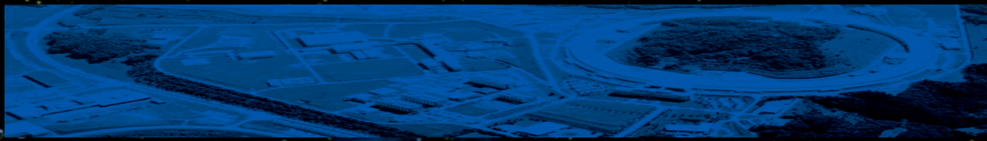


Inelastic X-Ray Scattering

PRELIMINARY VERSION

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 Techniques
- Resonant Techniques (Briefly)

Comment: Mostly no history

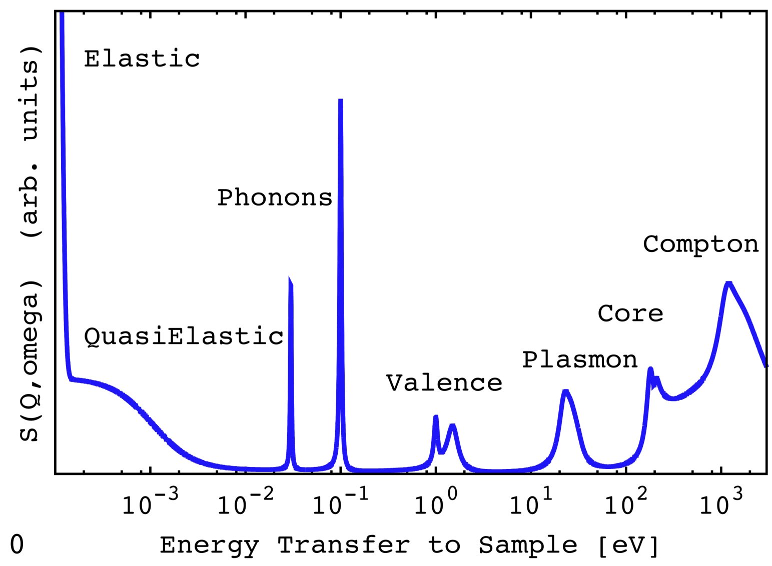
Table Of IXS Techniques/Applications

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
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
NIS Nuclear IXS	Atom Specific Via Mossbauer Nuclei	E_{in} ~ 14-25 keV ΔE ~ 1-100 meV	Element Specific Phonon Density of States (DOS)

Note: ΔE = Typical Energy Transfer (Not Resolution)

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

Excitations



Some References

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New York: Oxford University Press.
& References therein (RIXS, X-Ray Raman, NRIXS…)

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Spectroscopy
Absorption vs. Scattering

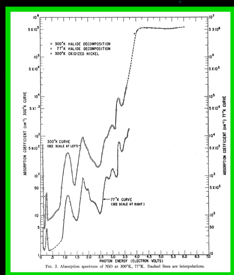
Absorption Spectroscopy

Optical, IR, NMR

Measure absorption as you scan the incident energy

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

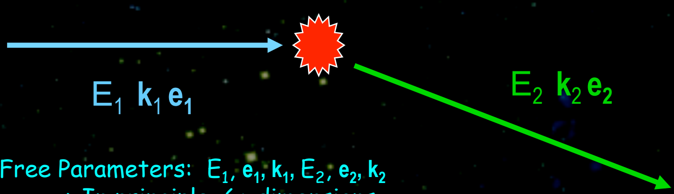
Free Parameters: E_1, e_1, k_1
-> In principle, 3+ dimensions
but in practice mostly 1 (E_1)



Optical Spect. NiO
Newman, PR 1959

Scattering Spectroscopy

IXS, Raman, INS

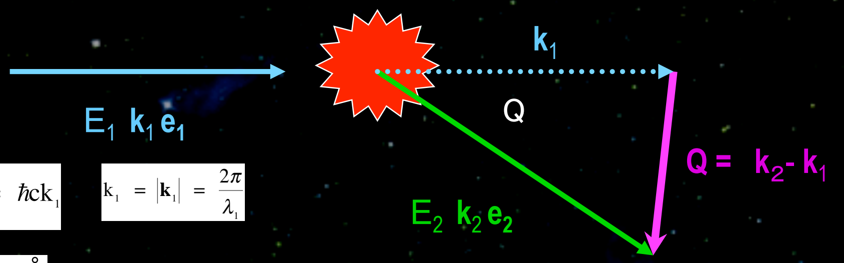


Free Parameters: E_1, e_1, k_1, E_2, e_2, k_2
-> In principle, 6+ dimensions
in practice, mostly 4: E_1-E_2, $\mathbf{Q} = \mathbf{k}_2$-$\mathbf{k}_1$

Scattering is more complex, but gives more information.

Note: Fluctuation Dissipation Theorem

X-Ray Scattering Diagram



$$E_1 = \hbar\omega_1 = \frac{hc}{\lambda_1} = \hbar c k_1 \qquad k_1 = |\mathbf{k}_1| = \frac{2\pi}{\lambda_1}$$

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

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

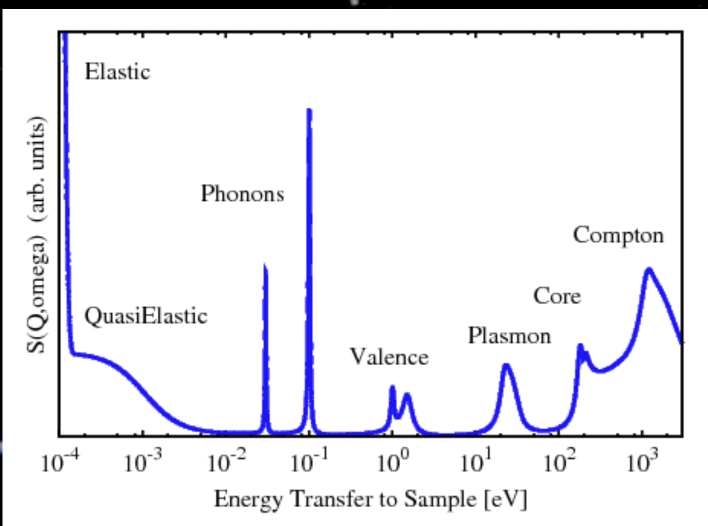
$$\mathbf{Q} \equiv \mathbf{k}_2 - \mathbf{k}_1$$

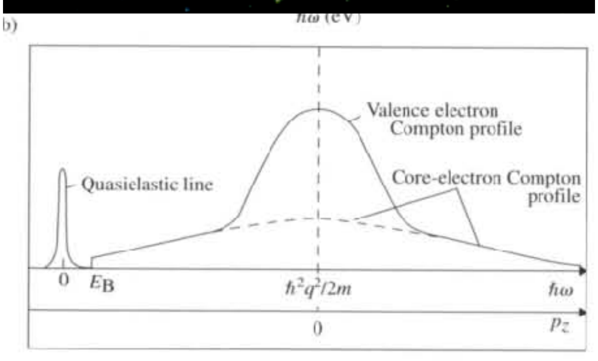
$$Q \equiv |\mathbf{Q}| \approx \frac{4\pi}{\lambda_1}\sin\left(\frac{\Theta}{2}\right)$$

Periodicity Probed

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

Excitations





"Low" Q (d ~ Å)
Collective Response

"High" Q (d<<1Å)
Single Particle Response

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)

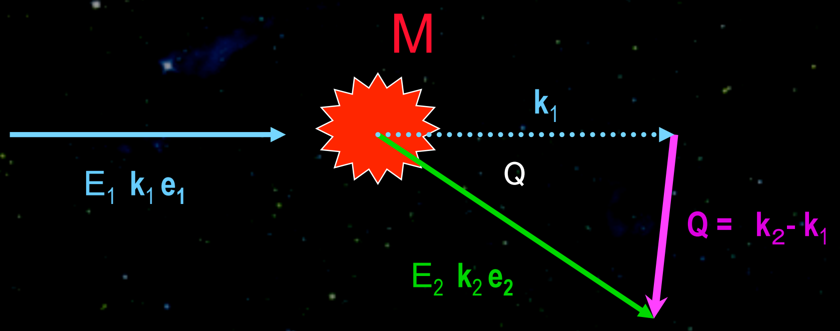
$$S(\mathbf{Q},\omega) = \sum_{\lambda,\lambda'} p_\lambda \left| \langle \lambda' | \sum_{\substack{electrons \\ j}} e^{i\mathbf{Q}\bullet\mathbf{r}_j} | \lambda \rangle \right|^2 \delta(E_{\lambda}' - E_\lambda - \hbar\omega)$$

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

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

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

Kinematics



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

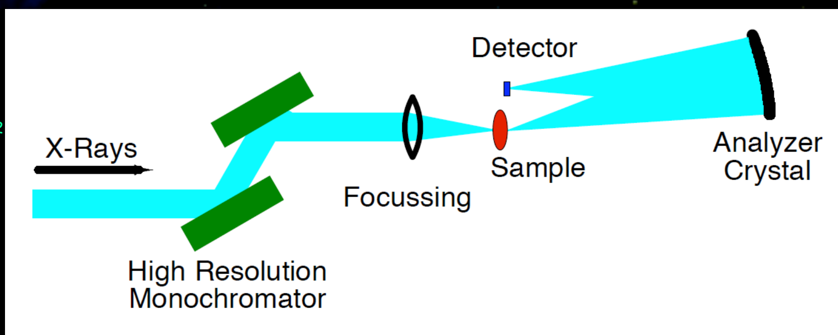
f-sum rule: $$\frac{\int d\omega\ \hbar\omega\ S(\mathbf{Q},\omega)}{\int d\omega\ S(\mathbf{Q},\omega)} = \frac{\hbar^2 Q^2}{2M}$$

Compton Form: $\lambda_2 - \lambda_1 = \frac{h}{Mc}(1-\cos\Theta)$ $\lambda_c = \frac{h}{m_e c} = 0.0243$Å

The IXS Spectrometer
An Optics Problem

Main Components

Monochromator:
- Modestly Difficult
- Only accepts 15x40 [illegible]rad^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

Basic Optical Concept

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

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

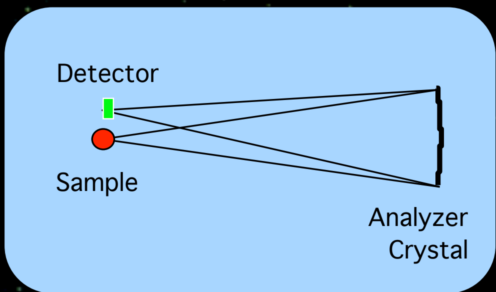
High Resolution Analyzer Crystals

The more difficult optic…

Require:

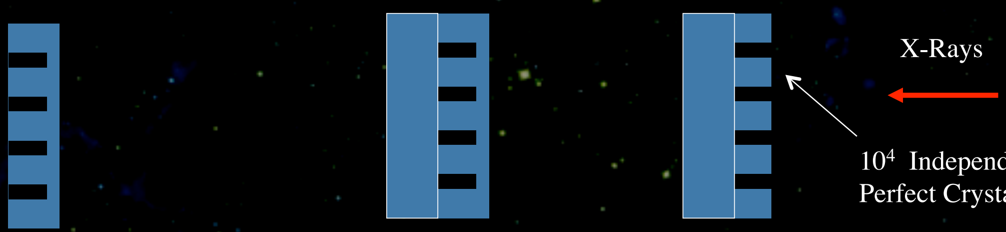
Correct Shape (Spherically Curved, R=9.8 m)

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



Method: Bond many small crystallites to a curved substrate.

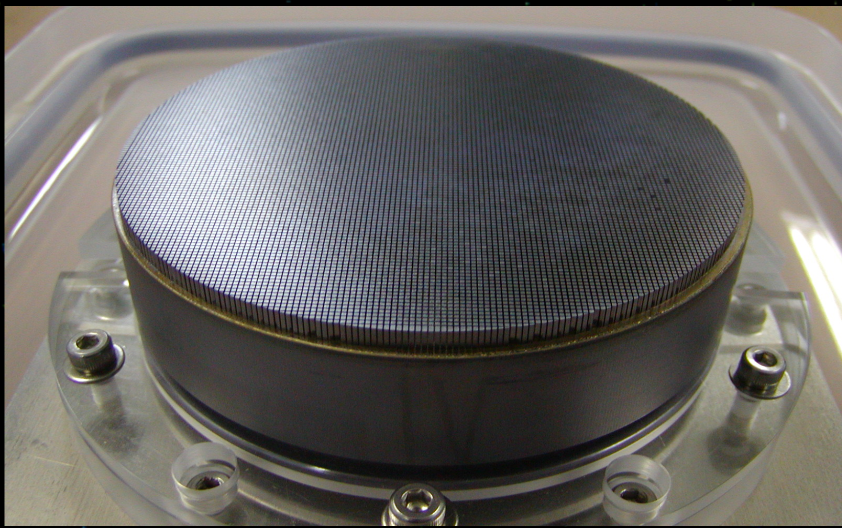
1. Cut 2. Etch 3. Bond to Substrate 4. Remove Back



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

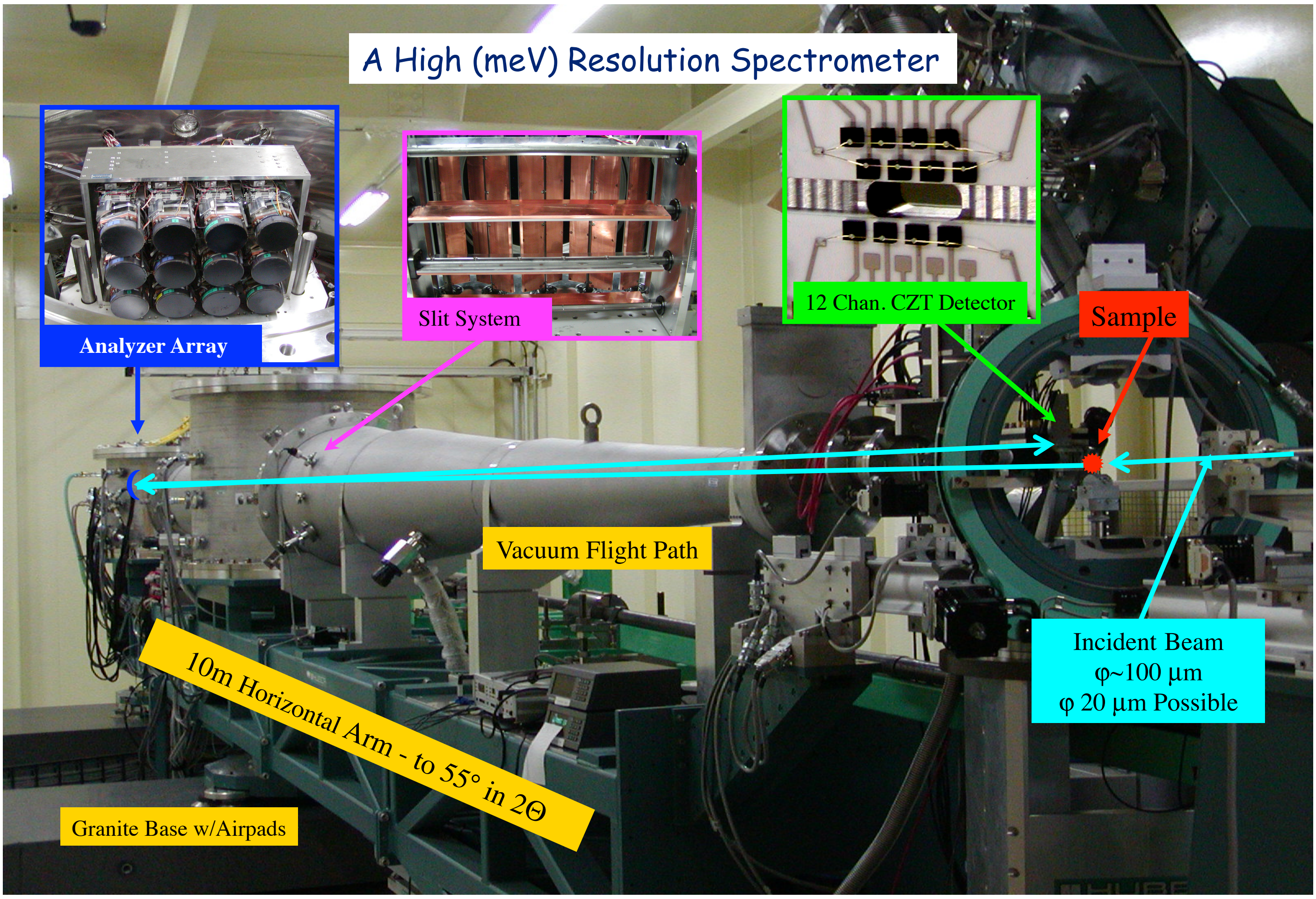
Analyzer Crystal

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

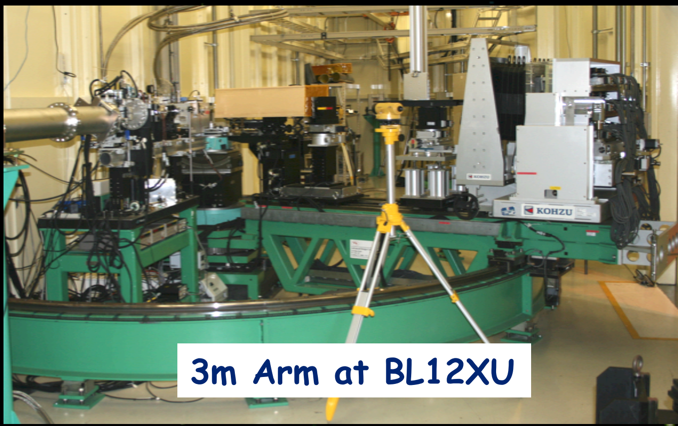


Present Parameters (9.8 m Radius, 10cm Diameter)

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 Medium Resolution Spectrometer

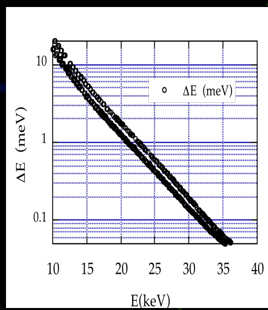


3m Arm at BL12XU

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

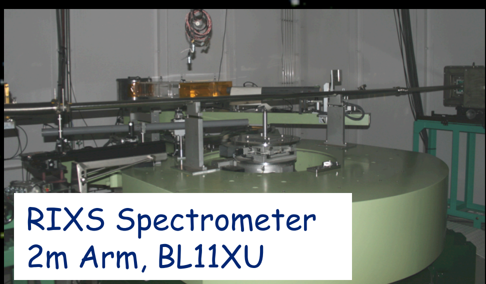
BL12XU BL11XU

Shorter Possible
(later, if time)

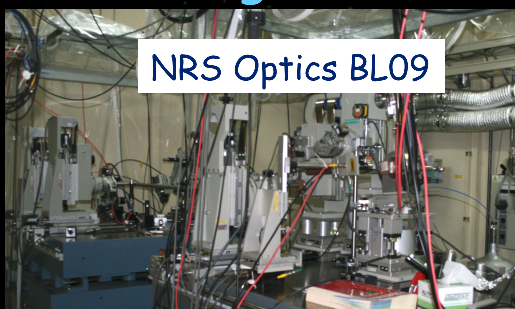


Note difference between RIXS and NRIXS
NRIXS: Choose the energy to match the optics
RIXS: Resonance chooses energy -> usually worse resolution

Other Spectrometers @ SPring-8

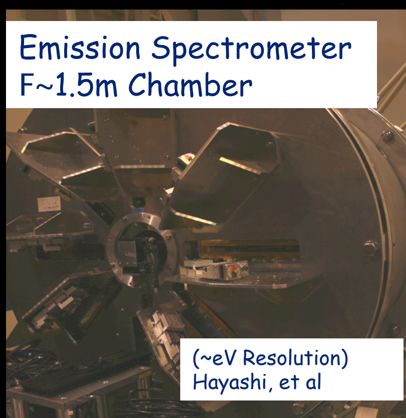


RIXS Spectrometer
2m Arm, BL11XU



NRS Optics BL09

Compton Spectrometer BL08



Emission Spectrometer
F~1.5m Chamber

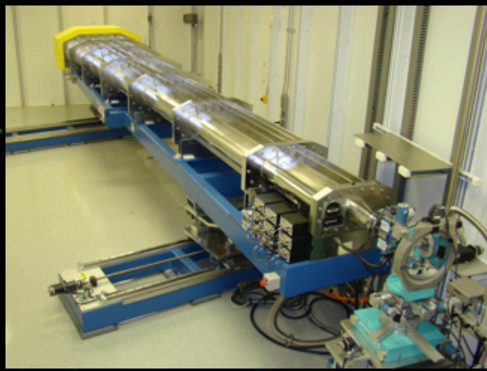
(~eV Resolution)
Hayashi, et al

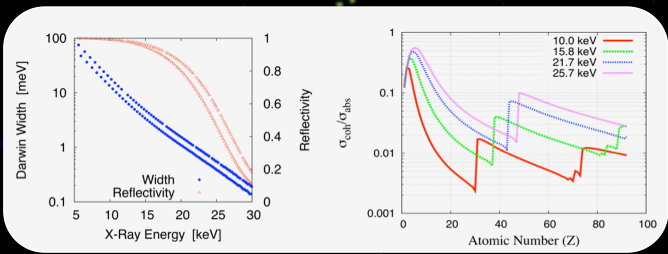
AQRB @ AOFSRR Cheiron School 2011

Other High Resolution Spectometers

ESRF

APS





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:

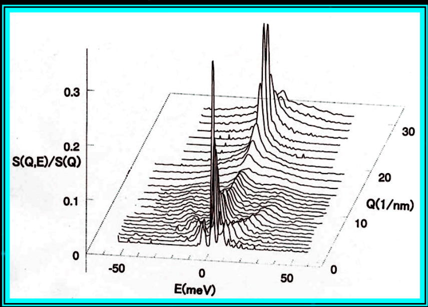
Basic phonon model does very well -> Specific questions needed.

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

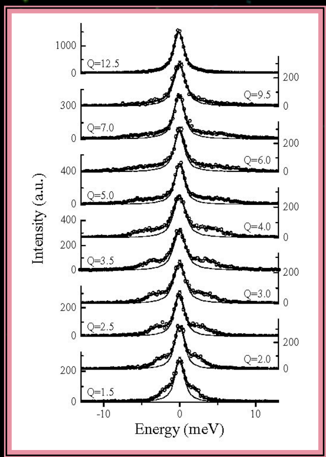
Disordered Materials

Liquids & Glasses

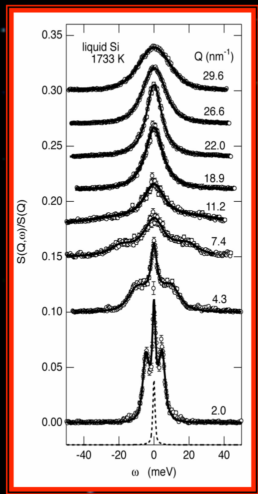
First Glance: Triplet response similar for most materials.
Dispersing Longitudinal Sound Mode
+ Quasi-Elastic peak



l-Mg (Kawakita et al)



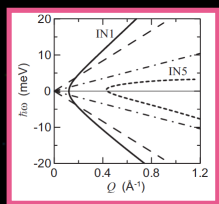
a-Se (Scopigno et al)



l-Si (Hosokawa, et al)

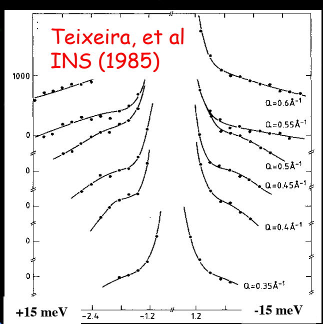
The IXS Advantage

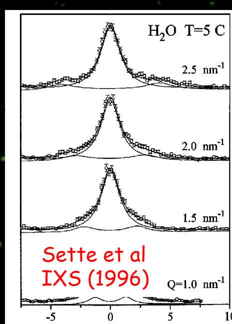
IXS has no kinematic limitations (DE<<<E_g)
Large energy transfer at small momentum transfer
-> excellent access to mesoscopic length scales



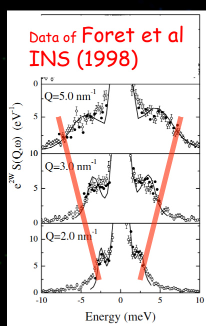
INS Diagram

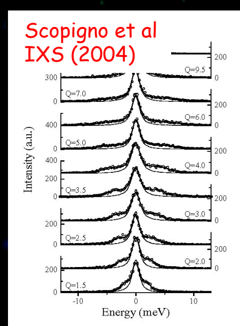
Water





Glassy-Se



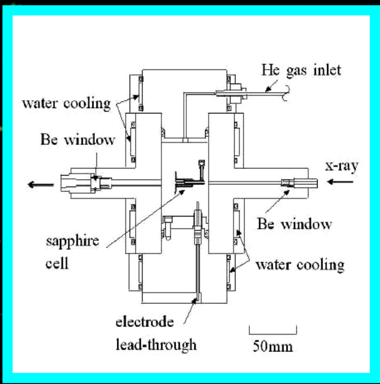


Also: No Incoherent Background
Small Beam Size (f<0.1mm)

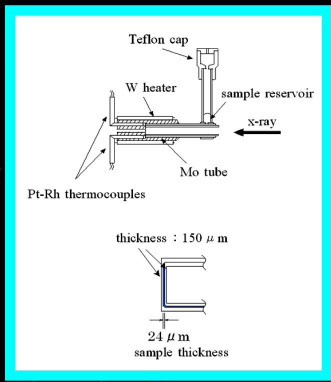
But: <1 meV resolution is hard
Low Rates for Heavy Materials

Metal to Insulator Transition in Liquid Mercury

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



For Hg
~1500 C & ~ 1.5 kbar

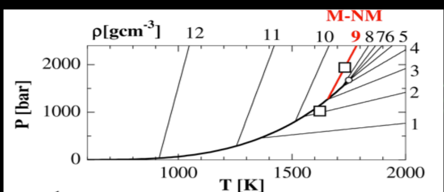


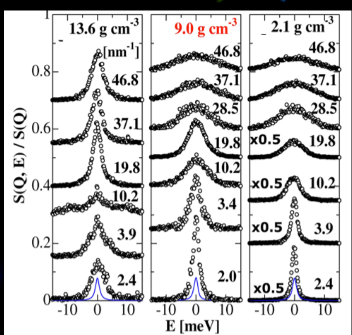
15 mm Be, 200 m He (STP), 0.15 mm Sapphire
~ 20 microns Hg

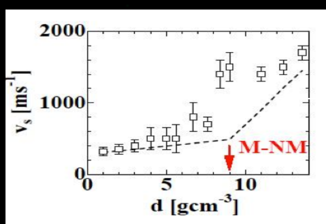
D. Ishikawa, M. Inui, K. Tamura, *et al.*

"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)

D. Ishikawa, *et al*, PRL 93 (2004) 97801

~2 months of beam time…

On Positive Dispersion

Very General feature:

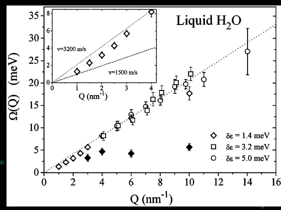
As Q increases the phase velocity of the acoustic mode becomes larger than the Low-Q (e.g. ultrasonic) sound velocity.

Casual explanation

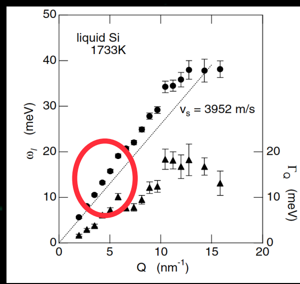
For smaller length scales (high Q) and higher frequencies, a liquid, locally, resembles a solid which has a faster sound velocity.

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

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

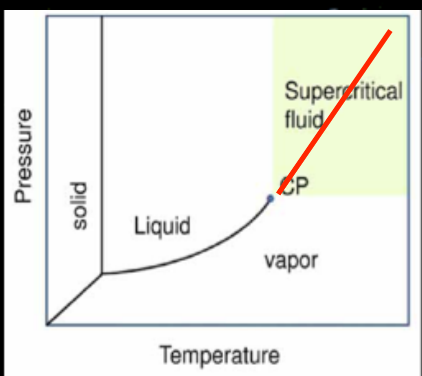


Sette et al

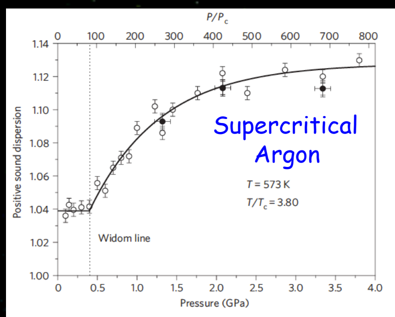


Hosokawa, et al

Dynamical Distinction



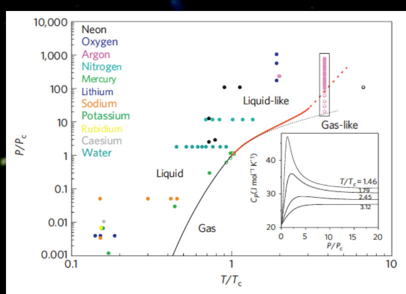
Widom Line
Maximum in C_p



Simeoni et al NPhys 2010

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

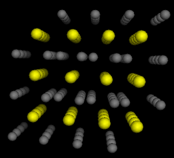
Gorelli et al, PRL (2006)
Simeoni et al, NPhys (2010)
Also Bencivenga et al EPL (2006)

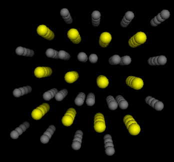


Shear Mode in a Simple Liquid

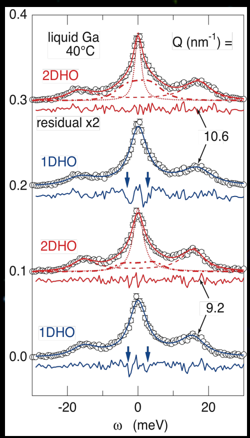
Pressure Wave in a Liquid:
Nearly Always Visible

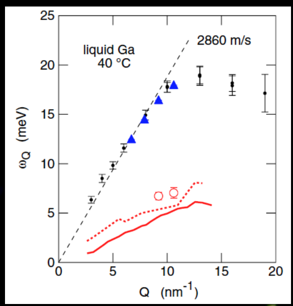
Shear Wave -> Harder...





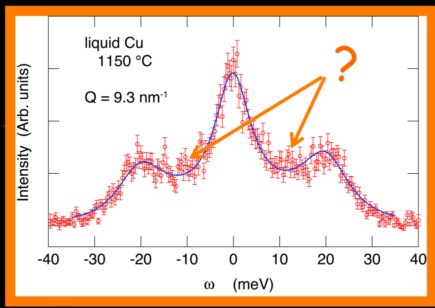
$$S(\mathbf{Q},\omega) \approx \int dt e^{-i\omega t} \int d\mathbf{r} \int d\mathbf{r}' \; e^{i\mathbf{Q}\bullet(\mathbf{r}-\mathbf{r}')} \langle \rho(\mathbf{r}',t)\rho(\mathbf{r},t=0)\rangle$$





Weak, but significant, signal.

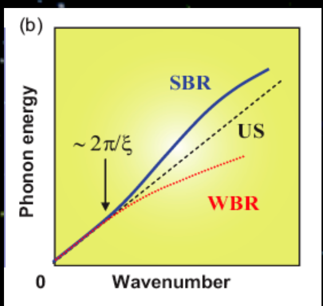
Hosokawa, et al, PRL (2009)

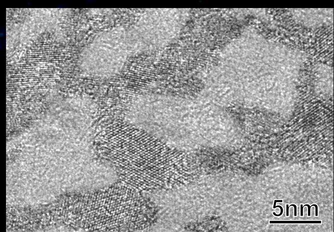


Next experiment: l-Cu
2.5 Days -> ?

Elastic Inhomogeneity in a Glass

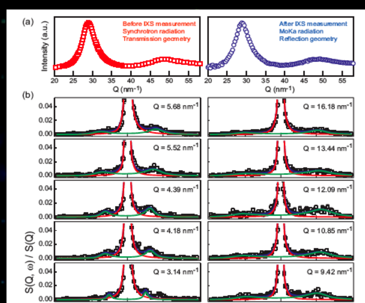
Ichitsubo, et al.



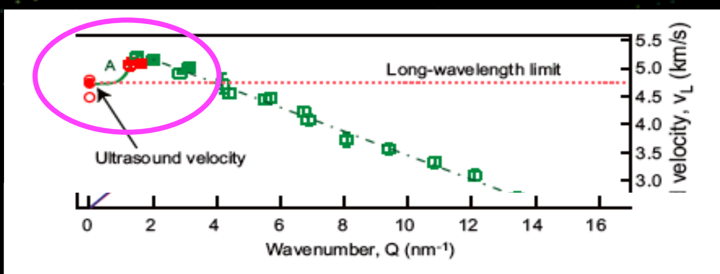


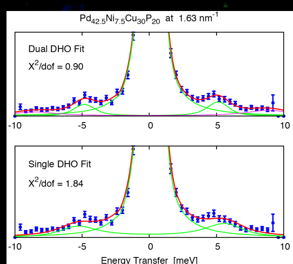
Electron Micrograph of a
Re-crystallized Sample

$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$



Note: ~1 Day/Spectrum @ Low Q
Subsidiary Structure in Spectra





Fast sound a signature of elastic inhomogeneity.
(Detailed analysis: possible failure of DHO Model)

Phonons in a Crystal

Normal Modes of Atomic Motion

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

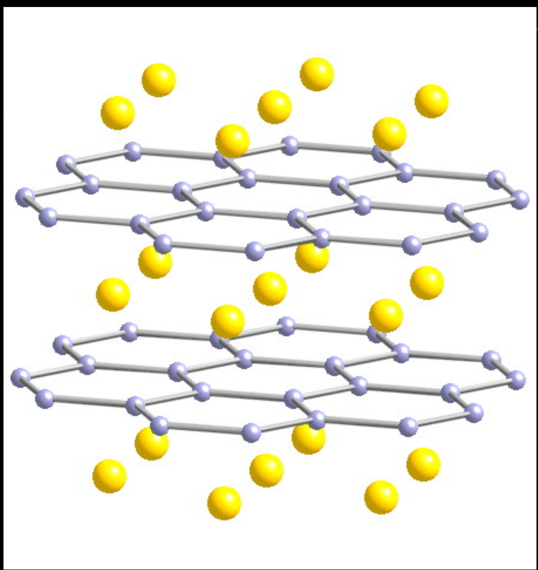
If a crystal has N unit cells and R atoms/Cell then it has 3NR Normal Modes

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

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

MgB_2 As An Example

Layered Material
Hexagonal Structure



B Layer

Mg Layer

B-B Bond is Short & Stronger

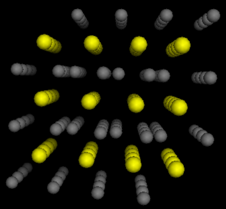
Mg-Mg Bond is Longer & Weaker

3 Atoms/cell -> 9 modes / Q Point

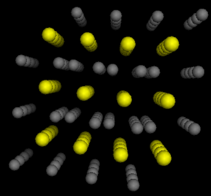
AQRB @ AOFSRR Cheiron School 2011

Acoustic and Optical Modes

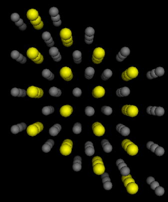
Acoustic Modes are Continuum (Smooth) Modes



LA Mode
Compression Mode

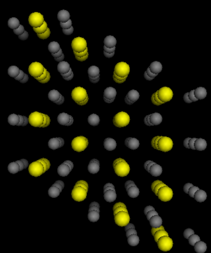


TA Mode
Shear Mode

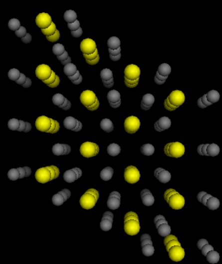


Optical Mode
Atoms in one unit cell
move against each-other

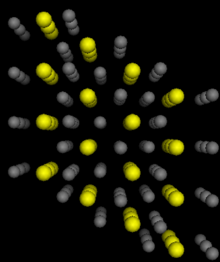
Dispersion of an Optical Mode



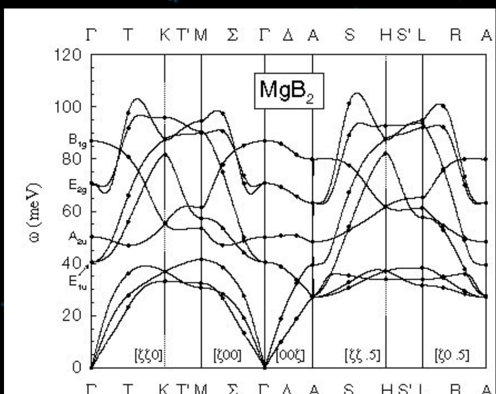
(0 0 0)



(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

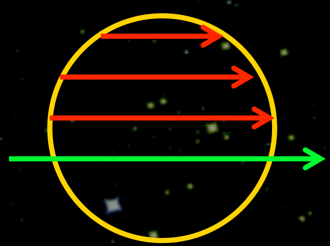
Electron Phonon Coupling

& 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 **$Q<2k_F$**

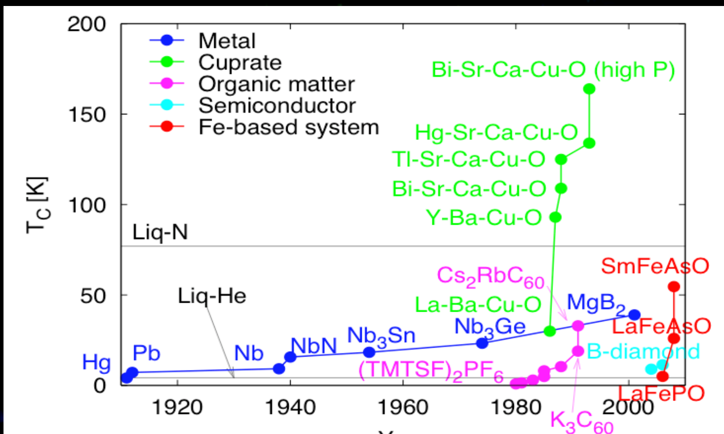


Large Momentum $Q>2k_F$ Can Not Couple to the Electronic system

Fermi Surface Diameter = $2k_f$

Superconductors @ BL35XU

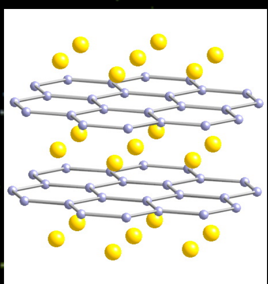
Systems Investigated at BL35XU include
MgB_2, Doped MgB_2, CaAlSi, B-Doped Diamond
Hg1201, LSCO, YBCO, LESCO, Tl2212, BKBO, NCCO,
Bi2201, Bi2212, Nickelates, Oxychlorides
Fe-As Systems: LaFeAsO, PrFeAsO, BaKFeAs



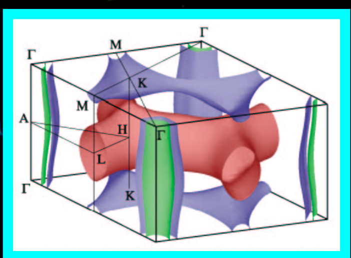
From T. Fukuda

Dark Blue Line: Conventional, Phonon-Mediated Superconductors

MgB_2



Electronic Structure



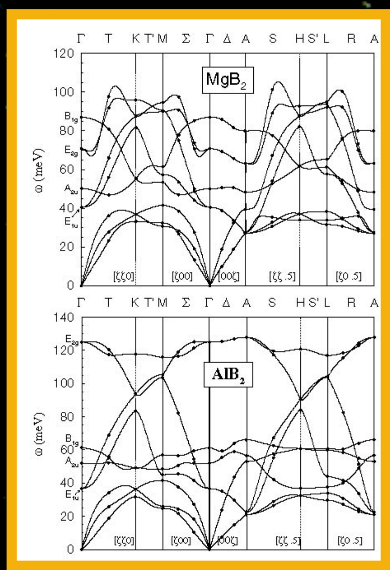
Kortus, et al, PRL 86 (2001)4656

High T_c (39K)

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

Simple Structure…
straightforward calculation.

Phonon Structure

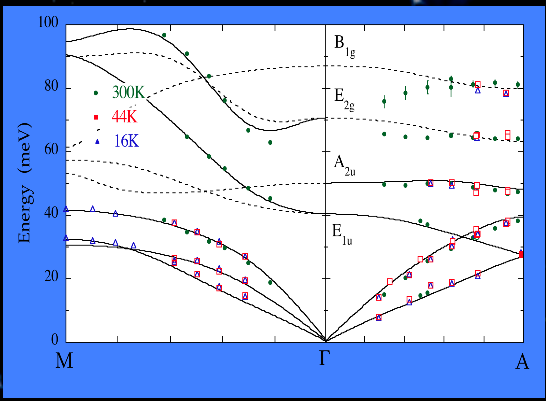


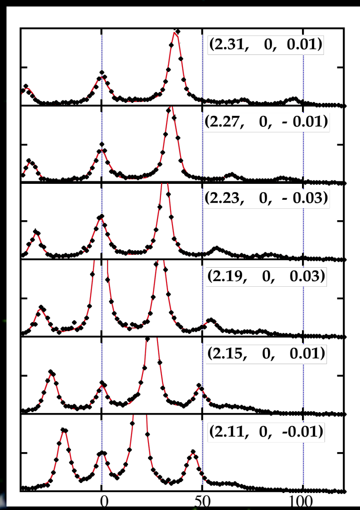
Bohnen, et al. PRL. **86**, (2001) 5771.

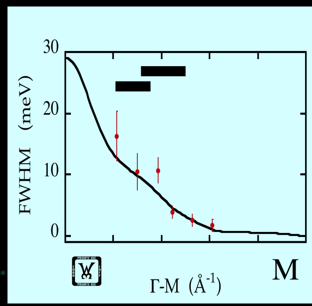
BCS (Eliashberg) superconductor with mode-specific electron-phonon coupling.

Electron-Phonon Coupling in MgB_2

Dispersion | Spectra | Linewidth







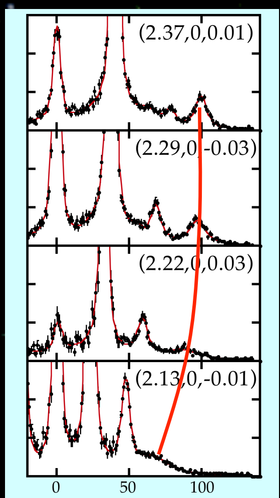
Clear correlation between
linewidth & softening.
Excellent agreement with LDA Pseudopotential calculation.

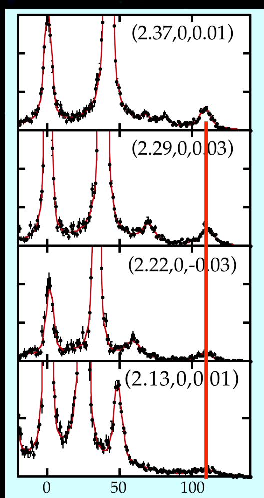
PRL 92(2004) 197004: Baron, Uchiyama, Tanaka, ... Tajima

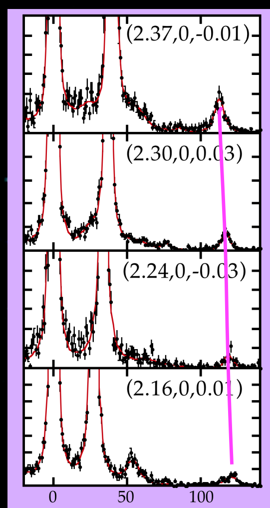
Carbon Doped $Mg(C_xB_{1-x})_2$

M

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







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

More Superconductors

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

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

Phonons in the Cuprates…

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

(0 0) (0.5 0)

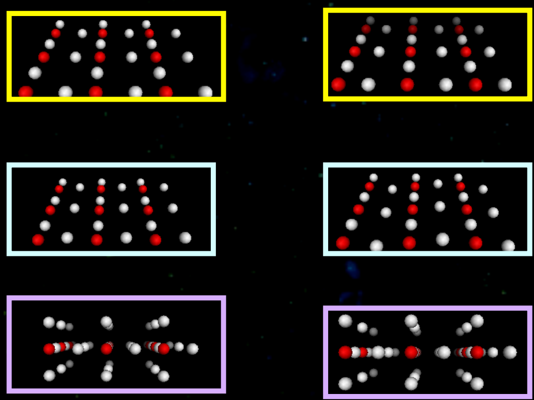
In-Plane Mode:

Stretching mode

Out of Plane Modes:

Buckling Mode

Apical Mode

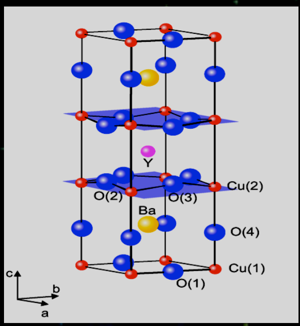


At the level of phonon spectra, the anomaly of the Bond Stetching Mode is very large

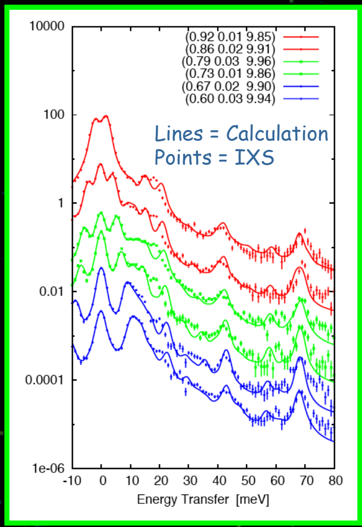
Copper Oxide Superconductors Remain Challenging…

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

T_c = 91 K

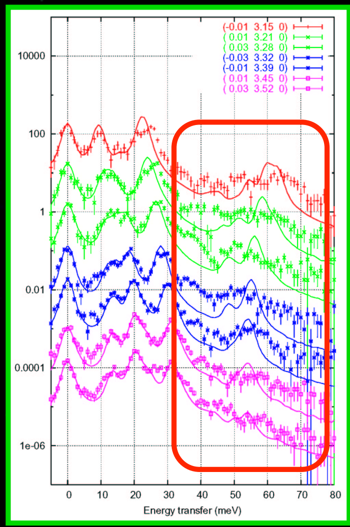


C-axis modes



Beautiful Agreement

In-Plane Modes

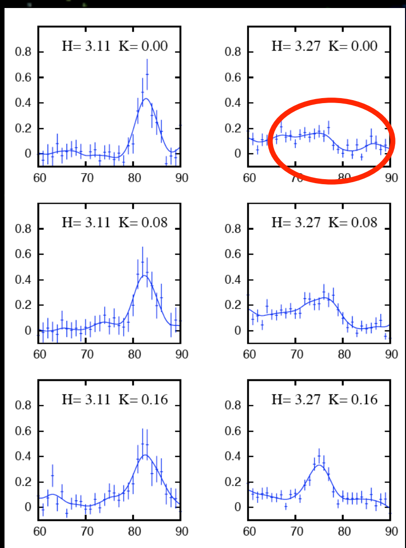


Problems

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

Compare IXS to Calculation
At low T (~30K) Bohnen, et al.

$La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$



D. Reznik, et al, Accepted
2.5 days

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

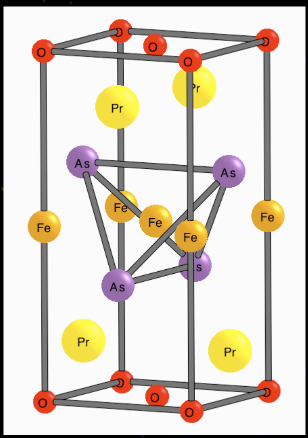
Expt done by a neutron scatterer because he could not get good enough resolution using neutrons

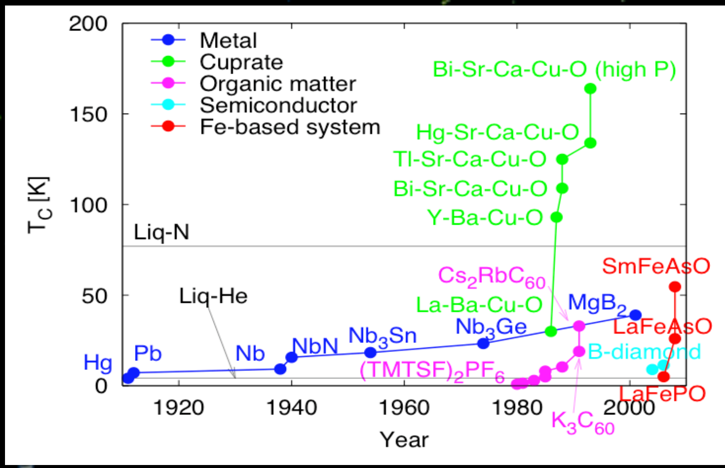
Forces a reinterpretation of some Neutron data (Reznik, Nature, 2006)

Note: IXS Q Resolution
Analyzer array
Count rate limited.

The Iron-Pnictide Superconductors

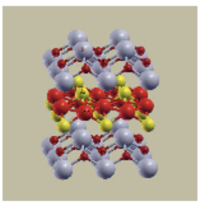
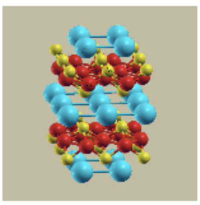
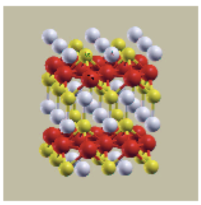
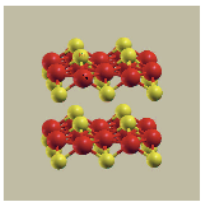
High-Tc demonstrated February 2008 (Hosono's group)
-> Research Explosion

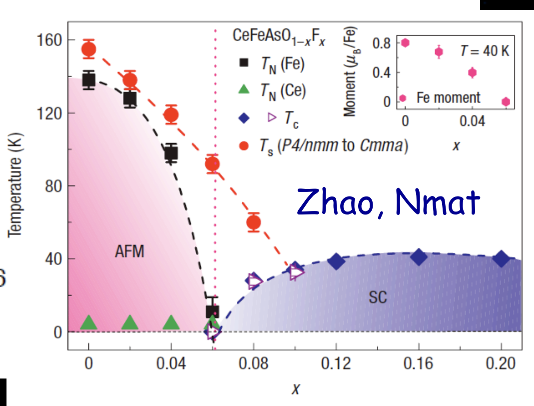




Fe Planes with Tetrahedral As
Parent (non SC) Shows Mag. Order & Tetragonal-> Orthorhombic Transition at ~140 K

Materials

	RFeAsO "1111"	AFe$_2$As$_2$ "122"	AFeAs "111"	FePn "11"
	R=La,Ce,Pr, Nd,Sm,Eu,Gd,Tb,Dy	A=Ba,Sr,Ca K,Cs,Na	A=Li,Na	Pn=Se,Te,S
				
T_N [K]	127∼141	140, 220, 173		
T_s [K]	150∼155	140, 220, 173		
T_c [K]	28, 55	25, 37		
T_R [K]	2∼14	-		
m [μ_B]	0.36∼0.9	0.8∼1.0		
Ref.	Y.Kamihara *et al.* JACS 130,3296 Z-A.Ren *et al.* CPL 25,2215	M.Rotter *et al.* PRL 101,107006		



Samples

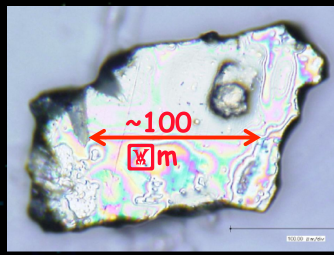
Single Crystals of $PrFeAsO_{1-y}$

Superconductor: T_c (onset) ~ 45 K

Parent: Resistivity Change at ~145 K

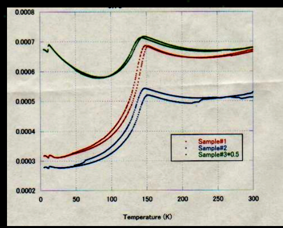
Typically "reasonable" crystal quality
~1 degree mosaic

Measurements
- 3 to 6 hours / spectrum (Fe&As!)
- Wide variety of Q and T<=300K
- Many small changes with doping & T

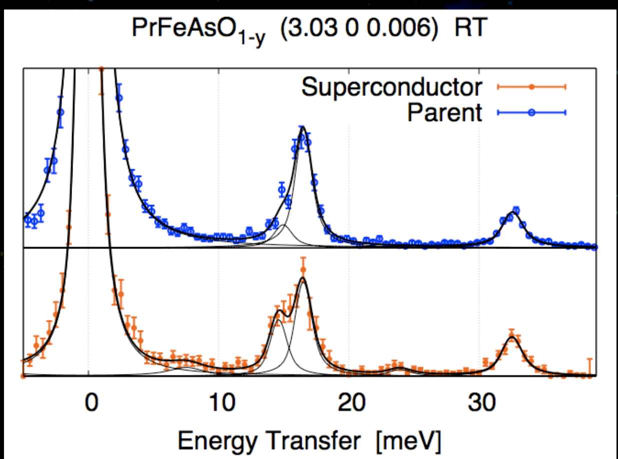


$PrFeAsO_{1-y}$
20 um Thick
Transverse: ~0.1 to ~0.5 mm

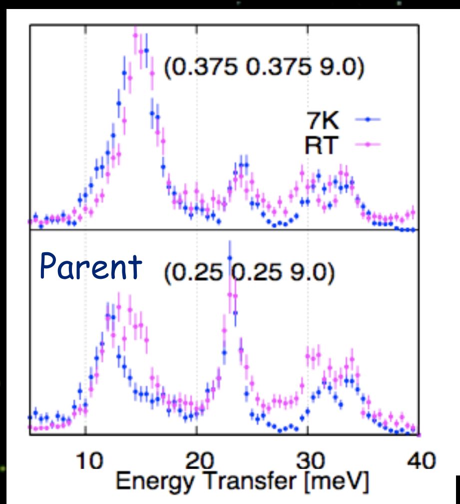
Ishikado, Kito, & Eisaki
(at AIST)



Some Examples of Measured Spectra:



In-Plane



C-axis

Generally: Differences in measured spectra (doping, temperature)
are smaller than difference between DFT calculations and Data...

Different Models:

Original: Straight GGA for Tetragonal stoichiometric PrFeAsO

Soft: As "Original" but soften the FeAs NN Force constant by 30%

Soft O7/8: Super cell 2x2x1 with one oxygen removed
and softened Fe-As NN Force constant
(31 atoms/prim cell, Tetragonal, No Magnetism)

Magnetic Orthorhombic: LSDA for LaFeAsO with
stripe structure of De la Cruz (16 atoms/prim. cell, 72 Ibam)

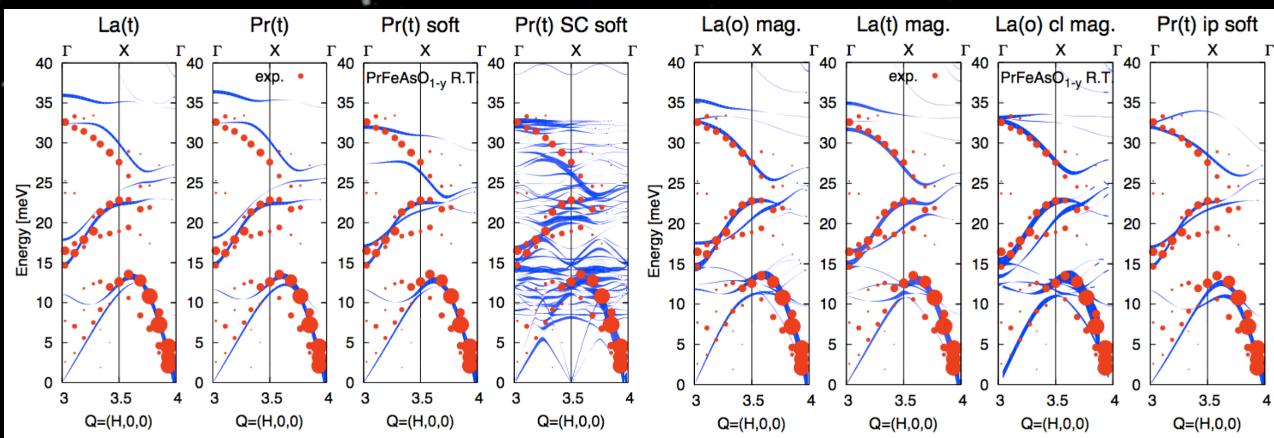
Magnetic Tetragonal: LSDA for LaFeAsO with stripes
Force a=b (to distinguish effects of structure vs magnetism)

Clipped: Mag. Ortho. with cut force constant

Soft IP: "Original" but soften FeAs NN *In Plane* components

Calculations: Nakamura & Machida

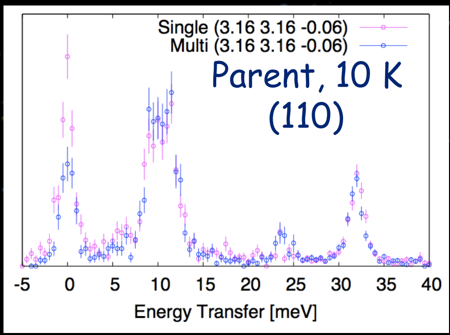
Compare dispersion with models

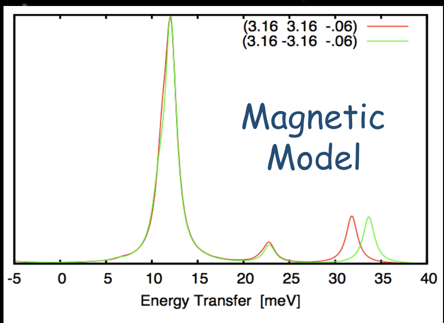


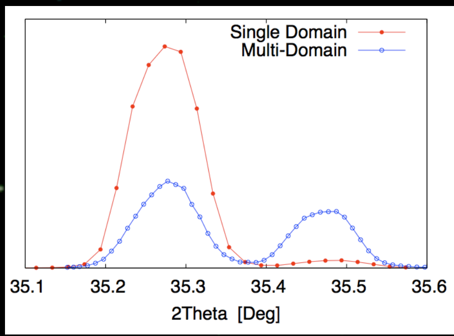
Red = Data (SC) Blue = Calc. Area/Height: Intensity

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

But: No evidence of magnetic anisotropy in the phonon spectra

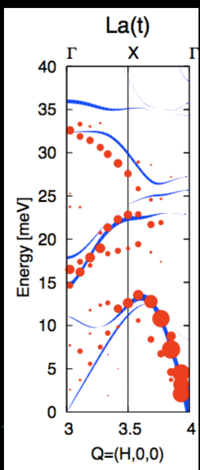




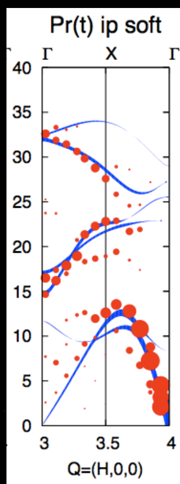


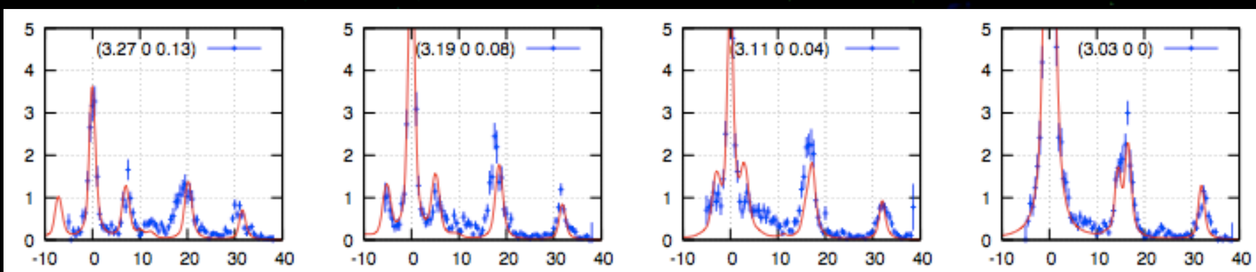
Splitting along the (110) direction is predicted but *not* observed, even in the parent materials…

Soften In-Plane Fe-Fe Force-Constant



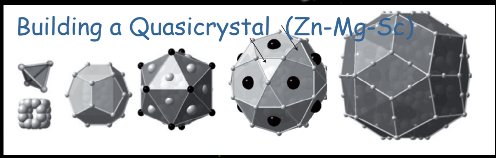
Softening the in-plane components of the force-constant matrix Avoids the anti-crossing



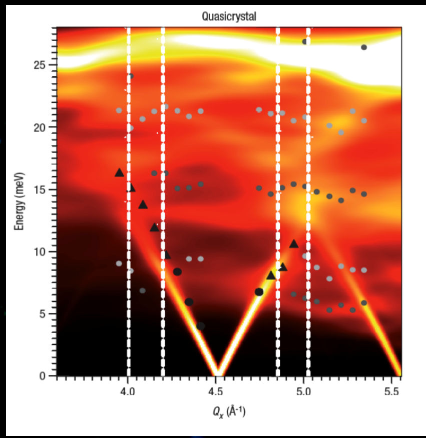


Phonons in a Quasicrystal

Mostly like a solid but some glassy character.

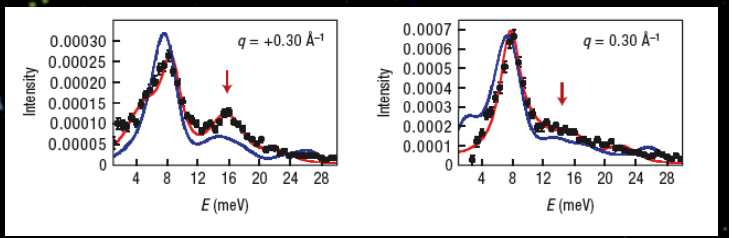


Periodic (BCC) -> **Crystalline** Approximant
Aperiodic -> **Quasicrystal**



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

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

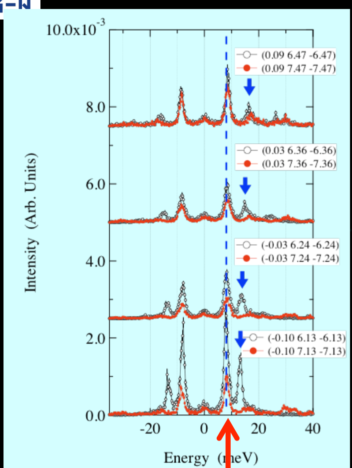


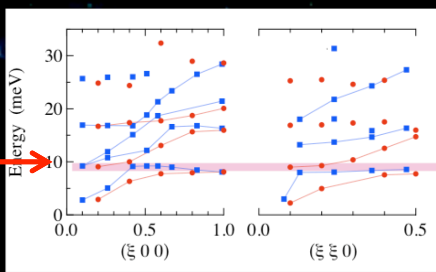
De Boissieu, *et al.*
Nature Materials, Dec 2007

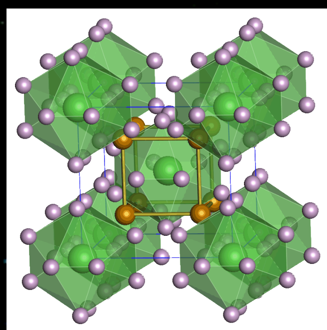
Red: Fits, Blue: Simulation

$SmRu_4P_{12}$

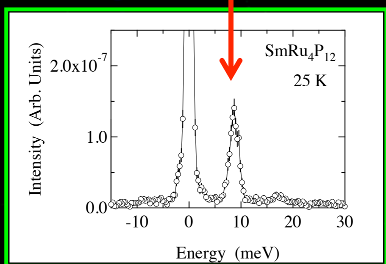
S. Tsutsui, et al.
JPSJ 77 (2008) 033601







"Localized" Rattling Mode



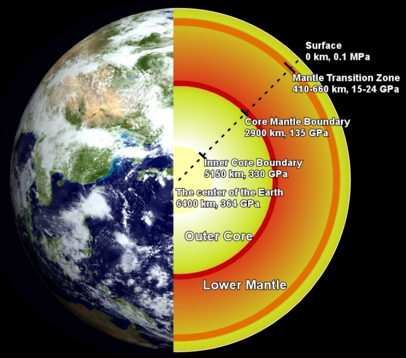
Localized Nature Confirmed by IXS
(No Frequency Dispersion, Weak Intensity Dispersion,
BUT Note Anticrossing!)

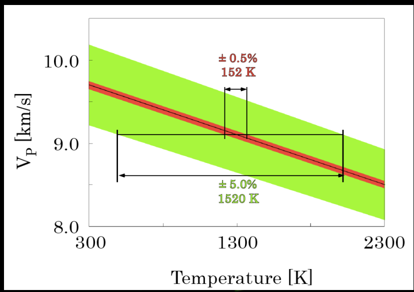
Sm Mode confirmed by (Sm specific)
Nuclear Inelastic Scattering

Anti-Crossing Subsequently Confirmed
Christensen et al, Nature Materials

Elastic Constants in Geological Conditions

Required for Modeling Earths Interior & Interpreting Seismic Data (v->T)
... but this is difficult to measure for samples in a DAC

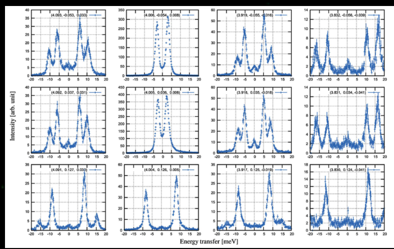




MgO
5% Uncertainty in v
-> 750K in T

Precision/Accuracy 0.2/0.8% using
Christoffel's Eqn & 12 Analyzer Array
H. Fukui, et al., JSR

~1 Order Improvement Over Previous IXS

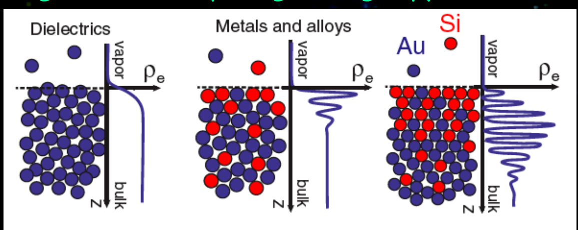


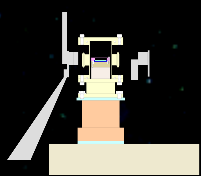
One Scan with 12-Analyzers

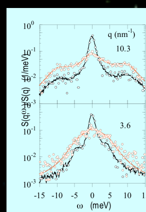
Liquid Surfaces

Surface Dynamics are different than bulk...
Surface Sensitivity (~5nm) is possible at Extreme Grazing Incidence

e.g. Surface Layering... (fig. Spyrko, et al)

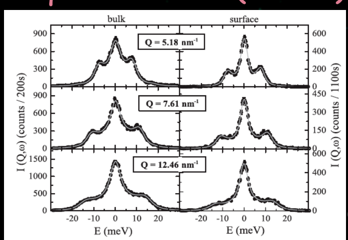




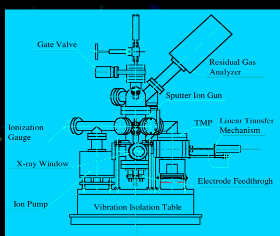


Favorable Tests in Air...
UHV Chamber now in Progress
(D. Ishikawa)

Liquid Indium (ESRF)



Reichert, et al, PRL 2007



Novel Uses of The Phonon *Intensity*

Phonon Cross Section:

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

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

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

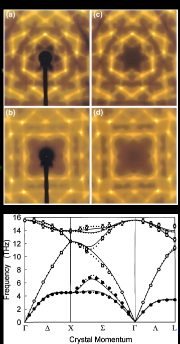
In principle, the phonon polarization is complex, but in some cases, it can be simple, or smooth, letting one get information about
e.g. the form factor from frequency resolved measurements or
sharp frequency changes from integrated measurements

Using Thermal Diffuse Scattering (TDS)

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

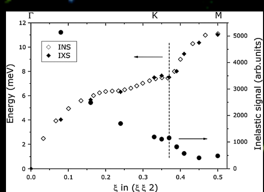
Long history... at least to Colella and Batterman PR 1970 (Va dispersion)

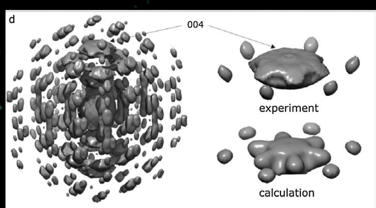
More sensitive -> See Kohn anomalies when phonons span the Fermi surface

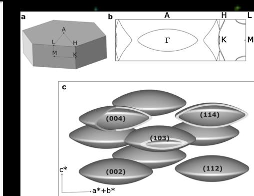


TDS from Silicon

Holt, et al, PRL 1999





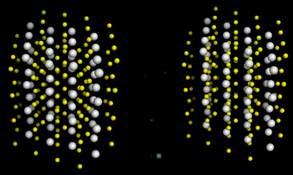


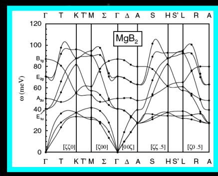
Zn, Bosak et al, PRL 2009

Detailed Phonon/FS behavior in SIMPLE materials
More generally very useful, but not so detailed
Learn where to look...

Atomic -> Electronic Dynamics

Atomic Dynamics



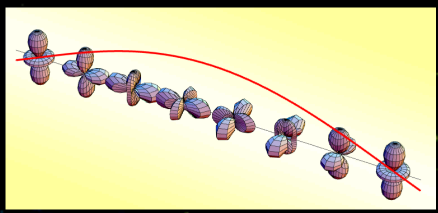


Correlated atomic motions (phonons) play a role in many phenomena
(e.g. superconductivity, CDWs, phase transitions, thermoelectricity, magneto-elastic phenomena etc)

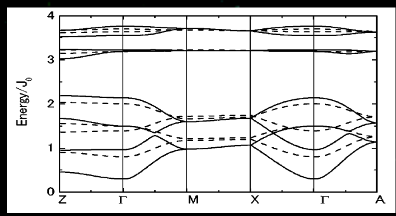
Electronic Excitations.... A New Field

High (~10 meV) Resolution
at Large Momentum Transfers

Orbiton Movie
S. Maekawa



1 electron-> Very Weak



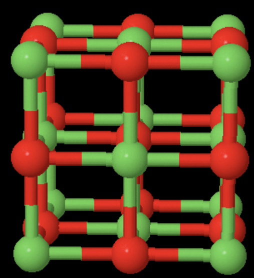
Calculated Orbiton Dispersion
Ishihara

Key is to see momentum dependence (dispersion) -> Not Yet.

First Attempt via IXS: NJP 2004

d-d Excitations in NiO

First something simple...

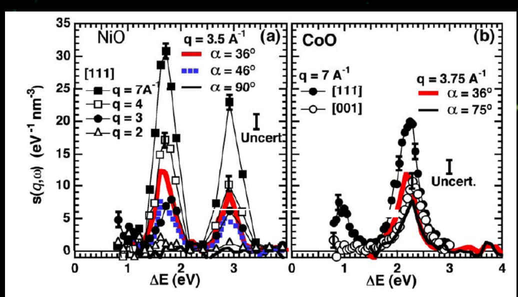


There exist well-defined excitations in the charge transfer gap of NiO
Antiferromagnet (T_N 523K), (111) Spin order

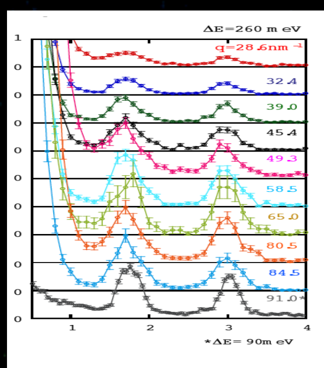
Long and Distinguished History

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

Non-Resonant IXS, ΔE~300 meV

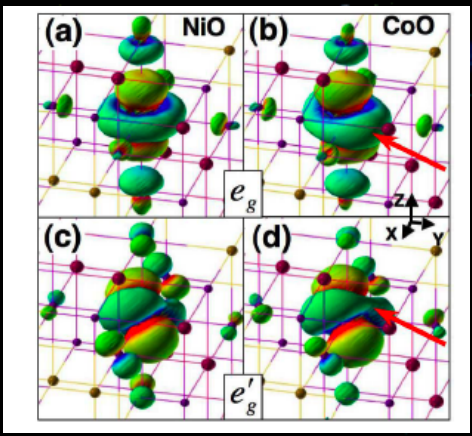


Larson, et al., PRL 99 (2007) 026401



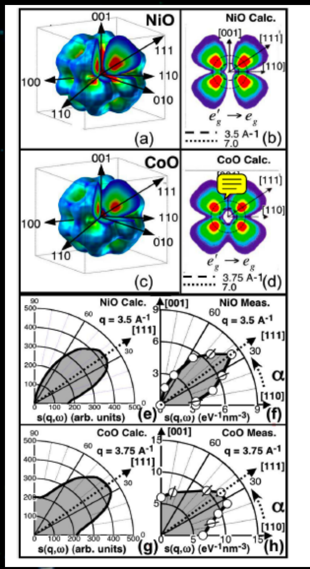
Cai, Hiraoka, et al, BL12XU
Unpublished

Orientation Dependence

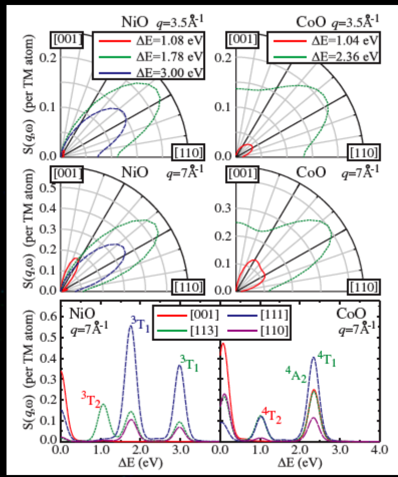


Orbitals

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



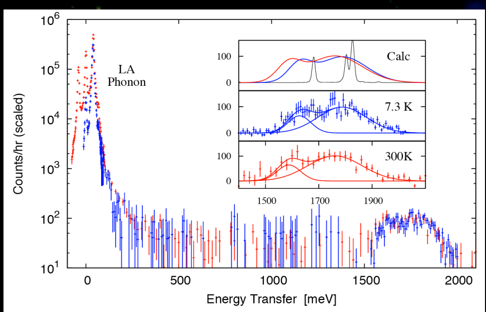
Scattered Intensity



Cluster calculations
Haverkort, et al PRL (2007)

High Resolution Experiment

7 meV resolution at 1800 meV energy transfer



d-d Excitation in NiO
Baron et al, Fall 07, 3 Days/Spectrum

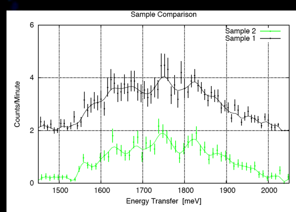
Cleaner "Optical Spectroscopy" due to

1. Non-resonant interaction $S(Q,\omega)$
2. Large Q & Q dependence
   -> selects multipole order.
   -> atomic correlations.

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

Collective interaction <-> dispersion
(d-d excitations -> "orbiton")

Relevance to correlated materials…
Gaps (Mott, Charge Transfer) and
Mid-IR band in high Tcs
f-electron transitions, etc



"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

NRIXS

MgB_2 Collective Excitation

PRL **97,** 176402 (2006) PHYSICAL REVIEW LETTERS week ending 27 OCTOBER 2006

Low-Energy Charge-Density Excitations in MgB_2: Striking Interplay between Single-Particle and Collective Behavior for Large Momenta

Y. Q. Cai,[1,*] P. C. Chow,[1,†] O. D. Restrepo,[2,3] Y. Takano,[4] K. Togano,[4] H. Kito,[5] H. Ishii,[1] C. C. Chen,[1] K. S. Liang,[1] C. T. Chen,[1] S. Tsuda,[6] S. Shin,[6,7] C. C. Kao,[8] W. Ku,[9] and A. G. Eguiluz[2,3]

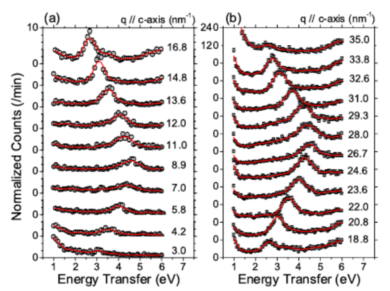


FIG. 1 (color online). NIXS spectra at various momentum transfers $q \parallel c^*$ axis showing the low-energy collective mode, where $q = 8.9\ \mathrm{nm}^{-1}$ corresponds to the first boundary of the extended BZ. The total energy resolution was 65 meV for (a), and 250 meV for (b).

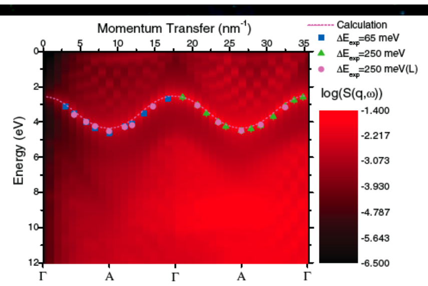
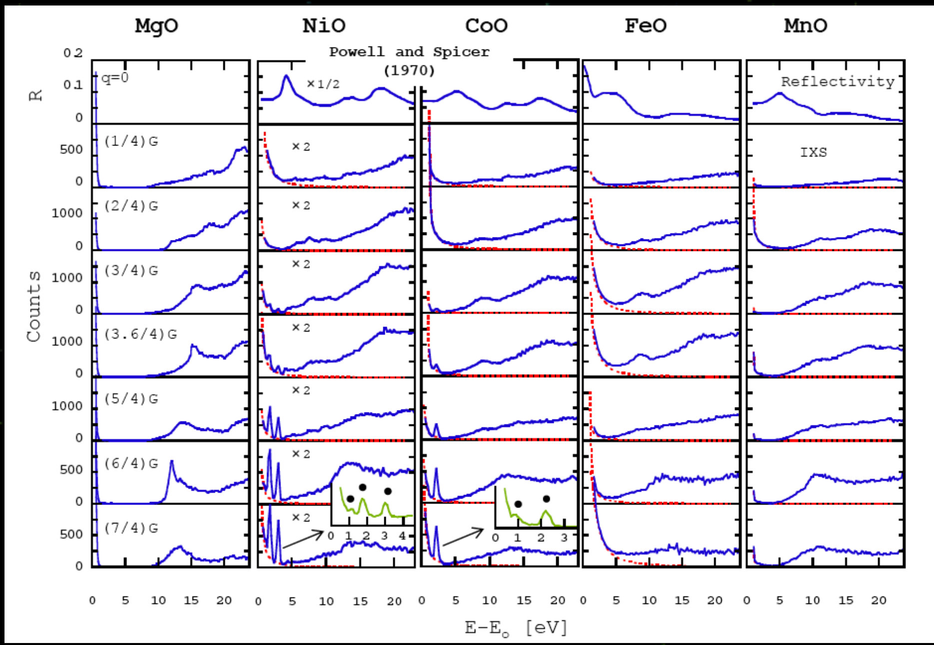


FIG. 2 (color). Theoretical $S(\mathbf{q}, \omega)$ calculated in the present work in false color log scale as a function of energy and momentum transfer showing the cosine energy dispersion of the low-energy collective mode. Filled squares and triangles mark the energy positions obtained from the NIXS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

Excitation repeats from one zone to the next…

Larger Energy Range



Hiraoka et al

RIXS & NRIXS

30 to 300 meV resolution

Both are Methods of Probing Electronic Structure
RIXS = Resonant IXS = Near an absorption edge
NRIXS = Non-Resonant IXS

RIXS: Higher Rate
Poorer Resolution (Optics must match resonance)
Element Specific (Somewhat)
More Complicated Data

NRIXS: Lower Rate
Higher Resolution (Choose energy to match optics)
Simpler & Cleaner Data

Slightly Different Experimental Setup

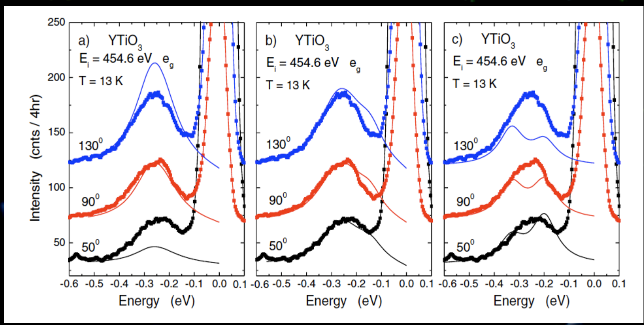
RIXS -> 2 Orbiton

This is different…

PRL **103,** 107205 (2009) PHYSICAL REVIEW LETTERS week ending 4 SEPTEMBER 2009

Momentum Dependence of Orbital Excitations in Mott-Insulating Titanates

C. Ulrich,[1] L. J. P. Ament,[2] G. Ghiringhelli,[3] L. Braicovich,[4] M. Moretti Sala,[4] N. Pezzotta,[4] T. Schmitt,[5] G. Khaliullin,[1] J. van den Brink,[2,6] H. Roth,[7] T. Lorenz,[7] and B. Keimer[1]

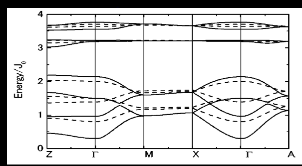


Ti L-Edge RIXS at the SLS

Signal from “2-orbiton”, some evidence of changes with Q

Nice,

…but not real orbiton dispersion.



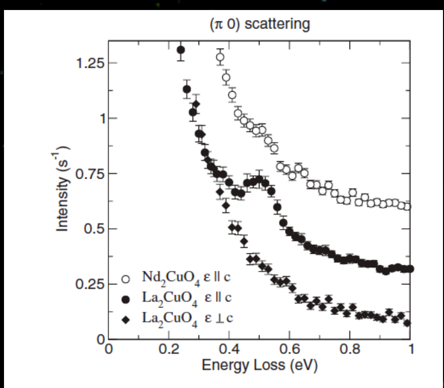
AQRB @ AOFSRR Cheiron School 2011

2-Magnon Peak?

PRL **100,** 097001 (2008) PHYSICAL REVIEW LETTERS week ending 7 MARCH 2008

Observation of a 500 meV Collective Mode in $La_{2-x}Sr_xCuO_4$ and Nd_2CuO_4 Using Resonant Inelastic X-Ray Scattering

J. P. Hill,[1,2] G. Blumberg,[3] Young-June Kim,[4] D. S. Ellis,[4] S. Wakimoto,[4] R. J. Birgeneau,[4] Seiki Komiya,[5] Yoichi Ando,[5,*] B. Liang,[6] R. L. Greene,[6] D. Casa,[7] and T. Gog[7]



Copper K-Edge RIXS

120 meV resolution, APS, Sector 9

Q Dependence (over zone) and polarization dependence

d-d Excitation or 2-Magnon?

AQRB @ AOFSRR Cheiron School 2011

X-Ray Raman Scattering

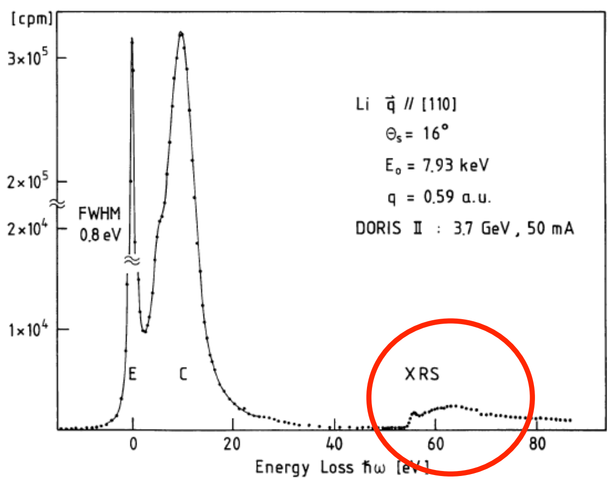


Fig. 1. Raw experimental data for Li single crystal obtained in the dispersion compensating case. The X-ray Raman spectrum (XRS) has an edge like onset at the binding energy of the Li K-electron of about 55 eV. E and C denote the quasielastically scattered Rayleigh line and the $S(\boldsymbol{q}, \omega)$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

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

X-Ray Raman Scattering

(Example of Ice Under Pressure)

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

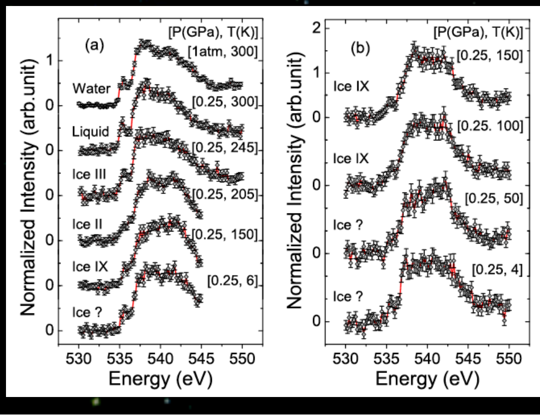
Diamond:

l_{abs} < 0.5 um 500 eV

l_{abs} ~ 2 mm 10 keV

Easier at 10 keV than 0.5 keV

Note: need dipole approx. (Q.r<1) to be good to compare with usual XAFS.



Ordering of Hydrogen Bonds in High-Pressure Low-Temperature H_2O

Y. Q. Cai,[1,*] H.-K. Mao,[2] P. C. Chow,[1,†] J. S. Tse,[3] Y. Ma,[3] S. Patchkovskii,[3] J. F. Shu,[2] V. Struzhkin,[2] R. J. Hemley,[2] H. Ishii,[1] C. C. Chen,[1] I. Jarrige,[1] C. T. Chen,[1] S. R. Shieh,[4] E. P. Huang,[4] and C. C. Kao[5]

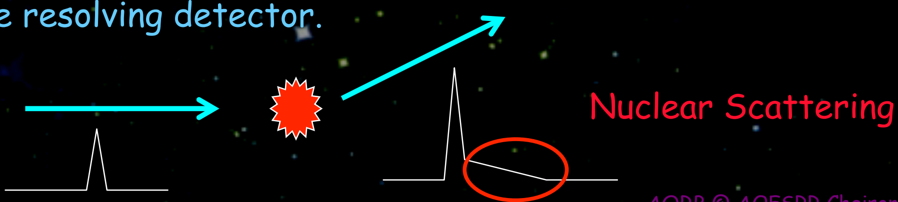
Nuclear Inelastic Scattering

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

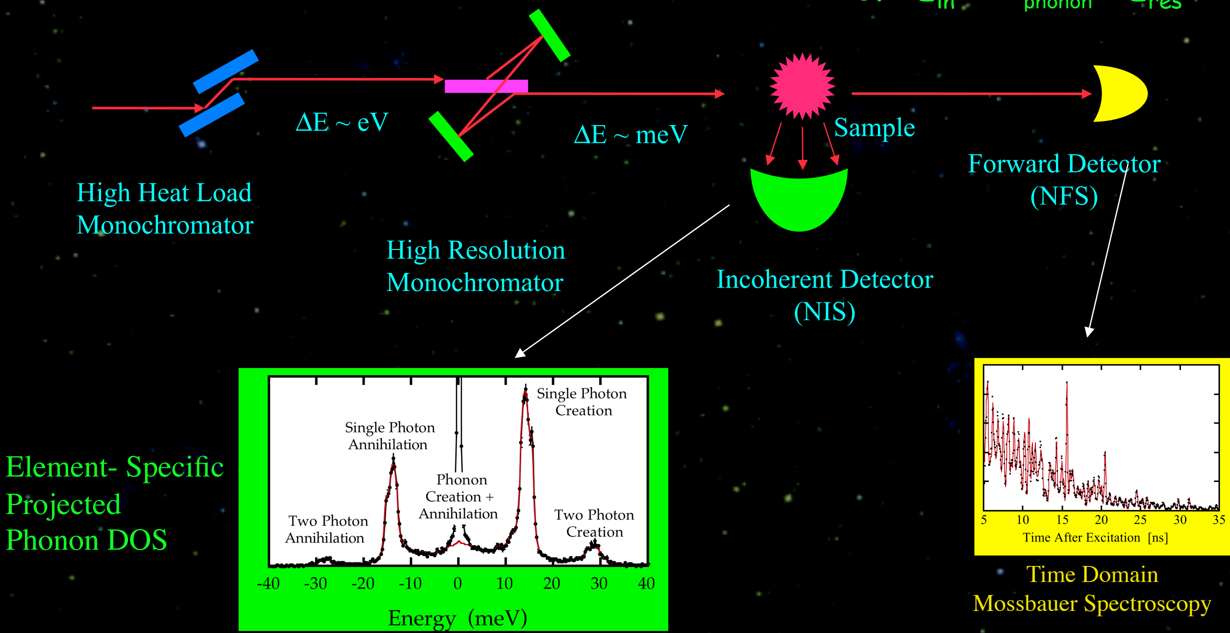
Resonances have relatively long lifetimes so that if one has a pulsed source, one can separate the nuclear scattering by using a fast time resolving detector.



NIS Setup

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

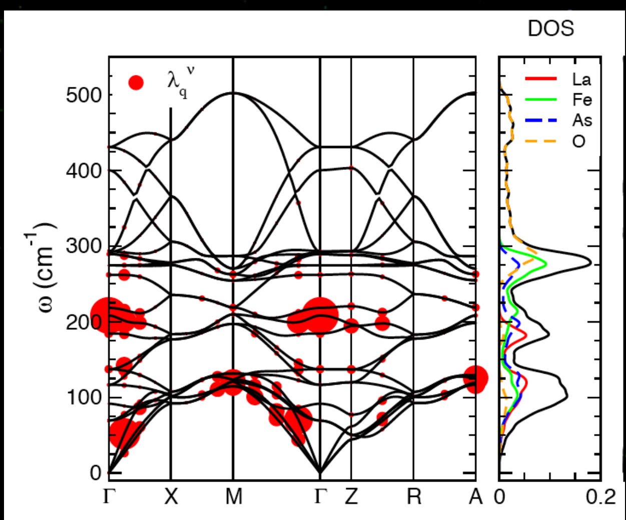
1. $E_{in} = E_{res}$
2. $E_{in} + E_{phonon} = E_{res}$
3. $E_{in} - E_{phonon} = E_{res}$



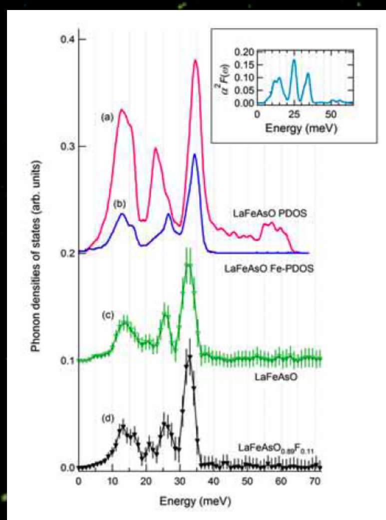
NIS Gives the Partial Projected DOS

Example of the Fe-As Superconductors

Partial= Element Specific   Projected= Weakly Directional $I \sim \varepsilon \bullet k_l$



Calculation: Boeri et al



Measurement: Higashitaniguchi et al

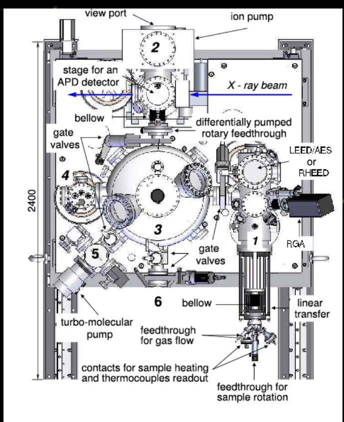
NIS: Good and Bad

Important things to note:

1. Element and isotope selective.
2. Gives Projected Density of states NOT Dispersion
   (But it does this nearly perfectly)

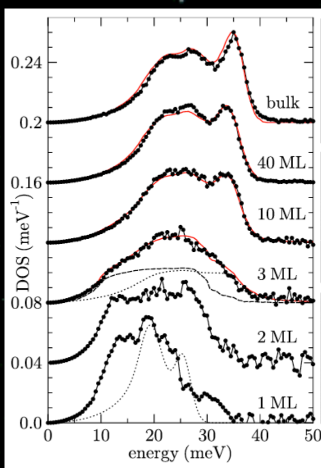
Surfaces by NIS

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



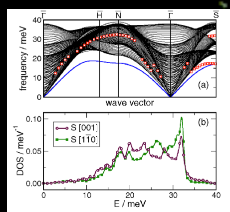
In-Situ Deposition @ ESRF

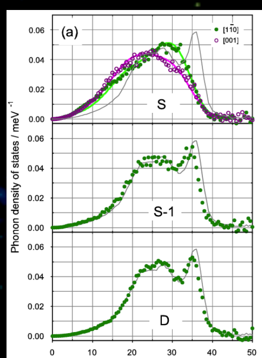
Stankov et al, JP 2010



^{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

NIS Example: Biological Macro-Molecules

e.g.

VOLUME 86, NUMBER 21 PHYSICAL REVIEW LETTERS 21 MAY 2001

Long-Range Reactive Dynamics in Myoglobin

J. Timothy Sage,[1,*] Stephen M. Durbin,[2] Wolfgang Sturhahn,[3] David C. Wharton,[1] Paul M. Champion,[1] Philip Hession,[2,3] John Sutter,[2,3] and E. Ercan Alp[3]

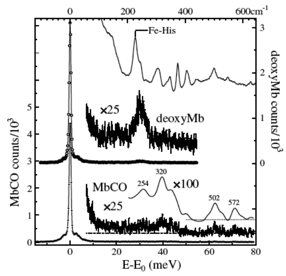


FIG. 1. NRVS data recorded from frozen solutions of ^{57}Fe-enriched MbCO (solid circles) at 110 ± 5 K and deoxyMb (open circles) at 35–70 K. Temperatures were estimated from the relative intensity of phonon creation and annihilation peaks. The MbCO (deoxyMb) spectrum is the sum of 20(16) independent scans sampled every 0.2 meV over an energy range extending from −15 meV to 80(55) meV with a total accumulation time of 189(160) sec/channel. The high frequency region of the MbCO spectrum is scaled up by an additional factor of 4, subjected to an 11-point smooth, and displayed as a solid curve. The solid curve at the top of the figure is the resonance Raman spectrum of deoxyMb at 100 K.

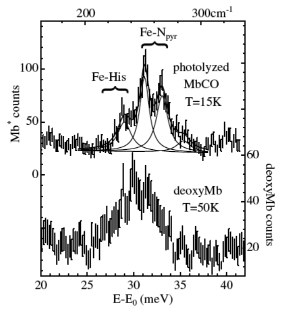


FIG. 2. Comparison of the 250 cm^{-1} mode clusters of deoxy-Mb and Mb*. The Mb* data were recorded under continuous illumination. The temperature of a sensor mounted in the sapphire sample block was 15 K.

σ_0 is the nuclear cross section and Γ_n is the linewidth of the recoilless resonance. The excitation probability per unit energy

Where element specificity can help a lot.

Compton Scattering

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

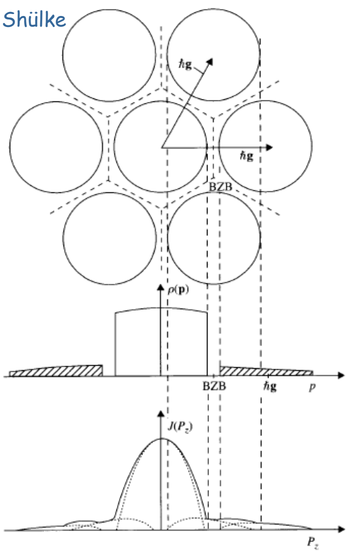
$$S(\mathbf{Q},\omega) = \frac{m}{\hbar Q} \iint dp_x dp_y \ \rho(p_z = p_Q)$$
$$\equiv \frac{m}{\hbar Q} J(p_Q)$$

Typical: Q~100Å^{-1}
E>100 keV

Ie: Compton scattering projects out the electron momentum density.

Typical of incoherent scattering...

From Shülke



Three-Dimensional Momentum Density Reconstruction

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

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

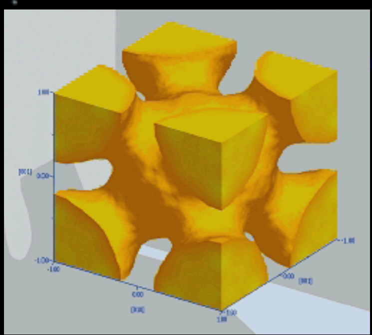
Reconstruction:

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

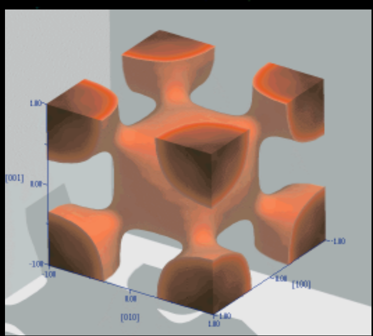
Momentum density, n(**p**)

From Y. Sakurai

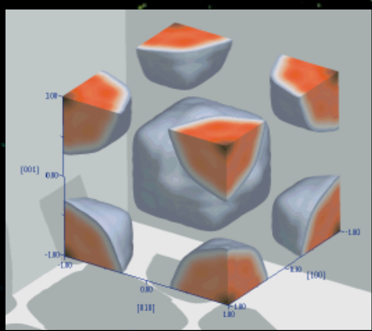
Fermi surfaces of Cu and Cu alloys



Cu-15.8at%Al



Cu



Cu-27.5at%Pd

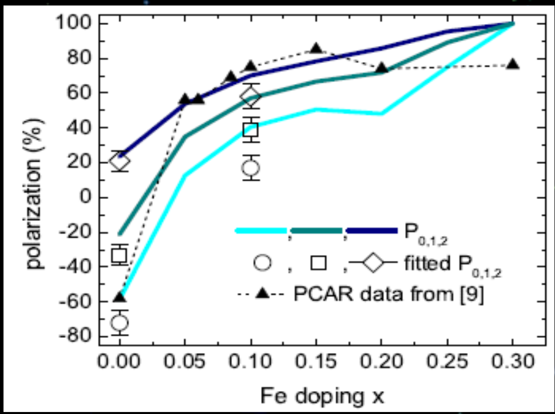
Determined by Compton scattering at KEK-AR

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

Spin Polarization by Magnetic Compton Scattering

Magnetic Compton scattering combined with *ab initio* electronic structure calculation is used to evaluate the degrees of spin polarization, P_n.

Spin Polarization of $Co_{2-x}Fe_xS_2$



C. Utfeld *et al.*, PRL

$$P_n = \frac{N_\uparrow v^n_{F,\uparrow} - N_\downarrow v^n_{F,\downarrow}}{N_\uparrow v^n_{F,\uparrow} + N_\downarrow v^n_{F,\downarrow}}$$

$N_{\uparrow/\downarrow}$: Spin - dependent DOS at Fermi level

$v_{F,\uparrow/\downarrow}$: Fermi velocity