Applications of XAFS to materials science and nanostructures

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Plan

• Why use XAFS as a structural tool in materials science & nanostructure research
• Examples of applications, using both
  - results which have “stood the test of time”
  - recent results
X-Ray Absorption Fine Structure

“XANES”: Absorber symmetry and valence/oxidation state
Electronic structure of unoccupied states
Medium range structure

“EXAFS”: Coordination numbers
Interatomic distances
Disorder of distances
EXAFS

- **Extended X-ray Absorption Fine Structure**
- Fit fine structure oscillations with

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

\[
k = \frac{\sqrt{2m(h\omega - E_B)}}{h}
\]

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

From *ab-initio* calculations or from reference compounds
XANES

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

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

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

(lin. pol. light)

\[
s \rightarrow p, \ p \rightarrow d \ (s)
\]

• “Molecular orbital” approach: 1 electron approximation, constant matrix element: probe site and symmetry projected density of states of final states

• “Multiple scattering” approach: structural interpretation through simulation
Characteristics of XAFS

- Atomic selectivity
  - most elements can be studied
- High resolution for first few coordination shells
  - signal from higher shells is damped
- Sensitivity to high dilutions
- Equally applicable to ordered or disordered matter

Today’s topics
- Dopants, defects
- Alloys, local distortions
- Thin films, interfaces
- Amorphous solids
- Phase transitions
- Vibrational dynamics
- Nanostructures
  - Ge quantum dots
  - Metallic clusters
  - Core-shell nanoparticles
Role of XAFS in Materials Science

Growth

MBE@TASC

Structure

Physical Properties


XAS
XAFS and dopants

• Only the structure around the photo-excited atom is probed
• Fluorescence detection greatly enhances sensitivity
• Present sensitivity limit
  - dopants in the bulk $\sim 10^{18}$ at/cm$^3$,
  - thin films (single layer) $\sim 10^{14}$ at/cm$^2$
Arsenic in a-Si:H

• As in a-Si expected to be 3-fold coordinated
• **But**: doping is observed
• Doping in c-Si due to 4-fold As
• Knights et al. observe increase in CN at 1% As concentration
  - evidence of active As
• Knights, Hayes, and Mikkelsen Jr.

![Graph showing As Coordination Number (CN) vs. Atomic % As]

**FIG. 2.** Silicon coordination of arsenic as a function of arsenic concentration in amorphous Si-H:As compounds. Points represent values determined from EXAFS; shaded bars represent range of values predicted from hydrogen content (see text).
Si/GaAs $\delta$-doped layers and superlattices

Boscherini, Ferretti, Bonanni, Orani, Rubini, Piccin, and Franciosi APL 81, 1639 (2002)

- $\delta$-doping: physical separation of dopants and charge carriers
  - Si-GaAs a technologically relevant case
- Number of charge carriers not proportional to number of dopants above a critical concentration
Si-GaAs: Open issue

• What is the structural origin of the defects which give rise to charge carrier saturation?

• Growth conditions optimized for Si/GaAs superlattice formation:
  - MBE, 540 °C, 4 nm/h, @TASC

• Si thickness: 0.02 ML - 4 ML; repetition optimized for XAS

• Fraction of electrically active Si atoms: $2 \times 10^{-4} - 6 \times 10^{-2}$
Si-GaAs: data

- Si K edge XAS @ LURE
- Fluorescence mode, bulk sensitivity
- Si - Si clustering apparent in raw data

![Graph showing Si-GaAs data with peaks at specific k values](image-url)
Si-GaAs: results

- Si – Si CN > 2 always
- Presence of Si clusters
- This is the origin of low concentration of charge carriers
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 for K and LIII edges.](Image)

**ALOISA beamline @ ELETTRA**
Dilute nitrides: $\text{GaAs}_{1-y}N_y$, $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}N_y$

Anomalous non-linear optical and electronic properties of III-V nitrides

- Red shift of the band gap by adding few % of nitrogen ($\approx 0.05-0.1\,\text{eV per N atomic percent in InGaAsN}$)
- Huge and composition dependent optical bowing
Hydrogen – nitrogen complexes in dilute nitrides

- Hydrogenation/deuteration leads to reversible changes
  - compressive strain
  - opening of band gap
- \([10^{18} \text{ ions/cm}^2, 100 \text{ eV}]\)
Hydrogen - nitrogen complexes in dilute nitrides

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

Some candidate low energy structures
N K edge experiment

- Full multiple scattering XANES simulations
- Good agreement for GaAsN
Hydrogen – nitrogen 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!!

![Graph showing absorption cross-section vs energy](image)
How many H atoms are there?

- Measurement of D concentration: in as-deuterated samples there are 3 D atoms per N!
  - Where is the third D atom?
  - What is its effect on lattice and gap?

Nuclear reaction analysis
Annealing studies

• 250 °C annealing:
  - 2 H/N
  - Compressive strain released
  - No effect on gap

• 328 °C annealing
  - 0 H/N
  - Strain back to tensile
  - Gap back to that of GaAsN
XANES: the optically active complex really is the $C_{2v}$ one
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
Bimodal distribution of bond lengths in InGaAs

- $\text{In}_x\text{Ga}_{1-x}\text{As}$: tuning of lattice parameter and band gap
- Does the local structure follow the average structure suggested by Vegard's law?
- NO! Bond lengths stay close to sum of covalent radii
XAS and amorphous solids

- Sensitivity only to very local coordination is useful to avoid overlap of RDF peaks
- In alloys, atomic selectivity is further help
XAFS vs. X-ray scattering

- Comparison between X-ray scattering and Si K-edge XAFS in a-Si$_{1-x}$C$_x$:H alloys

F. Boscherini,
Amorphous semiconductors: ordering

- Different possibilities for relative arrangement for $A_{1-x}B_x$ alloy (A,B equal $CN_{\text{tot}} = 4$):
  - Random: $CN_{A-B} = 4x$, $CN_{B-A} = 4(1-x)$
  - Clustering: $CN_{A-B} = 0$, $CN_{A-A} = CN_{B-B} = 4$
  - Chemical order: for $x < 0.5$, $CN_{B-A} = 4$, $CN_{B-B} = 0$

- Compare composition (from other method) with $CN_{i-j}$ (from XAFS)
Amorphous semic.: ordering

- Clustering never observed
- Degree of chemical ordering depends on enthalpy of heteroatomic bond, e.g.:
  - $a-Si_{1-x}C_x:H$, ordered
  - $a-Ge_{1-x}Sn_x$, random

Pascarelli, et al
Phys. Rev. B 45, 1650 (1992);
Using SR linear polarization to study thin films

\[ \sigma(\theta) \propto \cos^2 \theta \]
Hexagonal and cubic GaN
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
  - $C_{6v}$: $\sigma^{tot}(E,\theta) = \sigma^{iso}(E) + (3\cos^2\theta - 1)\sigma^1(E)$
GaN

CUBIC

HEXAGONAL

- Katsikini et. al., APL 69, 4206 (1996); JAP 83, 1440 (1998)
The Fe/NiO(001) interface

P. Luches, V. Bellini, S. Colonna, L. Di Giustino, F. Manghi, S. Valeri, and F. Boscherini,
FM/AFM systems

- Heating up to $T_N$
- Cooling in H

Exchange bias
The Fe/NiO(100) interface

NiO
AF \( T_N = 520 \) K

Fe
FM \( T_C = 1040 \) K

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

\( m = -2.8\% \)
Fe K-edge XAFS experiment
Fe local atomic environment

GILDA beamline @ ESRF

Polarization dependence of XAFS cross section

out-of-plane local environment

in-plane local environment
samples

ex-situ growth @ S3 laboratories

![Diagram showing layers: Ag(001), 10 ML NiO, Fe, 10 nm Au]
XANES

- deviation from metallic character
- shift of the white line towards FeO
XANES: polarization dependence

Fe K-edge

metallic Fe

2 ML θ=15°

2 ML θ=60°

FeO

photon energy (eV)

7080  7120  7160  7200

planar FeO phase

SILS School on SR, Duino (Trieste), Italy - September 2007
EXAFS

$\chi(k)$ vs. $k$ (Å$^{-1}$)

- Metallic Fe
- 10 ML
- 2 ML $\theta = 15^\circ$
- 2 ML $\theta = 75^\circ$
- FeO
EXAFS-quantitative analysis

<table>
<thead>
<tr>
<th>N</th>
<th>BCC Fe, R (Å)</th>
<th>BCT Fe, R (Å)</th>
<th>fit results, R (Å)</th>
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<tr>
<td>1st shell</td>
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<td>2.50</td>
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</tr>
<tr>
<td>8th shell</td>
<td>8</td>
<td>4.96</td>
<td>5.01</td>
</tr>
</tbody>
</table>

the epitaxial strain is partially released at 10 ML
2 ML sample

Mag. Fou. Trans. \[ k^3 \chi(k) \]

\[ R (\text{Å}) \]

2 ML $\theta = 15^\circ$

2 ML $\theta = 75^\circ$
The model

- buckled pseudomorphic FeO layer
- expanded FeO-NiO and FeO-Fe distance
XAS and highly correlated oxides

• Manganites, HT$_C$’s, perovskites
• High resolution in the determination of local structure
• Local distortions couple to physical properties
• Local deviations from 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 $T_c$
- The ferroelectric transition has a large order - disorder character: the orientation of local distortions changes at $T_c$
La$_{1-x}$Ca$_x$MnO$_3$ Manganites

- For $0.2 < x < 0.5$
  - Metallic ferromagnet $T < T_c$
  - Insulating paramagnet $T > T_c$
- Colossal Magneto Resistance
- Double exchange model: hopping conductivity between adjacent Mn ions is enhanced if Mn ions are spin aligned
La$_{1-x}$Ca$_x$MnO$_3$ Manganites

- Mn$^{3+}$O$_6$ octahedron in LaMnO$_3$ is Jahn-Teller distorted
  - Mn$^{4+}$ is not
- Conductivity in the presence of polarons: an electron + a lattice distortion
- Range of polaronic distortion?
La$_{1-x}$Ca$_x$MnO$_3$ Manganites

- Presence of localized structural distortions at MI transition

Booth, Bridges, Kwei, Lawrence, Cornelius and Neumeier
La$_{1-x}$Ca$_x$MnO$_3$ Manganites

Meneghini, Castellano, Mobilio, Kumar, Ray and Sarma,

- Magnetic field reduces local distortions
Thermal vibrations in crystals

- XAFS detects relative atomic motion
  - Useful to study of thermal vibrations
- In the harmonic approximation the effect of thermal motion on $\chi(k)$ is via

$$\sigma_{0j}^2 = \left\langle \left[ \hat{R}_{0j} \cdot (\vec{u}_o - \vec{u}_j) \right]^2 \right\rangle$$
Correlated atomic motion in AgI

Anharmonic vibrations in AgI

• High maximum wave-number leads to great sensitivity to details of radial distribution function
• Detect asymmetries in RDF connected to deviations from harmonic approximation to interatomic potential

Vibrations parallel & perpendicular to interatomic vector in Ge

- Distance measured in EXAFS is not equal to distance between average position of atoms:
  \[ C_1^* = R + \frac{\langle \Delta u_{\perp}^2 \rangle}{2R} \]

- Perpendicular motion does not contribute to \( \sigma^2 \), so that
  \[ \sigma^2 = \langle \Delta u_{\parallel}^2 \rangle \]


\[ \frac{\text{Å}^2}{0} \quad \frac{0.02}{0.04} \quad \frac{0.04}{600 \text{ K}} \]

\[ \langle u_{\perp}^2 \rangle \quad \langle u_{\parallel}^2 \rangle \]
Nanostructures
**XAS to study nanostructures**

- **XAS** is a local, short range, effect
  - Origin: core hole lifetime \((\tau_{\text{hole}} = 10^{-16} - 10^{-15} \text{ s})\) and electron mean free path \((5 - 10 \text{ Å})\).
  - EXAFS signal is damped by \(e^{-r/\lambda}\) where
    \[
    \frac{1}{\lambda} = \frac{1}{\lambda_{\text{mfp}}} + \left(\frac{m_e}{\hbar k}\right)\frac{1}{\tau_{\text{hole}}}
    \]
- 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 upon reduction of dimensions and/or dimensionality
Local nature of XAS
Semiconductor quantum dots

• The prototypical nanoscience system
• Self organized hetero-epitaxial growth can lead to quantum dots with narrow size distribution
• Due to small size the quantum dots exhibit new physical properties
Ge Quantum Dots


- Need for understanding of local bonding
- Preparation:
  - Ge/Si(001) by CVD @ 600 °C, Univ. Roma Tre
    - Ex-situ AFM used to characterize degree of relaxation
  - Ge/Si(111) by MBE @450 - 550 °C, Univ. Roma II
    In-situ STM/AFM
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"
Q. Dots: AFM

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

![Graph showing relaxed volume vs. equivalent thickness](image)

(1 ML = 0.135 nm, WL = 3 ML)
Q. Dots: Ge edge data

- Assuming random alloy average composition is Ge\(_{0.70}\)Si\(_{0.30}\)
Conventional SK growth
SK growth with interdiffusion
Physical origin of intermixing

- Keating potential

\[ V(\{R_{ij}\}, \{\theta_{ijk}\}) = \frac{\alpha}{2} \sum_{ij} (R_{ij} - R_{ij}^0)^2 + \frac{\beta}{8} \sum_{ijk} (\cos \theta_{ijk} + \frac{1}{3})^2 \]

- intermixing reduces the number of “stretched” bonds and hence the strain energy
- thermodynamical and kinetic effects
- strain enhanced diffusion
- intermixing is reproduced by MC simulations which include “atomic identity flips” (P. Kelires, 2001)

- Intermixing must be considered in realistic models of Stranski-Krastanov growth
Metallic nanostructures
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
  \[ \Delta R = -\frac{2}{3} f \frac{\kappa}{r} \]

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

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

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

- $\sigma^2$:
  - depends on thermal motion
  - can have structural contribution

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

X-ray absorption spectroscopy studies of Fe/Fe-oxide granular nanostructures
Granular Fe/Fe-oxide nanostructures

- Changes in structure and physical properties induced by reduced dimensions
- Effect of disorder on magnetic properties
- Comparison with 2D systems (surfaces)
- Applications
Sample deposition: IGC

Inert Gas Condensation

- Evaporation in He (133 Pa)
- \( \text{O}_2 \) passivation
- Cold compacted at 1.5 GPa

*In situ* compacting
Sample morphology

- Core: $\alpha$-Fe nanoparticles
  $<d> = 5 - 21$ nm
- Oxide matrix: ultra-fine grains (2-3 nm) with spinel structure
Sample morphology & structure

Inverse spinel structure
- Magnetite (Fe₃O₄)
  \( T_d: \text{Fe}^{3+}; \text{O}_h: \text{Fe}^{3+} \, \& \, \text{Fe}^{2+} \)
- Maghemite (\( \gamma \)-Fe₂O₃)
  \( \text{Fe}^{3+} \) in both \( T_d \) and \( O_h \) sites

BCC
\( \alpha \)-Fe
Matrix: magnetite or maghemite?

- Two oxides have significantly different properties (e.g. conductivity)
- XRD not sensitive (broad peaks)
- Use XAFS
  - Element and local sensitivity
  - Unaffected by morphology changes
O K-edge XANES

- O edge: information only on the matrix
- Clear variation of edge position with core size
  - 7 nm ~ maghemite (94%)
  - 21 nm ~ magnetite (83%)
Fe and O edge EXAFS

- **Fe edge: core & matrix**
  - Core
    - bcc Fe, $\sigma^2$ decreases with $<d>$
  - Matrix
    - 7nm similar to maghemite

- **O edge: matrix**
  - High values of $\sigma^2$ ($\sim 35 \times 10^{-3}$ Å$^2$)
  - magnetite $\rightarrow$ maghemite transition with decreasing $<d>$
Size-dependent magnetite to maghemite transformation

- \(\alpha\)-Fe core exposed to \(O_2\) → formation of \(Fe_3O_4\)
- Further exposure to \(O_2\) → formation of \(\gamma\)-\(Fe_2O_3\) on surface of grains
- Enhanced transformation due to higher disorder, grain boundaries in smaller particles
Thanks

- Funding: MIUR, INFM, Uni Bo, ESRF, EU
High resolution XAS @ N edge

- Vibrationally split $1s \rightarrow \pi^*$ transition for N implanted in compound semiconductors
$Y_2O_3$ thin films on Si(001)

M. Malvestuto, R. Carboni, and F. Boscherini F. D’Acapito S. Spiga, M. Fanciulli, A. Dimoulas, G. Vellianitis, and G. Mavrou, 
High-κ oxides

schematic representation of FET

direct tunneling across gate dielectric presents serious limitation for continued use of thermally-grown SiO₂

From: G. Lucovsky
XAFS and high-$\kappa$’s

• Local atomic and CB electronic structure of high-k films:
  - Similarity to bulk oxides?
  - Disorder, interdiffusion?

• Interfaces with Si:
  - nature of interface phases
The bixbyite structure

- Two inequivalent cation sites, both octahedral
  - site I: all O at same distance
  - site II: 3 different distances
$Y_2O_3/Si(001)$: growth


- Dimoulas group, Athens
- MBE from ceramic target at 450 °C
- 5 samples: 2, 4 and 20 nm
- Some annealed 30 min. 500 °C
$Y_2O_3/Si(001)$: Y K edge XANES

- Probes p-type CB DOS projected on Y
- Overall similarity to bulk spectrum
  - 2 nm samples: broader spectrum
$\text{Y}_2\text{O}_3/\text{Si}(001)$: Y XANES simulation

- Simulation within "full multiple scattering" theory (FEFF) for 20 nm sample
  - 150 atom cluster
  - self consistency up to 4 Å
- Good correspondence with 5p PDOS of Y in bixbyite cluster
- Similar PDOS for the two inequivalent sites
$Y_2O_3/Si(001)$: $Y$ EXAFS

- 4 and 20 nm samples
  - Sharper 2$^{nd}$ and 3$^{rd}$ shell peaks with increasing thickness and with annealing
- 2 nm samples
  - 1$^{st}$ shell peak shifts to lower energy
  - a combination of $Y$ - $O$ and $Y$ - $Si$ bonds
$Y_2O_3/Si(001)$: O XANES

- 4 and 20 nm samples: similar to bulk yttria
- 2 nm samples: contribution from $SiO_x$
- Good agreement with simulations
$Y_2O_3/Si(001)$: O EXAFS

- 20 nm sample
- Good agreement with bulk structure
  - 4 Y atoms, 2.2 – 2.3 Å
  - 10 O atoms, 2.9 – 3.7 Å
Y$_2$O$_3$/Si(001) conclusions: films

- For thickness $\geq$ 4 nm atomic and electronic structure correspond to bixbyite Y$_2$O$_3$
- Decreasing static disorder with increasing thickness and/or annealing (less defects seen in electron microscopy)
$Y_2O_3/\text{Si(001)}$ conclusions: interface

- Presence of $\text{SiO}_x$
- $Y - \text{Si}$ bonds with $R = 2.09 \text{ Å}$ (2.07 Å in $\text{YSi}_2$)
- At 610 °C deposition temperature $\text{YSi}_2$ seen from XRD
- $Y - \text{Si}$ bonds are “precursor bonds”
“Fingerprint approach” to XANES: Fe oxides

- Change of XANES lineshape with oxidation state, local symmetry
Evolution of XAFS

• XAFS has greatly benefited from
  - Improvements in SR sources
    • high brilliance, polarization, extended energy range, stability, reliability
  - full theoretical understanding and reliable analysis programs

\[
\sigma = \frac{\sigma_0}{3 \sin^2 \delta_0} \sum_m \text{Im} \{ T(1 - TG)^{-1} \}_{1m,1m}^{0,0}
\]

• XAFS a reliable tool, but still interesting as a physical effect