Applications of XAFS to materials and nano-science

Federico Boscherini
Department of Physics
University of Bologna, Italy
federico.boscherini@unibo.it
www.df.unibo.it/fismat/rad-sinc

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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

- "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

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

**Measure:**
- Coordination number
- Interatomic distance
- Debye Waller factor
  - thermal vibration
  - static disorder

From *ab-initio* calculations or from reference compounds

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

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

\[ \sigma(\hbar \omega) = 4\pi^2 \alpha \hbar \omega \left| \langle i | \hat{E} \cdot \vec{r} | f \rangle \right|^2 \rho(E_f) \]

\[ \Delta \ell = \pm 1, \; \Delta m_\ell = 0 \]

(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 μm spot size
  – ns, ps and …fs time resolution
Role of XAFS in Materials Science

Objective: an understanding of physical properties of novel materials based on knowledge of their local structure
Today’s topics

• Dopants, defects
• Alloys
  – local distortions
  – ordering
• Phase transitions
• Thin films, interfaces
• 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$^3$
    • XANES $\sim 10^{17}$ at/cm$^3$
  – thin films (single layer) $\sim 10^{14}$ at/cm$^2$
Si in GaAs

- 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)
  - Si:GaAs(311)A
- at low concentration
- Increasing [Si]

- XANES exhibit reasonable evolution with concentration
- Difference in lineshape between SiGa and SiAs 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


• 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 Fe$^{3+}$

High Fe content
- Appearance of Fe-Fe ($R_2$) coming from a precipitated Fe$_x$N phase
Si,Fe:GaN data

- For the same Fe content Si co-doping prevents the formation of Fe$_3$N
- No evidence of the Fe-Fe bond at R$_2$
Si affects the charge state of Fe

• Si addition causes partial reduction of Fe\(^{3+}\) ions to Fe\(^{2+}\)
• Notable ability of XAFS to determine structure and valence

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• Higher growth temperature favours formation of Fe$_x$N and $\alpha$-Fe
Fe:GaN conclusions (2010 paper)

• Magnetization due to various components, including one due to ferromagnetic nanocrystals of $\varepsilon$-Fe$_3$N, $\alpha$-Fe, $\gamma'$-Fe$_4$N, $\gamma$-Fe$_2$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
µ-XRF & µ-XAFS: two defects

~ 20 nm silicide

~ 10 µm oxide
Best process: slow cool (5 °C s⁻¹) from 1200 °C
µm 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

![Graph showing fluorescence yield vs. Z]

ALOISA beamline @ ELETTRA

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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 ($\approx$ 0.05-0.1 eV per N atomic percent in InGaAsN)
- Huge and composition dependent optical bowing
Hydrogen – nitrogen complexes in dilute nitrides

- Hydrogenation leads to reversible changes
  - compressive strain
  - opening of $E_g$

$E_K \sim 100$ eV

\[ \text{GaAsN} \]
\[ \text{GaAs} \]
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

- 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!!


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
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
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$_{1-x}$In$_x$P alloys


- 26 years later
  - Much better data
  - More sophisticated analysis
- Same conclusion!
Disorder in \( \text{Sr}_2\text{FeMoO}_6 \) double perovskites


\[
S = 2x - 1
\]

long range order parameter \( S \)
determined from powder XRD

A = Fe sublattice

B = Mo sublattice
Double perovskites: disorder from a local perspective

$S = 0.51$

- Fe on Mo lattice
- Mo on Fe lattice

$S$ takes into account only for the number of Anti Site defects ($\text{Fe}_B$ or $\text{Mo}_A$), not their arrangement.

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XAFS spectra very similar for all $S$

- Despite great variation of $S$ the local structure appears very similar.
- $\xi = N(\text{Fe-Mo})/N(\text{Fe})$

Local order parameter determined from XAFS

For random distribution of $AS$ $\xi_{\text{random}} = (1+S^2)/2$

$fitted \ \xi$

$\xi_{\text{random}}$
Local versus long range order

\[ \xi \] always higher than \( \xi_{\text{random}} \)
A model for local disorder

Randomly distributed defect clusters having average diameter $D$

$D$ is refined in order to obtain $S$ and $\xi$ close to their experimental values

• Fe-Mo antisite defects appear as small ($D \sim 1.5$ nm) domains with antiphase Fe/Mo order.
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 PbTiO$_3$


- At $T_c = 763$ K 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 PbTiO$_3$

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

• Phase change optical discs used in DVD-RAMs are based on Ge$_2$Sb$_2$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


• Sub nanosecond time resolved XAFS with μm 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
  - $C_{6v}$:

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

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GaN

• Katsikini et. al., APL 69, 4206 (1996); JAP 83, 1440 (1998)
Pentacene on Au(110)

Bavdek et al., Langmuir 24, 767 (2008)

- Polarization dependent XANES at C K edge to determine the orientation of pentacene with respect to substrate
- Spectra recorded at grazing incidence for two different azimuthal orientations as a function of polar angle for two coverages
  - Low coverage: 3 × 6 unit cell
  - High coverage: 6 × 8 unit cell
Transitions to $\pi^*$ molecular orbitals give rise to strong peak

Pentacene on Au(110)

- Marked dependence of $\pi^*$ feature on orientation
- At high coverage persistence of peak when beam along (1 -1 0) direction
Figure 6. The (3 × 6) phase (upper panel) is formed exclusively by flat-laying molecules (one molecule per unit cell), which align into chains extending in the [110] direction. The (6 × 8) phase (lower panel) also contains flat chains as the (3 × 6) phase, but is separated by chains of tilted molecules, forming regular arrays of nanorails (three molecules per unit cell). The corresponding unit cells are indicated by rectangles (thick lines).
The Fe/NiO(001) interface


heating up to $T_N$ + cooling in H

exchange bias
The Fe/NiO(100) interface

\[ a_{\text{Fe}} = 2.866 \, \text{Å} \]
\[ d_{\text{Fe}} = 4.053 \, \text{Å} \]
\[ a_{\text{NiO}} = 4.176 \, \text{Å} \]

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

Fe K-edge
metallic Fe
2 ML θ=15°
2 ML θ=60°
FeO

μ(E)

photton energy (eV)

7080 7120 7160 7200

planar FeO phase

θ

E
Fe/NiO 2 ML thickness
Fe/NiO: atomic structure of interface

- BCT Fe
- buckled pseudomorphic FeO layer
- expanded FeO-NiO and FeO-Fe distance
XAFS and nanostructures

• XAFS is a local, short range, effect
  – Origin: core hole lifetime \( t_{\text{hole}} = 10^{-16} - 10^{-15} \text{ s} \) 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


• 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

"Coverage"
AFM of Ge dots

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

![AFM images](b)

Relaxed volume (%) vs. equivalent thickness (nm)

Ge/Si(001) (1 ML = 0.135 nm, WL = 3 ML)

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Quantum Dots: Ge edge XAFS

![Graph showing Ge edge XAFS data for Ge in Si, dots, and bulk Ge.](image)

- Ge:Si
- (111)
- 1 nm
- (001)
- 7.8 nm
- (001)
- 38 nm
- Ge

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

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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

• A bond length contraction has been found for weakly supported metallic clusters (Ni, Cu, Au……) for d < 100 Å

Apai et. al.,

Montano et. al.,

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

• A macroscopic surface tension interpretation ("liquid drop") can explain the bond length contraction

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

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

- Montano et. al.
Balerna et. al.,
Dynamic properties of Au clusters

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

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

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

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
  – µm spot size now available and decreasing fast
  – Time resolution in the 10 -100 ps range available and with FELs decreasing to 10 fs