Inelastic X-ray Scattering: Past, present and future

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NSLS-II Director

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Acknowledgements

• Alfred Baron
• Valentina Bisogni
• Yong Cai
• Mark Dean
• Joe Dvorak
• Ignace Jarrige
• Jungho Kim
• Young Lee

• All my collaborators over the years
Impossible talk

Merriam Webster:

Definition of *impossible*

: Felt to be incapable of being done, attained or fulfilled: insuperably difficult
Impossible talk

“Inelastic x-ray scattering: Past, present and future”

1) Past, present and future each deserve their own talks = 3 talks
2) Non-resonant inelastic x-ray scattering and resonant inelastic x-ray scattering should be separate topics x2
3) Hard x-ray RIXS and soft x-ray RIXS should be their own topics x2
4) Direct and indirect RIXS should be their own topics x2
5) Theory and experiment should be their own topics x2
6) Total of 48 talks or 1 min on each!

7) Guaranteed to offend everyone in this room!
Impossible Burger
Excitations

A complete picture of a system requires knowledge of both its ground state and the excitations.

*(in high-energy physics parlance: Vacuum and particles)*

Biologists: Normal modes of a protein, or lipid bilayer, or....
Excitation Spectrum

• Excitations determine the dynamic response of a system (response functions).
• IXS can study all these excitations over the relevant \((q, \omega)\) regime for condensed matter systems.
• Bosons can be responsible for more exotic behavior (pairing).
• Stringent test of theoretical descriptions of the system.
Cross-section

\[ \frac{d^2\sigma}{d\Omega d\omega} \propto \langle f | H_{\text{int}} | i \rangle + \sum_{|n|} \frac{\langle f | H_{\text{int}} | n \rangle \langle n | H_{\text{int}} | i \rangle}{E_i - E_n + \hbar \omega_i + i\Gamma} \]

Non-resonant scattering (weak)

- Phonons with ~ 1 meV resolution

Resonant scattering (strong at \( E_i = E_n \))

- Electronic excitations with ~20 meV resolution
Electronic Excitations
First work

First measurement of valence electron excitations (plasmons) in 1968 by Priftis, Theddossiou and Alexopoulos

Tour de force measurement

Sparked a decades long debate as to the origins of the corrections to RPA many body theory

Cr Tube source
\[ \Delta E \sim 4-5 \text{ eV} \]
Count rate = \( \sim 0.1 \text{ cps} \)

Phil Platzman’s contributions

Drove the heated debate between many-body effects vs band structure effects as the origin of discrepancies with RPA

Pushed for X21 at NSLS to be tunable around Ni K-edge leading to the discovery of hard RIXS in NiO

Driving force behind early RIXS studies of high-Tc compounds

Eisenberger, Platzman and Pandy PRL (1973)

Julie Cross IXS98
First RIXS experiments

The discovery in the late 1990’s of large (x 100) resonant enhancements in the IXS cross-section transformed the study of electronic excitations:


Instrumentation advances in soft and hard RIXS have paralleled each other:

**Soft x-ray**

- 1996: High resolution
- 2000: Moderate resolution

**Hard x-ray**

- 1999: Highest resolution
- 2000, 2006, 2007: Moderate resolution

Resolution: 20 meV vs. 10 meV
Mirrored by advances in RIXS theory

\[
\frac{d^2\sigma}{d\Omega d\omega} \propto \left| \langle f | H_{\text{int}} | i \rangle + \sum_n \frac{\langle f | H_{\text{int}} | n \rangle \langle n | H_{\text{int}} | i \rangle}{E_i - E_n + \hbar \omega_i + i\Gamma} \right|^2
\]

Joint DOS

Multiplets

Anderson impurity model

Hubbard model

Series expansion

Cluster exact diagonalization

Diagrammatics

Community tools

CTM4RIXS
Quanty
EDRIXS

Abbamonte (1999)
Kotani and Shin (2001)
Nomura and Igarashi (2004), (2005)
Van Veenendaal (2006)
Tohyama (2005)
Markiewicz and Bansil (2006)

Ament (2007)
Haverkort (2010)
Chen (2010)
Jia (2011)
Chen (2016)
De Groot
Key advances that powered these RIXS developments

For both hard and soft RIXS, several things contributed:

1. 3rd generation synchrotrons
   - APS, ESRF, SLS
2. Use of dispersive optics and area detectors
3. Dedicated, purpose-built instruments
   - Ex: MERIX (APS), ADDRESS (SLS), ID20 (ESRF)....
4. Theoretical advances relating the cross-section to $S(q, \omega)$ and understanding of polarization dependencies
   - V. d. Brink, v. Veenendaal, Devereaux, Haverkort, Igarashi, Maekawa...

S. Huotari et al. J. Syn. Rad (2005),
C. Dallera et al., J. Syn Rad (1996),
D. Casa, Y. Shvyd’ko, T. Gog...
First observations of magnons: $\text{La}_2\text{CuO}_4$

Soft RIXS: Cu L-edge

Hill et al., PRL (2008)

Hard RIXS: Cu K-edge

These results energized the field, inspiring theoretical studies and in particular many Cu L-edge studies of magnons in cuprates

Braicovich et al., PRL (2010)
Next steps for magnetic excitations

Sr$_2$CuO$_3$  \hspace{2cm} Sr$_2$IrO$_4$

Schlappa et al., Nature (2012)

Kim et al., PRL (2012)

These measurements made strong connection with $S(q,\omega)$
Latest soft RIXS

CaCuO$_2$

Role of apical oxygen

La$_{1.875}$Ba$_{0.25}$CuO$_4$

Charge spin coupling

Bi$_{2212}$


SC gap

Bi$_{2201}$

Peng et al., PRB (2018)

Polarization dep

Miao et al., PNAS (2017)
Latest hard RIXS

Ca$_3$LiOsO$_6$

Taylor et al., PRL (2017)

$J_{\text{eff}}=3/2$ state in osmates

Sr$_2$IrO$_4$

Porras et al., PRB (2019)

2 meV magnon gap

SrRu$_2$O$_6$

Suzuki et al., Nat Mat (2019)

Magnons in 4d oxide

Li$_2$IrO$_3$

Clancy et al., npj Quant. Mat (2018)

Collapse of $J_{\text{eff}}=1/2$ state with pressure
SIX at NSLS-II: Highest Energy Resolution

Scattered Beam

Sample

Incoming Beam

38° < 2θ < 150°

ΔE=22 meV at Cu L-edge

LiCuVO₄ O K-edge

Phonon resonant harmonics

Bisogni et al. (unpublished)
Magnetic excitations of a quantum spin liquid

Previous neutron scattering

Spinon continuum in herbertsmithite

Zn-barlowite \((\text{Cu}_{3.44}\text{Zn}_{0.56}\text{OH})_6\text{FBr})\) crystal measured at SIX

1.2 gram co-aligned crystal of herbertsmithite

Spin-1/2 Kagome lattice

RIXS at SIX
Rebecca Smaha et al. (*June 2019*).

Charge transfer

Multi-spinon continuum

\(dd\) excitations

0.6 mm ~ 0.001 gram

Unpublished data

Young Lee group (Stanford and SLAC), SIX beamline team, NSLS-II
Atomic excitations
First Phonon measurements

Optical phonon mode in pyrolytic graphite in the hexagonal plane measured by INELAX

$\Delta E = 47 \text{ meV}$
$10^6 - 10^7 \text{ ph/s/meV}$

Dorner & Peisl, N. Instr. & Meth. 208, 587 (1983)
Burkel, Peisl & Dorner, EPL 3, 957 (1987)
Acoustic modes in disordered systems


Water

Observation of fast sound

ΔE = 1.5 meV
2x10^8 ph/s

Glycerol

Measurement of propagating modes led to improved microscopic understanding of the dynamics in glasses

Optical phonons and the CDW transition in YBa$_2$Cu$_3$O$_{7-\delta}$

Apply strain to drive the 3D CDW transition and observe a softening of an optical phonon

Kim et al., Science (2019)
Bond-Stretching Phonon: Optimally Doped YBa$_2$Cu$_3$O$_{7-\delta}$

T-Dependence: Broadening turns on at $T_c$

$10^{10}$ ph/s/meV with $\Delta E < 2$ meV

Flux/meV/ Resolution is $5 \times 10^4$ improvement from INELAX days!!

A. Baron & S. Tajima, et al. unpublished

Anomalous phonon behavior observed through $T_c$
Number of IXS papers continues to grow rapidly...

"inelastic x-ray scattering" papers

~ 180 papers/year
...as do their citations

Citations for "inelastic x-ray scattering"

~ 5000 citations/year
In which fields is IXS having impact?

Top 30 papers: 6 of which are technique reviews or instrumentation

**Graphite**
- Phonons: Mohr (2007) 271 citations
- Phonons: Lazzeri (2008) 192 citations
- Phonons: Bosak (2007) 169 citations
- Electronic b.s.: Carlisle (1995) 150 citations

**Hi Pressure**
- Iron: Mao (2001) 219 citations

**Other**
- TM complexes: Glatzel (2005) 541 citations
- Phonons: Fultz (2010) 248 citations
- Cathodes: Luo (2016) 208 citations

**Amorphous systems**
- Glasses: Sette (1998) 275 citations
- Fluids: Simeoni (2010) 192 citations
- Silica: Foret (1996) 183 citations
- Silica: Benassi (1996) 171 citations
- Water: Sette (1996) 143 citations

**Strongly correlated systems**
- Oxides: Kotani (2001) 552 citations
- Iridate: Kim (2012) 272 citations
- Fe$_2$O$_3$: Vayssieres (2005) 249 citations
- Cuprates: LeTacon (2011) 225 citations
- Cuprate: Braicovich (2010) 163 citations
- Cuprate: Schlappa (2012) 157 citations

Top 30 papers: 6 of which are technique reviews or instrumentation.
Inelastic neutron scattering impact

Top 30 papers, by citation. No technique reviews or instrumentation papers

<table>
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<tr>
<th>MOFs</th>
<th>Quantum magnetism and high Tc</th>
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<tr>
<td>Science</td>
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<td>J. Phys Cond Mat</td>
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Other

- Molecular magnets: 2175 citations
- Proton conduction: 1609 citations
- Myoglobin: 936 citations
- Discrete breathers: 913 citations
- Spin clusters: 718 citations
- Nano particles: 568 citations
- Semiconductors: 501 citations
- Spin clusters: 557 citations
- Ferro: 536 citations
- STO: 521 citations
IXS and INS

Complimentary techniques, providing similar information, but IXS has some real advantages:

• Requires (much) small samples
• Probe of electronic excitations
• Energy and momentum resolution decoupled. No multiple scatt effects
• Can work in applied fields, high pressure
• Can look at high energy transfers
• No need to deuterate
• ...

So, why less impact?

1) Number of spectrometers in the world
2) Difficulty in making the experiments work
3) Resolution hasn’t been well matched to problems of interest
4) Difficulty in obtaining appropriate analyzers for resonant edges

1) – 4) have all gotten much better in recent years. Expect IXS to diversify problems tackled and to have increased impact in the coming years...
Free electron lasers

- Non-equilibrium & time resolved
- V. high time-averaged flux (SR x 10^4)
- Stimulated RIXS, non-linear effects?

See Chi-Chang Kao’s talk Friday

M. Beye et al., Nature (2013)

Fletcher et al. (2013)
Time-resolved RIXS

“killer app” will be measuring spin-wave dispersions following a pump pulse (optical, IR, MIR, THz) to obtain a movie of $\mathcal{H}(t)$

Example question:
- How does the excitation spectrum of a transient superconductor differ from the equilibrium one?

Dean et al., Nat Mat (2018)

Chen et al., PRB (2019)

TR-RIXS theory being worked on:
Challenges and future directions for SR IXS

Storage rings maintain crucial advantages for IXS

• Ability to have large, dedicated spectrometers
• Large amounts of beamtime for complex expts

• Push to $\Delta E \sim 1\text{meV}$ for soft and hard RIXS
• Make polarization analysis routine in soft and hard RIXS
• Add nano diffraction capability
• Expand sample environments: Magnetic field, electric field, ultra low temperatures....
• Non-equilibrium (ns and longer)

See Thomas Gog’s talk Friday
Soft RIXS – what is next?

1. Combine with ARPES
2. Add spatial resolution

• Proposed “ARI” beamline at NSLS-II

3. Achieve $\Delta E=1$ meV

• Achieve 3 meV with 2nd order gratings and improved slope errors and detector resolution (x2.5)
• 1 meV also requires multilayer gratings in higher order

J. Dvorak et al.
Hard RIXS: towards 1 meV..

Analyzer resolution \( \Delta E = 3.9 \) meV

Builds on earlier work on quartz: Sutter et al. (2006)

Summary

• It has been 50 years of enormous advances, driven by the work of many in instrumentation, sources and theory
• Technique has matured: “it is not the beginning of the end, but the end of the beginning”
• FELs will be disruptive – in some areas
• Synchrotrons will remain the mainstay of the field
• Expect IXS to have major impact in the next decade across a range of disciplines
Back up slides
Comparison with Inelastic Neutron Scattering

"INELASTIC NEUTRON SCATTERING" PAPERS


350 papers/yr

CITATIONS OF "INELASTIC NEUTRON SCATTERING"


14,000 citations/year
FELs

Al