Inelastic X-Ray Scattering

These slide are for distribution to the Cheiron Summer School Students.

Alfred Q.R. Baron
Materials Dynamics Laboratory (RIKEN)
Research and Utilization Division (JASRI)
SPring-8

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

Resonant

Others (time permitting)

Some References

Shulke, W. (2007), Electron Dynamics by Inelastic X-Ray Scattering. New York: Oxford University Press.

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

Squires, G. L. (1978). Introduction to the Theory of Thermal Neutron Scattering. New York: Dover Publications, Inc.

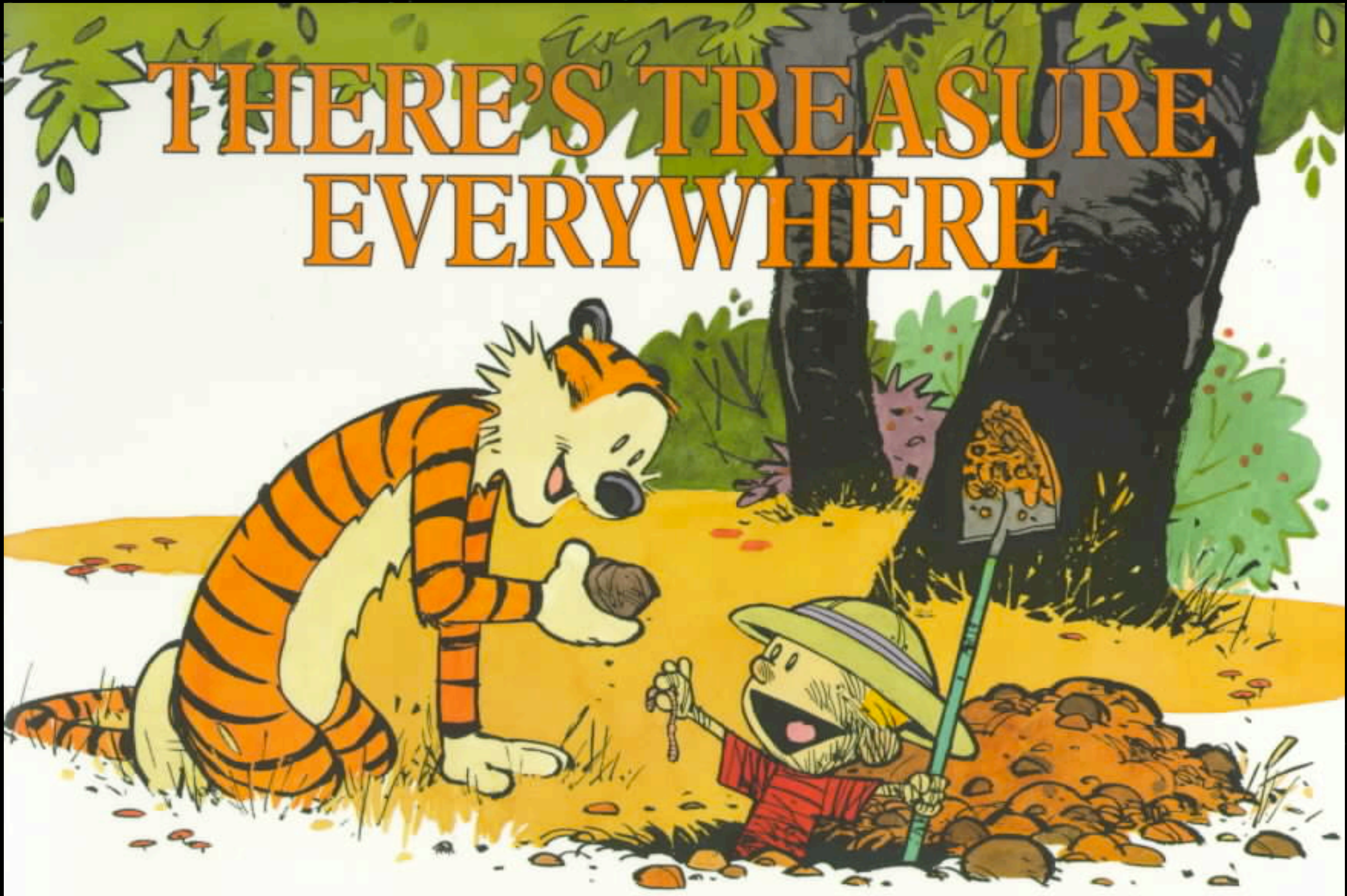
van Hove, L. (1954). Phys. Rev. **95**, 249-262.

Born, M. & Huang, K. (1954). Dynamical Theory of Crystal Lattices. Oxford: Clarendon press.

Bruesch, P. (1982). Phonons: Theory and Experiments, Springer-Verlag.

Cooper, M.J. (1985). Compton Scattering Rep. Prog. Phys. **48** 415-481

Ament, L.J., et al, (2011). RIXS, Rev. Mod. Phys. 83 705-767



Calvin & Hobbes (Watterson)

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 <-> Motions/transitions of electrons
- Chemical Bonding (Valence, etc)
- Electronic Energy Levels (atomic/molecular)
- Delocalized Electronic Excitations
- Generalized Dielectric Response
- Fermi-Surface Topology
- Magnetic structure
- Complex Materials

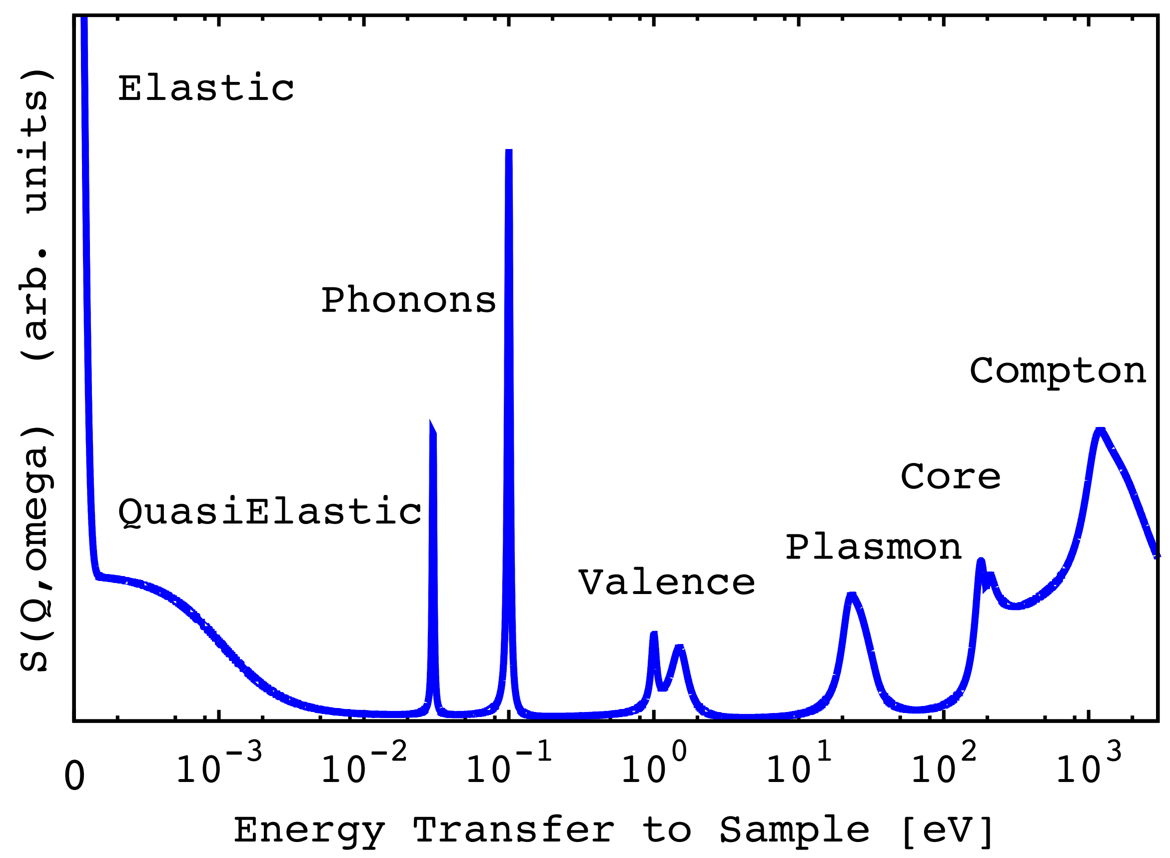
Table Of IXS Techniques/Applications

Technique	Comment	Energy Scale	Information
X-Ray Raman	(E)XAFS in Special Cases	E_{in}~10 keV ΔE~100-1000 eV	Edge Structure, Bonding
Compton	Oldest Note: Resolution Limited	E_{in} ~ 150 keV ΔE ~ keV	Electron Momentum Density Fermi Surface Shape
Magnetic Compton	Weak But Possible	E_{in} ~ 150 keV ΔE ~ keV	Density of Unpaired Spins
RIXS Resonant IXS	High Rate Somewhat Complicated	E_{in} ~ 4-15 keV ΔE ~ 1-50 eV	Electronic Structure
SIXS Soft (Resonant) IXS	Under Development Now Exploding	0.1-1.5 keV ΔE ~ 0.05 - 5 eV	Electronic & Magnetic Structure
NRIXS Non-Resonant IXS	Low Rate Simpler	E_{in}~10 keV ΔE ~ <1-50 eV	Electronic Structure
IXS High-Resolution IXS	Large Instrument	E_{in}~16-26 keV ΔE ~ 1-100 meV	Phonon Dispersion
			Element Specific

Note: ΔE = Typical Energy Transfer (Not Resolution)

Note also: Limit to FAST dynamics (~10 ps or faster)

Excitation Energy Scales



Spectroscopy

Absorption vs. Scattering

Absorption Spectroscopy

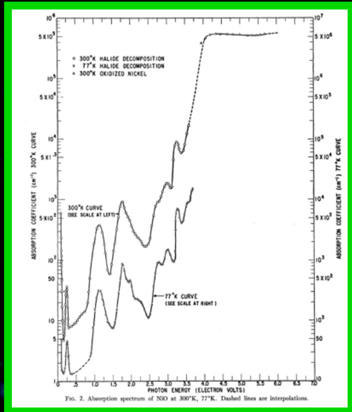
Optical, IR, NMR

Raman

Measure absorption as you scan the incident energy

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

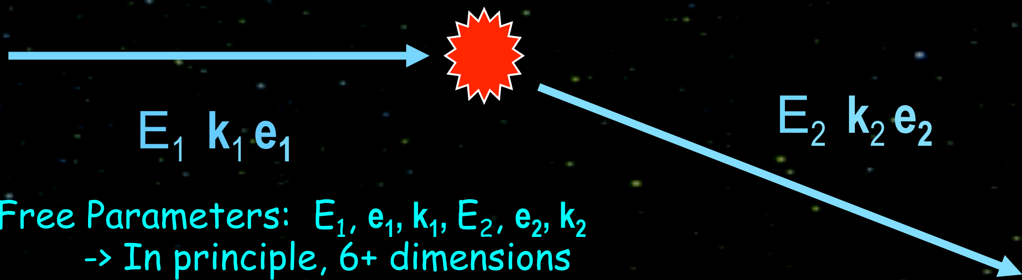
Free Parameters: E_1, e_1, k_1
-> In principle, 3+ dimensions
but in practice mostly 1 (E_1)



Optical Spect. NiO
Newman, PR 1959

Scattering Spectroscopy

IXS, INS



Free Parameters: E_1, e_1, k_1, E_2, e_2, k_2
-> In principle, 6+ dimensions
in practice, mostly 4: E_1-E_2, $\mathbf{Q} = k_2 - k_1$

Scattering is more complex, but gives more information.

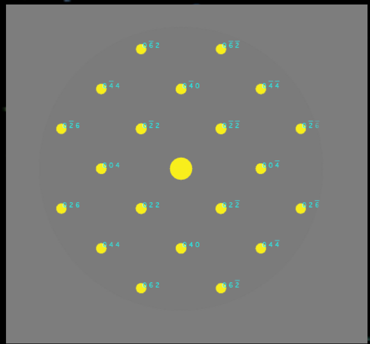
Energy scales PLUS spatial structure on scale of probe wavelength

Where We Are Measuring

Between the Bragg Peaks…

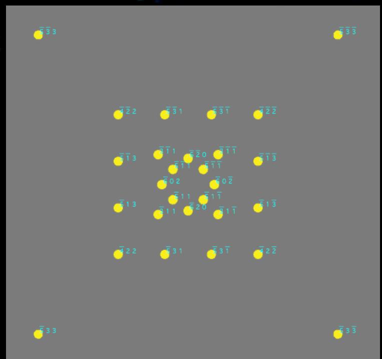
Conventional Diffraction

Linear Scale



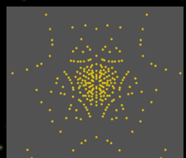
Precession Photo

Silicon



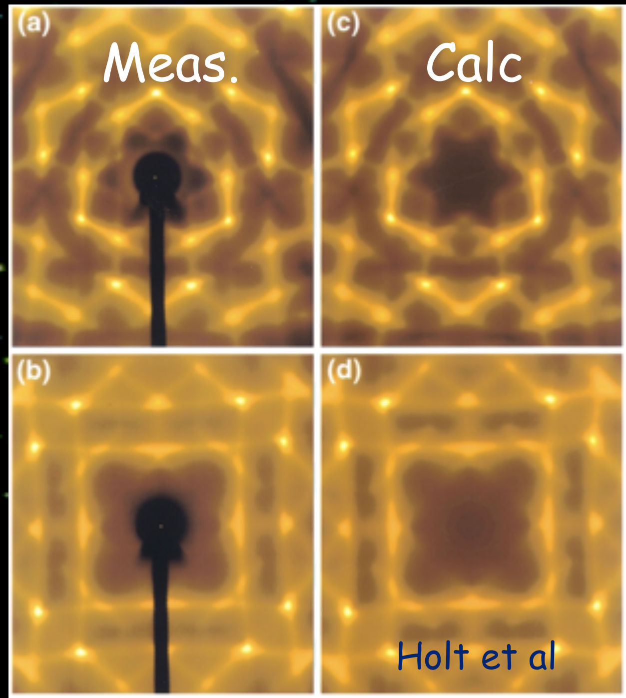
Laue Photo

Ruby



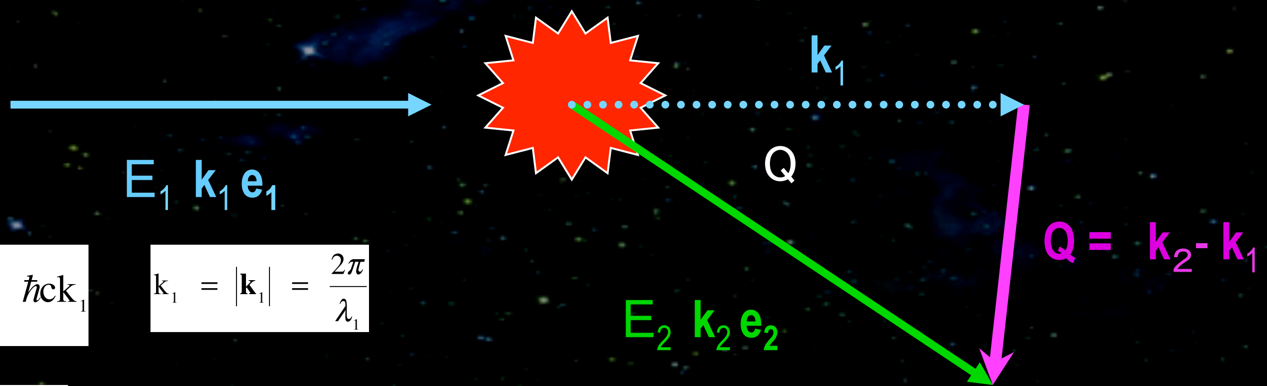
Bragg peaks

On Log Scale



For IXS we are usually measuring between the Bragg peaks where the intensity is weaker.
A strong signal is down by 10^7, weak by 10^{11}

X-Ray Scattering Diagram



$$E_1 = \hbar\omega_1 = \frac{hc}{\lambda_1} = \hbar c k_1$$

$$k_1 = |\mathbf{k}_1| = \frac{2\pi}{\lambda_1}$$

$$hc = 12.398 \ \text{keV} \bullet \text{Å}$$

Two Main Quantities:

Energy Transfer

$$E \ \text{or} \ \Delta E = E_1 - E_2 \equiv \hbar\omega$$

Note: For Resonant Scattering
E_1 and E_2 and Poln.
Are also important

Momentum Transfer

$$\mathbf{Q} \equiv \mathbf{k}_2 - \mathbf{k}_1$$

$$Q \equiv |\mathbf{Q}| \approx \frac{4\pi}{\lambda_1} \sin\left(\frac{\Theta}{2}\right)$$

Periodicity $d = \frac{2\pi}{|\mathbf{Q}|}$

Resonant vs Non-Resonant

Resonant:
RIXS
SIXS

Tune near an atomic transition energy
ie: K, L or M Edge of an atom
Generally High Rate
Complex interpretation
Energy fixed by resonance -> poorer resolution

Non-Resonant:
IXS
NRIXS

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

Different Experimental Setups -> Modern Specialization

Nuclear Resonant & Compton Scattering -> Different

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)

$$I_{scattered}(\mathbf{Q},\omega) \propto \frac{d^2\sigma}{d\Omega d\omega} = r_e^{\ 2} \left(e_2^{\ *} \bullet e_1\right)^2 \frac{\omega_2}{\omega_1} S(\mathbf{Q},\omega)$$

$$\sigma_{Thomson} = r_e^{\ 2}\left(e_2^{\ *} \bullet e_1\right)^2$$

Thomson Scattering
Cross Section
"A Scale Factor"

$$S(\mathbf{Q},\omega)$$

Dynamic Structure Factor
"The Science"

Different Views of S(Q,w)

$$S(\mathbf{Q},\omega) = \sum_{\lambda,\lambda'} p_\lambda \left| \langle \lambda' | \sum_{\substack{electrons \\ j}} e^{i\mathbf{Q}\bullet\mathbf{r}_j} | \lambda \rangle \right|^2 \delta(E_{\lambda}' - E_\lambda - \hbar\omega)$$

Transition between states

Fluctuations in electron density

$$= \frac{1}{2\pi\hbar} \int dt \; d^3r \; d^3r' \; e^{-i\mathbf{Q}\bullet r} \langle \rho(\mathbf{r}', t=0) \rho^+(\mathbf{r}+\mathbf{r}', t) \rangle \;\rightarrow\; N \sum_{\mathbf{q}} \sum_{Modes} \left| \sum_{\substack{d \\ Atoms \\ /Cell}} \frac{f_d(\mathbf{Q})}{\sqrt{2M_d}} \; e^{-W_d(\mathbf{Q})} \mathbf{Q} \bullet \mathbf{e}_{\mathbf{q}jd} \; e^{i\mathbf{Q}\bullet\mathbf{x}_d} \right|^2 \delta_{(\mathbf{Q}-\mathbf{q}),\tau} F_{\mathbf{q}j}(\omega)$$

$$= \frac{1}{\pi} \frac{1}{1-e^{-\hbar\omega/k_BT}} \mathrm{Im}\{-\chi(\mathbf{Q},\omega)\} \quad = \quad \frac{1}{\pi} \frac{1}{1-e^{-\hbar\omega/k_BT}} \frac{1}{v(\mathbf{Q})} \mathrm{Im}\{-\varepsilon^{-1}(\mathbf{Q},\omega)\}$$

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 (sometimes) be preferred.

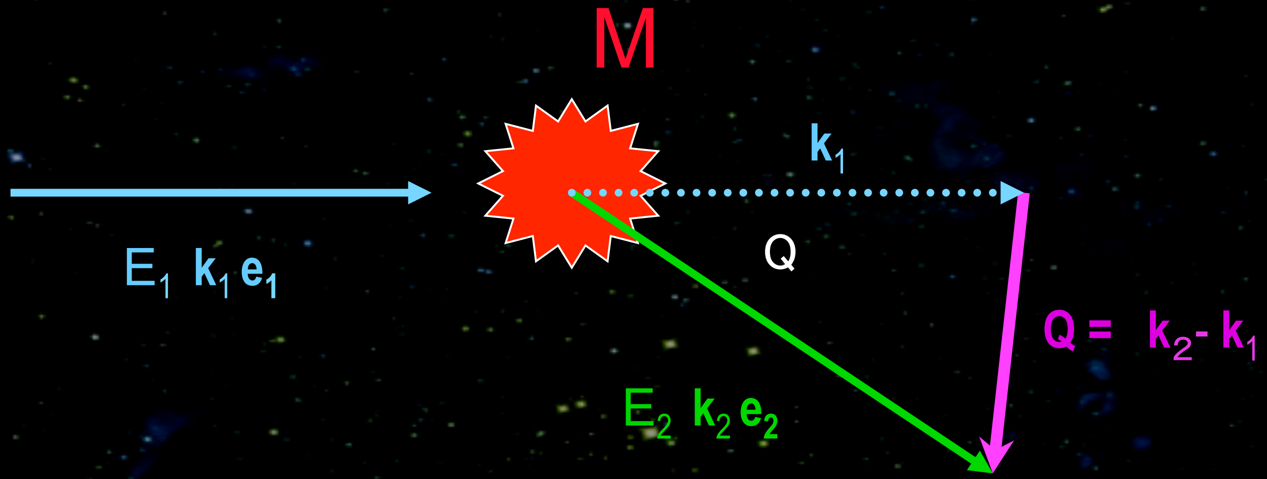
Equilibrium Dynamics: Q,E space is what you want.
Normal modes -> peaks in energy space -> clear and "easy"
Periodicity of crystals -> Excitations are plane waves
-> Q is well defined

Non-equilibrium dynamics -> Real space (x,t) can be better.

Non-periodic (disordered) materials -> Expand in plane waves. (oh well)

Kinematics

Conservation of Energy



Kinetic Energy Given to Sample:

$$E_{recoil} = \frac{p^2}{2M} = \frac{\hbar^2 \mathbf{Q}^2}{2M}$$

Take: M=57 amu, Q/c = 7 Å^{-1} -> E_r=2.3 meV

f-sum rule:

$$\frac{\int d\omega \;\; \hbar\omega \; S(\mathbf{Q},\omega)}{\int d\omega \; S(\mathbf{Q},\omega)} = \frac{\hbar^2 Q^2}{2M}$$

Compton Form:

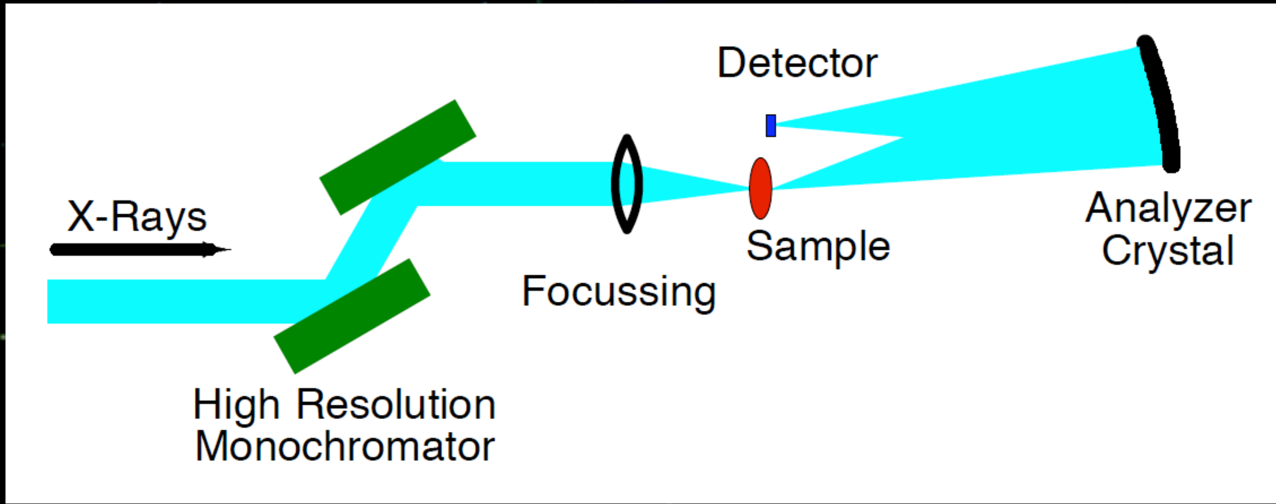
$$\lambda_2 - \lambda_1 = \frac{h}{Mc}(1 - \cos\Theta)$$

$$\lambda_c = \frac{h}{m_e c} = 0.0243\text{Å}$$

The IXS Spectrometer
An Optics Problem

Main Components

Monochromator:
- Modestly Difficult
  - Accepts 15x40 μrad^2



Sample Stages
- Straightforward
- Only Need Space

Analyzer:
- Large Solid Angle
  - Difficult

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...

Basic Optical Concept

(Hard x-rays)

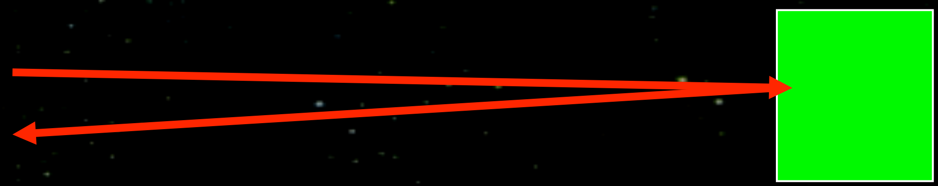
Bragg's Law : $\lambda = 2d\sin(\Theta_B)$ => $\Delta\theta = \tan\left(\Theta_B\right)\dfrac{\Delta E}{E}$

Working closer to Θ_B~90 deg. maximizes the angular acceptance for a given energy resolution…

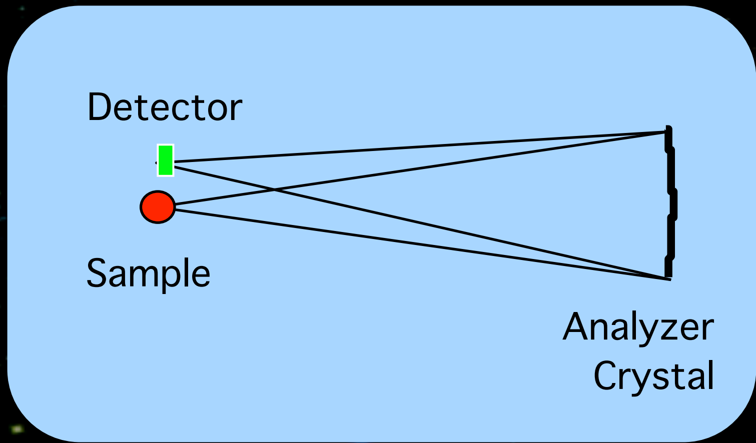
Better energy resolution

-> Closer to 90 degrees

-> Large Spectrometer



High Resolution Analyzer Crystals



The more difficult optic…

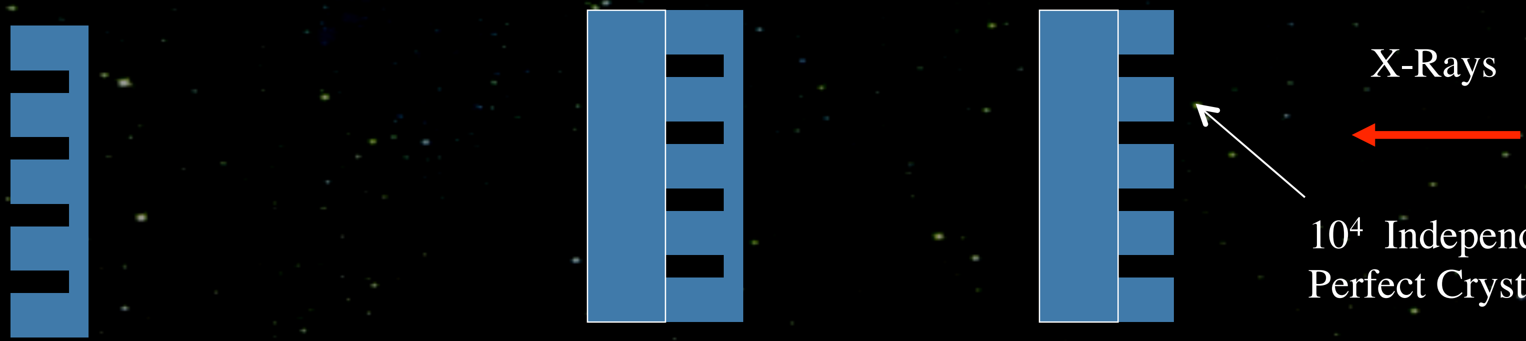
Require:

Correct Shape (Spherically Curved, R=9.8 m)

Not Strained ($\Delta E/E \sim$few 10^{-8}-> $\Delta d/d <<$few10^{-8})

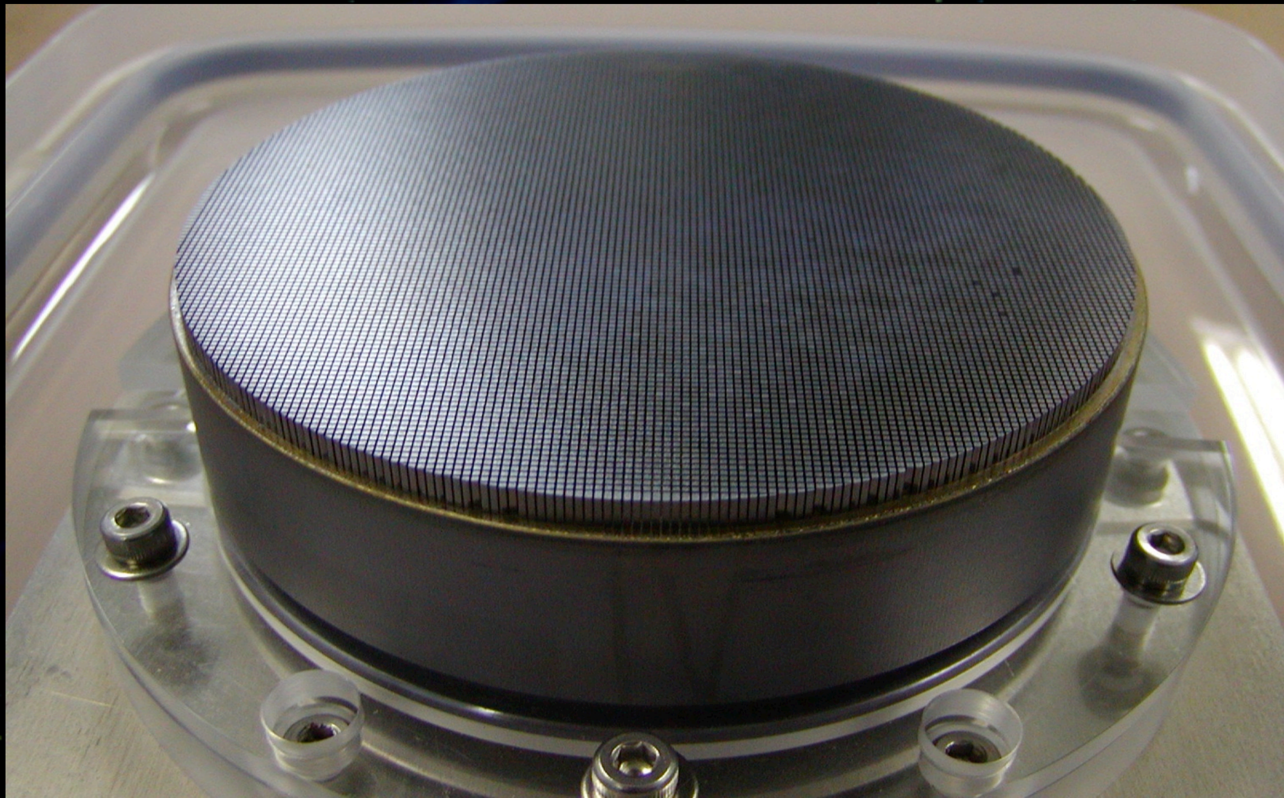
Method: Bond many small crystallites to a curved substrate.

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



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

Analyzer Crystal



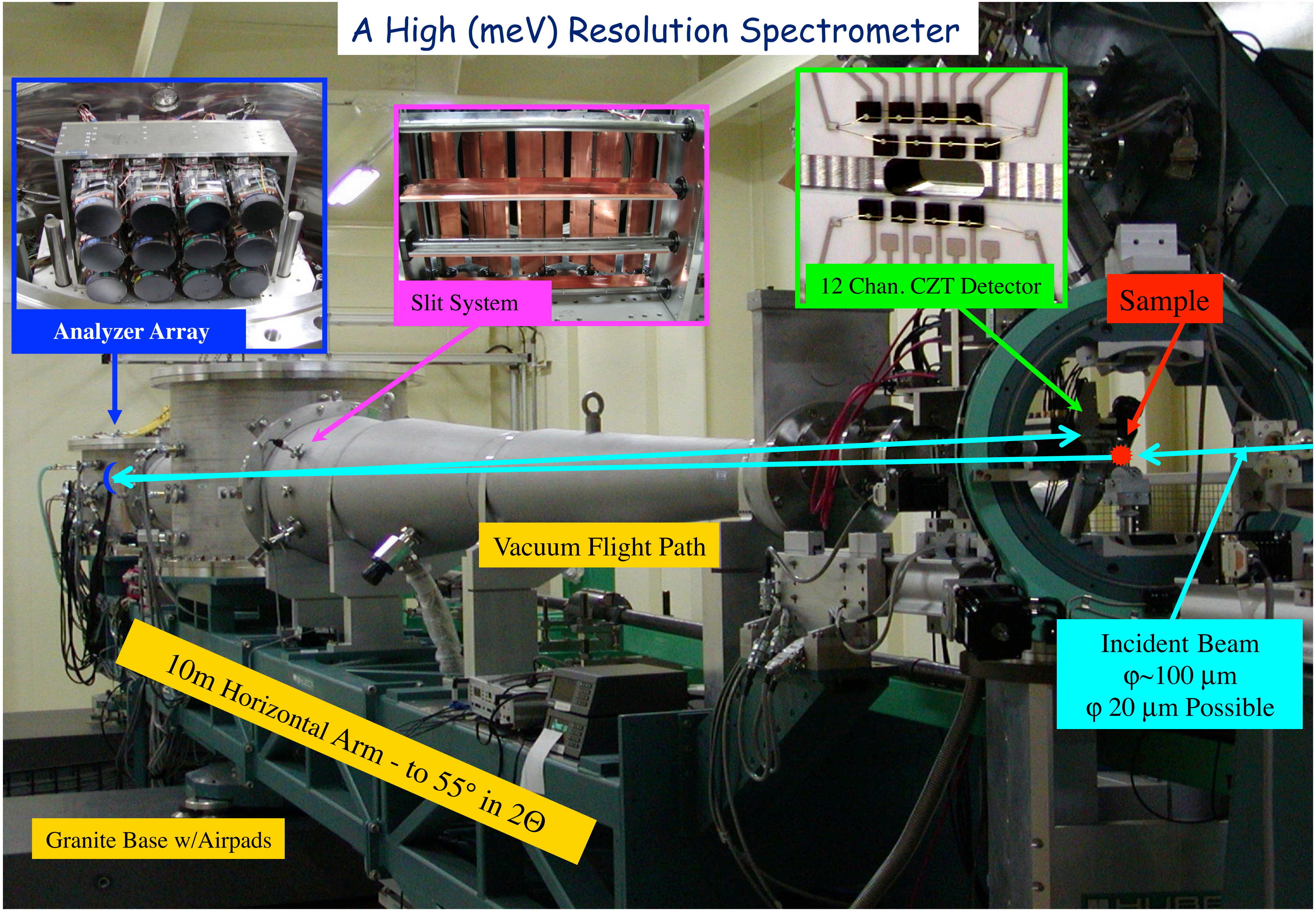
9.8 m Radius, 10cm Diameter

50 or 60 µm blade, 2.9 mm depth, 0.74 mm pitch

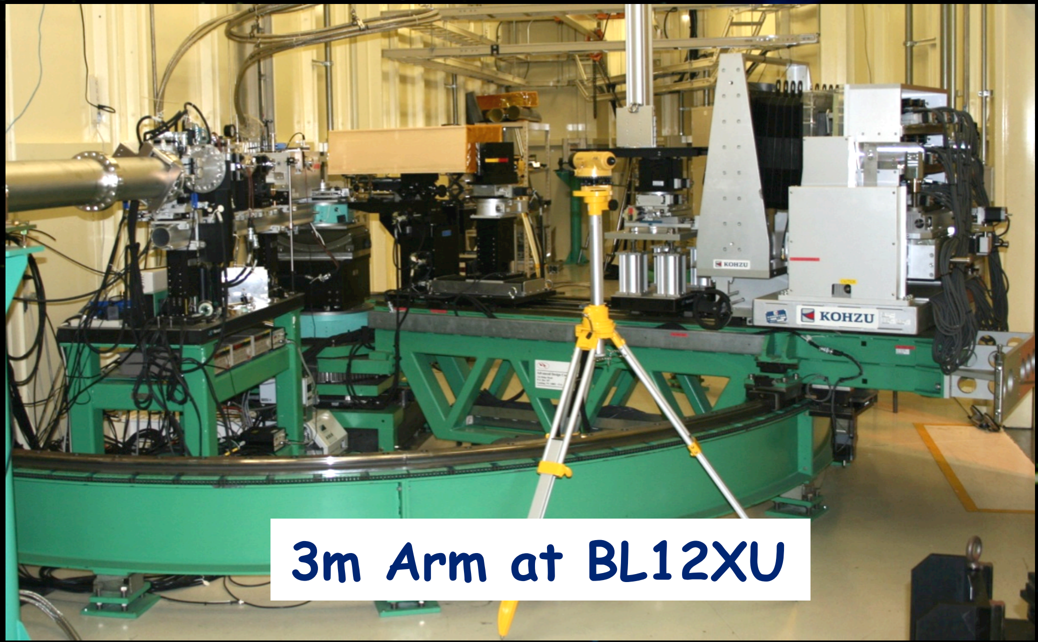
Channel width (after etch): ~ 0.15 mm

60 to 65% Active Area

A High (meV) Resolution Spectrometer



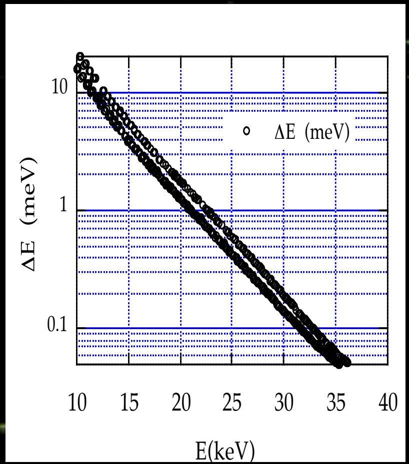
A Medium Resolution Spectrometer


3m Arm at BL12XU

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

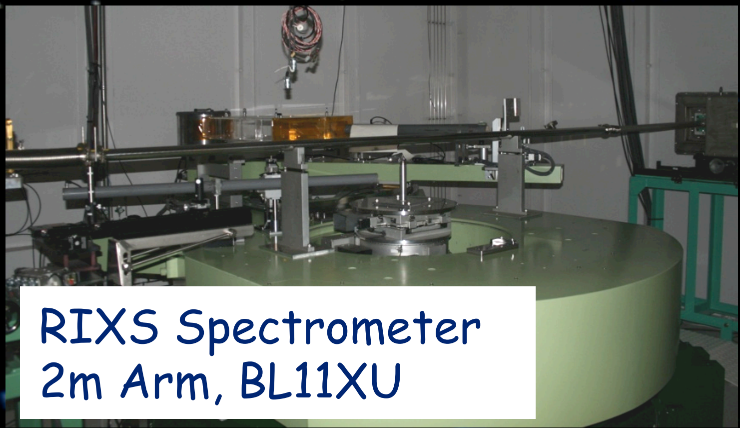
BL12XU BL11XU BL43LXU

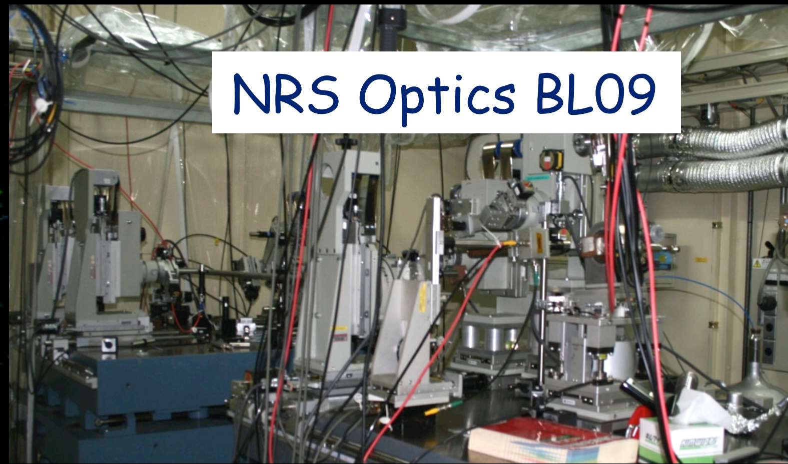
Shorter Possible
(later, if time)

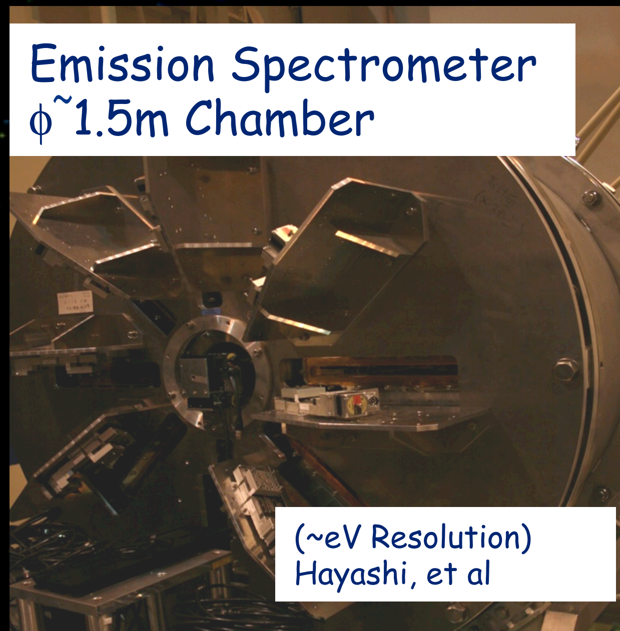


Note difference between RIXS and NRIXS
NRIXS: Choose the energy to match the optics
RIXS: Resonance chooses energy -> usually worse resolution

Other Spectrometers @ SPring-8



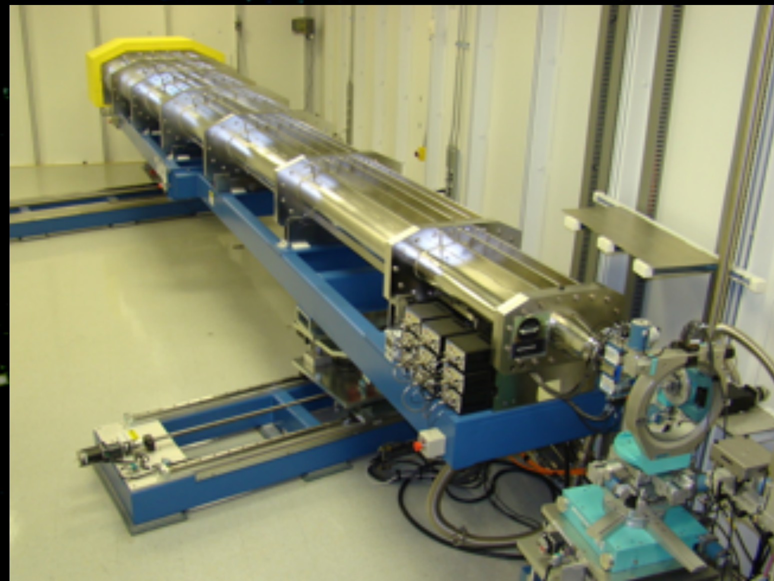


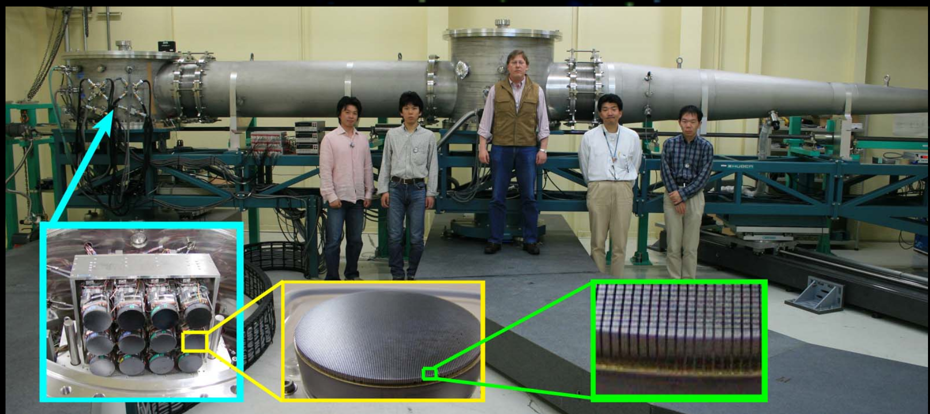


High Resolution Spectrometers

ESRF (ID28)

APS (Sector 30)

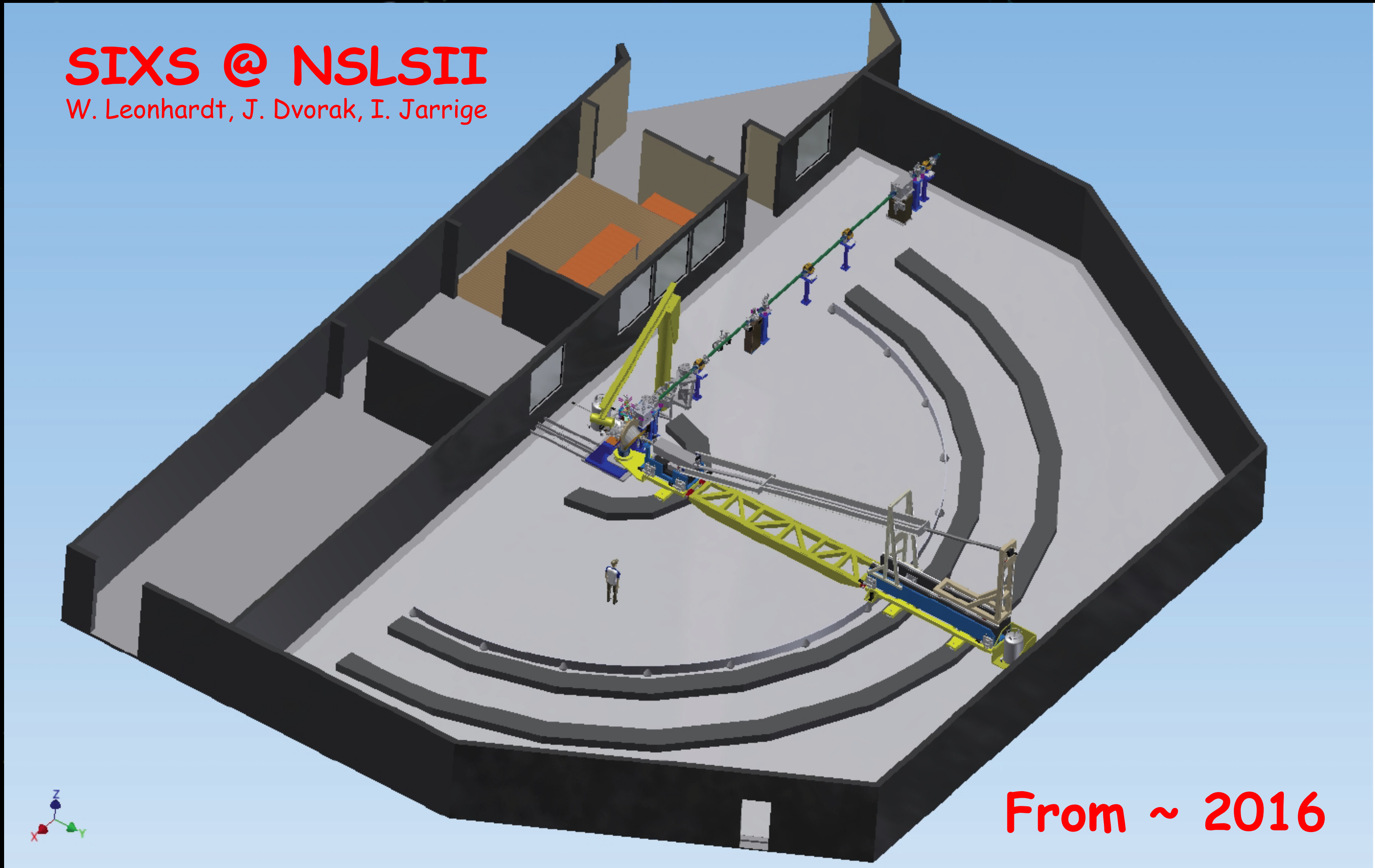




SPring-8 BL35XU

HRIXS
~10m scale instruments

Softer and Bigger...



Soft inelastic x-ray scattering: 10 meV resolution at 1 keV via gratings

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:

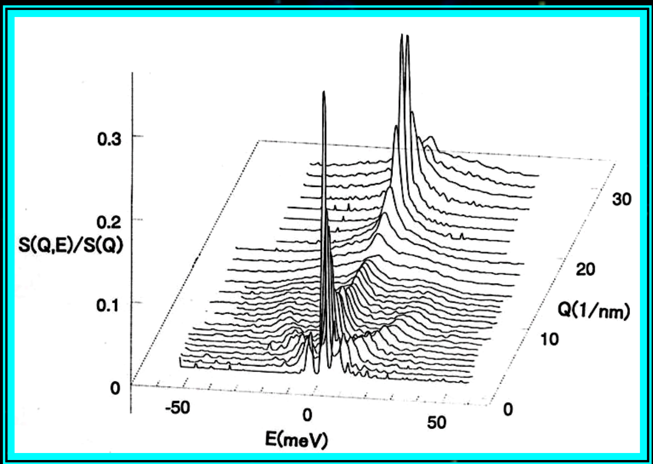
Basic phonon model does very well -> Specific questions needed.

Phonon softening & Phase transitions (e.g. CDW Transition)
Thermal Properties: Thermoelectricity & Clathrates
Sound Velocity in Geological Conditions
Pairing mechanism in superconductors

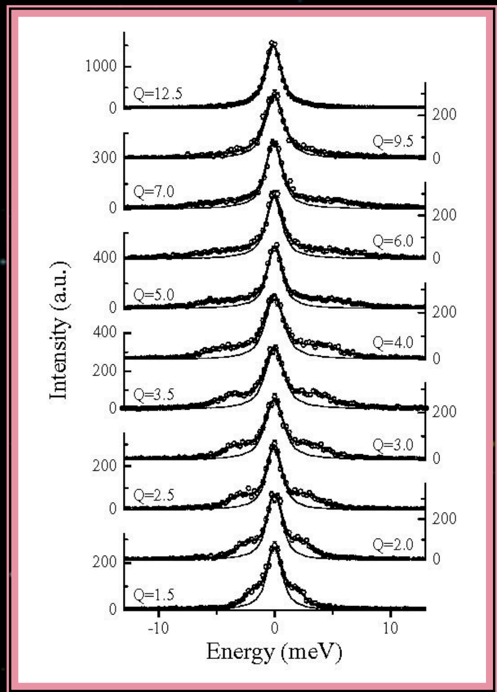
Disordered Materials

Liquids & Glasses

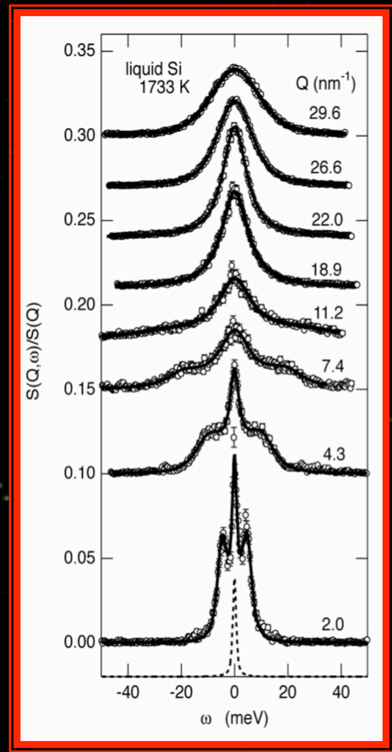
First Glance: Triplet response similar for most materials.
Dispersing Longitudinal Sound Mode
+ Quasi-Elastic peak



l-Mg (Kawakita et al)



a-Se (Scopigno et al)



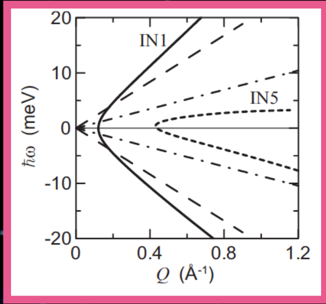
l-Si (Hosokawa, et al)

The IXS Advantage

IXS has no kinematic limitations ($\Delta E <<< E_\gamma$)

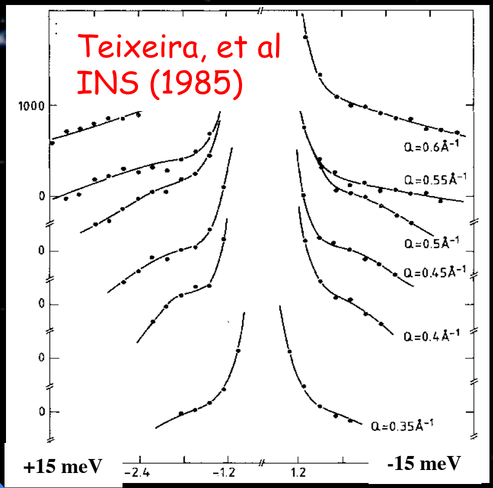
Large energy transfer at small momentum transfer

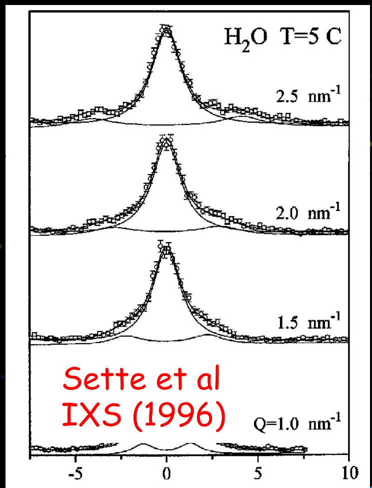
-> excellent access to mesoscopic length scales



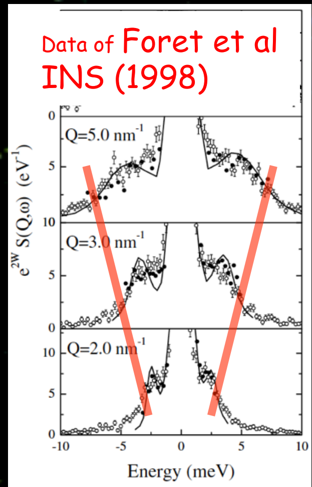
INS Diagram

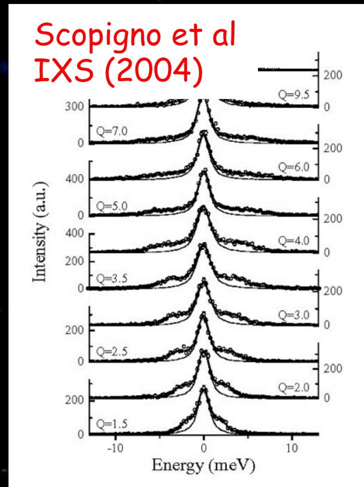
Water





Glassy-Se





Also: No Incoherent Background

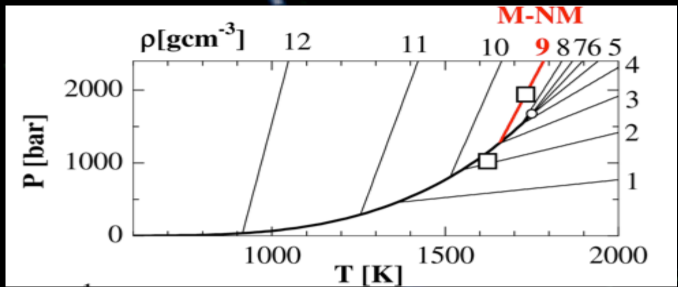
Small Beam Size (ϕ<0.1mm)

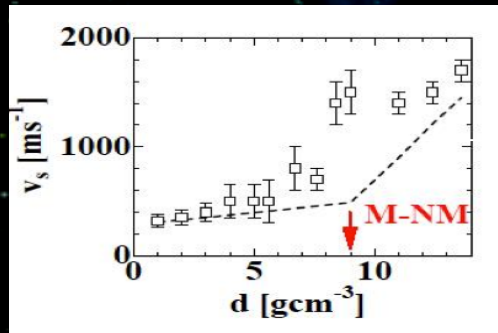
But: <1 meV resolution is hard

Low Rates for Heavy Materials

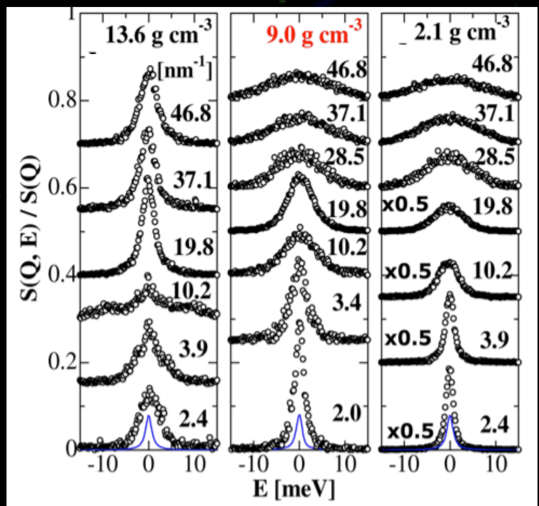
"Fast Sound" at the Metal-Non-Metal Transition in Liquid Hg

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





Ultrasonic Velocity



Suggests a change in the microscopic density fluctuations...

Probably general phenomenon...
but no confirmation yet.
(Next M-I transition under discussion)

Ishikawa, Inui, *et al*, PRL 93 (2004) 97801

~2 months of beam time...

On Positive Dispersion

Very General feature:

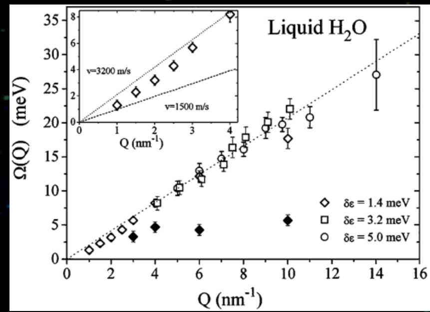
As Q increases the phase velocity of the acoustic mode becomes larger than the Low-Q (e.g. ultrasonic) sound velocity.

Casual explanation

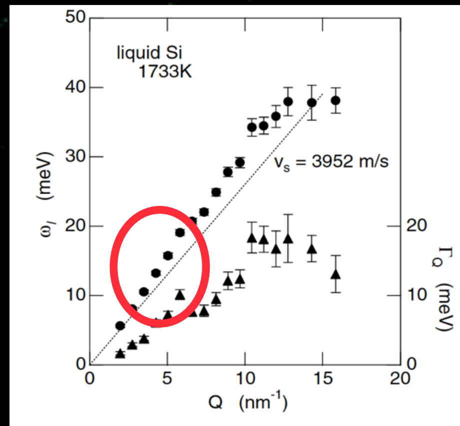
For smaller length scales (high Q) and higher frequencies, a liquid, locally, resembles a solid which has a faster sound velocity.

Partial explanation in terms of a visco-elastic model...

Scopigno & Ruocco RMP 2005
Ruocco & Sette CMP 2008
Bryk et al JCP 2010

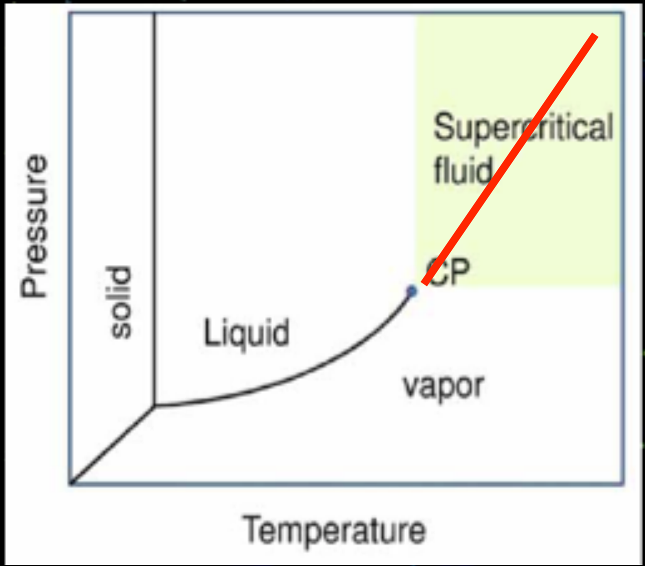


Sette et al

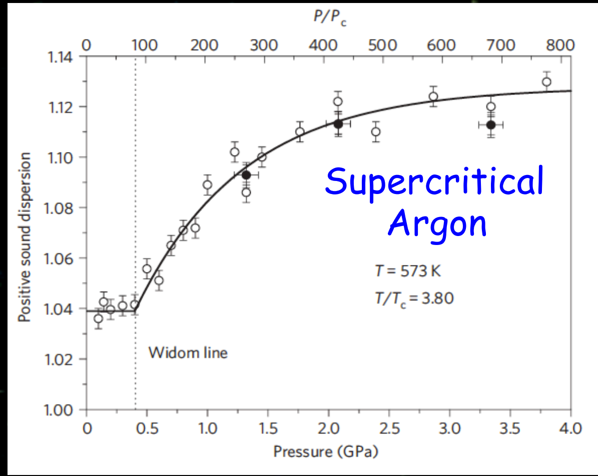


Hosokawa, et al

Dynamical Distinction



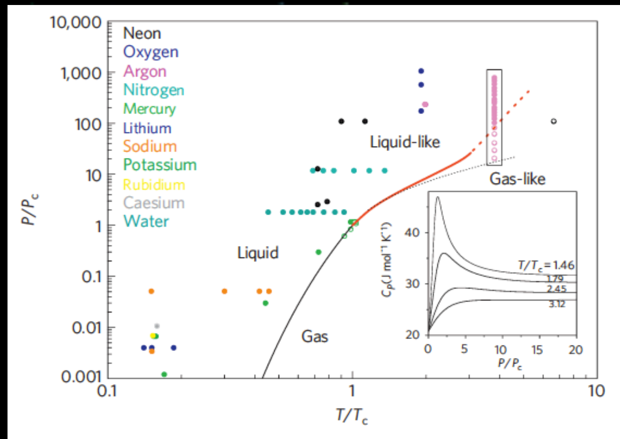
Widom Line
Maximum in C_p



Simeoni et al NPhys 2010

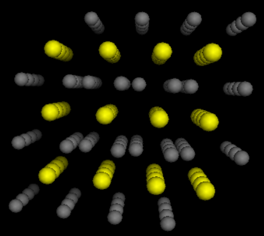
Take the presence of Positive Dispersion as the definition of liquid-like behavior

Gorelli et al, PRL (2006)
Simeoni et al, NPhys (2010)
Also Bencivenga et al EPL (2006)

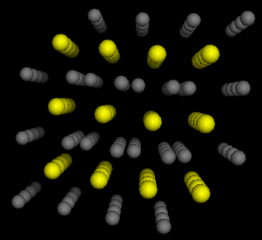


Shear Mode in a Simple Liquid

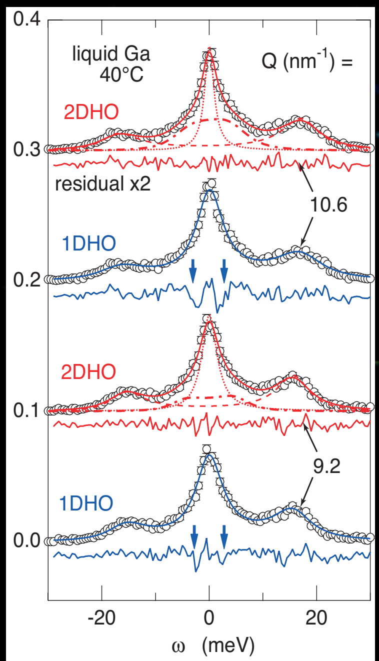
Pressure Wave in a Liquid:
Nearly Always Visible

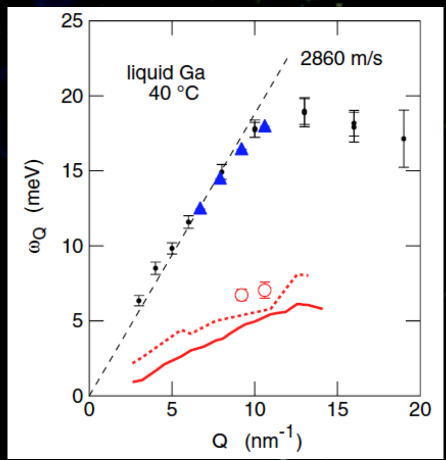


Shear Wave -> Harder...



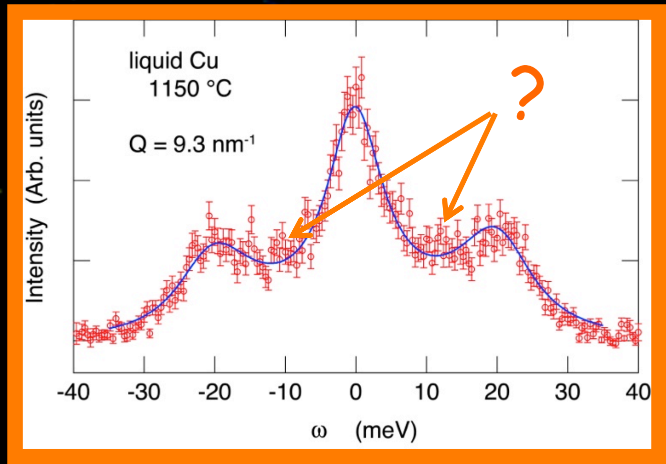
$$S(\mathbf{Q},\omega) \approx \int dt e^{-i\omega t} \int d\mathbf{r} \int d\mathbf{r}' \, e^{i\mathbf{Q}\bullet(\mathbf{r}-\mathbf{r}')} \langle \rho(\mathbf{r}',t)\rho(\mathbf{r},t=0) \rangle$$





Weak, but significant, signal.

Hosokawa, et al, PRL (2009)

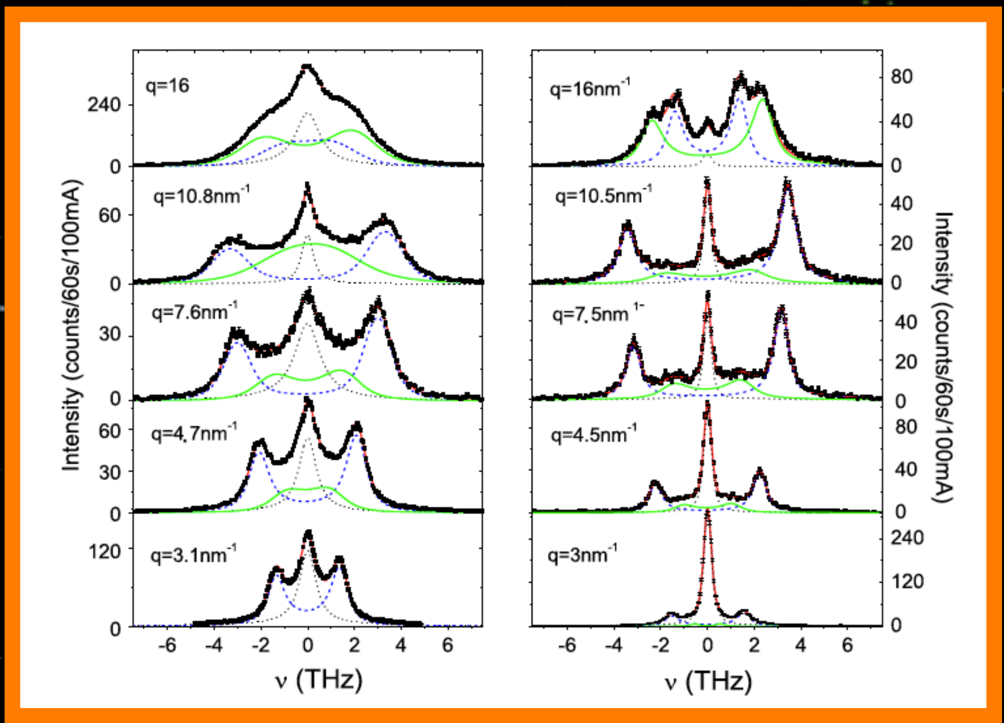


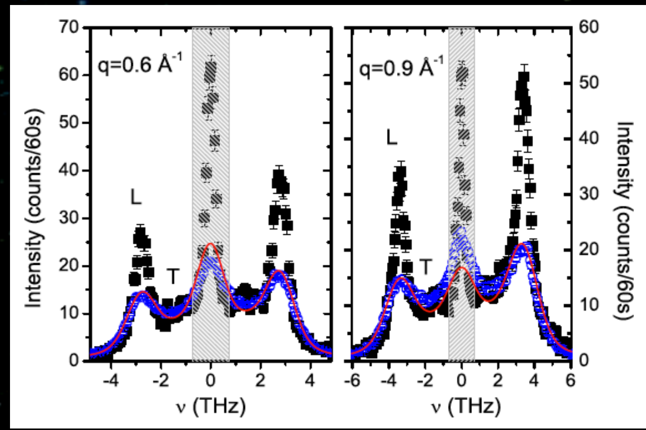
Next experiment: l-Cu
2.5 Days -> ?

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.

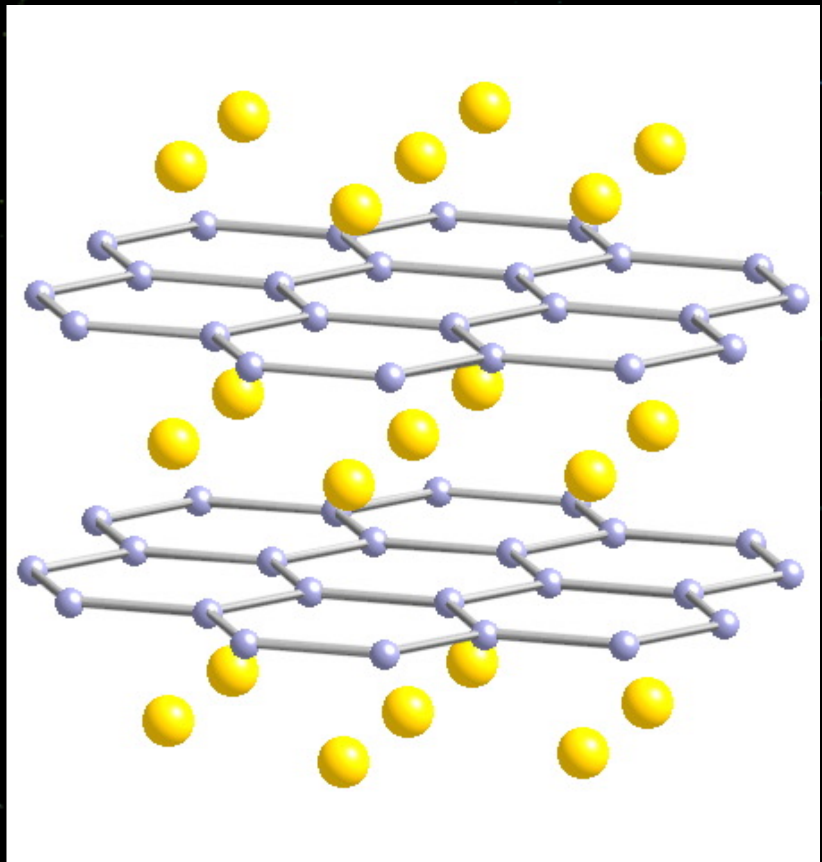
If a crystal has N unit cells and R atoms/Cell then it has 3NR Normal Modes

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

-> 3R modes for any given **q**

MgB_2 As An Example

Layered Material
Hexagonal Structure



B Layer

B-B Bond is Short
& Stronger

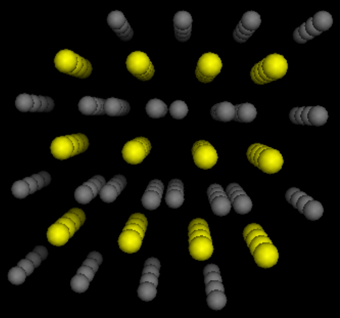
Mg Layer

Mg-Mg Bond is
Longer & Weaker

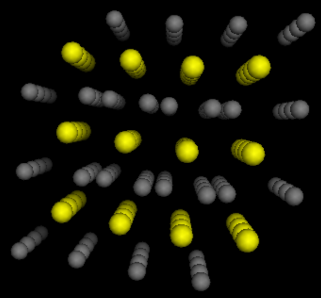
3 Atoms/cell -> 9 modes / Q Point

Acoustic and Optical Modes

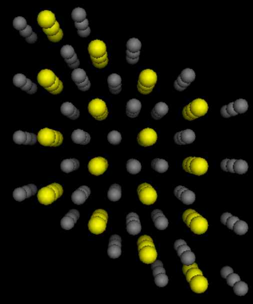
Acoustic Modes are Continuum (Smooth) Modes



LA Mode
Compression Mode

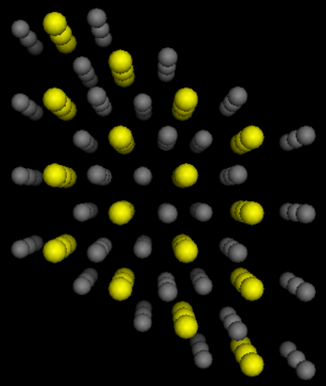


TA Mode
Shear Mode

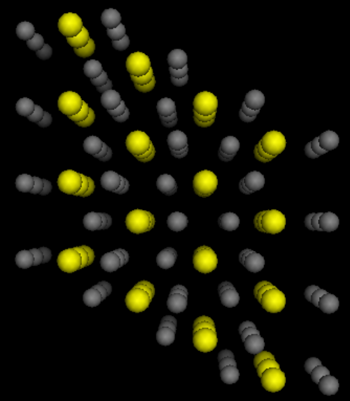


Optical Mode
Atoms in one unit cell
move against each-other

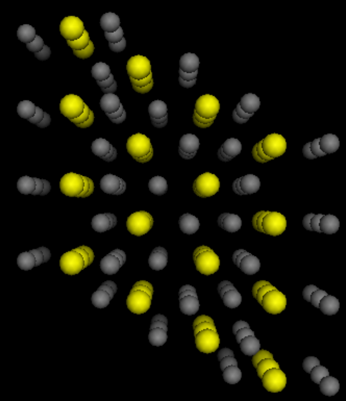
Dispersion of an Optical Mode



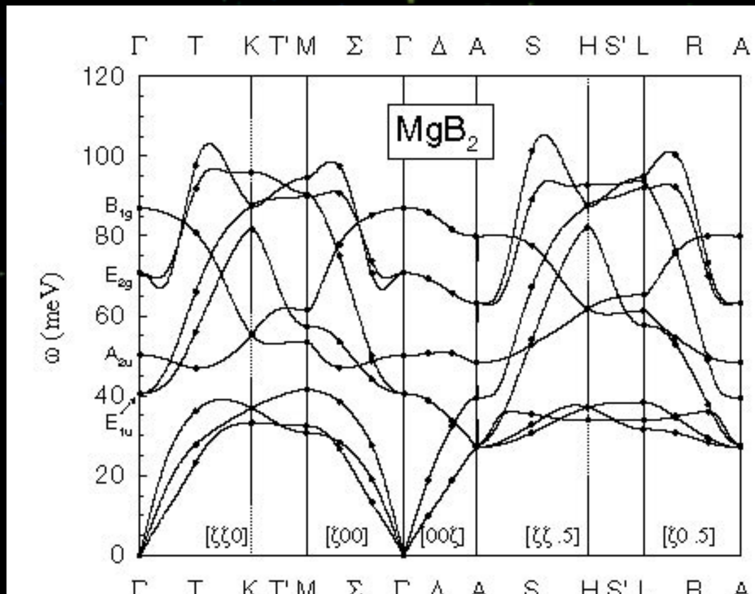
(0 0 0)



(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 <=> Kohn Anomaly)

Broadening: Additional decay channel (phonon->e-h pair) reduces the phonon lifetime

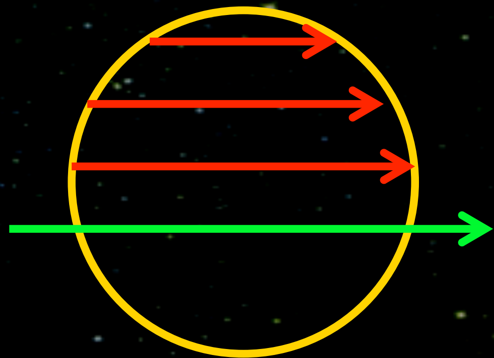
Electron Phonon Coupling

& 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.

Phonon
Momenta
$Q<2k_F$



Large Momentum
$Q>2k_F$
Can Not Couple to the Electronic system

Fermi Surface
Diameter = $2k_f$

Superconductors

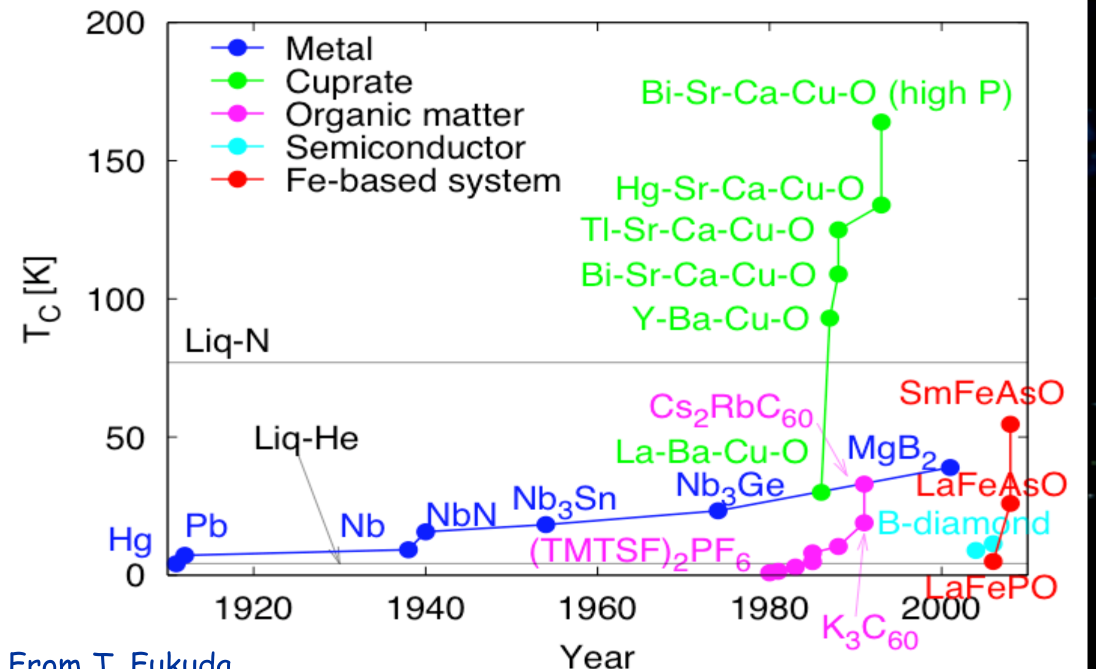
Systems Investigated include

MgB_2, Doped MgB_2, CaAlSi, B-Doped Diamond

Hg1201, LSCO, YBCO, LESCO, Tl2212, BKBO, NCCO,

Bi2201, Bi2212, Nickelates, Oxychlorides

Fe-As Systems: LaFeAsO, PrFeAsO, BaKFeAs



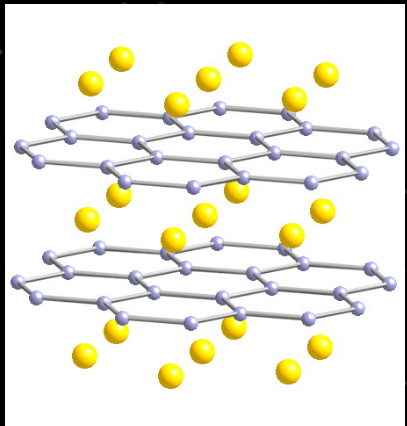
From T. Fukuda

Dark Blue Line: Conventional, Phonon-Mediated Superconductors

MgB_2

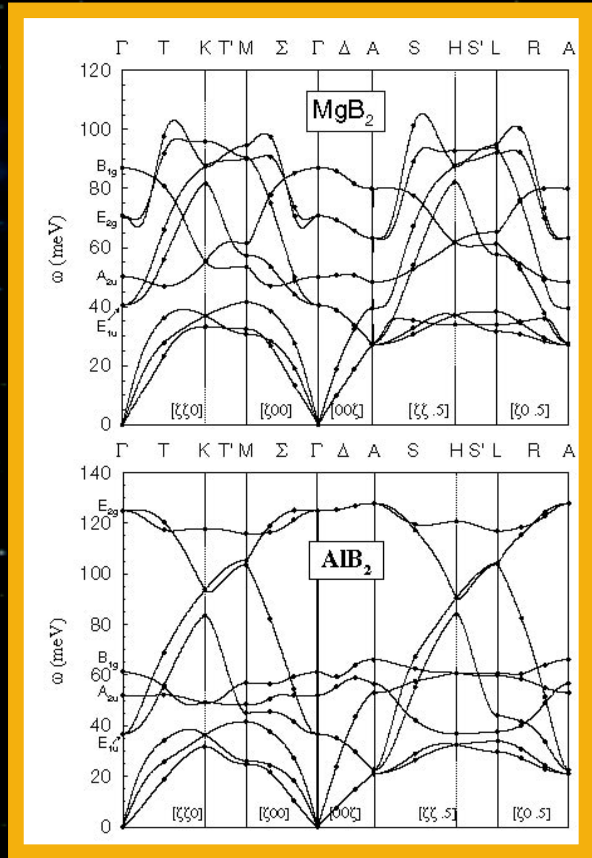
High T_c (39K)

Nagamatsu, et al, Nature **410**, (2001) 63.



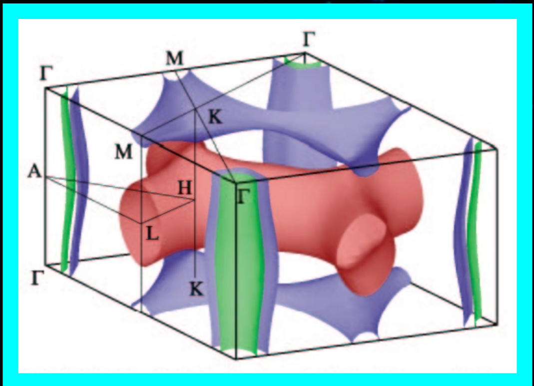
Simple Structure…
straightforward calculation.

Phonon Structure



Bohnen, et al. PRL. **86**, (2001) 5771.

Electronic Structure

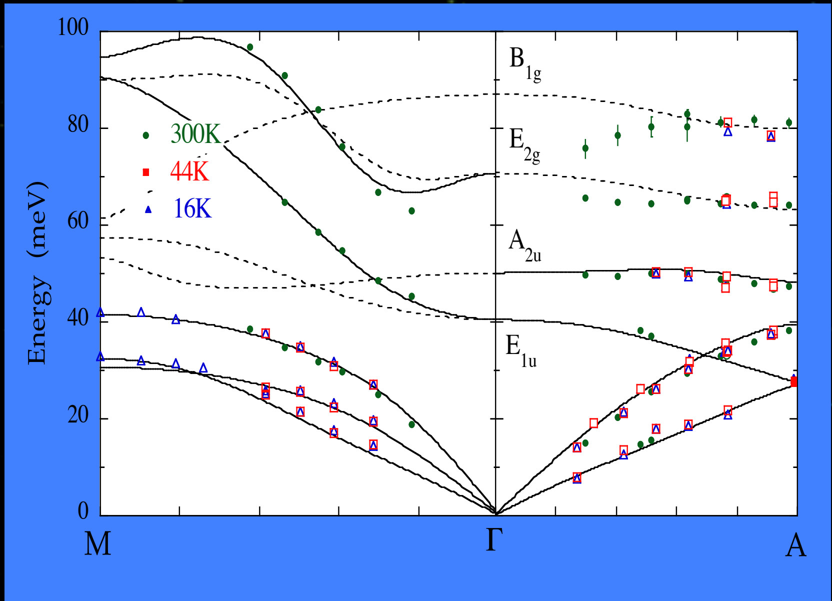


Kortus, et al, PRL 86 (2001)4656

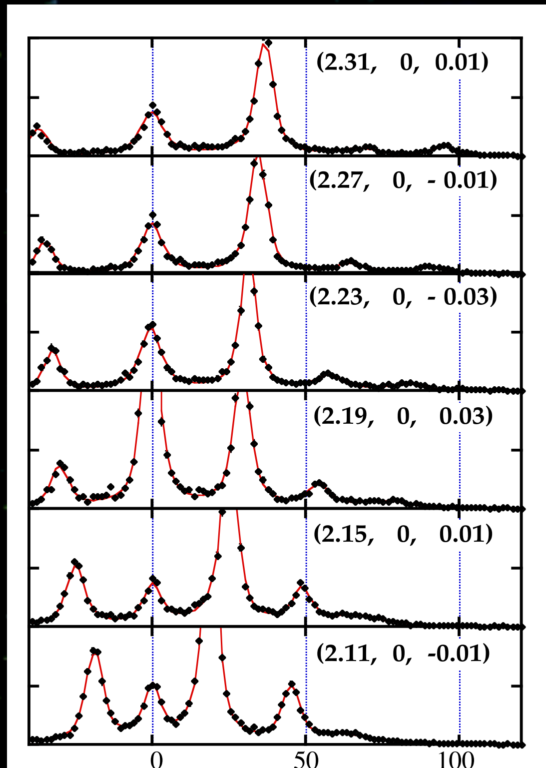
BCS (Eliashberg) superconductor with mode-specific electron-phonon coupling.

Electron-Phonon Coupling in MgB_2

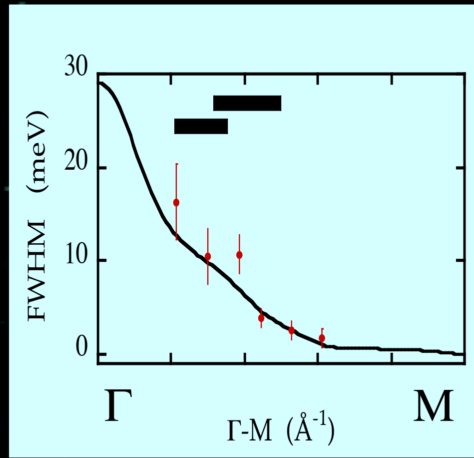
Dispersion



Spectra



Linewidth



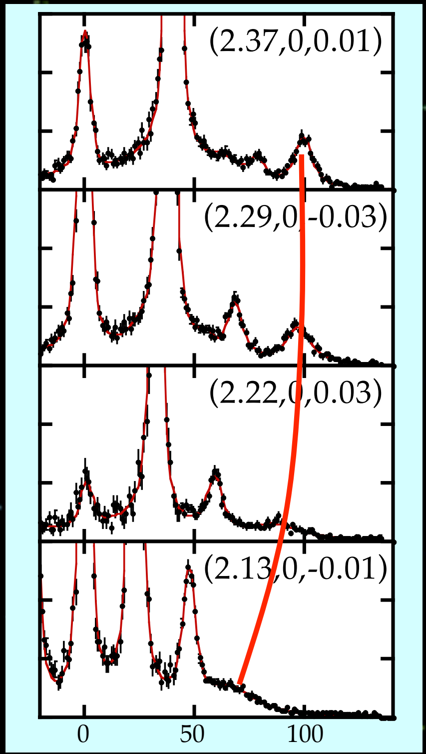
Clear correlation between
linewidth & softening.
Excellent agreement with LDA Pseudopotential calculation.

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

Carbon Doped $Mg(C_xB_{1-x})_2$

2%C, T_c=35.5K   12.5% C, T_c=2.5K AlB_2 (Not SC)

M



Γ

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

(0 0) (0.5 0)

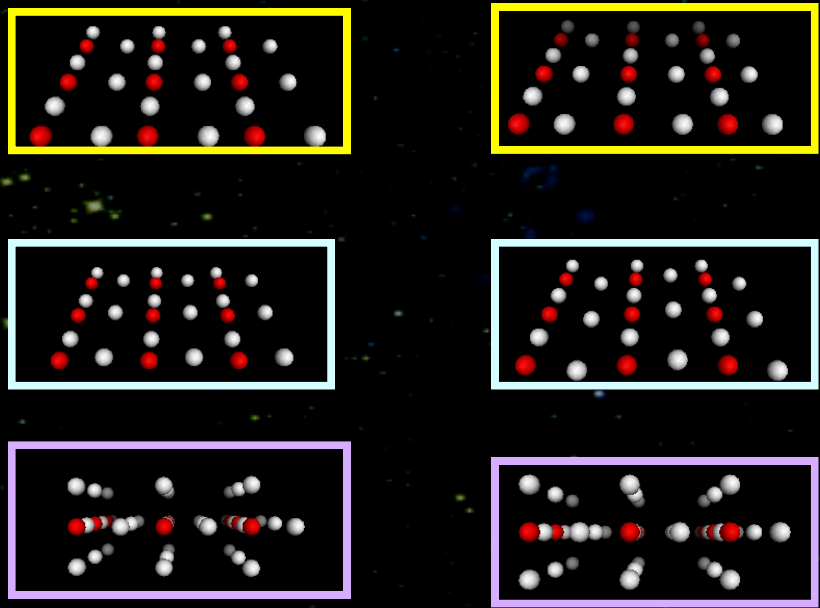
<u>In-Plane Mode:</u>

Stretching mode

<u>Out of Plane Modes:</u>

Buckling Mode

Apical Mode

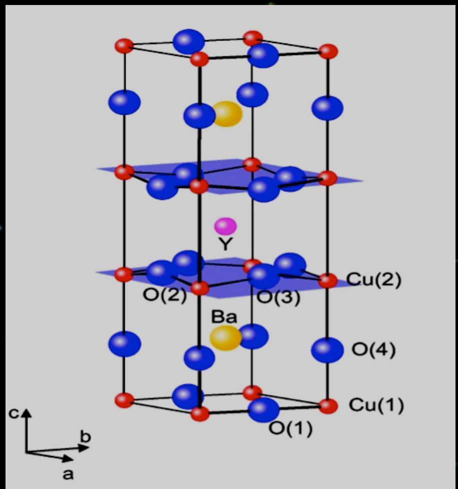


At the level of phonon spectra, the anomaly of the Bond Stetching Mode is very large

Copper Oxide Superconductors Remain Challenging…

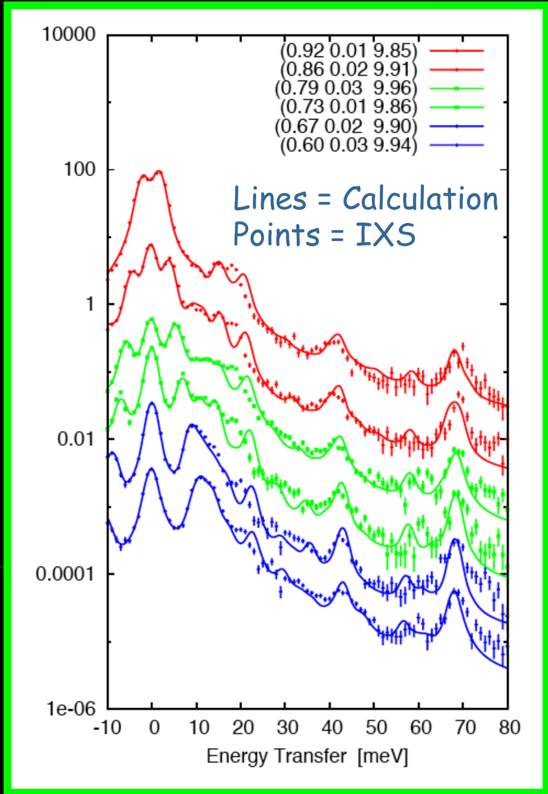
De-Twinned YBCO:
$YBa_2Cu_3O_{7-\delta}$

T_c = 91 K



C-axis modes

In-Plane Modes



Beautiful Agreement

Problems

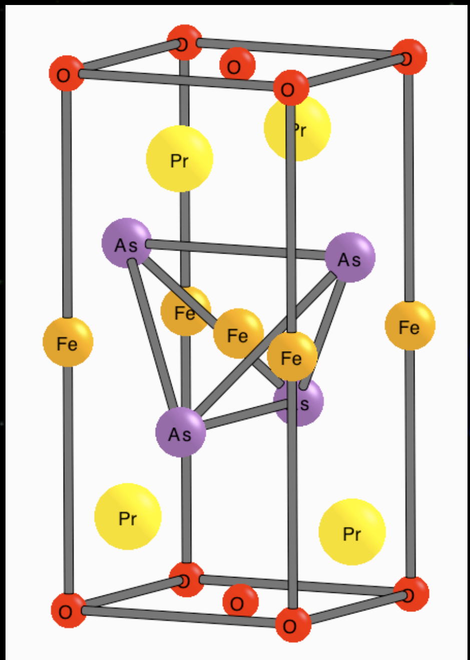
Shows Bond Stretching Anomaly
Is Huge (>> Buckling Anomaly)

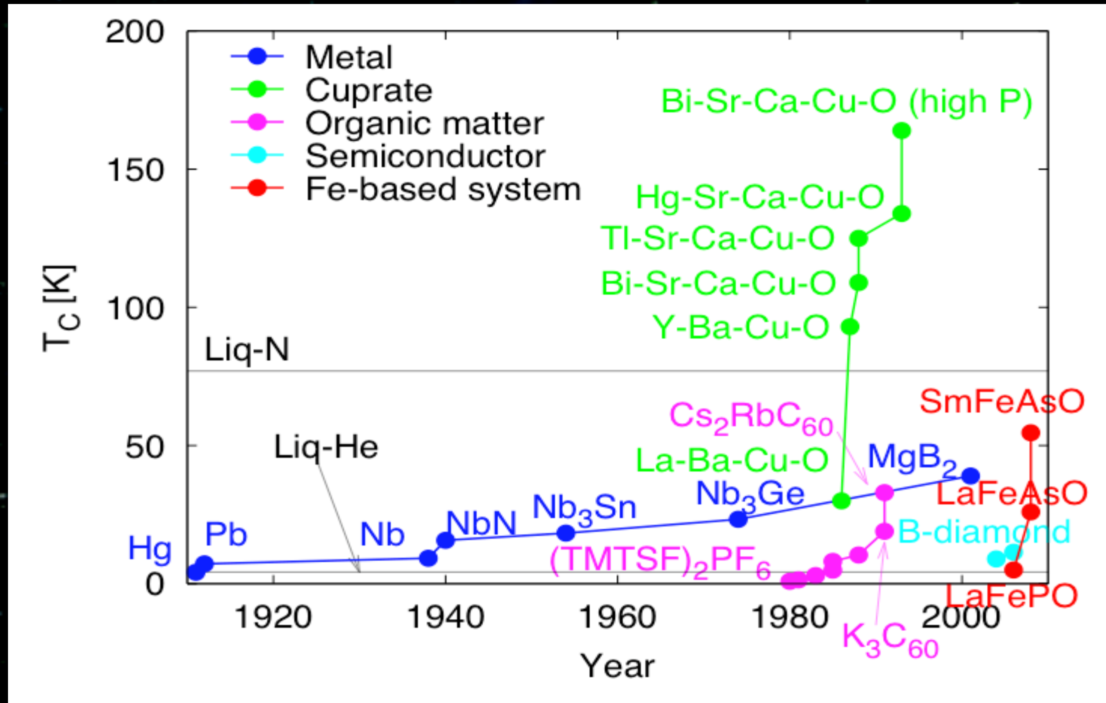
Compare IXS to Calculation
At low T (~30K)

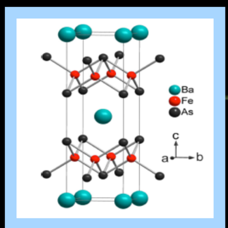
Bohnen, et al.

Iron-Pnictide Superconductors

High-T_c demonstrated February 2008 (Hosono's group)
(T_c saturated within months…)



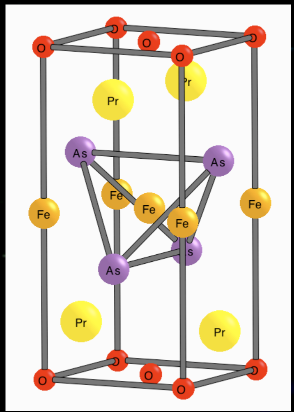




Several families: Fe with Tetrahedral As (or Se)

Proximity to Magnetic Order

Phonons in the Iron Pnictides



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.

Phonon response, in itself, is remarkably plain:

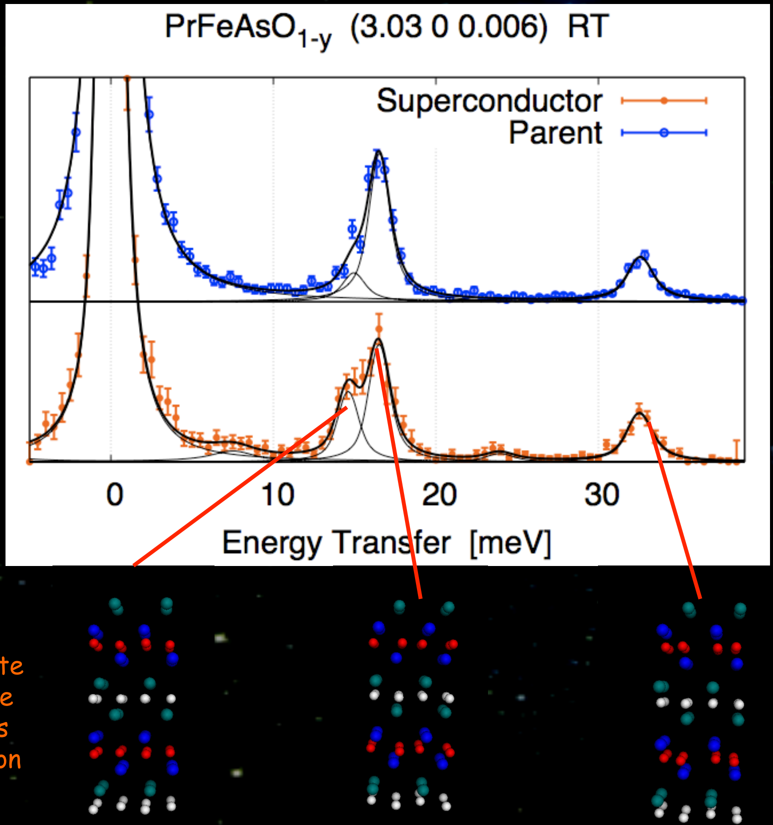
NO very large line-widths

NO obvious anomalies

NO asymmetric Raman lines

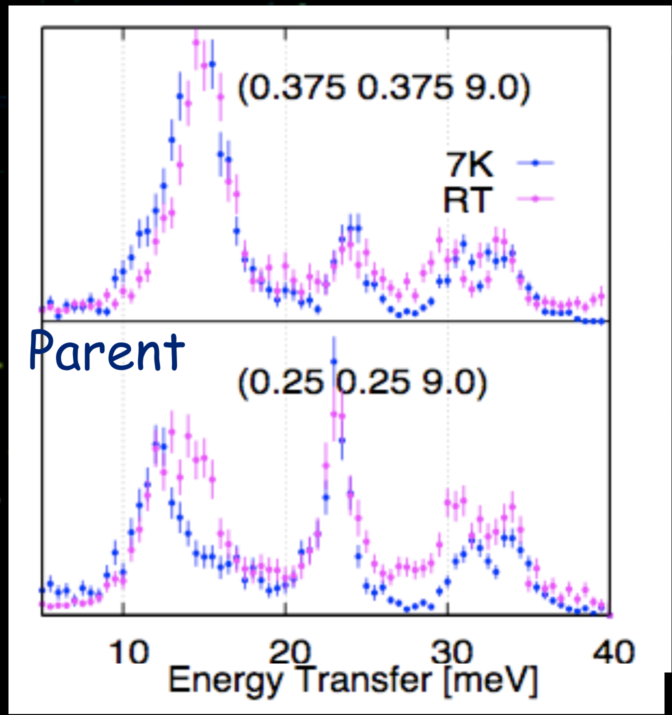
Some Examples of Measured Spectra:

In-Plane



Estimate of mode motions based on calc

C-axis



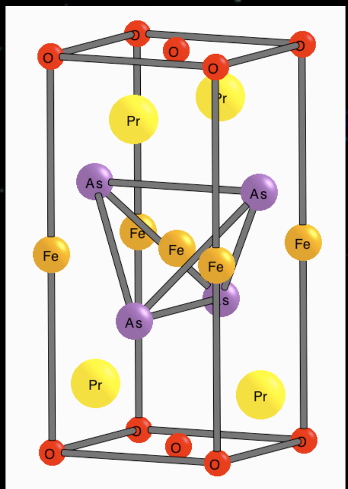
Clear differences in measured spectra (with doping, temperature)
-> interpretations requires modeling...

Basic DFT (GGA) for PrFeAsO

(No Magnetism)

Some agreement, but details are poor

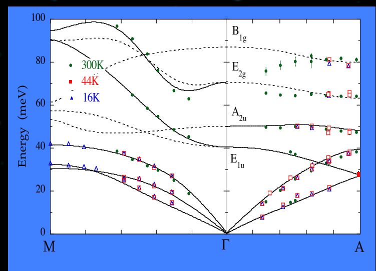
Also, fails to get correct As height above the Fe planes.

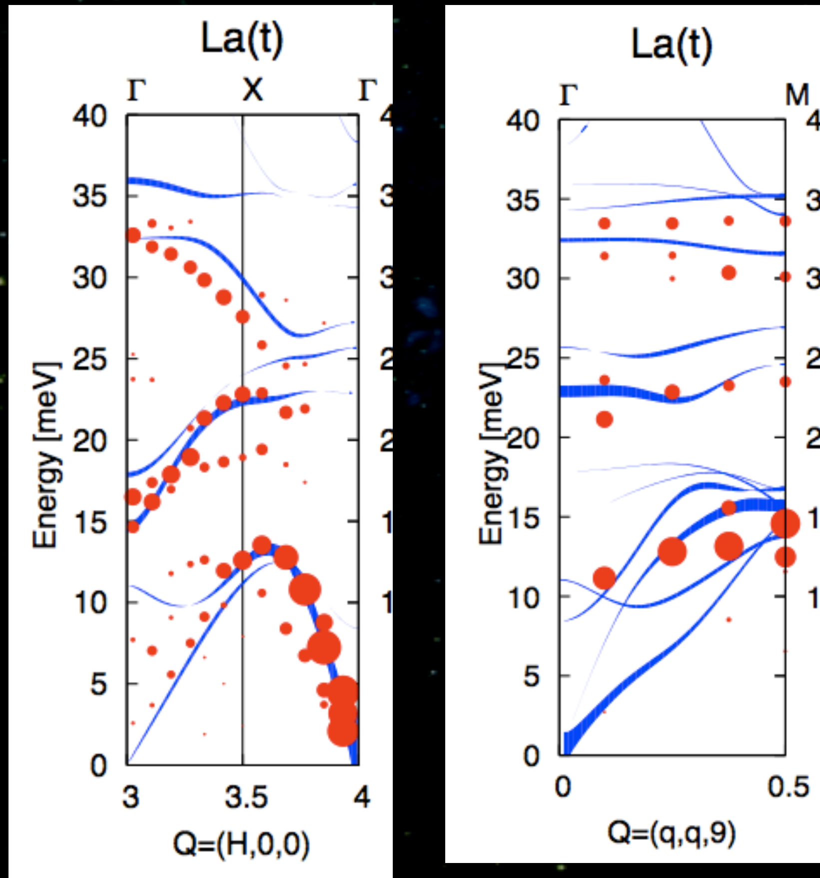


Fe-As Bond Length

Expt: 2.41 Å

GGA: 2.31 - 2.33 Å





A Better Model is Needed

Symbol size: Measured Intensity

Line Thickness: Calculated Intensity

Different Models:

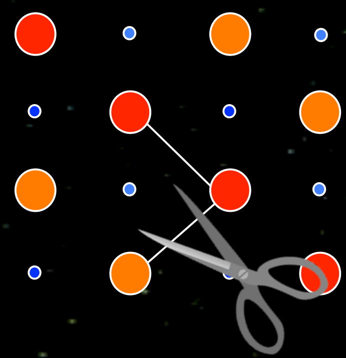
Original: Straight GGA for Tetragonal stoichiometric PrFeAsO

$O_{7/8}$: 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, 72 Ibam)

Magnetic Tetragonal: LSDA for LaFeAsO with stripes
Force a=b (to distinguish effects of structure vs magnetism)

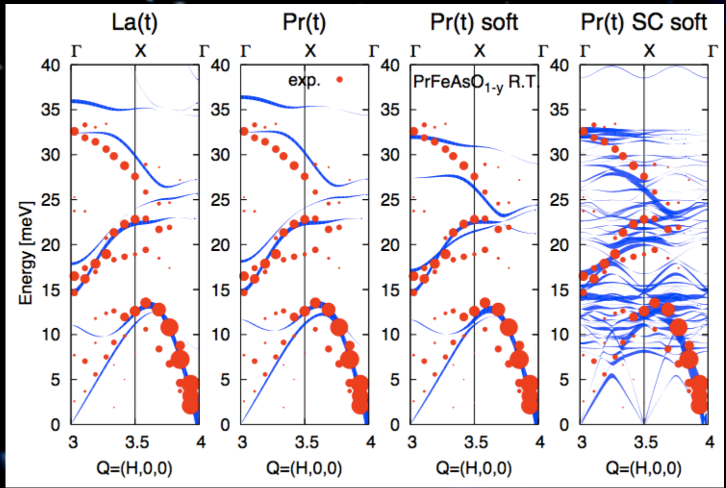
- Soft: As "Original" but soften the FeAs NN Force constant by 30%
- Clipped: Mag. Ortho. with cut force constant
- Soft IP: "Original" but soften FeAs NN ***In Plane*** components

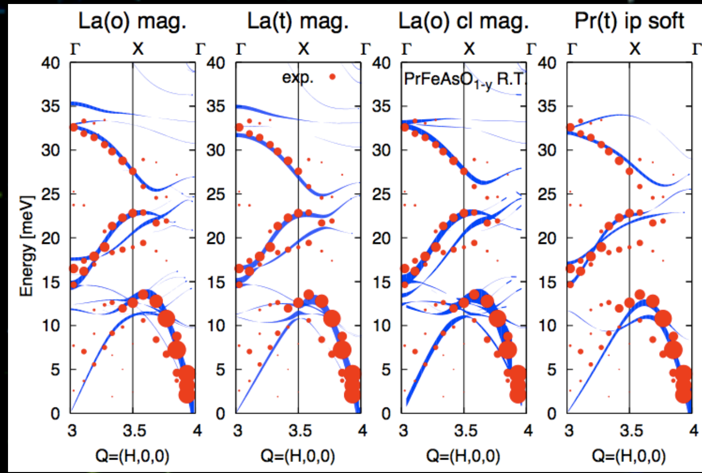


Original *ab-initio* Calculations: Nakamura & Machida

Compare dispersion with various models

In-Plane

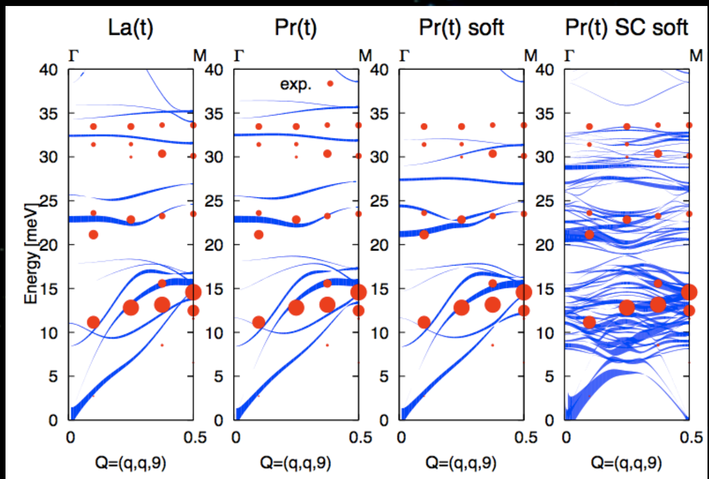


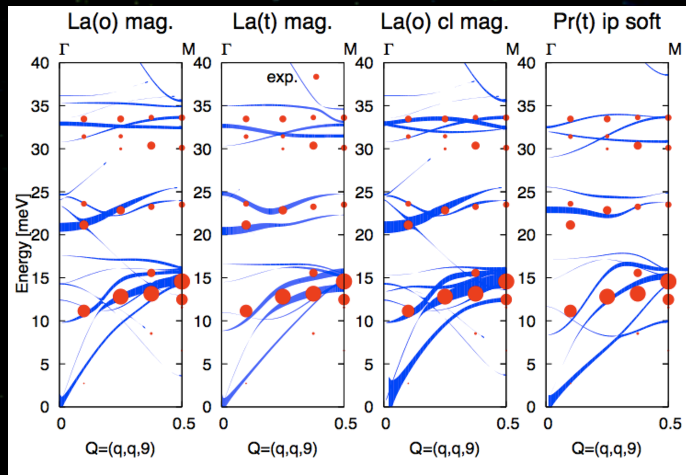


Red = Data (SC)

Blue = Calc.

C-axis





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 ferrmagnetically 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?

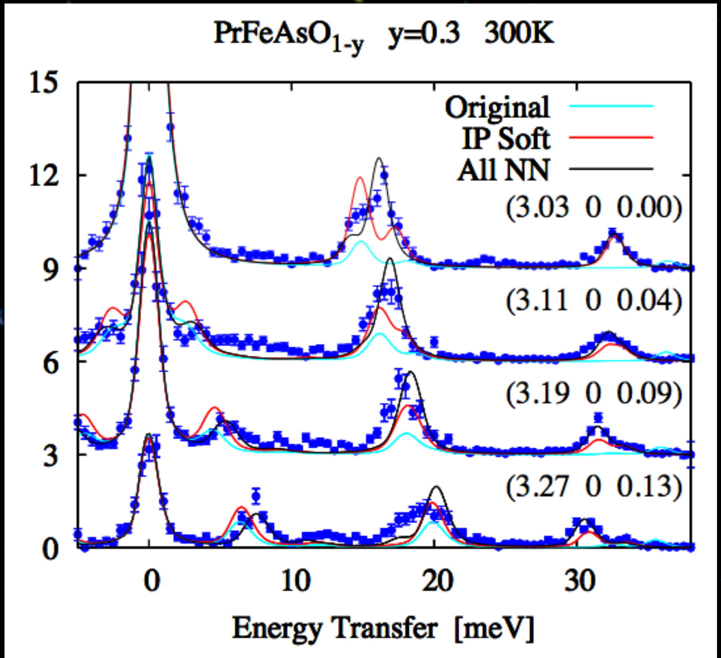
Fitting of full spectra: intensity vs energy transfer.

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

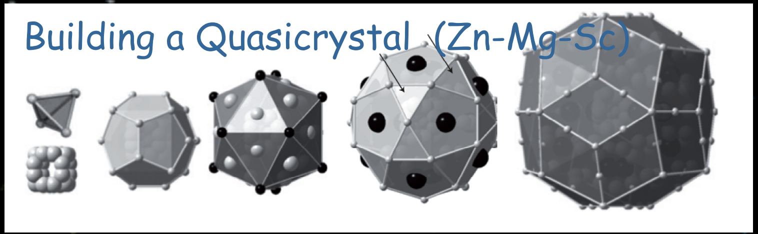


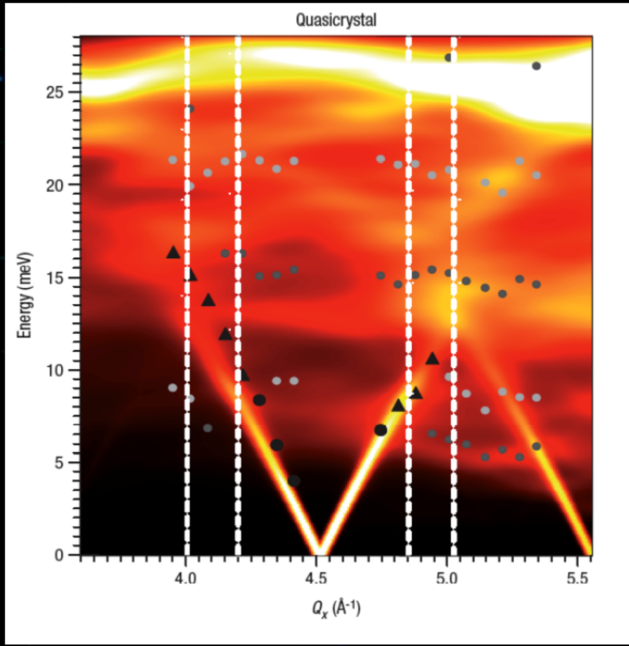
In-Plane Soft is
NOT bad but also
But also *NOT* great.

Some improvement by
allowing parts of nearly all
NN bonds to change.

Phonons in a Quasicrystal

Mostly like a solid but some glassy character.

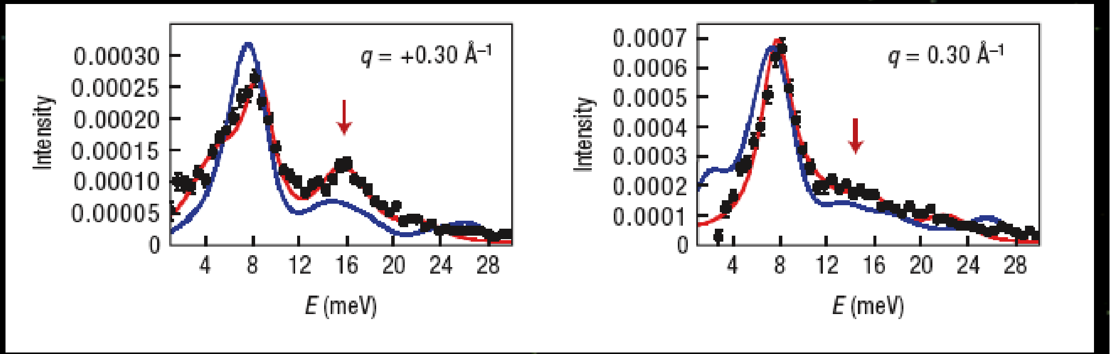




Periodic (BCC) -> **Crystalline** Approximant
Aperiodic -> **Quasicrystal**

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

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



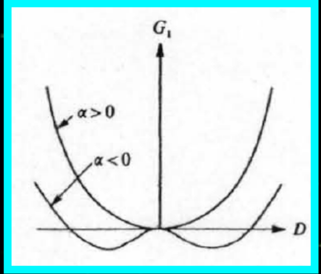
De Boissieu, *et al.*
Nature Materials, Dec 2007

Red: Fits, Blue: Simulation

Ferroelectrics

Develop spontaneous polarization over macroscopic (>~um) domains when T is below the ferroelectric transition temperature (T_0). The origin is a displacement (off-centering) of ions. This is switchable by an external (electric) field.

Zeroth Approximation -> Two types of transitions



"Displacive" transition where there is a "continuous" below T

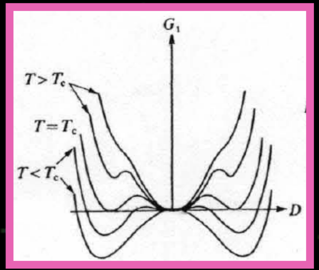
"Soft Mode" transition   Examples: $BaTiO_3$, $KTaO_3$, Gd $(MoO_4)_3$

Soft Mode Nomenclature

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

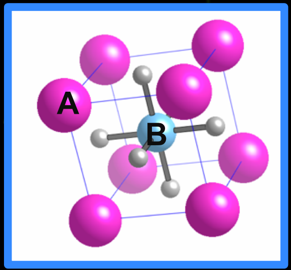
Antiferrodistortive involves softening of zone boundary mode (unit cell size increases)

Lines & Glass



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

Examples KH_2PO_4(KDP), $NaNO_2$, Organics



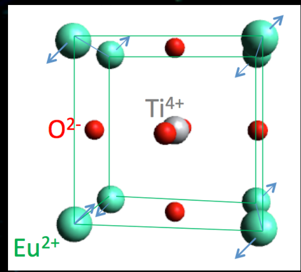
Perovskite structure (ABO_3) popular as it is ***relatively*** simple and the cubic structure is inherently unstable.. Why?

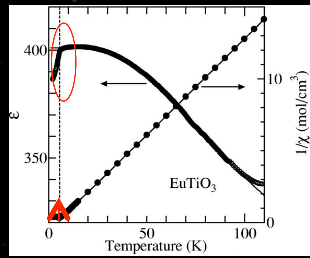
(3 atoms & one lattice constant)

Multiferroic $EuTiO_3$

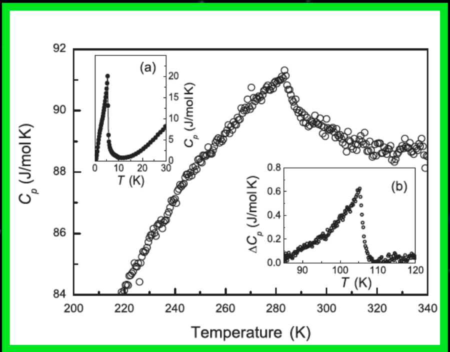
Perovskite – Similar to $SrTiO_3$

But with magnetism & coupling of magnetic & dielectric response

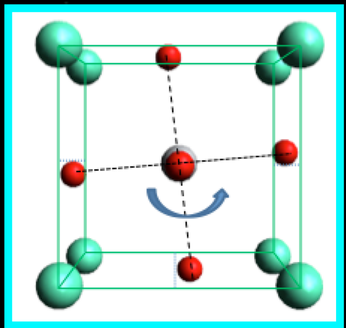


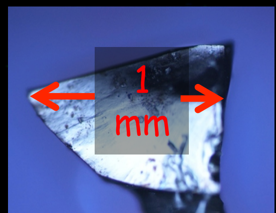


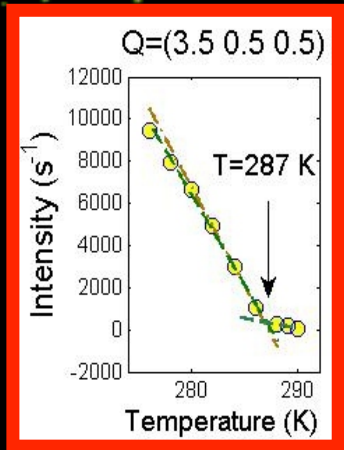
Katsufuji & Takagi , PRB,2001

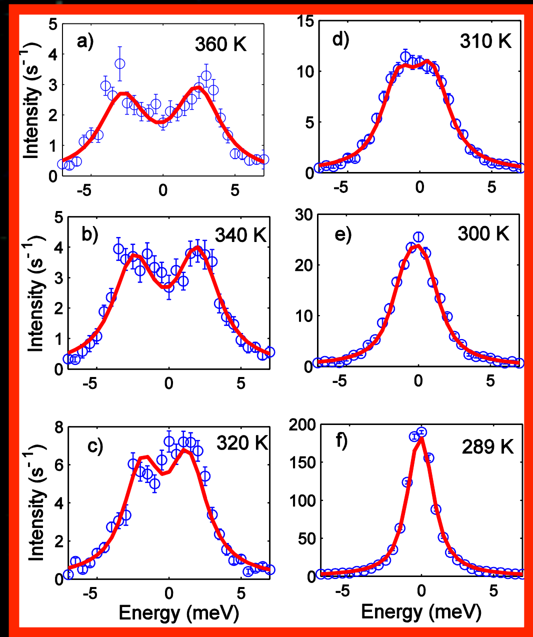


Phase transition just below RT – putative rotation oxygen octahedra.
Calculations say disorder-order.
Bussman-Holder, PRB, 2011



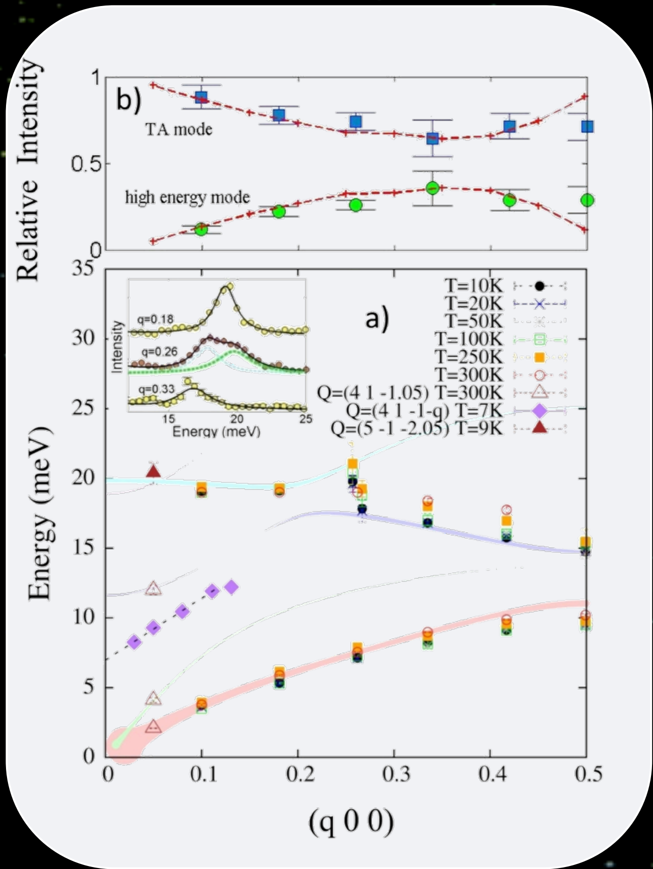


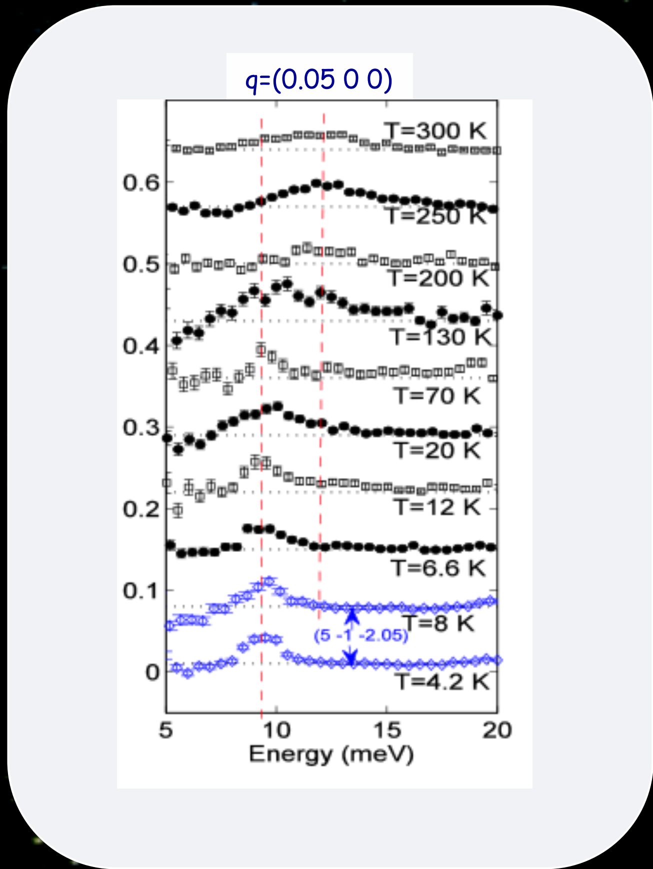




IXS -> Phonon Softening-> Displacive

Dispersion, Shell Model, & Approaching T_N



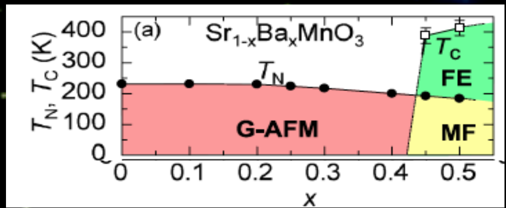


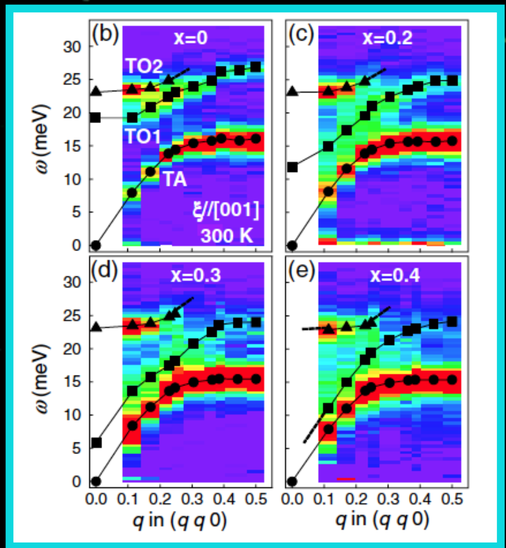
Shell model -> Good agreement
Suggests "soft" mode has Slater character.

"Softening" (or weight shift) as T is reduced toward T_N consistent with gradual change in dielectric response

Multiferroics

$Sr_{1-x}Ba_xMnO_3$

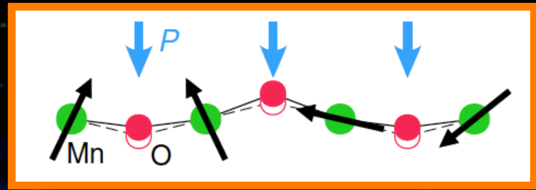




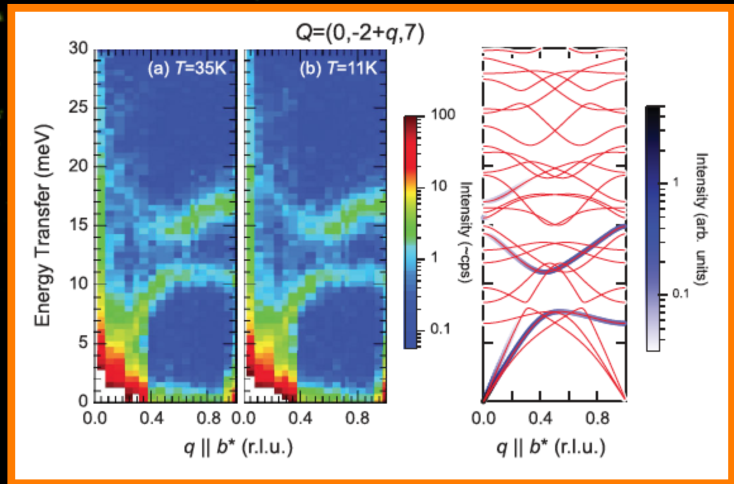
Classical ferroelectric soft mode

Sakai, et al. PRL 2011 (Tokura-lab)

$TbMnO_3$



Cycloidal spin structure coupled to development of polarization below 28K



No observed phonon softening may suggest a different (magnetic) driving force

Kajimoto, et al. PRL 2009 (Tokura-lab)

IXS under High Pressure

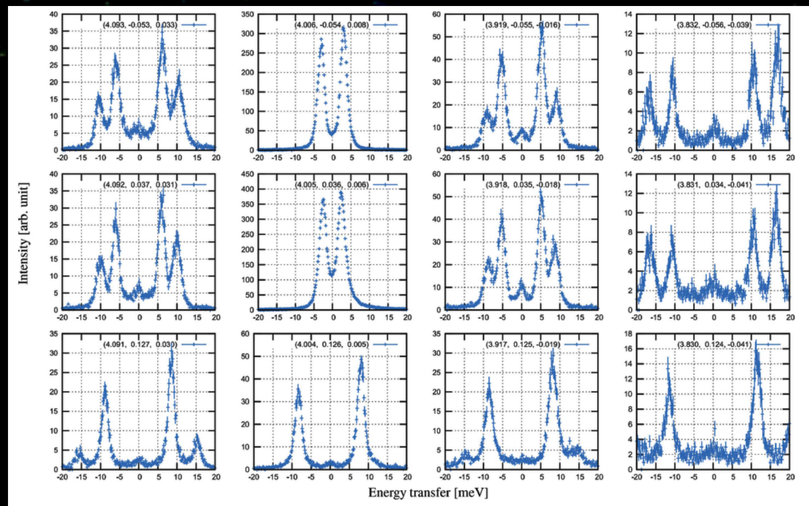
General Viewpoint: Just another thermodynamic variable.

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
H. Fukui, et al., JSR

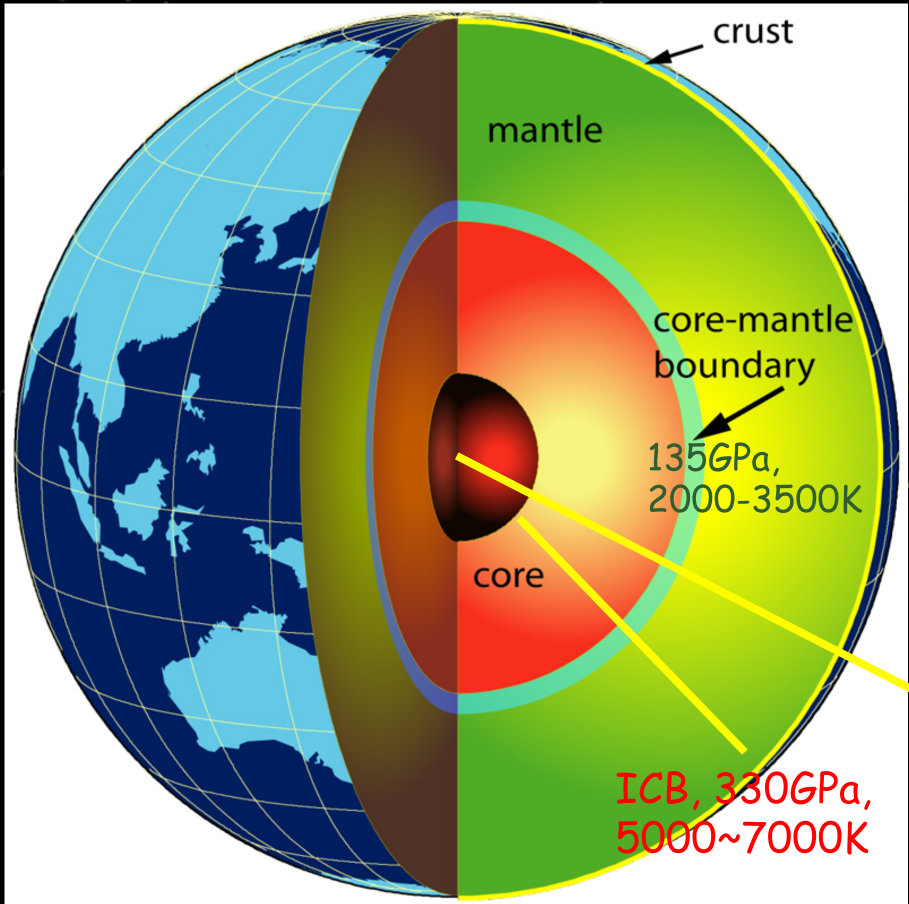
~1 Order Improvement in Precision
Over Previous IXS

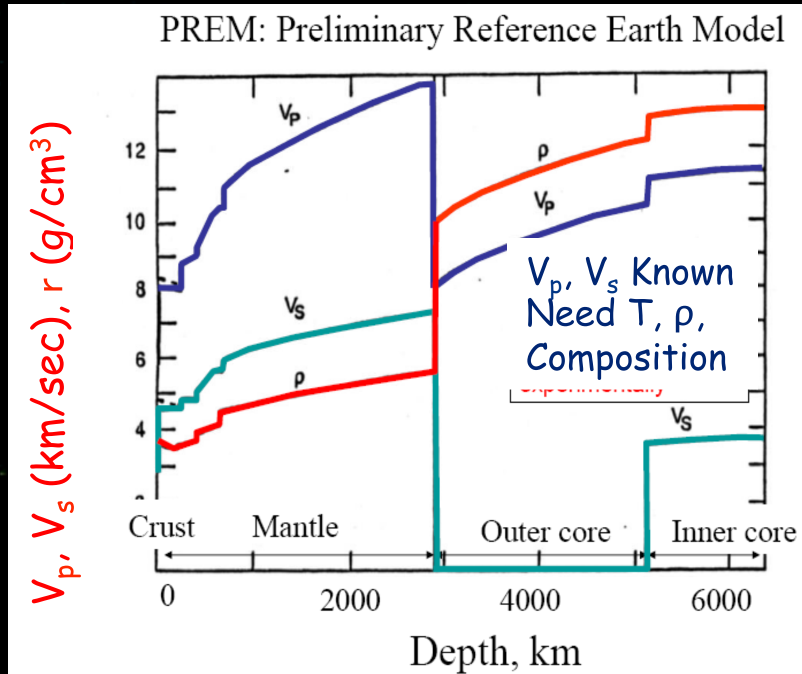
MgO Single Crystal in Ambient Conditions



One Scan with 12-Analyzers

High Pressure & Temperature for Geology





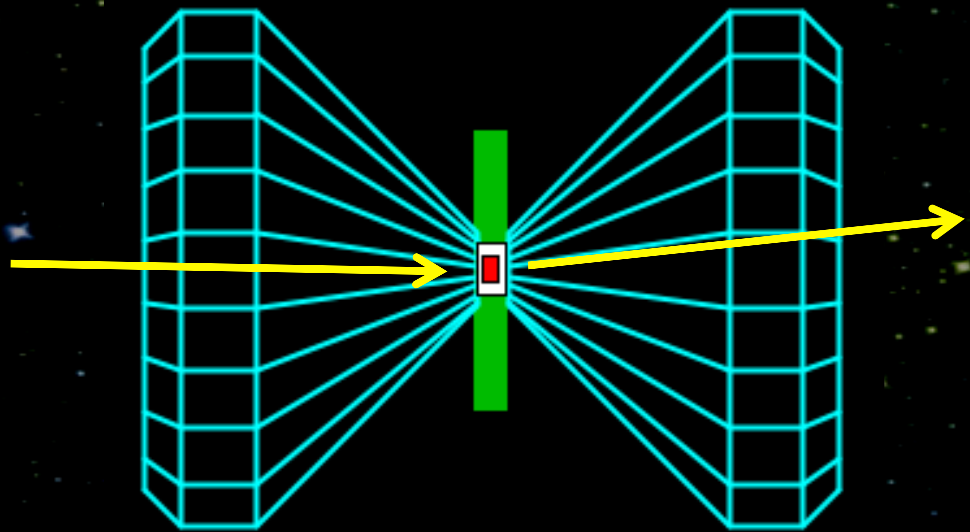
Earth's Center, 365 GPa
6000~8000 K

Needed: Lab measurements relating T, Density & Composition to V

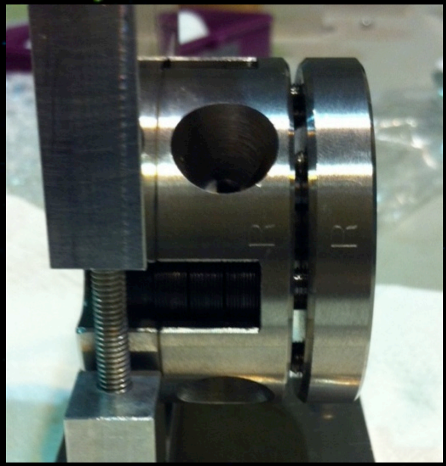
Diamond Anvil Cells

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

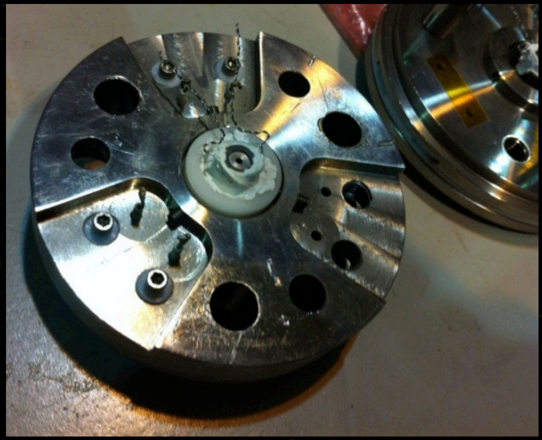
So far with IXS:
170 GPa or 1800K



Diamonds: 2 x 1.5mm Thk
Sample: ~ Φ20 μm x 5μm Thk
Also Gasket & Pressure Medium
P increases -> Smaller Sample & Gasket Hole



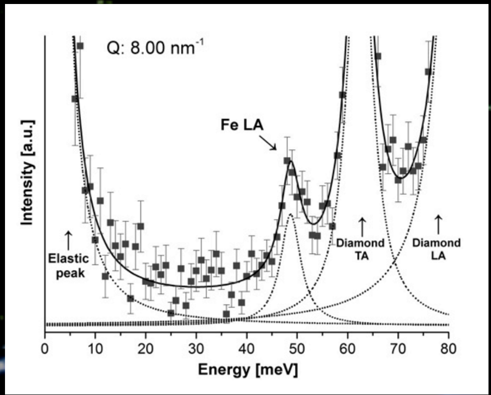
Std Cell
Laser



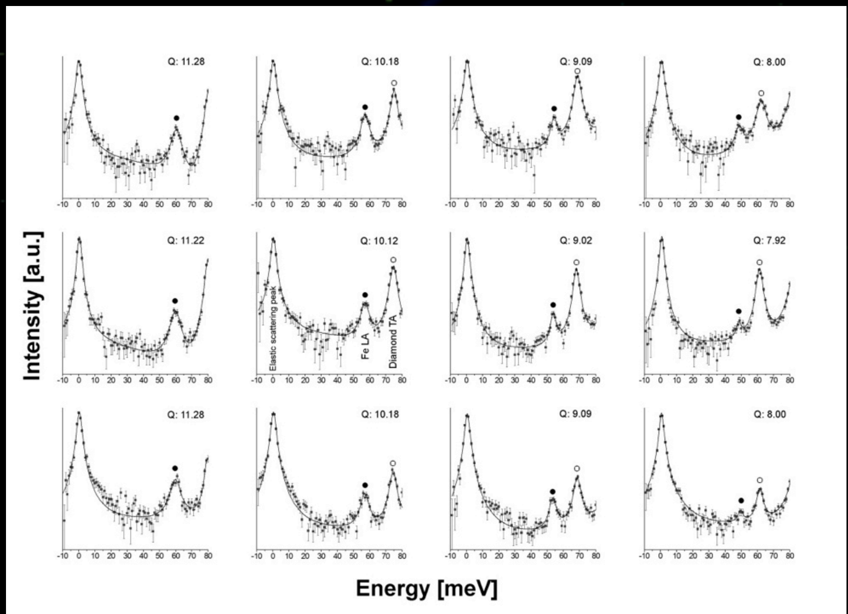
Cell with Internal Heating

Small samples, Signal low, Poor signal to noise

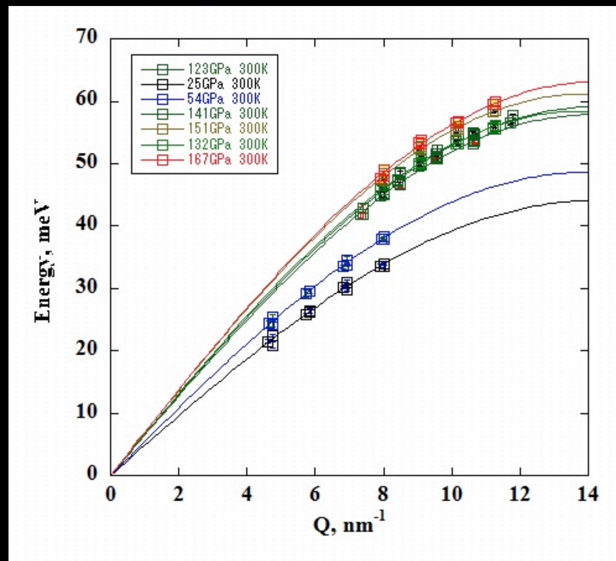
IXS Data for Iron at 167 GPa



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

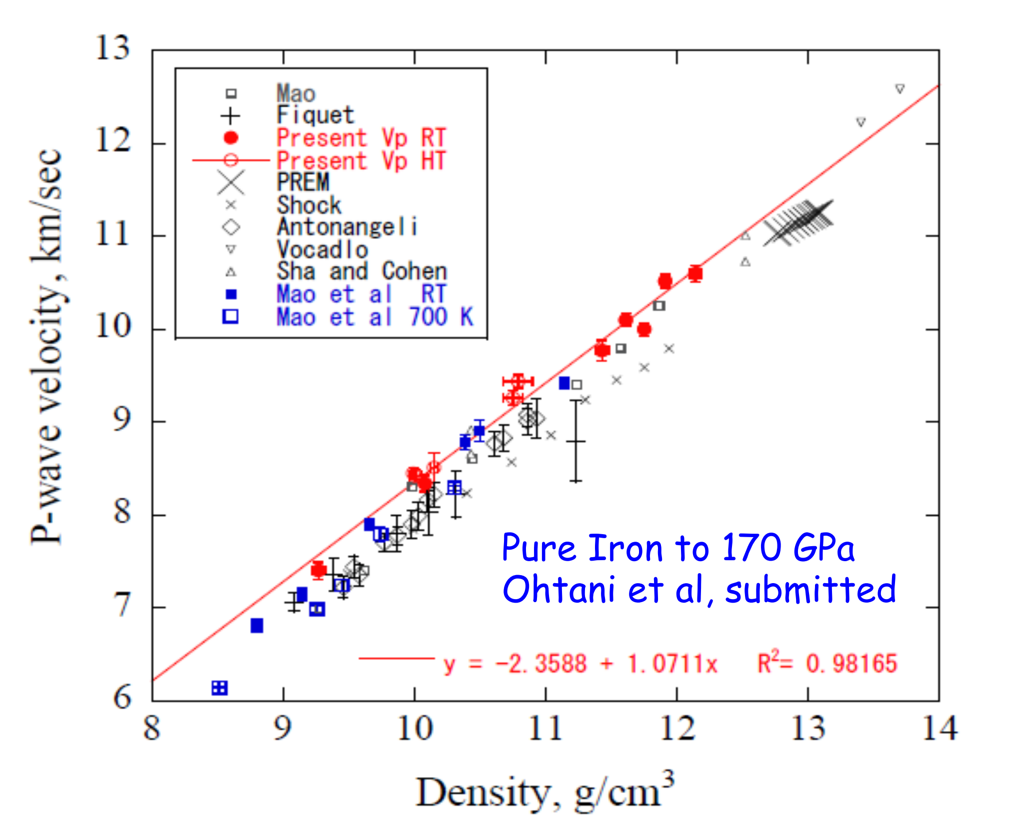


Sine fit gives velocity (V_p)



Sound Velocity in Pure Iron

Birch's Law: 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.

Discussion is needed -> workshop

Novel Uses of The Phonon *Intensity*

Phonon Cross Section:

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\mathbf{k}_1\varepsilon_1 \to \mathbf{k}_2\varepsilon_2} = \frac{k_2}{k_1}\, r_e^{\,2} \left|\varepsilon_1^{*} \bullet \varepsilon_2\right|^2 S(\mathbf{Q},\omega)$$

$$S(\mathbf{Q},\omega)_{1p} = N \sum_{\substack{\mathbf{q}\\ 1st\ Zone}} \sum_{\substack{j\\ 3r Modes}} \left| \sum_{\substack{d\\ Atoms\\ /Cell}} \frac{f_d(\mathbf{Q})}{\sqrt{2M_d}}\, e^{-W_d(\mathbf{Q})}\, \mathbf{Q}\bullet\mathbf{e}_{\mathbf{q}jd}\, e^{i\mathbf{Q}\bullet\mathbf{x}_d} \right|^2 \delta_{(\mathbf{Q}-\mathbf{q})\tau}\, F_{\mathbf{q}j}(\omega)$$

$$F_{\mathbf{q}j}^{Harmonic}(\omega) = \frac{1}{\omega_{\mathbf{q}j}}\left[\left\langle n_{\omega_{\mathbf{q}j}} + 1\right\rangle \delta\left(\omega - \omega_{\mathbf{q}j}\right) + \left\langle n_{\omega_{\mathbf{q}j}}\right\rangle \delta\left(\omega + \omega_{\mathbf{q}j}\right)\right]$$

In principle, the phonon polarization is complex, but in some cases, it can be simple, or smooth, letting one get information about

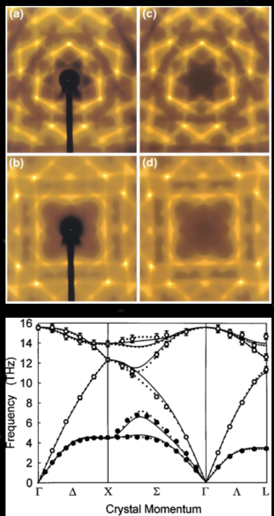
e.g. the form factor from frequency resolved measurements or
sharp frequency changes from integrated measurements

Using Thermal Diffuse Scattering (TDS)

Phonon Intensity ~ 1/w -> In simple materials can use intensity to gain insight about phonon frequencies

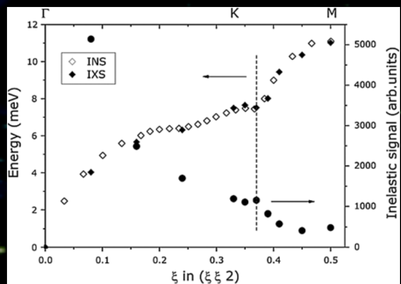
Long history… at least to Colella and Batterman PR 1970 (Va dispersion)

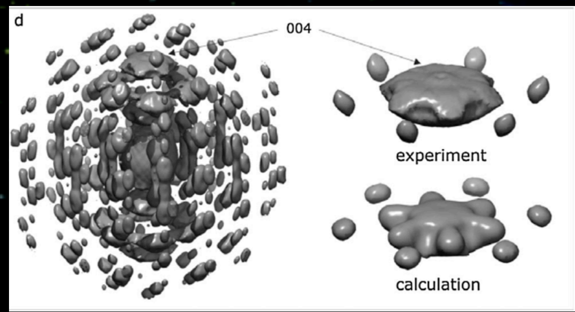
More sensitive -> See Kohn anomalies when phonons span the Fermi surface

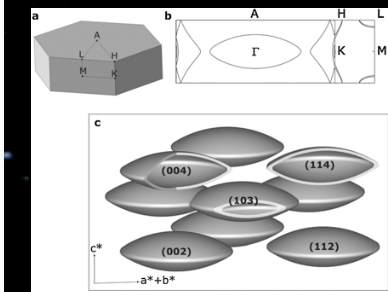


TDS from Silicon

Holt, et al, PRL 1999





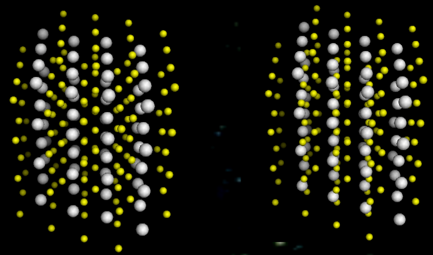


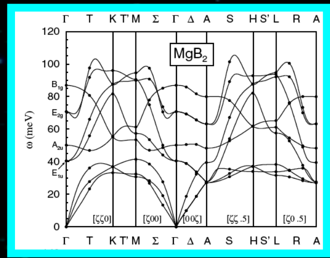
Zn, Bosak et al, PRL 2009

Detailed Phonon/FS behavior in SIMPLE materials
More generally very useful, but not so detailed
… use it to learn where to look…

Atomic -> Electronic Dynamics

Atomic Dynamics

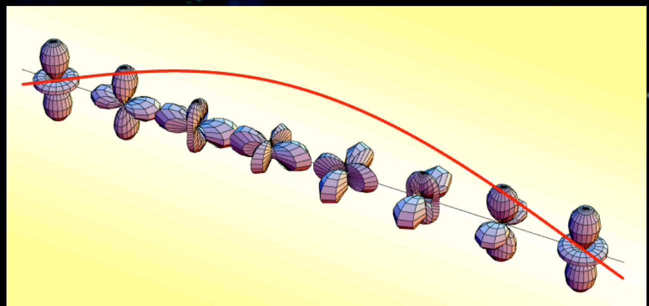




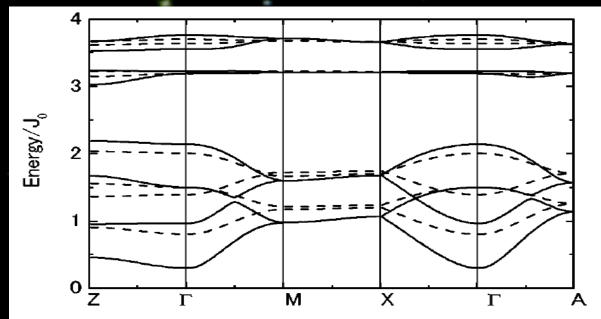
Correlated atomic motions (phonons) play a role in many phenomena
(e.g. superconductivity, CDWs, phase transitions, thermoelectricity, magneto-elastic phenomena etc)

Electronic excitations similar: Orbitons...?

Orbiton Movie
S. Maekawa



1 electron-> Very Weak



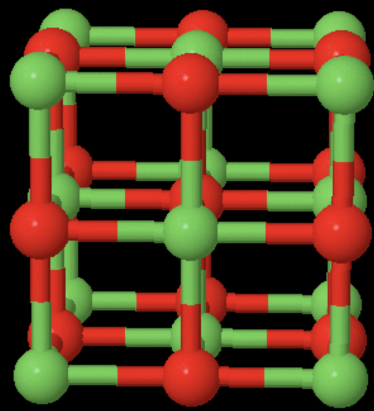
Calculated Orbiton Dispersion
Ishihara

Key is to see momentum dependence (dispersion).

First Attempt via IXS: NJP 2004

d-d Excitations in NiO

First something simple...



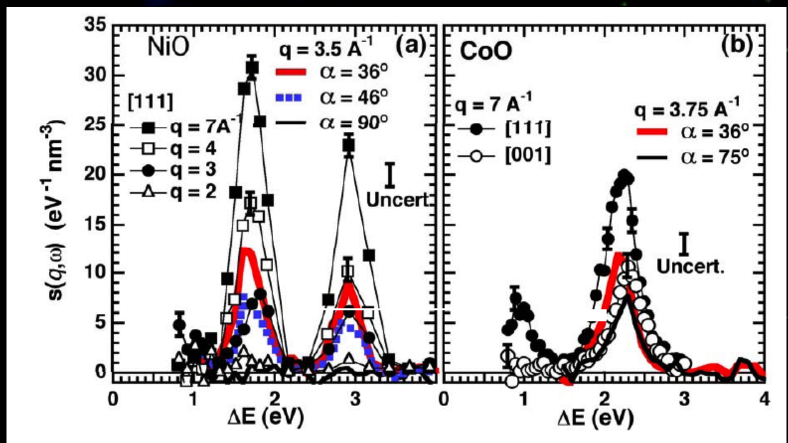
There exist well-defined excitations in the charge transfer gap of NiO

Antiferromagnet (T_N 523K), (111) Spin order

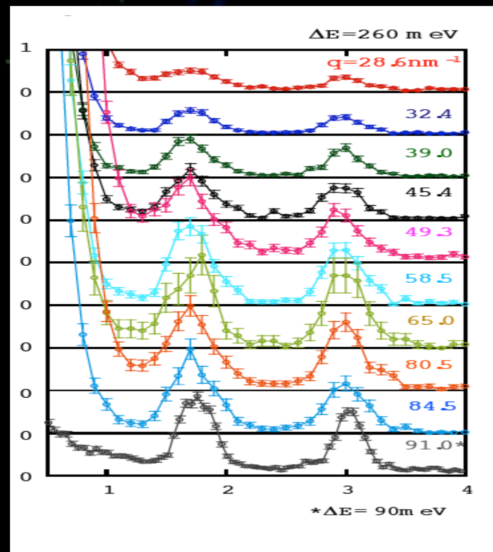
Long and Distinguished History

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

Non-Resonant IXS, ΔE~300 meV

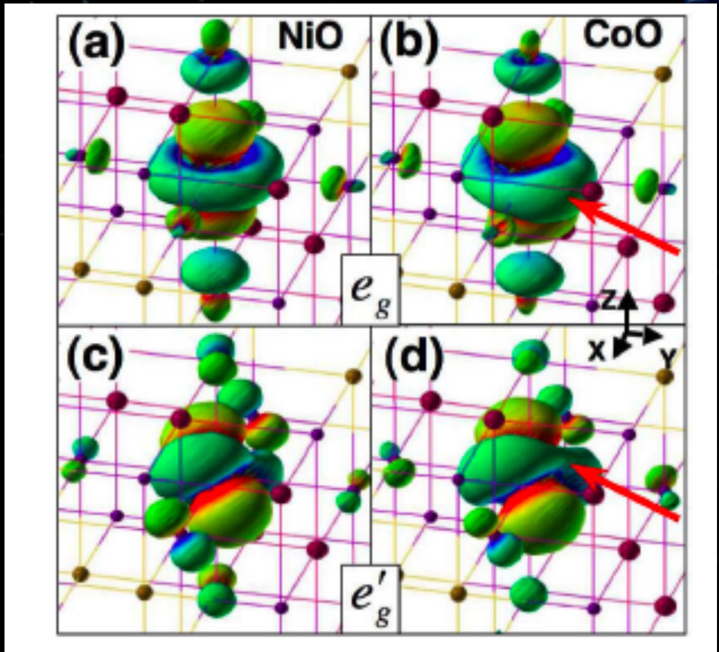


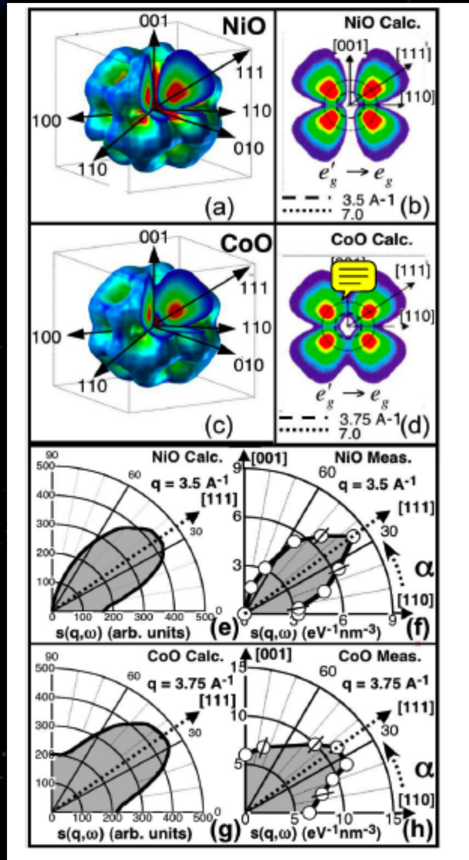
Larson, et al., PRL 99 (2007) 026401

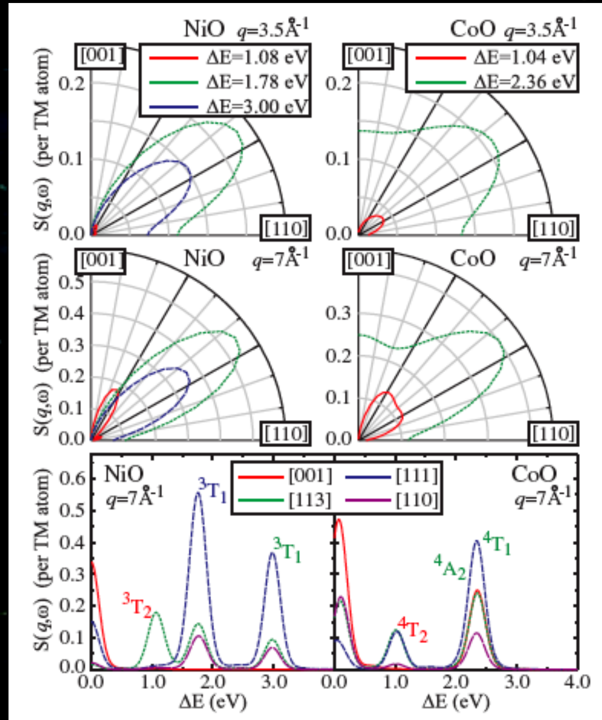


Cai, et al, BL12XU, Unpublished

Orientation Dependence







Orbitals

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

Scattered Intensity

Cluster calculations
Haverkort, 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 -> information about environment

- Spin fluctuations
- Lattice interactions (Franck-Condon)

d-d Excitation in NiO

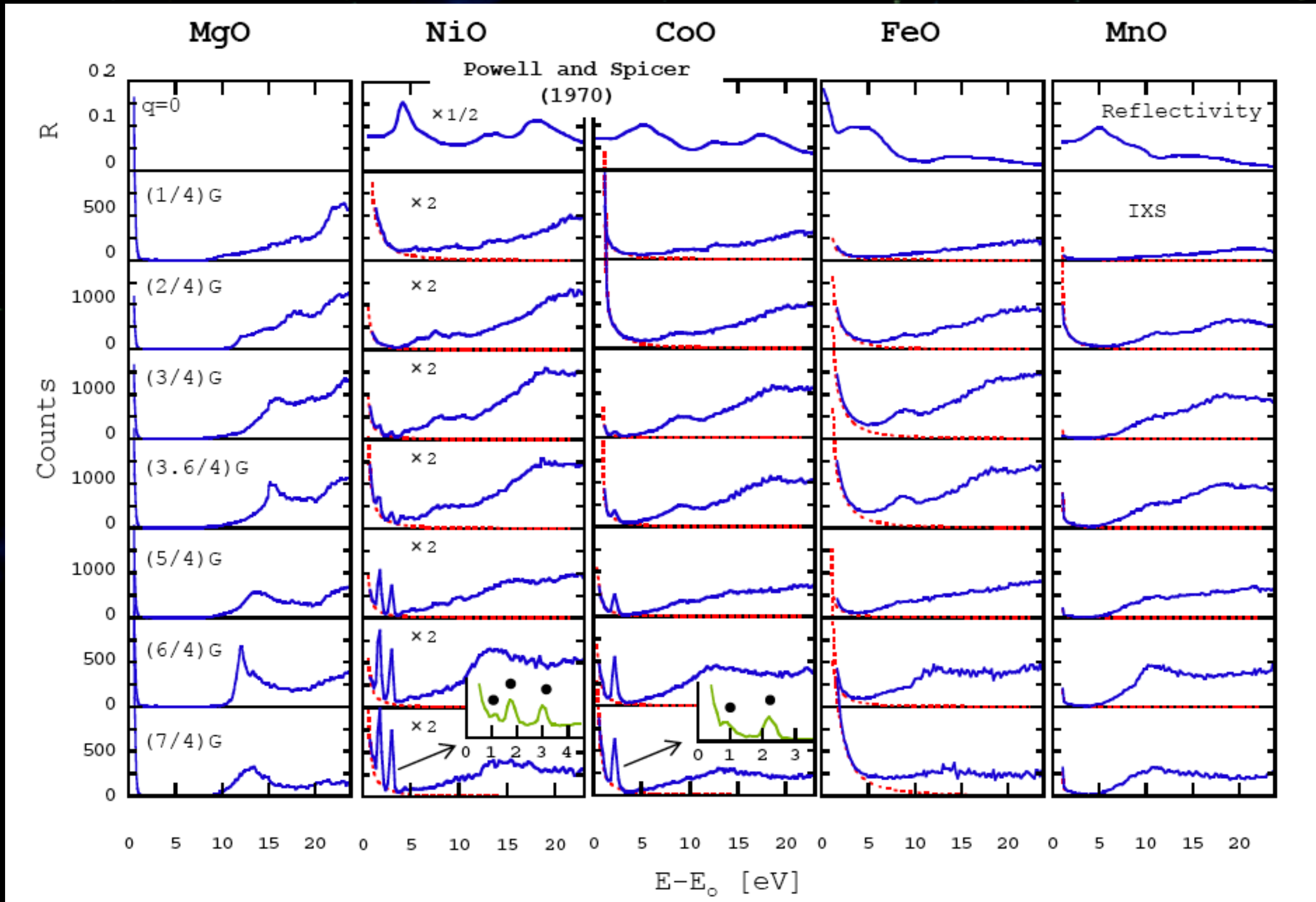
3 Days/Spectrum

Collective interaction <-> dispersion

Relevance to correlated materials…

- Gaps (Mott, Charge Transfer, SC) and
- Mid-IR band in high Tcs
- f-electron transitions, etc

Larger Energy Range



Hiraoka et al

"Momentum Resolved Optical Spectroscopy"

Conventional Optical Spectroscopy:

(Absorption, Reflectivity)

Information on electronic energy levels but *without* information on inter-atomic correlations or atomic structure

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?

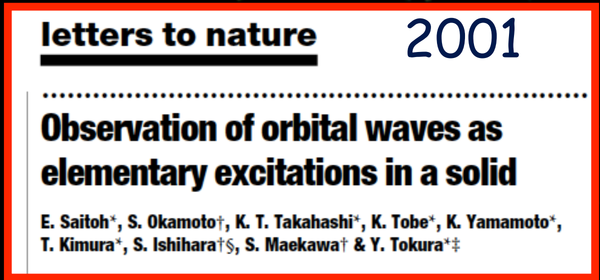
Resonant experiment vs non-resonant IXS experiment.

Non-resonant experiment is simpler and can have higher resolution
… but badly flux limited

The Orbiton Story
(One, mostly experimental, viewpoint)

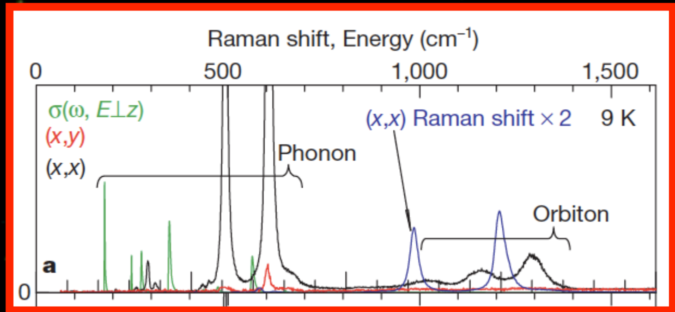
Orbital order exists -> there should be an equivalent excitation

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

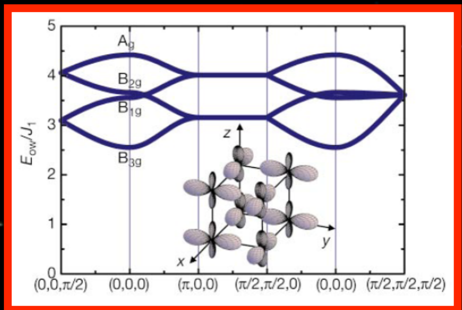

letters to nature 2001

Observation of orbital waves as elementary excitations in a solid

E. Saitoh*, S. Okamoto†, K. T. Takahashi*, K. Tobe*, K. Yamamoto*, T. Kimura*, S. Ishihara†§, S. Maekawa† & Y. Tokura*‡



LaMnO$_3$



Calculated Dispersion

But some dissent:

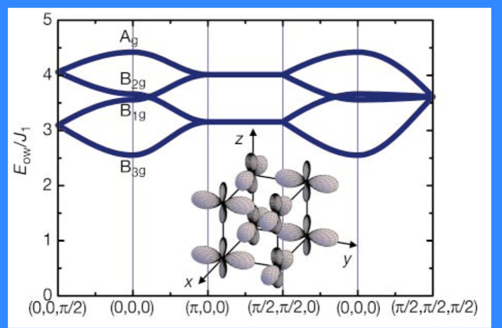
Two phonon peak?

Gruninger (n), Kruger (prl), Marin-Carron (prl)

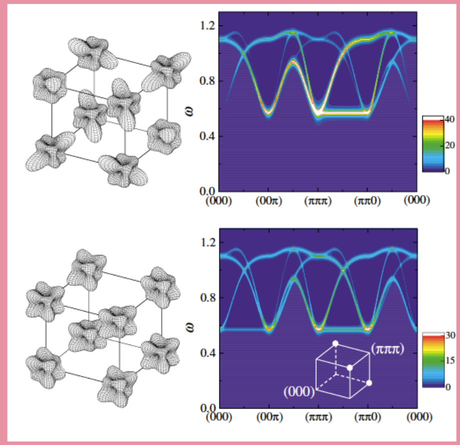
And also corroboration

Raman spectra from different materials

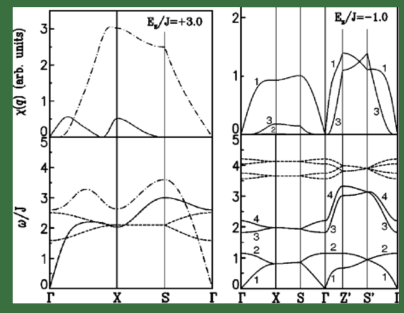
Calculated Orbiton Dispersion



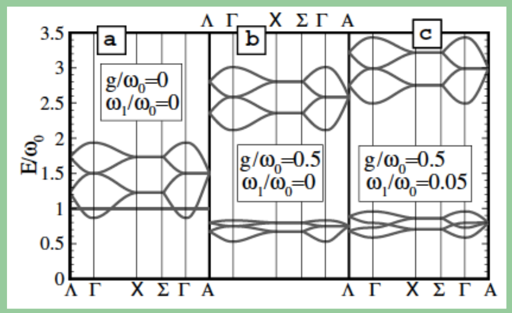
Saitoh et al, (N 2001)



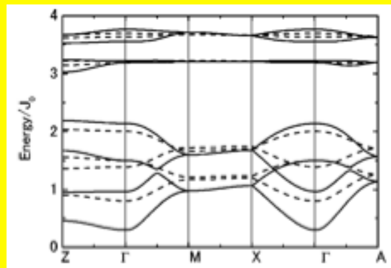
Khaliullin & Okamoto (PRL 2002)



Oles, Feiner, Zaanen (PRB 2000)



van den Brink (PRL 2001)



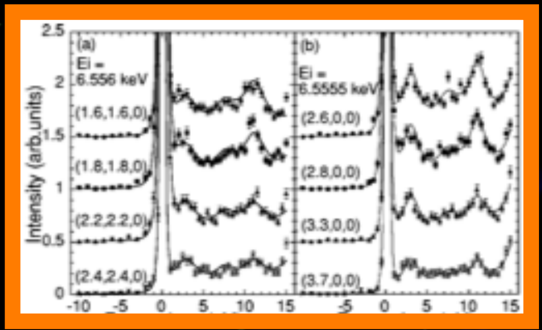
Ishihara (PRB 2004)

Still Some Debate:

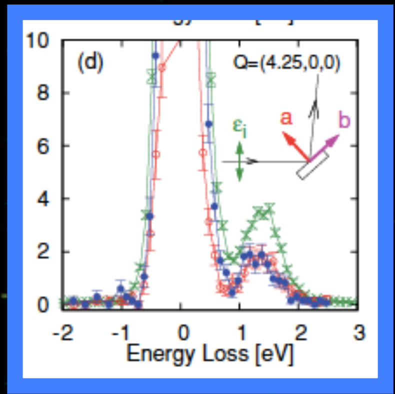
- Energy scale?
- Coupling to phonons and/or spin?
- Linewidth small or large?

Resonant IXS (RIXS)

K-Edge RIXS (d-d excitations)



$LaMnO_3$ Inami, et al (prb 2003)

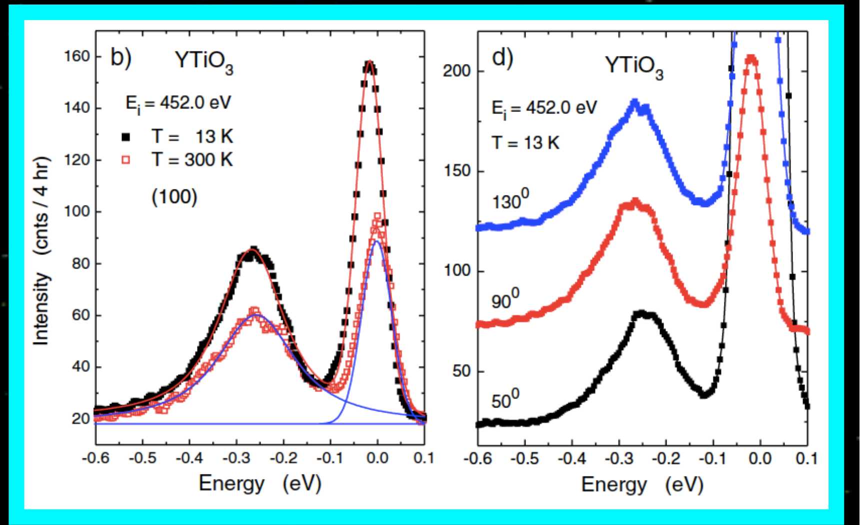


$KCuF_3$ Ishii, et al (PRB 2011)

Soft x-ray RIXS (SRIXS)

Ulrich, Ament, et al (PRL 2009)
At SLS/ADDRESS

L_3 in YTiO3, 55 meV Resolution at 450 eV



2-orbiton signal at 250 meV...

Resolution Improving:
1000 -> 250 meV -> 70 meV

2011: STILL NO DISPERSING EXCITATIONS

Recent Work

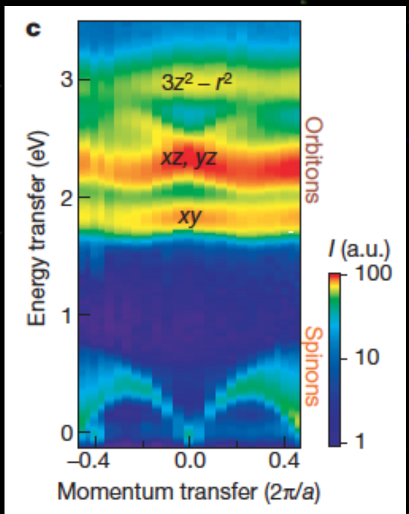
LETTER

May, 2012

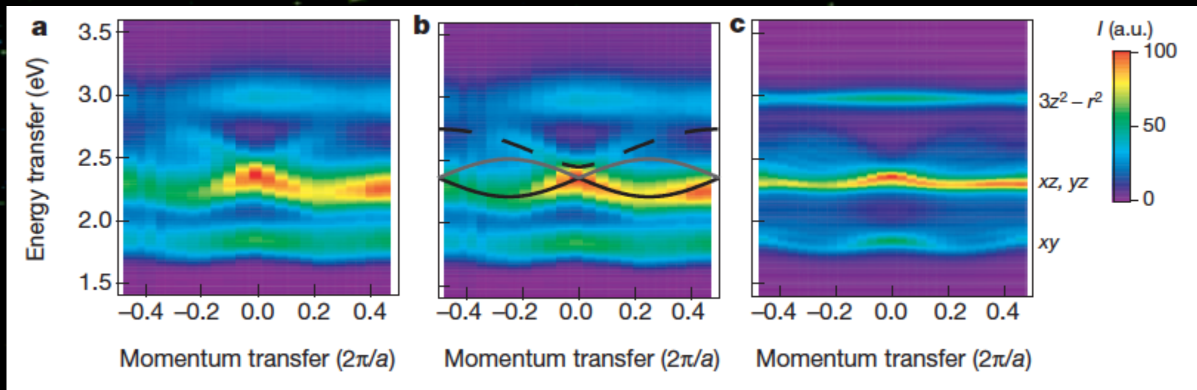
doi:10.1038/nature10974

Spin–orbital separation in the quasi-one-dimensional Mott insulator Sr_2CuO_3

J. Schlappa[1,2], K. Wohlfeld[3], K. J. Zhou[1]†, M. Mourigal[4], M. W. Haverkort[5], V. N. Strocov[1], L. Hozoi[3], C. Monney[1], S. Nishimoto[3], S. Singh[6]†, A. Revcolevschi[6], J.-S. Caux[7], L. Patthey[1,8], H. M. Rønnow[4], J. van den Brink[3] & T. Schmitt[1]



High Energy Excitation in Sr_2CuO_3



Resonant IXS
(RIXS/SIXS)

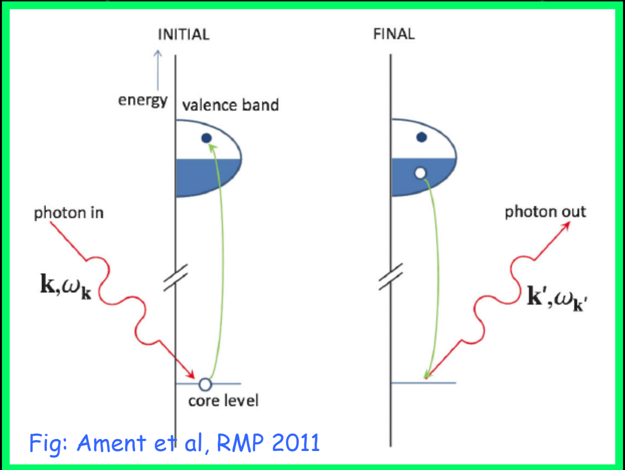


Fig: Ament et al, RMP 2011

Direct RIXS

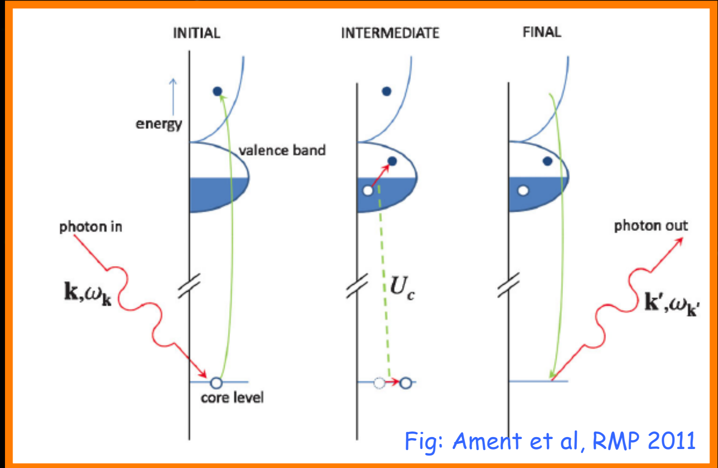


Fig: Ament et al, RMP 2011

*In*Direct RIXS

K Lines: Stronger, easier to reach for transition metals
L Lines: Weaker, lower energy

Photons: Orbital angular momentum change, Δl=1, dominates: s-> p or p->d

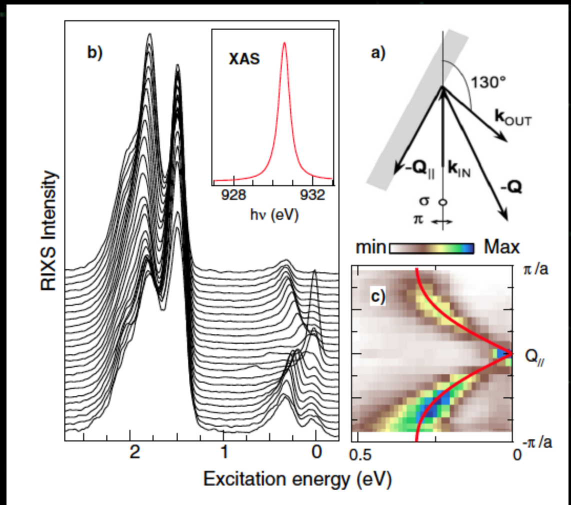
Science: Most interest is in d-orbitals

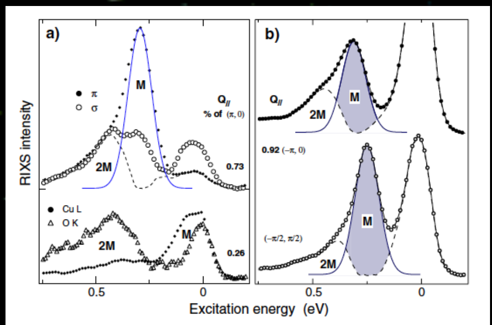
Spin Waves Possible

PRL 105, 157006 (2010) PHYSICAL REVIEW LETTERS week ending 8 OCTOBER 2010

Measurement of Magnetic Excitations in the Two-Dimensional Antiferromagnetic $Sr_2CuO_2Cl_2$ Insulator Using Resonant X-Ray Scattering: Evidence for Extended Interactions

M. Guarise,[1] B. Dalla Piazza,[1] M. Moretti Sala,[2] G. Ghiringhelli,[2] L. Braicovich,[2] H. Berger,[1] J. N. Hancock,[3] D. van der Marel,[3] T. Schmitt,[4] V. N. Strocov,[4] L. J. P. Ament,[5] J. van den Brink,[5] P.-H. Lin,[1] P. Xu,[1] H. M. Rønnow,[1] and M. Grioni[1]





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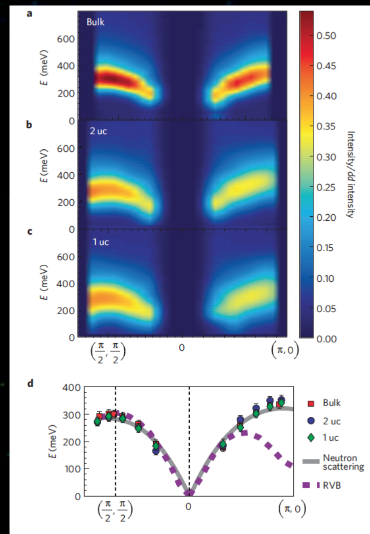
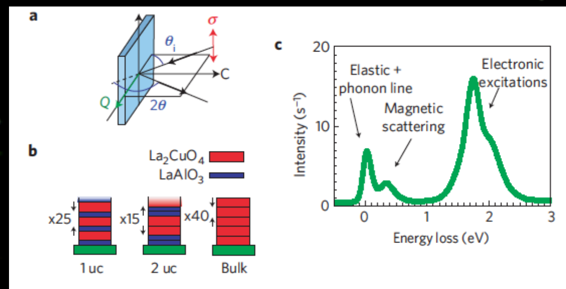
Spin excitations in a single La_2CuO_4 layer

M. P. M. Dean[1]*, R. S. Springell[2,3], C. Monney[4], K. J. Zhou[4†], J. Pereiro[1†], I. Božović[1], B. Dalla Piazza[5], H. M. Rønnow[5], E. Morenzoni[6], J. van den Brink[7], T. Schmitt[4] and J. P. Hill[1]*





X-Ray Raman Scattering

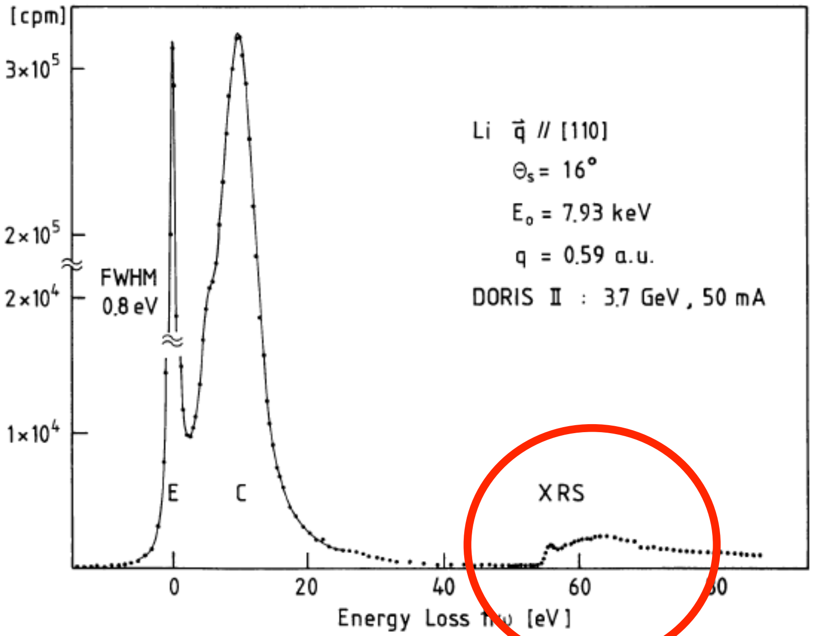


Fig. 1. Raw experimental data for Li single crystal obtained in the dispersion compensating case. The X-ray Raman spectrum (XRS) has an edge like onset at the binding energy of the Li *K*-electron of about 55 eV. E and C denote the quasielastically scattered Rayleigh line and the *S*(*q*, *ω*) profile from the valence electrons, respectively.

Nagasawa, et al, J. Phys. Soc. Jpn. 58 (1989) pp. 710-717

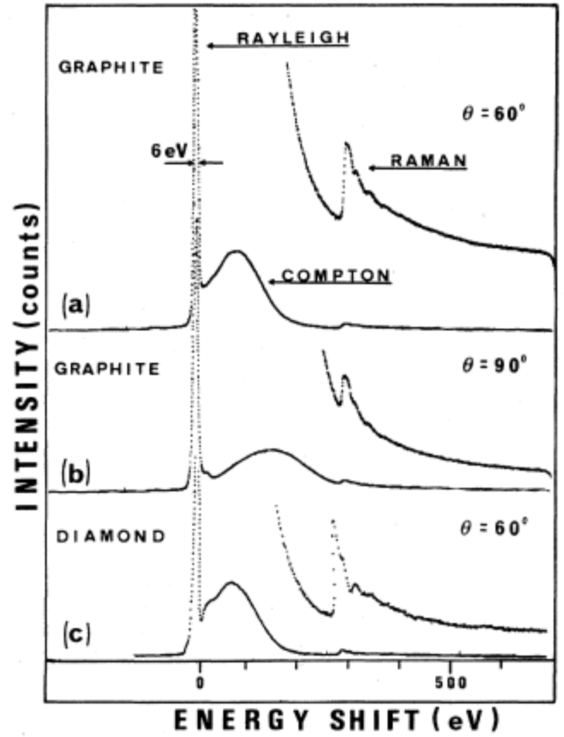


FIG. 2. (a) Inelastic-scattering spectrum from graphite observed at 60°. (b) Inelastic-scattering spectrum from graphite observed at 90°. (c) Inelastic-scattering spectrum from diamond observed at 60°. The Raman parts are inserted with an expanded scale. (a) and (b) were obtained with a Ge(440) dispersing crystal at 8900 eV excitation and (c) was obtained with a Ge(333) crystal at 8400 eV excitation. The Compton shift at 60° scattering does not coincide exactly for graphite and diamond because the excitation energy is slightly different.

Tohji&Udagawa, PRB 39 (1989) 7590

X-Ray Raman Scattering

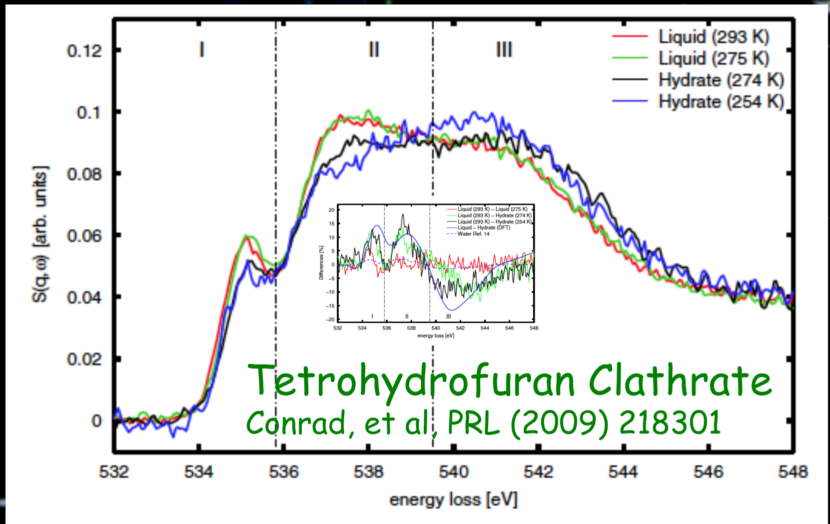
Suppose you would like to measure the structure of the oxygen k-edge (at 532 eV) of a sample inside of complex sample environment…

Diamond:

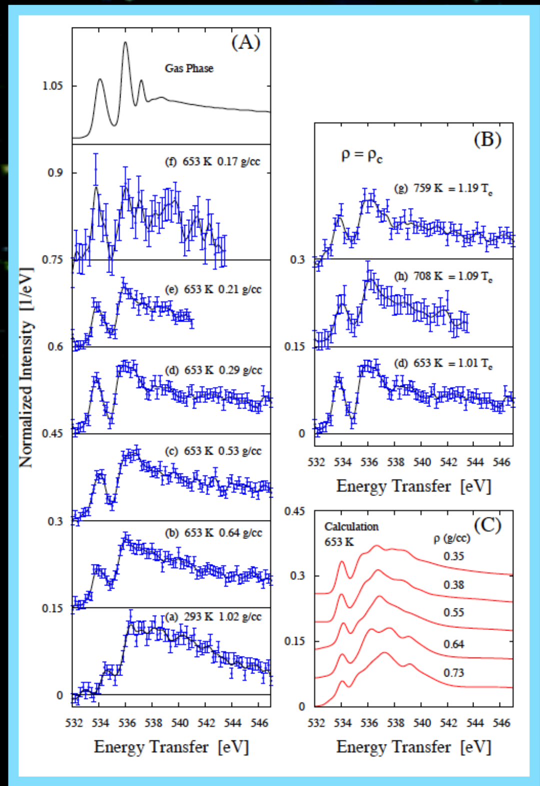
l_{abs} < 0.5 um 500 eV

l_{abs} ~ 2 mm 10 keV

Easier at 10 keV than 0.5 keV



Tetrohydrofuran Clathrate
Conrad, et al, PRL (2009) 218301



Supercritical Water

Ishikawa, et al, Submitted

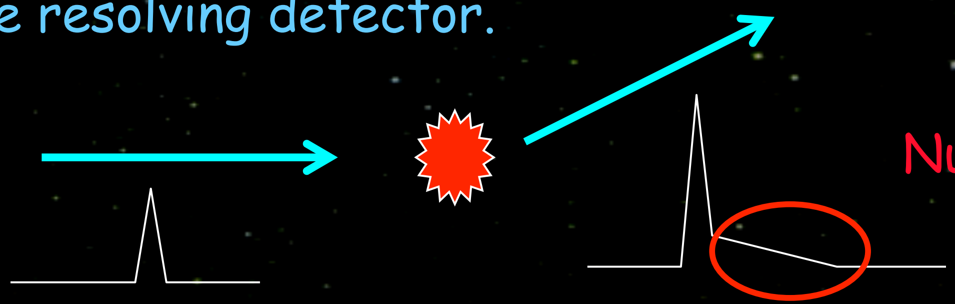
Nuclear Inelastic Scattering

First Demonstrated (Clearly) by Seto et al 1995

Mössbauer Resonances Exist in Different Nuclei…

Isotope	Transition energy (keV)	Lifetime (ns)	Alpha	Natural abundance (%)
^{181}Ta	6.21	8730	71	100
^{169}Tm	8.41	5.8	220	100
^{83}Kr	9.40	212	20	11.5
^{57}Fe	14.4	141	8.2	2.2
^{151}Eu	21.6	13.7	29	48
^{149}Sm	22.5	10.4	~ 12	14
^{119}Sn	23.9	25.6	~ 5.2	8.6
^{161}Dy	25.6	40	~ 2.5	19

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.

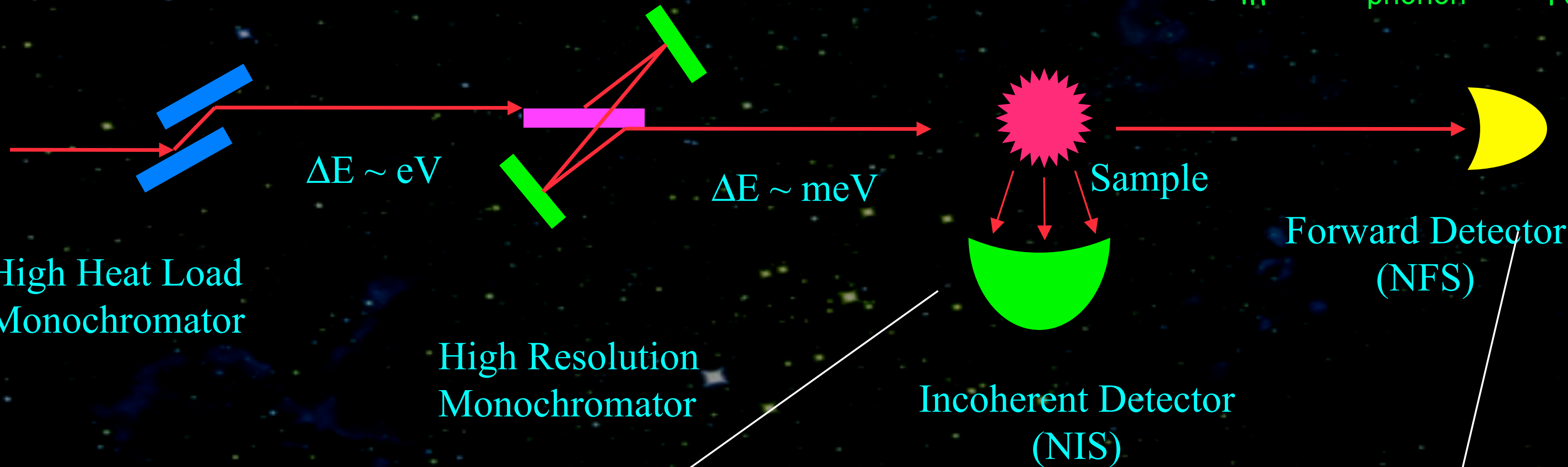


Nuclear Scattering

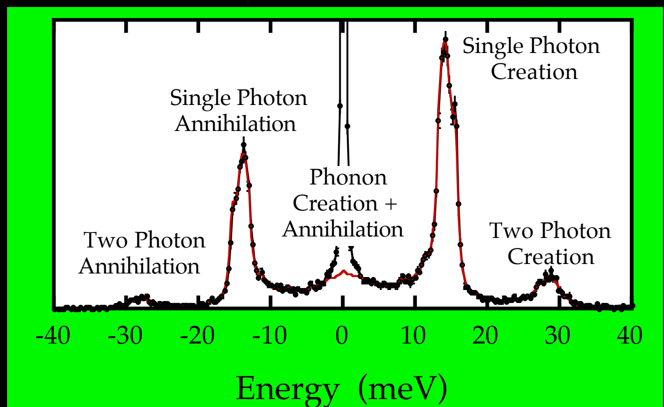
NIS Setup

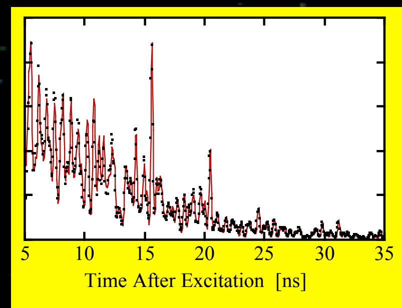
Use a narrow bandwidth monochormator
The nucelar resonance becomes the analyzer.

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



Element- Specific
Projected
Phonon DOS





Time Domain
Mossbauer Spectroscopy

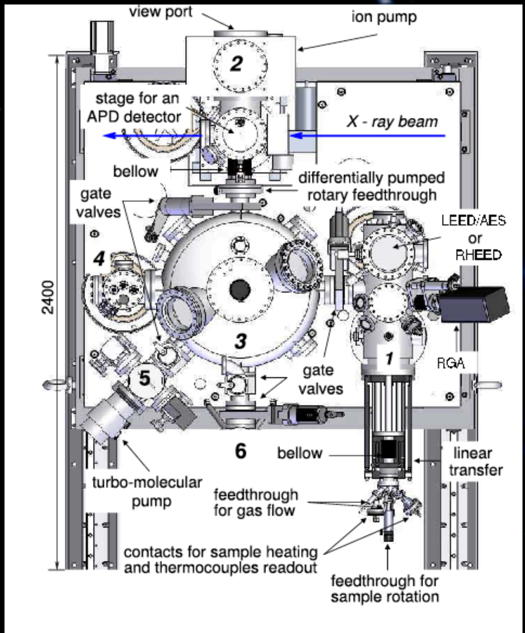
NIS: Good and Bad

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 ~ueV)
   Easier optics but setup not optimized
   (compensated by large cross section)

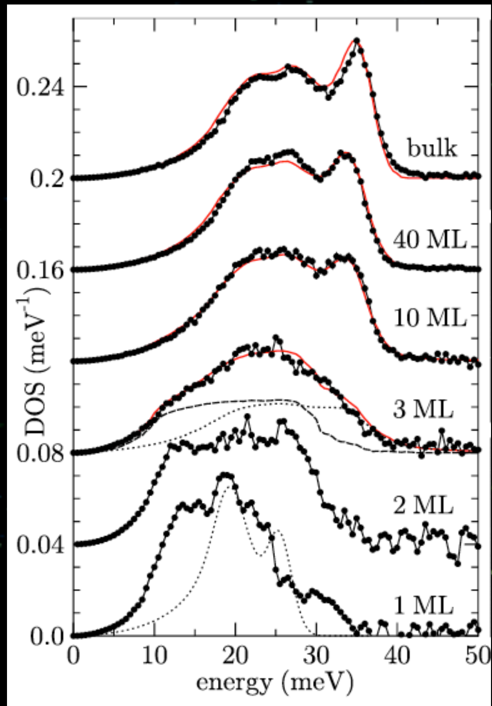
Surfaces by NIS

The large nuclear cross section allows sensitivity even to monolayers with relatively low backgrounds

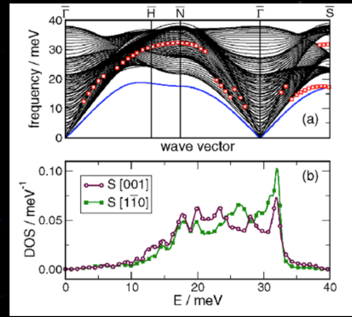


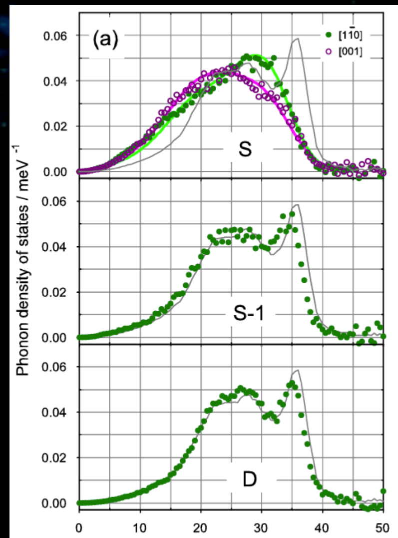
In-Situ Deposition
@ ESRF

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

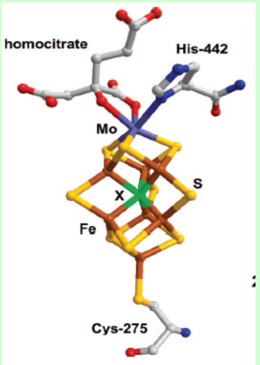
Example (NRVS/NIS/NRIXS) In Biology

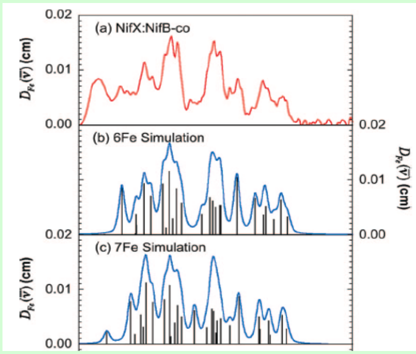
S. Cramer, et al, JACS

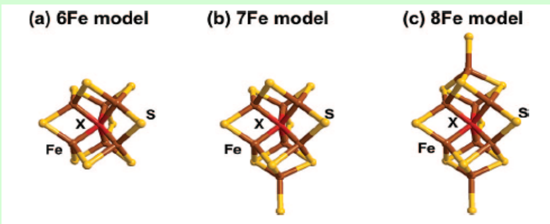
Measurement to determine the products of biological reactions via ***site-selective*** vibrational spectroscopy and comparison against calcs and model compound:

A compound in the nitrogen cycle…

Is X present? How many irons?

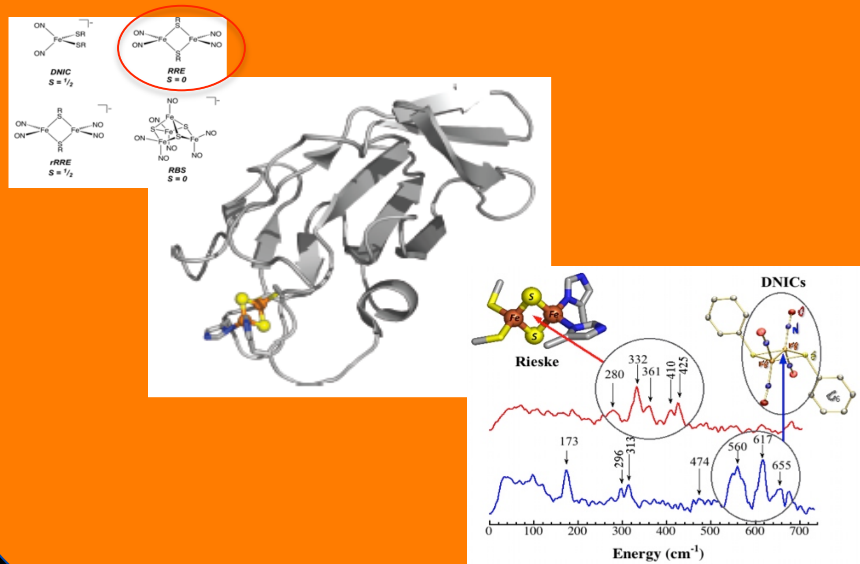






Toxicity of Nitric Oxide (NO)

-> Reaction products previously believed to be mononuclear are dinuclear



Compton Scattering

For very large Q and ΔE<<E one can take

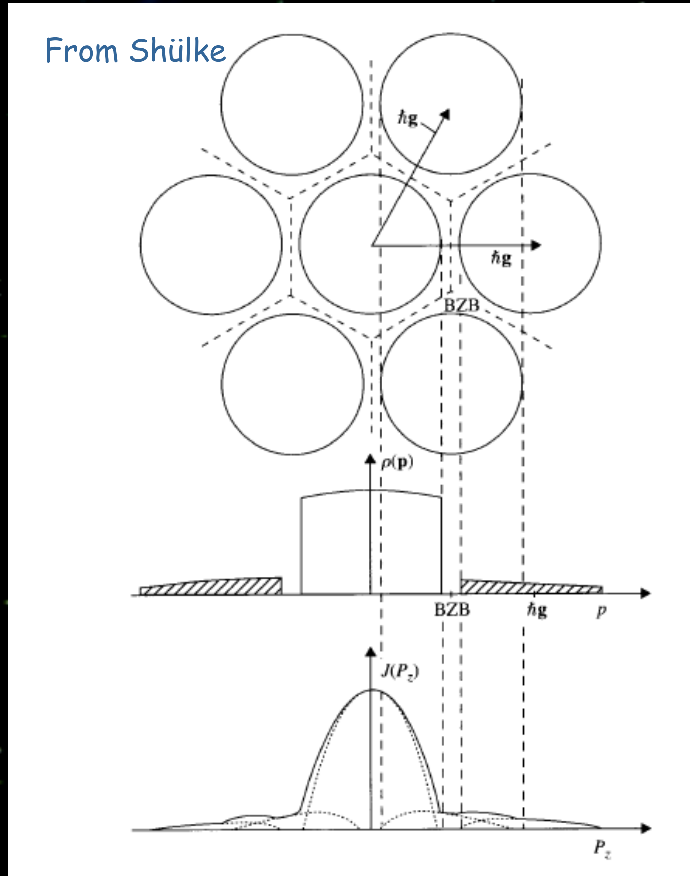
$$S(\mathbf{Q},\omega) = \frac{m}{\hbar Q} \iint dp_x dp_y \;\; \rho(p_z = p_Q)$$

$$\equiv \frac{m}{\hbar Q} J(p_Q)$$

Typical: $Q \sim 100 Å^{-1}$
$E > 100$ 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 ~10 Compton profiles.

$$J(p_z) = \iint n(\mathbf{p})\,dp_x\,dp_y$$

Reconstruction:

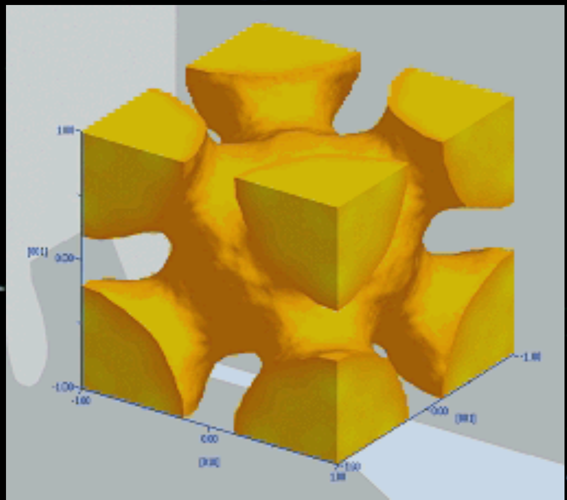
- Direct Fourier Method
- Fourier-Bessel Method
- Cormack Method
- Maximum Entropy Method

Momentum density, n(**p**)

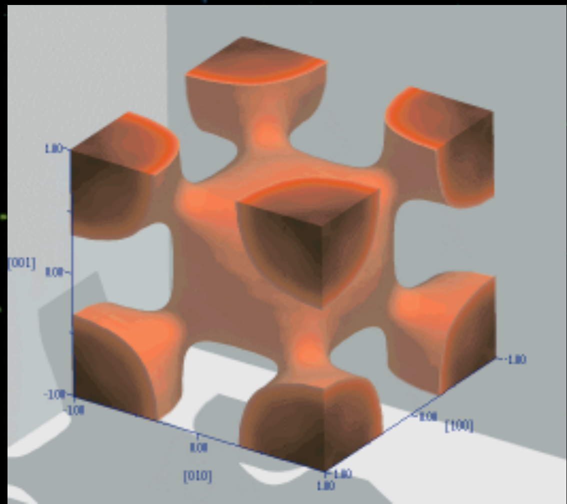
Note: a bulk probe that is tolerant of sample imperfections.

From Y. Sakurai

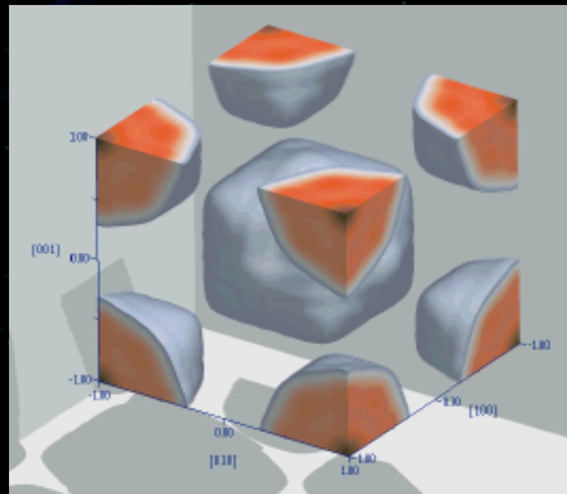
Fermi surfaces of Cu and Cu alloys



Cu-15.8at%Al



Cu



Cu-27.5at%Pd

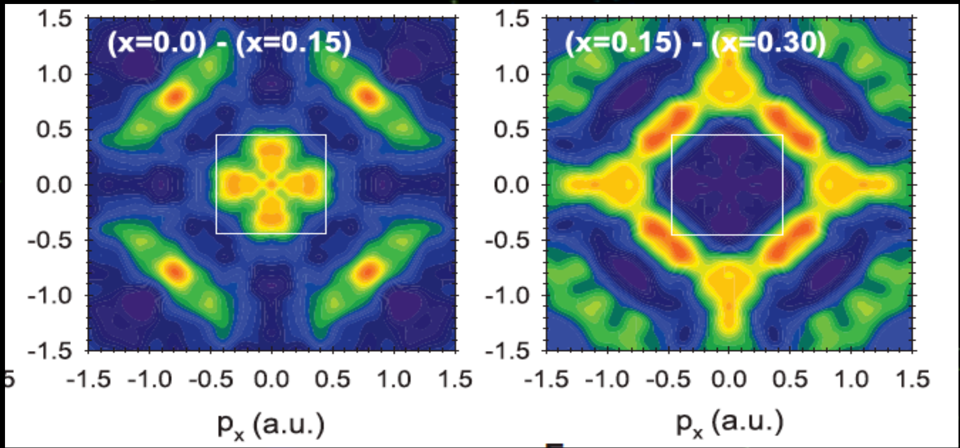
Determined by Compton scattering at KEK-AR

J. Kwiatkowska *et al.*, Phys. Rev. B 70, 075106 (2005)

Hole Locations in $La_{2-x}Sr_xCuO_4$

Sakurai, et al, Science 2011

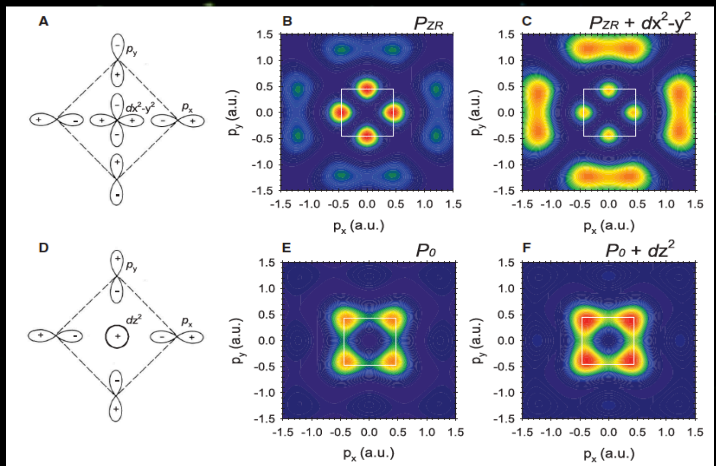
Measured Results for Different Doping



Parent vs Optimal Doping:
Holes in ZR singlet state

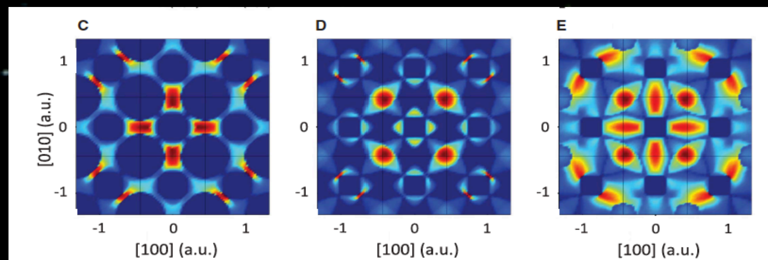
Optimal vs Overdoped
Holes in Cu dz^2 orbital

Cluster Calculations



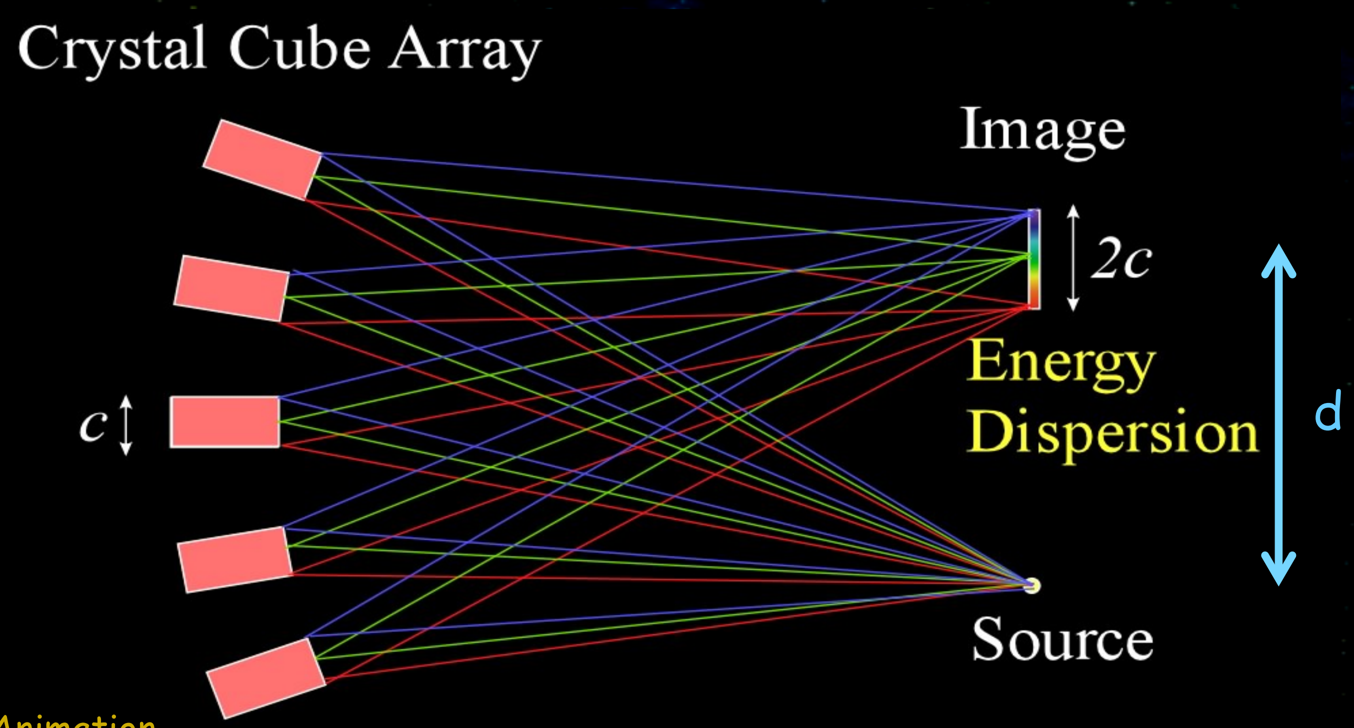
& Some density that is not yet understood

Band Structure Calculations

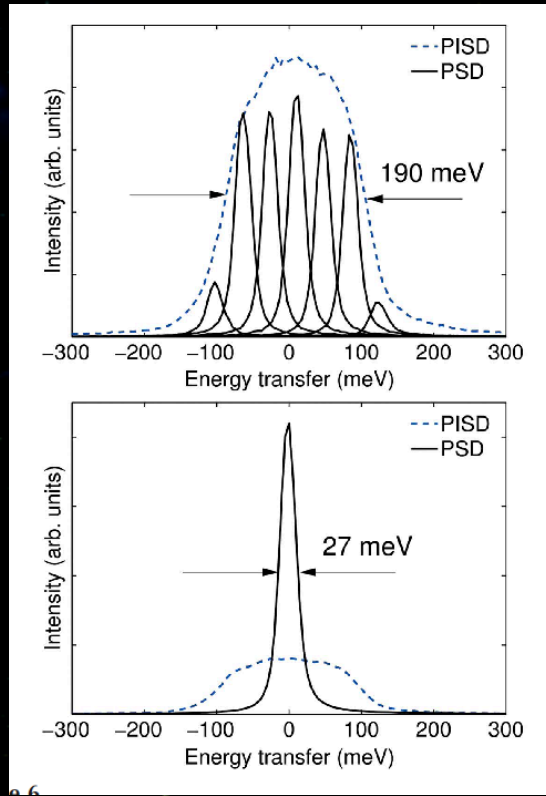


Reducing the Two-Theta Arm Size

Dispersion Compensation: Houtari, et al JSR (2005)



Animation
D. Ishikawa

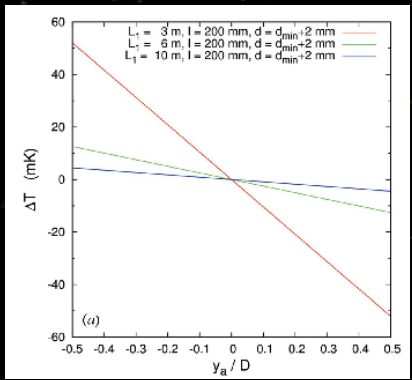


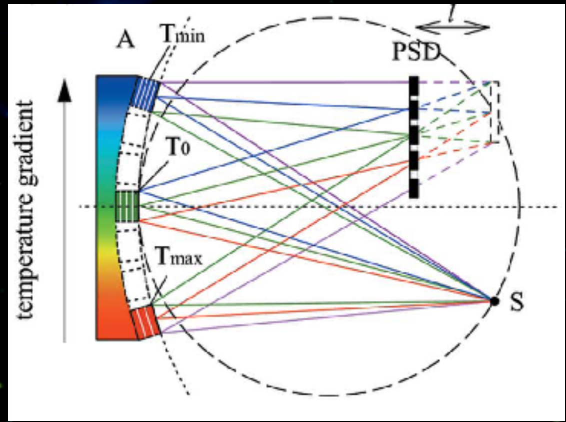
$$d = \frac{4R^2}{p}\frac{\Delta E}{E}$$

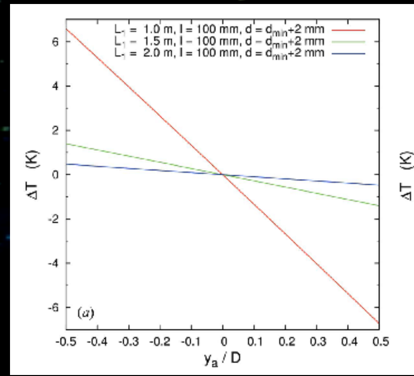
5 meV at 16 keV
R=2m, p=0.1 -> d=50 mm

Temperature Gradient Analyzer

(Ishikawa & Baron, JSR 2010)



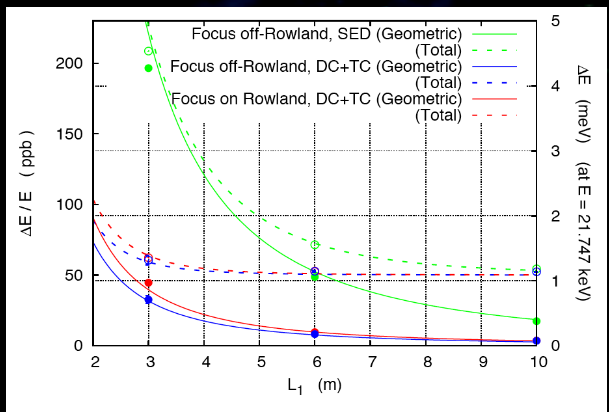


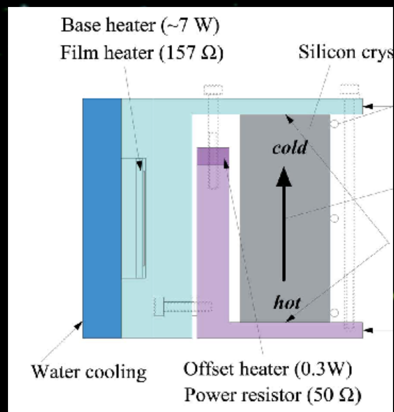


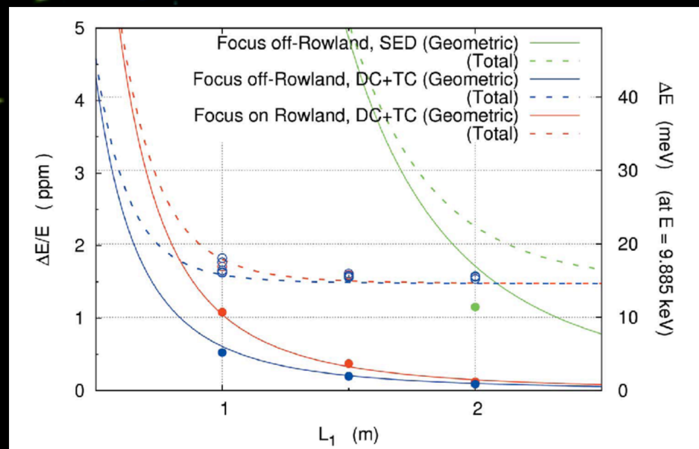
Longer Arm: DT~0.1C

l=150 to 200mm

Short Arm: DT: 1 to 10C





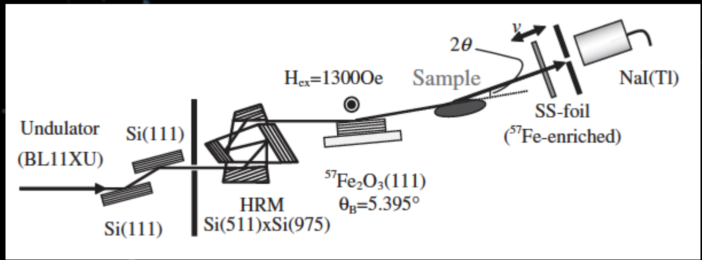


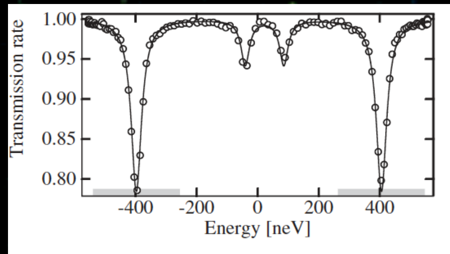
~ meV resolution at 3m

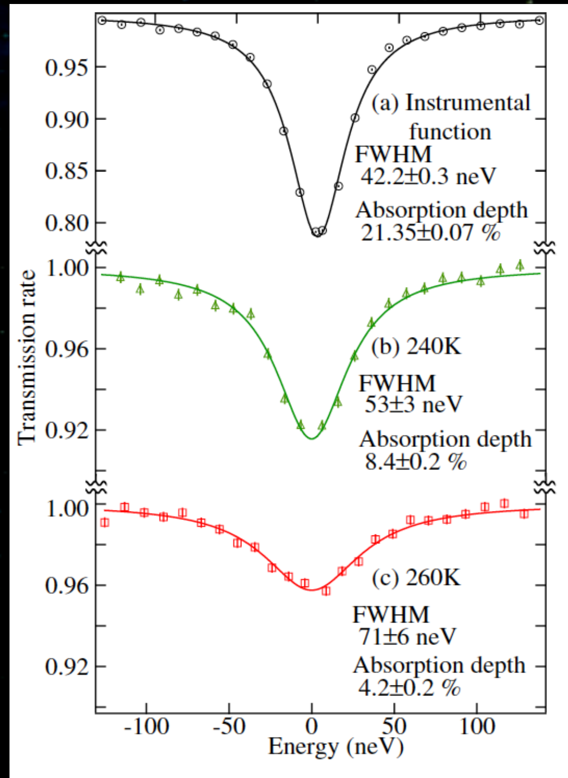
~5 meV at 1m

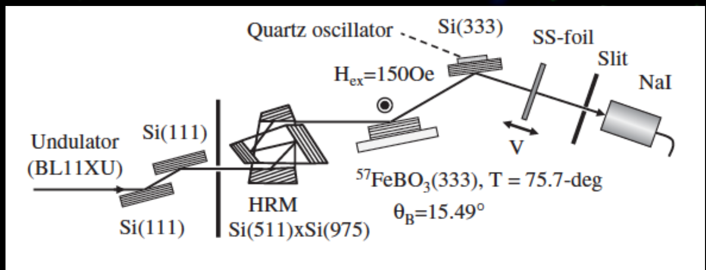
A Nano-Volt Spectrometer

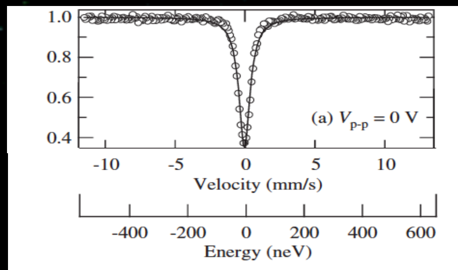
Rayleigh Scattering of Synchrotron Mossbauer Radiation (RSSMR)











Masuda, Mitsui, Seto, et al, JJAP (2008, 2009)

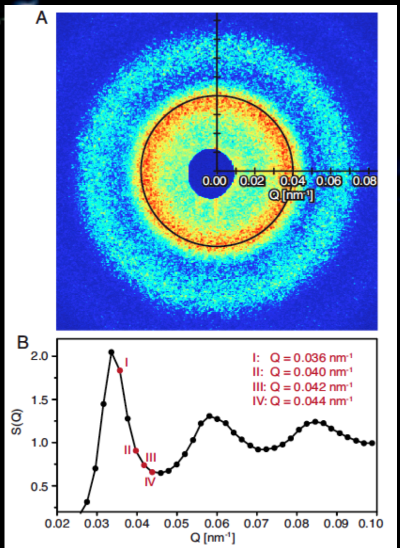
Beyond Plane Waves

Usual Measurement is a
two-point correlation function:

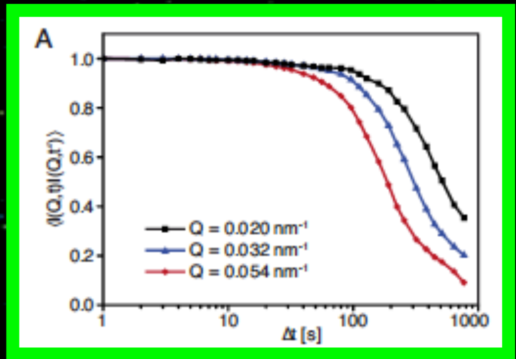
$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\int dt\; e^{-i\omega t}\int d\mathbf{r}\int d\mathbf{r}'\; x\; e^{i\mathbf{Q}\bullet(\mathbf{r}-\mathbf{r}')}\langle\rho(\mathbf{r}',t)\rho(\mathbf{r},t=0)\rangle$$

Complete picture includes higher order correlation functions

$$I(\mathbf{Q},t)I(\mathbf{Q}',t') \propto \langle\rho(\mathbf{r}',t)\rho(\mathbf{r},0)\rho(\mathbf{s}',t')\rho(\mathbf{s},0)\rangle$$



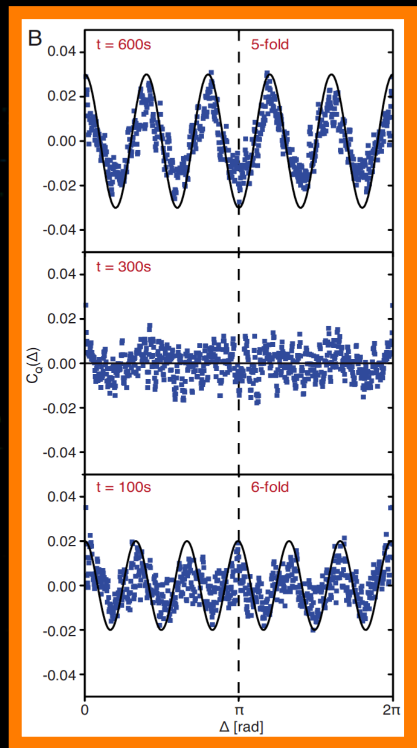
Wochner et al, PNAS (2009)



(A) Autocorrelation at One Q

(B) Cross-Correlation, Different Q

$$C_Q(\Delta) = \frac{\langle I(Q,\varphi)I(Q,\varphi+\Delta)\rangle_\varphi - \langle I(Q,\varphi)\rangle_\varphi^2}{\langle I(Q,\varphi)\rangle_\varphi^2}$$

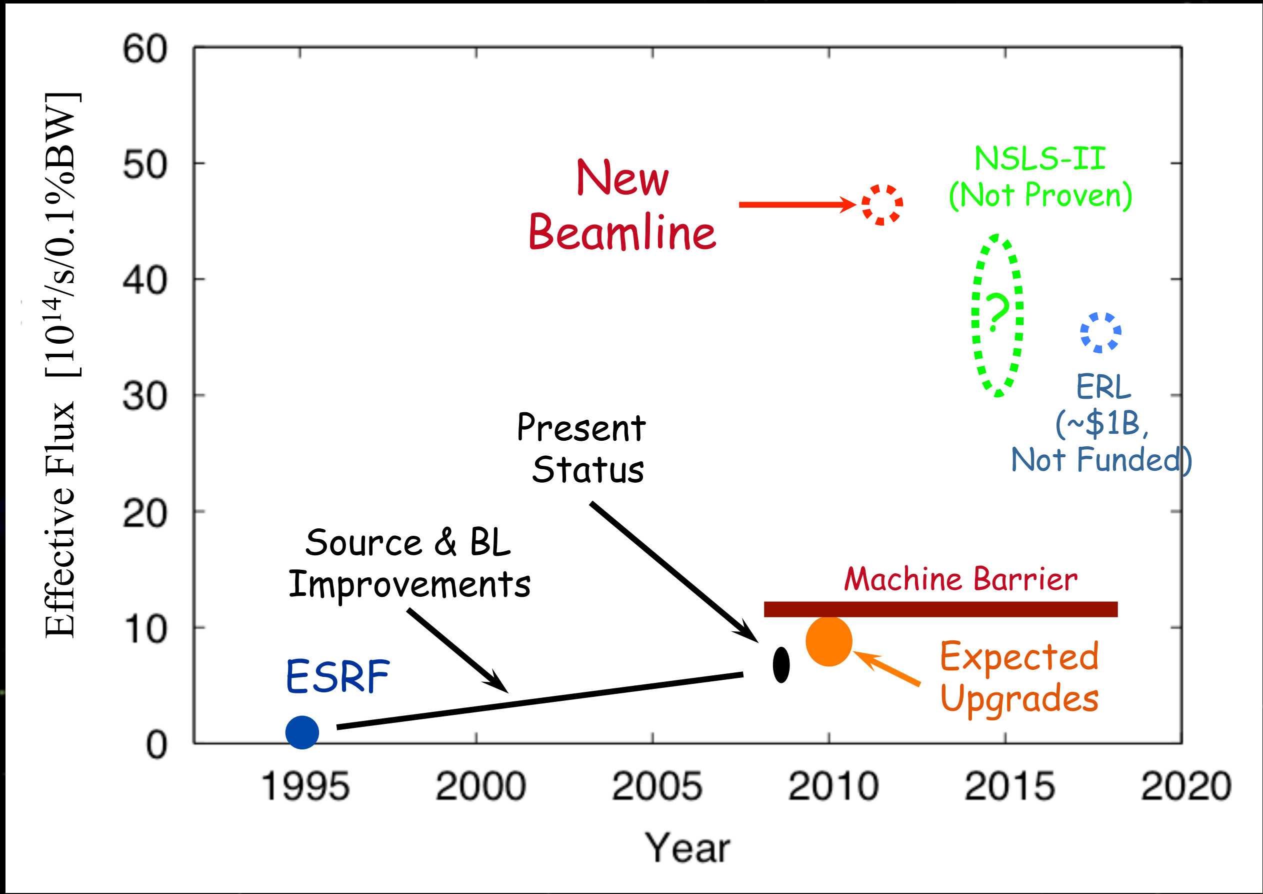


Ps Scales

XFEL
Or
XFELO

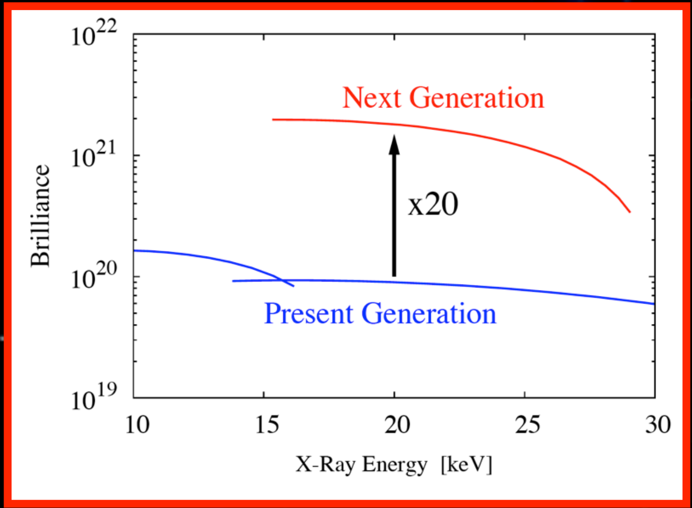
IXS Beamline Evolution

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

<u>Improvements</u>

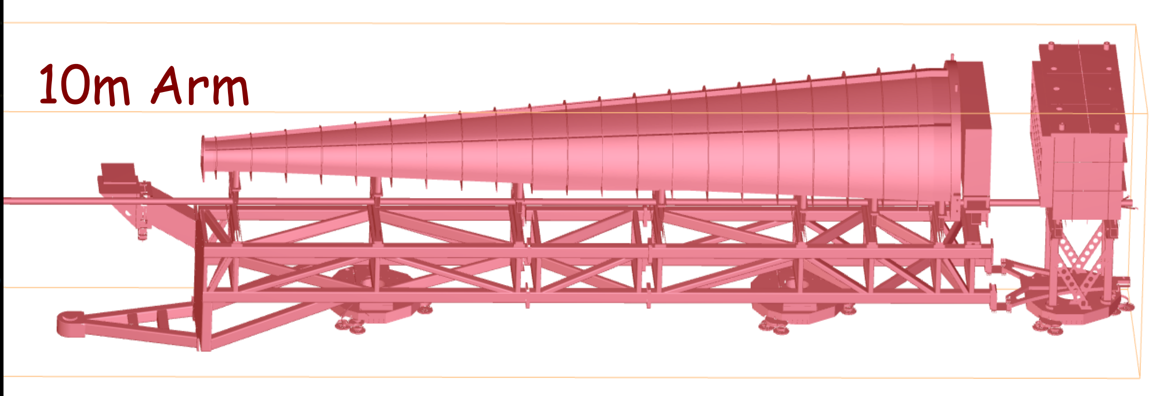
Flux On Sample: x10
Parallelization: x3
Small Spot Size: x5

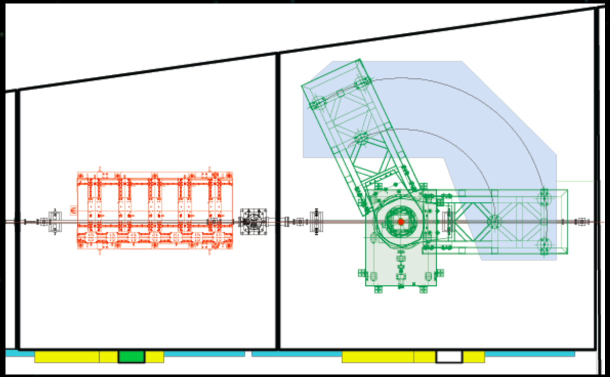
Quantum NanoDynamics Beamline

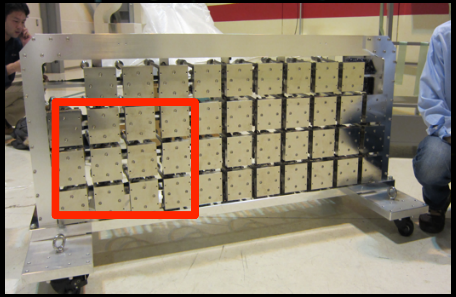
(BL43LXU)

High resolution spectrometer: <1 to 6 meV
10 m Arm, Good Q Resolution, to 12 $Å^{-1}$
Large (42 element) analyzer array.

Medium resolution: 10-100 meV
2m Arm, Large Q Accepta
Good tails using (888)





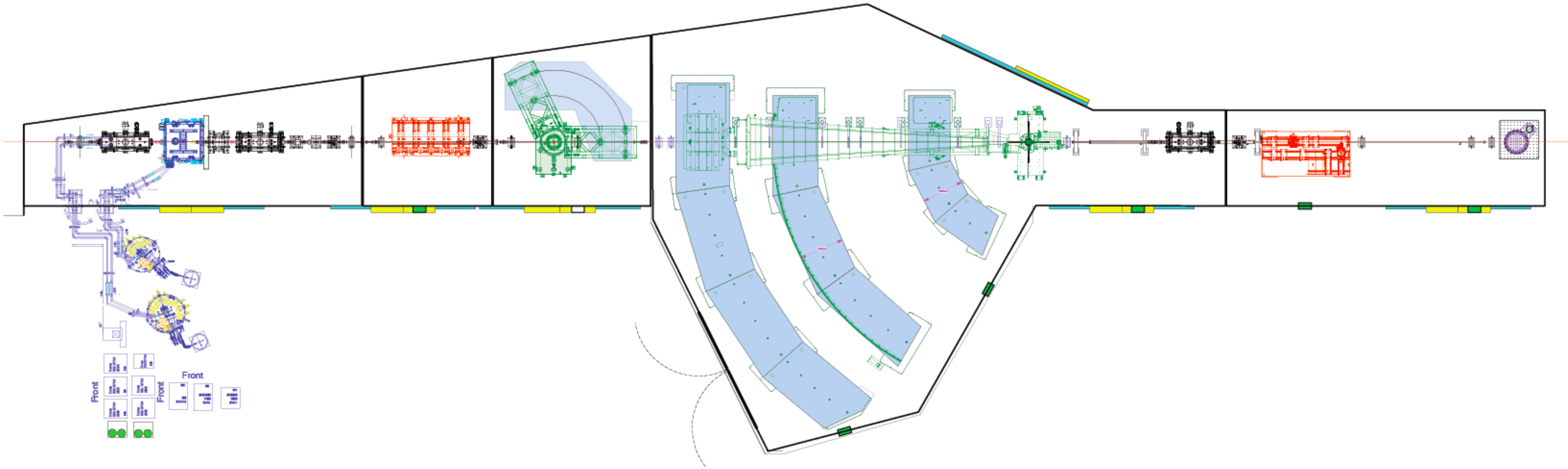


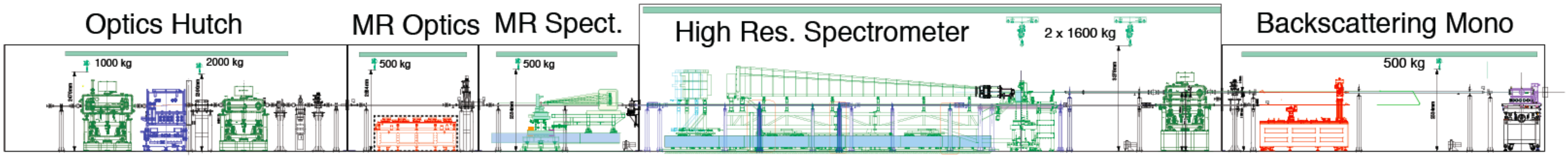
First Monochromatic Light: Sunday

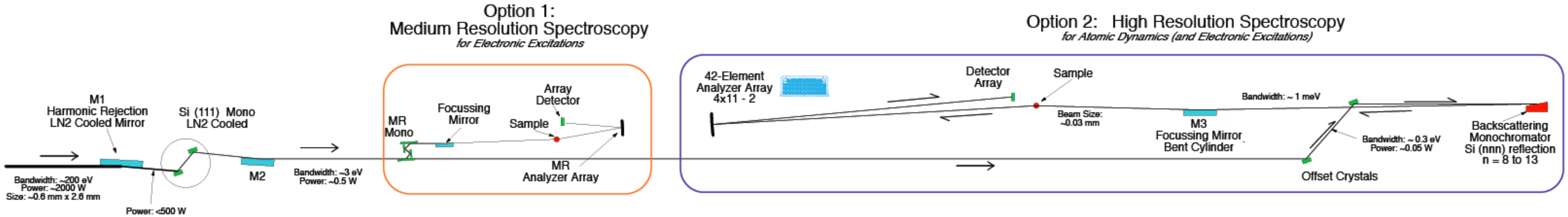
BL43LXU: RIKEN Quantum NanoDynamics (RQD) Beamline

for High-Resolution Non-Resonant Inelastic X-Ray Scattering

A.Q.R. Baron, http://user.spring8.or.jp/sp8info/?p=3138








Thanks for Your Attention!