Applications of XAFS to materials and nano – science

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Plan

• Examples of applications, using both
  – results which have “stood the test of time”
  – recent results
Today’s topics

• Dopants, defects
• Alloys
• Phase transitions
• Thin films, interfaces
• Nanostructures
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 \( \sim 10^{18} \text{ at/cm}^3 \)
    • XANES \( \sim 10^{17} \text{ at/cm}^3 \)
  – thin films (single layer) \( \sim 10^{14} \text{ at/cm}^2 \)
Si in GaAs


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

- Samples studied
  - Si:GaAs(001)
    - at low concentration $\text{Si}_{\text{Ga}}$
  - Si:GaAs(311)A
    - at low concentration $\text{Si}_{\text{As}}$
- XANES exhibit reasonable evolution with concentration
- Difference in lineshape between $\text{Si}_{\text{Ga}}$ and $\text{Si}_{\text{As}}$ 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
Fe:GaN conclusions

• 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: \((\text{Ga,Fe})\text{N} \) nanocomposites, not real doping
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 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 $E_g$

$E_K \approx 100 \text{ eV}$
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!!


Combined XAFS and XES
Amidani et al., Phys. Rev. B 89, 085301 (2014), talk MS 103.O05

XAS

XES

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$_{0.5}$Ga$_{0.5}$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
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

![Graph showing the intensity of the white line for different phases](image)

- Crystallized band
- As-deposited amorphous
- Amorphous marks
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
Transitions to $\pi^*$ molecular orbitals give rise to strong peak

Use of linear dichroism

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

- Typical application: determination of the orientation of molecules on single crystal surfaces
- \( \text{N}_2 \) on Ni(110)
- Molecules are "vertical"

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
• Need for understanding of local bonding
• Analysis of aspect ratio provides measurement of relative amount of relaxed islands

Ge/Si(001)
(1 ML = 0.135 nm, WL = 3 ML)
Quantum Dots: Ge edge XAFS

- Assuming random alloy average composition is Ge$_{0.70}$Si$_{0.30}$
Conventional SK growth
SK growth with interdiffusion
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
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

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

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

From *ab-initio* calculations or from reference compounds

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

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

$$\sigma(\hbar\omega) = 4\pi^2 \alpha \hbar\omega \left| \langle i | \hat{\mathbf{e}} \cdot \mathbf{r} | f \rangle \right|^2 \rho(E_f)$$

$$\Delta \ell = \pm 1, \quad \Delta m_\ell = 0$$

(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