Inelastic X-Ray Scattering

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SPring-8

Acknowledgement:
Y. Sakurai (Compton)

Scope & Outline

Main Goal: Introduce Capabilities & Put them in Context
- Introduction & Relation to Other SR Work
- What relevant properties of samples can be measured?
- When/why would someone consider these techniques?

Outline:
- Introduction
- Brief comments about instrumentation.
- Non-Resonant Techniques
- Resonant Techniques (Briefly)

Note: limit to some aspects of photon-in -> photon out scattering

Note: Huge & Complex Topic - Appropriate for a semester, not an hour…

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 ~ 0.001-100 meV	Phonon Dispersion
NIS Nuclear IXS	Atom Specific Via Mossbauer Nuclei	E_{in} ~ 14-25 keV ΔE ~ 0.001-100 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)

Some References

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

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 1. Berlin: Springer-Verlag.

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

Spectroscopy

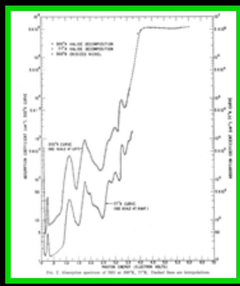
Absorption vs. Scattering

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

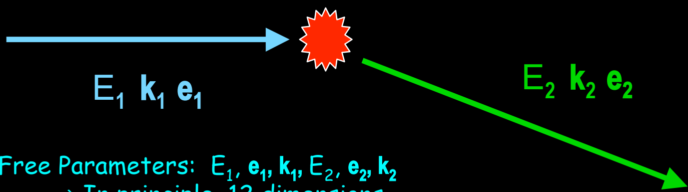


Optical Spect. NiO
Newman, PR 1959

Free Parameters: E_1, $\mathbf{e}_1$, $\mathbf{k}_1$
-> In principle, 6 dimensions
but in practice mostly 1 (E_1)

Scattering Spectroscopy

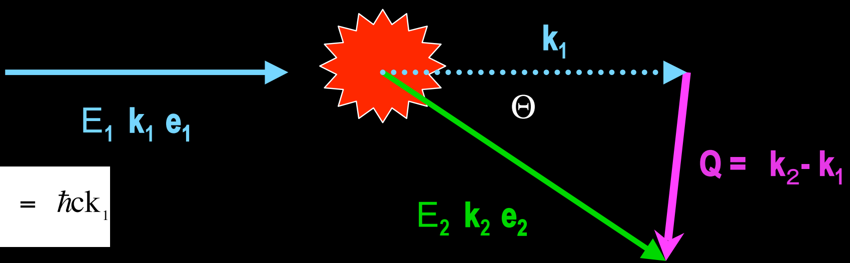
IXS, Raman, INS



Free Parameters: E_1, $\mathbf{e}_1$, $\mathbf{k}_1$, E_2, $\mathbf{e}_2$, $\mathbf{k}_2$
-> In principle, 12 dimensions
in practice, mostly 4, E_1-E_2, $\mathbf{Q} = \mathbf{k}_2 - \mathbf{k}_1$

Scattering is much more complex, but gives more information.

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:

Momentum Transfer

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

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

Energy Transfer

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

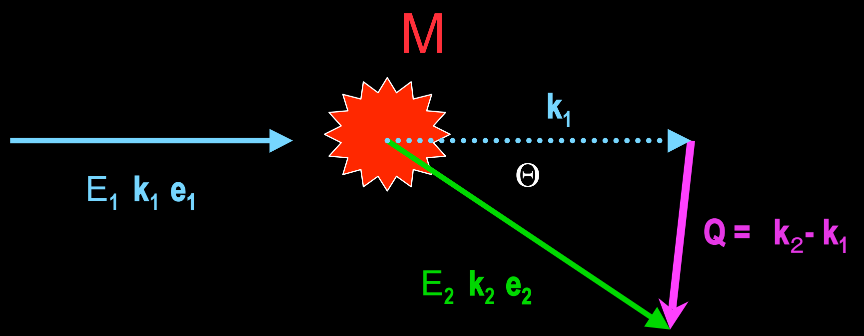
Periodicity Probed in Sample

$$d = \frac{2\pi}{|\mathbf{Q}|} \quad \text{or} \quad d = \frac{2\pi}{|\mathbf{q} = \mathbf{Q} - \tau|}$$

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

Kinematics:

Simplistic energy-momentum relations



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

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

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)

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

Note: For resonant $\omega \to \omega_2$

$$\sigma_{\mathrm{Thomson}} = r_e^{\ 2}\left(e_2^{\ *} \bullet e_1\right)\frac{\omega_2}{\omega_1}$$

Thomson Scattering Cross Section

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

Dynamic Structure Factor

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

The IXS Spectrometer
An Optics Problem

Main Components

Monochromator:

Modestly Difficult

Only needs to accept 15x40 mrad^2

Sample Stages

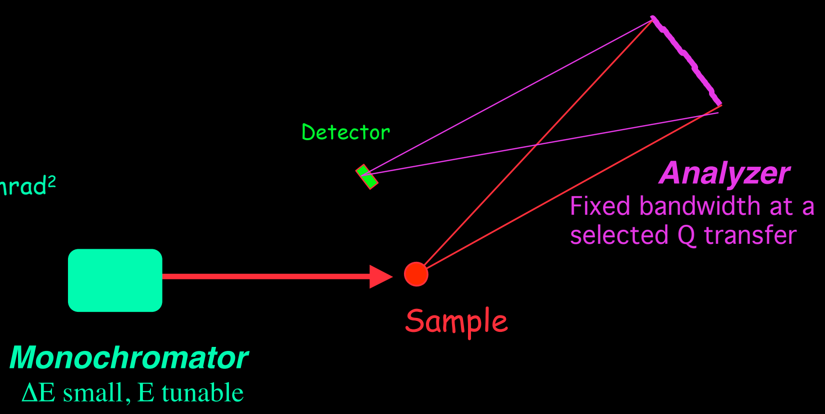
Straightforward

Only Need Space

Analyzer:

Large Solid Angle

Difficult



The Goal: Put it all together and

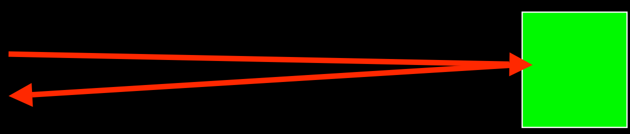
Keep Good Resolution, Not Lose Flux

Basic Optical Concepts

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

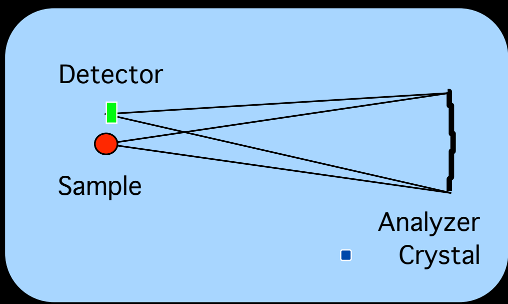
Working closer to Θ_B~90 deg. maximizes the angular acceptance for a given energy resolution…

Better energy resolution
-> Closer to 90 degrees
-> Large Spectrometer



Analyzer Crystals

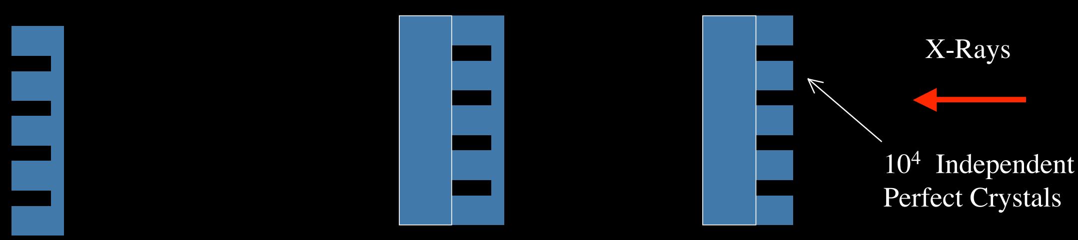
The more difficult optic…



Require:
Correct Shape (Spherically Curved, R=9.8 m)
Not Strained ($\Delta E/E$~few 10^{-8}-> $\Delta d/d$<<few10^{-8})

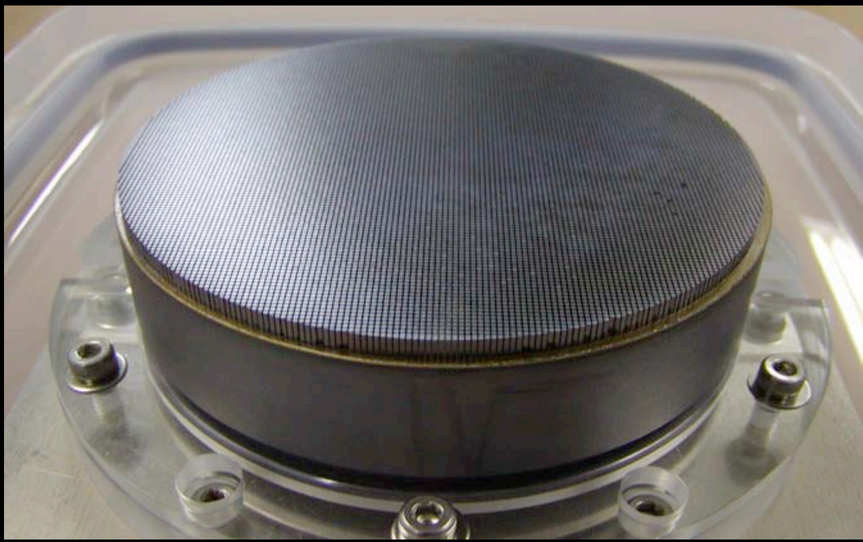
Method: Bond many small crystallites to a curved substrate.

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



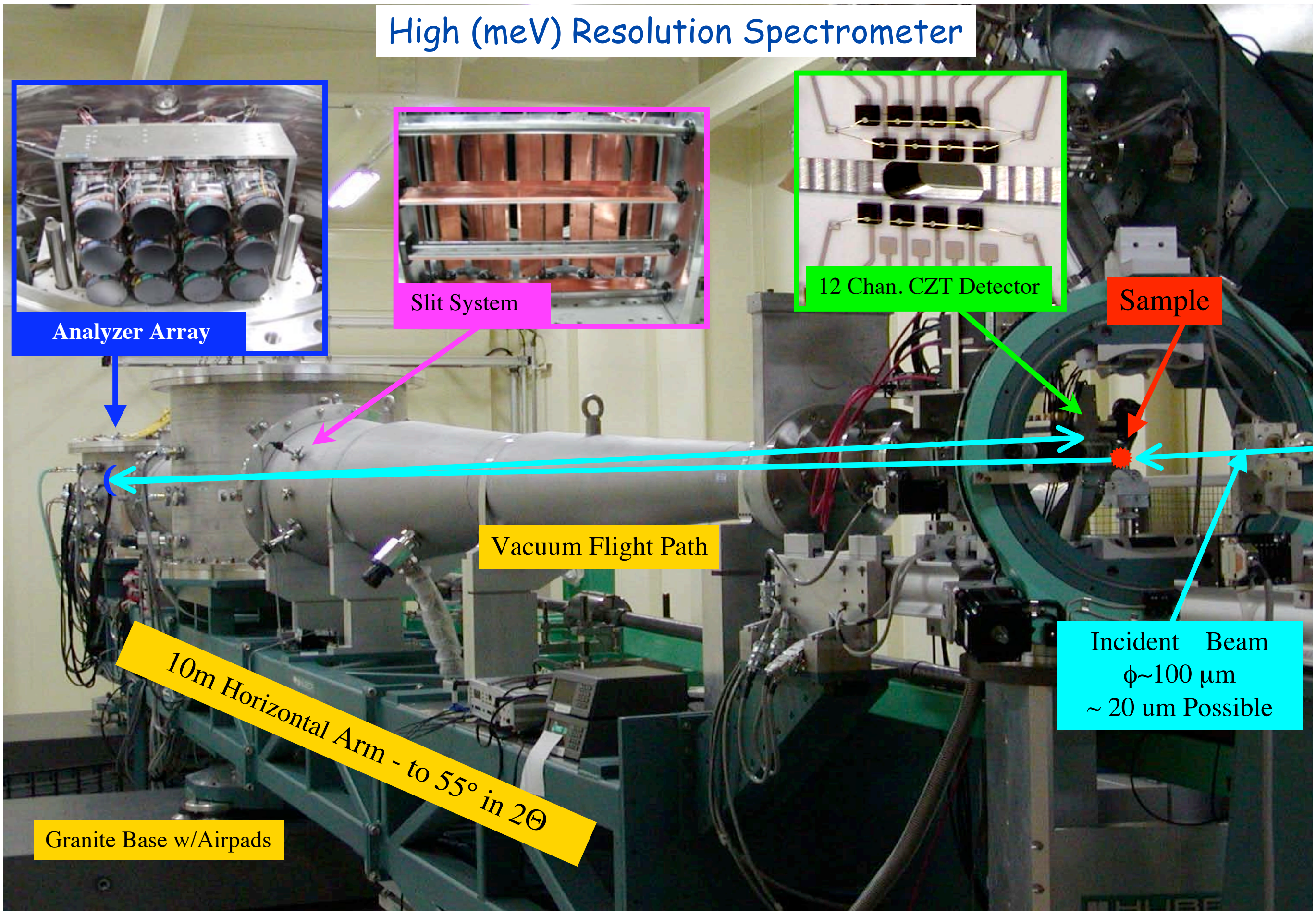
Analyzer Crystal

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

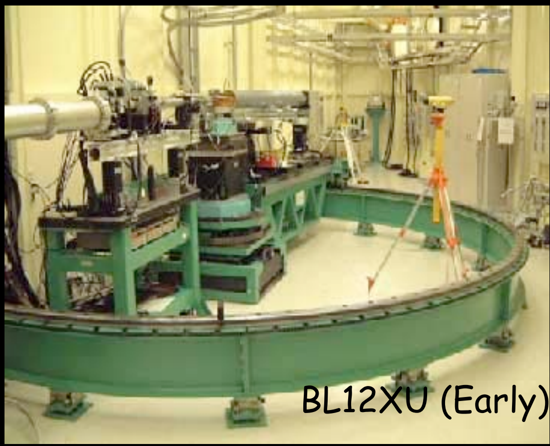


Present Parameters (9.8 m Radius, 10cm Diameter)

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

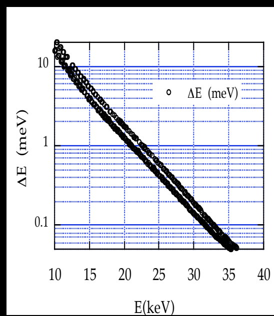


Medium Resolution



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

BL12XU (Cai, et al)
BL11XU (Ishii, et al)
Also: BL39XU (Hayashi, et al)



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

Atomic Dynamics: Systems and Questions

Disordered Materials (Liquids & Glasses):

Still a new field -> Nearly all new data is interesting.

How do dynamical modes survive the cross-over from the long-wavelength continuum/hydrodynamic regime to atomic length scales?

Crystalline Materials:

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

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

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**

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?

<u>Softening</u>: Screening lowers the energy of the mode (abrupt change <=> Kohn Anomaly)

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

Electron Phonon Coupling

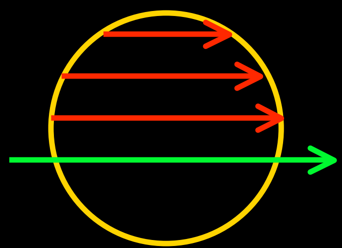
& Kohn Anomalies

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.

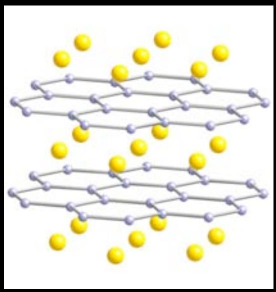
Phonon Momenta **$Q<2k_F$**



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

Fermi Surface Diameter = $2k_f$

MgB_2

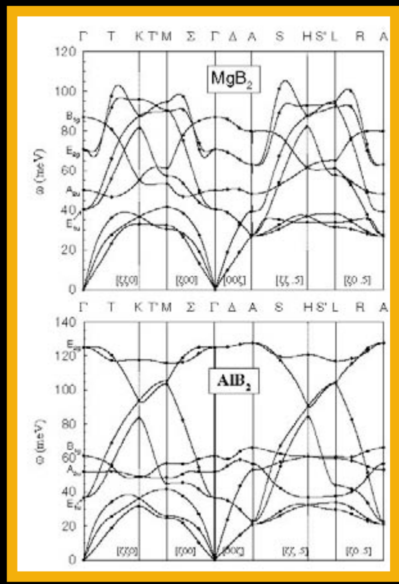


High T_c (39K)

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

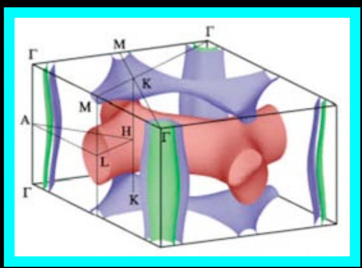
Simple Structure…
straightforward calculation.

Phonon Structure



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

Electronic Structure

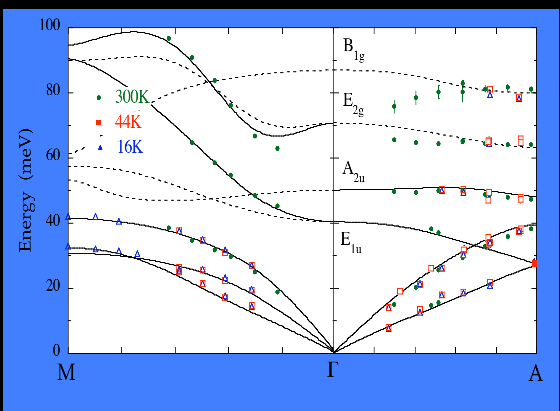


Kortus, et al, PRL 86 (2001)4656

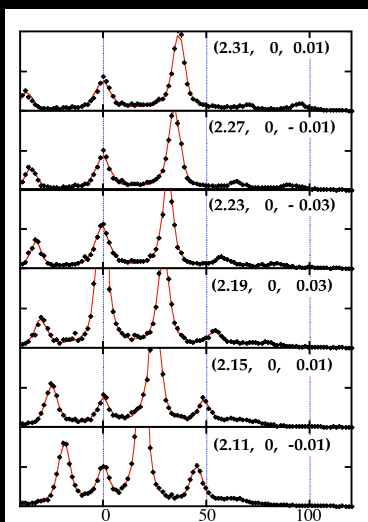
BCS (Eliashberg) superconductor with mode-specific electron-phonon coupling.

Electron-Phonon Coupling in MgB_2

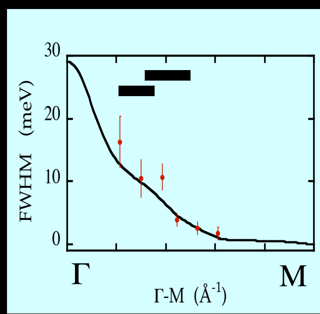
Dispersion



Spectra



Linewidth



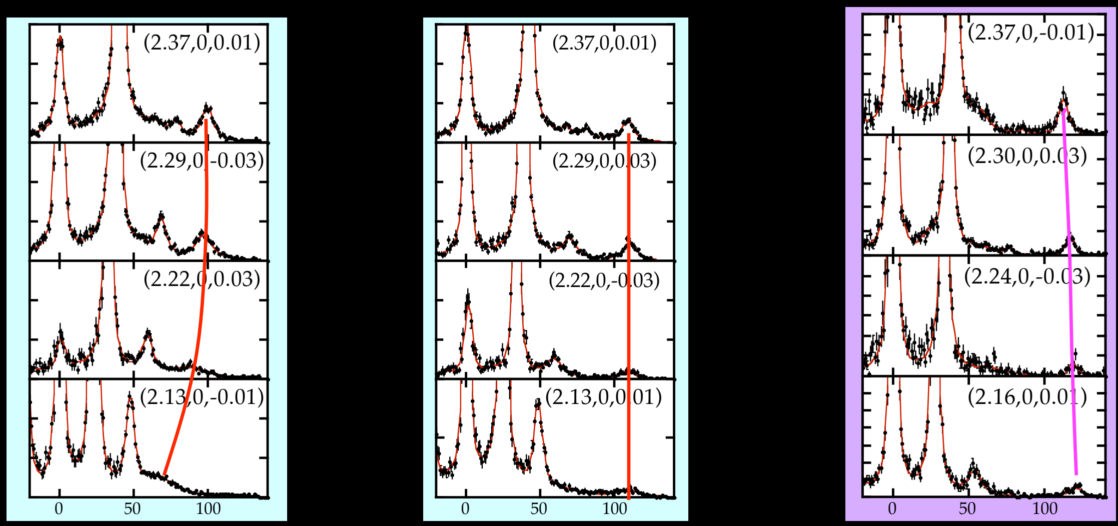
Clear correlation between
linewidth & softening.
Excellent agreement with LDA Pseudopotential calculation.

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

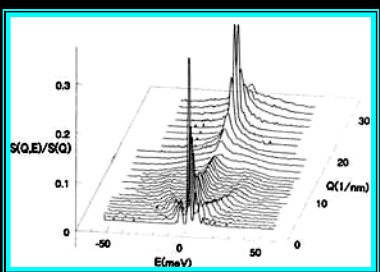
Similar types of results for
- Mn Doped MgB_2
- CaAlSi
- Boron Doped Diamond

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

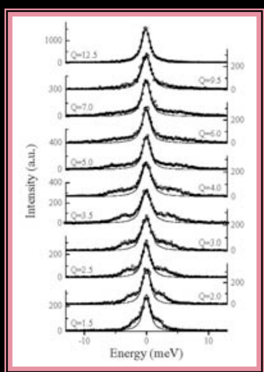
Disordered Materials

Hydrodynamic/Continuum (Q->0) Limit ->
Brillouin Triplet: Quasi-Elastic Peak + Sound Mode

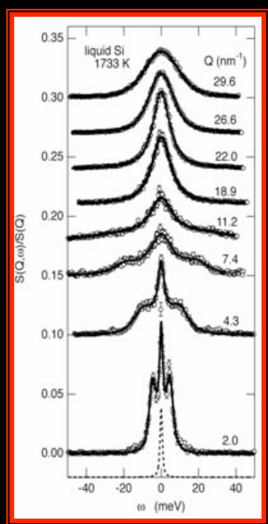
How does this evolve at larger Q?
"DHO model" = Lorentzian
+ Damped Harmonic Oscillator



l-Mg (Kawakita et al)



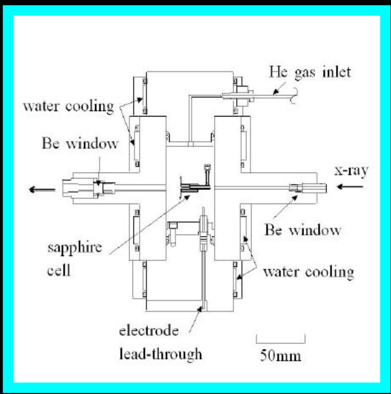
a-Se (Scopigno et al)



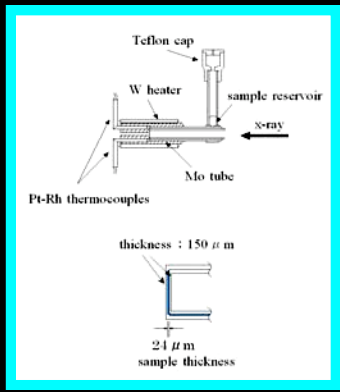
l-Si (Hosokawa, et al)

Metal to Insulator Transition in Liquid Mercury

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



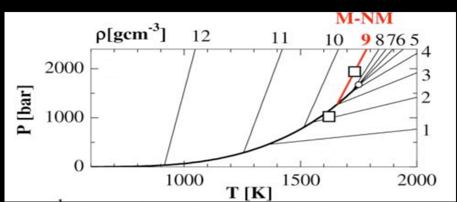
For Hg
~1500 C & ~ 1.5 kbar

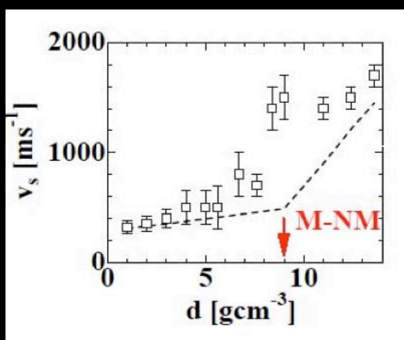


15 mm Be, 200 m He (STP), 0.15 mm Sapphire
~ 20 microns Hg

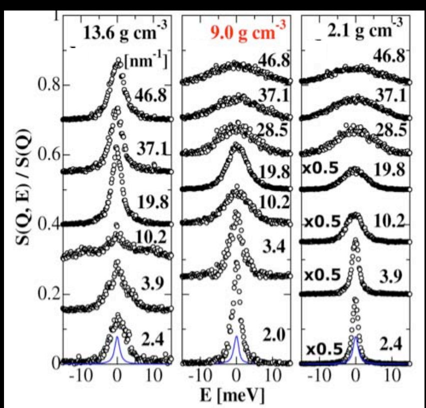
D. Ishikawa, M. Inui, K. Tamura, *et al.*

"Fast Sound" at the Metal-Non-Metal Transition





Ultrasonic Velocity

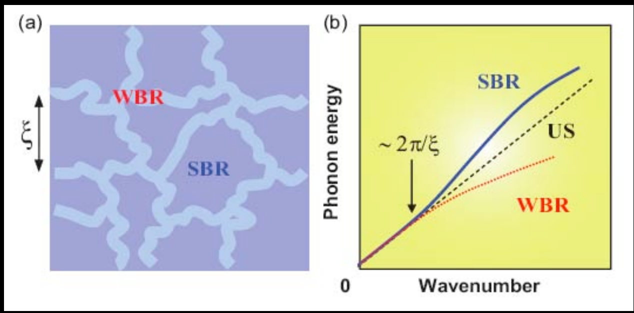


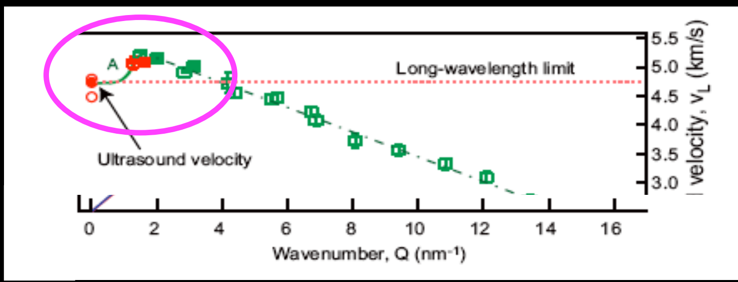
Suggests a change in the microscopic density fluctuations, possibly due to a modification of the pair potential…

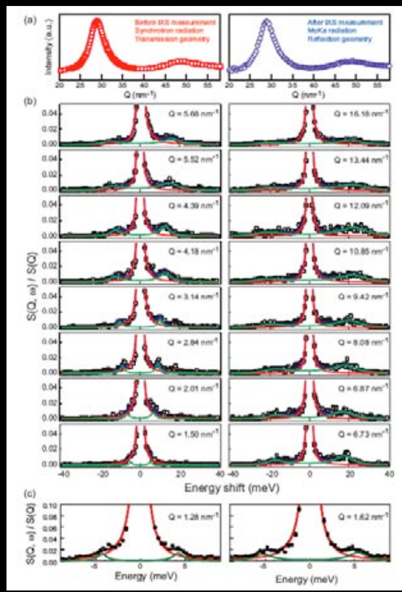
D. Ishikawa, *et al*, PRL 93 (2004) 97801

Elastic Inhomogeneity in a Glass

Ichitsubo, et al.







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

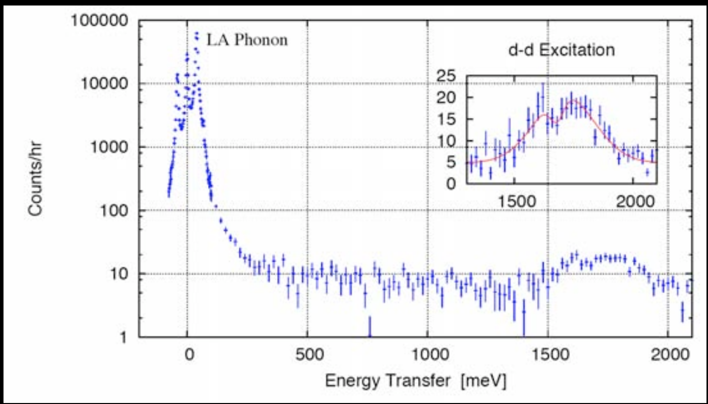
(More detailed analysis: possible failure of DHO Model)

AQRB @ AOFSRR Cheiron School 2008

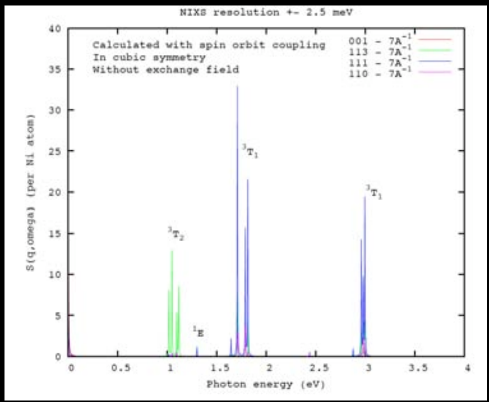
NRIXS

High Resolution Measurement

8 meV resolution at 15.8 keV, Si(888)
Temperature scan of mono over 2 eV or 60K



Baron, et al, April 2007 @ BL35XU
Detwinned Sample



Havercourt, Sawatzky, et al, May 07
NiO_6 cluster calculation
Note splitting of 1700 meV excitation.

NRIXS at Smaller (~eV) Energy Transfers

"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?

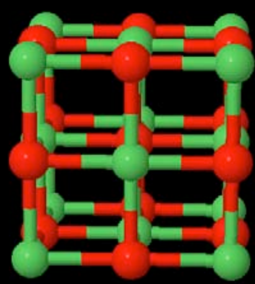
Resonant experiment -> non-resonant IXS experiment.

Non-Resonant is simpler and can have higher resolution

But badly flux limited

d-d Excitations in NiO

First something simple…



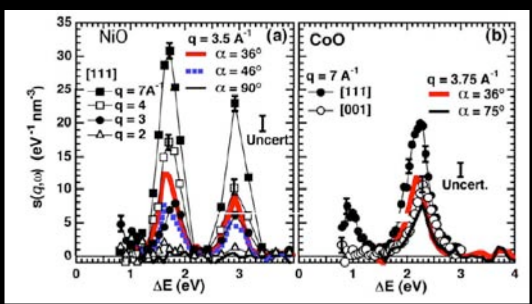
There exist well-defined excitations in the charge transfer gap of NiO

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

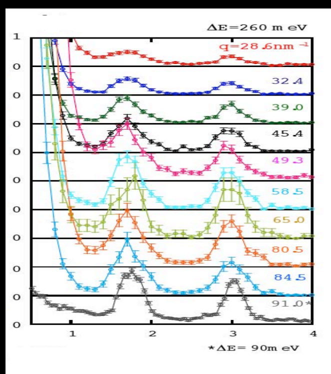
Long and Distinguished History

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

Non-Resonant IXS, ΔE~300 meV

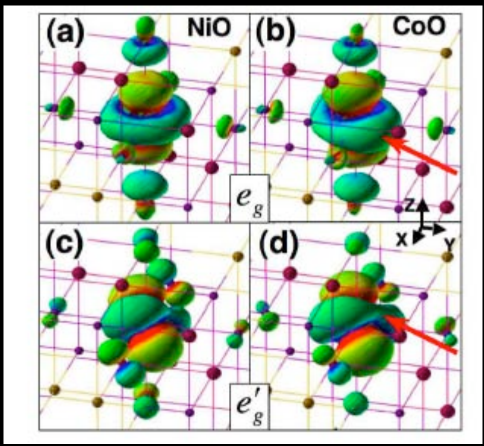


Larson, et al., PRL 99 (2007) 026401



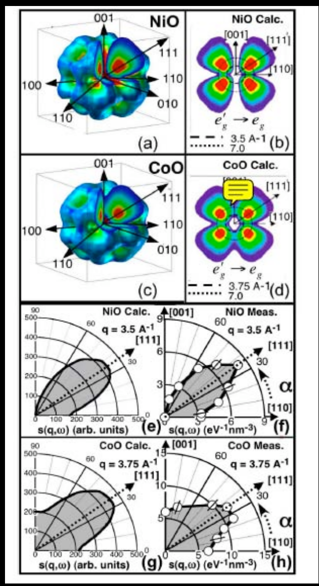
Cai, Hiraoka, et al, BL12XU Unpublished

Orientation Dependence

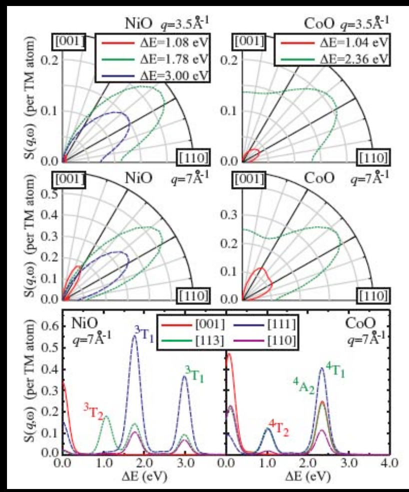


Orbitals

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



Scattered Intensity



Cluster calculations
Haverkort, et al PRL (2007)

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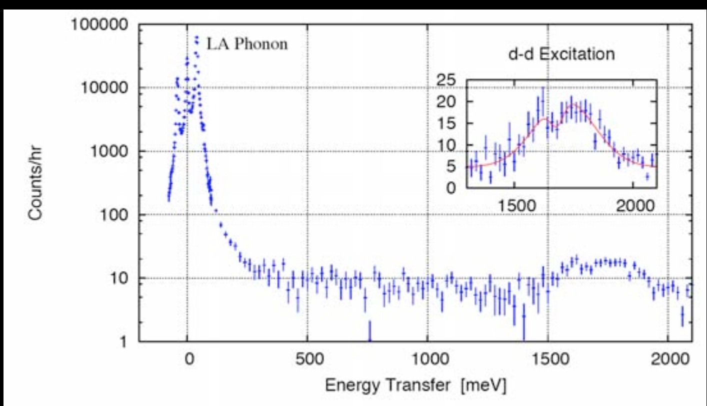

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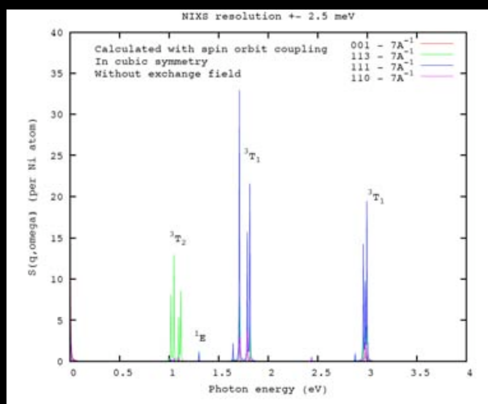

Havercourt, Sawatzky, et al, May 07
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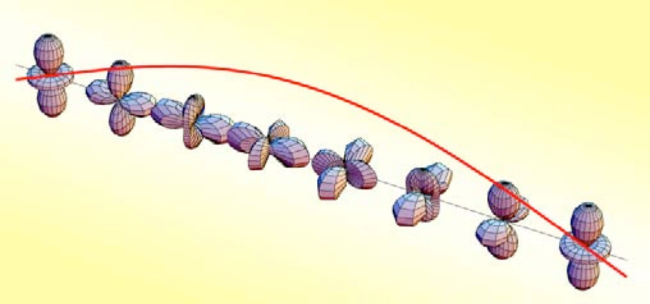
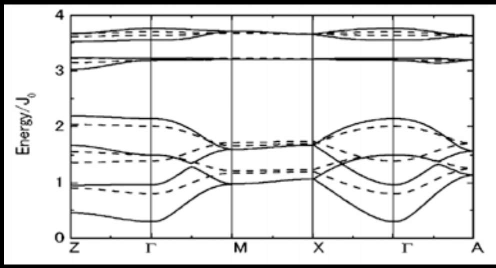
AQRB @ AOFSRR Cheiron School 2008

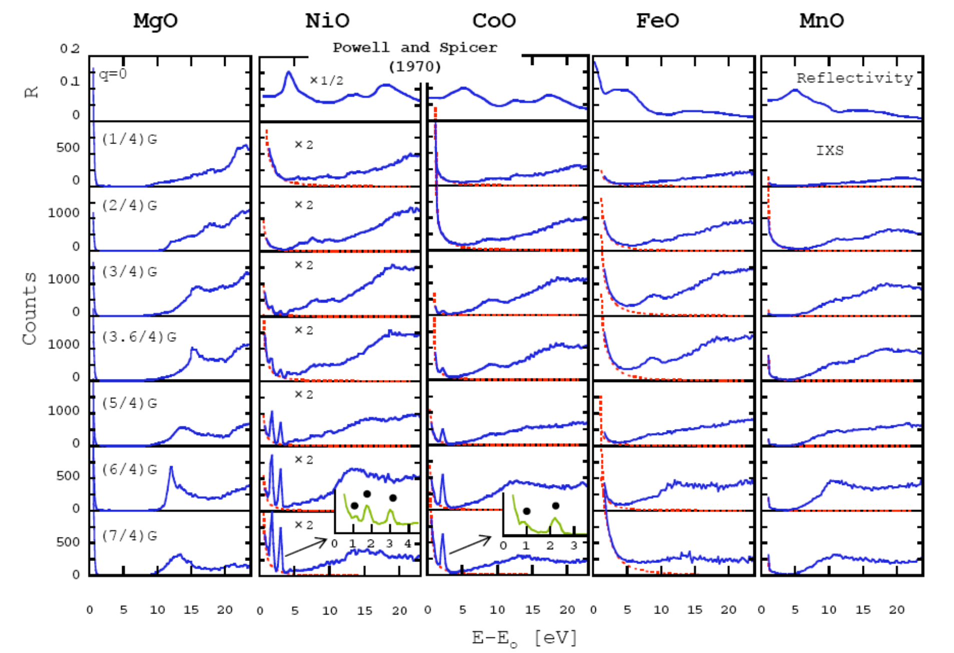
Towards a Dispersive Excitation?





Orbiton: Movie Maekawa, Dispersion Ishihara

Larger Energy Range



Hiraoka et al, Submitted

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]

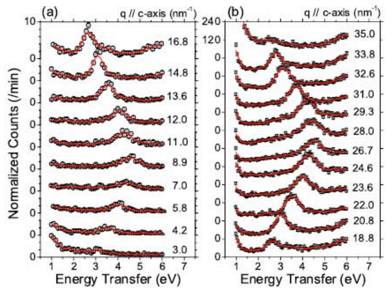


FIG. 1 (color online). NIXS spectra at various momentum transfers $q \parallel c^*$ axis showing the low-energy collective mode, where $q = 8.9\ \mathrm{nm}^{-1}$ corresponds to the first boundary of the extended BZ. The total energy resolution was 65 meV for (a), and 250 meV for (b).

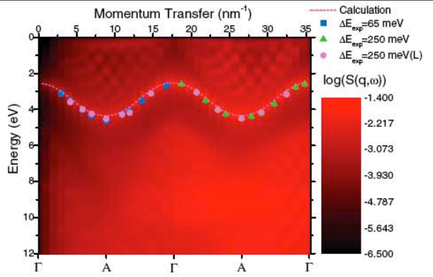


FIG. 2 (color). Theoretical $S(\mathbf{q}, \omega)$ calculated in the present work in false color log scale as a function of energy and momentum transfer showing the cosine energy dispersion of the low-energy collective mode. Filled squares and triangles mark the energy positions obtained from the NIXS 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…

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X-Ray Raman Scattering

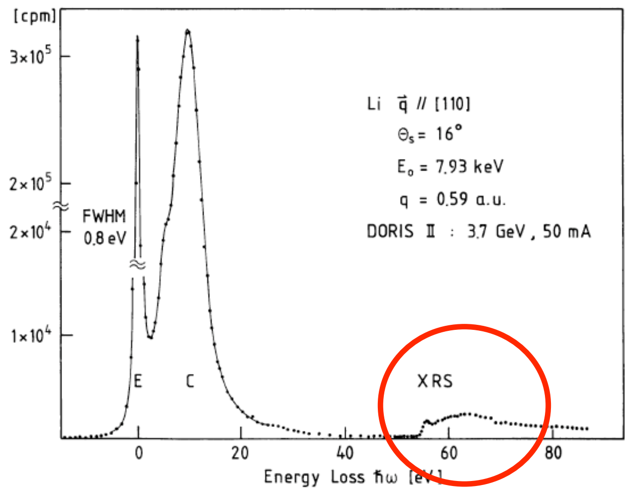


Fig. 1. Raw experimental data for Li single crystal obtained in the dispersion compensating case. The X-ray Raman spectrum (XRS) has an edge like onset at the binding energy of the Li *K*-electron of about 55 eV. E and C denote the quasielastically scattered Rayleigh line and the $S(q, \omega)$ profile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

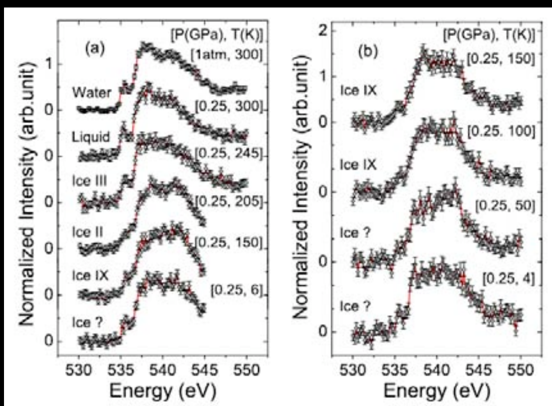
Diamond:

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.



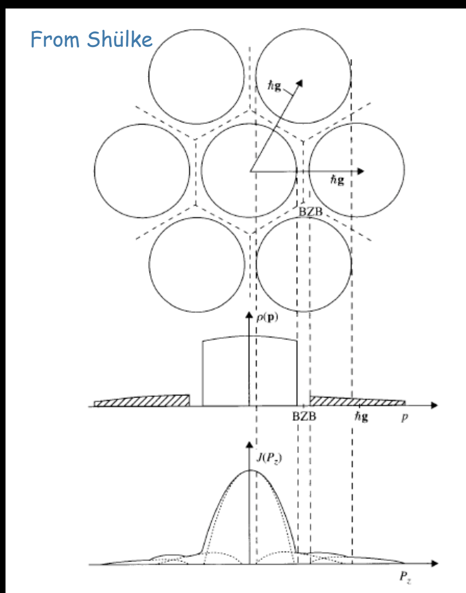
Ordering of Hydrogen Bonds in High-Pressure Low-Temperature H_2O

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]

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...

Three-Dimensional Momentum Density Reconstruction

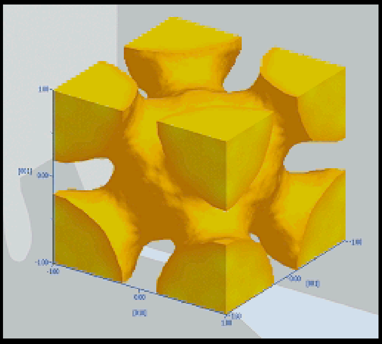
Three-dimensional momentum density, n(p), can be reconstructed from ~10 Compton profiles.

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

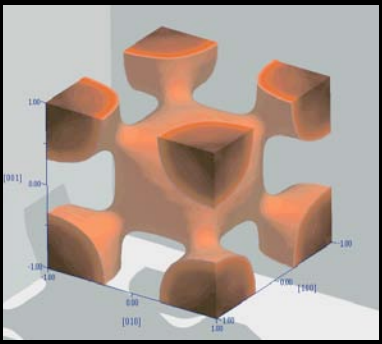
Reconstruction:
- Direct Fourier Method
- Fourier-Bessel Method
- Cormack Method
- Maximum Entropy Method

Momentum density, n(p)

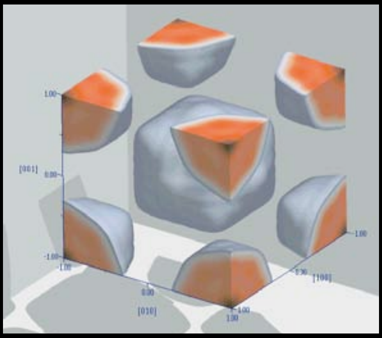
Fermi surfaces of Cu and Cu alloys



Cu-15.8at%Al



Cu



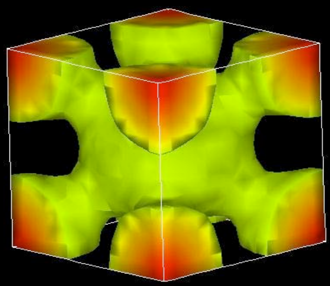
Cu-27.5at%Pd

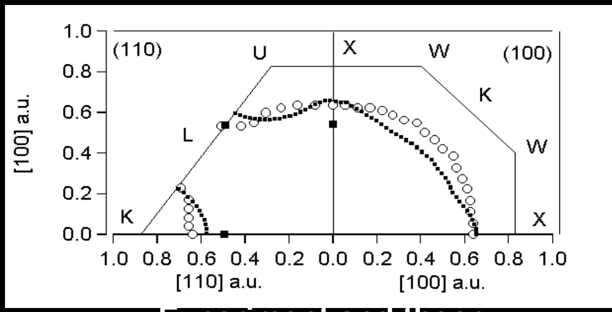
Determined by Compton scattering at KEK-AR

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

Fermi Surface of $PdH_{0.84}$

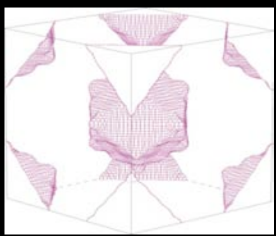
Exp.



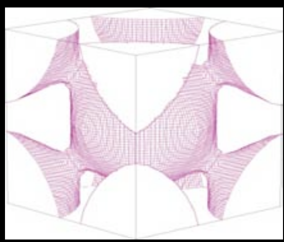


Experiment and theory

The Fermi surface is similar to that of Ag,
but the size of neck is about 2 times larger.

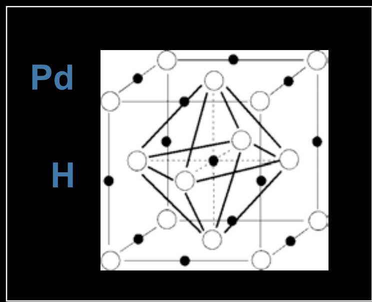


fcc-Pd



fcc-Ag

Theory



S. Mizusaki *et al.* Phys. Rev. B 73(2006)113101

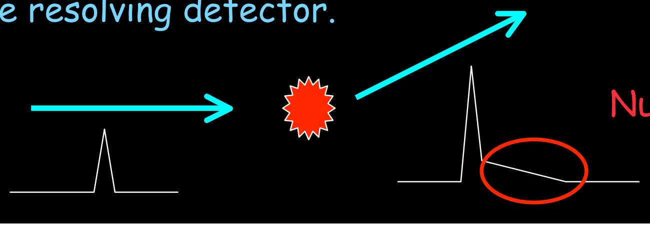
Nuclear Inelastic Scattering

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.

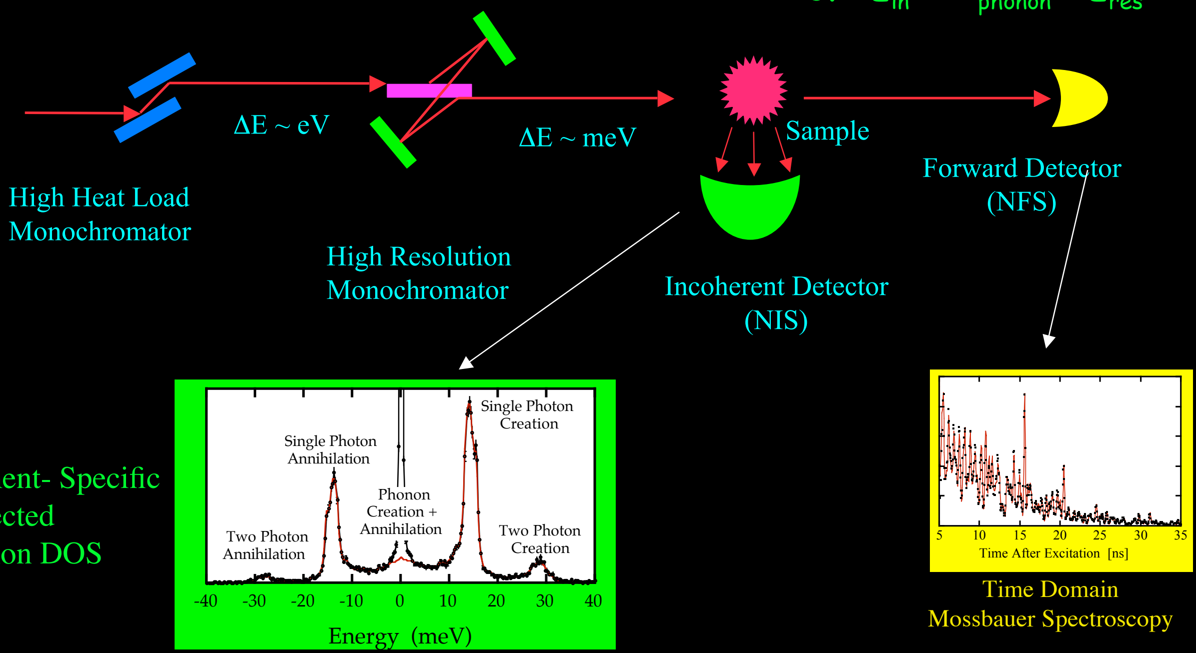


Nuclear Scattering

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. $E_{in} - E_{phonon} = E_{res}$



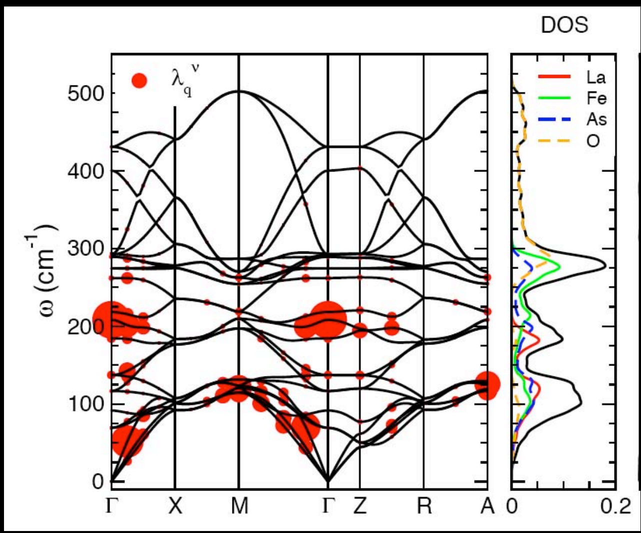
Element- Specific Projected Phonon DOS

Time Domain Mossbauer Spectroscopy

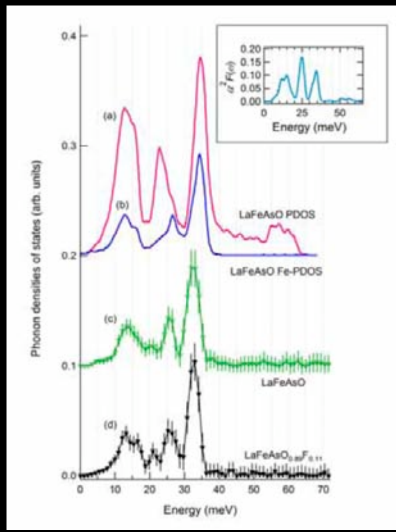
NIS Gives the Partial Projected DOS

Example of the Fe-As Superconductors

Partial= Element Specific   Projected= Weakly Directional $I \sim \varepsilon \bullet \mathbf{k}_l$



Calculation: Boeri et al



Measurement: Higashitaniguchi et al

NIS: Good and Bad

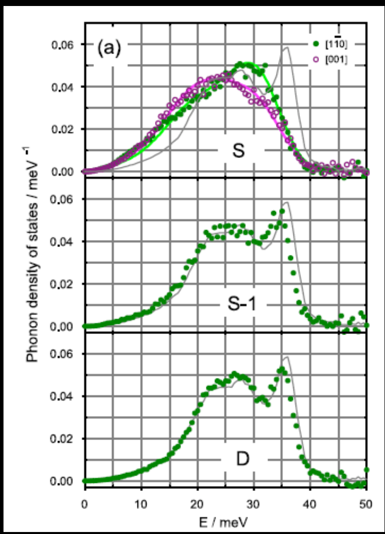
Important things to note:

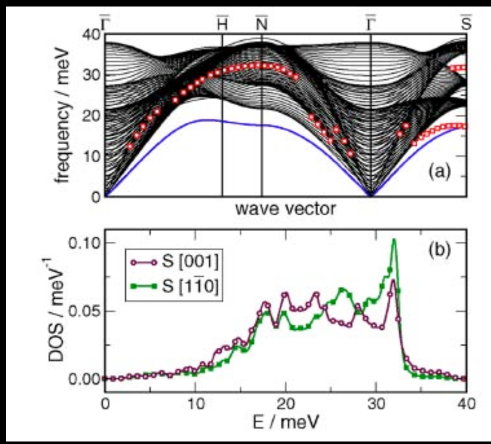
1. Element and isotope selective.
2. Gives Projected Density of states NOT Dispersion
   (But it does this nearly perfectly)

NIS Example: Surface DOS

Slezak et al PRL 99 (2007) 066103

^{57}Fe monolayers near the surface of ^{56}Fe





Note projection!

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]

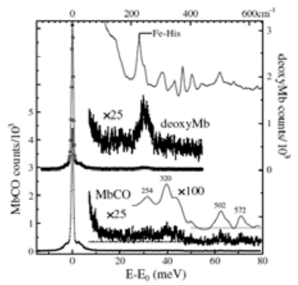


FIG. 1. NRVS data recorded from frozen solutions of ^{57}Fe-enriched MbCO (solid circles) at 110 ± 5 K and deoxyMb (open circles) at 35–70 K. Temperatures were estimated from the relative intensity of phonon creation and annihilation peaks. The MbCO (deoxyMb) spectrum is the sum of 20(16) independent 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.

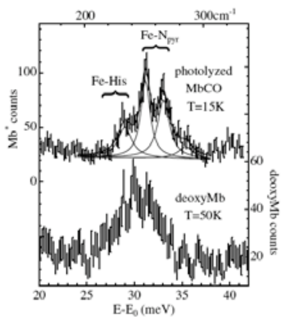


FIG. 2. Comparison of the 250 cm^{-1} mode clusters of deoxy-Mb and Mb*. The Mb* data were recorded under continuous illumination. The temperature of a sensor mounted in the sapphire sample block was 15 K.

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.