Inelastic X-Ray Scattering

Scope & Outline

Main Goal: Introduce Capabilities & Put them in Context
   Introduction & Relation to Other SR Work
   What relevant properties of samples can be measured?
   When/why would someone consider these techniques?

Outline:
   Introduction
   Brief comments about instrumentation.
   Non-Resonant Techniques
   Resonant Techniques (Briefly)

Note: limit to some aspects of photon-in -> photon out scattering

Note: Huge & Complex Topic - Appropriate for a semester, not an hour...
Table Of IXS Techniques/Applications

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Note: $\Delta E$ = Typical Energy Transfer (Not Resolution)
Note also: Limit to FAST dynamics (~10 ps or faster)

Some References

& References therein


**Absorption Spectroscopy**

Measure absorption as you scan the incident energy

When energy hits a resonance, or exceeds a gap, or... get a change

Free Parameters: $E_1, \epsilon_1, k_1$

→ In principle, 6 dimensions
  but in practice mostly 1 ($E_1$)

**Scattering Spectroscopy**

IXS, Raman, INS

Free Parameters: $E_1, \epsilon_1, k_1, E_2, \epsilon_2, k_2$

→ In principle, 12 dimensions
  in practice, mostly 4, $E_1-E_2$, $Q = k_2-k_1$

Scattering is much more complex, but gives more information.

**X-Ray Scattering Diagram**

Energy Transfer

$E$ or $\Delta E = E_1 - E_2 = \hbar \omega$

Momentum Transfer

$Q = k_2 - k_1$

$Q = |Q| \approx \frac{4\pi}{\lambda} \sin\left(\frac{\Theta}{2}\right)$

Periodicity Probed in Sample

$d = \frac{2\pi}{|Q|}$ or $d = \frac{2\pi}{q = Q - \tau}$

Note: For Resonant Scattering

$E_1$ and $E_2$ and Poln.

Are also important
**Kinematics:**

Simplistic energy-momentum relations

![Kinematics Diagram](image)

Kinetic Energy Given to Sample:

\[
E_{\text{recoil}} = \frac{p^2}{2M} = \frac{\hbar^2 Q^2}{2M}
\]

Take: \(M=57\) amu, \(Q/c = 7\,\text{Å}^{-1}\) \(\rightarrow E_r=2.3\) meV

Compton Form:

\[
\lambda_2 - \lambda_1 = \frac{\hbar}{Mc}(1 - \cos \Theta)
\]

\[
\lambda_c = \frac{\hbar}{m_e c} = 0.0243\,\text{Å}
\]

**Dynamic Structure Factor**

It is convenient, especially for non-resonant scattering, to separate the properties of the material and the properties of the interaction of the photon with the material (electron)

\[
\frac{d^2\sigma}{d\Omega d\omega} = r_e^2 \left( e_2^* \cdot e_1 \right) \frac{\omega_2}{\omega_1} S(Q,\omega)
\]

\[
\sigma_{\text{Thomson}} = r_e^2 \left( e_2^* \cdot e_1 \right) \frac{\omega_2}{\omega_1}
\]

Note: For resonant scattering \(\omega \rightarrow \omega_2\)

**Thomson Scattering Cross Section**

Dynamic Structure Factor

\[
S(Q,\omega) = \frac{1}{4\pi} \int dt \ e^{-i\omega t} \int dr \int dr' \ e^{i\omega(r-r')} \langle \rho(r',t)\rho(r,t=0) \rangle
\]

\[
\int d\omega \ h\omega S(Q,\omega) = \frac{\hbar^2 Q^2}{2M}
\]

AQRB © QOFSSRR Cheiron School 2008
The IXS Spectrometer

An Optics Problem

Main Components

**Monochromator:**
Modestly Difficult
Only needs to accept 15x40 mrad$^2$

Sample Stages
Straightforward
Only Need Space

**Analyzer:**
Large Solid Angle
Difficult

$\Delta E$ small, $E$ tunable

The Goal: Put it all together and
Keep Good Resolution, Not Lose Flux
Basic Optical Concepts

Bragg’s Law: \( \lambda = 2d \sin(\Theta_B) \Rightarrow \Delta \Theta = \tan(\Theta_B) \frac{\Delta E}{E} \)

Working closer to \( \Theta_B \sim 90 \text{ deg.} \) maximizes the angular acceptance for a given energy resolution...

Better energy resolution
  - Closer to 90 degrees
  - Large Spectrometer

Analyzer Crystals

The more difficult optic...

Require:
  Correct Shape (Spherically Curved, R=9.8 m)
  Not Strained (\( \Delta E/E \sim \text{few} 10^{-8} \Rightarrow \Delta d/d < \text{few} 10^{-8} \))

Method: Bond many small crystallites to a curved substrate.

1. Cut
2. Etch
3. Bond to Substrate
4. Remove Back

X-Rays

10^4 Independent Perfect Crystals
Analyzer Crystal

Collaborative R&D with NEC Fundamental Research Laboratory, H. Kimura, F. Yamamoto

Present Parameters (9.8 m Radius, 10 cm Diameter)

50 or 60 µm blade, 2.9 mm depth, 0.74 mm pitch
Channel width (after etch): ~ 0.15 mm
60 to 65% Active Area

High (meV) Resolution Spectrometer

Analyzer Array
Slit System
12 Chan. CZT Detector
Sample
Vacuum Flight Path
Incident Beam φ~100 µm
~ 20 µm Possible
Granite Base w/Airpads

10 m Horizontal Arm - to 55° in 2Θ
Medium Resolution

Medium Resolution Spectrometer:
Arm Radius: 1 to 3 m
Resolution: ~0.1 to 1 eV
Used for RIXS and NRIXS

BL12XU (Cai, et al)
BL11XU (Ishii, et al)
Also: BL39XU (Hayashi, et al)

Note difference between RIXS and NRIXS
NRIXS: Choose the energy to match the optics
RIXS: Resonance chooses energy -> usually worse resolution
Atomic Dynamics: Systems and Questions

Disordered Materials (Liquids & Glasses):
Still a new field -> Nearly all new data is interesting.
How do dynamical modes survive the cross-over from the long-wavelength continuum/hydrodynamic regime to atomic length scales?

Crystalline Materials:
Basic phonon model does very well -> Specific questions needed.
Phonon softening & Phase transitions (e.g. CDW Transition)
Thermal Properties: Thermoelectricity & Clathrates
Sound Velocity in Geological Conditions
Pairing mechanism in superconductors

Phonons in a Crystal

Normal Modes of Atomic Motion

Must have enough modes so that each atom in a crystal can be moved in either x, y or z directions by a suitable superposition of modes.

If a crystal has N unit cells and R atoms/Cell then it has 3NR Normal Modes

Generally: Consider the unit cell periodicity separately by introducing a continuous momentum variable, q.

-> 3R modes for any given q
Phonons in a Superconductor

Conventional superconductivity is driven by lattice motion. "Phonon Mediated" - lattice "breathing" allows electron pairs to move without resistance.

Original Picture: Limited interest in specific phonons...
Now: Lots of interest as this makes a huge difference. Particular phonons can couple very strongly to the electronic system.

How does this coupling appear in the phonon spectra?

- **Softening**: Screening lowers the energy of the mode (abrupt change <=> Kohn Anomaly)
- **Broadening**: Additional decay channel (phonon->e-h pair) reduces the phonon lifetime

Electron Phonon Coupling & Kohn Anomalies

On the scale of electron energies, a phonon has nearly no energy. A phonon only has momentum.

So a phonon can move electrons from one part of the Fermi surface to another, but NOT off the Fermi surface.
**MgB$_2$**

High $T_c$ (39K)


Simple Structure... straightforward calculation.

Electronic Structure


**Phonon Structure**

BCS (Eliashberg) superconductor with mode-specific electron-phonon coupling.

---

**Electron-Phonon Coupling in MgB$_2$**

Dispersion  

Spectra  

Linewidth

Clear correlation between linewidth & softening. Excellent agreement with LDA Pseudopotential calculation.

PRL 92(2004) 197004: Baron, Uchiyama, Tanaka, ... Tajima

AQRB @ AOFSRR Cheiron School 2008
Carbon Doped Mg(C_xB_{1-x})_2

\[ \begin{align*}
2\% C, & \quad T_c=35.5K \\
12.5\% C, & \quad T_c=2.5K \\
\text{AlB}_2 \quad (\text{Not SC})
\end{align*} \]

Phonon structure correlates nicely with \( T_c \) for charge doping.
(Electron doping fills the sigma Fermi surface)

More Superconductors

Similar types of results for
- Mn Doped MgB_2
- CaAlSi
- Boron Doped Diamond

Extrapolation to the High \( T_c \) Copper Oxide Materials....
1. Much More Complex
2. Calculations Fail so interpretation in difficult
Disordered Materials

Hydrodynamic/Continuum (Q→0) Limit →
Brillouin Triplet: Quasi-Elastic Peak + Sound Mode

How does this evolve at larger Q?
“DHO model” = Lorentzian
+ Damped Harmonic Oscillator

I-Mg (Kawakita et al)
a-Se (Scopigno et al)
I-Si (Hosokawa, et al)
Metal to Insulator Transition in Liquid Mercury

Universal Phenomenon in Liquids:
Expand a liquid metal enough and it becomes an insulator.

For Hg
~1500°C & ~1.5 kbar

15 mm Be, 200 m He (STP), 0.15 mm Sapphire
~ 20 microns Hg


“Fast Sound” at the Metal-Non-Metal Transition

Suggests a change in the microscopic density fluctuations, possibly due to a modification of the pair potential...

Elastic Inhomogeneity in a Glass
Ichitsubo, et al.

Pd$_{42.5}$Ni$_{7.5}$Cu$_{30}$P$_{20}$

(More detailed analysis: possible failure of DHO Model)
High Resolution Measurement

8 meV resolution at 15.8 keV, Si(888)
Temperature scan of mono over 2 eV or 60K

Baron, et al, April 2007 © BL35XU
Detwinned Sample

Havercourt, Sawatzky, et al, May 07
NiO$_6$ cluster calculation
Note splitting of 1700 meV excitation.
NRIXS at Smaller (~eV) Energy Transfers

“Momentum Resolved Optical Spectroscopy”

Conventional Optical Spectroscopy: Information on electronic energy levels but without information on inter-atomic correlations or atomic structure

(Absorption, Reflectivity)

With x-rays, the short wavelength allows direct probe at atomic scale:

Is an excitation collective or local (does it disperse)?
What is the atomic symmetry of an excitation?
How does it interact with the surrounding environment?

Resonant experiment -> non-resonant IXS experiment.
Non-Resonant is simpler and can have higher resolution
But badly flux limited

d-d Excitations in NiO

First something simple...

There exist well-defined excitations in the charge transfer gap of NiO Antiferromagnet (T_N 523K), (111) Spin order

Long and Distinguished History
First (resonant) IXS experiments (Kao, et al)

Non-Resonant IXS, ΔE~300 meV


Cai, Hirooka, et al, BL12XU Unpublished
**Orientation Dependence**

Orbitals

Results of Wanneir function analysis of LDA+U calcs of Larson et al/PRL (2007)

Cluster calculations


Scattered Intensity

**High Resolution Measurement**

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Temperature scan of mono over 2 eV or 60K

Baron, et al, April 2007 @ BL35XU

Detwinned Sample

Havercourt, Sawatzky, et al, May 07

NiO\textsubscript{6} cluster calculation

Note splitting of 1700 meV excitation.
Towards a Dispersive Excitation?

Orbiton: Movie Maekawa, Dispersion Ishihara

Larger Energy Range

Hiraoka et al, Submitted
Low-Energy Charge-Density Excitations in MgB$_2$: Striking Interplay between Single-Particle and Collective Behavior for Large Momenta

Y. Q. Cai,$^{1,8}$ P. C. Chow,$^{1,6}$ O. D. Restrepo,$^{2,3}$ Y. Takano,$^{4}$ K. Togano,$^{4}$ H. Kitao,$^{4}$ H. Ishii,$^{3}$ C. C. Chen,$^{1}$ K. S. Liang,$^{1}$ C. T. Chen,$^{1}$ S. Tsuda,$^{6}$ S. Shin,$^{6}$ C. C. Kao,$^{6}$ W. Kuo,$^{7}$ and A. G. Eguiluz$^{2,3}$

FIG. 1 (color online). NIXS spectra at various momentum transfers $q$ in $c^*\parallel$ axis showing the low-energy collective mode, where $q = 8.9$ meV$^{-1}$ corresponds to the first boundary of the extended BZ. The total energy resolution was 65 meV for (a), and 250 meV for (b).

FIG. 2 (color). Theoretical $S(q,w)$ calculated in the present work in false color log scale as a function of energy and momentum transfer showing the cosine energy dispersion of the low-energy collective mode. Filled squares and triangles mark the energy positions obtained from the NIXS spectra shown in Fig. 1, whereas filled circles are data from another set of spectra taken with the total energy resolution of 250 meV.

Excitation repeats from one zone to the next...
Suppose you would like to measure the structure of the oxygen k-edge (at 532 eV) of a sample inside of a high pressure cell with 1mm thick diamond windows?

Diamond:

- $I_{abs} < 0.5 \text{ um } 500 \text{ eV}$
- $I_{abs} \sim 2 \text{ mm } 10 \text{ keV}$

Easier at 10 keV than 0.5 keV

Note: need dipole approx. ($Q_r < 1$) to be good to compare with usual XAFS.
Compton Scattering

For very large $Q$ and $\Delta E \ll E$ one can take

$$S(Q,\omega) = \frac{m}{\hbar Q} \iiint dp_x dp_y \rho(p_z = p_\omega)$$

$$= \frac{m}{\hbar Q} J(p_\omega)$$

Typical: $Q \sim 100 \text{Å}^{-1}$

$E > 100$ keV

Ie: Compton scattering projects out the electron momentum density.

Typical of incoherent scattering...
Three-Dimensional Momentum Density Reconstruction

Three-dimensional momentum density, \( n(p) \), can be reconstructed from \( \sim 10 \) Compton profiles.

\[
J(p_z) = \iiint n(p) \, dp_x \, dp_y
\]

Reconstruction:
- Direct Fourier Method
- Fourier-Bessel Method
- Cormack Method
- Maximum Entropy Method

Momentum density, \( n(p) \)

Fermi surfaces of Cu and Cu alloys

Cu-15.8at%Al  Cu  Cu-27.5at%Pd

Determined by Compton scattering at KEK-AR

The Fermi surface is similar to that of Ag, but the size of neck is about 2 times larger.

Exp.  

The Fermi Surface of PdH$_{0.84}$ 

Experiment and theory 

fcc-Pd  

fcc-Ag 

Nuclear Inelastic Scattering
First Demonstrated (Clearly) by Seto et al 1995

Mössbauer Resonances Exist in Different Nuclei...

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<th>Lifetime (ns)</th>
<th>Alpha</th>
<th>Natural abundance (%)</th>
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<td>$^{161}$Ta</td>
<td>6.21</td>
<td>87.30</td>
<td>71</td>
<td>100</td>
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<tr>
<td>$^{169}$Tm</td>
<td>8.41</td>
<td>5.8</td>
<td>220</td>
<td>100</td>
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<tr>
<td>$^{89}$Kr</td>
<td>9.40</td>
<td>212</td>
<td>20</td>
<td>11.5</td>
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<tr>
<td>$^{57}$Fe</td>
<td>14.4</td>
<td>141</td>
<td>8.2</td>
<td>2.2</td>
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<tr>
<td>$^{151}$Eu</td>
<td>21.6</td>
<td>13.7</td>
<td>29</td>
<td>48</td>
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<tr>
<td>$^{146}$Sm</td>
<td>22.5</td>
<td>10.4</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>$^{156}$Sm</td>
<td>23.9</td>
<td>25.6</td>
<td>5.2</td>
<td>8.6</td>
</tr>
<tr>
<td>$^{151}$Dy</td>
<td>25.6</td>
<td>40</td>
<td>2.5</td>
<td>19</td>
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</table>

Resonances have relatively long lifetimes so that if one has a pulsed source, one can separate the nuclear scattering by using a fast time resolving detector.

NIS Setup

Use a narrow bandwidth monochromator
The nuclear resonance becomes the analyzer.

1. $E_{\text{in}} = E_{\text{res}}$
2. $E_{\text{in}} + E_{\text{phonon}} = E_{\text{res}}$
3. $E_{\text{in}} - E_{\text{phonon}} = E_{\text{res}}$

Element-Specific Projected Phonon DOS
NIS Gives the Partial Projected DOS
Example of the Fe-As Superconductors

Partial = Element Specific  Projected = Weakly Directional

Calculation: Boeri et al
Measurement: Higashitaniguchi et al

NIS: Good and Bad

Important things to note:
1. Element and isotope selective.
2. Gives Projected Density of states NOT Dispersion
   (But it does this nearly perfectly)
NIS Example: Surface DOS
Slezak et al PRL 99 (2007) 066103

$^{57}$Fe monolayers near the surface of $^{56}$Fe

![Graph showing phonon density of states](image)

Note projection!

NIS Example: Biological Macro-Molecules

e.g.

Where element specificity can help a lot.

![Graph showing long-range reactive dynamics in myoglobin](image)