Resonant X-ray Diffraction (REXD)

where Diffraction meets Spectroscopy

Yezhou Shi

Department of Materials Science and Engineering, Stanford University

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outline

1. motivation: why do we/you care?

2. technique: how does this work?

3. design experiments: what to consider?
site-specific chemical information important to understanding properties

- materials property depends directly on site occupancies
- complex oxides: multiple sites, multiple cations & anions

perovskite: $\text{ABO}_3$

spinel: $\text{A}_2\text{BO}_4$
requirements of an ideal technique

- **elemental/chemical selectivity**
  - different elements and/or oxidation states

- **site selectivity**:
  - site A vs. site B
  - substitution vs. interstitial
Large-range diffraction + Rietveld refinement

- relatively *fast* to perform and can refine both elemental and site information

- refine a variety of structural parameters (occupancy, strain, displacement, *etc* …)

- limitations
  - have to deal with all phases/structures in the sample
  - elements with similar \( z \) → chemical selectivity lost
  - Alternative: neutron scattering → best with large mass
outline

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principles of resonant X-ray diffraction

\[ I(E) \propto |F_{hkl}|^2 \]

\[ F_{hkl} = \sum_{i} x_i f_i(Q,E) e^{2\pi i (hx+ky+lz)} \]

Bragg \((h,k,l)\) site selectivity

Element selectivity

\[ f = f_o(\bar{Q}) + f_1(E) + if_2(E) \]
model fitting to extract site occupancies

\[ I(E) \propto |F_{hkl}|^2 \quad \rightarrow \quad F_{hkl} = \sum_{i} x_i f_i(Q, E) \cdot e^{2\pi i (hx + ky + lz)} \]

**real part: \( f_1 \)**

**imag. Part: \( f_2 \)**

Combine the best of two worlds: simultaneously chemical and structural info.
data collection: diffraction scans at various incident X-ray energies

incident x-ray (tunable energy)

sample

diffracted x-ray

Co K edge

Energy (eV)

Intensity (a.u.)

phi (deg)

achieving the grand challenge of materials and nanostructures by design
The other half of the story: experimentally determined $f_1$ & $f_2$

measured spectra near the abs. edge

Absorption coefficients

Stitched to theoretical values

imaginary: $f_2$

real part: $f_1$

Achieving the grand challenge of materials and nanostructures by design
outline

1. motivation: why do we/you care?

2. technique: how does this work?

3. design considerations
designing your experiments:
practical considerations

○ is resonant diffraction the tool?

• Sr vs Ti in STO
• Fe vs Ti in Fe doped STO
• 0.1% doped Fe?
designing your experiments: practical considerations (cont’d)

- ideally, single phase with known composition
- can you identify one or a set of Bragg peaks to extract site-specific information?
- trade off between absorption and diffracted intensity
  - textured thin films: easiest to work with
  - powder/nanocrystals: fine
  - polycrystalline film: diffraction too weak

<table>
<thead>
<tr>
<th>Material/Mass</th>
<th>More</th>
<th>Less</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>More (bad)</td>
<td>Less (good)</td>
</tr>
<tr>
<td>Diffraction Singal</td>
<td>Strong (good)</td>
<td>Weak (bad)</td>
</tr>
</tbody>
</table>
designing your experiments: drawbacks and limitations

- insensitive to low Z elements or O vacancy (generally true to hard X-ray based techniques)

- relatively long data acquisition time (30 to 50 energies per element → 6 to 15 hrs) – plan your experiments carefully

- model fitting is required to understand the data (no commercial software to do this)
designing your experiments: resources at SSRL

<table>
<thead>
<tr>
<th>beamline</th>
<th># motors</th>
<th>sample form</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Two-circle</td>
<td>Powder / nanocrystals</td>
<td>Less crowded</td>
</tr>
<tr>
<td>10-2</td>
<td>Four-circle</td>
<td>Thin film/single crystal</td>
<td>Sufficient for most purposes</td>
</tr>
<tr>
<td>7-2</td>
<td>Six-circle</td>
<td>Thin film/single crystal</td>
<td>Strange geometries available</td>
</tr>
</tbody>
</table>

- *in-situ* experiments possible (elevated T, gas environments…)
- “sweet spot” elements: **Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge**
  - $K$ edges readily accessible with large photon flux
- who to talk to?
  - Kevin Stone, Badri Shyam and me
BONUS (Example): Mn occupancies in $\text{Cr}_2\text{MnO}_4$ spinels
spinel structure and anti-site defects

- two structurally inequivalent sites: tetrahedral vs. octahedral
- intrinsic anti-site defects created by cross-substitution

\[
(A^{3+})_{2}^{Oh} [B^{2+}]_{2}^{Td} O_{4}
\]

\[
(A_{1-x}B_{x})_{2}^{Oh} [A_{y}B_{1-y}]_{2}^{Td} O_{4}
\]

- \( B^{2+}_{Oh} \) acceptor states
- \( A^{3+}_{Td} \) donor states

(422) peak

(222) peak

Achieving the grand challenge of materials and nanostructures by design
spinel oxide thin film fabrication

• pulsed laser deposition of $\text{Cr}_2\text{MnO}_4$ on top of SrTiO$_3$ single crystal substrate

• two different compositions from two PLD targets

• XRD confirm the film is biaxially textured

$\text{Cr}_2\text{MnO}_4$ (a = 8.4 Å)
SrTiO$_3$ substrate (a = 3.9 Å)
Cr$_2$MnO$_4$ spinel: spectroscopy offers a qualitative yet incomplete picture

$$(Mn_{1-x}Cr_x)^{Oh}_2[Mn_yCr_{1-y}]^{Td}_4$$

Cr edge: Cr (III) only

Mn edge: (II) + (III)

site-dependent chemical shifts near Mn edge

- chemical shift related to Mn oxidation states
- a larger shift is observed for Mn$_{Oh}$ than the Mn$_{Td}$ in both samples

Cr$_2$MnO$_4$

- theoretical edge: 6539 eV
- Td site dip: 6546 eV
- Oh site dip: 6549 eV

Cr$_{1.5}$Mn$_{1.5}$O$_4$

- Td site dip: 6546 eV
- Oh site dip: 6549 eV
fitted site occupancies for \( \text{Cr}_2\text{MnO}_4 \)

• how do we know Mn are indeed (II) on \( Td \) sites and (III) on \( Oh \) sites?
  → compare dip position and fine features

• \( Td \) site data (422 reflections) are very similar to the simulated REXD of \( \text{Fe}_2\text{MnO}_4 \) with Mn(II)

• \( Oh \) site data (222 reflections) are very similar to the simulated REXD of \( \text{Mn}_2\text{O}_3 \) with Mn(III)
fitted site occupancies for Cr$_2$MnO$_4$

- compare Mn edge data to references: Td site is Mn(II) whereas Oh site is Mn(III)
- four data sets are fitted independently to give site occupancies – occupancies sum up to unity for both sites

complimentary information from absorption & emission spectroscopies

<table>
<thead>
<tr>
<th>Film Composition (XRF)</th>
<th>Site Occupancies (REXD)</th>
<th>Calculated Mn Ox. States (REXD)</th>
<th>Averaged Mn Ox. States (XANES)</th>
<th>Averaged Mn Ox. States (XES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$<em>{1.83}$Mn$</em>{1.17}$O$_4$</td>
<td>Cr$<em>{1.7}$Mn$</em>{1.3}$O$_4$</td>
<td>2.23 ± 0.02</td>
<td>2.13 ± 0.12</td>
<td>2.25 ± 0.04</td>
</tr>
<tr>
<td>Cr$<em>{1.33}$Mn$</em>{1.67}$O$_4$</td>
<td>Cr$<em>{1.4}$Mn$</em>{1.6}$O$_4$</td>
<td>2.38 ± 0.03</td>
<td>2.26 ± 0.11</td>
<td>2.33 ± 0.04</td>
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Thank you for your attention.