National Synchrotron Light Source II

Inelastic X-ray Scattering: Past, present and future

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NSLS-II Director

IXS2019 June 24th 2019

U.S. DEPARTMENT OF ENERGY | Office of Science

BROOKHAVEN NATIONAL LABORATORY

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*)

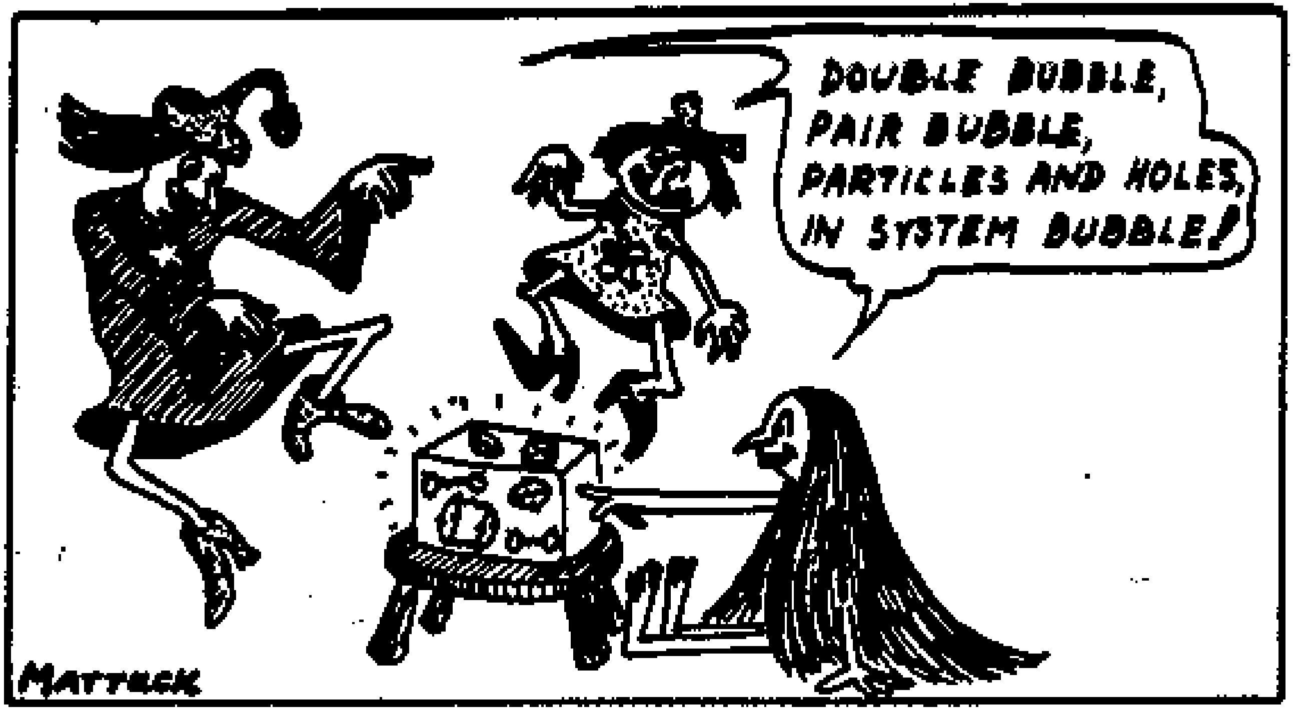
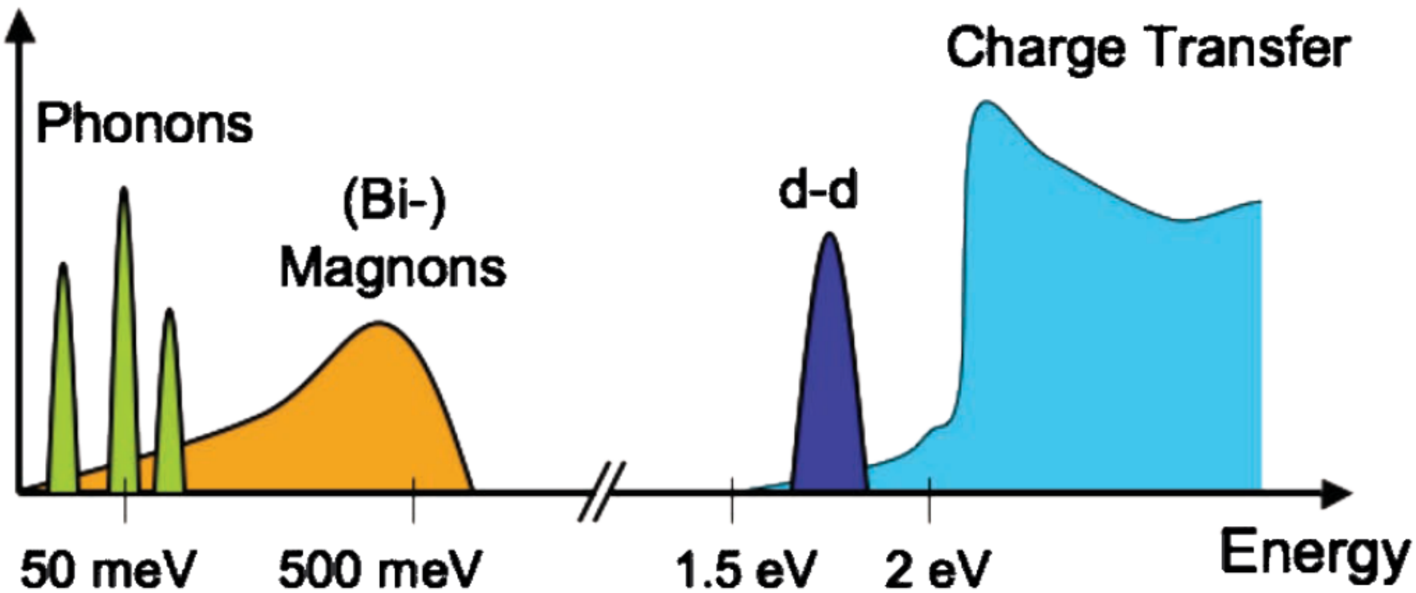


Fig. 1.5 ***Modern View of a Many-body System in its Ground State***

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

Excitation Spectrum

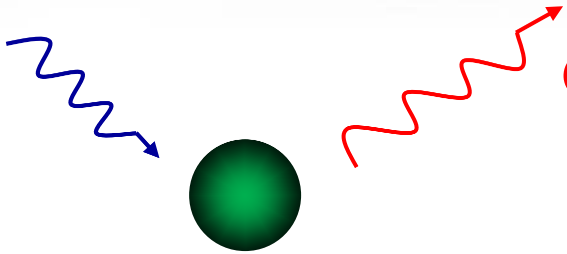


- Excitations determine the dynamic response of a system (response functions)
- Bosons can be responsible for more exotic behavior (pairing)
- Stringent test of theoretical descriptions of the system

IXS can study all these excitations over the relevant (**q**,ω) regime for condensed matter systems

Cross-section

ω_i, k_i



ω_f, k_f

$q = k_i - k_f$

$\omega = \omega_i - \omega_f$

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

Non-resonant scattering (weak)

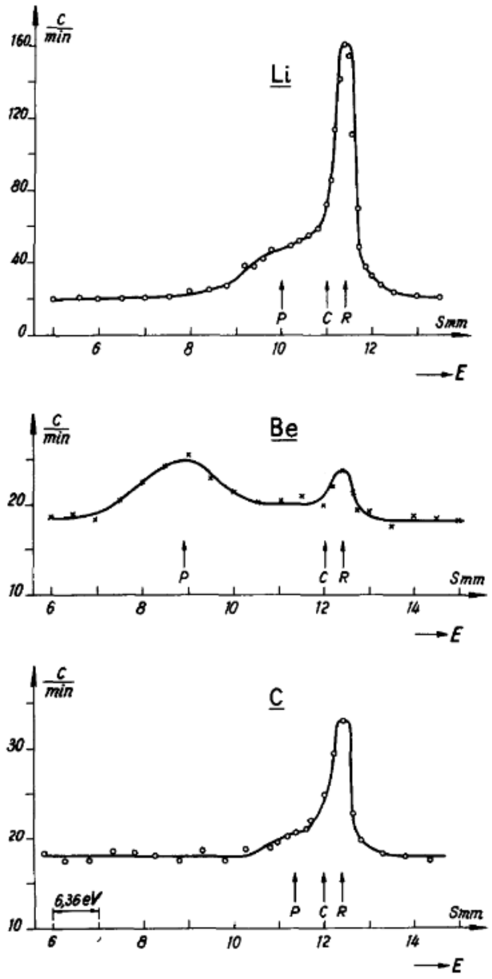
Resonant scattering (strong at $E_i = E_n$)

Mostly → Phonons with ~ 1 meV resolution

Mostly → Electronic excitations with ~20 meV resolution

Electronic Excitations

First work



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

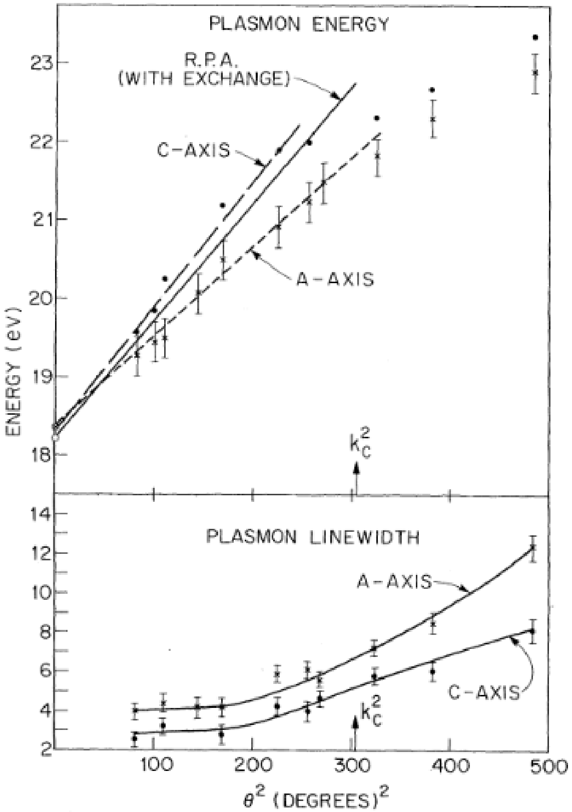
Tour de force measurement

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

Cr Tube source
ΔE ~ 4-5 eV
Count rate = ~0.1 cps

Priftis *et al.*, Phys. Lett A (1968)

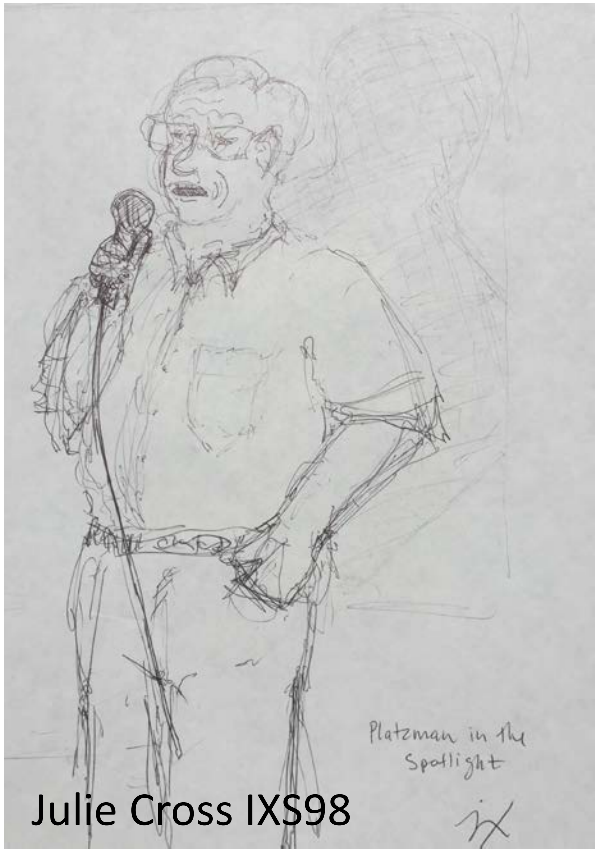
Phil Platzman's contributions



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

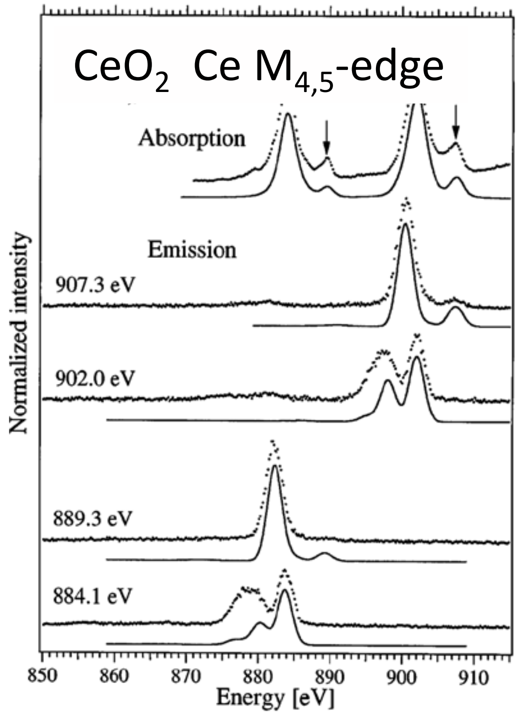


Eisenberger, Platzman and Pandy PRL (1973)

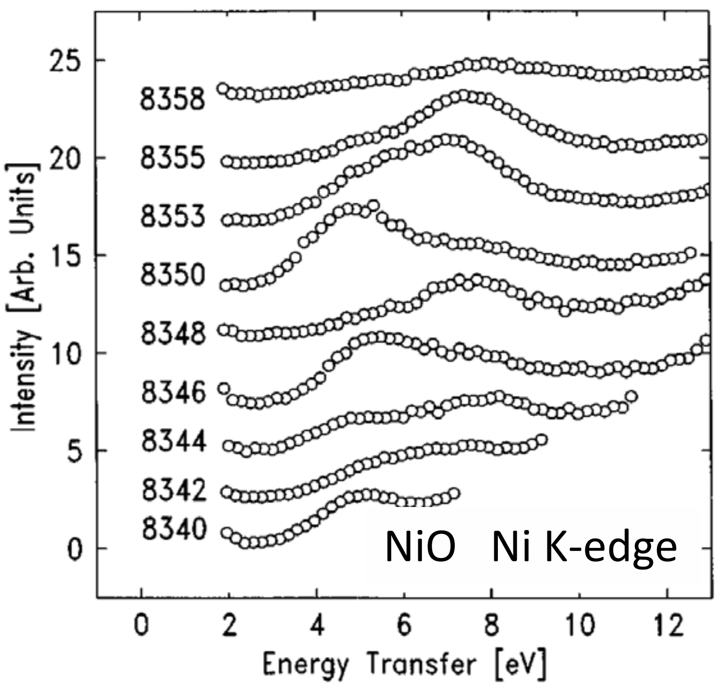
First RIXS experiments

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

Soft RIXS



Hard RIXS

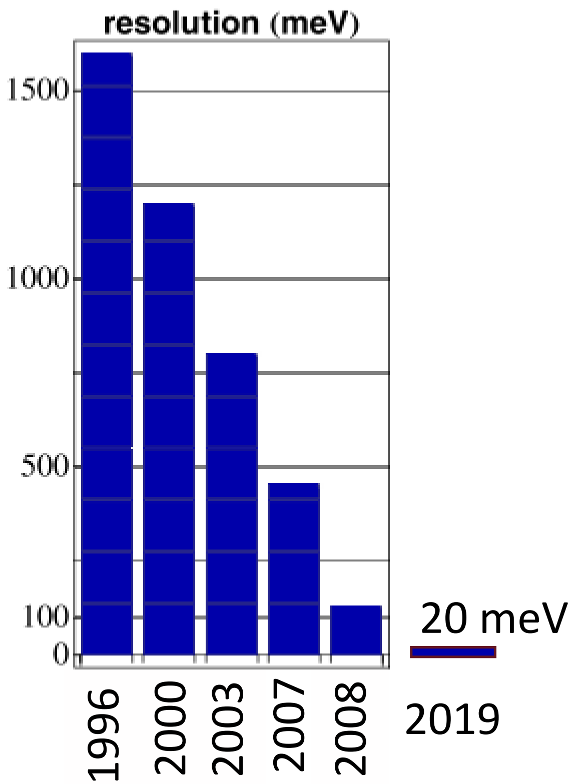


S.M. Butorin *et al*., Phys. Rev. Lett. (1996)

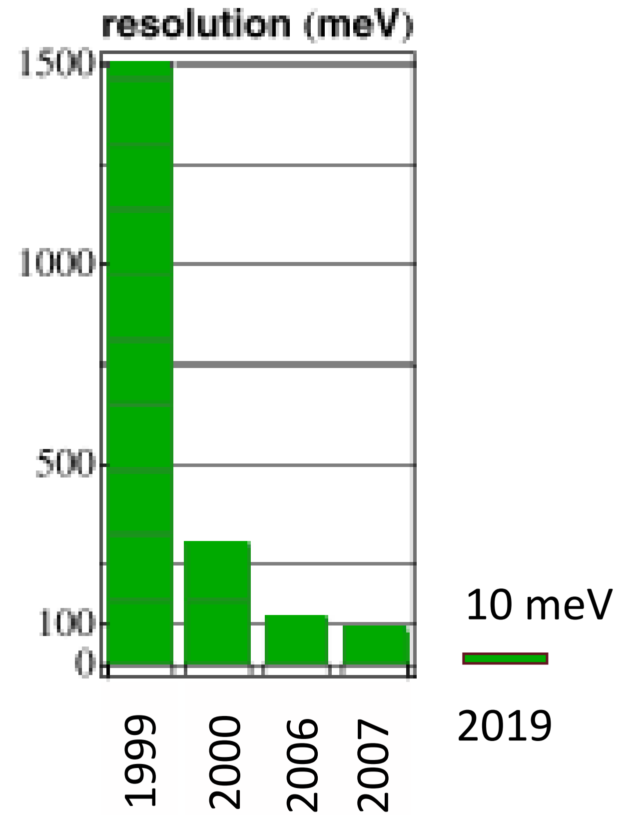
C.-C. Kao *et al*., Phys. Rev. B (1996)

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

Soft x-ray

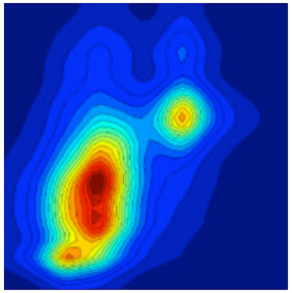


Hard x-ray



Mirrored by advances in RIXS theory

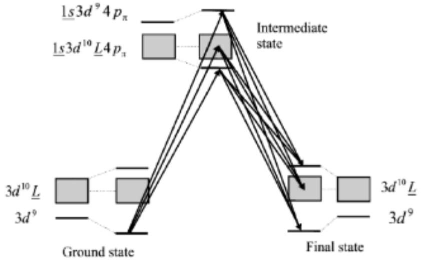
Multiplets



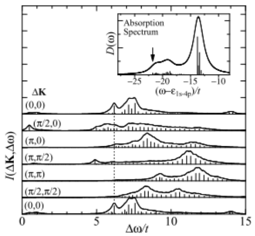
Joint DOS

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

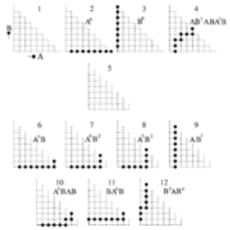
Anderson impurity model



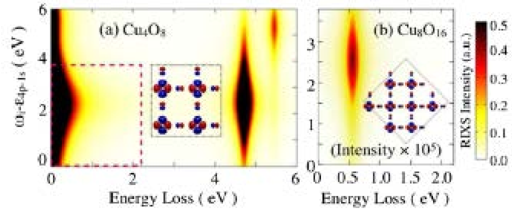
Hubbard model



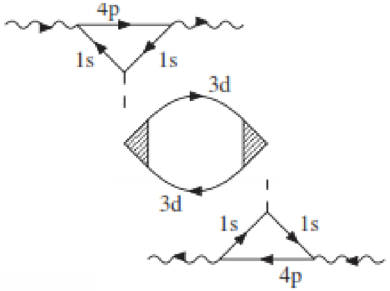
Series expansion



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)

V. d. Brink and v. Veenendaal (2005), (2006)

Ament (2007)

Haverkort (2010)

Chen (2010)

Jia (2011)

Chen (2016)

De Groot

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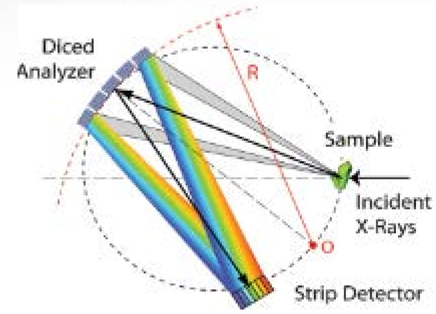
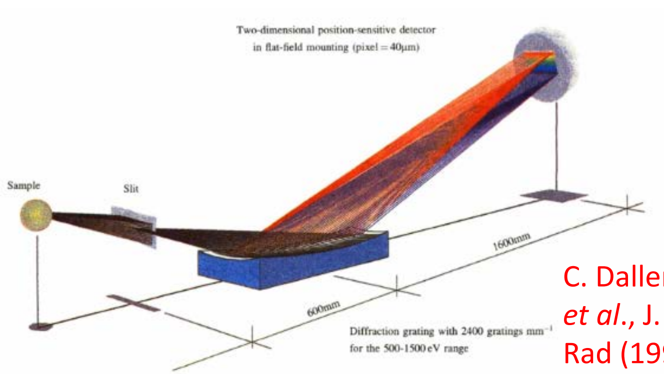
Key advances that powered these RIXS developments



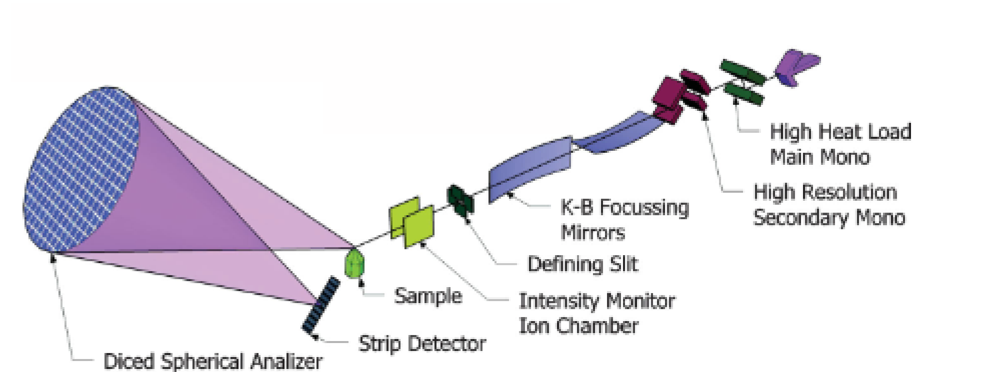
S. Huotari *et al*. J. Syn. Rad (2005),

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,ω) and understanding of polarization dependencies
   V. d. Brink, v. Veenendaal, Devereaux, Haverkort, Igarashi, Maekawa…



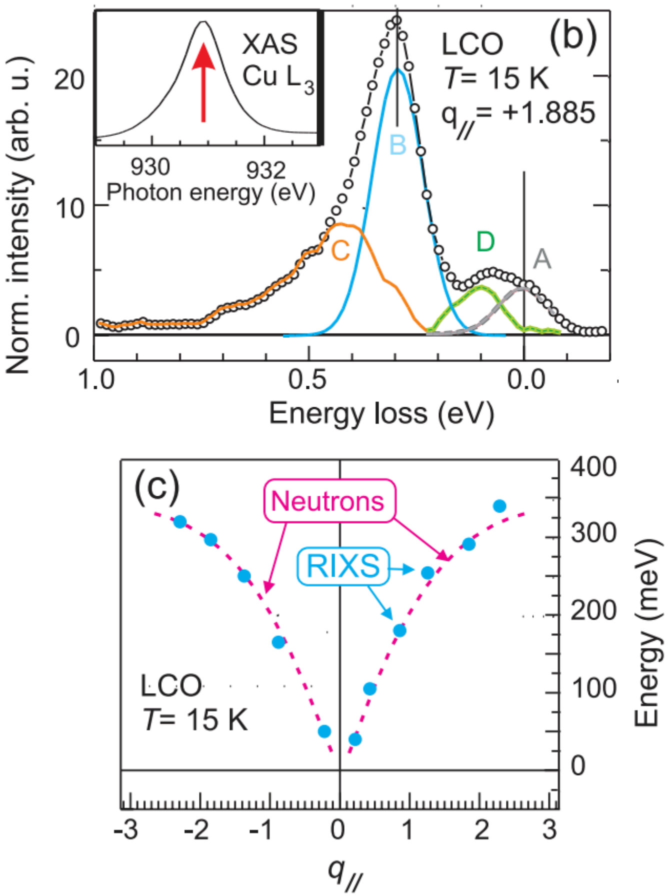
C. Dallera *et al*., J. Syn Rad (1996)



D. Casa, Y .Shvyd'ko, T. Gog…

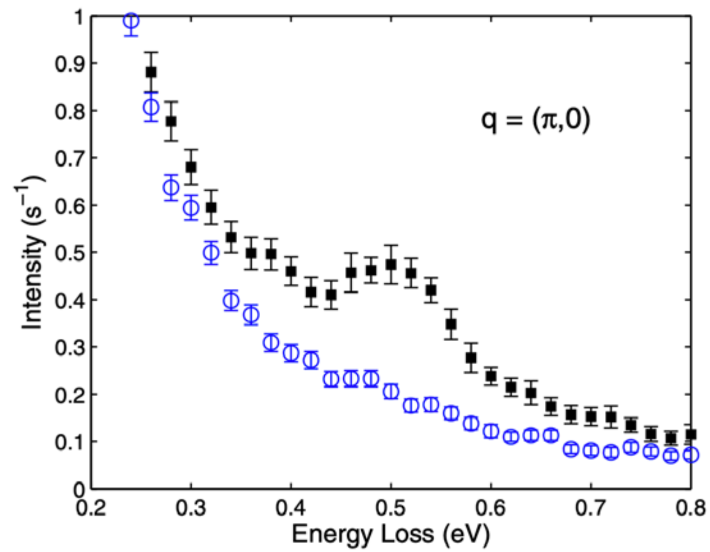
First observations of magnons: La_2CuO_4

Soft RIXS: Cu L-edge



Braicovich et al., PRL (2010)

Hard RIXS: Cu K-edge



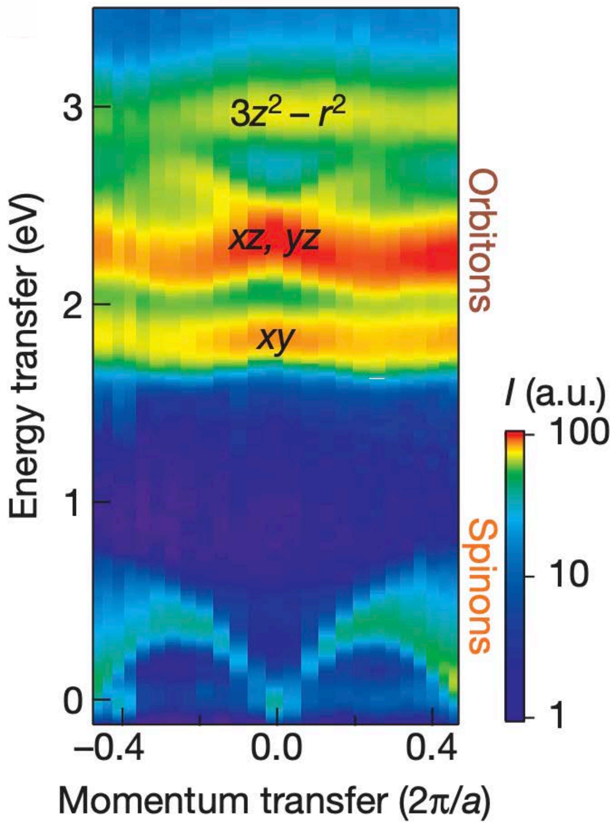
Hill et al., PRL (2008)

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

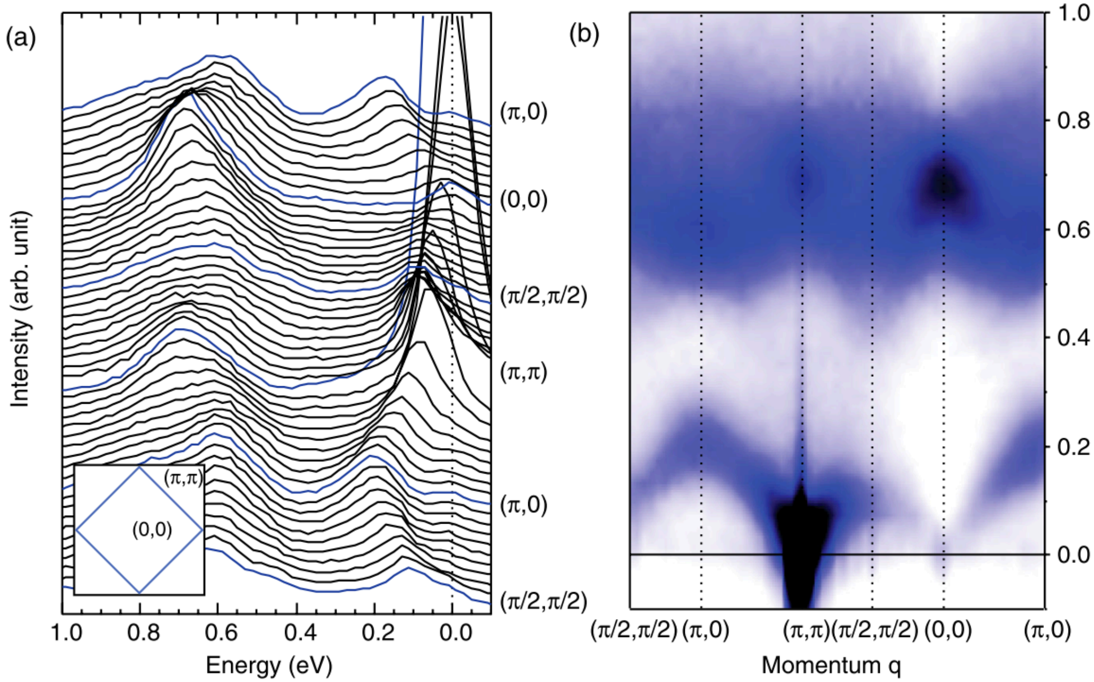
Next steps for magnetic excitations

Sr_2CuO_3

Sr_2IrO_4



Schlappa *et al*., Nature (2012)

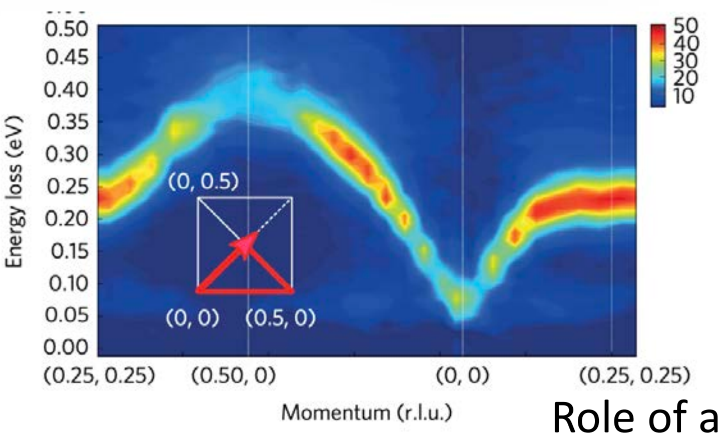


Kim *et al*., PRL (2012)

These measurements made strong connection with S(q,ω)

Latest soft RIXS

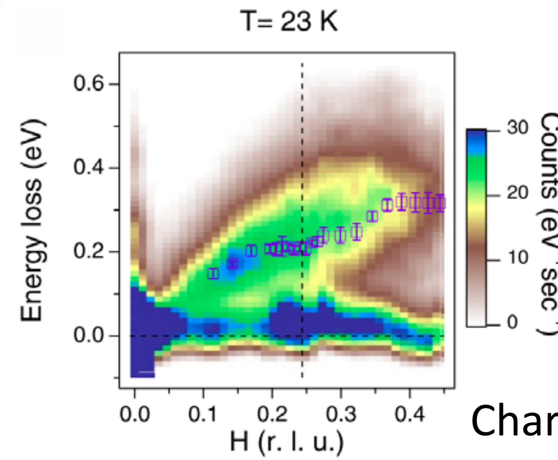
$CaCuO_2$



Peng *et al.*, Nature Physics (2017)

Role of apical oxygen

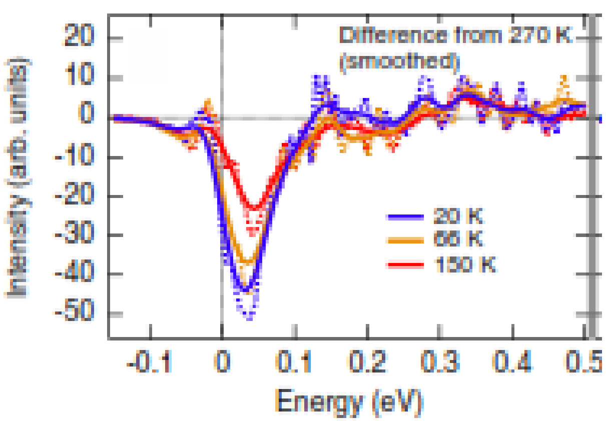
$La_{1.875}Ba_{0.25}CuO_4$



Miao *et al.*, PNAS (2017)

Charge spin coupling

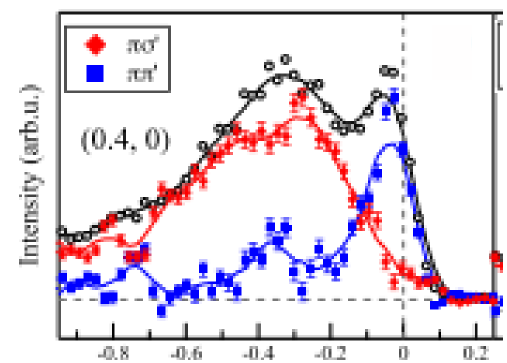
Bi2212



Suzuki *et al. npj Quantum mat. (2018)*

SC gap

Bi2201

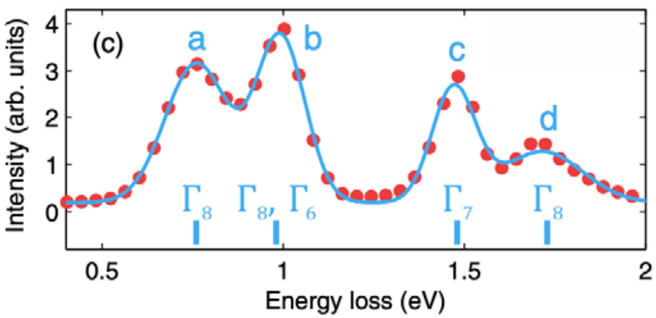


Peng *et al.* PRB (2018)

Polarization dep

Latest hard RIXS

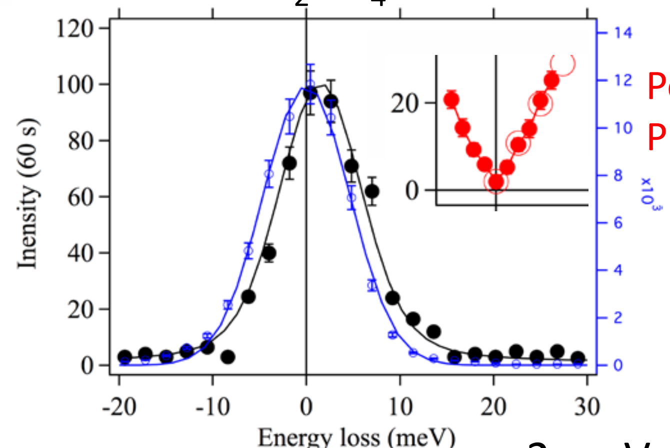
Ca_3LiOsO_6



Taylor *et al.*, PRL (2017)

J_{eff}=3/2 state in osmates

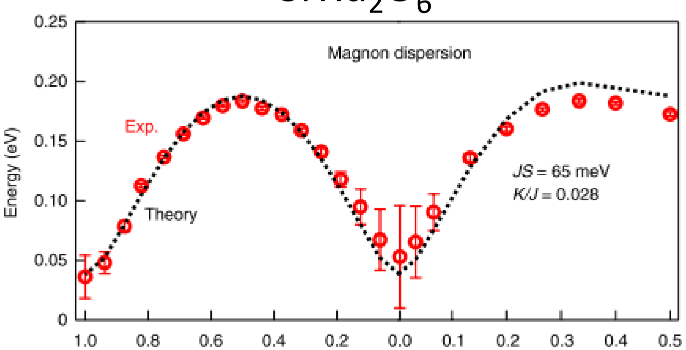
Sr_2IrO_4



Porras *et al.*, PRB (2019)

2 meV magnon gap

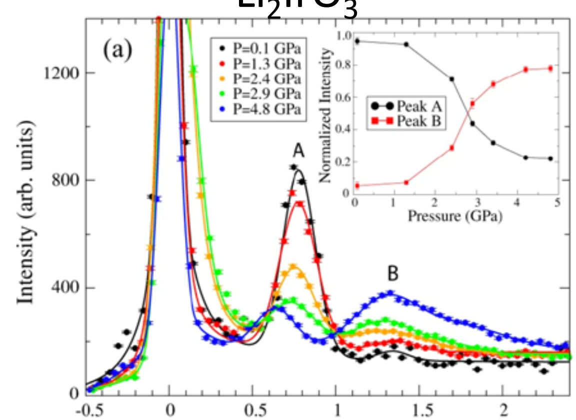
$SrRu_2O_6$



Suzuki *et al.*, Nat Mat (2019)

Magnons in 4d oxide

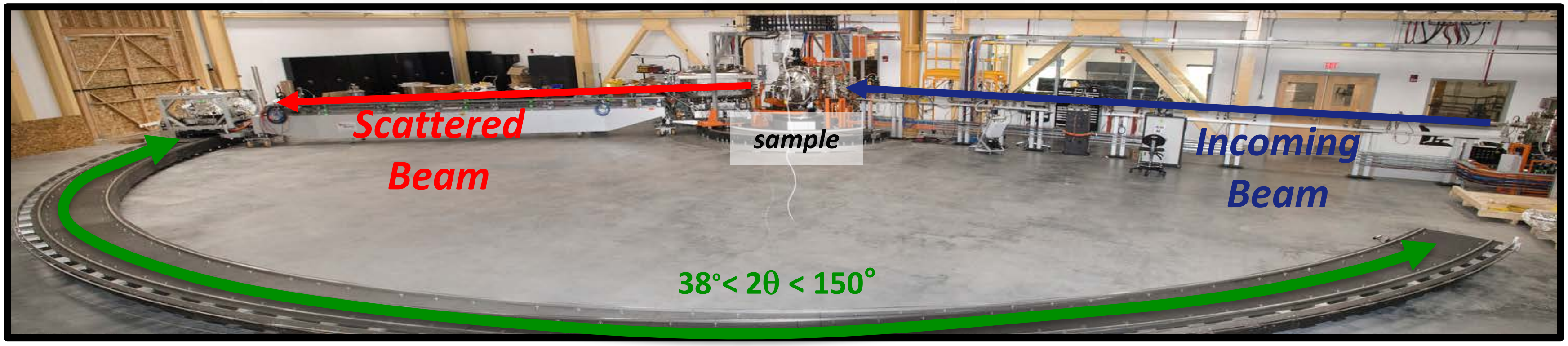
Li_2IrO_3

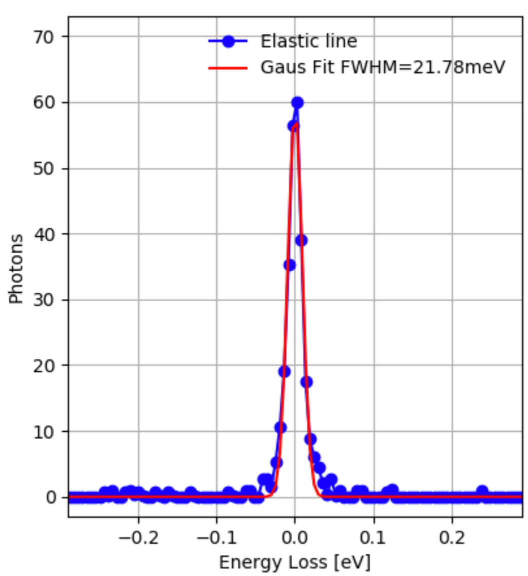


Clancy *et al.*, npj Quant. Mat (2018)

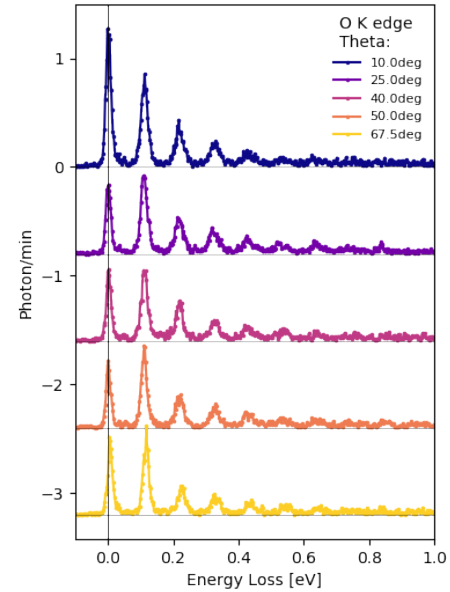
Collapse of J_{eff}=1/2 state with pressure

SIX at NSLS-II: Highest Energy Resolution





ΔE=22 meV at
Cu L-edge



$LiCuVO_4$
O K-edge

Phonon resonant harmonics

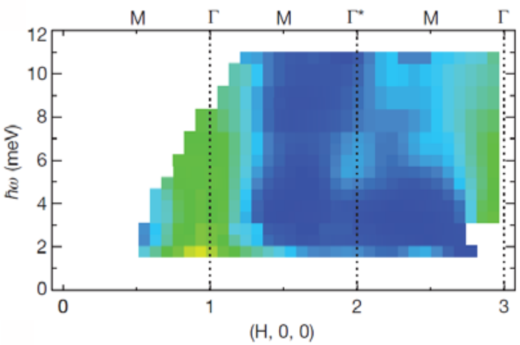
Bisogni *et al.*
(unpublished)

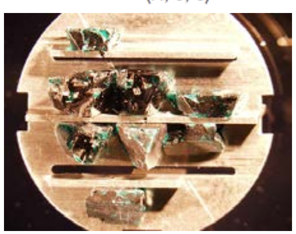
Magnetic excitations of a quantum spin liquid

Previous neutron scattering

Spinon continuum in herbertsmithite

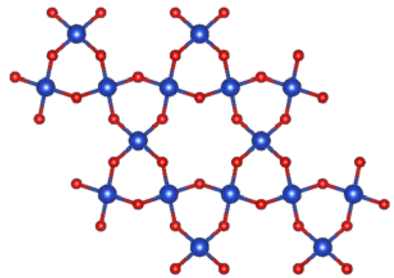
T.-H. Han *et al.* *Nature* **492**, 406-410 (2012)





1.2 gram co-aligned crystal of herbertsmithite

Spin-1/2 Kagome lattice

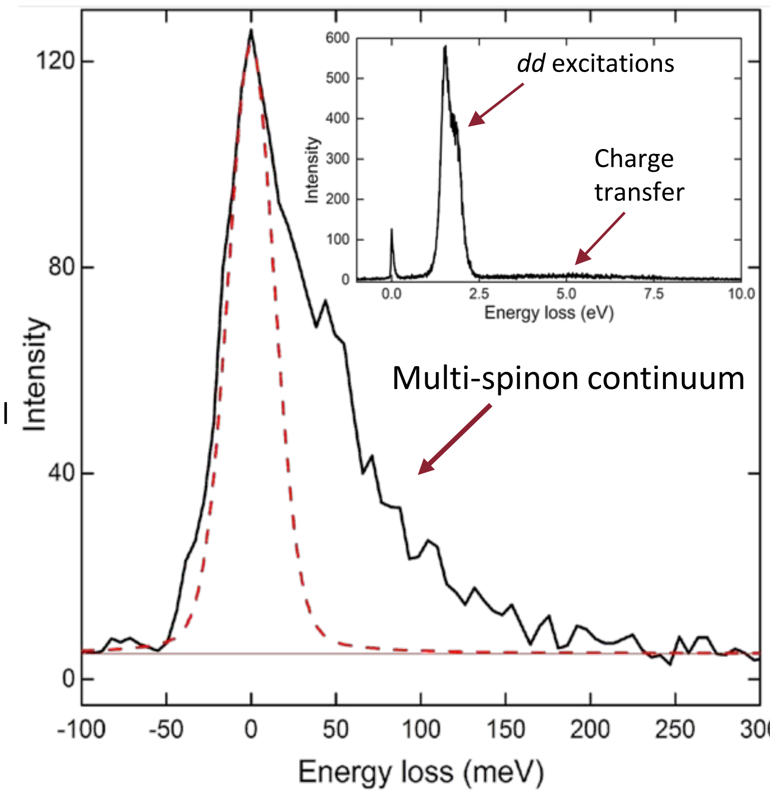


Zn-barlowite ($(Cu_{3.44}Zn_{0.56}OH)_6FBr$) crystal measured at SIX

0.6 mm
~ 0.001 gram

RIXS at SIX

Rebecca Smaha *et al. (June 2019)*.



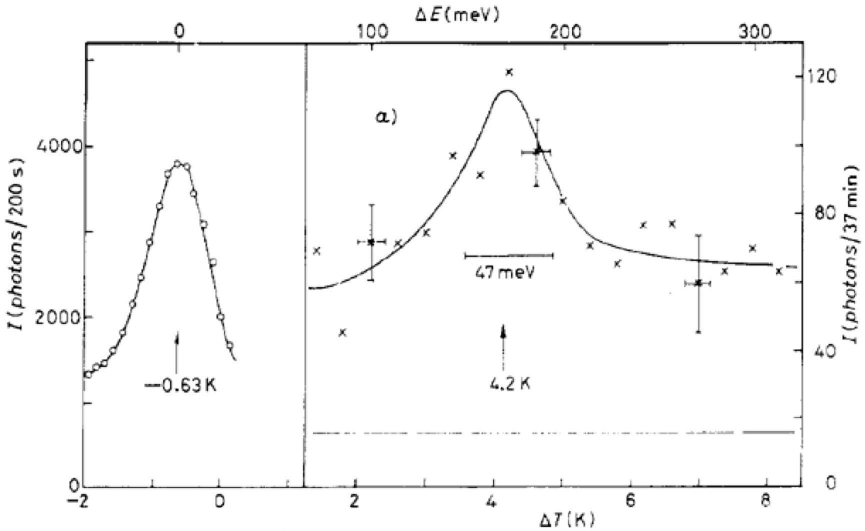
Unpublished data

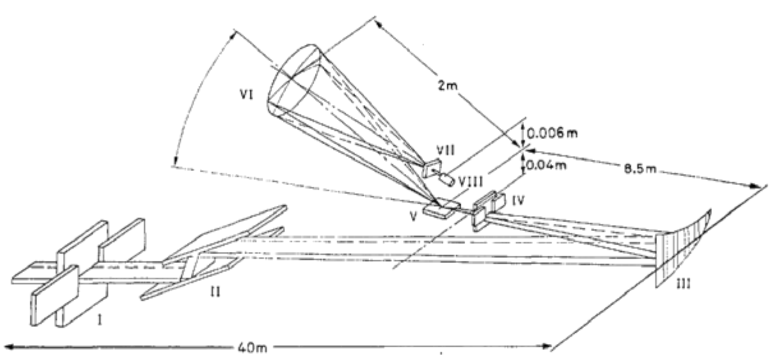
Young Lee group (Stanford and SLAC), SIX beamline team, NSLS-II

Atomic excitations

First Phonon measurements

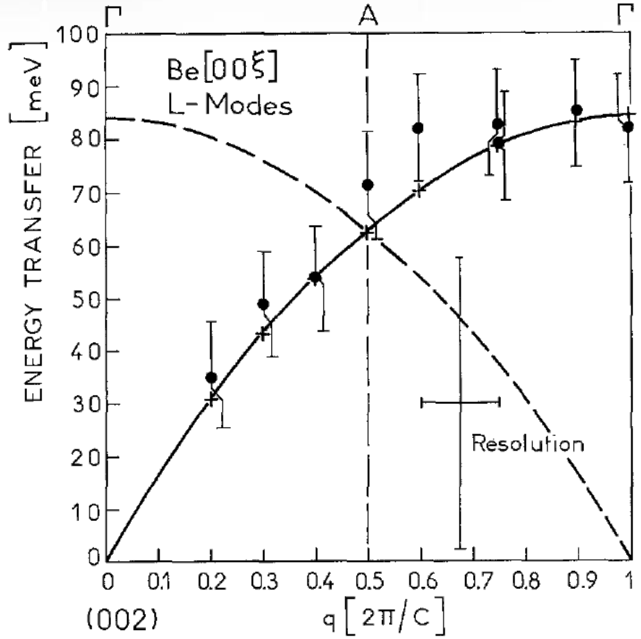
Optical phonon mode in pyrolytic graphite in the hexagonal plane measured by INELAX





INELAX @ HASYLAB

1^{st} Phonon dispersion in Be by INELAX



ΔE = 47 meV

$10^6 – 10^7$ ph/s/meV

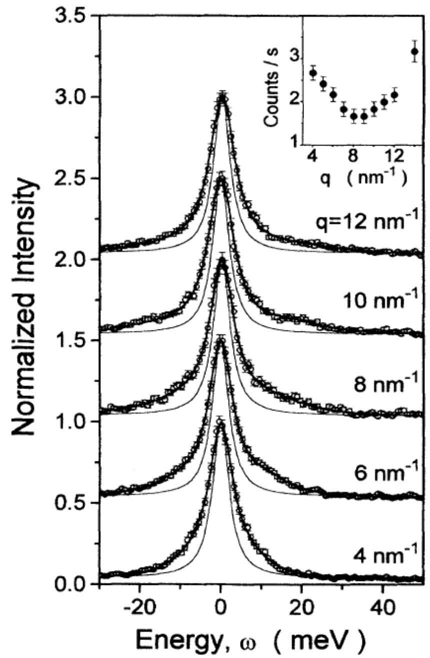
Dorner & Peisl, N. Instr. & Meth. 208, 587 (1983)

Burkel, Peisl & Dorner, EPL 3, 957 (1987)

Dorner et al, Z. Phys. B 69, 179 (1987)

Acoustic modes in disordered systems

Water



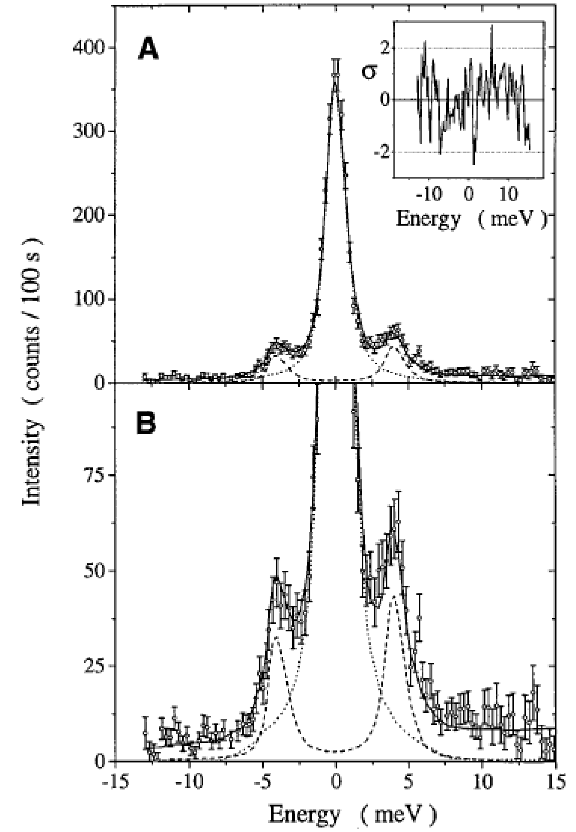
Sette *et al*, PRL (1995)

Observation of fast sound

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

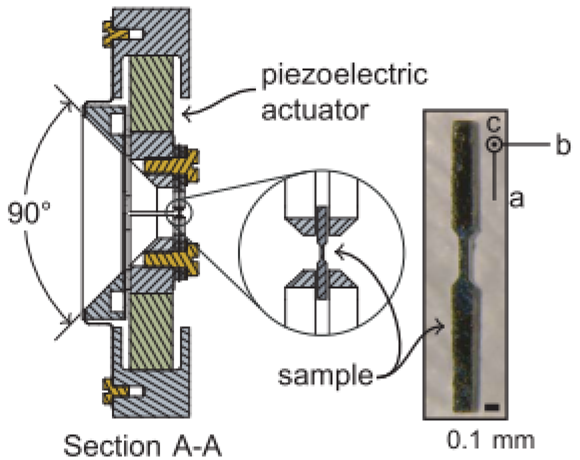
ΔE = 1.5 meV
$2x10^8$ ph/s

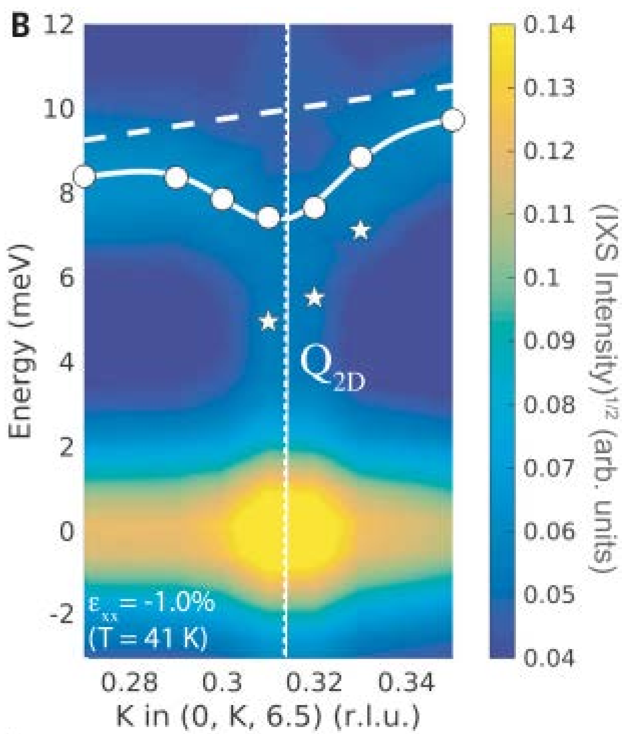
Glycerol



Sette *et al*, Science (1998)

Optical phonons and the CDW transition in $YBa_2Cu_3O_{7-\delta}$

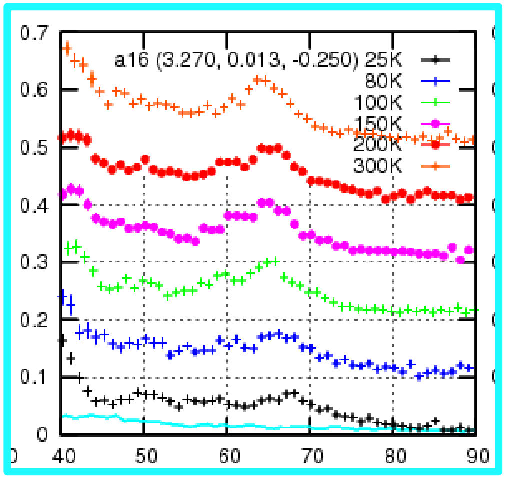




Kim *et al., Science (2019)*

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

Bond-Stretching Phonon: Optimally Doped $YBa_2Cu_3O_{7-\delta}$

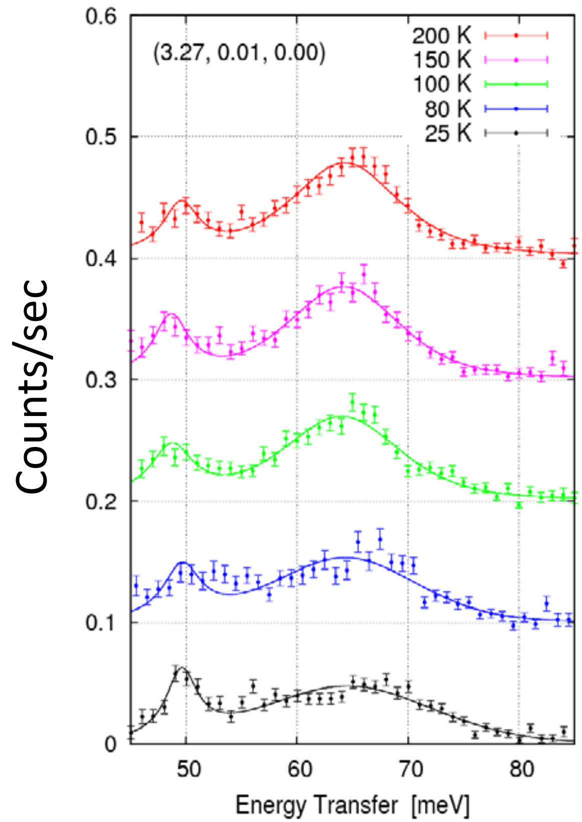


BL43LXU <24 hours/trace

10^{10} ph/s/meV with ΔE < 2 meV

Flux/meV/ Resolution is 5 x 10^4 improvement from INELAX days!!

T-Dependence: Broadening turns on at T_c



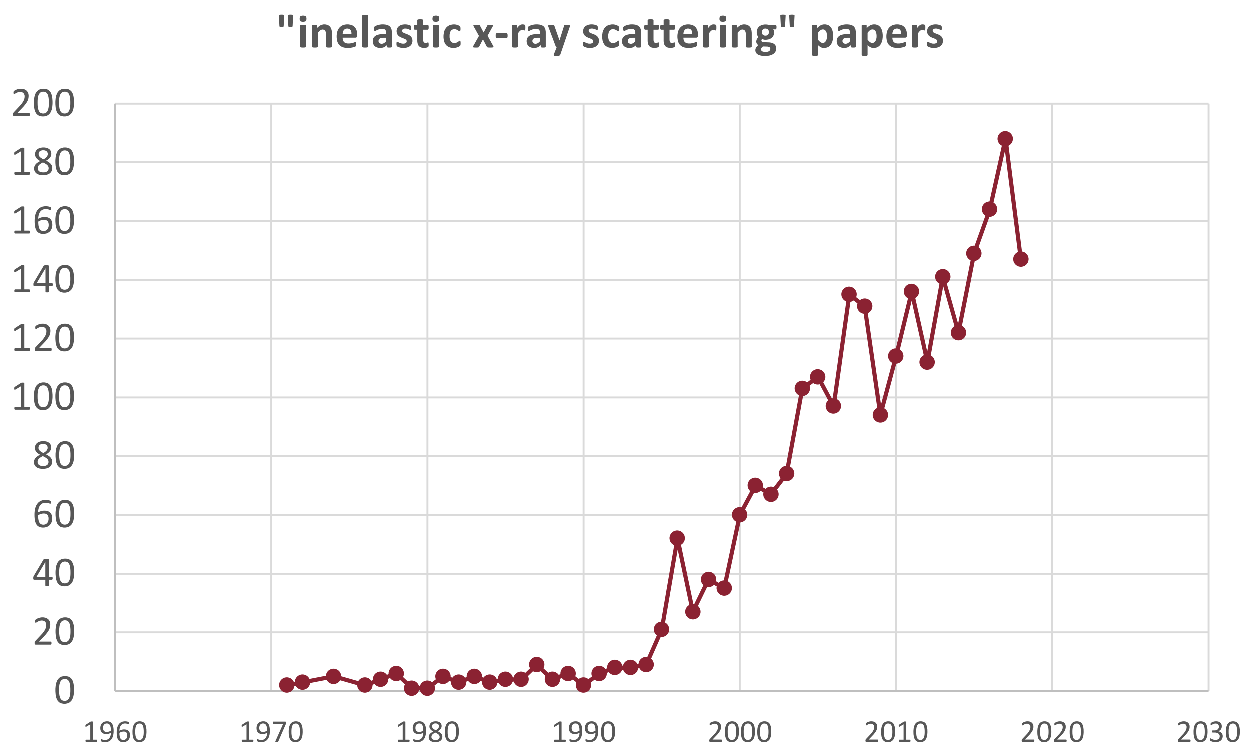
(tails of low-energy modes subtracted)

Anomalous phonon behavior observed through Tc

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

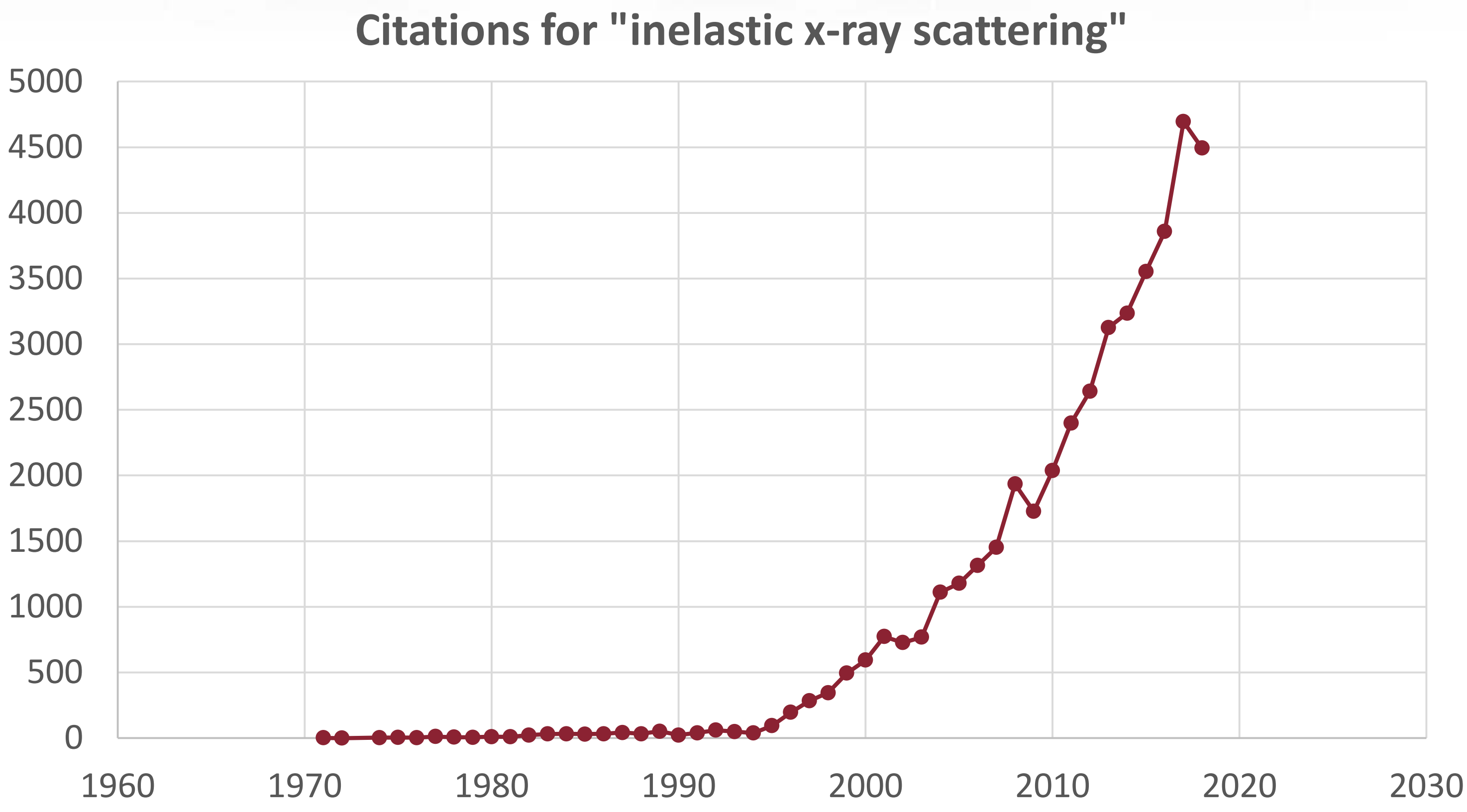
FUTURE

Number of IXS papers continues to grow rapidly…



~ 180 papers/year

…as do their citations



~ 5000 citations/year

In which fields is IXS having impact?

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

Graphite

Phonons : Maulzsch (2004)	354 citations
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
Iron: Badro (2007)	157 citations

Other

TM complexes: Glatzel(2005)	541 citations
Phonons: Fultz (2010)	248 citations
Cathodes: Luo (2016)	208 citations
Iron pnictides: Wang (2009)	151 citations

Amorphous systems

Glasses: Sette (1998)	275 citations
Water: Sette (1995)	202 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_2O_3: Vayssieres (2005)	249 citations
Cuprates: LeTacon (2011)	225 citations
Cuprate: Hasan (2000)	173 citations
Cuprate: Braicovich (2010)	163 citations
Cuprate: Schlappa (2012)	157 citations

Inelastic neutron scattering impact

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

MOFs

Science	3445 citations
Chem Soc Rev	3200 citations
Chemical comm.	835 citations
JACS	561 citations
Ange Chem Int	518 citations

Glasses and liquids

Science	3118 citations
J. Phys. Chem	1619 citations
J. Appl. Phys	1470 citations
J. Phys Cond Mat	662 citations

Quantum magnetism and high Tc

RMP	1038 citations
RMP	937 citations
PRL	697 citations
Physica C	685 citations
PRL	527 citations
PRL	508 citations

Graphite and Fullerines

RMP	807 citations
PRB	564 citations

H2 absorption

Chem reviews	602 citations
Ange Chem Int	602 citations

Other

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

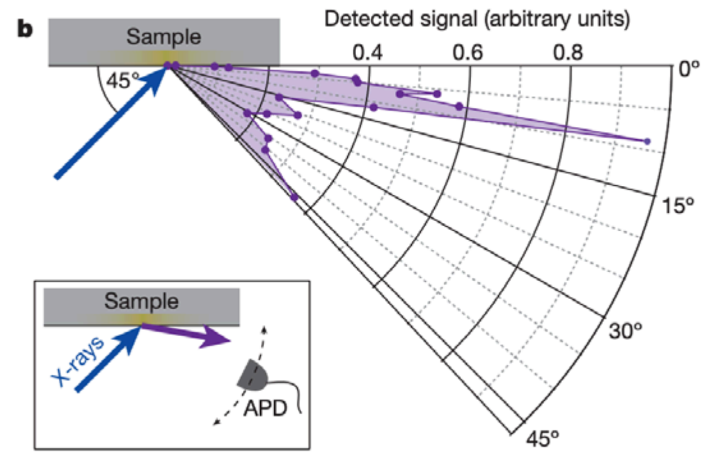
1) Number of spectrometers in the world
2) Difficulty in making the experiments work
3) Resolution hasn't been well matched to problems of interest
4) Difficulty in obtaining appropriate analyzers for resonant edges

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…

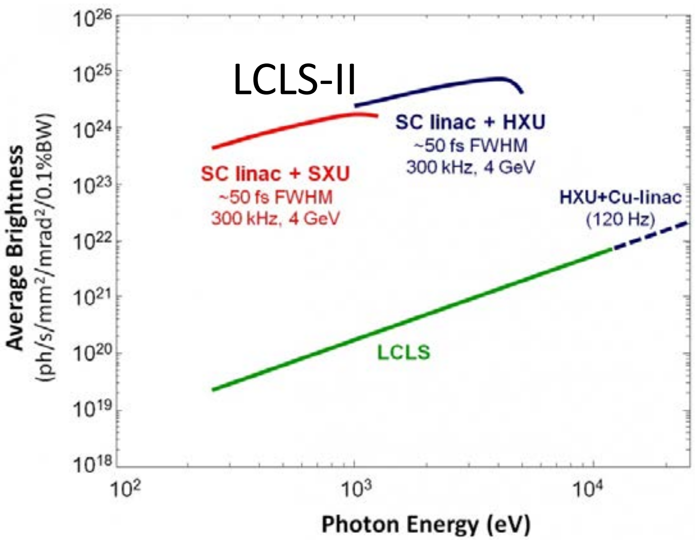
Free electron lasers

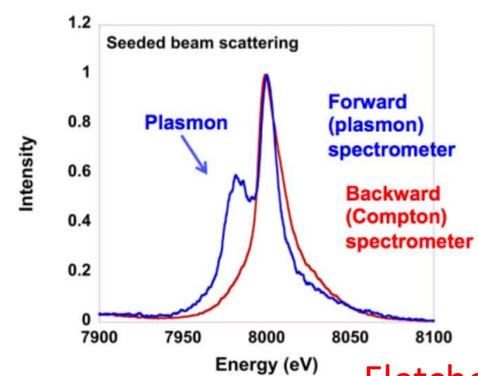
- Non-equilibrium & time resolved
- V. high time-averaged flux (SR x10^4)
- Stimulated RIXS, non-linear effects?

Stimulated emission



M. Beye *et al.*, Nature (2013)

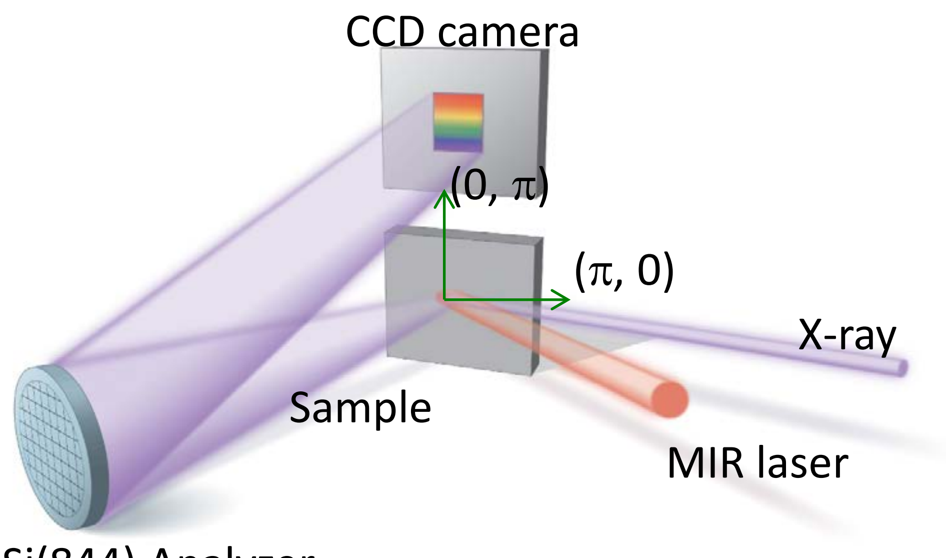




Fletcher *et al.* (2013)

See Chi-Chang Kao's talk Friday

Time-resolved RIXS



Dean *et al.*, Nat Mat (2018)

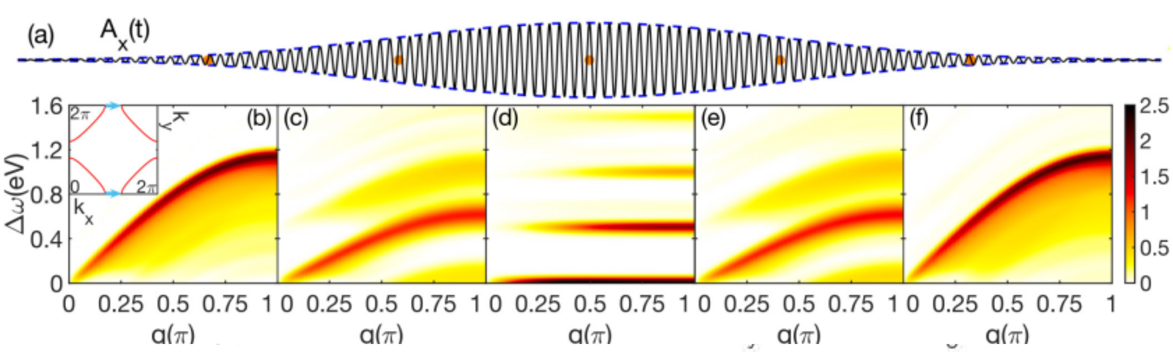
"killer app" will be measuring spin-wave dispersions following a pump pulse (optical, IR, MIR, THz) to obtain a movie of $\mathcal{H}(t)$

Example question:

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

TR-RIXS theory being worked on:

Chen *et al.*, PRB (2019)



Challenges and future directions for SR IXS

Storage rings maintain crucial advantages for IXS

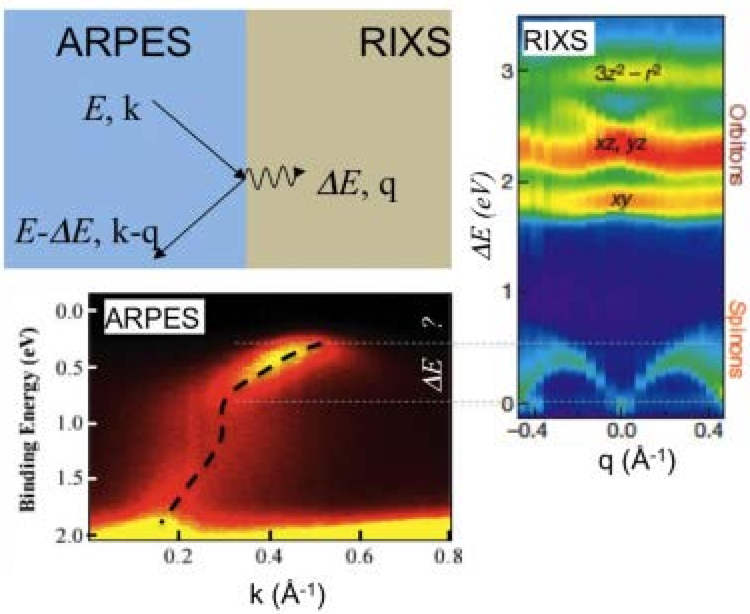
- Ability to have large, dedicated spectrometers
- Large amounts of beamtime for complex expts

- Push to $\Delta E\sim$ 1meV 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

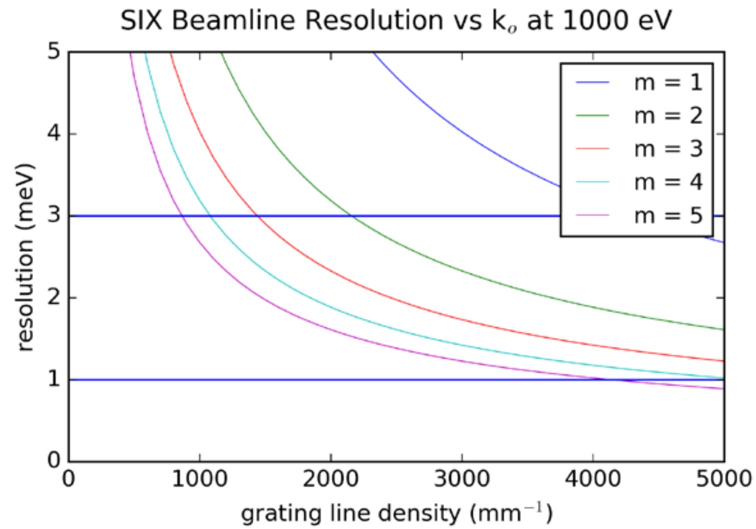
Soft RIXS – what is next?

1. Combine with ARPES
2. Add spatial resolution



- Proposed “ARI” beamline at NSLS-II

3. Achieve ΔE=1 meV

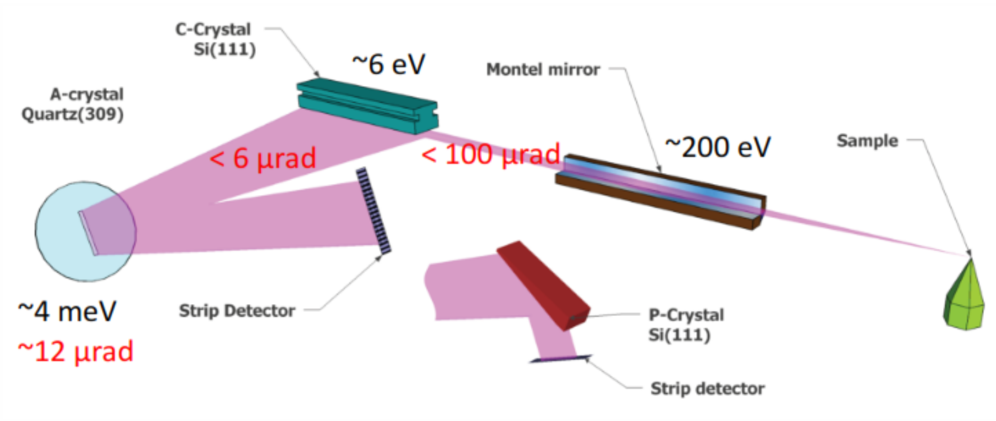


- Achieve 3 meV with 2nd order gratings and improved slope errors and detector resolution (x2.5)
- 1 meV also requires multilayer gratings in higher order

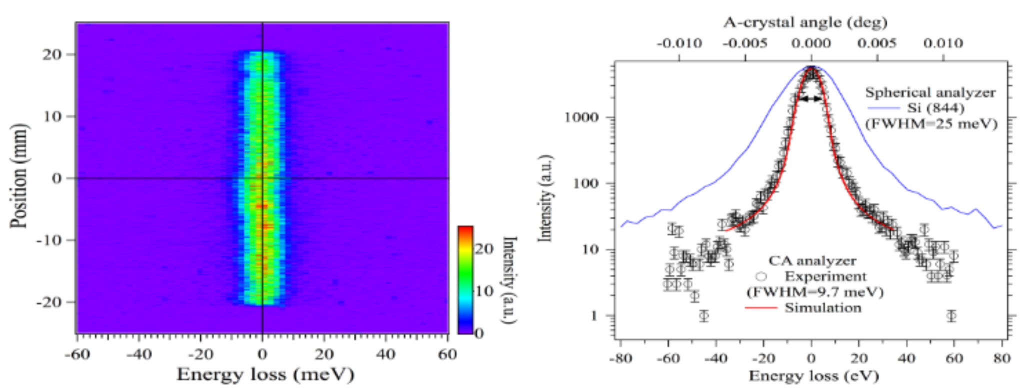
J. Dvorak *et al.*

Hard RIXS: towards 1 meV..

Post-sample-collimation
: Large enough collecting solid angle (<10 mrad)
: Smaller divergence (< 6μrad) than the analyzer acceptance angle.



Analyzer resolution ΔE=3.9 meV



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

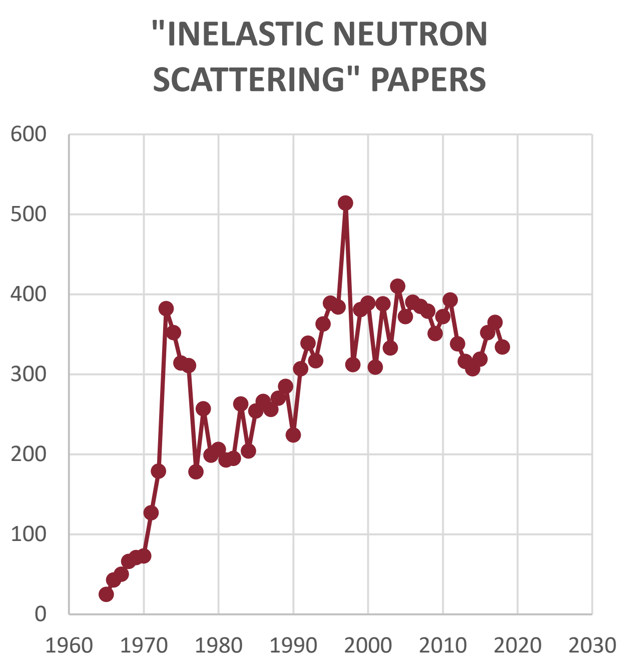
J. Kim et al., Scientific Reports 8, 1958 (2018)

Summary

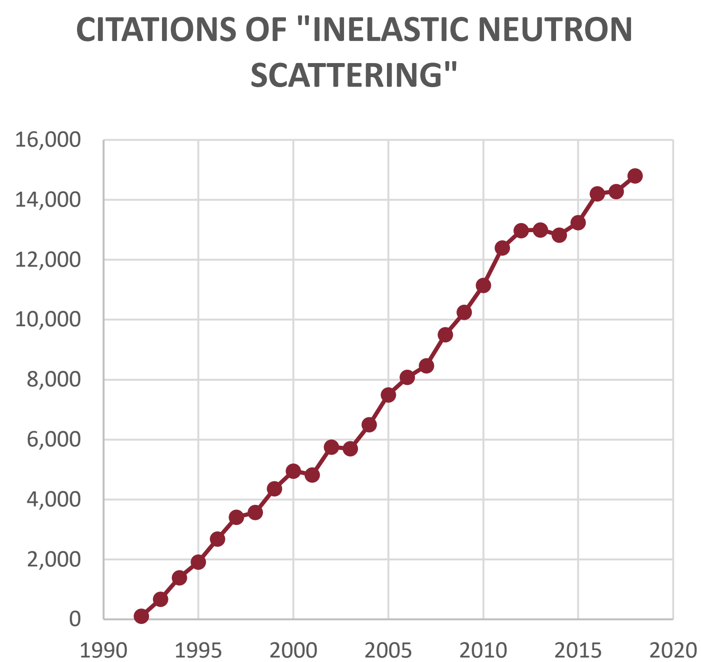
- It has been 50 years of enormous advances, driven by the work of many in instrumentation, sources and theory
- Technique has matured: "it is not the beginning of the end, but the end of the beginning"
- FELs will be disruptive – in some areas
- Synchrotrons will remain the mainstay of the field
- Expect IXS to have major impact in the next decade across a range of disciplines

Back up slides

Comparison with Inelastic Neutron Scattering



350 papers/yr



14,000 citations/year

FELs

Al