SLAC NATIONAL ACCELERATOR LABORATORY

LELAND STANFORD JUNIOR UNIVERSITY
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site occupancy determination by resonant elastic X-ray scattering

Yezhou Shi

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6th SSRL School on Synchrotron X-ray Scattering Techniques

name change: AXRD → REXS

- diffraction measurements at various incident X-ray energies near an absorption edge
- different names for the same technique
  - **anomalous X-ray diffraction**
  - resonant anomalous X-ray diffraction
  - **resonant elastic X-ray scattering (REXS)**

outline

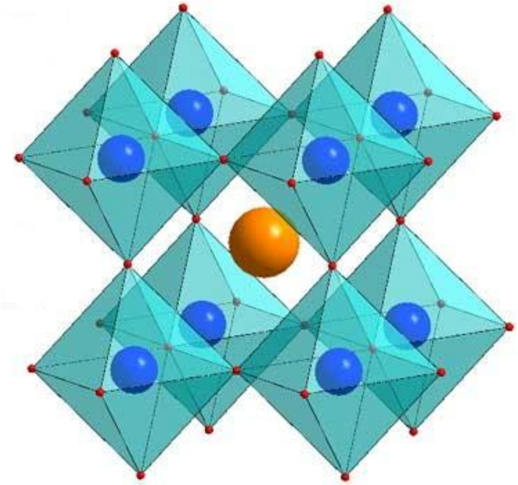
1. motivation: why do we care?

2. technique: how does this work?

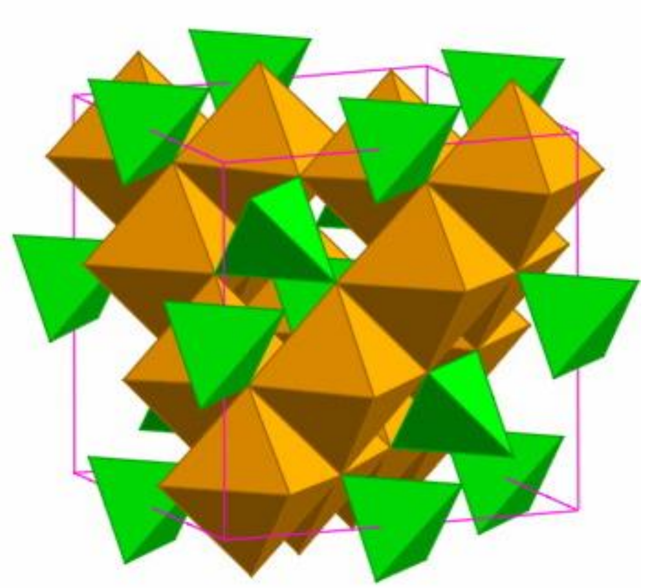
3. design experiments: what to consider?

importance of site occupancy

- materials property depends on site occupancies
- multiple sites, multiple cations/anions



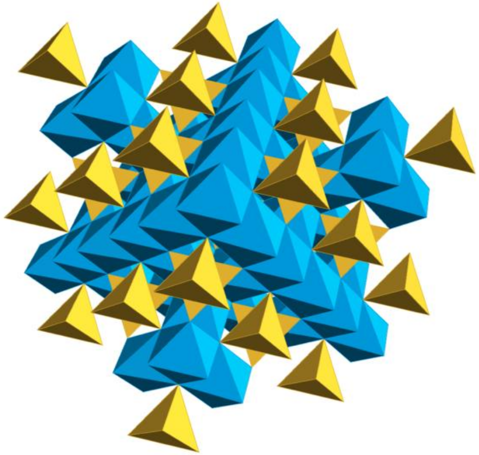
perovskite: ABO_3

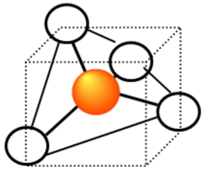


spinel: A_2BO_4

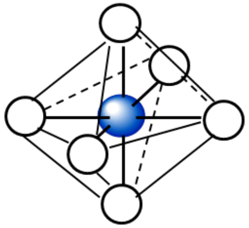
anti-site defects in A_2BO_4 spinel

- electronic conductivity of spinels depends on structure
- *intrinsic* anti-site defects created by cross-substitution

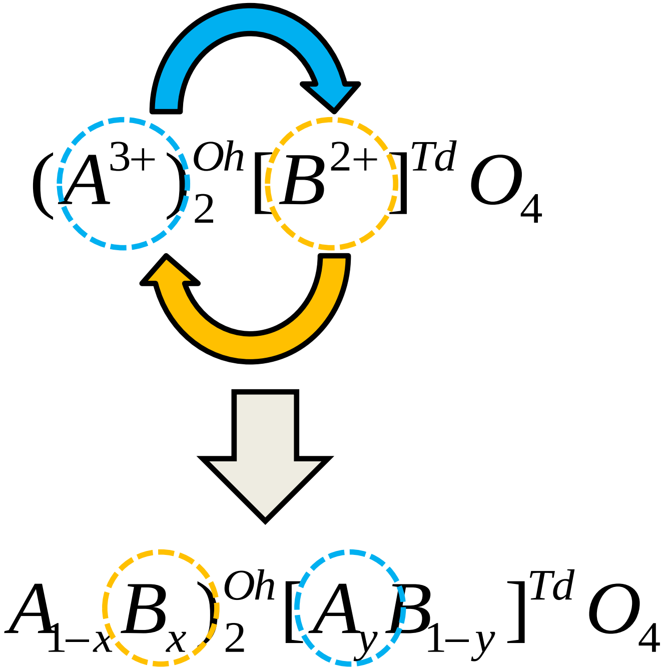




Tetrahedral



Octahedral



$$(A^{3+})_2^{Oh}[B^{2+}]^{Td}O_4$$

$$(A_{1-x}B_x)_2^{Oh}[A_yB_{1-y}]^{Td}O_4$$

B_{Oh}^{2+} acceptor states

donor states A_{Td}^{3+}

attributes of an ideal technique

- **chemical selectivity**: distinguish elements with similar atomic numbers
- **site selectivity**:
  - site A *vs*. site B
  - substitution *vs*. interstitial
- common techniques
  - extended X-ray absorption fine structures (EXAFS)
  - diffraction + Rietveld refinement
    - X-ray diffraction
    - neutron diffraction

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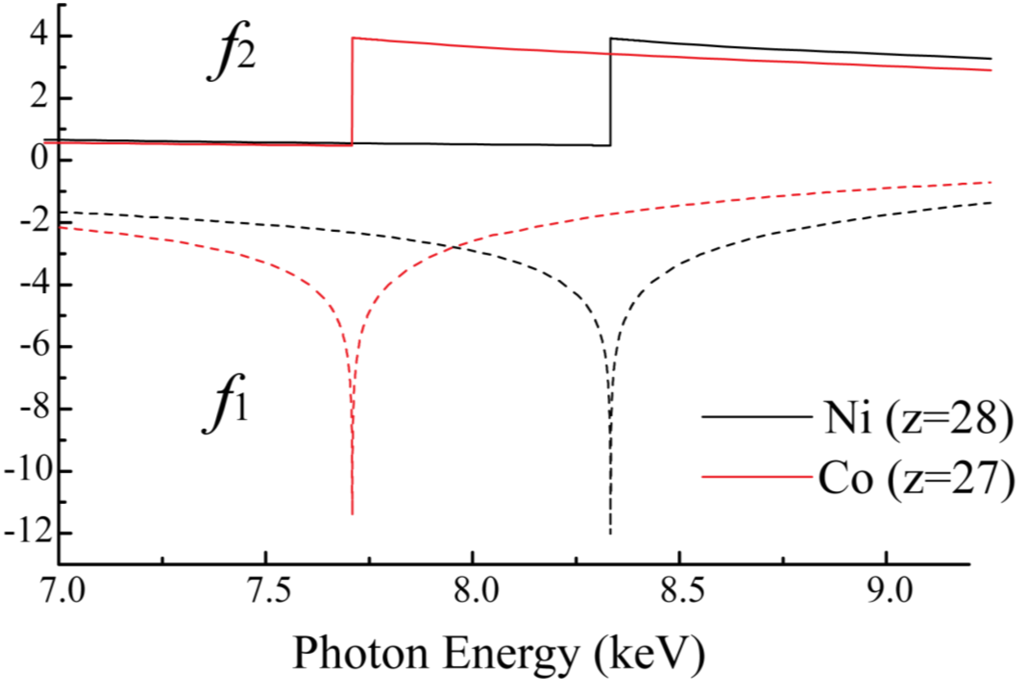
REXS: chemical selectivity

- offers both chemical and site selectivities

$$I(E) \propto \left|F_{hkl}\right|^2 \qquad F_{hkl} = \sum_i x_i \boxed{f_i(q,E)} \cdot e^{2\pi i(hx+ky+lz)}$$

chemical selectivity

$$f = f_o(q) + f_1(E) + if_2(E)$$



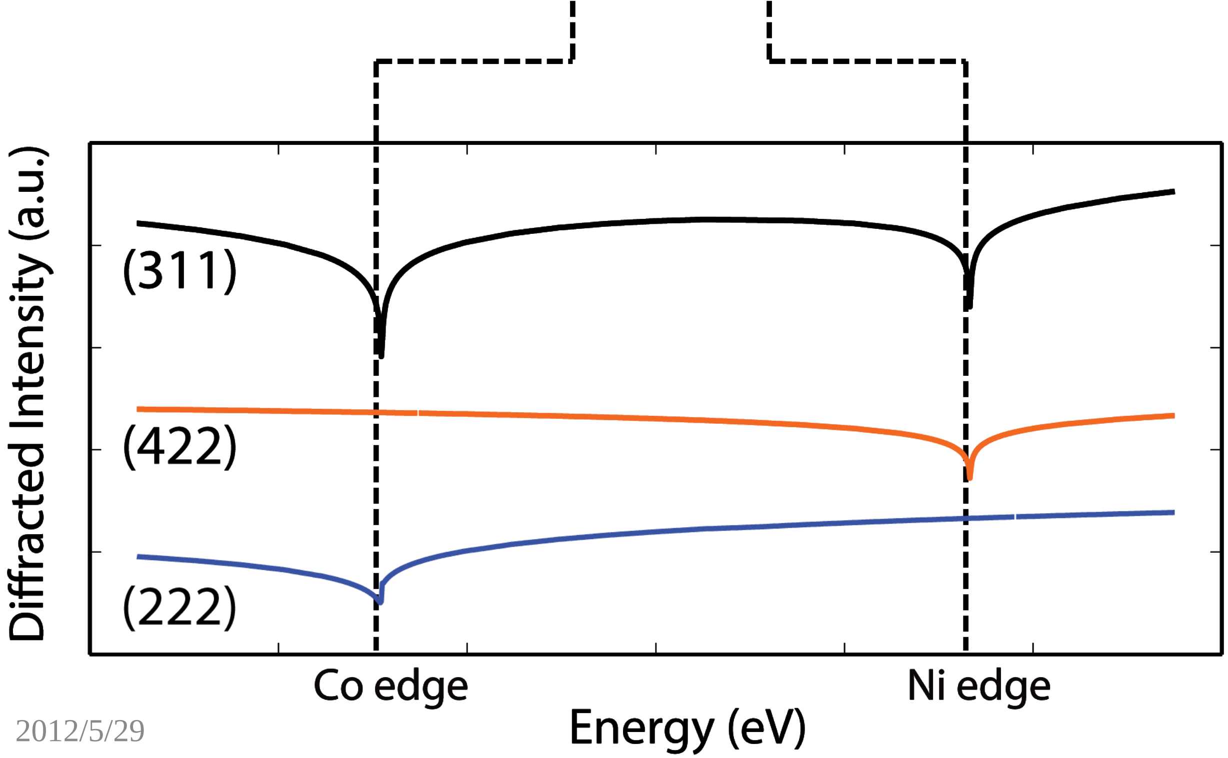
REXS: site selectivity

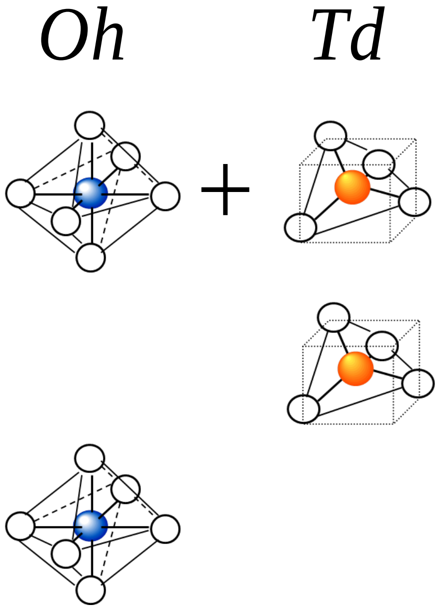
- offers both chemical and site selectivities

$$F_{hkl} = \sum_i x_i f_i(q,E)\cdot e^{\boxed{2\pi i(hx+ky+lz)}}$$

cation site selectivity

$$Co_2^{Oh}Ni^{Td}O_4$$

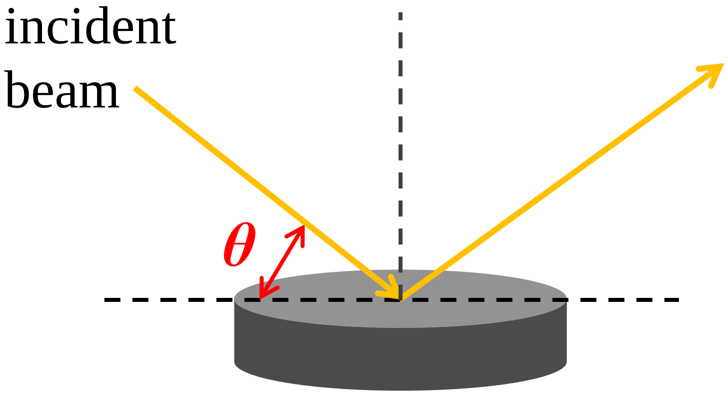




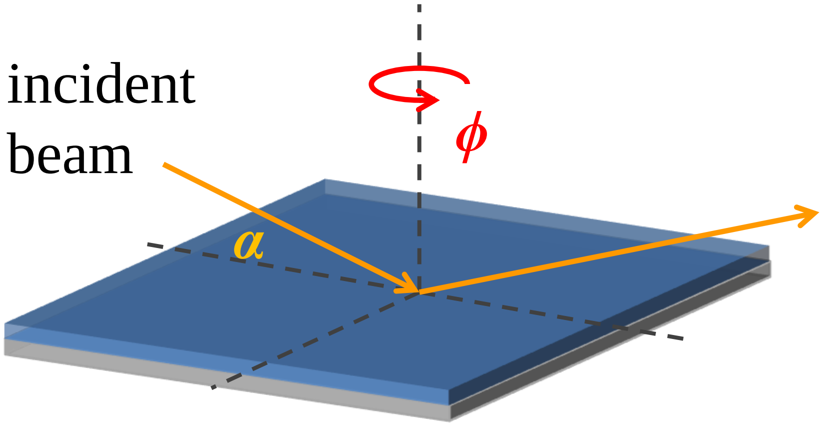
REXS: multiple-energy scans

$$I(E) \propto \left| F_{hkl} \right|^2 \qquad F_{hkl} = \sum_i x_i f_i(q,E) \cdot e^{2\pi i(hx+ky+lz)}$$

Powder



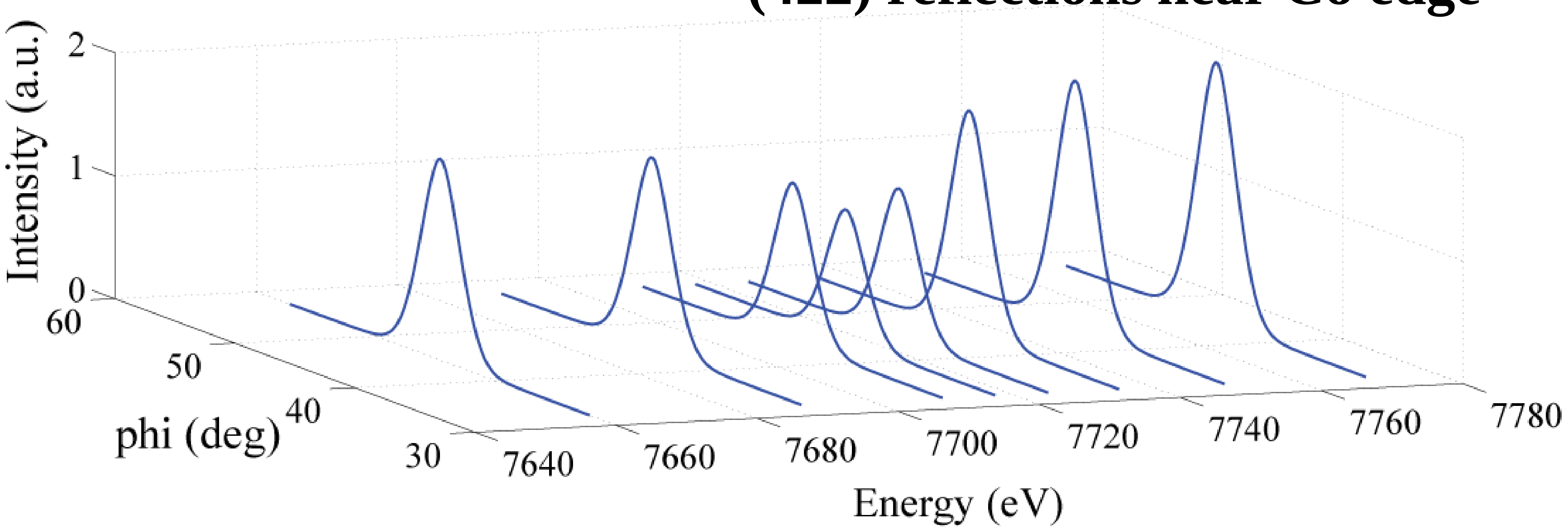
Thin films



REXS: multiple-energy scans

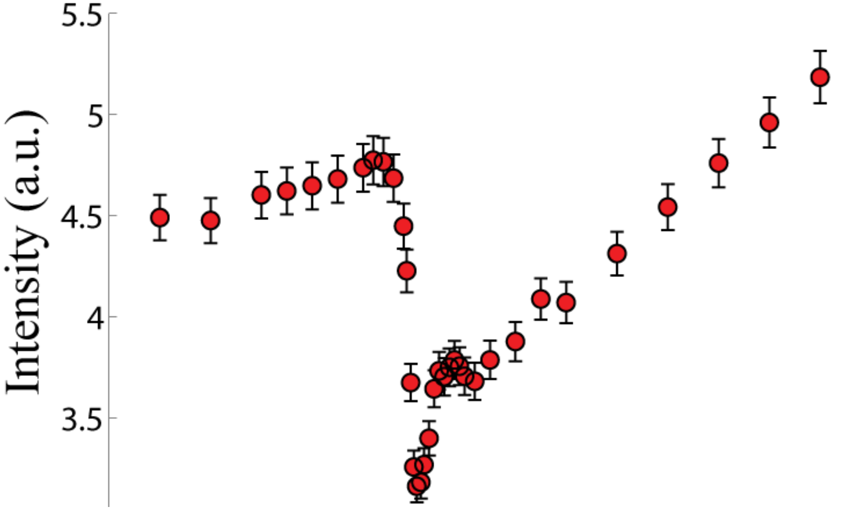
$$I(E) \propto \left|F_{hkl}\right|^2 \qquad F_{hkl} = \sum_i \underbrace{x_i}_{\text{occupancy}} f_i(q,E) \cdot e^{2\pi i(hx+ky+lz)}$$

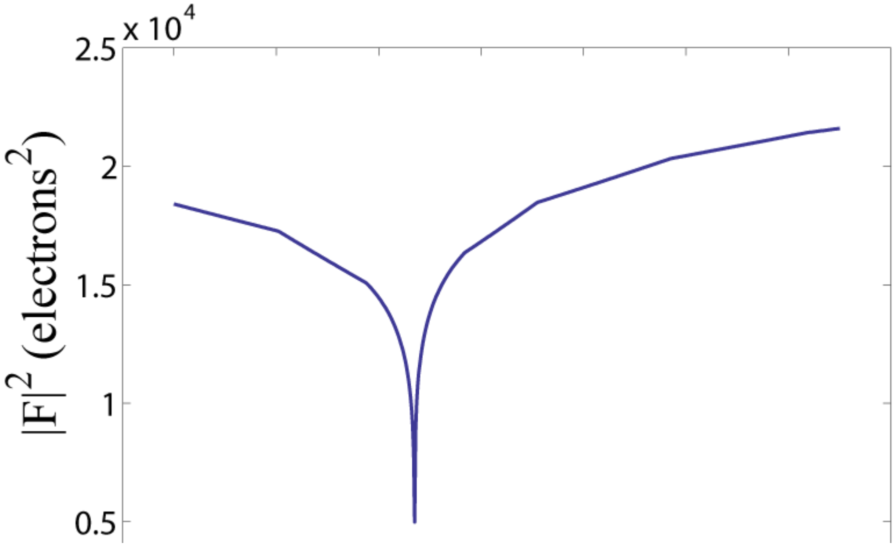
(422) reflections near Co edge



Y. Shi *et al*. *manuscript in preparation*.

experiment vs. simulation: Cr_2MnO_4





- ○ $$I_{obs}(E) = C \cdot \boxed{I_{calc}(E,x)}$$

$$\uparrow$$

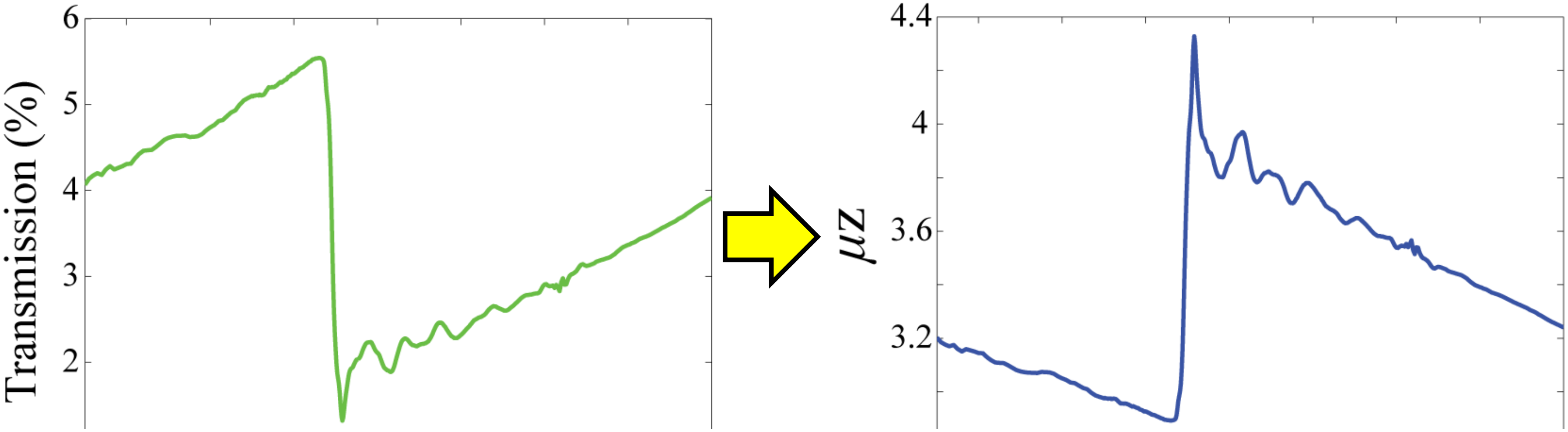
$$f_{calc}(q,E) = f_o(q) + \boxed{f_{1,\exp}(E) + f_{2,\exp}(E)}$$

$$\uparrow$$

obtain f_1 and f_2 with fine features

measuring X-ray abs. spectroscopy

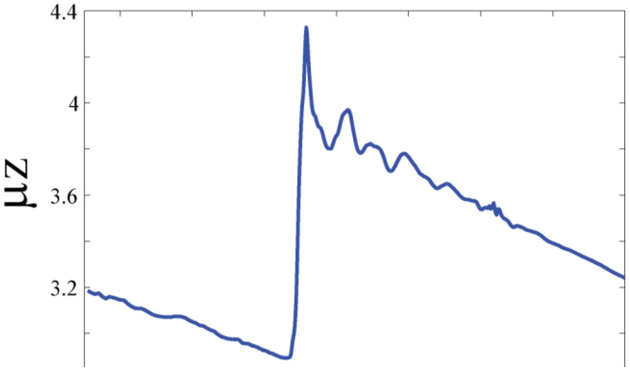
Beer-Lambert's Law $\boxed{transmission} = \frac{I}{I_o} = \exp(-\boxed{\mu \cdot z_{sample}})$



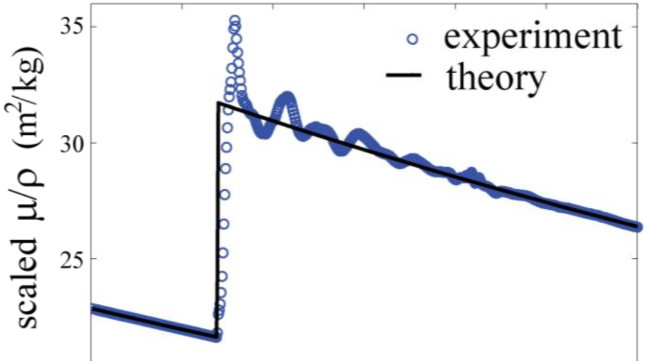
- powder samples: transmission XAS
- thin films: fluorescence XAS

scaling: μz → μ/ρ → f_2

measured ***μz***



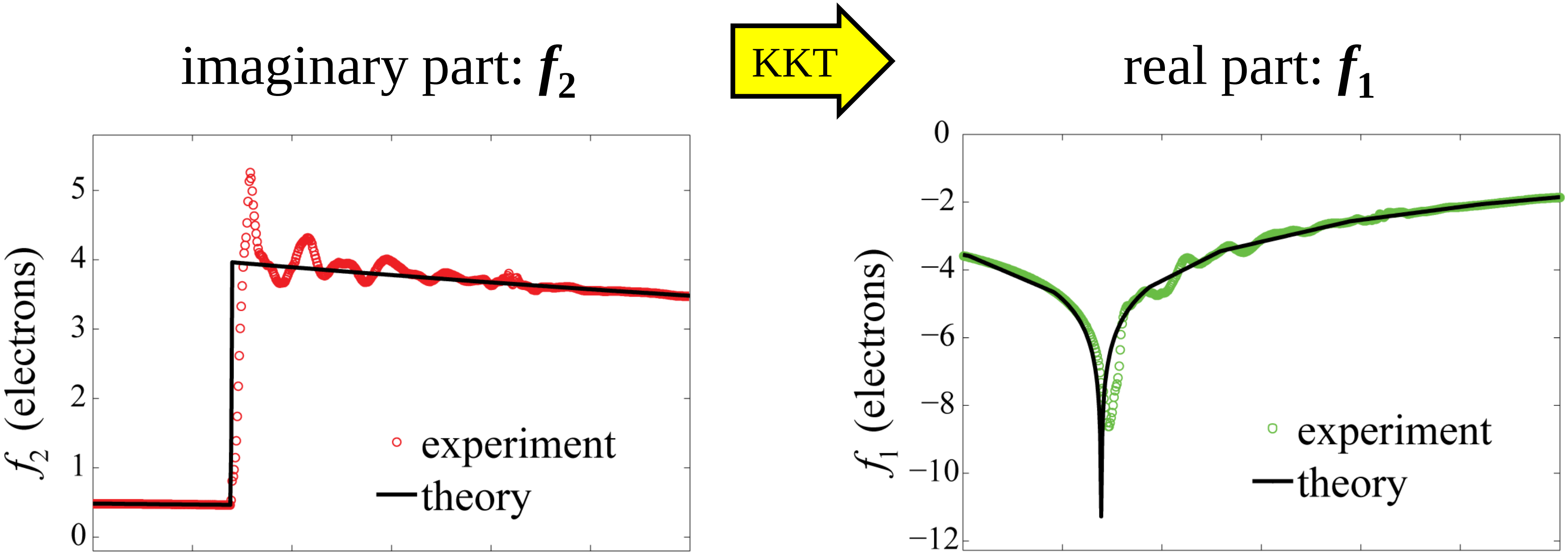
scale ***μ*** to
theoretical ***μ/ρ***



- calculate f_2 from mass. abs. coeff.

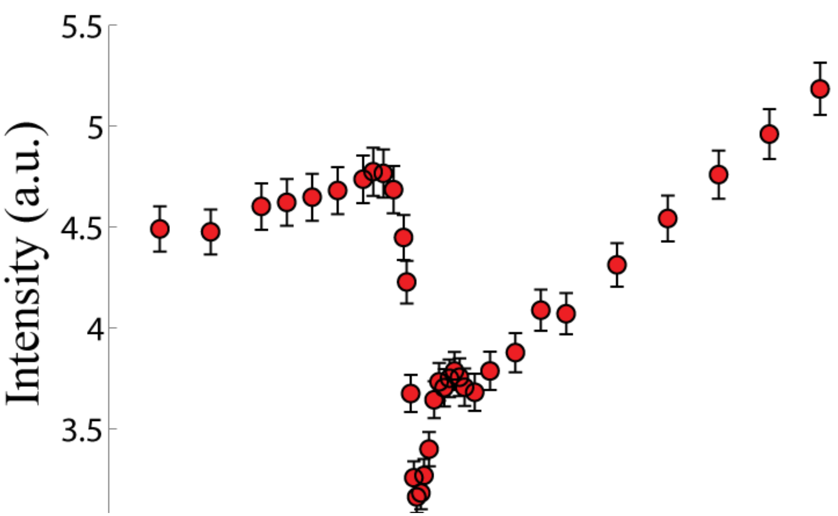
$$(\frac{\mu}{\rho})_{element} = \frac{2 f_{2,element} r_e \lambda}{A m_u}$$

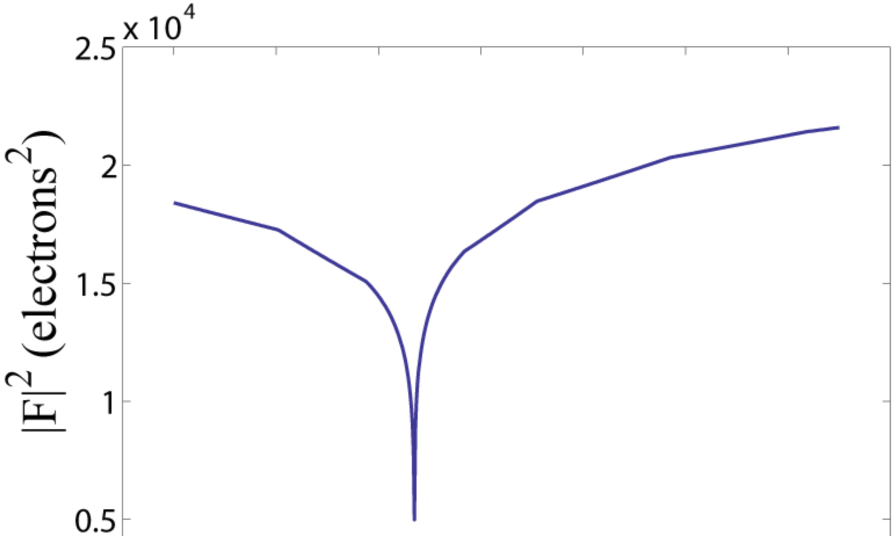
converting f_2 to f_1



- ○ Kramers-Krönig transform (KKT): $f_1(E_o) = \frac{2}{\pi}\int_0^\infty \frac{E\cdot f_2(E)}{E_o^2 - E^2}\,dE$
- ○ near edge: resonant features
- ○ away from edge: good agreement

experiment vs. simulation: Cr_2MnO_4

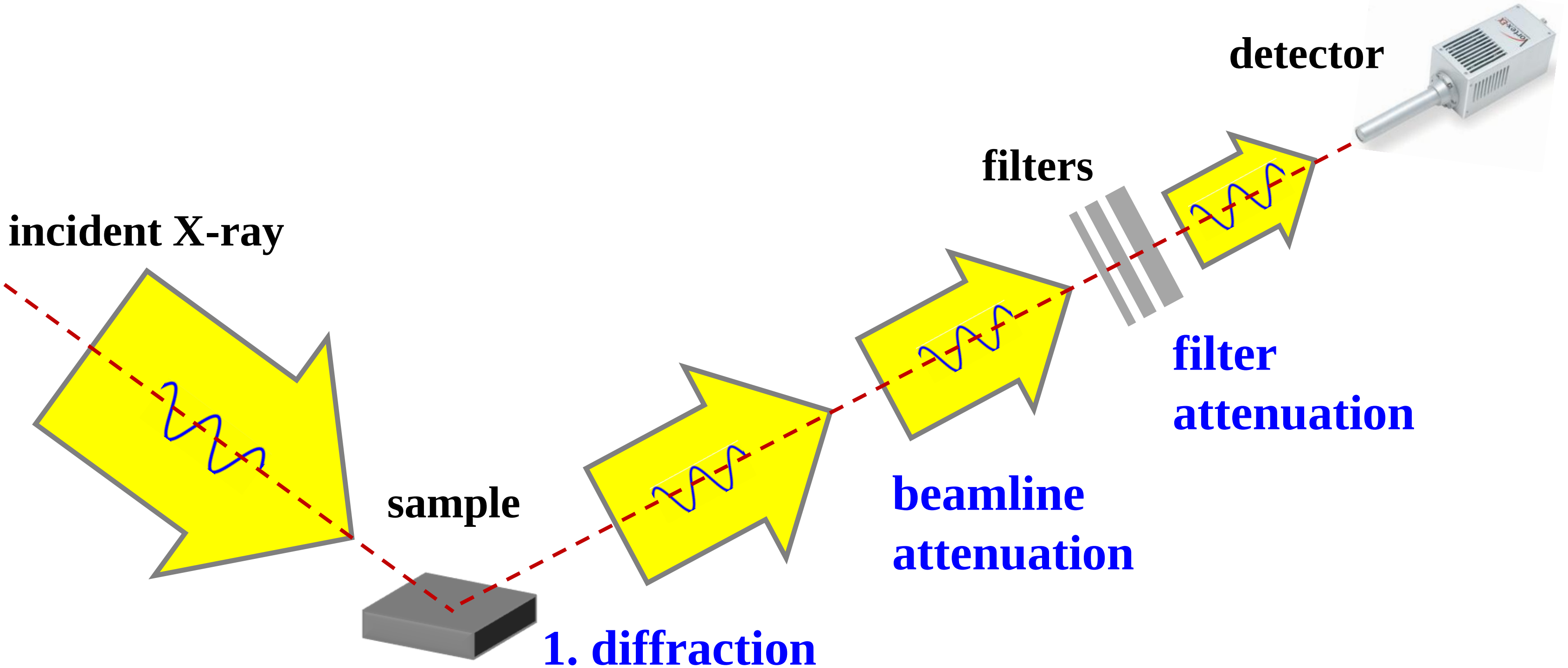




- ○ evident differences: slope, step, and near-edge fine features
- ○ $I_{obs}(E) = C \cdot I_{calc}(E, x) \cdot \boxed{A(E)}$

correct for absorptions

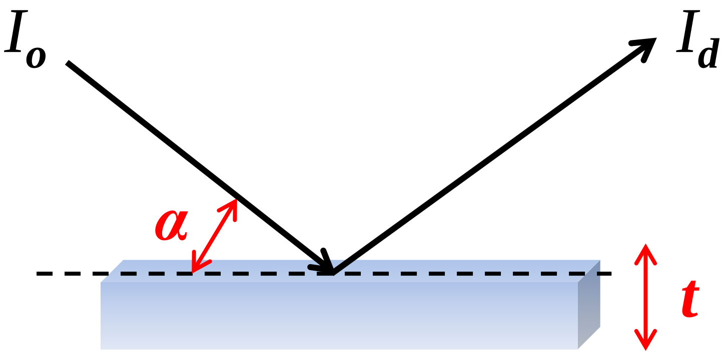
absorptions in the experiment



- size of the arrows symbolizes light intensity
- filter attenuation: can be measured
- beamline attenuation: need control samples

correct sample absorption

- calculate absorption in the sample
- tricky because *both* resonant diffraction and strong absorption features are near the edge



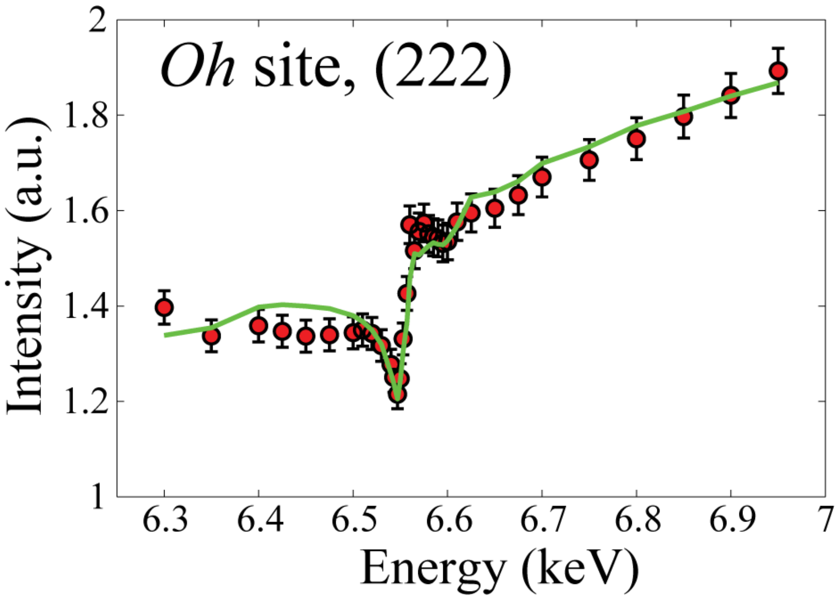
Powder

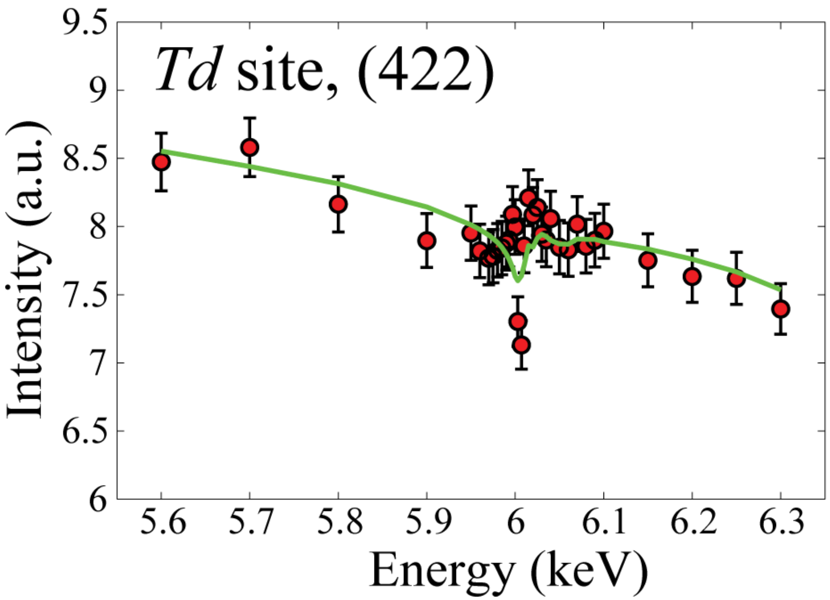
$$\frac{I_d}{I_o} \propto \frac{1}{\mu_{(E)}}$$

Thin films

$$\frac{I_d}{I_o} \propto \frac{1-\exp(-2\mu_{(E)}t/\sin\alpha_{(E)})}{2\mu_{(E)}}$$

fit calculation to experiment





- good agreement between data and fit
- capture the near-edge features and the slope

outline

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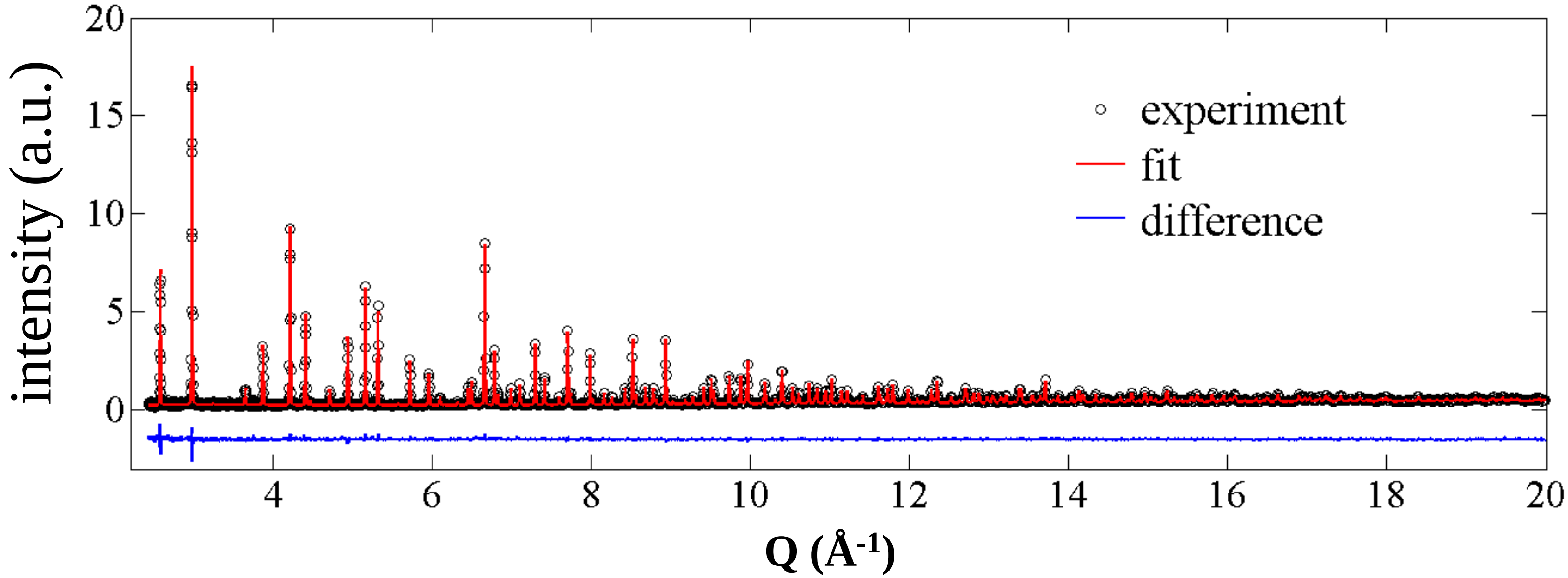
practical considerations

- fraction site occupancy in multiple cation and/or multiple site
- energy compatibility with beamlines
- forms of samples
  - single phase with known composition
  - polycrystalline films or nanocrystals: very difficult
  - powder/bulk ceramic: OK
  - textured thin films/single crystals: the best
  - surfaces: good?

- is this the appropriate technique?

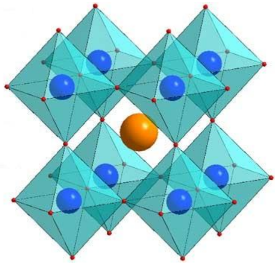
powder sample: co-refinement of XRD and neutron data

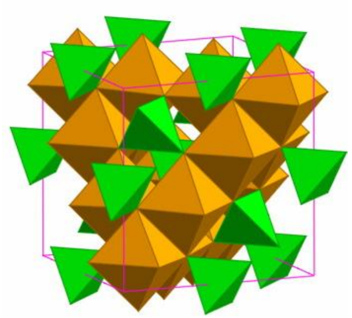
- material: Li doped Cr_2MnO_4 powder
- refine cation site occupancy: $(Cr_{1-x-y}Mn_xLi_y)_2^{Oh}[Mn_{1-z}Li_z]^{Td}O_4$
- neutron diffraction done at Oak Ridge National Lab
- complimentary XRD at SSRL



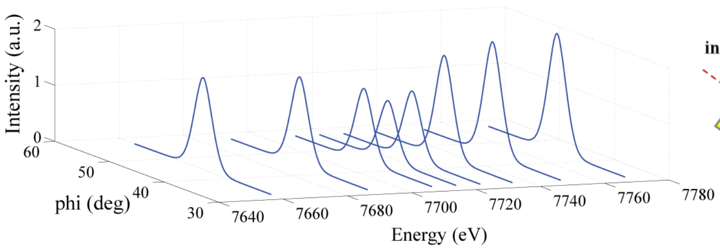
summary

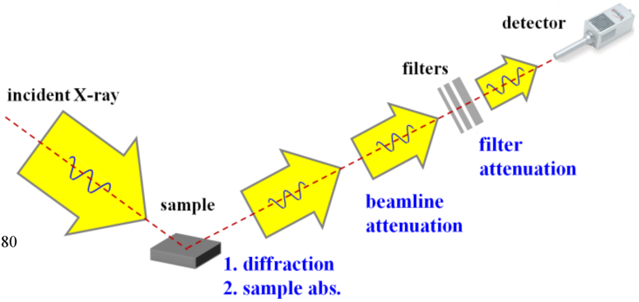
1. motivation

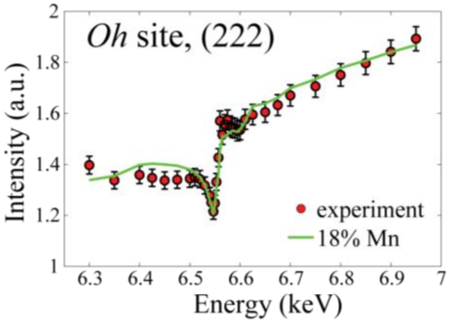




2. technique







3. design experiments
   - sample form
   - energy compatibility

acknowledgment

- Toney group at SLAC
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  Achieving the grand challenge of materials and nanostructures by design
- beamline staff at SSRL
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thank you for the attention