Investigating Dynamics via meV-Resolution Inelastic X-Ray Scattering

Edited Version

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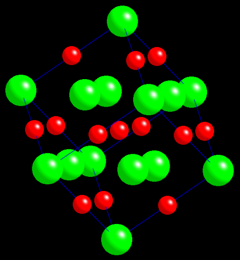
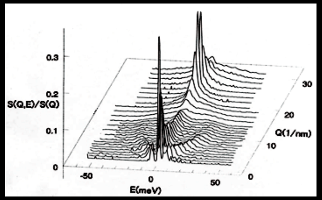
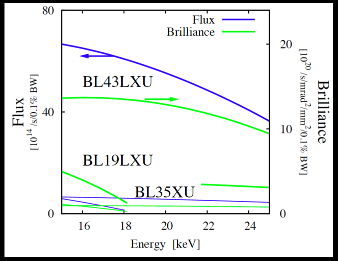
APSE2010 4th Yamada Symposium
16 June 2010, Harima, Japan







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Partially Complete

Outline

Introduction

Disordered Materials:
Increasing Detail at Low Q
-> TA in Liquid Ga, LO in Liquid NaI

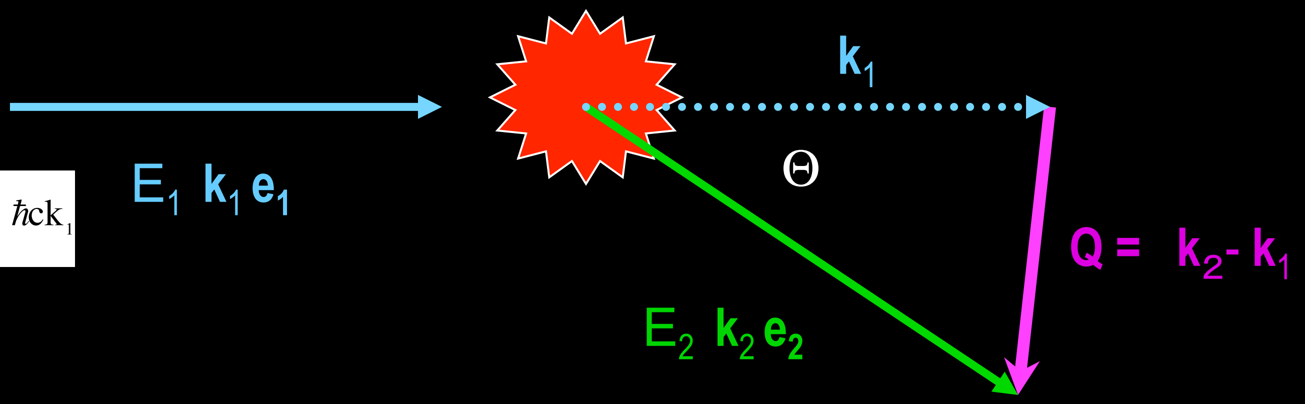
Crystalline Materials:
Phonons as a very sensitive probe of atomic interactions
-> Superconducting Pnictides, Antiferromagnetic NiO

A Move Toward Electronic Dynamics

The RIKEN Quantum NanoDynamics Beamline

X-Ray Scattering Diagram

(Non-Resonant)



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

Two Main Quantities:

Energy Transfer

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

Scale: 1 to >100 meV
or 1 to <0.01 ps

Momentum Transfer

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

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

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

Scale: 1 to 100 nm^{-1}
or 50 to ~0.5 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)

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

Thomson Scattering

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

Dynamic Structure Factor
"The Science"

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

Density-Density Correlation

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

Generalized Response Thy

$$S(\mathbf{Q},\omega) = \sum_{\lambda,\lambda'} p_\lambda \left| \langle\lambda'| \sum_{\substack{electrons\\ j}} e^{i\mathbf{Q}\bullet\mathbf{r}_j} |\lambda\rangle \right|^2 \delta\left(E_{\lambda}' - E_\lambda - \hbar\omega\right) = \frac{1}{\pi}\frac{1}{1-e^{-\hbar\omega/k_BT}} \mathrm{Im}\left\{-\chi(\mathbf{Q},\omega)\right\} = \frac{1}{\pi}\frac{1}{1-e^{-\hbar\omega/k_BT}}\frac{1}{v(\mathbf{Q})} \mathrm{Im}\left\{-\varepsilon^{-1}(\mathbf{Q},\omega)\right\}$$

One Phonon

$$S(\mathbf{Q},\omega)_{1p} = N \sum_{\substack{\mathbf{q}\\ 1st\\ Zone}} \sum_{\substack{j\\ 3rModes}} \frac{1}{\omega_{\mathbf{q}j}} \left| \sum_{\substack{\mathbf{d}\\ Atoms\\ /Cell}} \frac{f_d(\mathbf{Q})e^{-W_\mathbf{d}} e^{-i\mathbf{q}\bullet\mathbf{d}}}{\sqrt{2M_\mathbf{d}}} \mathbf{Q}\bullet\mathbf{e}_{\mathbf{q}j\mathbf{d}} \right|^2 \left\{ \begin{array}{l} \langle n_{\mathbf{q}j}+1\rangle\ \delta_{\mathbf{Q}-\mathbf{q},\tau}\delta\left(\omega-\omega_{\mathbf{q}j}\right) \\ +\ \langle n_{\mathbf{q}j}\rangle\ \delta_{\mathbf{Q}+\mathbf{q},\tau}\delta\left(\omega+\omega_{\mathbf{q}j}\right) \end{array} \right\}$$

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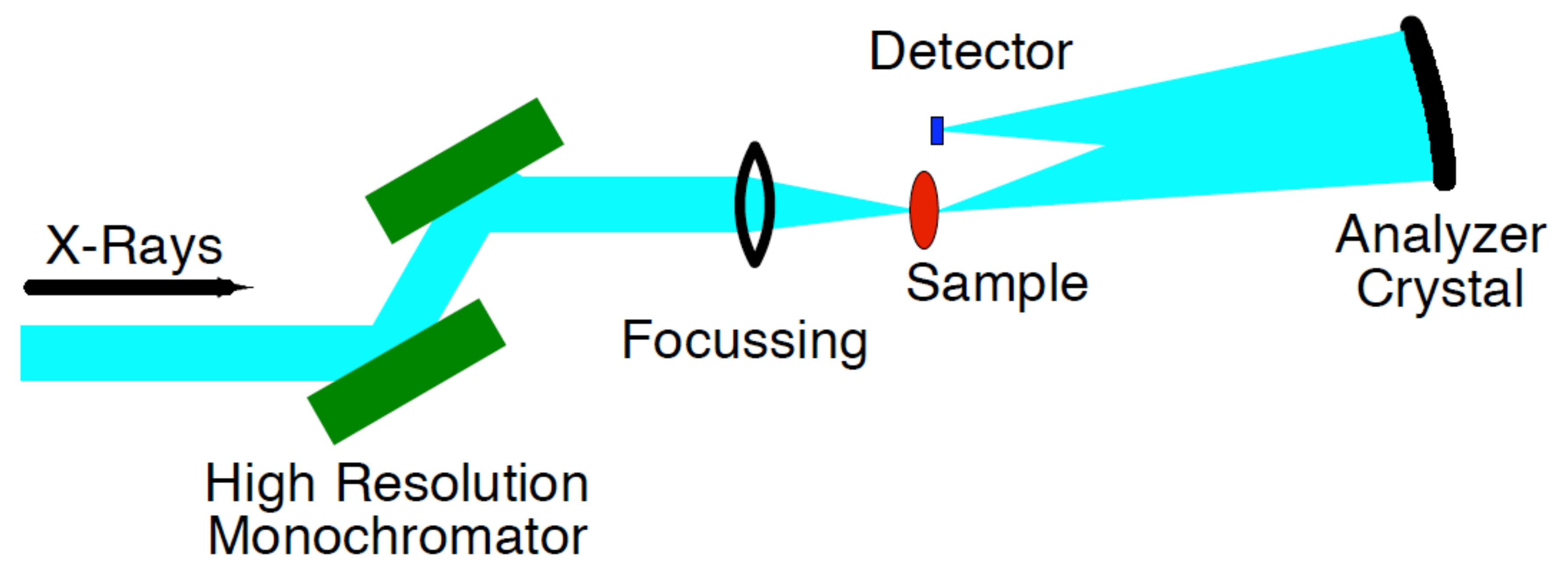
Generic Triple Axis Spectrometer

(IXS and INS)



For x-rays, resolution, ~ 1meV / 20 keV ~ 5×10^{-8}, is severe.

Analyzers crystals with large angular acceptance are the limiting optic

IXS vs INS:	Smaller Samples (to 0.01 mm) No Kinematic Constraints Smaller Backgrounds

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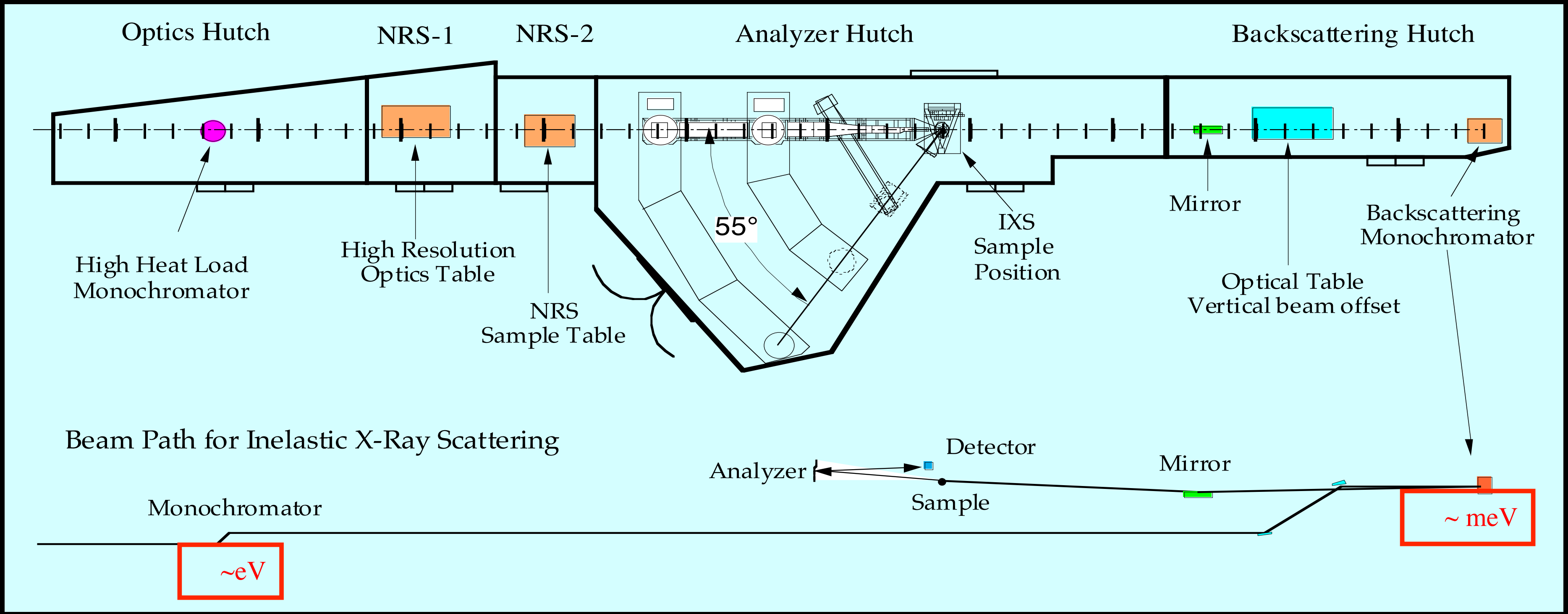
SPring-8 BL35XU



Energy (keV)	Si Order	Resolution (meV)	Rel. Flux
15.816	**(8 8 8)**	**6**	**10**
17.794	**(9 9 9)**	**3**	**3**
21.747	**(11 11 11)**	**1.5**	**1**
25.702	(13 13 13)	1.0	0.2

Experiments: 3 to 8 Days
Scan Times: 1 to 72 hours

Beam Spot on Sample (Bent Cylindrical Mirror): 50 μm V x 70 μm H (FWHM)
KB Setup: ϕ~15 microns

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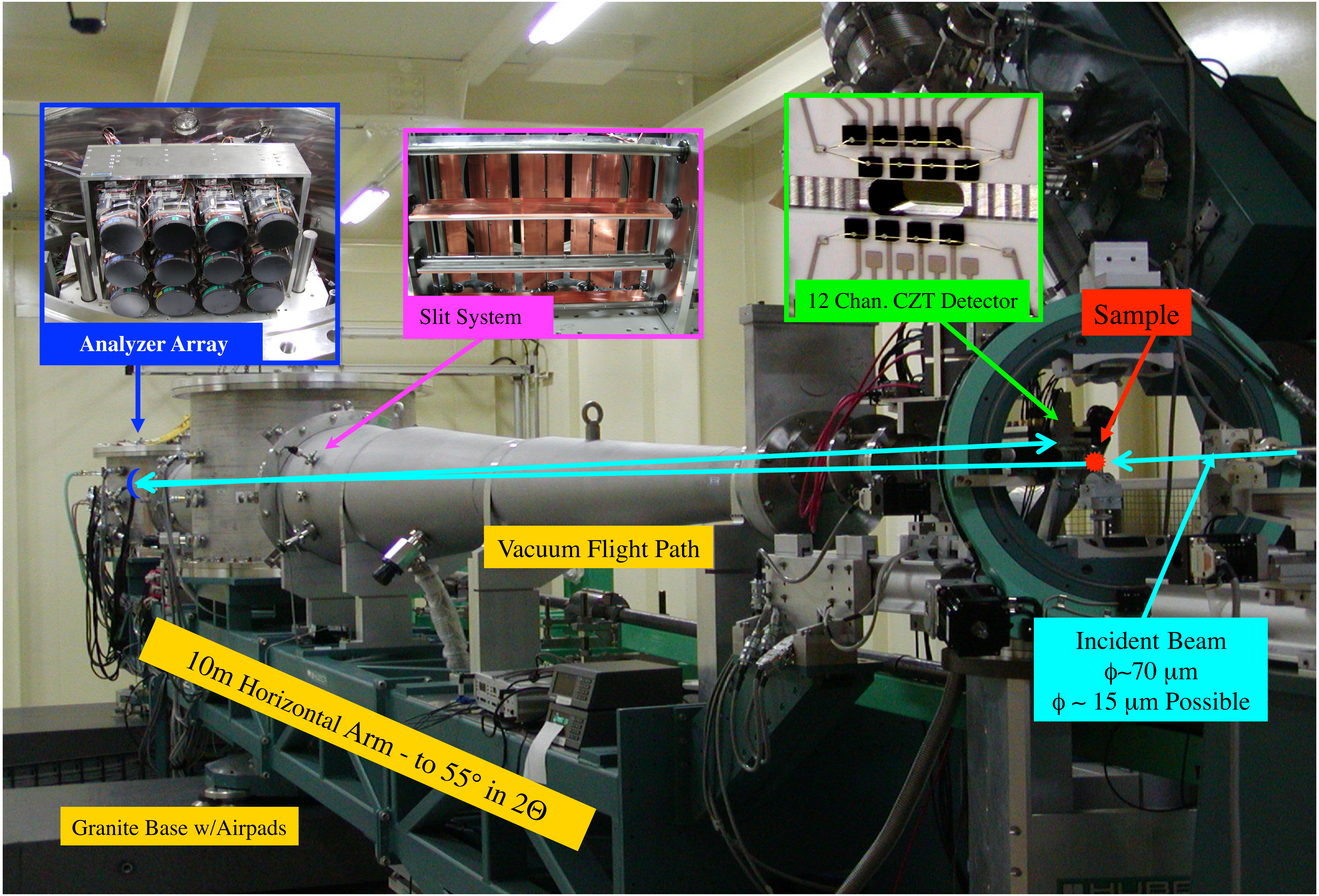
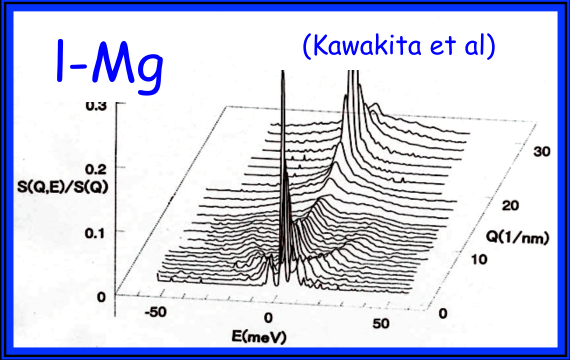

Analyzer Array
Slit System
12 Chan. CZT Detector
Sample
Vacuum Flight Path
10m Horizontal Arm - to 55° in 2Θ
Granite Base w/Airpads
Incident Beam
ϕ~70 µm
ϕ ~ 15 µm Possible

Disordered Materials

Liquids & Glasses

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

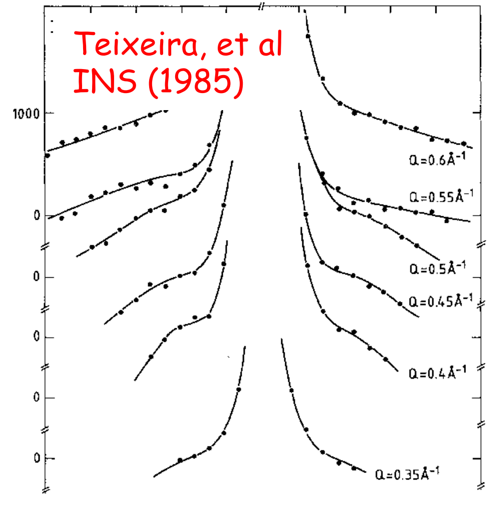
- Large energy transfer at small momentum transfer
- -> excellent access to mesoscopic length scales
  - Q<10 nm^{-1} (d from 5 to 50 Å)



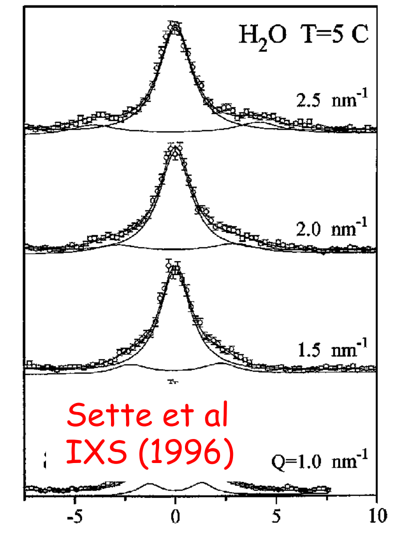
l-Mg

(Kawakita et al)

Water

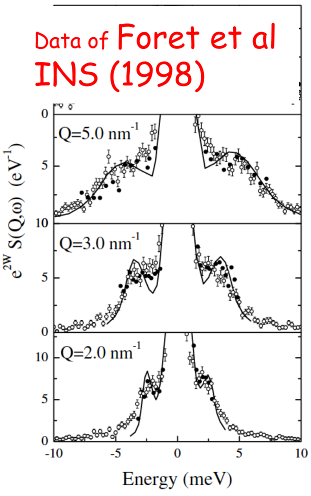


Teixeira, et al INS (1985)

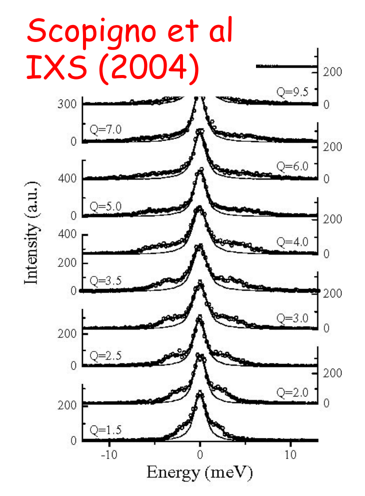


Sette et al IXS (1996)

Glassy-Se



Data of Foret et al INS (1998)

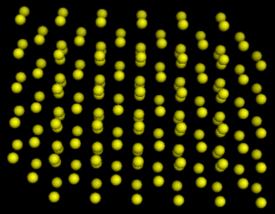


Scopigno et al IXS (2004)

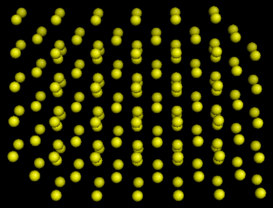
Investigating Finer Details…

Beyond the Quasi-Elastic + “LA” model

Pressure Wave

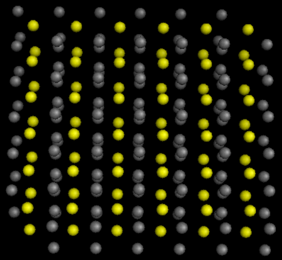


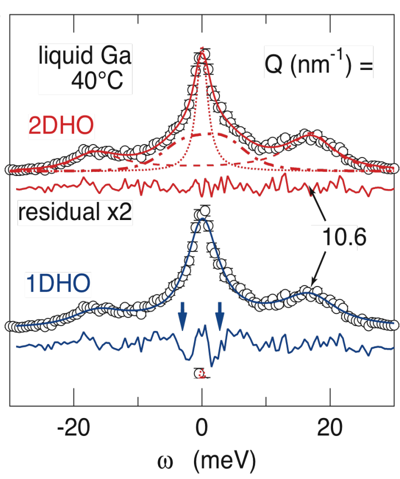
Shear Wave

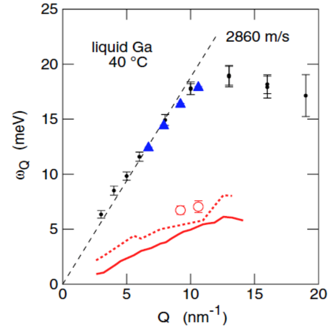


Animations for a crystal

Optic mode
(at low Q!)







Weak, but significant.
Good agreement with MD

S. Hosokawa

Partially Complete

Phonons via IXS

Phonon spectra & dispersion are a sensitive probe of inter-atomic interactions.
The more so in correlated materials where they are influenced
by interaction with other systems
(electron phonon coupling, magneto-elastic coupling…)

The X-Ray Advantage

Small Samples (micro-grams).
Nearly No Background.
Large energy transfer with good energy resolution.
Simple & good momentum resolution (up to rate).

Where X-Rays Are Less Good

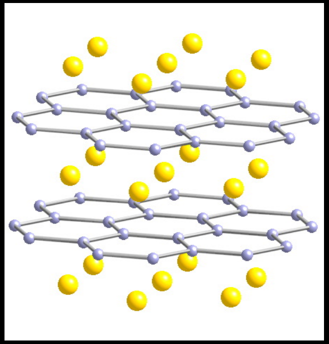
Light-Atom modes in heavy materials (absorption).
Sub-meV resolution is difficult.
Very few instruments (5) & limited beam time.

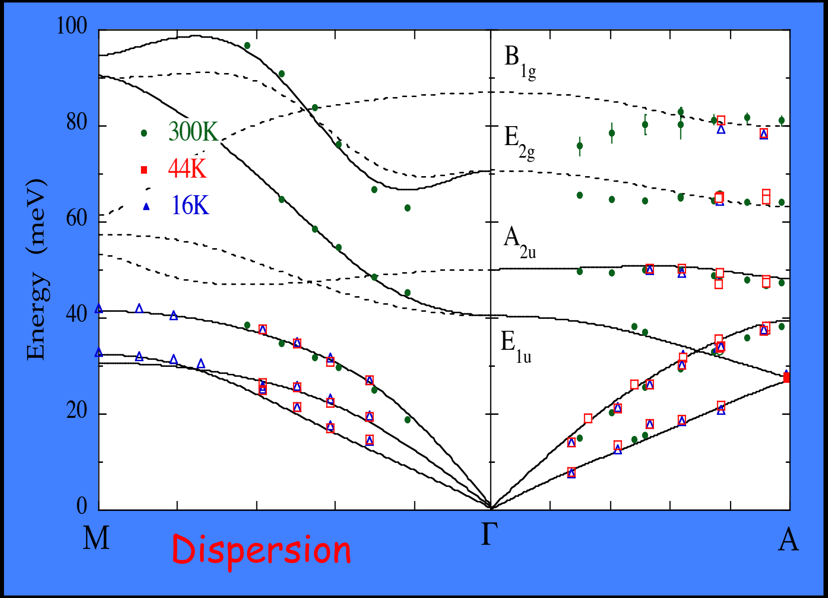
Note: phonons are complex compared to magnetism
Phonons: All atoms in a cell contribute
Magnons: Typically only one or two magnetic atoms/cell

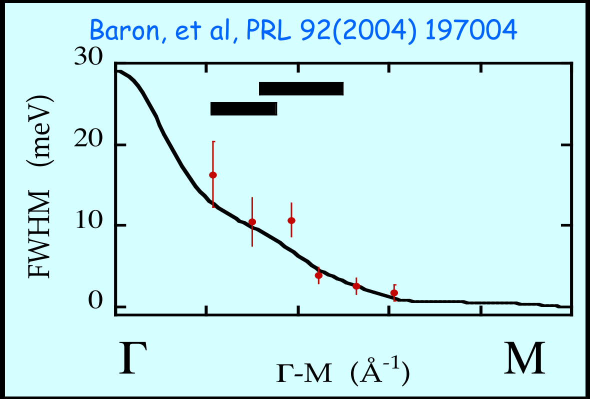
Examples of Conventional Materials

MgB_2: Strong electron-phonon to a specific phonon mode drives the high T_c

MgB_2
T_c = 39K
Akimitsu et al



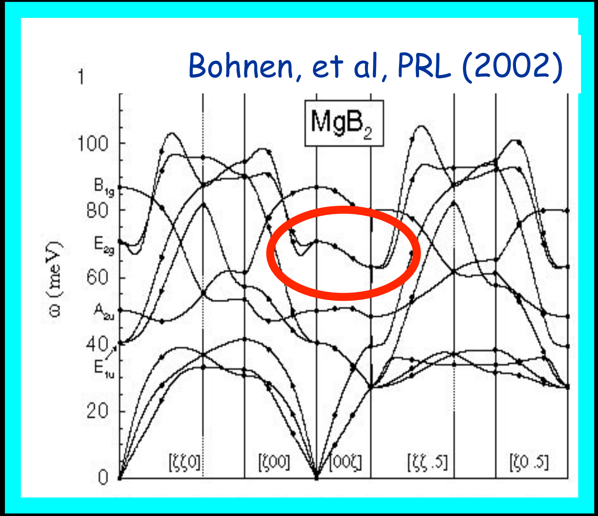


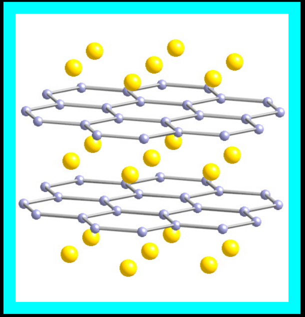

Baron, et al, PRL 92(2004) 197004

E_{2g} Linewidth

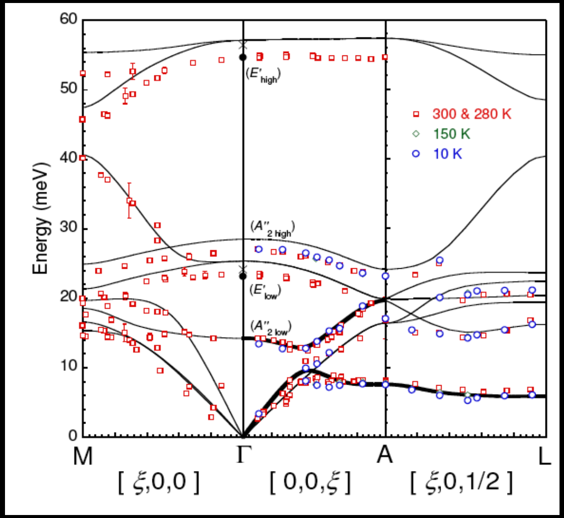
Good Agreement With LDA – Dispersion & Linewidth
-> Consistent picture of phonon mediated superconductivity

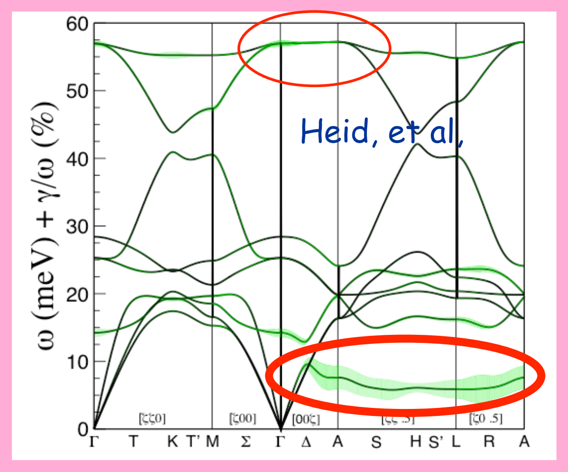
CaAlSi: Soft Mode Driven Superconductor


Bohnen, et al, PRL (2002)

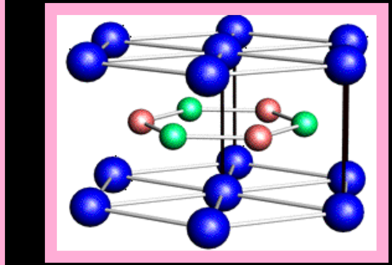


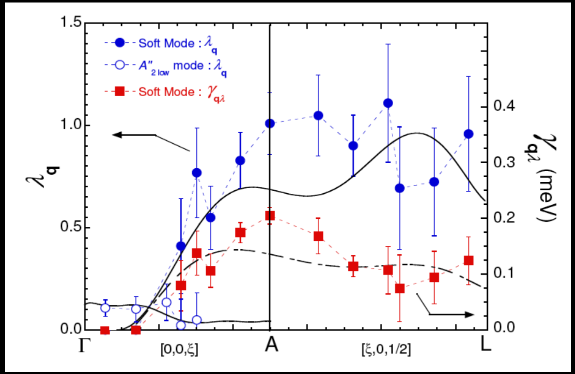
MgB$_2$




Heid, et al,

1H - CaAlSi



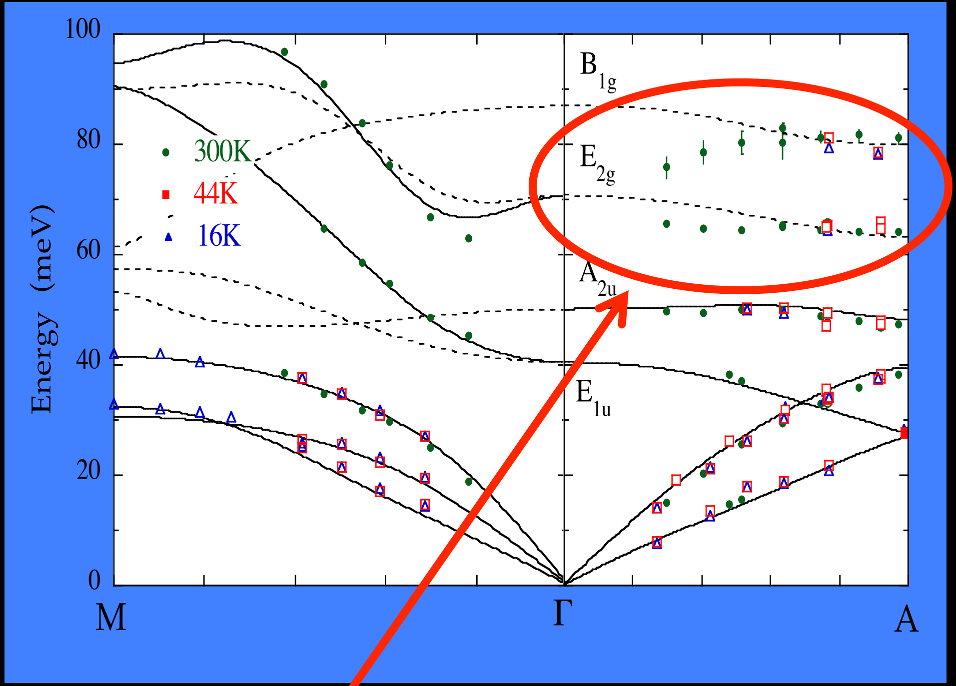


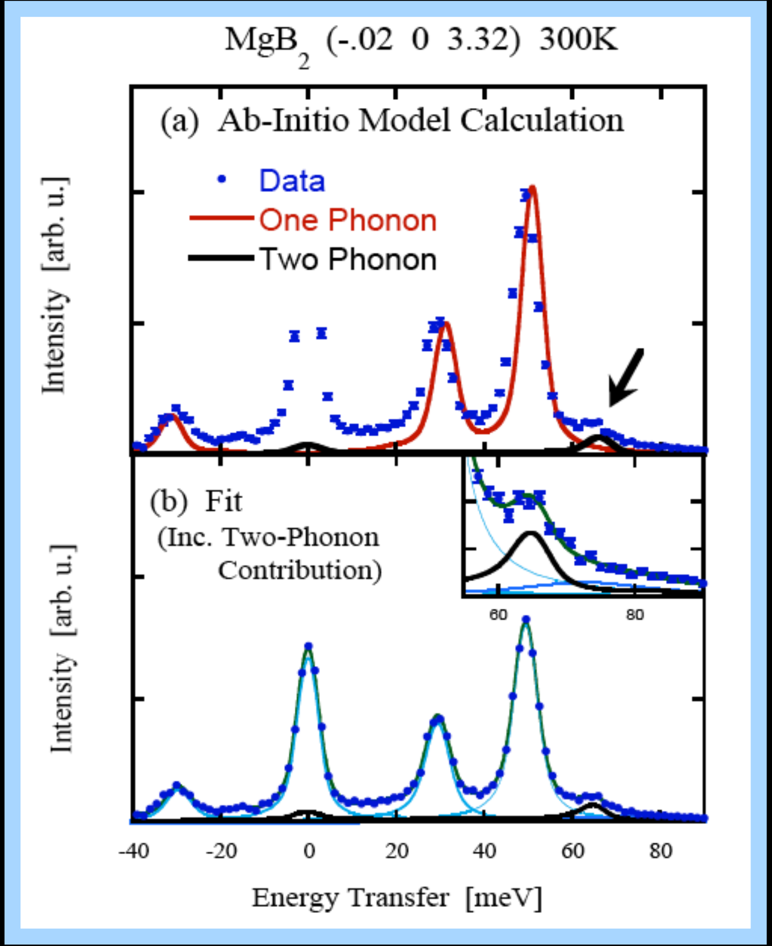
Kuroiwa et al, PRB (R), 2008

Proximity to a Structural Phase Transition Leads to a Soft Mode & Higher Tc

Two-Phonon Contribution

Baron, et al, PRB (2007)





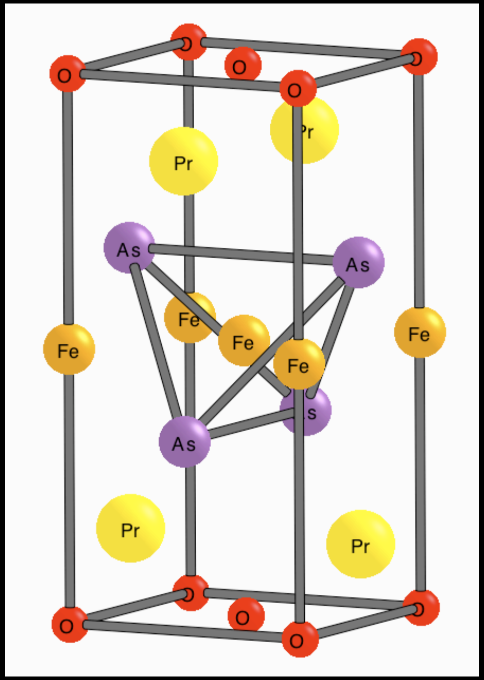
Modes that, by symmetry, should not be observed!

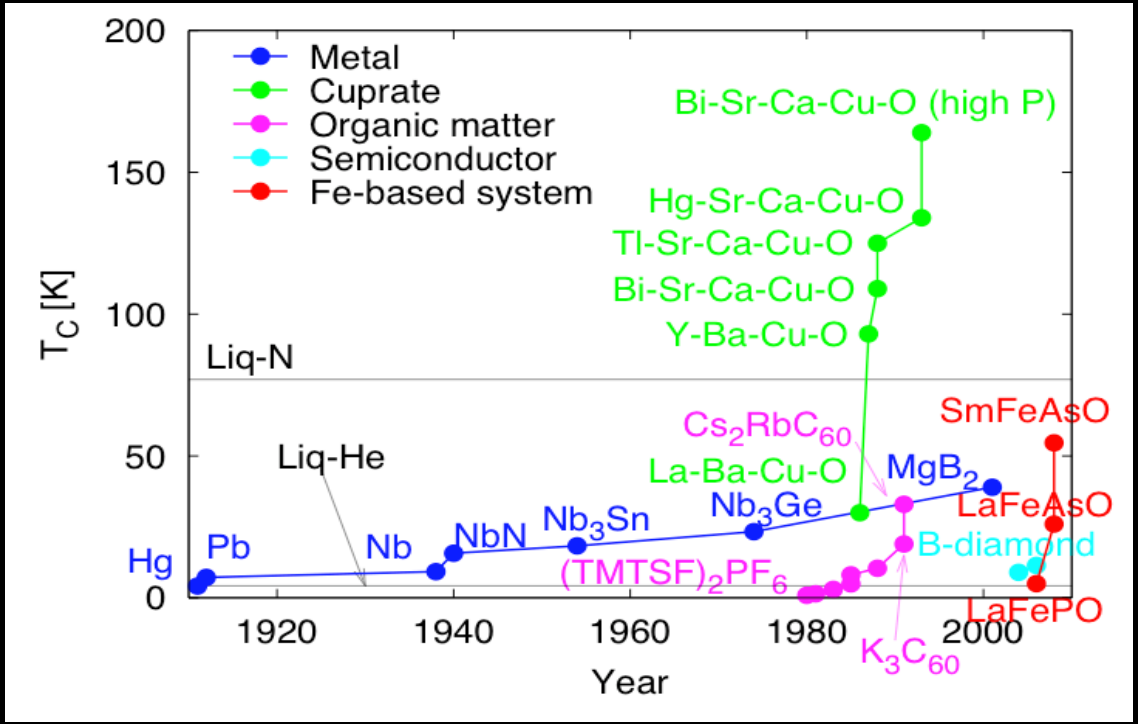
(at the selected momentum transfers
c-axis geometry, Q||c*)

The IXS spectra are reliable for rather subtle features…

The Iron-Pnictide Superconductors

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





Fe Planes with Tetrahedral As

Parent (non SC) Shows Mag. Order & Tetragonal-> Orthorhombic Transition at ~140 K

Phonons In the Iron Pnictides

Phonon response, in itself, is remarkably plain:

NO very large line-widths (typically < 2 meV)

NO obvious anomalies (yet).

NO asymmetric Raman lines

But also: Rather poor agreement with calculation

Iron Isotope Effect:

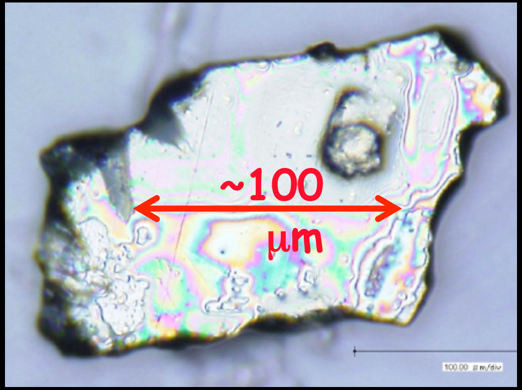
Liu et al. (Nature): BCS Effect on Tc & Resistive Transitions (1111, 122)
Shirage et al. (PRL): Small and negative effect in 122

Samples

Single Crystals of $PrFeAsO_{1-y}$

Superconductor: T_c (onset) ~ 45 K

Parent: Resistivity Change at ~145 K

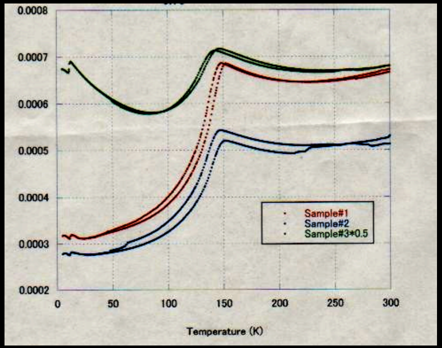


$PrFeAsO_{1-y}$
20 um Thick
Transverse: ~0.1 to ~0.5 mm

Typically “reasonable” crystal quality
~1 degree mosaic

Ishikado, Kito, & Eisaki
(at AIST)

Measurements
- Wide variety of Q and T<=300K
- Many small changes with doping & T



First question: what is important?
-> Compare with calculation…

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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
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Iron Pnictides: WIP

Still basic questions.

Over-All:

Phonons agree better with “pure” magnetic calculations

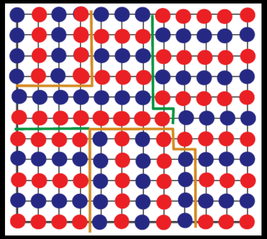
But these seem to over-estimate effects, even in Parent

If allow modifications, IP soft model also OK

But: seems like there is an ingredient missing

One possibility: Fluctuating magnetism

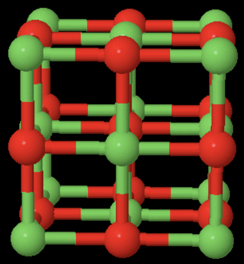
Upper limit for lifetime:
~ ns from Mossbauer
(Kitao, et al, JPSJ)



Model of anti-phase domains
Mazin&Johannes, Nat. Phys.

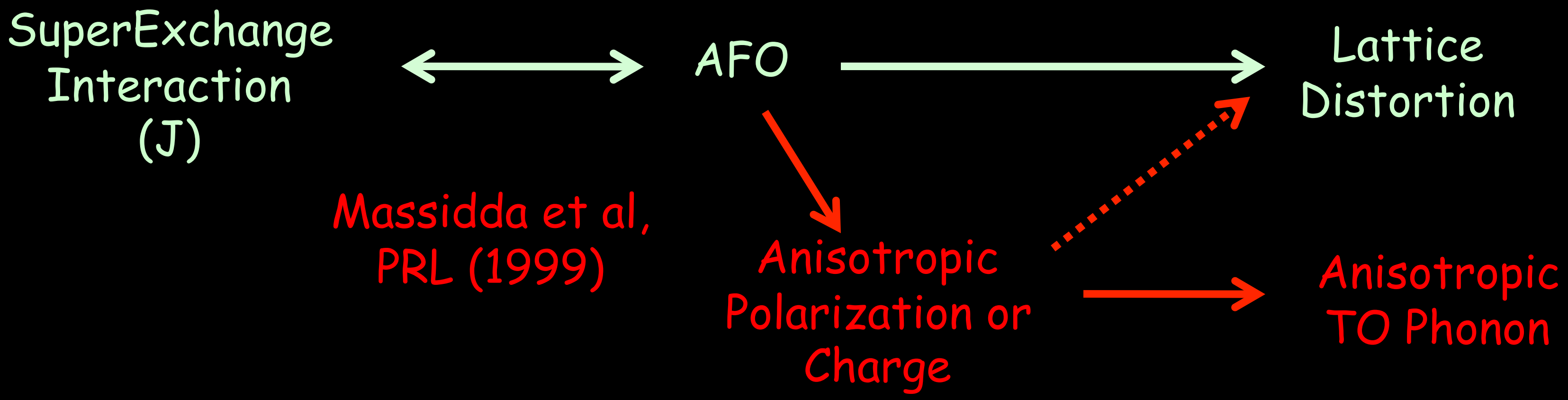
Magneto-Elastic Coupling & Anisotropic Polarizability

(Polarization)



Classic cubic transition metal oxides (TMO) (MnO, NiO) show trigonal (few%) distortion when anitiferromagnetic (AFO) order appears below T_N (MnO: 116K, NiO:525K)

AFO: Ferromagneteic Planes Perpendicular to [111] Ordering Direction



SuperExchange Interaction (J)

AFO

Lattice Distortion

Massidda et al, PRL (1999)

Anisotropic Polarization or Charge

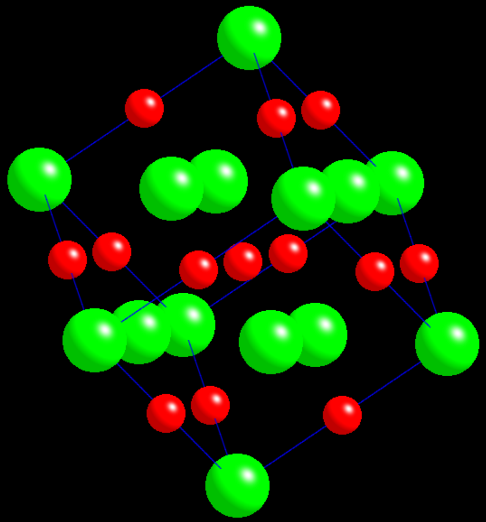
Anisotropic TO Phonon

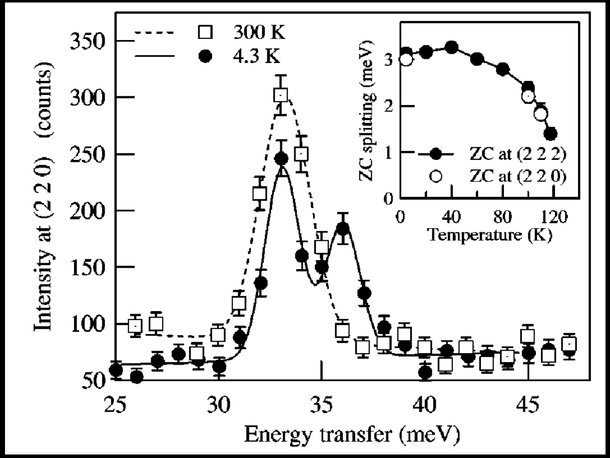
Argument based on “Modern Thy. of Ferroelectrics” (Berry phase calc)

Resta, 1992, King-Smith & Vanderbilt 1993

INS Results from MnO & NiO

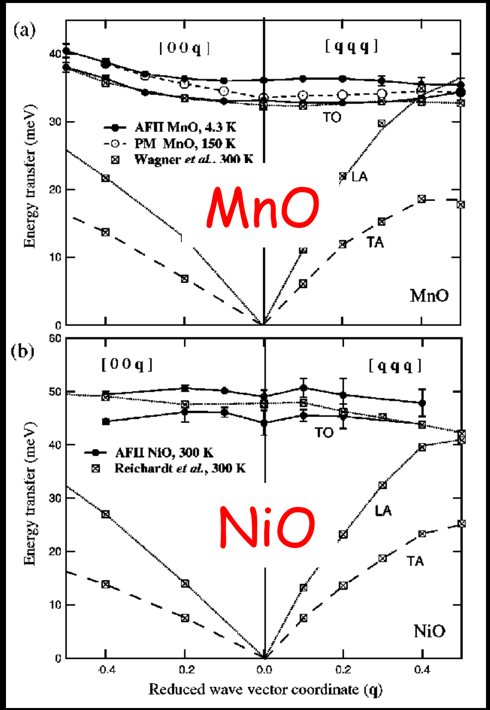
E. Chung et al., PRB (2003)





Twinned MnO:

$$\boxed{E_{ll} - E_{\perp} \sim 3.5 \;\; meV}$$



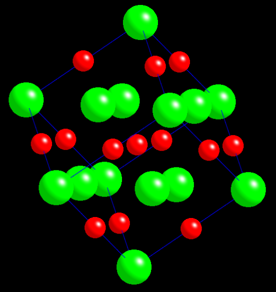
First IXS Results:
No obvious splitting in NiO (1.5 meV Resolution)

NiO: $\boxed{E_{ll} - E_{\perp} \sim 5 \;\; meV}$

Raw Data not shown

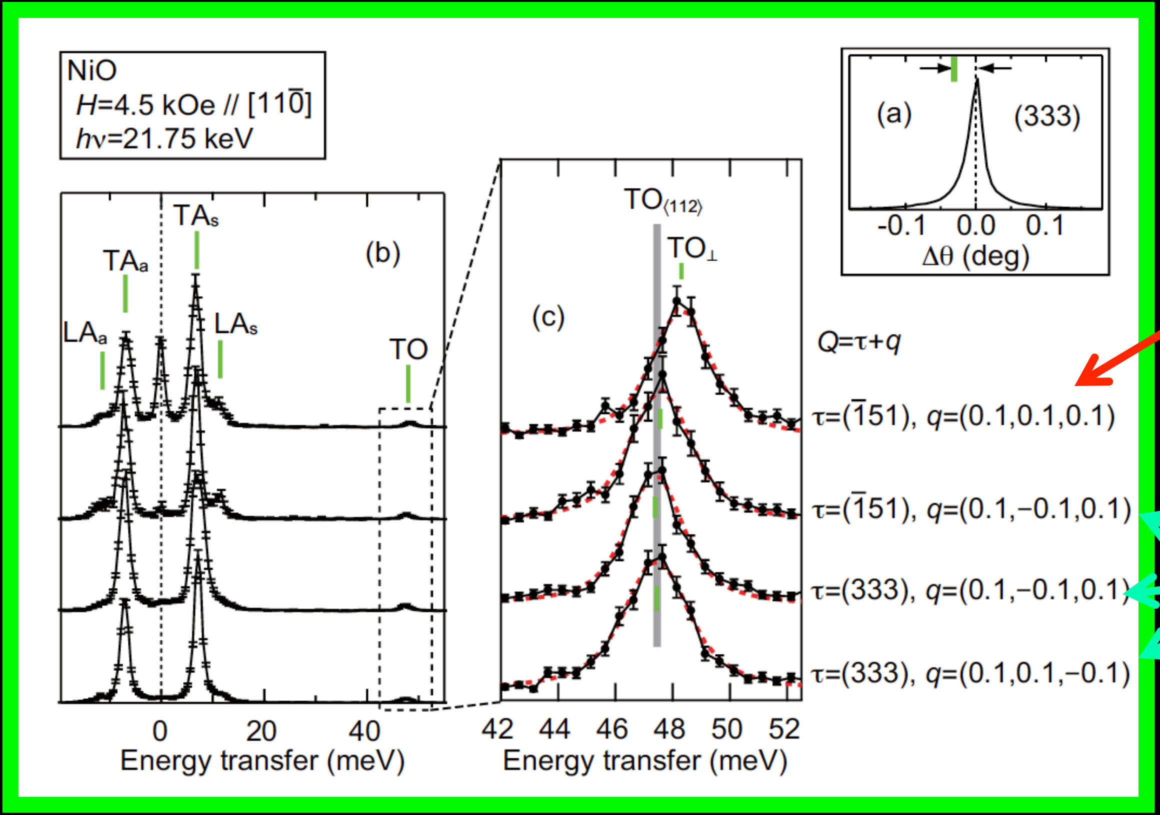
LSDA+U	MnO	NiO
Luo et al (2007)	3.8	-1.8
Park & Choi (2009)	2.6	-1.8

Careful Experiment



De-Twinned NiO Crystal

Trigonal [111] Axis selected from annealing & pressure
Magnetic Orientation from weak applied field



Selection Rule
-> Perp. Poln.

$\boxed{E_{\perp}}$

Selection & Calc
-> Mostly ll Poln.

$\boxed{E_{ll}}$

$$E_{ll} - E_{\perp} \sim -1\ meV$$

Uchiyama et al, 2010

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Calculation Compared to Experiment

LSDA+U	MnO	NiO
Luo et al (2007)	3.8	-1.8
Park & Choi (2009)	2.6	-1.8

Experiment	MnO	NiO
Chung et al (INS)	3.5	~5.0
Uchiyama et al (IXS)	**~3.5**	**-1.0 (RT)**

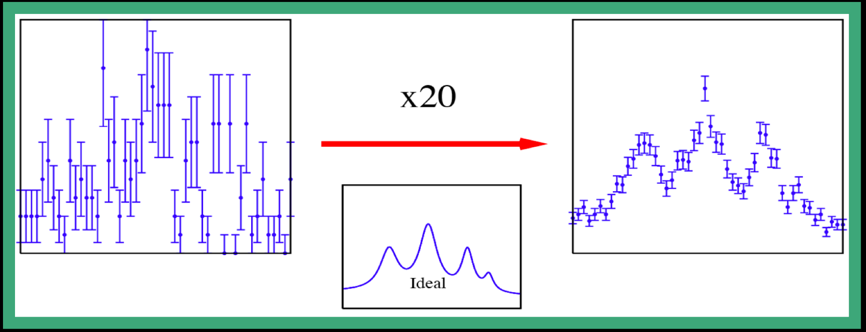
-> Anisotropic polarizability is reasonable

Also helps reconcile measured/calculated exchange interactions with observed lattice contraction

RIKEN
Quantum NanoDynamics Beamline
(BL43LXU)

Atomic Dynamics: Many experiments now flux limited.

Phonons in complex materials
Extreme environments (HT, HP liquids)
High pressure DAC work (Geology)
Excitations in metal glasses
Super-cooled liquids
Surface Dynamics of Liquids & Solids
Dynamics of thin films (Graphene)



New: Electronic Excitations, NRIXS
Extend Optical, Raman Spectroscopy to finite momentum transfers.

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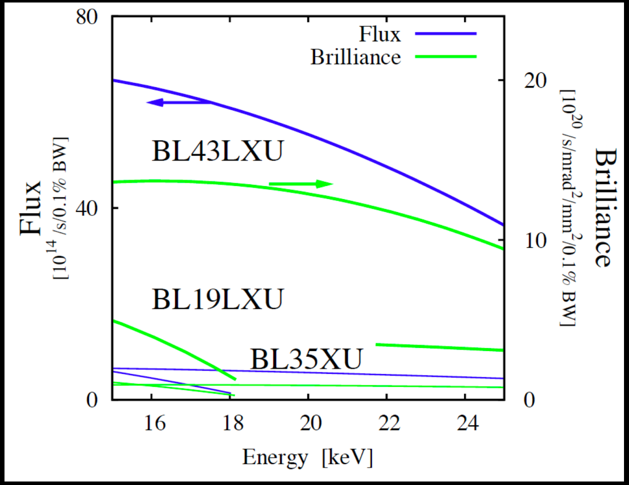
Beamline Design

Goal: Take advantage of the unique characteristics of SPring-8 to
Significantly improve experimental possibilities

Take advantage of

1. Long Straight Section (30m)
2. High Energy (8 GeV)
3. In-Vacuum (Small Gap) Undulators
4. Selective Tuning Range (15 to 25 keV)
5. New (but proven) Optical Ideas
6. Modern area detectors



Gives:
1. The most brilliant hard x-ray beamline in the world
2. The highest flux source for IXS

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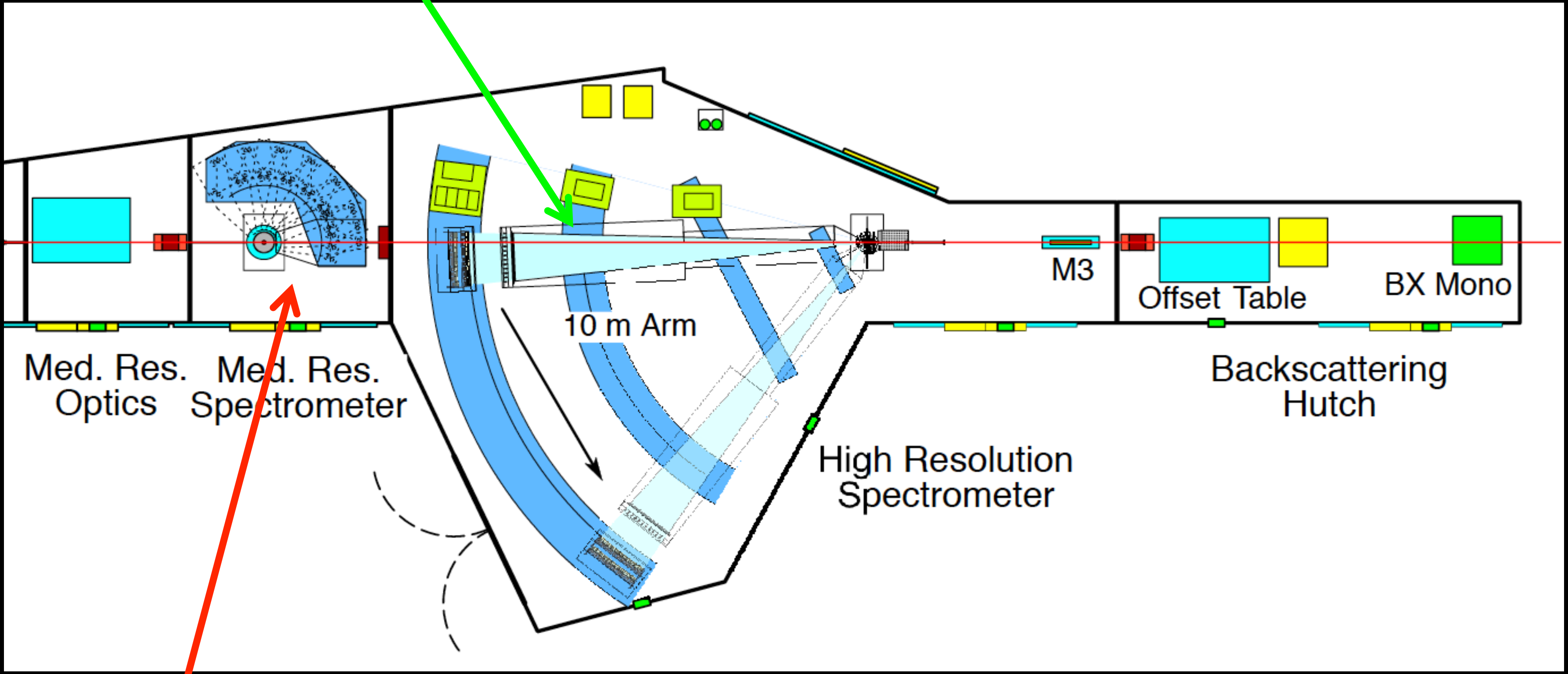
Two Spectrometers

"High-Resolution" = Large, 10m Arm.
Resolution from <1 meV to ~40 meV, ΔQ Small (x1)



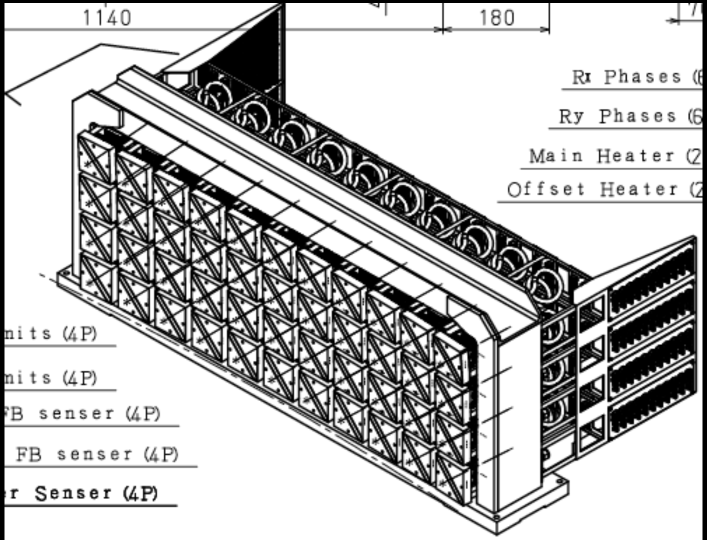
"Medium resolution" = Smaller (2m) arm.
Resolution 10 to 100 meV, ΔQ Large (x25)

Partially Complete

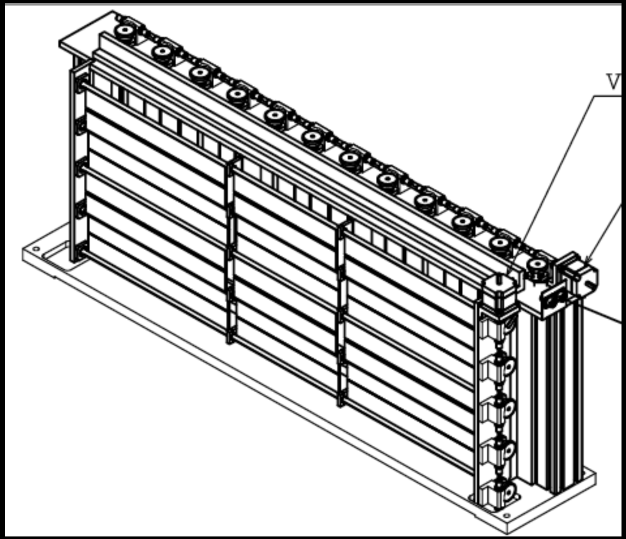
High Resolution Spectrometer

Based on a 10m Arm

Energy resolution: <1 to 40 meV (Backscattering mono.)
Analyzers From Si(888) – Si(13 13 13) 15.8-25.7 keV
Aim at 0.7 meV resolution with a Temperature Gradient
Designed to have good momentum resolution (0.01-0.1 Å^{-1})
Maximum momentum transfer ~7 to 12 Å^{-1}



42 Element
Analyzer Array

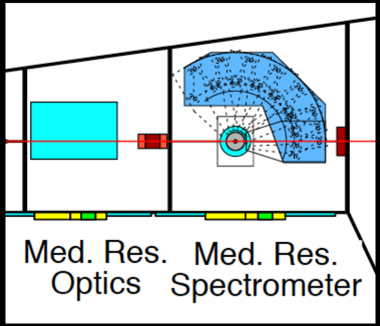


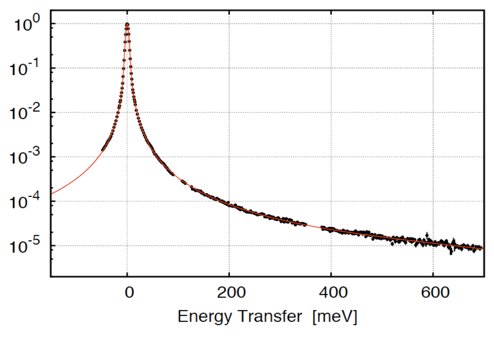
Partially Complete

Medium Resolution Spectrometer

Based on a 2m Arm

Energy resolution: ~10 to 100 meV (mono dependent)
Analyzers at Si(888) at 15.816 keV (reduced tails)
Dispersion compensation with Temperature Gradient
keeps high resolution with large space near sample.
Maximum momentum transfer ~15 Å





Target: Momentum resolved optical spectroscopy
Localized Excitations, (sub-eV) Gaps, Orbitons

Partially Complete

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Partially Complete

Thank You !

for Your Attention