Scope & Outline

Huge & Complex Topic - Appropriate for a semester, not an hour...

Main Goal:
Introduce Capabilities & Put them in Context
What properties can be measured?
Why consider these techniques?

Outline:
Introduction
Instrumentation
Non-Resonant Techniques
Resonant Techniques (Briefly)

Some References

& References therein (RIXS, X-Ray Raman, NRIXS...)


Scientific Information
(from IXS)

Atomic Dynamics → Motions of atoms in a solid (phonons) or liquid.
Phase transitions, thermal properties, fundamental science  (Atomic binding)
Electron-phonon coupling, Magneto-elastic coupling
Superconductors, Ferroelectrics, multiferroics, etc

Electronic Dynamics
Chemical Bonding (Valence, etc)
Electronic Energy Levels (atomic/molecular)
Delocalized Electronic Excitations
Generalized Dielectric Response
Fermi-Surface Topology
Magnetic structure

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)

Energy Scale of Excitations
**Spectroscopy**

Absorption vs. Scattering

- Measure absorption as you scan the incident energy.
- When energy hits a resonance, or exceeds a gap, or... get a change.

**Absorption Spectroscopy**
- Optical, IR, NMR

**Scattering Spectroscopy**
- IXS, Raman, INS

Free Parameters: $E_1, k_1, e_1$
- In principle, 3+ dimensions
- In practice, mostly 1 ($E_1$)

Free Parameters: $E_2, k_2, e_2$
- In principle, 6+ dimensions
- In practice, mostly 4: $E_1, E_2, Q = k_2 - k_1$

Scattering is more complex, but gives more information.

Where We Are Measuring

- Between the Bragg Peaks...
- On Log Scale

X-Ray Scattering Diagram

Two Main Quantities:
- Energy Transfer: $E$ or $\Delta E = E_1 - E_2 \equiv h\omega$
- Momentum Transfer: $Q = k_2 - k_1$

Periodicity: $d = \frac{2\pi}{k_1}$

Resonant vs Non-Resonant

- Resonant: RIXS, SIXS
  - Tune near an atomic transition energy
  - Generally High Rate
  - Complex interpretation
  - Energy fixed by resonance -> poorer resolution

- Non-Resonant: IXS, NRIS
  - Far from any atomic transition.
  - Small cross-section
  - Interpretation directly in terms of electron density
  - Choose energy to match optics -> good Resolution

Slightly Different Experimental Setup

- Nuclear Resonant -> Different entirely... later.
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).

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

\[ \sigma_{\text{Thom.}} = r_e^2 \left( e_2^* \cdot e_1 \right)^2 \]

Different Views of \( S(Q,\omega) \)

Transition between states

Fluctuations in electron density

\[ = \frac{1}{2\pi} \int dt \ e^{-i\mathbf{r}_1 \cdot \mathbf{r}} e^{-i\omega t} \delta(E_{\mathbf{q},\omega} - E_{\mathbf{q},\omega}) \]

Generalized Response (e.g. Dielectric functions)

See Squires, Lovesy, Shulke, Sinha (JPCM 13 (2001) 7511)

Why is it Better to Measure in Momentum/Energy Space?

For diffraction (and diffractive/coherent imaging), one goes to great lengths to convert from momentum space to real space. If possible, a direct real-space measurement would be preferred.

Equilibrium Dynamics: \( Q,E \) space is what you want.
- Normal modes \( \rightarrow \) peaks in energy space \( \rightarrow \) clear and "easy"
- Periodicity of crystals \( \rightarrow \) Excitations are plane waves
- \( Q \) is well defined

Non-equilibrium dynamics \( \rightarrow \) Real space (\( X,t \)) can be better.
- Non-periodic (disordered) materials \( \rightarrow \) Expand in plane waves.
- (oh well)

Kinematics

Conservation of Energy

Kinetic Energy Given to Sample:

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

Compton Form:

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

Where \( \frac{\hbar}{M_c} = 0.0243 \text{Å} \)
The IXS Spectrometer
An Optics Problem

Main Components

Monochromator:
- Modestly Difficult
- Accepts 15x40 µrad²

Sample Stages
- Straightforward
- Only Need Space

Analyzer:
- Large Solid Angle
- Difficult
- Keep Good Resolution, Not Lose Flux

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

Note: small bandwidth means starting flux reduced by 2 to 3 orders of magnitude...

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

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

Better energy resolution
\( \rightarrow \) Closer to 90 degrees
\( \rightarrow \) Large Spectrometer

High Resolution Analyzer Crystals

The more difficult optic...

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

Method: Bond many small crystallites to a curved substrate.

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

Note: For resolution >300 meV, bending can be OK.

Analyzer Crystal

9.8 m Radius, 10cm 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
A High (meV) Resolution Spectrometer

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

Other Spectrometers @ SPring-8
RIXS Spectrometer
2m Arm, BL11XU

Compton Spectrometer BLO8
(+eV Resolution)
Hoyashi, et al

Emission Spectrometer
Φ 1.5m Chamber

Other High Resolution Spectrometers
ESRF (ID28)
APS (Sector 30)

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

First Glance: Triplet response similar for most materials.
Dispersing Longitudinal Sound Mode + Quasi-Elastic peak

The IXS Advantage

IXS has no kinematic limitations (ΔE<<E).
Large energy transfer at small momentum transfer
-> excellent access to mesoscopic length scales

Water
Also: No Incoherent Background Small Beam Size (φ<0.1mm)
But: <1 meV resolution is hard Low Rates for Heavy Materials

Glassy-Se
Sette et al INS (1996)
Teixeira, et al INS (1985)

“Fast Sound” at the Metal-Non-Metal Transition in Liquid Hg

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


Water

On Positive Dispersion

Very General feature:
As $Q$ increases the phase velocity of the acoustic mode becomes larger than the Low-$Q$ (e.g. ultrasonic) sound velocity.

Casual explanation
For smaller length scales (high $Q$) and higher frequencies, a liquid, locally, resembles a solid which has a faster sound velocity.

Partial explanation in terms of a visco-elastic model...
Scopigno & Ruocco RMP 2005
Bryk et al JCP 2010

Shear Mode in a Simple Liquid
Pressure Wave in a Liquid: Shear Wave \rightarrow Harder...
Nearly Always Visible

$S(Q,\omega) = \int \int \int e^{-i\omega t} e^{iQ \cdot (r - r')} \rho(r',t) \rho(r,t = 0) d^3 r' d^3 r$

Weak, but significant, signal.

Next experiment: l-Cu
2.5 Days \rightarrow ?

Liquid Excitations = Solid + Disorder?
Giordano & Monaco, PNAS (2010)

IXS from Na: Above & Below $T_M$
Black = Polycrystalline Na
Blue = Liquid Na
Red = Polycrystal + Scaling by Density, T, & Blurring...
Not bad...
Phonons in a Crystal

Normal Modes of Atomic Motion = Basis set for small displacements

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, $q$.

$\rightarrow 3R$ modes for any given $q$

MgB$_2$ As An Example

Layered Material
Hexagonal Structure

B Layer
B-B Bond is Short & Stronger

Mg Layer
Mg-Mg Bond is Longer & Weaker

3 Atoms/cell $\Rightarrow 9$ modes / Q Point

Acoustic and Optical Modes

Acoustic Modes are Continuum (Smooth) Modes.

LA Mode
Compression Mode

TA Mode
Shear Mode

Optical Mode
Atoms in one unit cell move against each-other

Dispersion of an Optical Mode

(0 0 0) (0.25 0 0) (0.5 0 0)
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 $\Rightarrow$ Kohn Anomaly)

- **Broadening**: Additional decay channel (phonon-$\rightarrow$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.

- Phonon Momenta $Q < 2k_F$
- Large Momentum $Q > 2k_F$

From T. Fukuda

Superconductors

Systems Investigated include:

MgB$_2$, Doped MgB$_2$, CaAlSi, B-Doped Diamond

Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_{10}$, YBCO, LSCO, Tl$_2$2212, Bi$_2$2212, Bi$_2$2201, Bi$_2$2212, Nickelates, Oxychlorides

Fe-As Systems: LaFeAsO, PrFeAsO, BaFeAs

MgB$_2$

High $T_c$ (39K)


Simple Structure... straightforward calculation.

Phonon Structure

Electronic 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: Baran, Uchiyama, Tanaka, ... Tajima

Carbon Doped Mg(C$_{x}$B$_{1-x}$)$_2$

- 2% C, $T_c$=35.5K
- 12.5% C, $T_c$=2.5K
- AIB$_2$ (Not SC)

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

Phonons in the Cuprates...

Everyone has their favorite mode, or modes, usually focus on Cu-O planes

- In-Plane Mode:
- Out of Plane Modes:

At the level of phonon spectra, the anomaly of the Bond Stetching Mode is very large
Phonons in the Cuprates...

Everyone has their favorite mode, or modes, usually focus on Cu-O planes

In-Plane Mode:
- (0 0)
- (0.5 0)

Out of Plane Modes:
- Stretching mode
- Buckling Mode
- Apical Mode

At the level of phonon spectra, the anomaly of the Bond Stretching Mode is very large

Copper Oxide Superconductors Remain Challenging...

De-Twinned YBCO: YBa2Cu3O7-

\[ T_c = 91 \text{ K} \]

C-axis modes

In-Plane Modes

Beautiful Agreement

Compare IXS to Calculation

Problems

At low T (~30K) Bohnen, et al.

La1.48Nd0.4Sr0.12CuO4

Phonon anomaly (blurring) is highly localized in momentum space...

Expt done by a neutron scatterer because he could not get good enough resolution using neutrons

Forces a reinterpretation of some Neutron data (Reznik, Nature, 2006)

La1.48Nd0.4Sr0.12CuO4

Iron-Pnictide Superconductors

High-\( T_c \) demonstrated February 2008 (Hosono’s group)

(T\( _c \) saturated within months)

Several families: Fe with Tetrahedral As (or Se)

Proximity to Magnetic Order

Note: Analyzer array Count rate limited.
Phonons in the Iron Pnictides

Phonon response, in itself, is remarkably plain:
- NO very large line-widths
- NO obvious anomalies
- NO asymmetric Raman lines

Materials -> 8 Atoms/cell
- 24 Modes (6 mostly oxygen)

Magnetism -> 16 Atoms / 48 Modes
- No ab mirror plane
- Complex motions appear quickly as one moves away from gamma.

1111 Materials -> 8 Atoms/cell
- 24 Modes (6 mostly oxygen)

Magnetism -> 16 Atoms / 48 Modes
- No ab mirror plane
- Complex motions appear quickly as one moves away from gamma.

Basic DFT (GGA) for PrFeAsO
(No Magnetism)

Some agreement, but details are poor
Also, fails to get correct As height above the Fe planes.

Fe-As Bond Length
Expt: 2.41 Å
GGA: 2.31 - 2.33 Å

Some Examples of Measured Spectra:

Clear differences in measured spectra (with doping, temperature)
- interpretations requires modeling...

Different Models:

- Original: Straight GGA for Tetragonal stoichiometric PrFeAsO
- Soft: As /g15 Original but soften Fe-As NN Force constant by 30%
- O7/8: Super cell 2x2x1 with one oxygen removed
- and softened Fe-As NN Force constant
- (31 atoms/prim cell, Tetragonal, No Magnetism)
- Magnetic Orthorhombic: LSDA for LaFeAsO with stripe structure of De la Cruz (16 atoms/prim. cell, Tetragonal, 72 Ibam)
- Magnetic Tetragonal: LSDA for LaFeAsO with stripes
- Force a=b (to distinguish effects of structure vs magnetism)
- Soft: As “Original” but soften FeAs NN In Plane components
- Clipped: Mag. Ortho. with cut force constant
- Soft IP: “Original” but soften FeAs NN In Plane components

A Better Model is Needed
Compare dispersion with various models

Red = Data (SC)
Blue = Calc.
Size: Intensity

Over all: Better fit with magnetic calculations
And best fit with either “clipped” or “IP Soft” model

Comments

Of the straight ab-initio calculations, magnetic models do better than non-magnetic due to softening of ferrimagnetically polarized modes
However, they get details wrong, including too high an energy for AF polarized modes & predicting splitting that is not observed

Of the modified calculations, the in-plane soft generally seems best, but still data-calc difference are larger than doping/T effects.

Many people have suggested some sort of fluctuating magnetism, especially when magnetic calculations were seen to be better than non-magnetic calcs for the (non-magnetic) superconducting materials.

However, phonon response of parent and SC are nearly the same, and it seems unlikely that fluctuating magnetism is the answer in the parent material which shows static magnetism.

Still some missing ingredient(s) in the calculation → Interpretation Difficult

Towards A Better Model?

Fitting of full spectra: intensity vs energy transfer.

Zeroth Approximation: All Samples are the Same
Doping and Temperature Dependence are Weak
Differences between samples is generally much smaller than between any calculation and the data

→ Fit all spectra to a common model and then fit subsets of the data to determine effects of doping or phase transitions.

Fit Full Spectra

Some improvement by allowing parts of nearly all NN bonds to change.
Phonons in a Quasicrystal
Mostly like a solid but some glassy character.

Building a Quasicrystal (Zn-Mg-Sc)

Periodic (BCC) $\rightarrow$ Crystalline Approximant
Aperiodic $\rightarrow$ Quasicrystal

Compare to crystalline approximant & Simulation (2000 atoms/cell)

General Trend: Blurring out past a cutoff energy “Pseudo-Brillouin” zone size

De Boissieu, et al.
Nature Materials, Dec 2007

Ferroelectrics
Develop spontaneous polarization over macroscopic (~um) domains when T is below the ferroelectric transition temperature ($T_d$). The origin is a displacement (off-centering) of ions. This is switchable by an external (electric) field.

Zeroth Approximation $\rightarrow$ Two types of transitions

“Displacive” transition where there is a “continuous” below $T$

Soft Mode transition Examples: BaTiO$_3$, KTaO$_3$, Gd (MoO$_4$)$_3$

Order-Disorder transition where displacements occur first metastably and then condense. No soft mode.

Examples KH$_2$PO$_4$(KDP), NaNO$_2$, Organics

Ferrodistortive transition involves softening of gamma point mode (ferroelectric modes)

Antiferrodistortive involves softening of zone boundary mode (unit cell size increases)

Multiferroic EuTiO$_3$
Perovskite - Similar to SrTiO$_3$
But with magnetism & coupling of magnetic & dielectric response

Katsufuji & Takagi, PRB, 2001

Perovskite structure (ABO$_3$) popular as it is relatively simple and the cubic structure is inherently unstable. Why?

Lines & Glass
3 atoms & one lattice constant

Dispersion, Shell Model, & Approaching $T_N$

Katsufuji & Takagi, PRB, 2001

IXS $\rightarrow$ Phonon Softening $\rightarrow$ Displacive

Shell model $\rightarrow$ Good agreement Suggests “soft” mode has Slater character.

“Softening” (or weight shift) as T is reduced toward $T_N$ consistent with gradual change in dielectric response.
**IXS under High Pressure**

General Viewpoint: Just another thermodynamic variable.

Specific: elastic properties in extreme (geological) conditions based on IXS sound velocity measurements

Often: Just want the sound velocity

Precision/Accuracy: 0.2/0.8\% using Christoffel’s Eqn & 12 Analyzer Array

~1 Order Improvement in Precision Over Previous IXS

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**Diamond Anvil Cells**

P > 200 GPa
T > 2000K (Laser Heating)

Diamonds: 2 x 1.5mm Thk
Sample: \( \phi 20 \text{ mm} \times 5 \text{ mm} \) Thk
Also Gasket & Pressure Medium
P increases \( \rightarrow \) Smaller Sample & Gasket Hole

-Small samples, Signal low, Poor signal to noise

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**IXS Data for Iron at 167 GPa**

Very clear iron peak, but significant backgrounds
(Note diamond background can be tricky \( \rightarrow \) careful orientation is required)

Sine fit gives velocity (\( V_p \))
Birch's Law: Approximate Linear relation between density and velocity.

SIMPLE, in principle
- But 3 Facilities -> mostly different results
- SP8 is faster than ESRF and similar to APS
- ESRF recently became faster than before

T-Dependence:
- APS is sensitive.
- SP8 and ESRF are not.

Pure Iron to 170 GPa
Ohtani et al, submitted

Sound Velocity in Pure Iron

Using Thermal Diffuse Scattering (TDS)
Phonon Intensity ~ 1/ν -> In simple materials can use intensity to gain insight about phonon frequencies

Long history... at least to Colella and Batterman PR 1970 (Va dispersion)

More sensitive -> See Kohn anomalies when phonons span the Fermi surface

TDS from Silicon
Holt, et al, PRL 1999

Electronic excitations similar: Orbitons...

Correlated atomic motions (phonons) play a role in many phenomena (e.g. superconductivity, CDWs, phase transitions, thermoelectricity, magneto-elastic phenomena etc)

First Attempt via IXS: NJP 2004

Atomic Dynamics

Electronic excitations similar: Orbitons...

Key is to see momentum dependence (dispersion).
**d-d Excitations in NiO**

There exist well-defined excitations in the charge transfer gap of NiO.

Antiferromagnet \( T_N = 523 \text{K} \), \((111)\) Spin order

**Long and Distinguished History**

First (resonant) IXS experiments (Kao, et al)

Non-Resonant IXS, \( \Delta E \approx 300 \text{meV} \)


Cai, et al., BL12XU, Unpublished

**Orientation Dependence**

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

**First High Resolution Experiment**

7 meV resolution at 1800 meV energy transfer

Cleaner “Optical Spectroscopy” due to
1. Non-resonant interaction \( S(Q,w) \)
2. Large \( Q \) & \( Q \) dependence
   - selects multipole order.
   - atomic correlations.

Linewidth \( \rightarrow \) information about environment
Spin fluctuations
Lattice interactions (Franck-Condon)

**Larger Energy Range**

Hiraoka et al
“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 vs non-resonant IXS experiment.
Non-resonant experiment is simpler and can have higher resolution ... but badly flux limited

The Orbiton Story
(One, mostly experimental, viewpoint)

Essential picture is of a correlated d-d excitation - change in electronic wave function on one atom is correlated with change at other atoms.

LaMnO$_3$

But some dissent:
Two phonon peak?
Gruninger (n), Kruger (prl), Marin-Carron (prl)

And also corroboration
Raman spectra from different materials

Calculated Orbiton Dispersion

Calculated Dispersion

Still Some Debate:
Energy scale?
Coupling to phonons and/or spin?
Linewidth small or large?

Resonant IXS (RIXS)

K-Edge RIXS (d-d excitations)

Resolution Improving:
1000 → 250 meV → 70 meV

2011: STILL NO DISPERSING EXCITATIONS
Recent Work

LETTER
May, 2012

Spin-orbital separation in the quasi-one-dimensional Mott insulator Sr$_2$CuO$_3$

High Energy Excitation in Sr$_2$CuO$_3$

SIXS $\rightarrow$ Spin Waves Possible

X-Ray Raman Scattering


Tohji & Udagawa, PRB 39 (1989) 7590
X-Ray Raman Scattering

Suppose you would like to measure the structure of the oxygen k-edge (at 532 eV) of a sample inside of complex sample environment...

Diamond:
- \( I_{abs} \approx 0.5 \text{ um} 500 \text{ eV} \)
- \( I_{abs} \approx 2 \text{ mm} 10 \text{ keV} \)
- Easier at 10 keV than 0.5 keV

Supercritical Water
Ishikawa, et al, Submitted

Nuclear Inelastic Scattering

First Demonstrated (Clearly) by Seto et al 1995

\[
\begin{array}{cccc}
\text{Isotope} & \text{Transition energy (keV)} & \text{Lifetime (ns)} & \text{Alpha} \\
\text{^{16}_8^8O} & 6.21 & 8730 & 71 \\
\text{^{18}_8^8O} & 8.41 & 5.8 & 220 \\
\text{^{17}_9^3F} & 9.40 & 212 & 20 \\
\text{^{19}_9^3F} & 14.4 & 131 & 8.2 \\
\text{^{57}_27^7Co} & 21.5 & 13.7 & 29 \\
\text{^{56}_26^8Ni} & 22.5 & 10.4 & 12 \\
\text{^{150}_70^3Sm} & 23.9 & 25.6 & 5.2 \\
\text{^{151}_70^3Sm} & 25.6 & 40 & 2.5 \\
\end{array}
\]

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. \( E_{in} = E_{res} \)
2. \( E_{in} + E_{phonon} = E_{res} \)
3. \( E_{in} - E_{phonon} = E_{res} \)

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)
3. Resolution given only by monochromator
   (analyzer is \(~\text{meV}\))
   Easier optics but setup not optimized
   (compensated by large cross section)
Surfaces by NIS
The large nuclear cross section allows sensitivity even to monolayers with relatively low backgrounds.

In-Situ Deposition @ ESRF
Stankov et al., JP 2010

$^{57}$Fe on W(110)
Stankov et al. PRL (2007)

$^{57}$Fe with $^{56}$Fe
Slezak et al. PRL 2007

Also: Multilayers - Cuenya et al., PRB 2008

Example (NRVS/NIS/NRIXS) In Biology
S. Cramer, et al., JACS

Toxicity of Nitric Oxide (NO)

Measurement to determine the products of biological reactions via site-selective vibrational spectroscopy and comparison against calcs and model compounds.

A compound in the nitrogen cycle...
Is X present? How many irons?

Compton Scattering
For very large Q and $\Delta E < E$ one can take

$$ S(Q,\omega) = \frac{m}{\hbar Q} \int \rho(p_\omega = p_x) \int d\rho_x dy$$

Typical: $Q \approx 100 \AA^{-1}$
$E \approx 100$ keV

I.e.: Compton scattering projects out the electron momentum density.

Typical of incoherent scattering.

From Shülke

Three-Dimensional Momentum Density Reconstruction

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

$$ J(p_x) = \int n(p) dp_y dp_z$$

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

Momentum density, $n(p)$

Note: a bulk probe that is tolerant of sample imperfections.

From Y. Sakurai
Fermi surfaces of Cu and Cu alloys

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

Determined by Compton scattering at KEK-AR


Hole Locations in La$_{2-x}$Sr$_x$CuO$_4$

Sakurai, et al, Science 2011

Measured Results for Different Doping

- Parent vs Optimal Doping: Holes in ZR singlet state
- Optimal vs Overdoped: Holes in Cu dz$^2$ orbital

Cluster Calculations & Some density that is not yet understood

Band Structure Calculations

Reducing the Two-Theta Arm Size


Crystal Cube Array

Image

Energy Dispersion

Source

Animation

D. Ishikawa

5 meV at 16 keV

$d = \frac{4R^2}{p} \frac{\Delta E}{E}$

$R=2m, p=0.1 \rightarrow d=50 \text{ mm}$
**Temperature Gradient Analyzer**
(Ishikawa & Baron, JSR 2010)

- Longer Arm: $DT \approx 0.1 \text{C}$
- Short Arm: $DT: 1$ to $10 \text{C}$
- $\sim$ meV resolution at $3 \text{m}$
- $\sim 5 \text{ meV}$ at $1 \text{m}$

**A Nano-Volt Spectrometer**

Rayleigh Scattering of Synchrotron Mossbauer Radiation (RSSMR)


**Beyond Plane Waves**

Usual Measurement is a two-point correlation function:

$$S(Q, \omega) = \frac{1}{2\pi} \int d\omega \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \rho(x', t) \rho(x', t = 0) e^{i Q \cdot (x - x')}$$

Complete picture includes higher order correlation functions:

$$I(Q, \tau) / (Q', \tau') \propto \langle \rho(x', t) \rho(s, t) \rangle$$

- (A) Autocorrelation at One Q
- (B) Cross-Correlation, Different Q

Wochner et al, PNAS (2009)

Ps Scales
XFEL
Or
XFELO
**IXS Beamline Evolution**

For meV Resolution at 20 keV

**A Next Generation Beamline**

Dramatic Improvement to Source and Spectrometer allows new science...

- **New Field:** Electronic excitations
- **Also many expts now flux limited:**
  - Phonons in complex materials
  - Extreme environments (HT, HP liquids)
  - High pressure DAC work (Geology)
  - Excitations in metal glasses
  - Super-cooled liquids
  - etc

**Improvements**

- Flux On Sample: x10
- Parallelization: x3
- Small Spot Size: x5

**Quantum NanoDynamics Beamline**

(BL43LXU)

- High resolution spectrometer: <1 to 6 meV
- Medium resolution: 10-100 meV
- 10 m Arm, Good Q Resolution, to 12 Å⁻¹
- 2m Arm, Large Q Acceptance
- Large (42 element) analyzer array.

- Good tails using (888)
- High resolution: <1 to 6 meV (mono dependent)
- Dispersion compensation with Temperature Gradient keeps high resolution with large space near sample.
- Maximum momentum transfer ~15 Å⁻¹ (phase plate needed @ 90 Deg.)
- Solid Angle Gain: x25/Analyzer compared to high res spectrometer
- Commissioning to begin late in 2012

**Medium Resolution Spectrometer**

- Based on a 2m Arm & 3x3 Array Of Analyzers:
- Energy resolution: ~10 to 100 meV (mono dependent)
- Analyzers at Si(888) at 15.816 keV (reduced tails compared to lower order)
- Dispersion compensation with Temperature Gradient keeps high resolution with large space near sample.
- Maximum momentum transfer ~15 Å⁻¹ (phase plate needed @ 90 Deg.)
- Solid Angle Gain: x25/Analyzer compared to high res spectrometer
- Commissioning to begin late in 2012
Thanks for Your Attention!