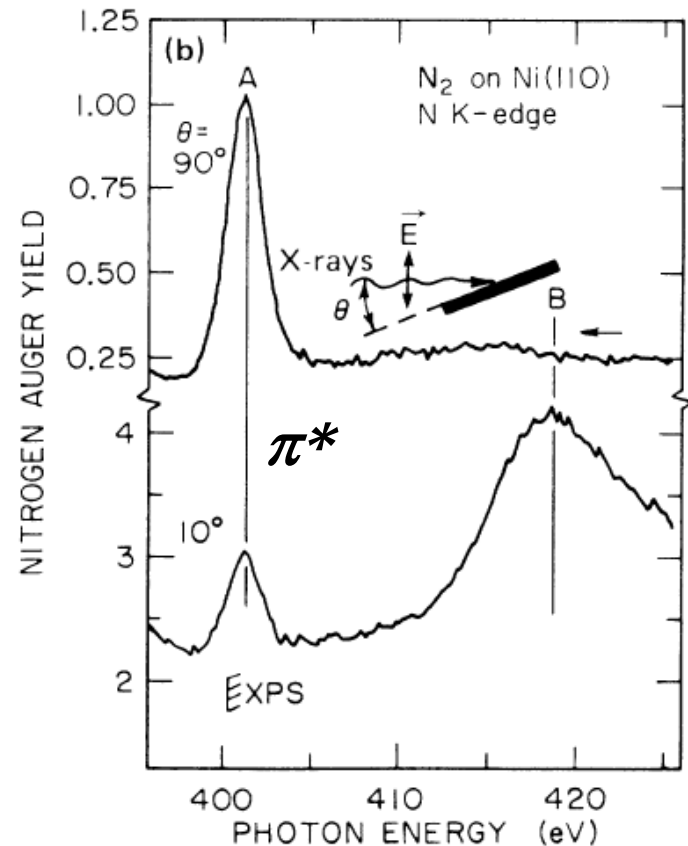
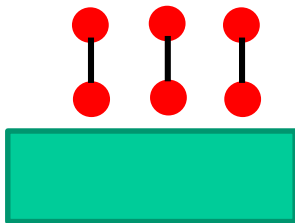


- Very clear dependence of peak due to transitions to  $\pi^*$  orbitals on orientation
- $\pi^*$  are perpendicular to surface plane
- Rosenberg et al, Phys. Rev. B33, 4034 (1986)

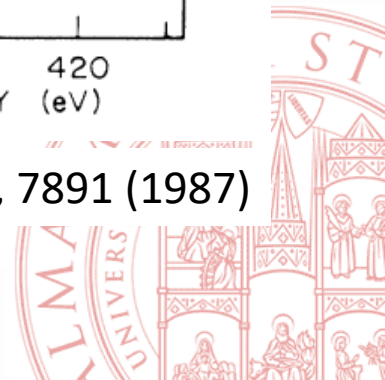


# Orientation of molecules on surfaces

- Typical application: determination of the orientation of molecules on single crystal surfaces
- $N_2$  on Ni(110)
- Molecules are "vertical"

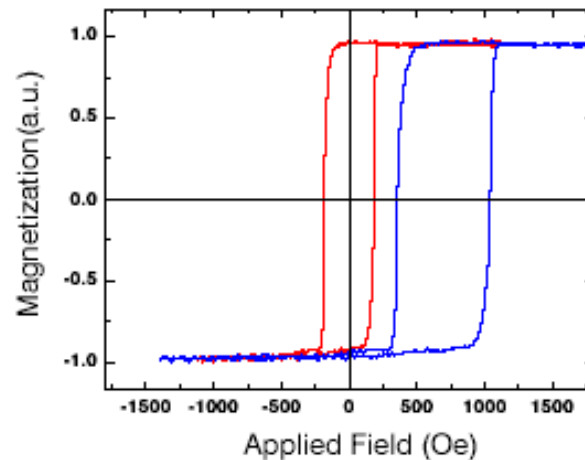
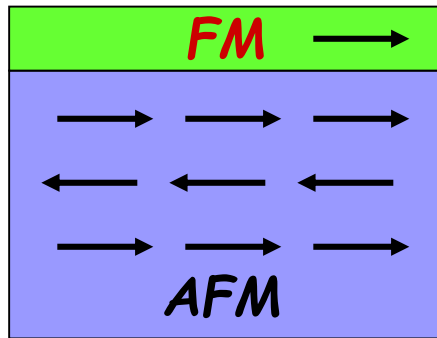


Stöhr & Oukta, Phys. Rev. B 36, 7891 (1987)



# The Fe/NiO(001) interface

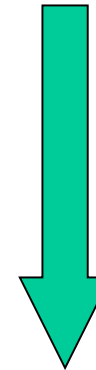
P. Luches, V. Bellini, S. Colonna, L. Di Giustino, F. Manghi, S. Valeri, and F. Boscherini,  
Phys. Rev. Lett. 96, 106106 (2006).



heating up to  $T_N$

+

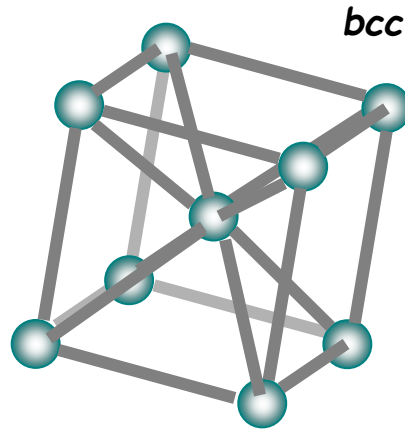
cooling in H



exchange bias

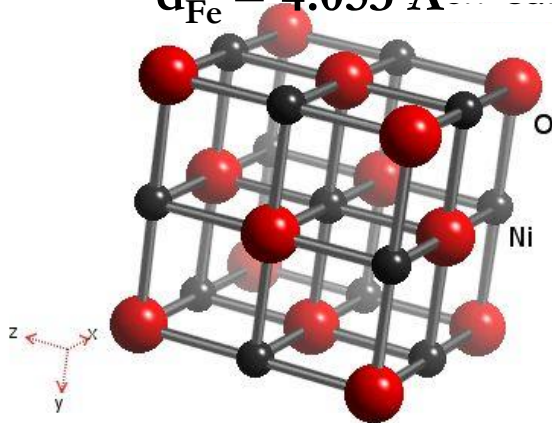


# The Fe/NiO(100) interface



$$a_{\text{Fe}} = 2.866 \text{ \AA}$$

$$d_{\text{Fe}} = 4.053 \text{ \AA}$$



$$a_{\text{NiO}} = 4.176 \text{ \AA}$$

Fe

FM  $T_C = 1040 \text{ K}$

$m = -2.8\%$

NiO

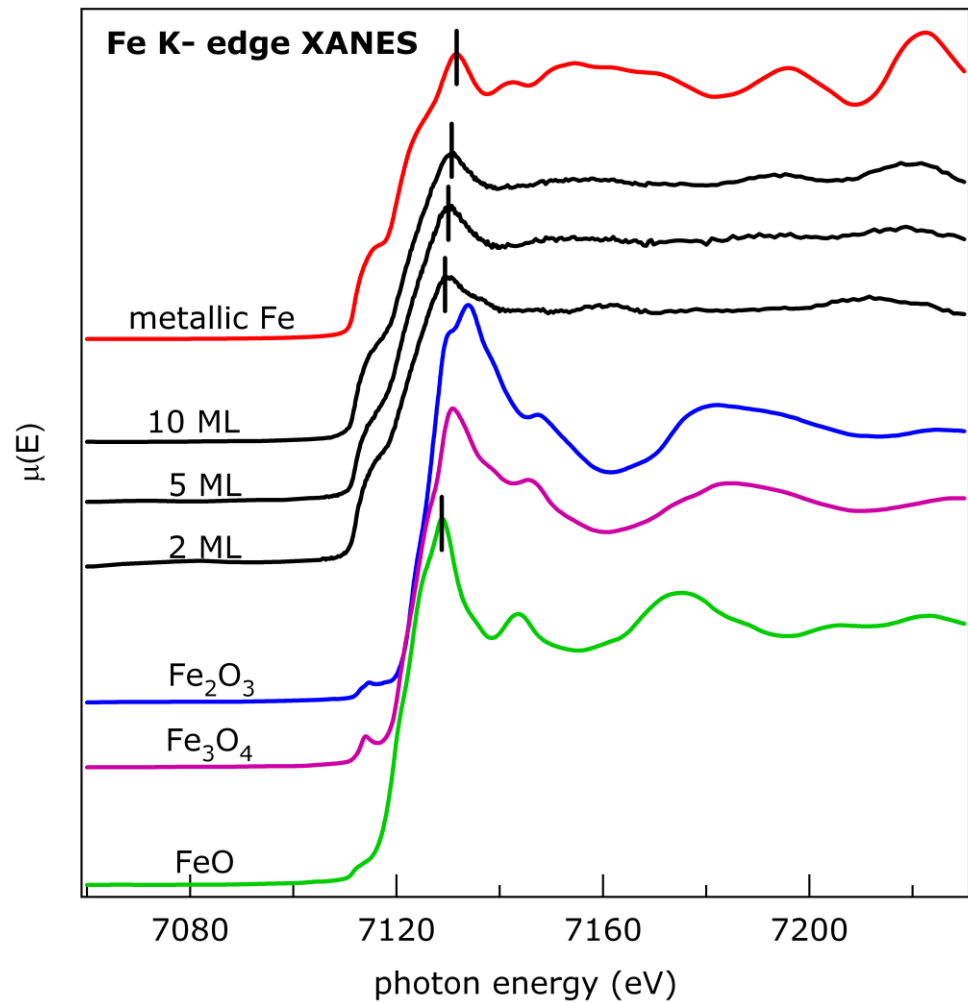
AF  $T_N = 520 \text{ K}$



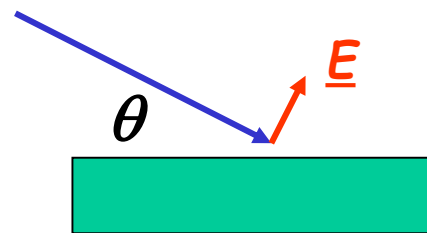
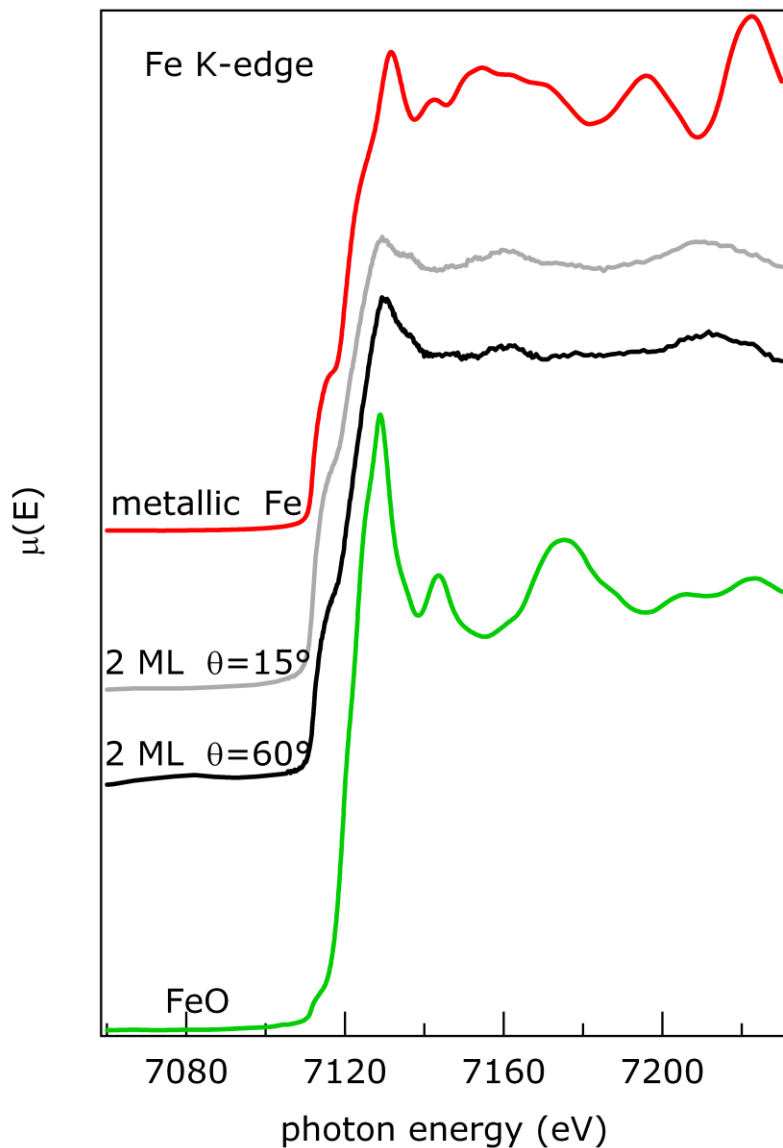
# Fe/NiO XANES

- deviation from metallic character

- shift of the white line towards FeO



# Fe/NiO XANES: polarization dependence

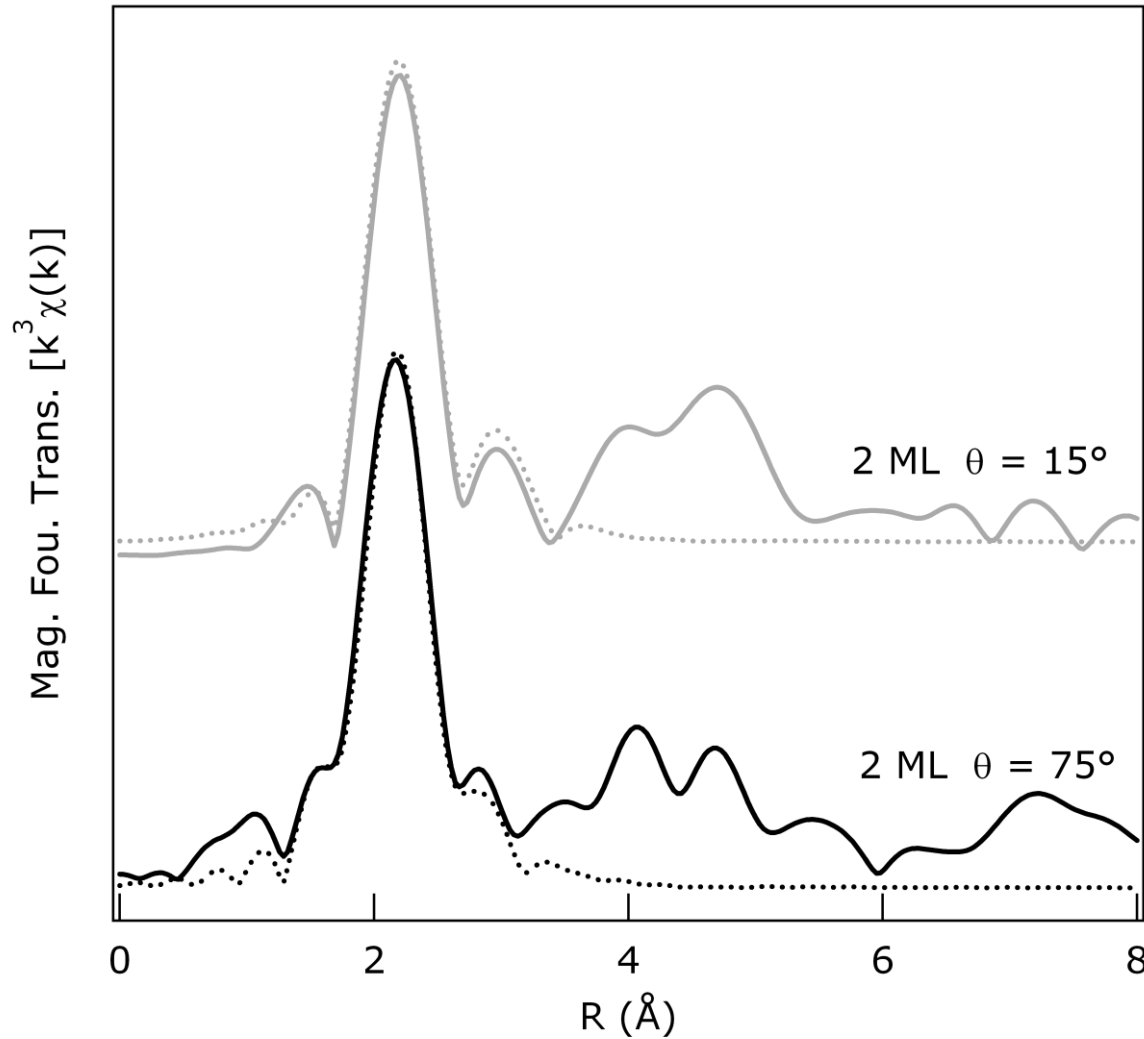


planar FeO phase

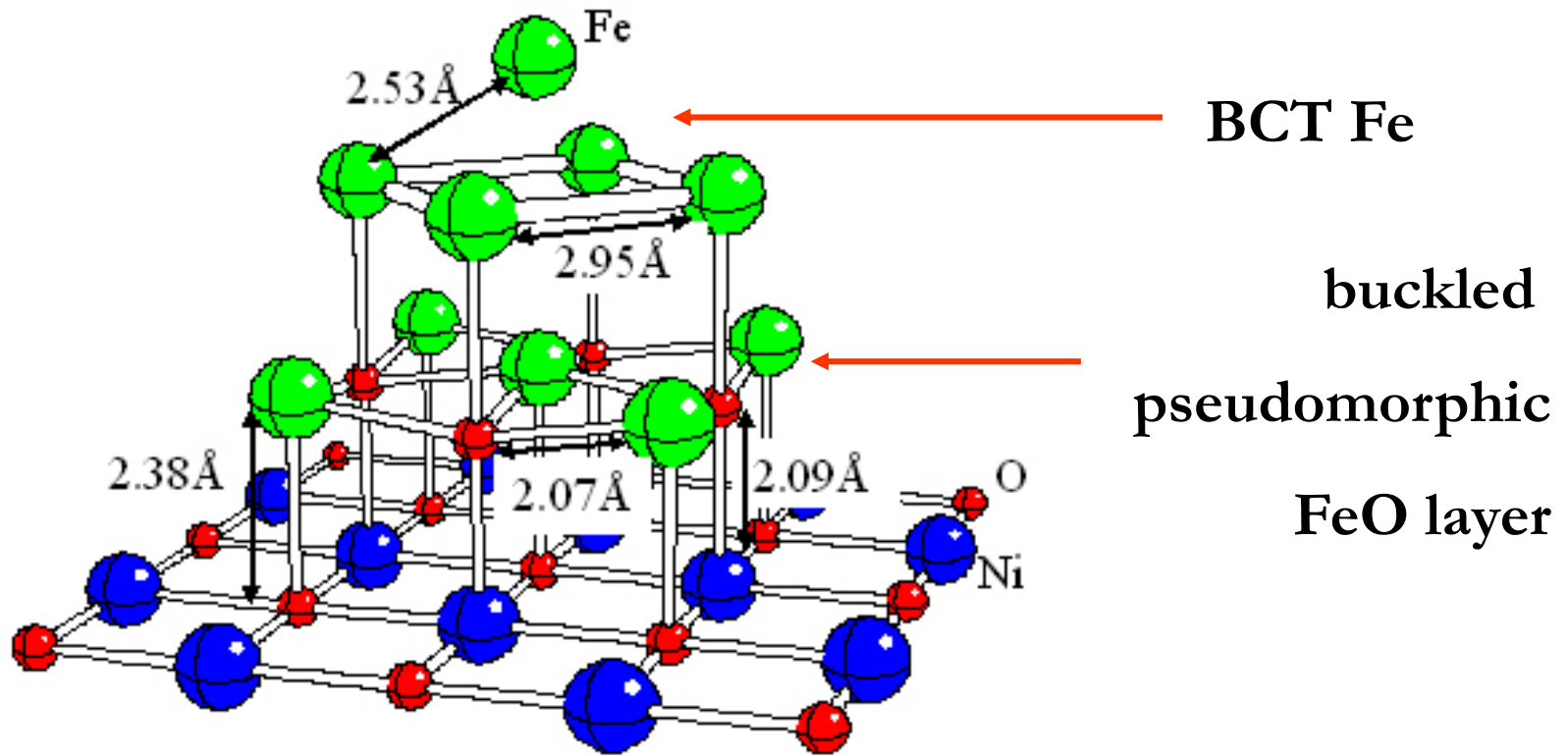




# Fe/NiO 2 ML thickness



# Fe/NiO: atomic structure of interface



- expanded FeO-NiO and FeO-Fe distance



# XAFS and nanostructures

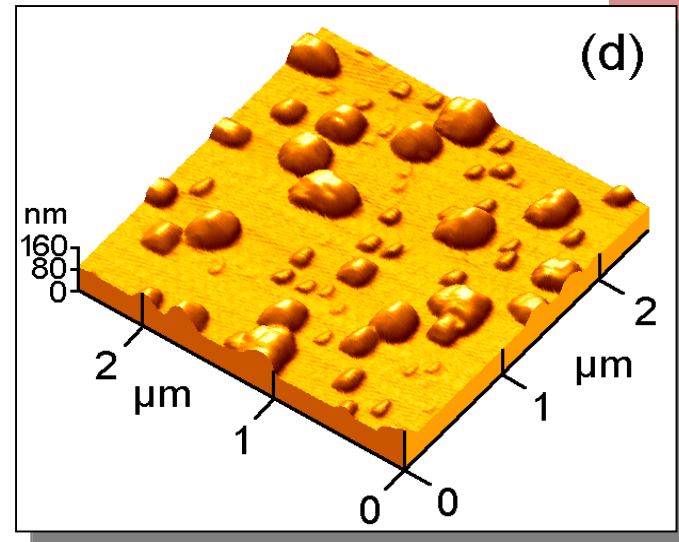
- XAFS is a local, short range, effect
  - Origin: core hole lifetime ( $t_{hole} = 10^{-16} - 10^{-15}$  s) and electron mean free path (5 – 10 Å).
- Same formalism applies to molecule, cluster or crystalline solid
  - insensitive to variations of morphology
  - sensitive to low thicknesses, high dilutions
- Excellent probe of **variations** in local environment due to
  - Size effects
  - Change 3D / 2D / 1D



# Ge Quantum Dots

F. Boscherini, G. Capellini, L. Di Gaspare, F. Rosei, N. Motta, and S. Mobilio, Appl. Phys. Lett. **76**, 682 (2000)

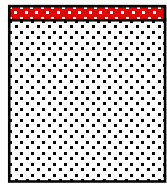
- Need for understanding of local bonding
- Preparation:
  - Ge/Si(001) by CVD @ 600 °C, Univ. Roma Tre
  - Ge/Si(111) by MBE @ 450 - 550 °C, Univ. Roma II



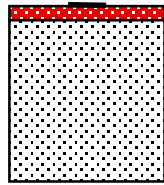
# Energetics of island formation

- Competing energies:
  - strain
  - surface
  - dislocations

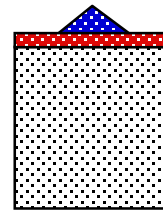
- Contributions from:
  - wetting layer
  - islands



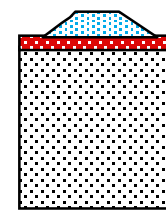
Wetting layer



WL+2D platelet



WL+Strained island

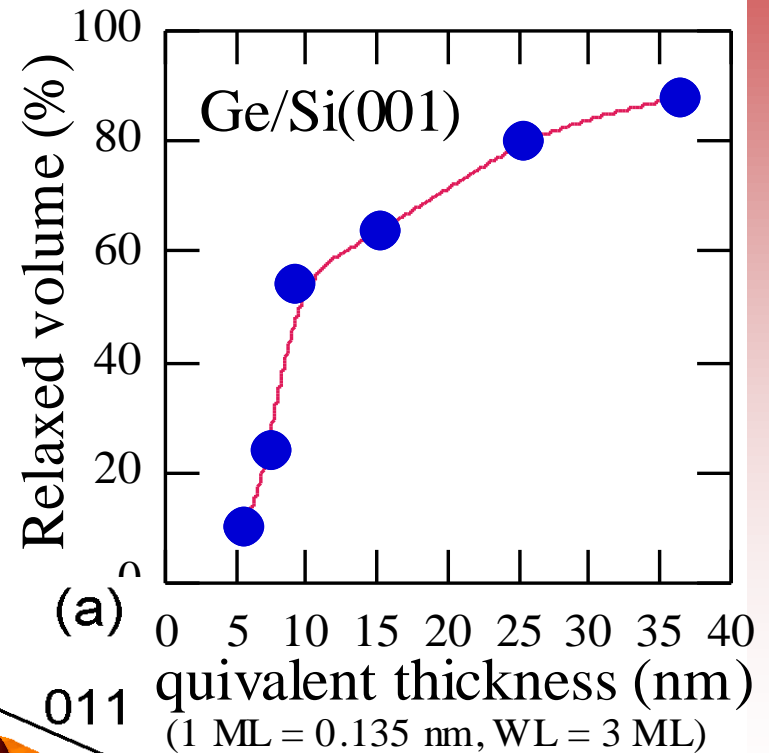
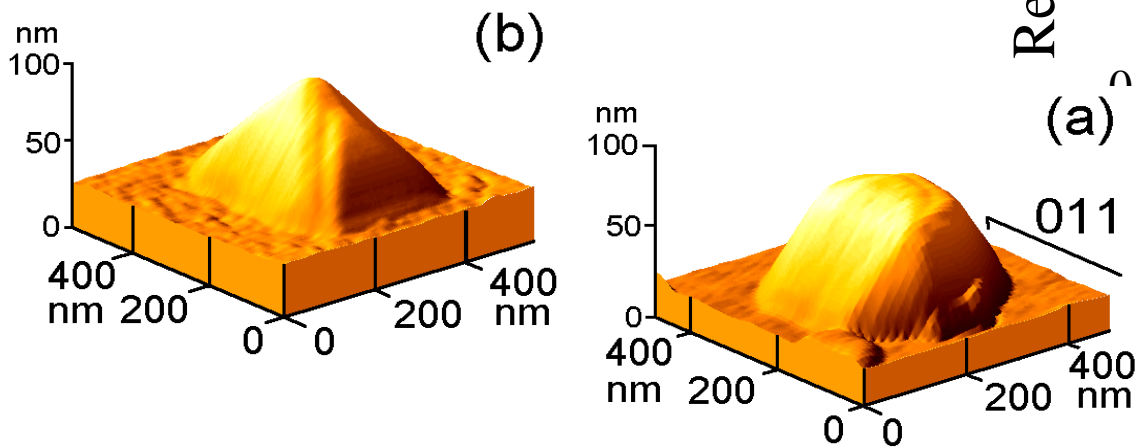


WL+Relaxed island

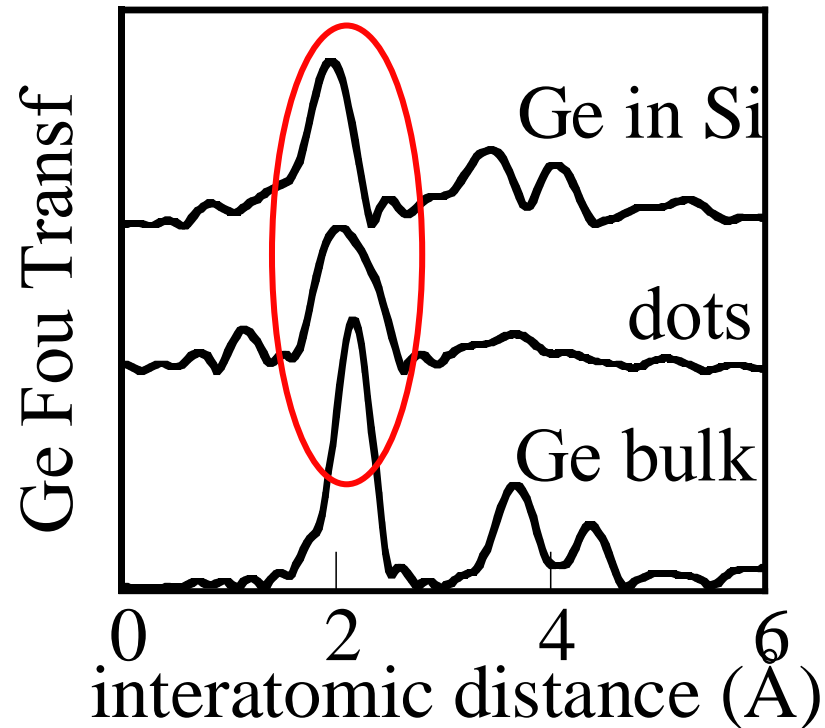


# AFM of Ge dots

- Analysis of aspect ratio provides measurement of relative amount of relaxed islands
- Ge/Si(001): Full range of relaxation examined



# Quantum Dots: Ge edge XAFS

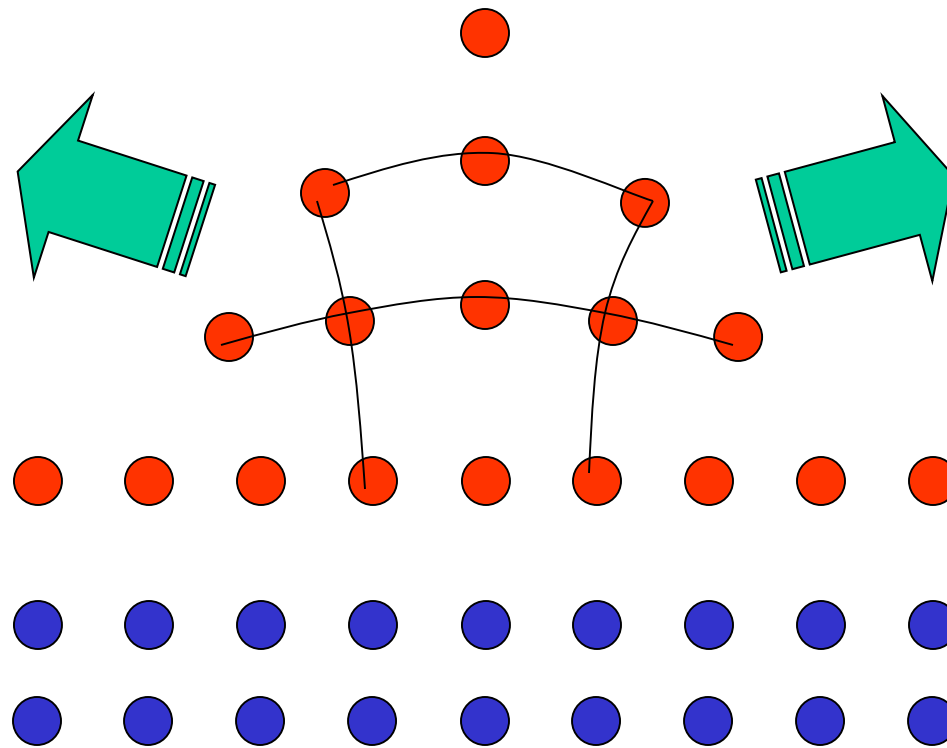


- Assuming random alloy average composition is  $\text{Ge}_{0.70}\text{Si}_{0.30}$

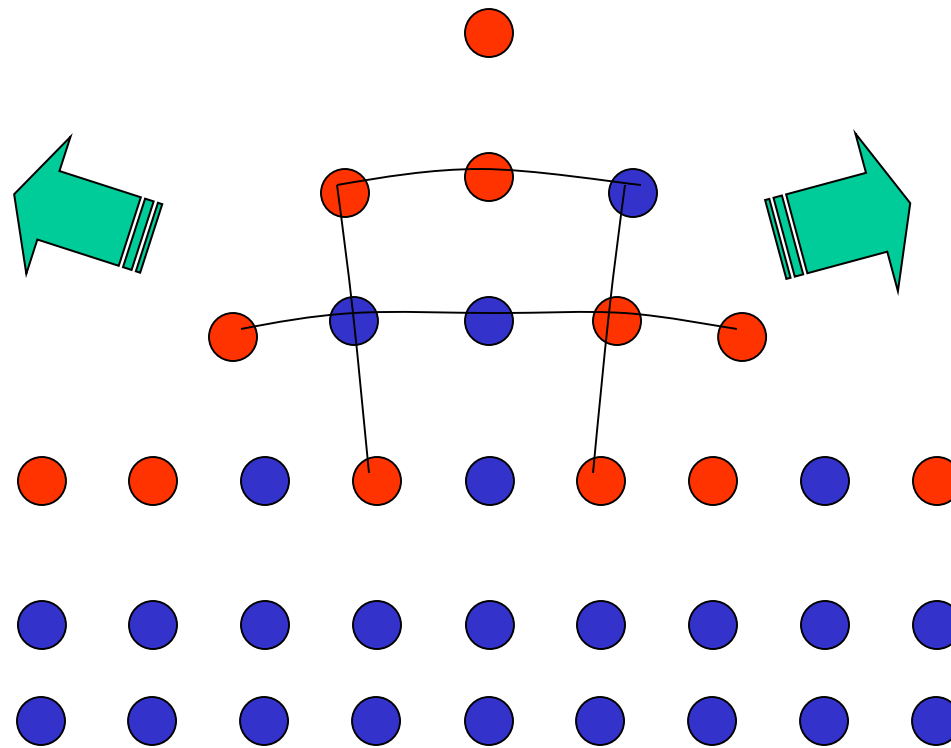




# Conventional SK growth



# SK growth with interdiffusion



# Metallic nanostructures

- One of the first applications of XAFS
- Exploits high resolution in first coordination shells



# Clusters: bond length contraction

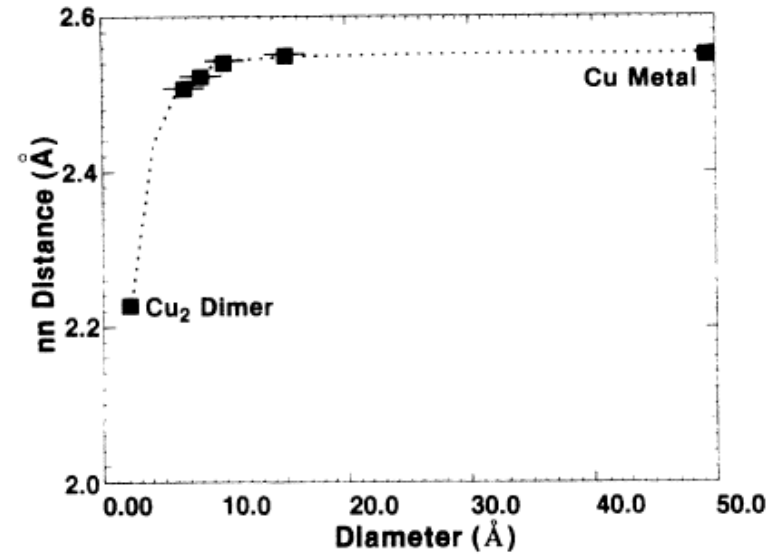
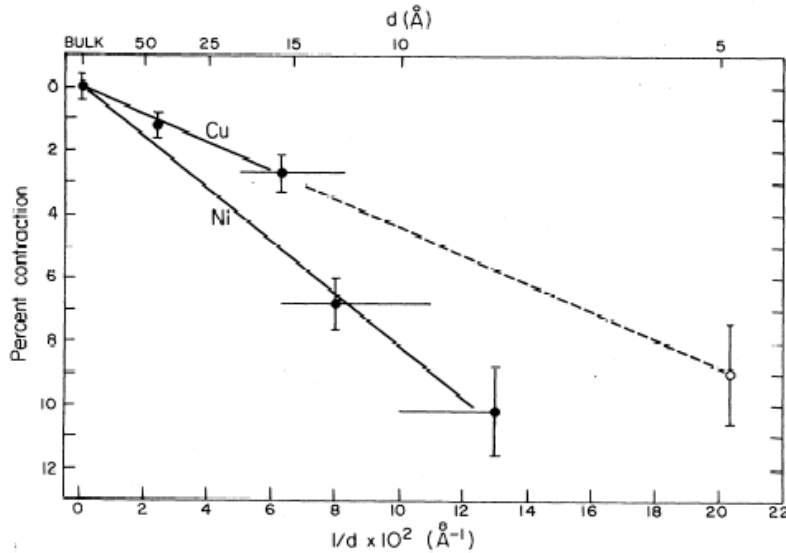


FIG. 4. Variation in interaction distance as a function of particle size.

Apai et. al.,  
Phys. Rev. Lett. **43**, 165 (1979)

Montano et. al.,  
Phys. Rev. Lett. **56**, 2076 (1986)

- A bond length contraction has been found for weakly supported metallic clusters (Ni, Cu, Au.....) for  $d < 100 \text{\AA}$



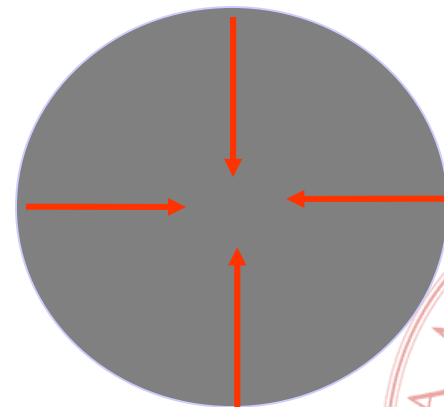
# Bond length contraction

- A macroscopic surface tension interpretation (“liquid drop”) can explain the bond length contraction

- $f$  surface tension,  
 $\kappa$  bulk modulus  
 $r$  radius of spherical particle

$$\frac{\Delta R}{R} = -\frac{2}{3} f \frac{\kappa}{r}$$

- Montano et. al.  
Phys. Rev. B **30**, 672 (1984)  
Balerna et. al.,  
Phys. Rev. B **31** 5058 (1985)

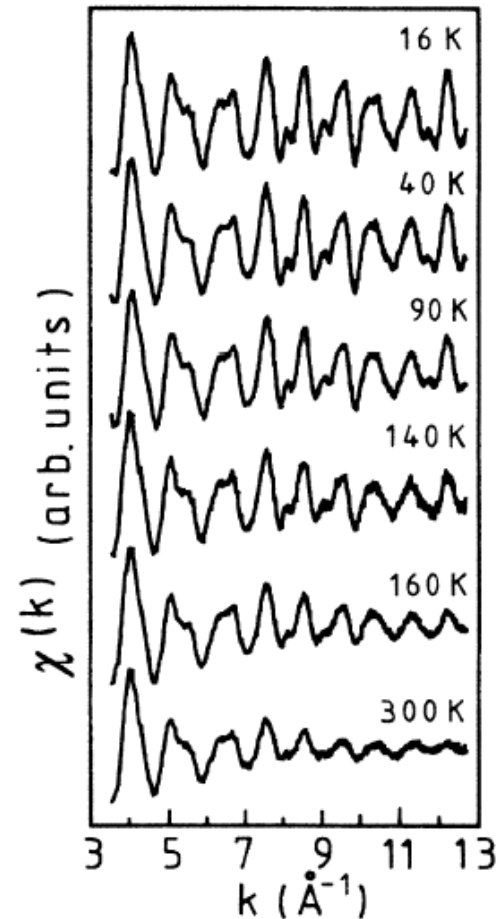
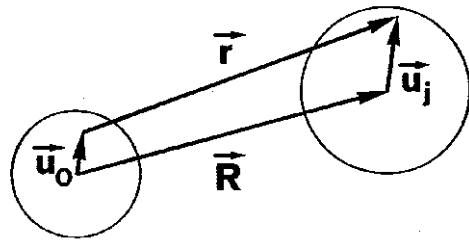


# Dynamic properties of Au clusters

- In the harmonic approximation, the Mean-Square-Relative-Displacement,  $\sigma^2$ , damps the EXAFS signal with a term

$$e^{-2k^2\sigma^2}$$

$$\sigma_{0j}^2 = \left\langle \left| (\vec{u}_0 - \vec{u}_j) \cdot \hat{R}_{0j} \right|^2 \right\rangle$$

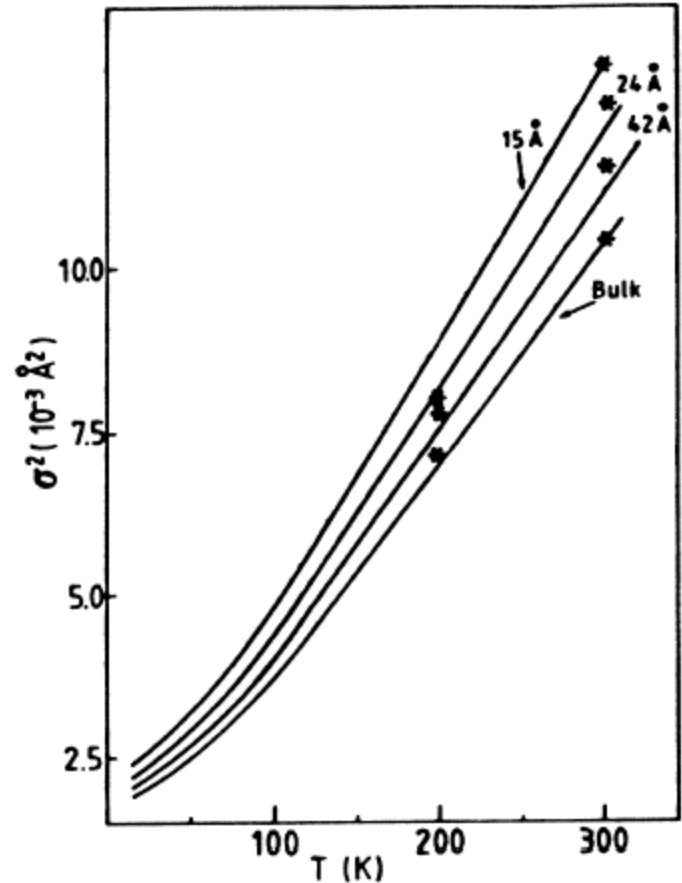


Bulk Au

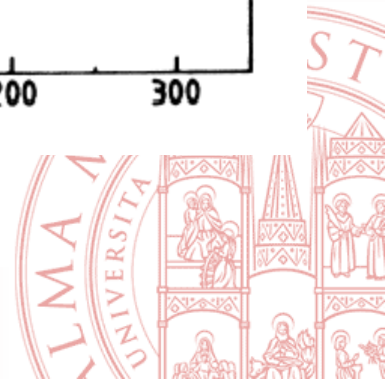


# Dynamic properties of Au clusters

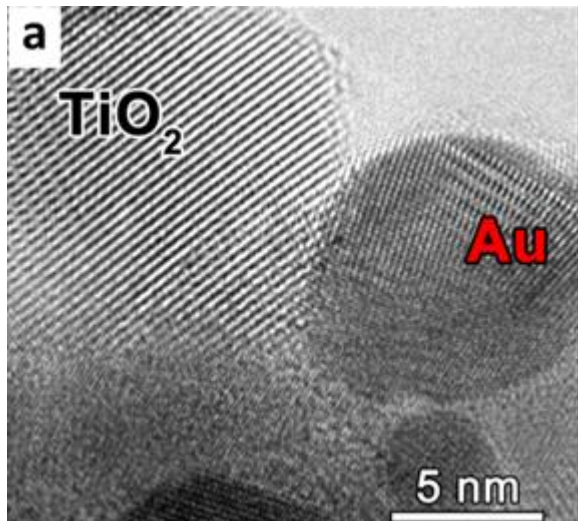
- As the cluster dimensions decrease an enhancement of  $\sigma^2$  is evident
- Surface atoms have less motion constraints
- High surface-to-volume ratio for nanoclusters
- Values reproduced by numerical model for free sphere phonon DOS which includes surface modes



Balerna and Mobilio,  
Phys. Rev. B **34**, 2293 (1986)



# High resolution inelastic x-ray scattering at Ti K-edge to study light – induced plasmonic electron transfer processes in Au/TiO<sub>2</sub> nanocomposites

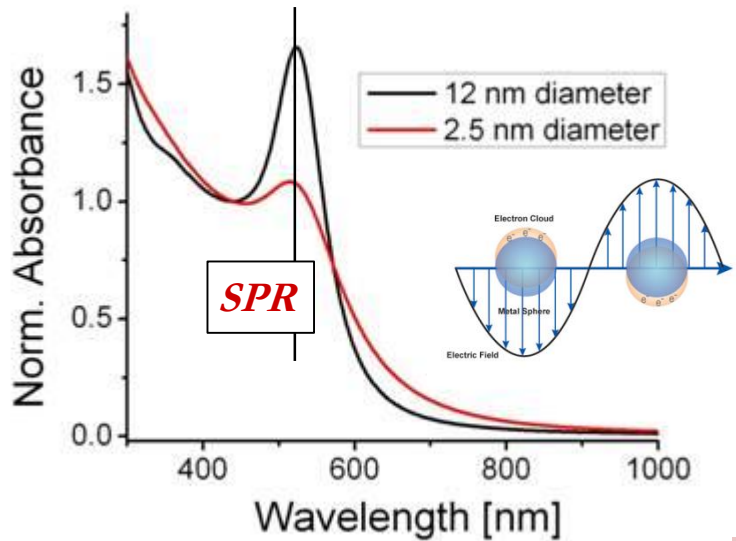
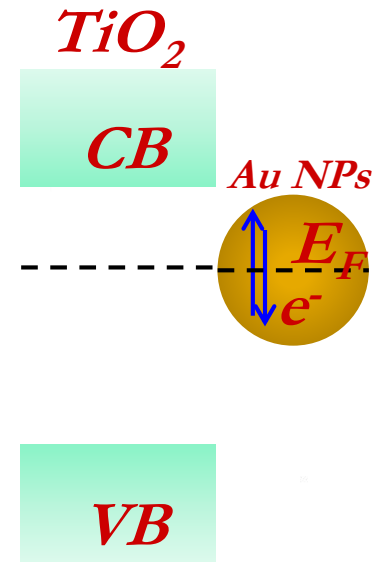
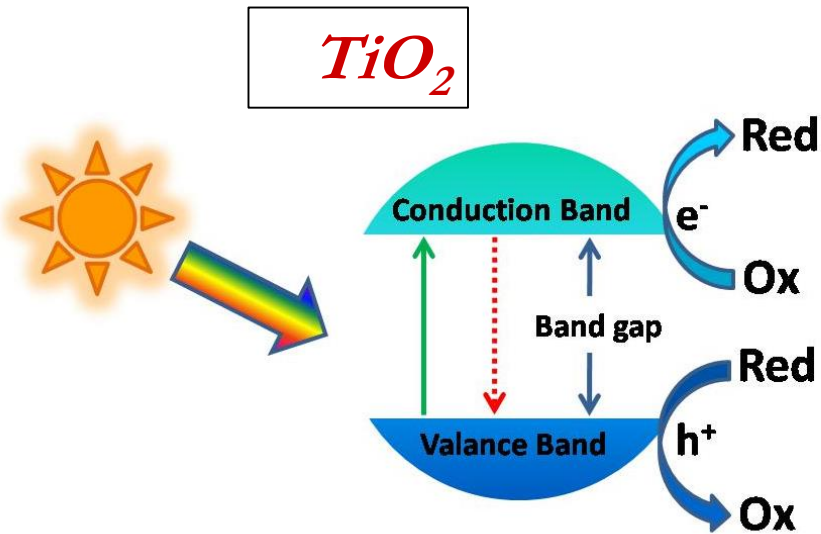


Amidani et al.,  
Angew. Chem. Int. Ed. 54, 5413 (2015)





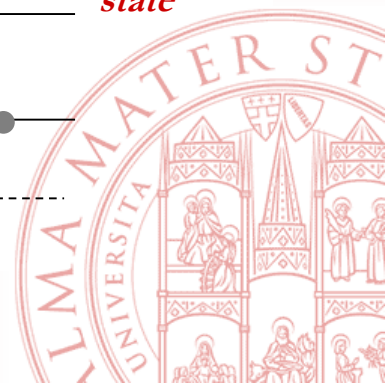
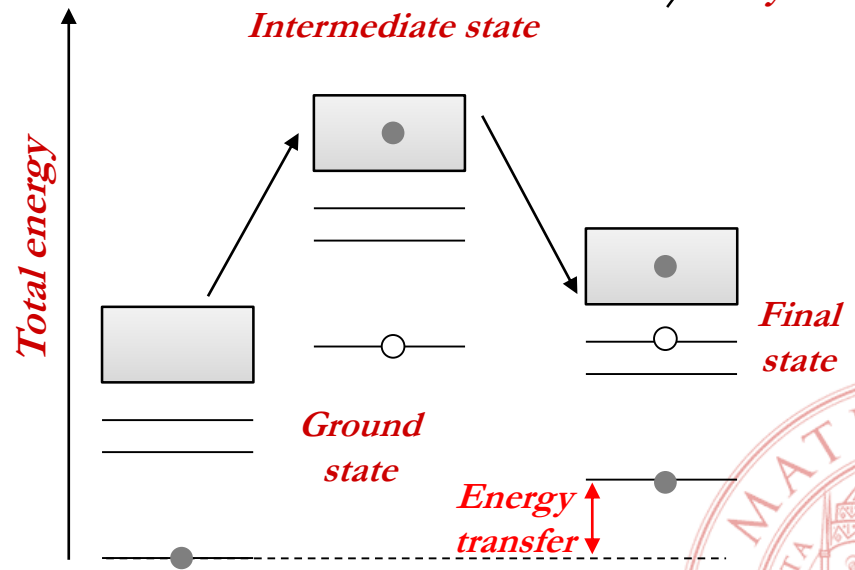
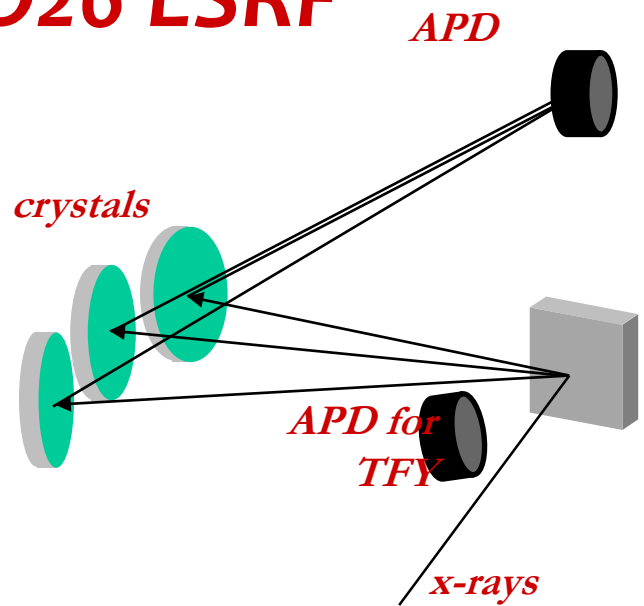
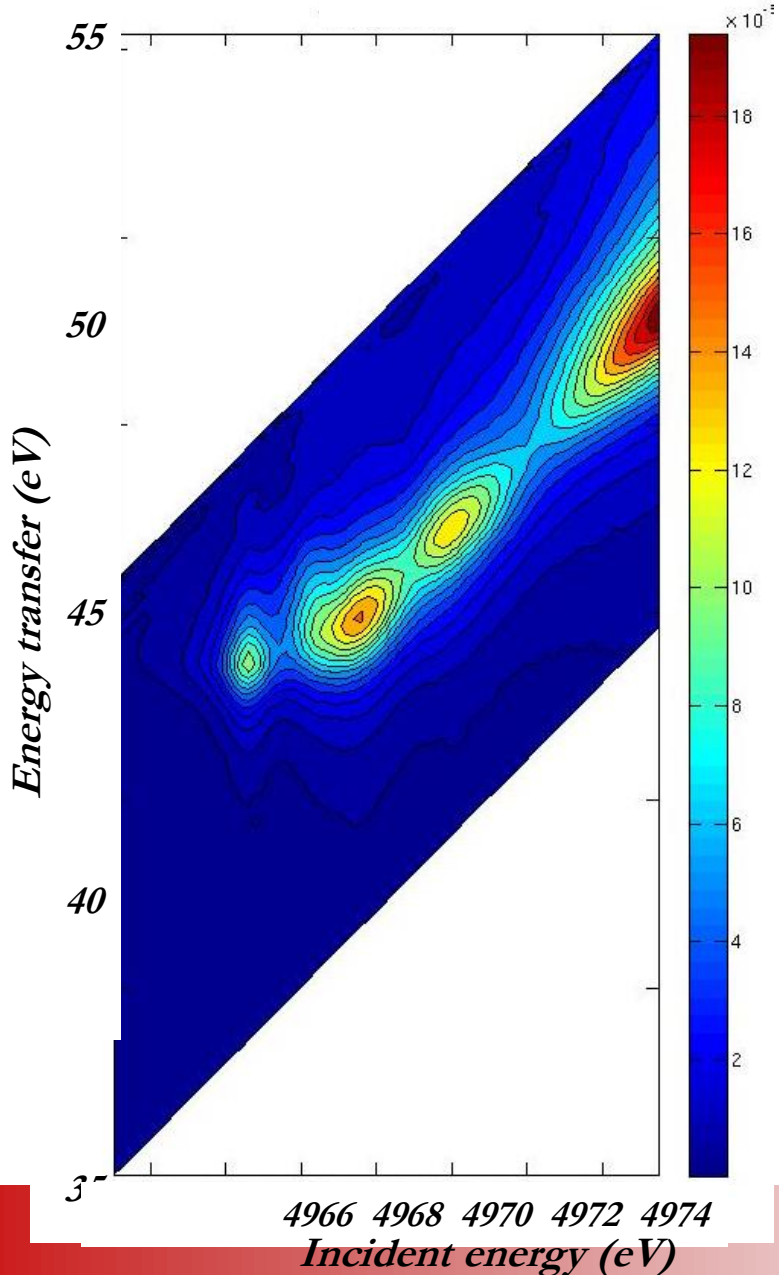
# Motivation



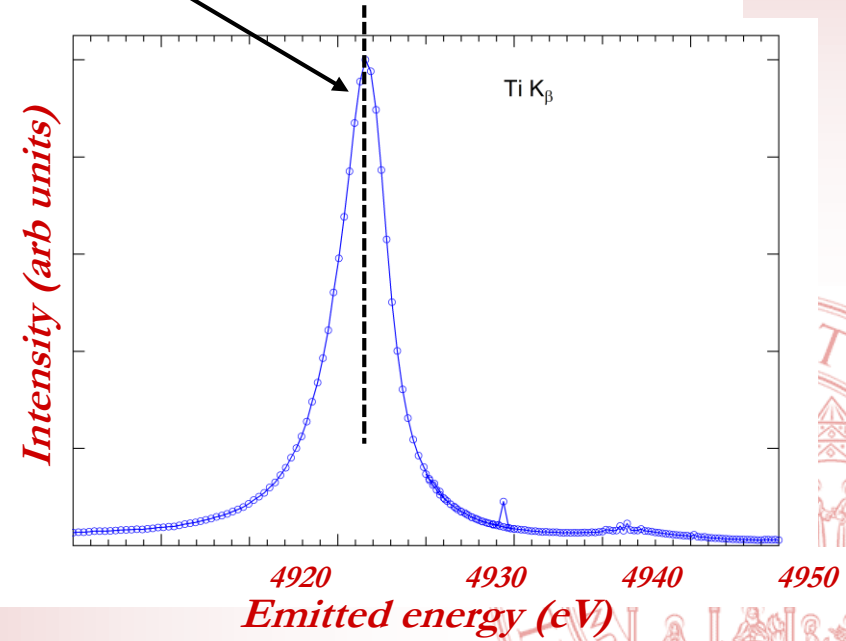
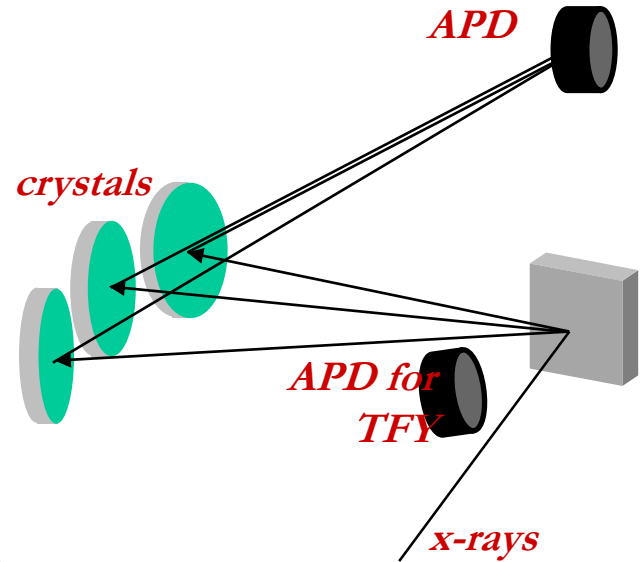
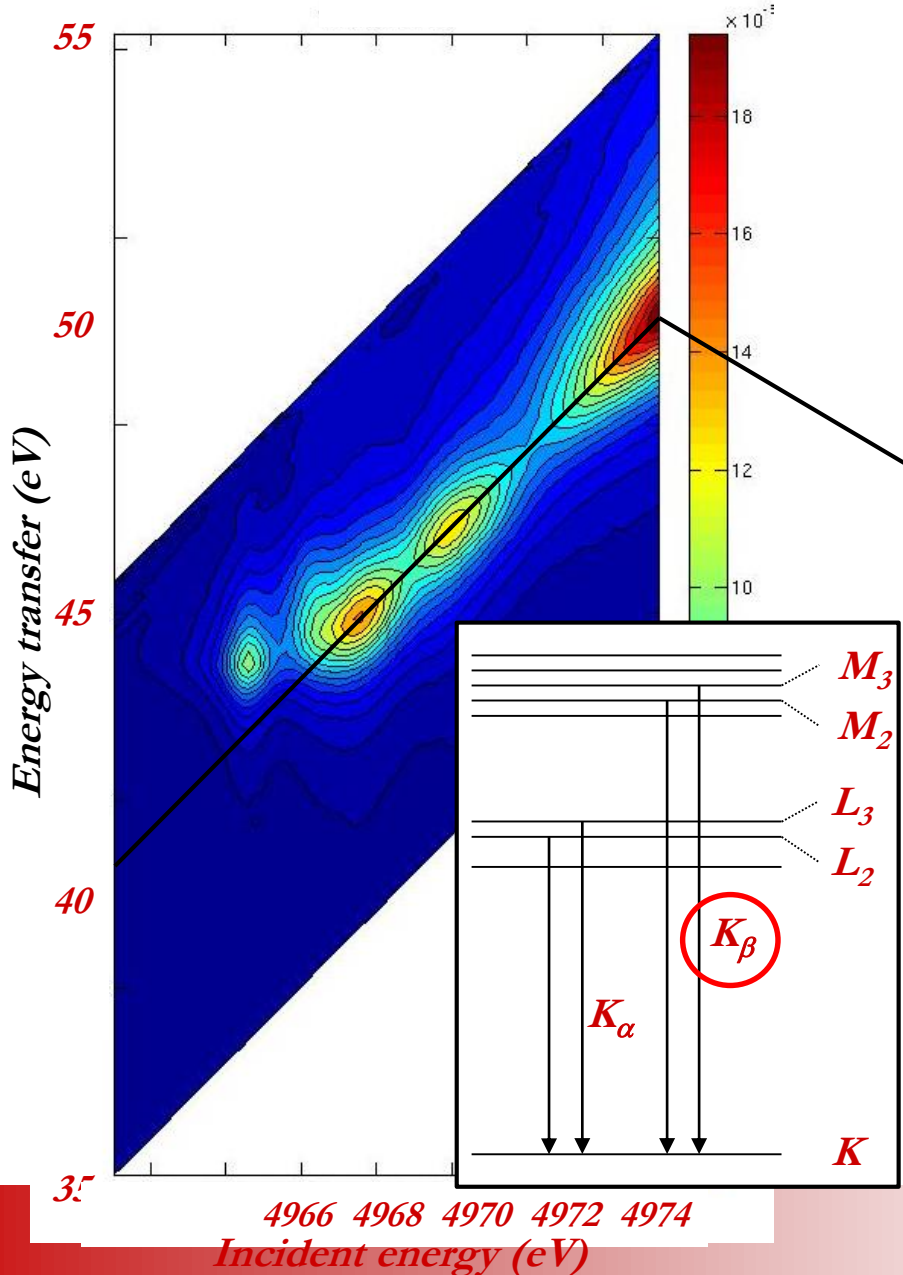
sensitize TiO<sub>2</sub> to visible light  
by coupling TiO<sub>2</sub> with  
metallic nanoparticles to  
exploit the surface plasmon  
resonance



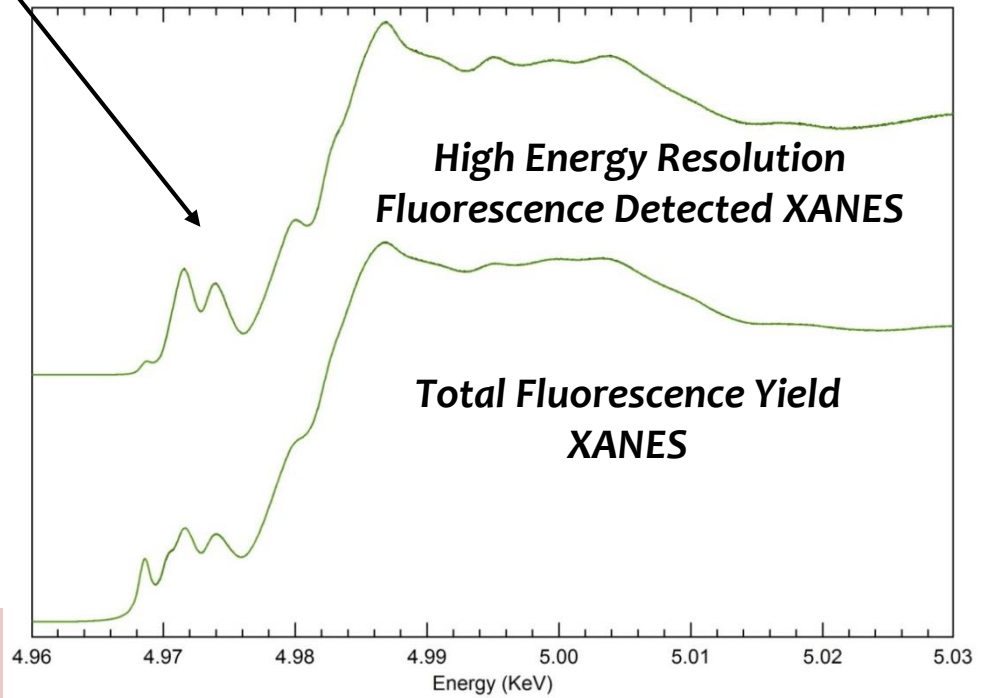
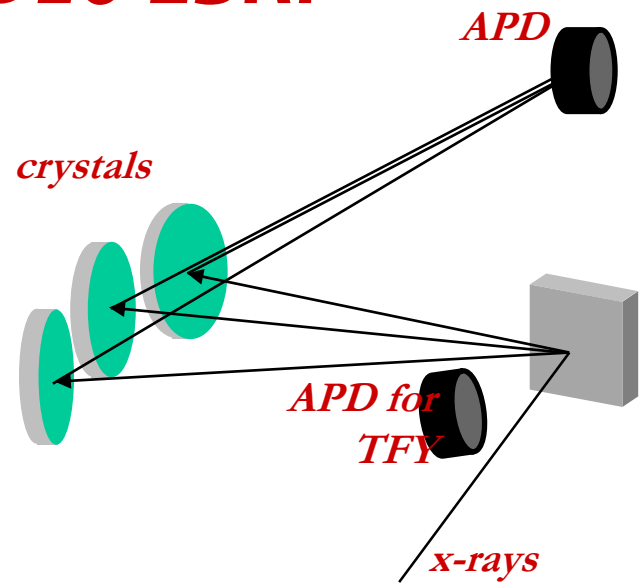
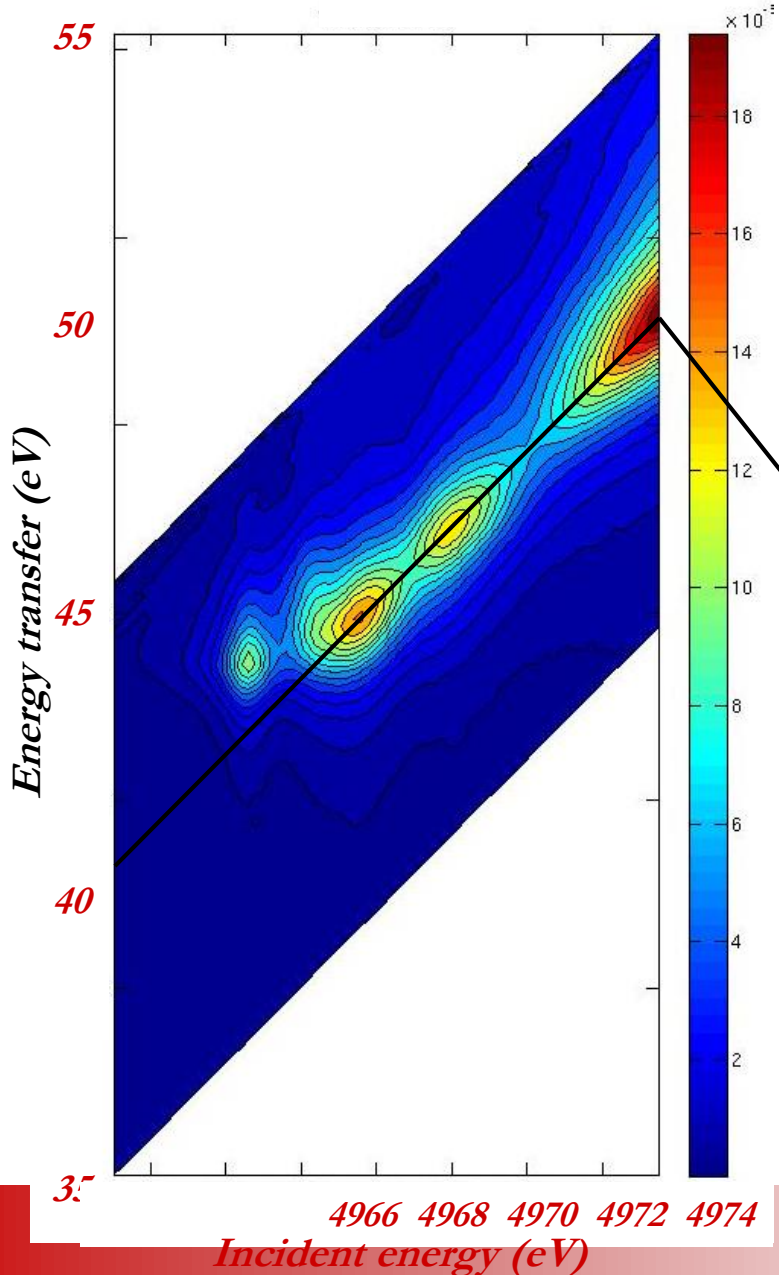
# RIXS @ ID26 ESRF



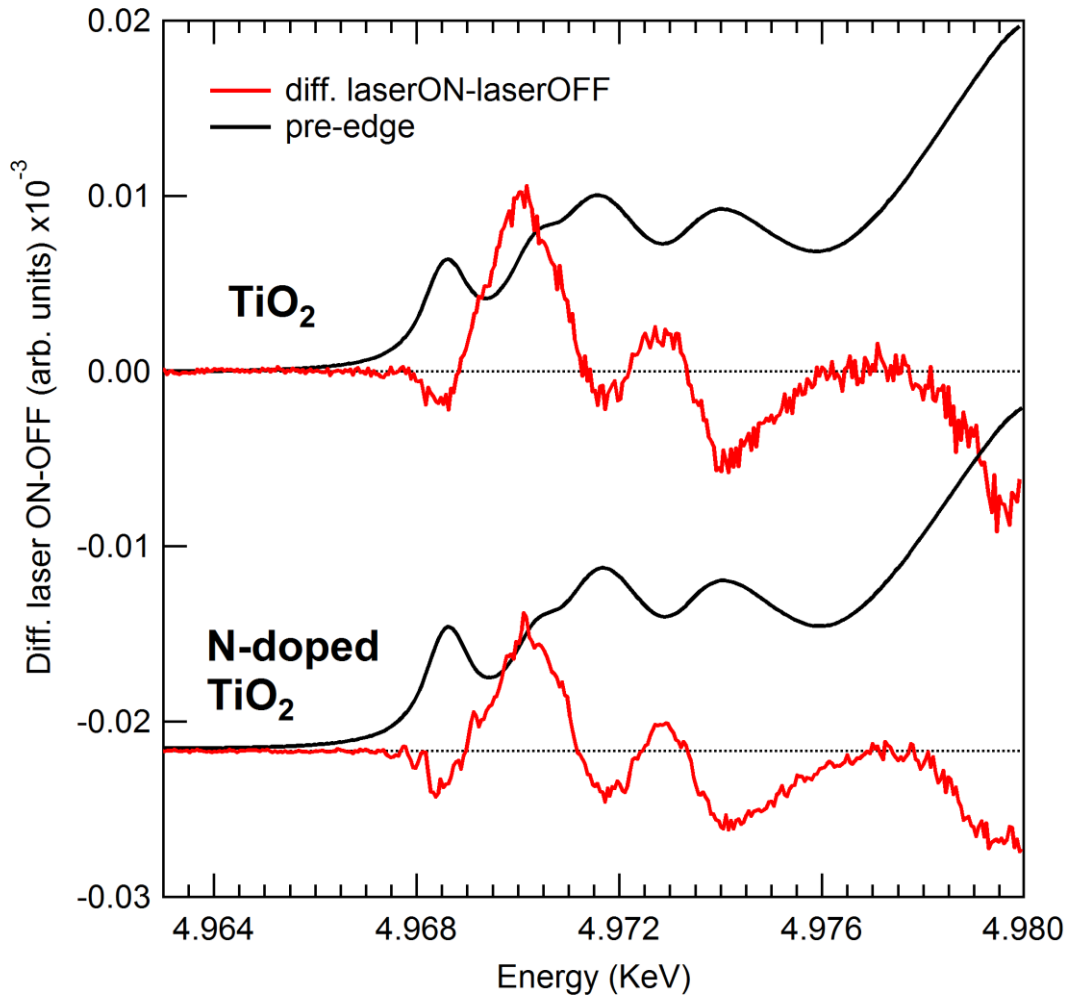
# RIXS @ ID26 ESRF



# RIXS @ ID26 ESRF



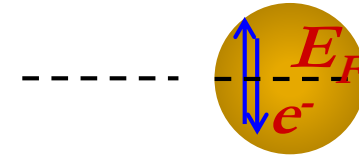
# Differential spectra



*TiO<sub>2</sub>*

*CB*

*Au NPs*



*VB*

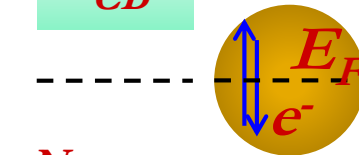
*CW laser, 532 nm,*

*200 mW, 2 mm diameter spot*

*N-TiO<sub>2</sub>*

*CB*

*Au NPs*



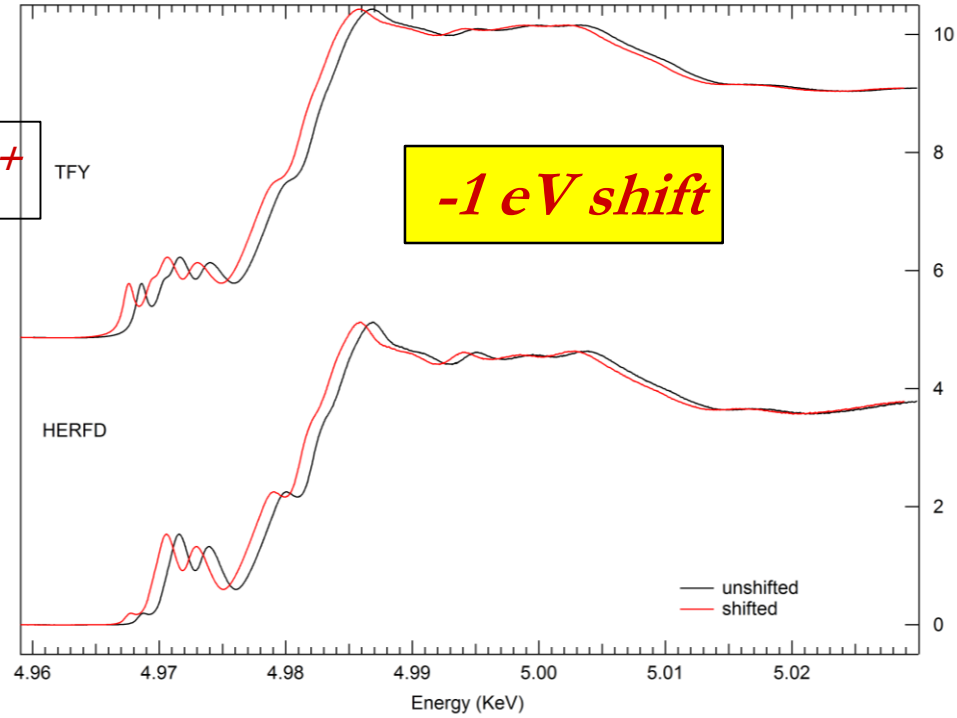
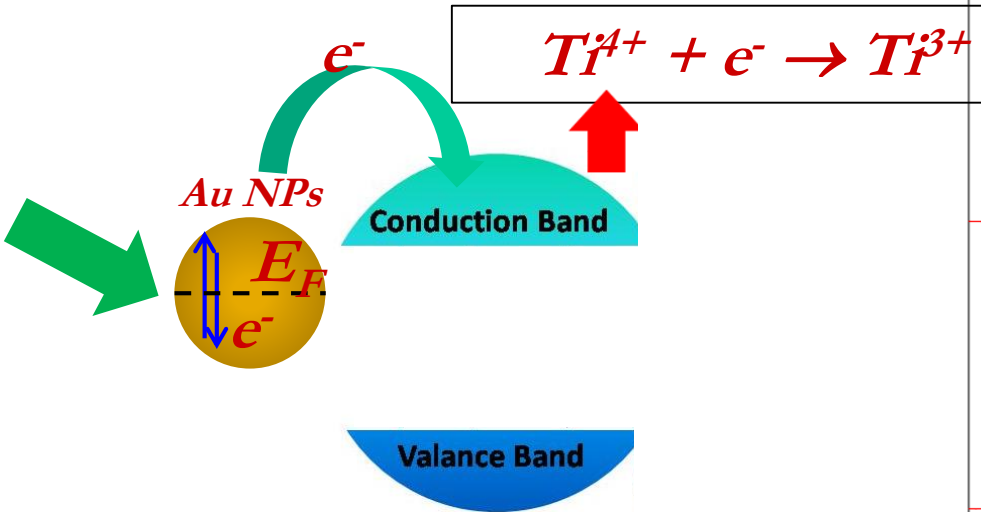
*N*

*VB*

- 1. Significant differences detected on samples with Au*
- 2. No / small spectral differences on samples without Au*

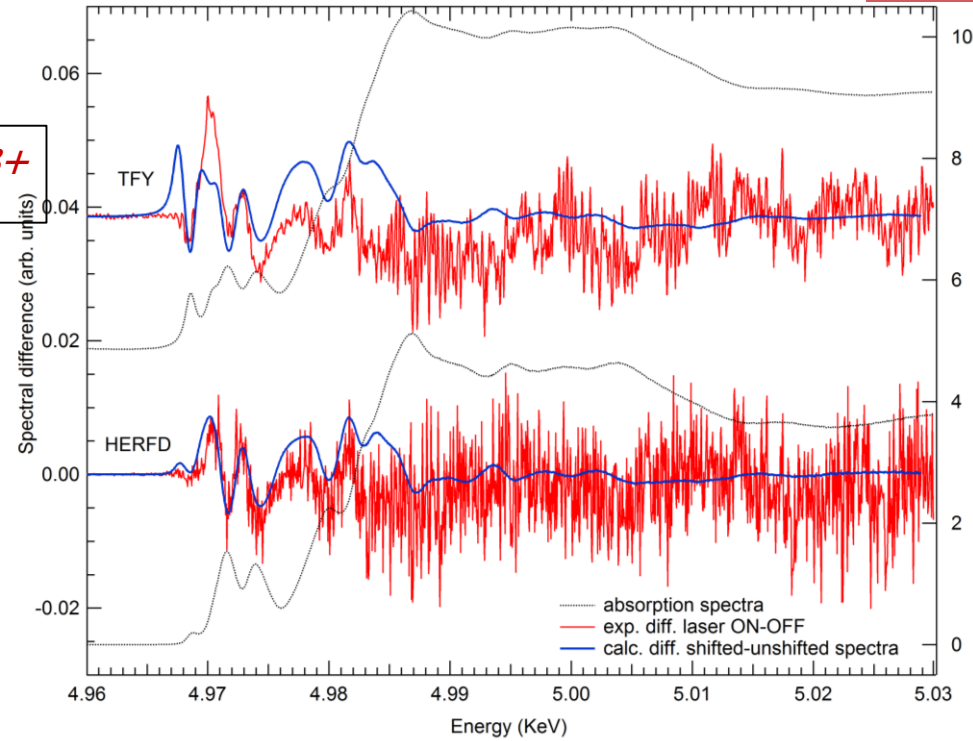
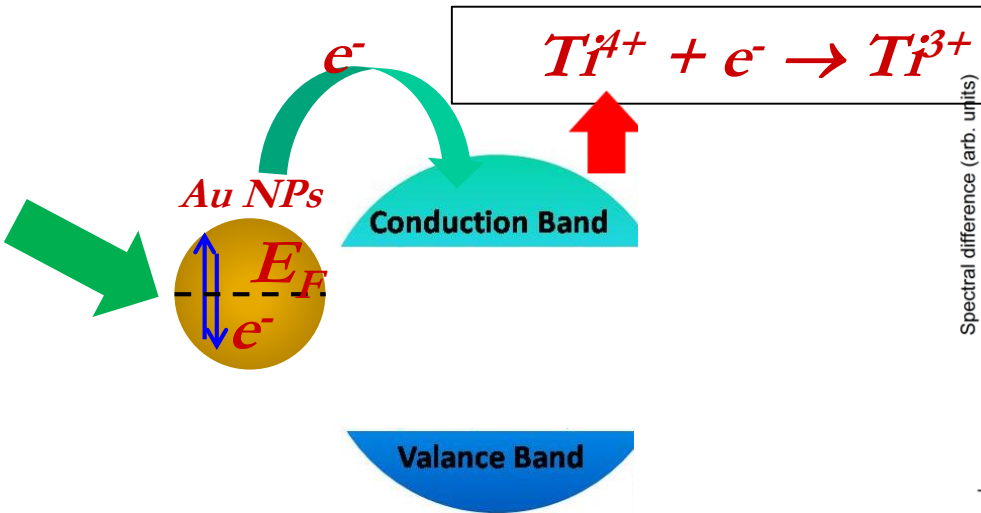


# Electron transfer from Au to TiO<sub>2</sub>





# Electron transfer from Au to TiO<sub>2</sub>

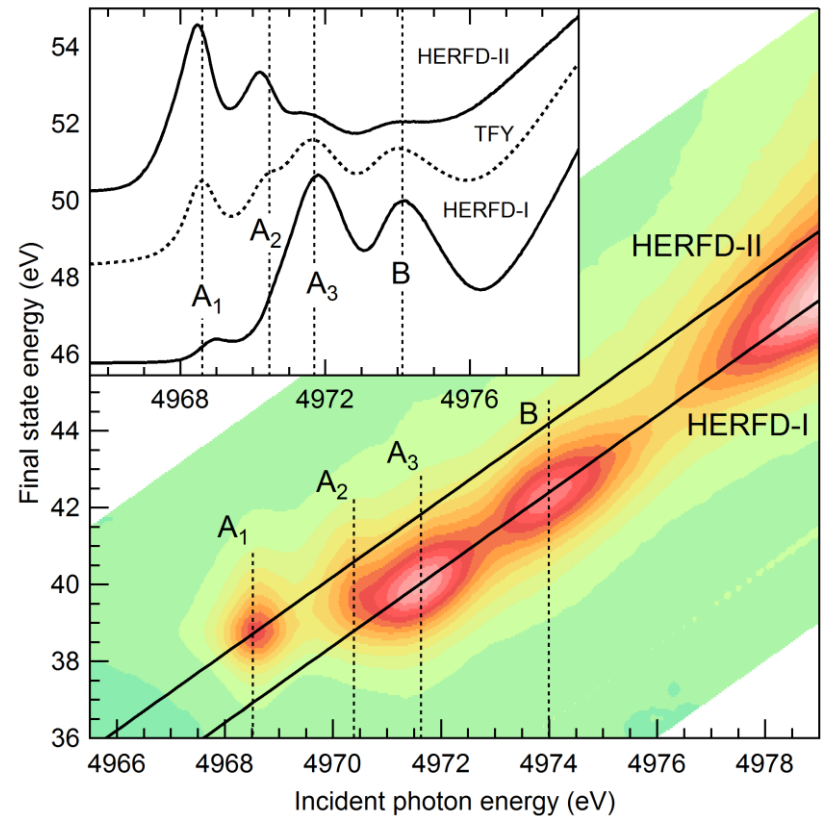


**Evidence for hot electron transfer to Ti sites**



## More in depth....

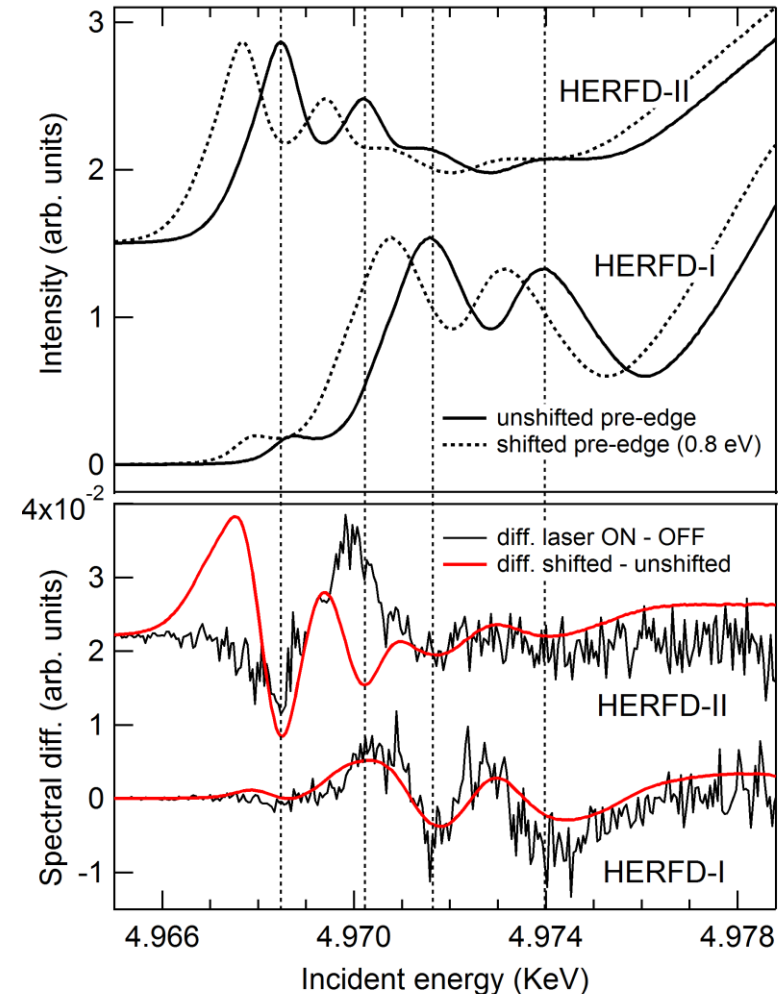
- Different «cuts» in the RIXS plane probe the effect of transitions to different final states
- HERFD-I
  - Mainly A<sub>3</sub> and B: delocalized final states
- HERFD-II
  - Mainly A<sub>1</sub> and A<sub>2</sub>: Localized final states





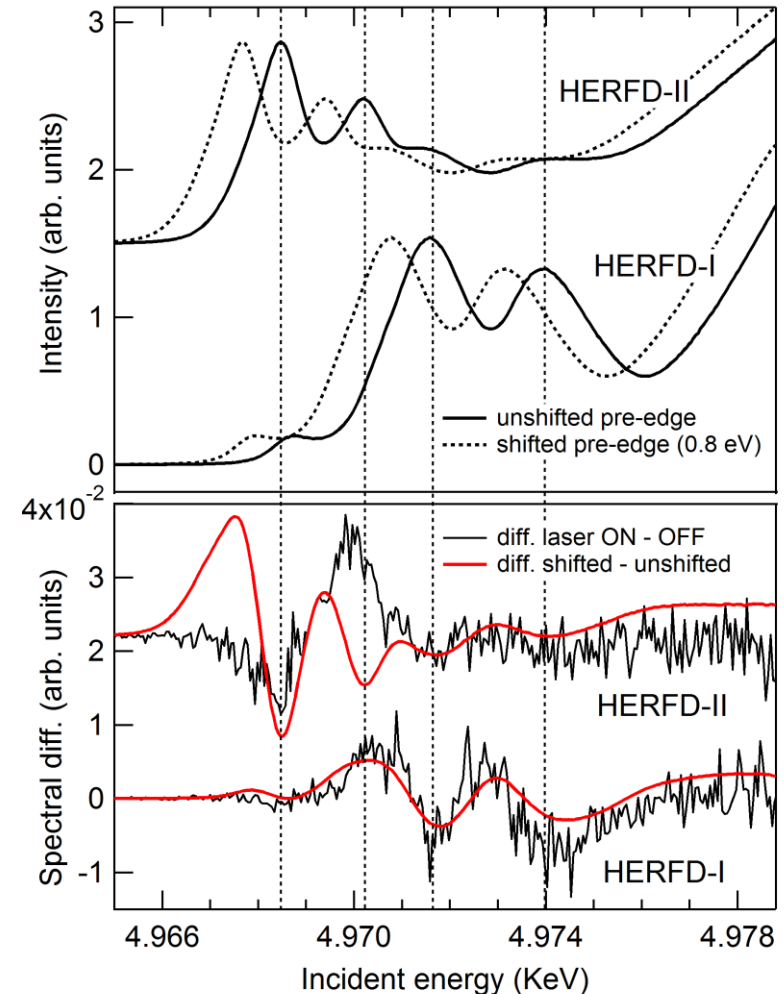
## More in depth...

- HERFD-I differential spectra in excellent agreement with «shifted – unshifted»: charge transfer to delocalized states, without change in structure



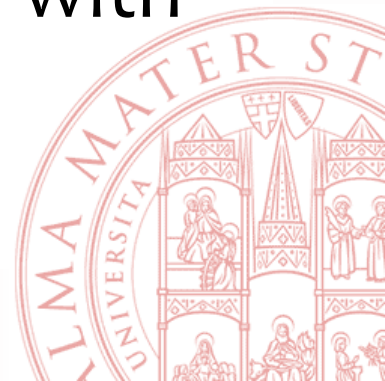
## More in depth...

- HERFD-II differential spectra in not so good agreement with «shifted – unshifted»: charge transfer to localized states involves structural rearrangement



# Conclusions on electron transfer in TiO<sub>2</sub> NP

- Electron transfer processes from Au NP to TiO<sub>2</sub> detected via differential HERFD XANES
- Different «cuts» in the RIXS plane can identify transitions to different final states
- Transitions to delocalized TiO<sub>2</sub> states corresponds to simple charge transfer with no structural rearrangement



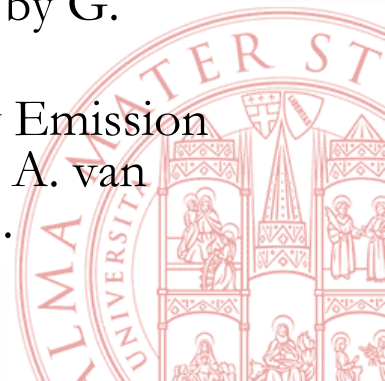
# Conclusions

- XAFS has been used to address important structural issues in materials/nano science
- It has specific advantages, especially
  - Atomic selectivity
  - Sensitivity to high dilutions & surfaces/interfaces
  - Equally applicable to ordered or disordered matter
  - EXAFS: high resolution for first few coordination shells
  - XANES:
    - valence/oxidation state
    - 3D structural sensitivity
  - $\mu\text{m}$  spot size now available and decreasing fast
  - Time resolution in the 10 -100 ps range available and with FELs decreasing to 10 fs
  - Combined use of XAFS, XES & RIXS



## Some useful review works by the author

- F. Boscherini, “XAFS in the study of semiconductor heterostructures and nanostructures” in *Characterization of Semiconductor Heterostructures and Nanostructures*, 2nd edition, edited by C. Lamberti and G. Agostini. ISBN 978-0-444-59551-5. DOI 10.1016/B978-0-444-59551-5.00007-8. Elsevier, 2013.
- F. Boscherini, “Dopants” in *X-ray Absorption Spectroscopy of Semiconductors*, edited by C.S. Schnor and M. Ridgway, Springer Series in Optical Sciences 190, 2015; ISBN-10: 3662443619 DOI 10.1007/978-3-662-44362-0\_4. Springer, 2015.
- F. Boscherini, “Applications of XAFS to nanostructures and materials science”, in *Synchrotron Radiation: Basics, Methods and Applications*, edited by F. Boscherini, C. Meneghini and S. Mobilio,. ISBN: 978-3-642-55314-1. DOI 10.1007/978-3-642-55315-8\_17. Springer, 2015
- G. Ciatto and F. Boscherini, “Structure of nitrogen – hydrogen complexes from x-ray and synchrotron radiation techniques” in *Hydrogenated dilute nitride semiconductors: theory, properties and applications*, edited by G. Ciatto, Pan Stanford Publishing, 2015. ISBN 978-981-4463-45-4
- F. Boscherini, “Semiconductors”, in *X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications*, First Edition. Edited by J. A. van Bokhoven and C. Lamberti. Published 2015 by John Wiley & Sons.



# Bologna



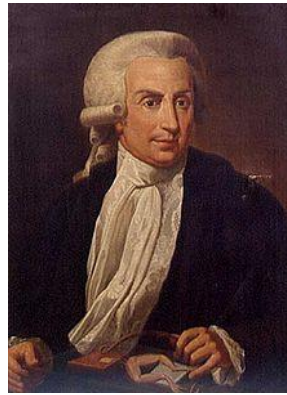


# What is Bologna famous for?

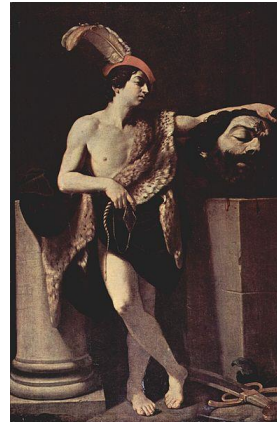
- University: Alma Mater Studiorum –1088 AD



Guglielmo Marconi  
(1874 – 1937): radio



Luigi Galvani  
(1737 – 1798)  
bioelectricity



Guido Reni  
(1575 – 1642)  
painter



Lamborghini cars



Mortadella



Tagliatelle al ragù



Ducati motorbikes

