Measurement of excitations – phonons and magnons

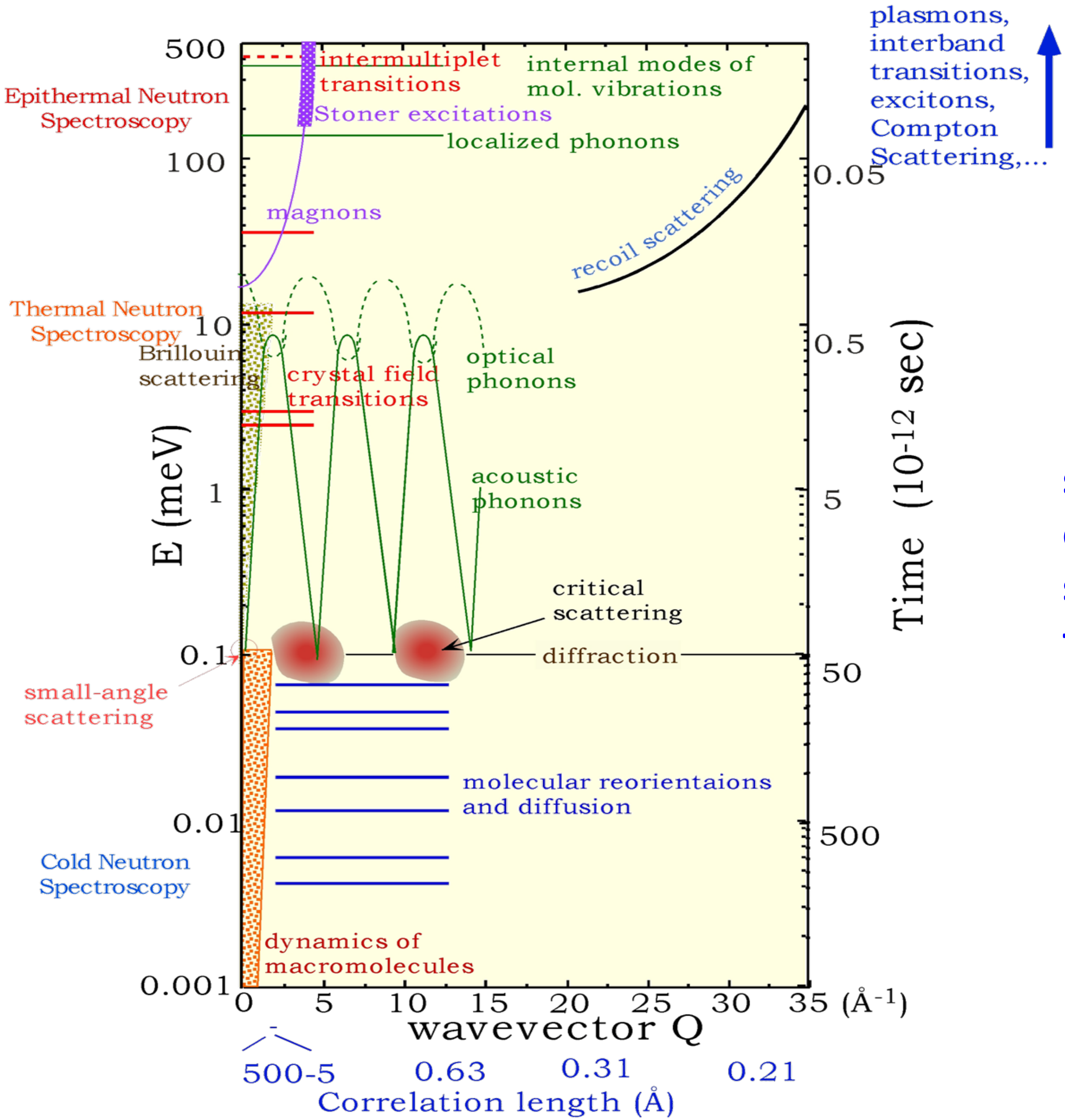
G. H. Lander

Institut Laue Langevin, Grenoble, France

What are excitations?

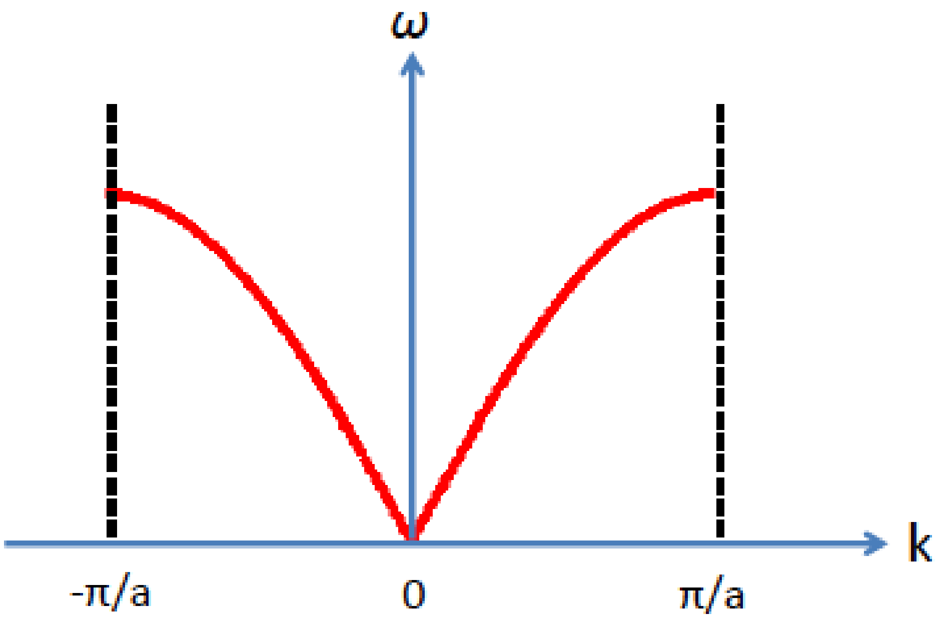
What do they tell us about condensed matter?

- Forces between atoms: ionic or covalent crystals, metals, H-bonds
- Why structures are what they are: how (and when) do they melt?
- Elastic constants
- Bulk modulus & compressibility
- Thermal conductivity
- …….. and many more (also for magnetism)



Identify the length & time scales of your problem, choose the appropriate spectrometer(s) to achieve the measurements.

Phonons on a 1-D chain



$$\omega_{ph} = 2\sqrt{\frac{K}{M}}\left|\sin\left(\frac{k_{ph}\,a}{2}\right)\right|$$

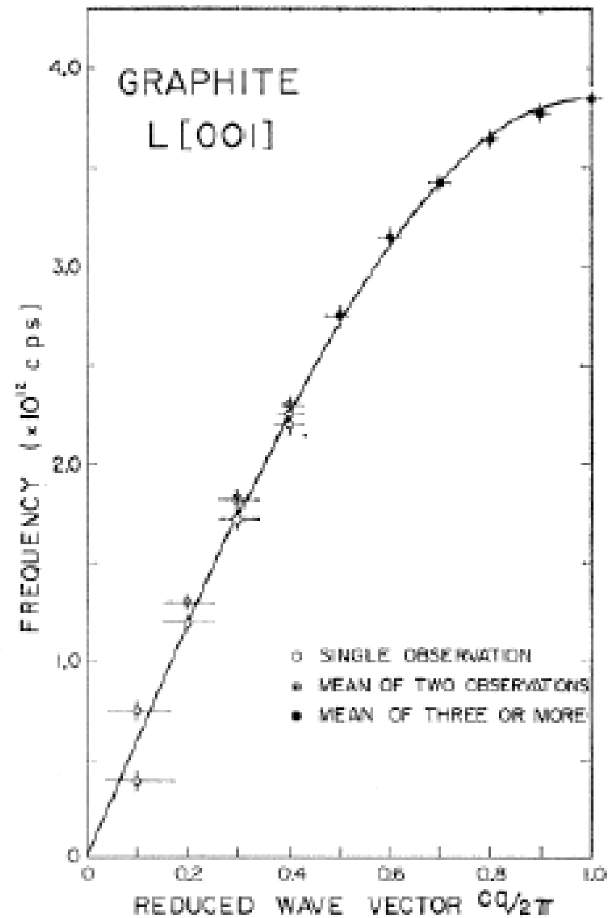


FIG. 3. Dispersion curve for the $L[001]$ modes in which the planes move as rigid units. The solid line is the best fitting (simple) sine wave to the experimental points. The assignment of errors is discussed in the text.

Dolling and Brockhouse., Phys. Rev. 128, 1120 (1962)

Neutron inelastic scattering

Two equations are: : $\vec{Q} = \vec{k}_i - \vec{k}_f$ $\hbar\omega = \Delta E = \hbar/(2m_n)\left(k_i^{\,2} - k_f^{\,2}\right)$

Elastic scattering has $k_i = k_f$

In terms of space-time correlation functions *elastic* scattering measures at t = 0 the position of particles j and j′

$$S(\vec{Q},0) \propto \sum_{jj'} \left\langle \exp[-i\vec{Q} \bullet \vec{R}_j(0)]\, x \exp[+i\vec{Q} \bullet \vec{R}_{j'}(0)] \right\rangle$$

We will now extend this to measure the correlation of particle j at t = 0 with particle j′ at t = t

$$S(\vec{Q},\omega) \propto \int_{-\infty}^{+\infty} \exp(-i\omega t)\,dt \sum_{jj'} \left\langle \exp[-i\vec{Q} \bullet \vec{R}_j(0)]\, x \exp[+i\vec{Q} \bullet \vec{R}_{j'}(t)] \right\rangle$$

In a crystal there is a periodic arrangement of atoms; we write this as $\vec{R}_l = \vec{l} + \vec{u}_l$ where $\boldsymbol{u_l}$ is the displacement of the atoms from their mean position $\boldsymbol{l}$

The correlations between particles l and l' depends only on their vector difference $|\boldsymbol{l} - \boldsymbol{l}'|$ so the sum over j and j' is the same

$$\sum_{jj'} \left\langle \exp[-i\vec{Q} \bullet \vec{R}_j(0)] \; x \; \exp[+i\vec{Q} \bullet \vec{R}_{j'}(t)] \right\rangle$$

$$= N \sum_j \exp(i\vec{Q} \bullet \vec{l}_j) \left\langle \exp[-\vec{Q} \bullet \vec{u}_o(0)] \; x \; \exp[+\vec{Q} \bullet \vec{u}_j(t)] \right\rangle$$

leading to:

$$S(\vec{Q},\omega) \propto \sum_j \exp(i\vec{Q} \bullet \vec{l}_j) \int_{-\infty}^{+\infty} \exp(-i\omega t) dt \; x \left\langle e^U e^V \right\rangle$$

where $\sum_j \exp(i\vec{Q} \bullet \vec{l}_j)$ is the ***elastic structure factor.***

$\left\langle e^U e^V \right\rangle$ where $U = -i\vec{Q} \bullet \vec{u}_o(0)\ and\ V = +i\vec{Q} \bullet \vec{u}_j(t)$

We assume the displacements are *small* and can be described in terms of an harmonic oscillator. Then we can use the identity

$\left\langle e^U e^V \right\rangle = e^{\langle U^2 \rangle} e^{\langle UV \rangle}$ and note that $e^{\langle U^2 \rangle}$ is independent of **t**

This term is the Debye-Waller factor representing uncorrelated motions of the nuclei from their mean positions $e^{\langle U^2 \rangle} = \left\langle \left[\vec{Q} \bullet \vec{u}_o(0) \right]^2 \right\rangle = e^{-2W}$

Finally $e^{\langle UV \rangle} = 1 + \langle UV \rangle + \frac{1}{2} \langle UV \rangle^2 + \ldots.$

One phonon **two phonon**

Final phonon cross section

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right) = \frac{\sigma_{coh}}{4\pi}\frac{k_f}{k_i}\frac{(2\pi)^3}{v_0}\frac{1}{2M}\exp(-2W)$$

$$x\sum_s\sum_\tau \frac{\left(\vec{Q}\bullet\hat{u}_s\right)^2}{\omega_s}\left(n_s+\frac{1}{2}\pm\frac{1}{2}\right)\delta(\omega\mp\omega_s)\,\delta(\vec{Q}\mp\vec{q}-\tau)$$

Intensity $\propto |Q|^2 \quad \left(\vec{Q}\bullet\hat{u}_s\right)^2$ **Selects phonon displacements || $\vec{Q}$**

$\propto \sigma_{coh}/\omega$

$\propto \langle n_s + 1/2 \pm 1/2 \rangle$ gives the population of phonon states. There are more phonons at high T as phonons and magnons are bosons, no limit to population. **Detailed balance**

$\propto \delta(\omega \quad \omega_s)$ gives Stokes and anti-Stokes lines

$\propto \delta(\vec{Q}\mp\vec{q}-\tau)$ gives conservation of momentum

for phonon of wavevector ***q***; note $|\vec{q}| = 2\pi/\lambda_{phonon}$

Ways to measure excitations

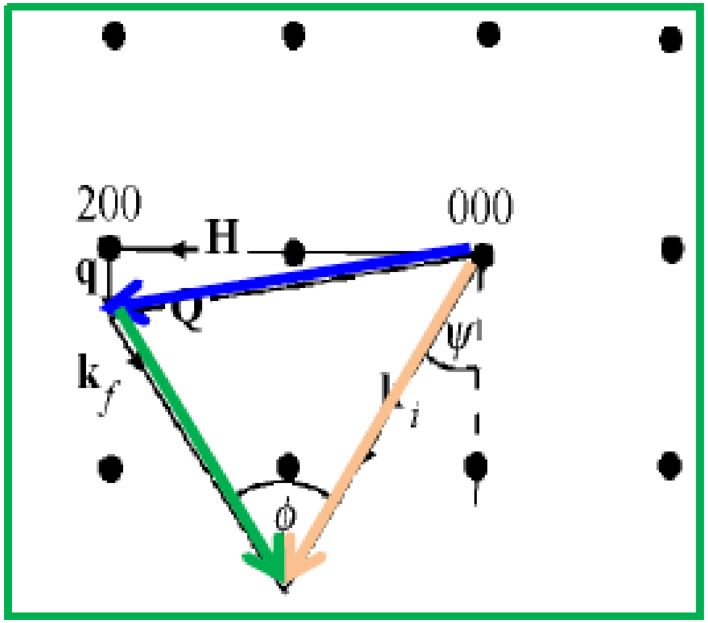
- Triple axis spectrometer
- Time-of-flight chopper spectrometer

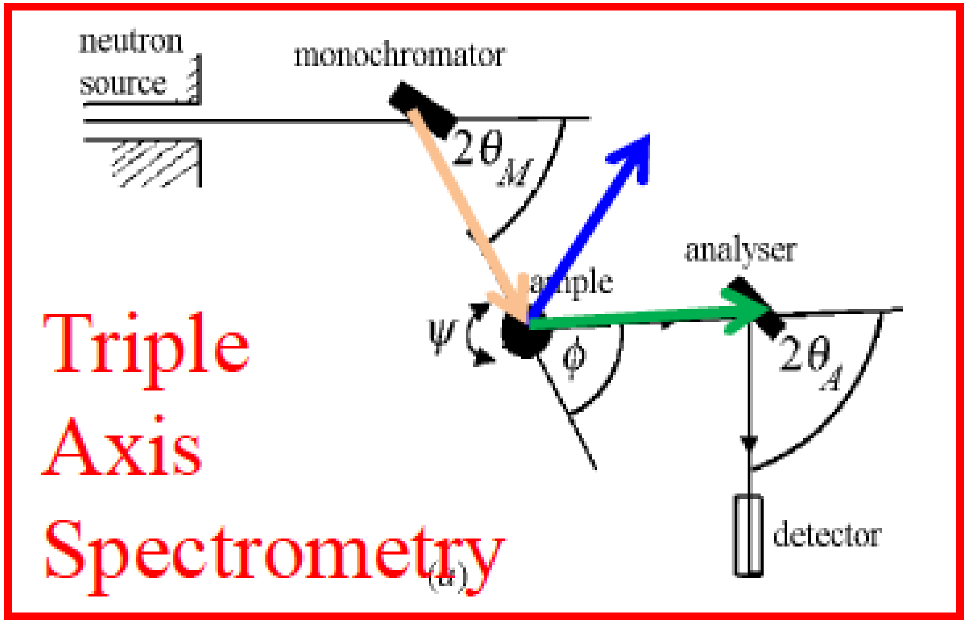
Special Instruments that have a more constrained energy or Q window

Back-scattering spectrometer
Spin-echo spectrometer
Crystal-analyzer spectrometer
Compton spectrometer

How do we measure these points?

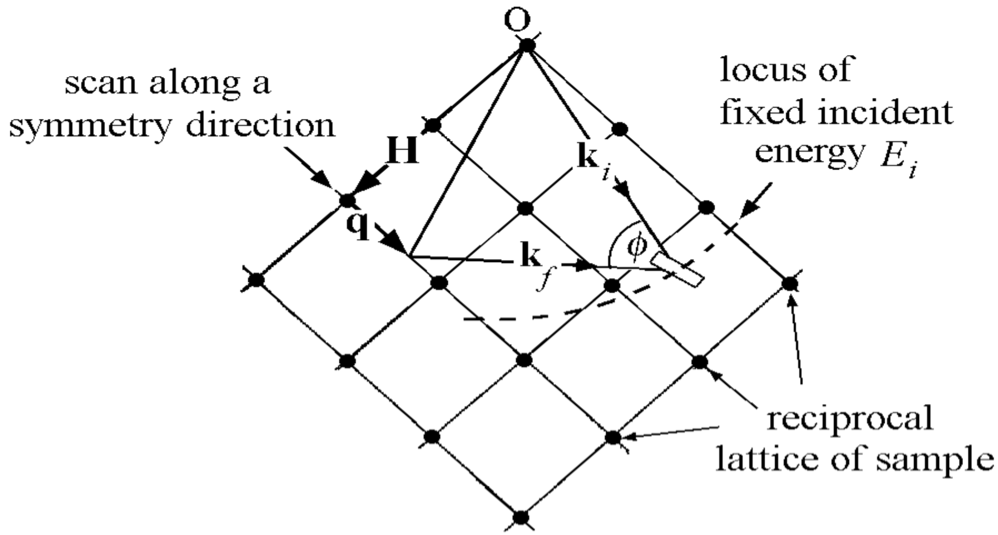
- Momentum transfer $\hbar\mathbf{Q} = \hbar(\mathbf{k}_i - \mathbf{k}_f)$
- Energy transfer $\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m}(k_i^2 - k_f^2)$



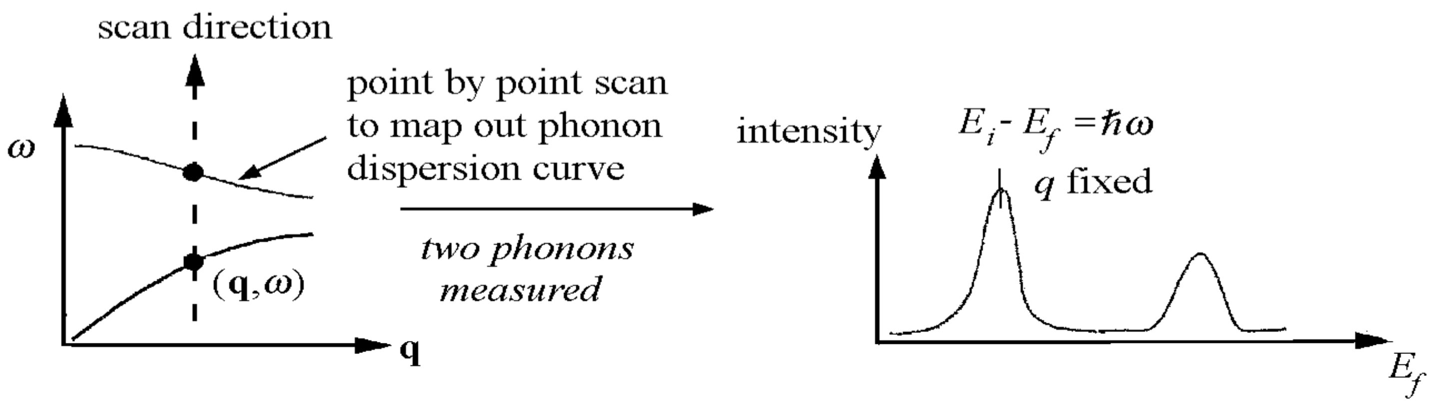


$$|\mathbf{Q}|^2 = |\boldsymbol{k}_i|^2 + |\boldsymbol{k}_f|^2 - 2\,|\boldsymbol{k}_i||\boldsymbol{k}_f|\cos(2\theta)$$

Techniques of the triple-axis spectroscopy

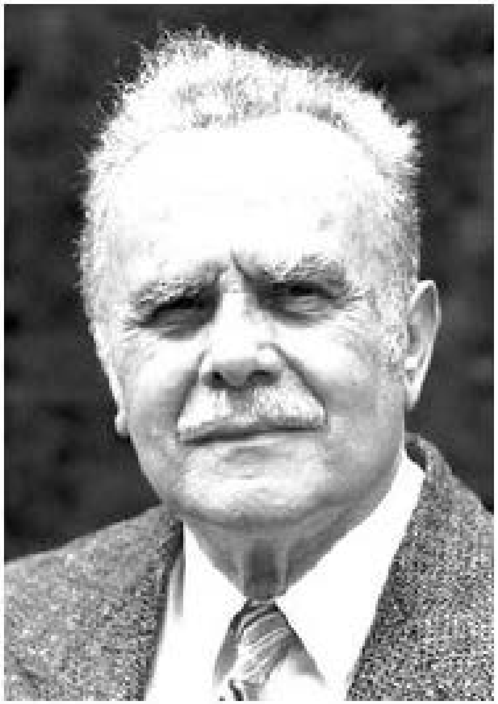


Focusing



The Nobel Prize in Physics 1994
Bertram N. Brockhouse, Clifford G. Shull

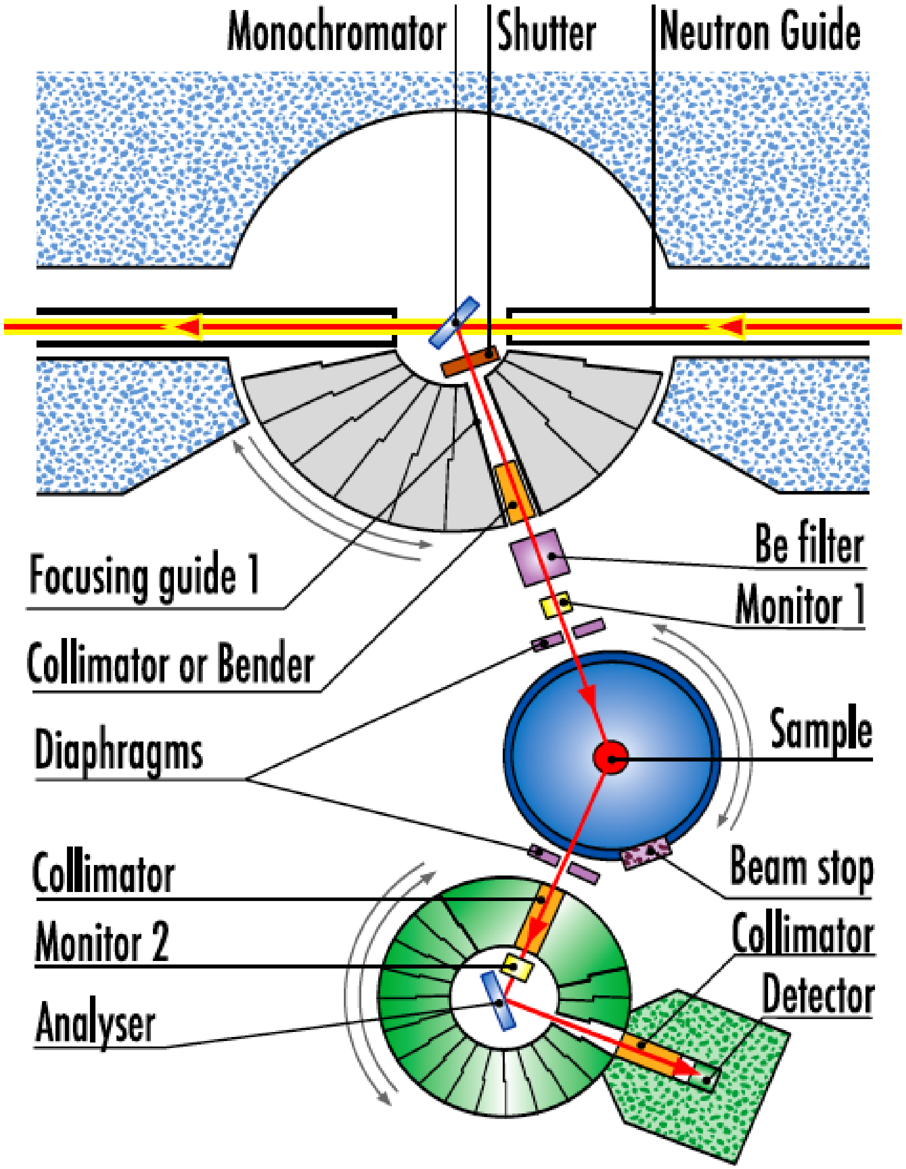
Bertram N. Brockhouse - Facts



Source: Atomic Energy of Canada Limited, Chalk River, Ontario (CC BY-NC-ND 2.0)

Bertram N. Brockhouse. *Nobelprize.org*. Nobel Media AB 2013.

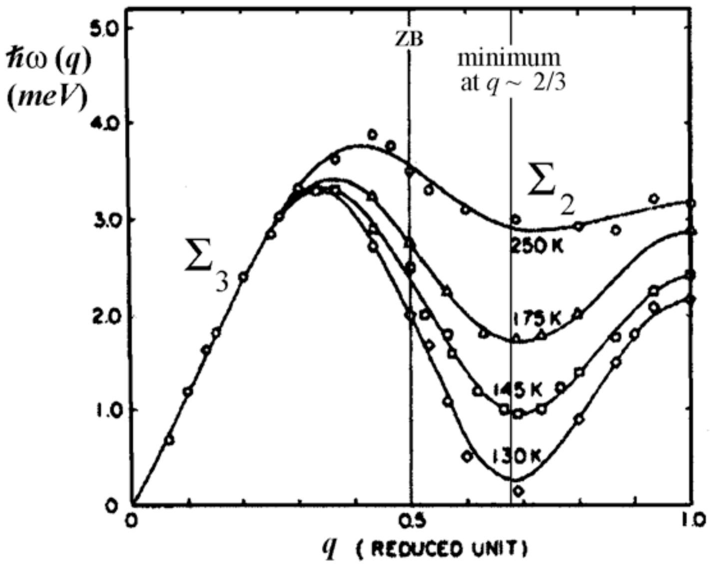
Schematic of triple-axis spectrometer



Note that the Be filter, which is used with cold neutrons, can either be before the sample (constant k_i) or after the sample (constant k_f)

The IN14 triple-axis spectrometer at the ILL

Phase transitions in solids



Dispersion relations of the Σ_2 soft mode and the Σ_3 acoustic mode in K_2SeO_4 plotted in an extended zone. Z.B. indicates the original zone boundary. The solid lines show the results of fitting force constant models to the data.

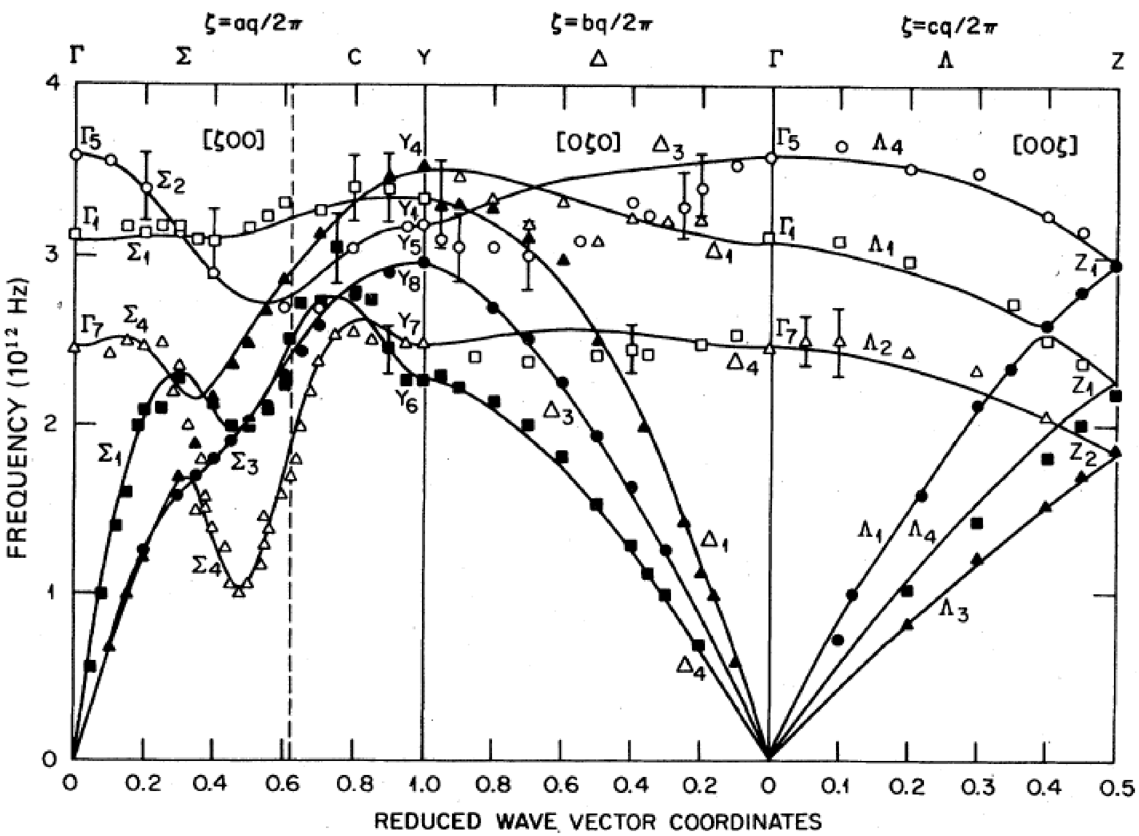
If one looks carefully at these data one can see that the initial "soft" point is not at q = 2/3, but rather at q = 2/3 + δ
This is an example of an incommensurate phase transition, stabilised by higher-order terms in the Landau expansion.

M. Iizumi, J. D. Axe, G. Shirane, and K. Shimoaka,
Phys. Rev.B 15,4392 (1977)

Phonons in alpha-Uranium at T=300 K

Note the anomaly in the ***a*** direction [100] and the incipient minimum of the Σ_4 mode. The other two directions are 'normal'

At low temperature the material transforms in a complex way, developing a charge-density wave.



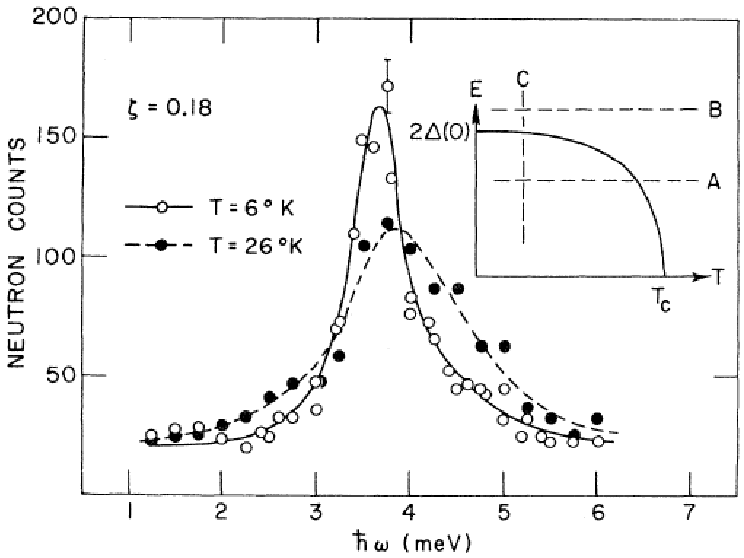
Crummett *et al.* Phys. Rev. B (1979)

Phonons and superconductivity

In the BCS theory (1957) of *s*-wave superconductivity the lattice vibrations (phonons) mediate the attraction between electrons and form the Cooper pairs. Thus the measurements of phonons, in particular, the total phonon-density of states, is important to understand the overall mechanism of superconductivity.

Many phonon studies using neutrons have been done with this motivation.

An example of an electron-phonon interaction as measured by neutrons



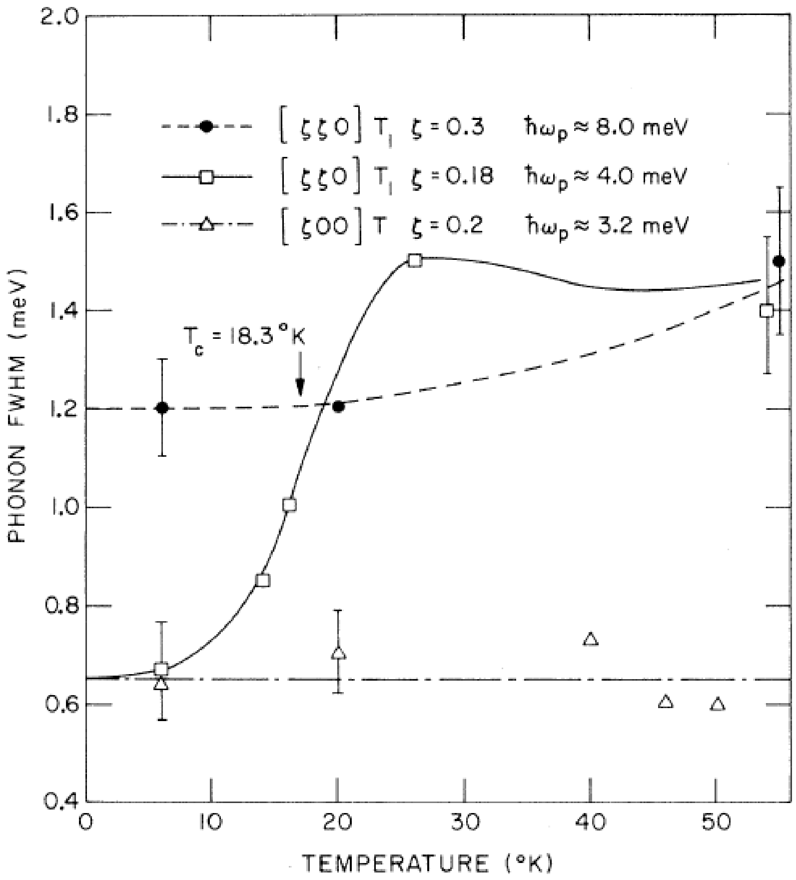
Inelastic scattering from Nb_3Sn, T_c = 18.3 K.

For phonons with E < 2 Δ(T), where Δ(T) is the s/c energy gap, there is a loss of a damping mechanism as the low-energy electron states form Cooper pairs.

Notice how this phonon is *much* broader for $T > T_{c.}$

Axe & Shirane, PRL <u>30</u>, 214 (1973)

Electron-phonon interaction in Nb_3Sn

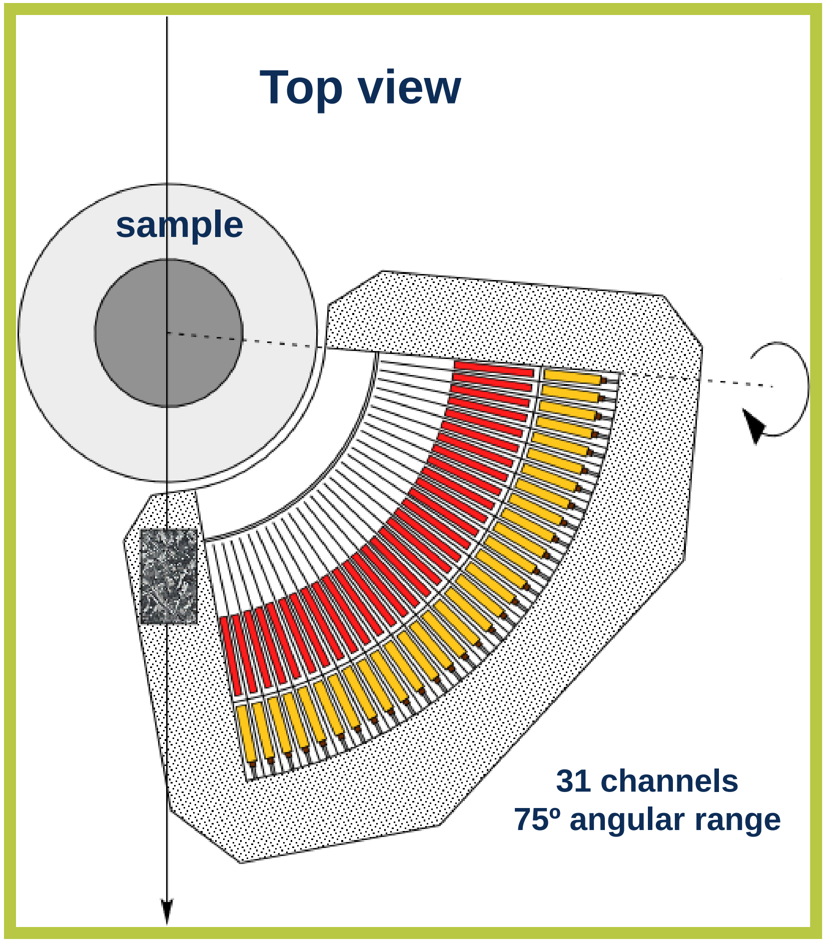


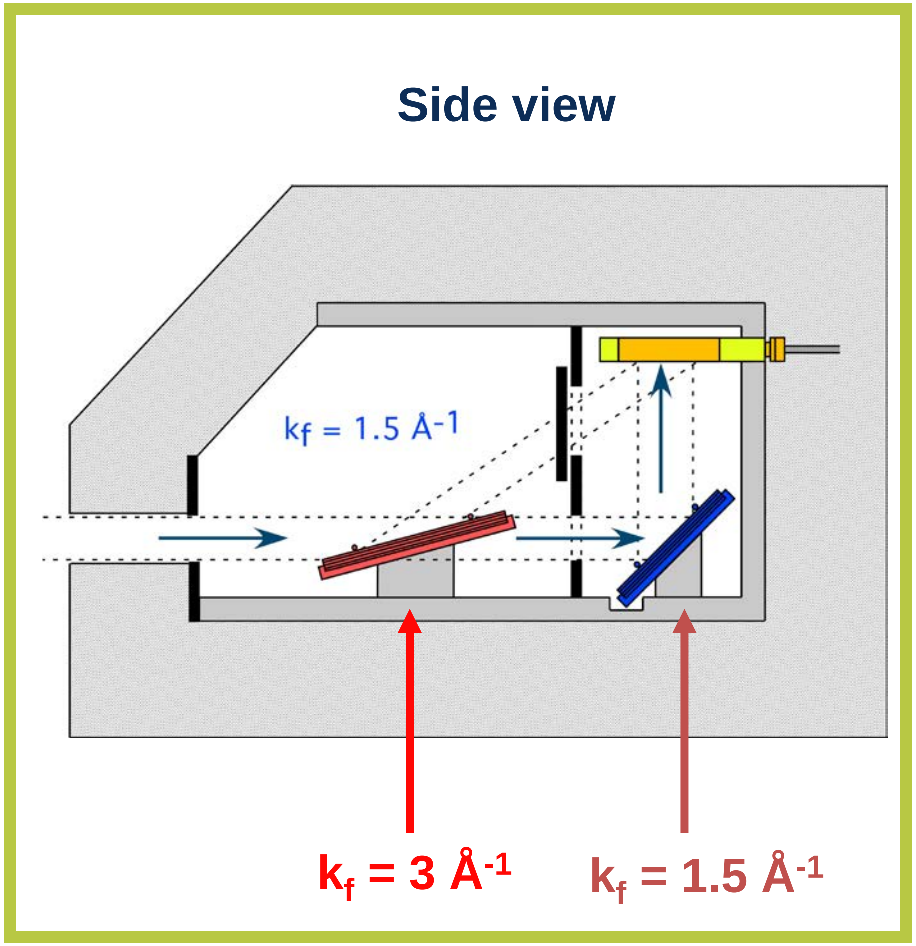
Summary of line-widths as f(T)
Note that there is *anisotropy* in the damping mechanism. No measurable effect is observed along [100], but a large effect along [110]

No effect is observed for a phonon of E = 8 meV. This is above 2 Δ(0).

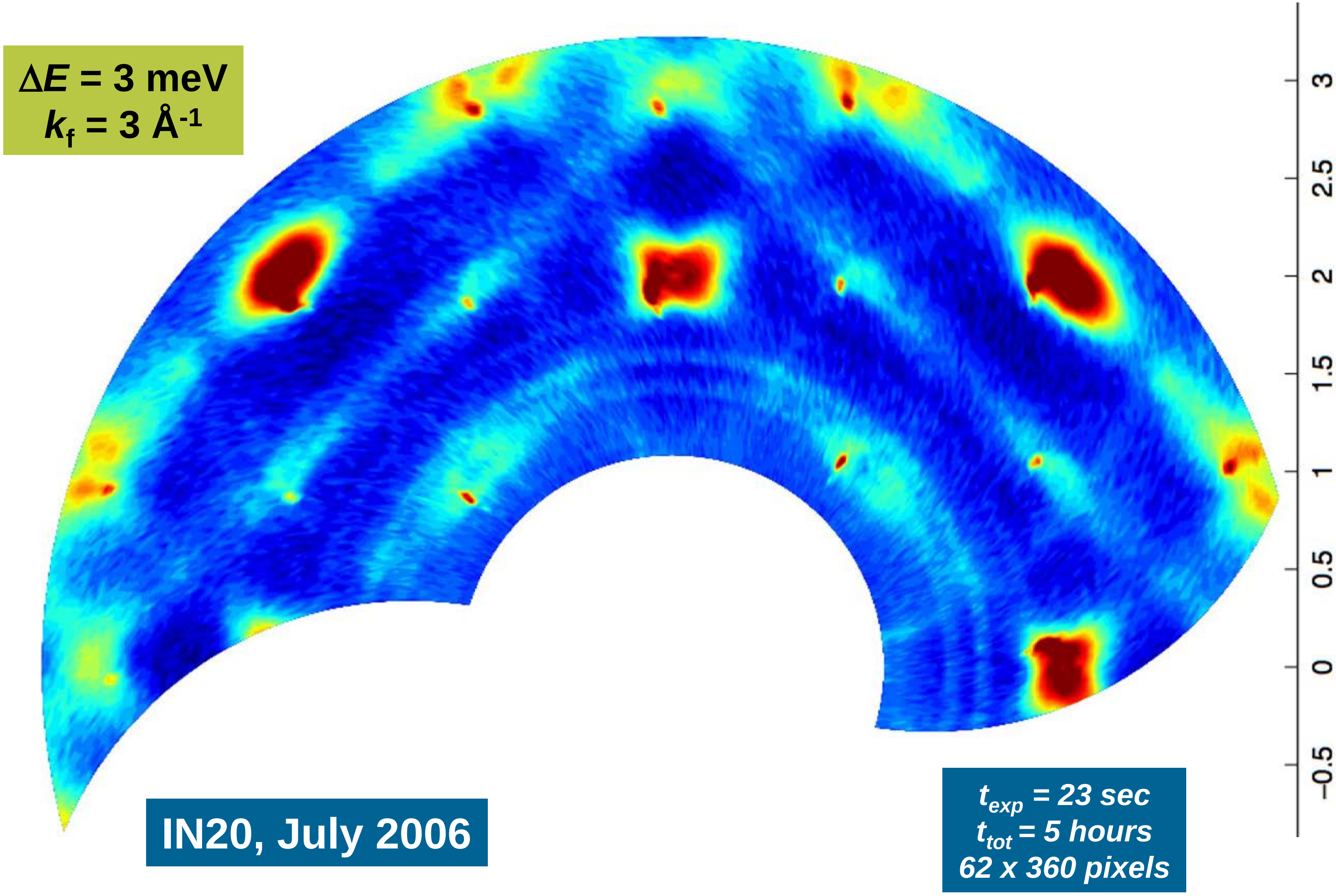
The gap is well determined as 2 Δ(0) = 7 ± 1 meV = (4.4 ± 0.6) $k_B T_c$ in excellent agreement with the specific heat value of 4.8 $k_B T_c$.

FLAT CONE II


Top view
sample
31 channels
75º angular range


Side view
kf = 1.5 Å-1
k_f = 3 Å^{-1}
k_f = 1.5 Å^{-1}

PZN-8%Pt relaxor



Beware of spurions

ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Physica B 350 (2004) 11–16

PHYSICA B

www.elsevier.com/locate/physb

Chasing ghosts in reciprocal space—a novel inelastic neutron multiple scattering process

H.M. Rønnow[a,b,*], L.-P. Regnault[b], J.E. Lorenzo[c]

[a] *NEC Laboratories, Princeton and University of Chicago, USA*
[b] *MDN/SPSMS/DRFMC, CEA-Grenoble, 38054 Grenoble, France*
[c] *Laboratoire de Cristallographie, CNRS, 38042 Grenoble, France*

Abstract

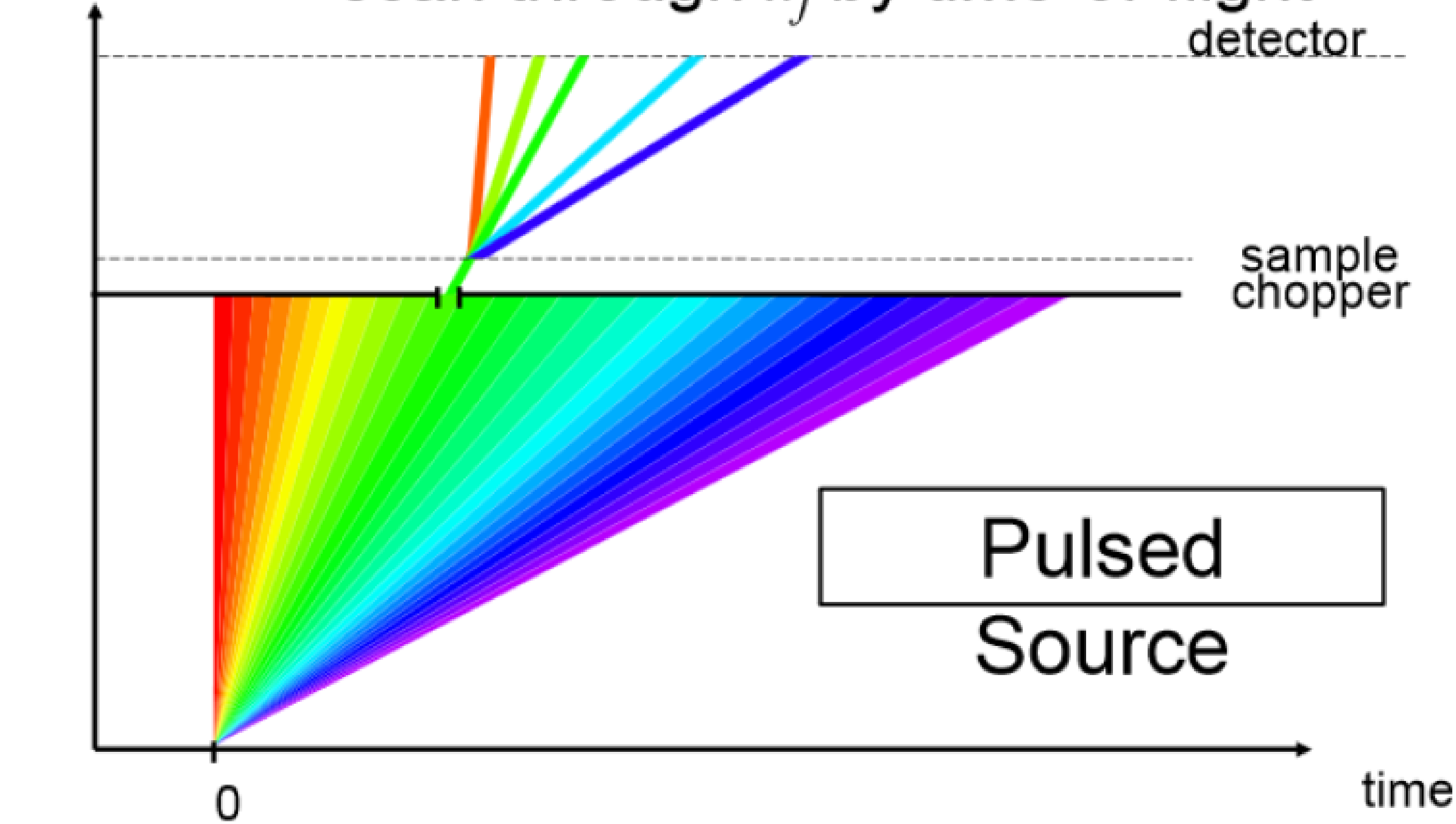
We have discovered that a recently reported weak excitation branch in the spin-Peierls material $CuGeO_3$ is in fact a ghost image of the primary magnetic excitation shifted in reciprocal space by a novel multiple scattering process. A model is developed that predicts the occurrence of such multiple scattering and accounts for the observations in $CuGeO_3$. New 'ghostons' can occur when the magnetic unit cell is smaller than the structural, while mixing of intensities from different reciprocal space zones jeopardize accurate polarisation analysis and the study of weak modes in general.
© 2004 Elsevier B.V. All rights reserved.

Time-of-flight spectroscopy

Direct geometry:

fix k_i by chopper phasing

scan through k_f by time-of-flight

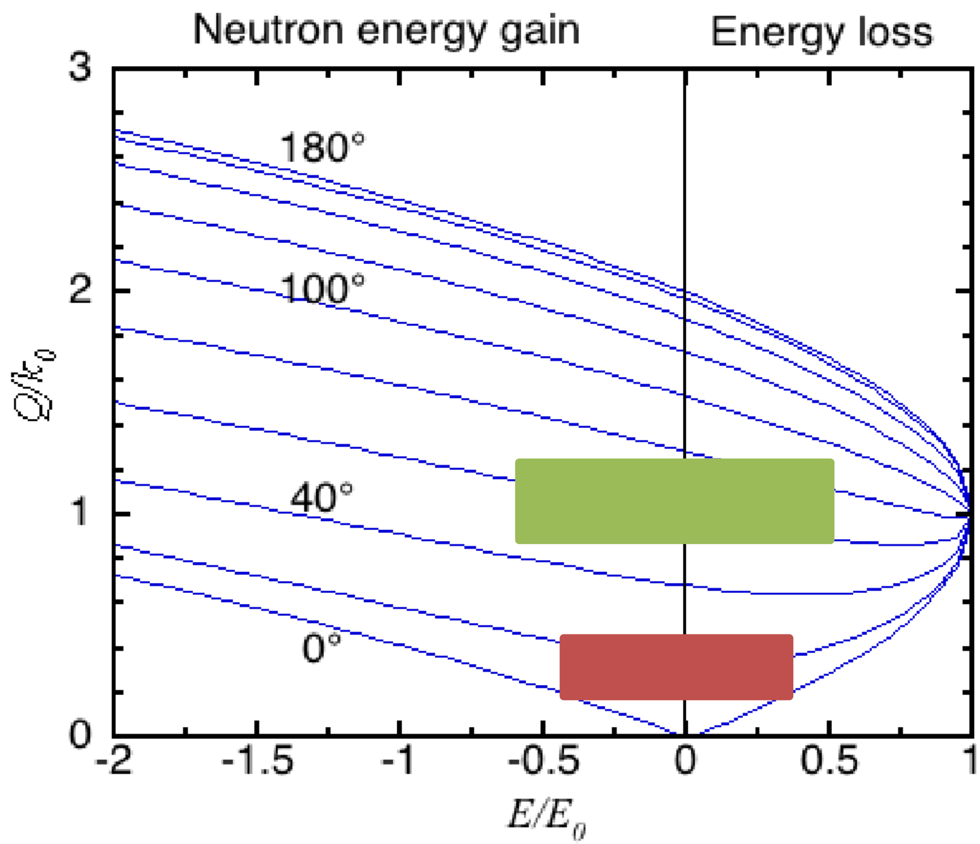


from Ken Andersen

Constraints on Q and ΔE in inelastic scattering

Direct Geometry: $$\left(\frac{Q}{k_0}\right)^2 = 2 - \frac{E}{E_0} - 2\cos\phi\sqrt{1-\frac{E}{E_0}}$$

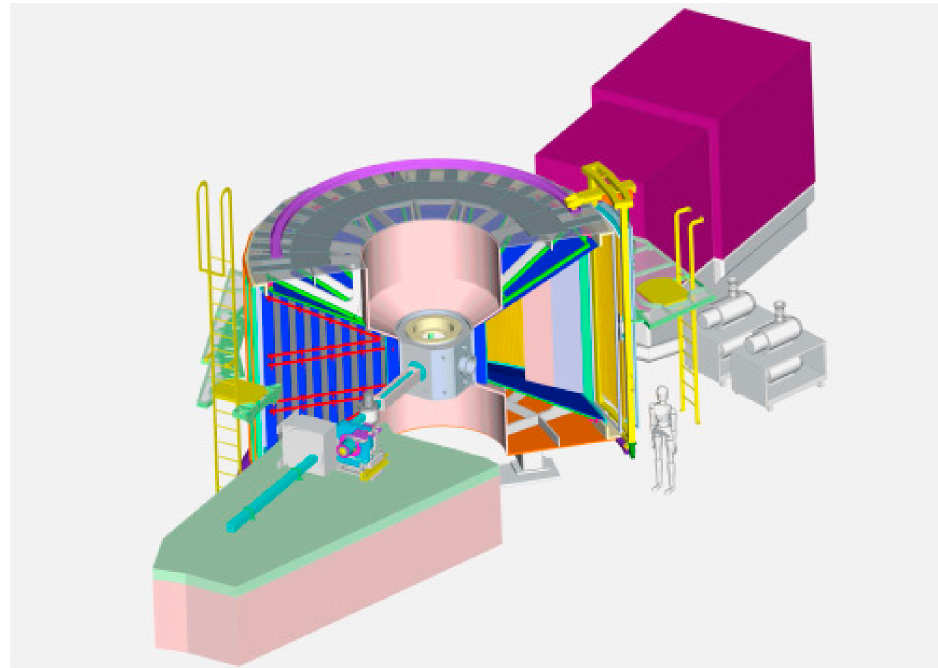
E = 2.072 k²



ΔE = 20 – 50 meV
E_0 = 100 meV, k_0 = 7 Å^{-1}
6 < Q < 8 Å^{-1}: Res ~ 3 meV

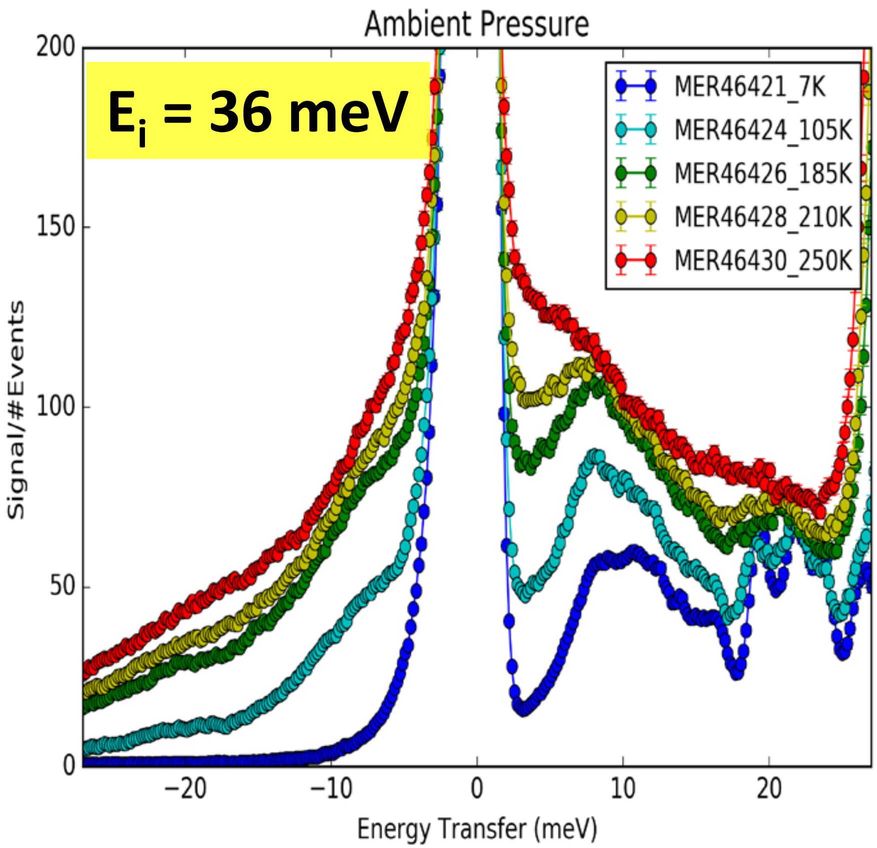
ΔE = 100 – 200 meV
E_0 = 300 meV, k_0 = 12 Å^{-1}
Q ~ 4 Å^{-1} Res: ~ 10 meV

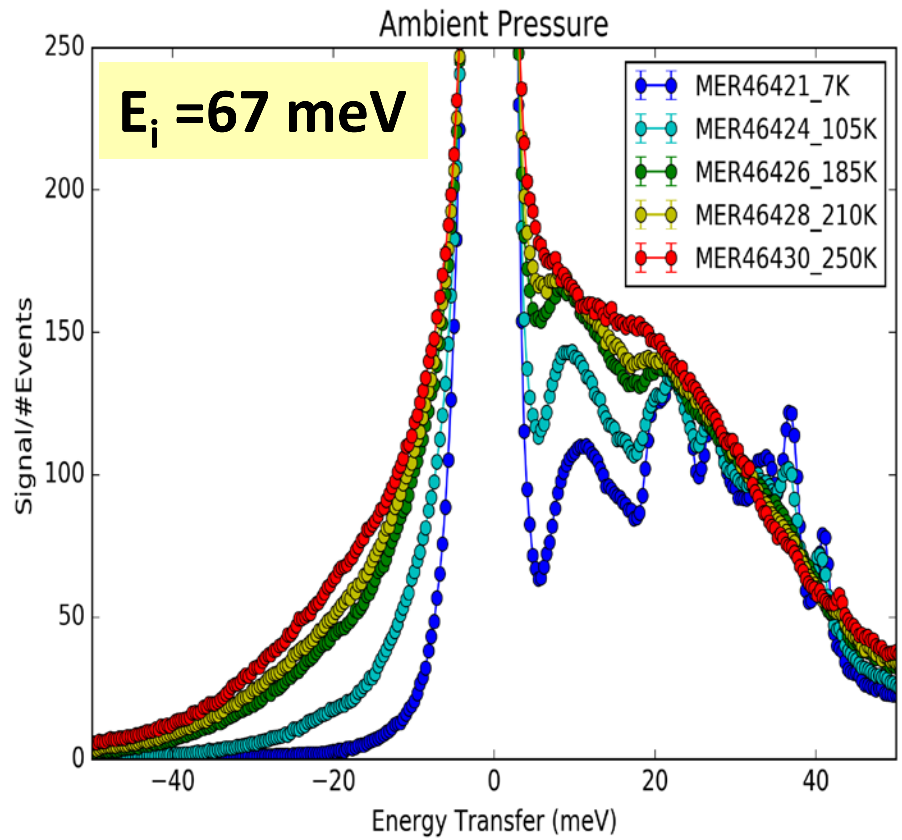
MERLIN chopper spectrometer at ISIS, RAL



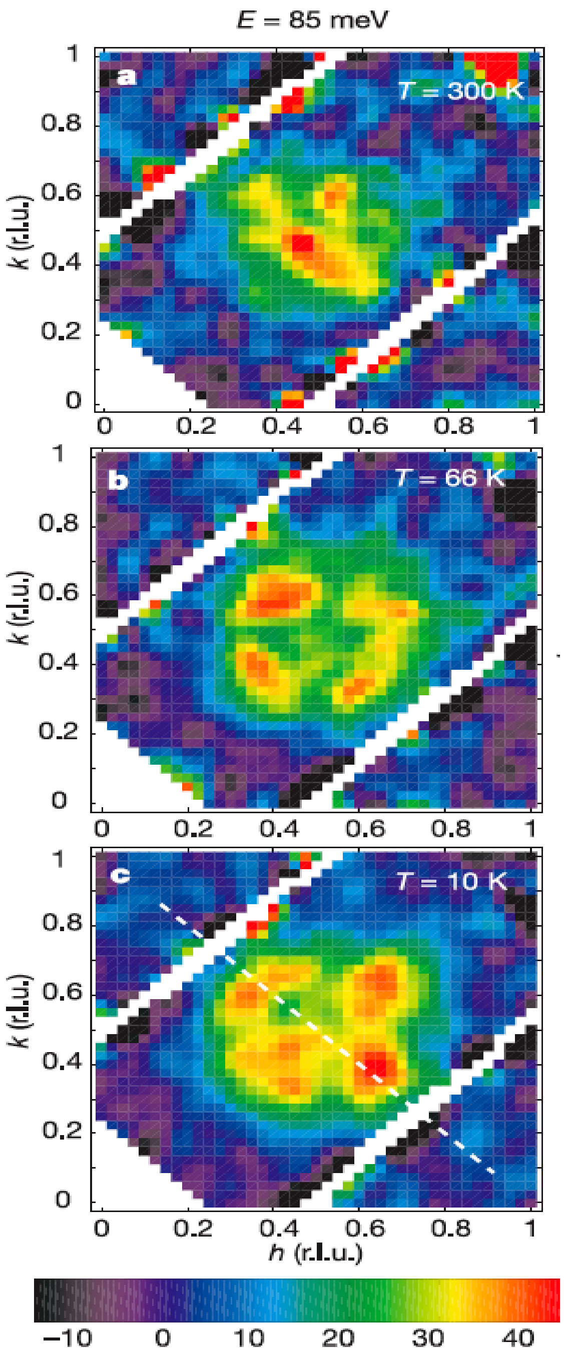
Wide angle coverage, high intensity and moderate resolution
direct chopper spectrometer
Also can run in special mode to allow more than
one incident energy to be measured at same time

Phonons from $(NH_4)_2SO_4$ measured on MERLIN





Note these data are at ambient pressure;
pressures up to several GPa were measured



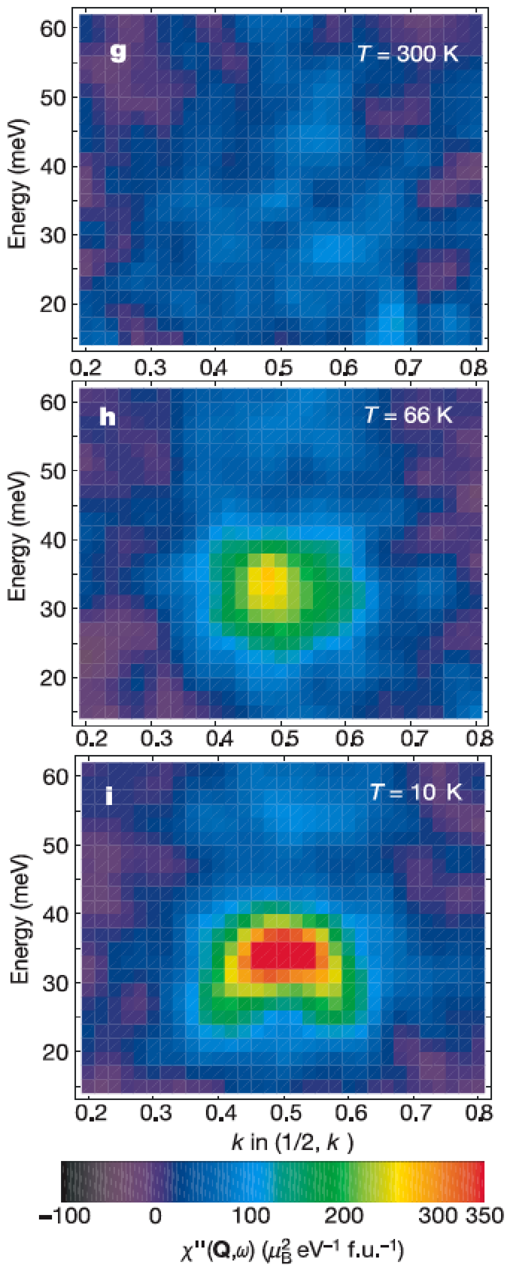
Magnetic fluctuations in superconducting $YBa_2Cu_3O_{6+x}$

The excitations are incommensurate below T_c even at high energies, in fact to 100 meV.

These data have be taken on the MAPS spectrometer at ISIS and show the great advantage of the multidetector system coupled to a pulsed source.

E_i = 170 meV; crystal 25 g. T_c = 63 K

S. M. Hayden *et al.*, *Nature* 429, 531 (2004)



Magnetic fluctuations in superconducting $YBa_2Cu_3O_{6+x}$

Although there are magnetic excitations over a wide range of energies near (1/2 1/2), they are by far the strongest at the resonant energy, in this case 34 meV, and below T_c = 63 K

This is an integration so cannot show the incommensurate nature.

S. M. Hayden *et al.*, *Nature* 429, 531 (2004)

Magnetic fluctuations in superconducting $YBa_2Cu_3O_{6+x}$

What causes these excitations and are they related to the special superconductivity in these materials?

(1) Incipient spin-charge separation leading to “stripes”

(2) Electron-hole pair excitations governed by the underlying Fermi surface.

Many theories are presently trying to reproduce these effects. Together with photoemission (ARPES), these neutron scattering experiments are probably the most important set of data in the quest to understand high T_c mechanism.

Inelastic X-ray scattering

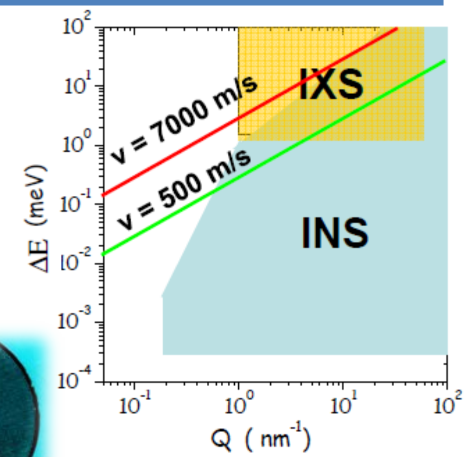
Recall that a **1 Å x-ray beam** has an energy of 12.4 **keV** –
in case you missed it, that is 12.4 x **10^6 meV.**

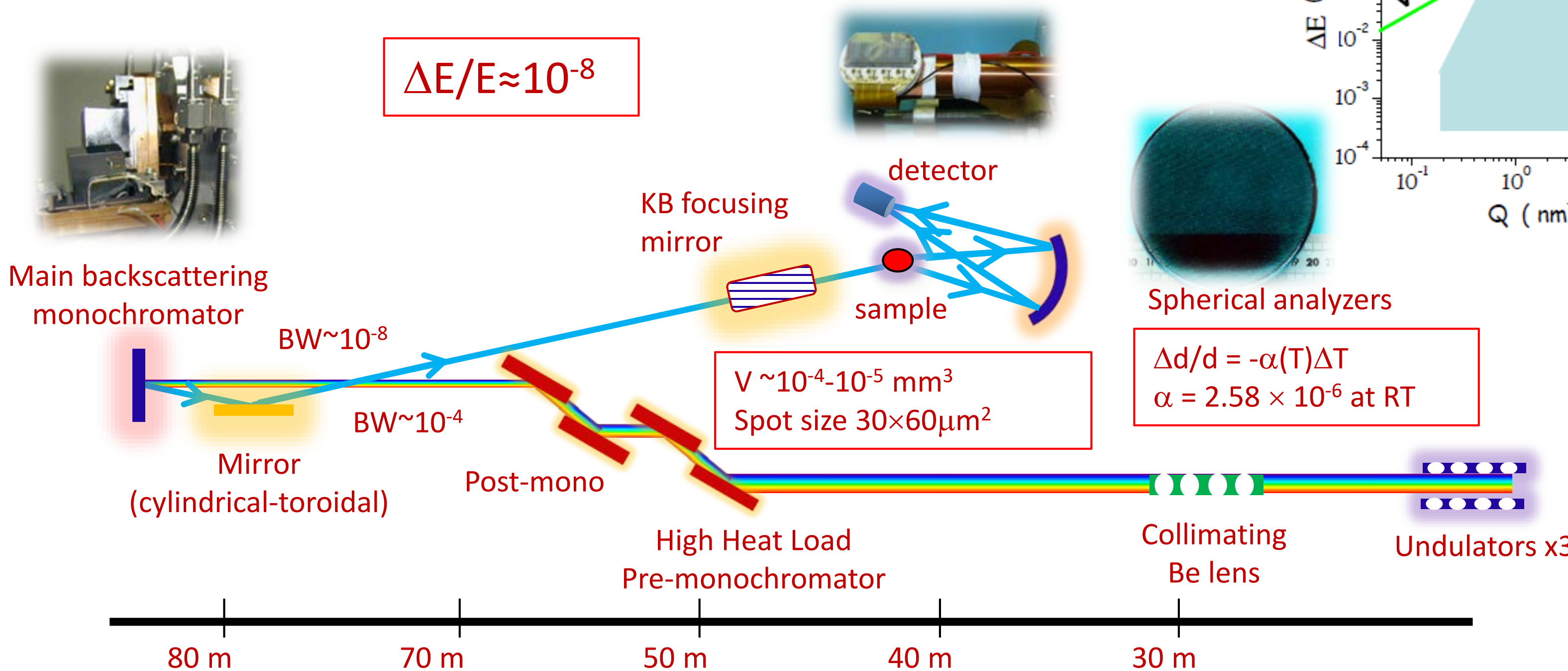
Since we know that there are **excitations at the eV level** in solids, plasmons, inter-multiplet levels etc., these can be investigated with x-rays, and this resolution is relatively easy to achieve.

But to get to **meV** is clearly very hard. The solution comes from large perfect crystals developed by the semiconducting industry, and to rely on **Backscattering techniques.** There are only 3 such instruments in the world, at ESRF, APS (Argonne), and Spring-8 (Osaka).

ID28 IXS beamline at ESRF

Energy resolution decoupled from the energy transfer
Energy independent momentum transfer
Focusing capabilities



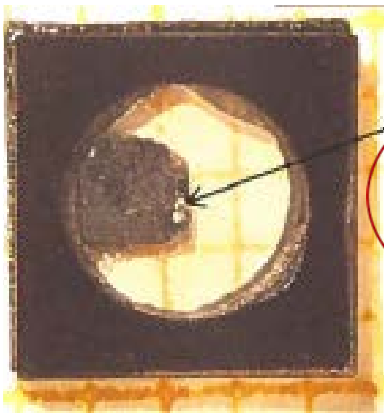


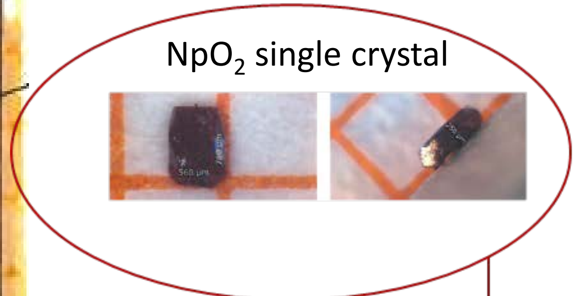
Si(9 9 9)
ΔE=3 meV
E=17.79 keV

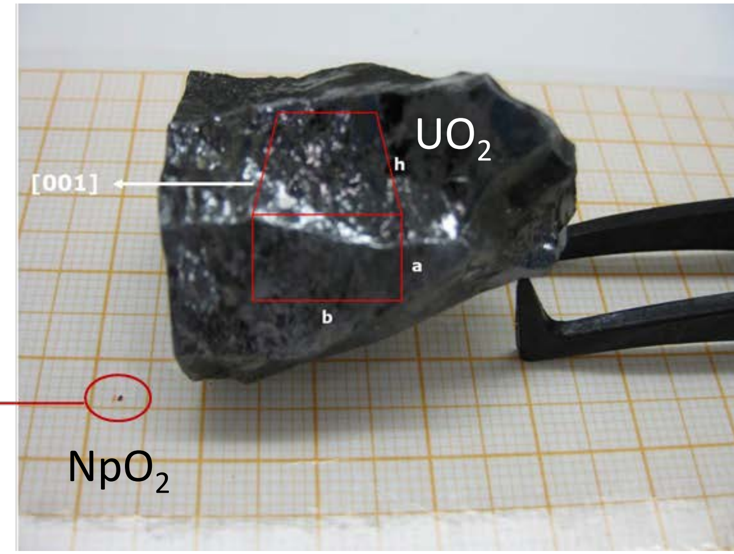
Si(12 12 12)
ΔE=1.5 meV
E=23.72 keV

IXS on Actinides: Safety issues

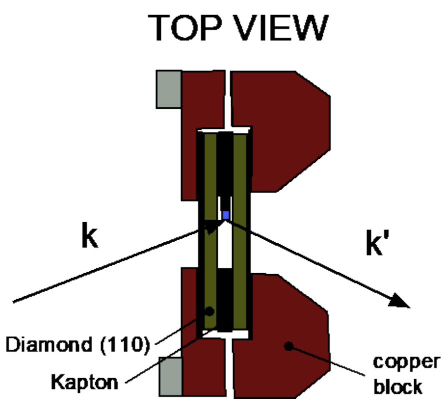
Sample handling, cutting and surface preparation follows strict safety rules
Restricted scattering geometry due to the sample encapsulation







Crystal sealed in a diamond wafer



Courtesy of G. Pagliosa, ITU

NpO_2:
Mass = 0.863 mg
Activity = 19.8 kBq

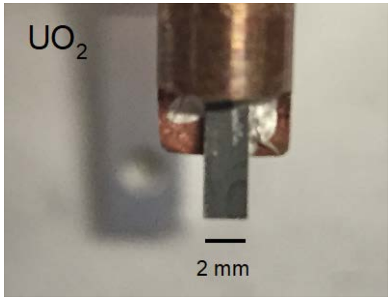
UO_2:
Mass = 99000 mg

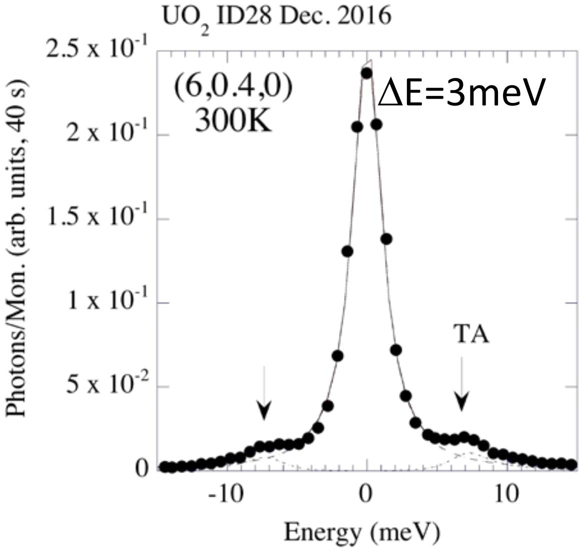
Strong L_3 photo-absorption at working energies
L_3(Np) = 17.610 keV, L_3(U) = 17.166 keV

UO_2: sample quality

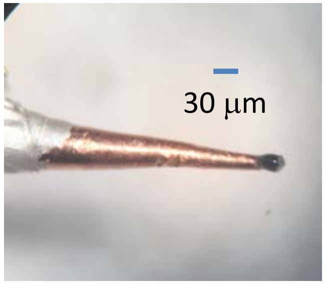
Sample quality affects the elastic line and prevents measurements at low energy

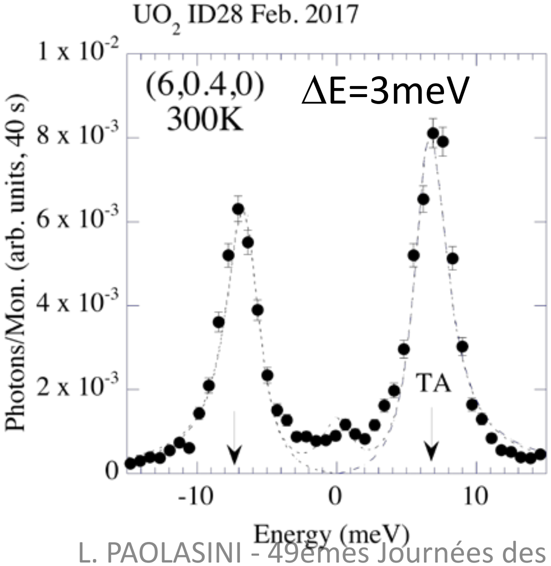
1st Exp. at Si(999)
Crystal cut from large UO_2 sample
Bad crystal surface



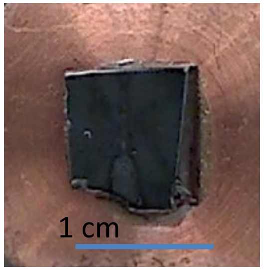


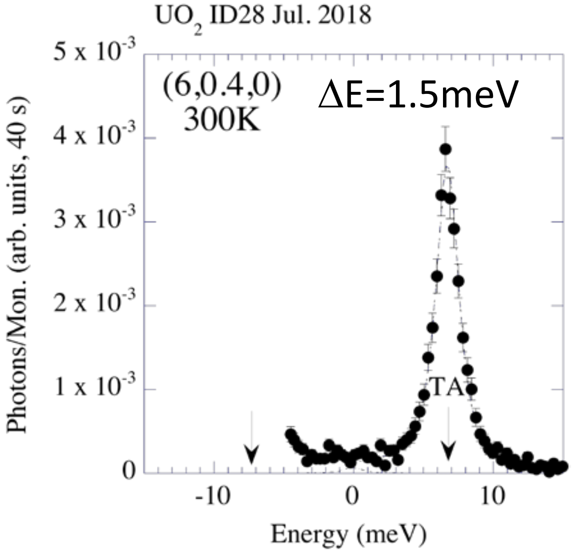
2nd Exp. at Si(999)
Single crystal grown by vapor transport
Slightly off-stoichiometric (T_N=29.8K)



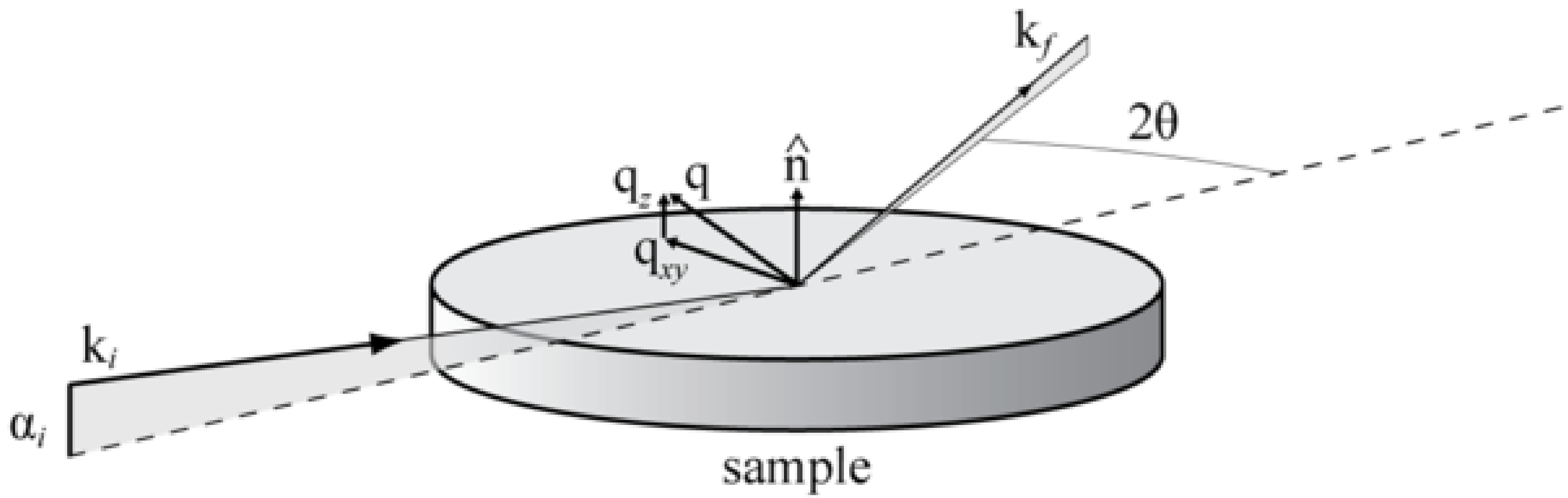


3rd Exp. at Si(12 12 12)
Good quality single crystal.
Stoichiometric sample
T_N=30.8K





Inelastic scattering from thin films: phonons in irradiated UO_2 thin films

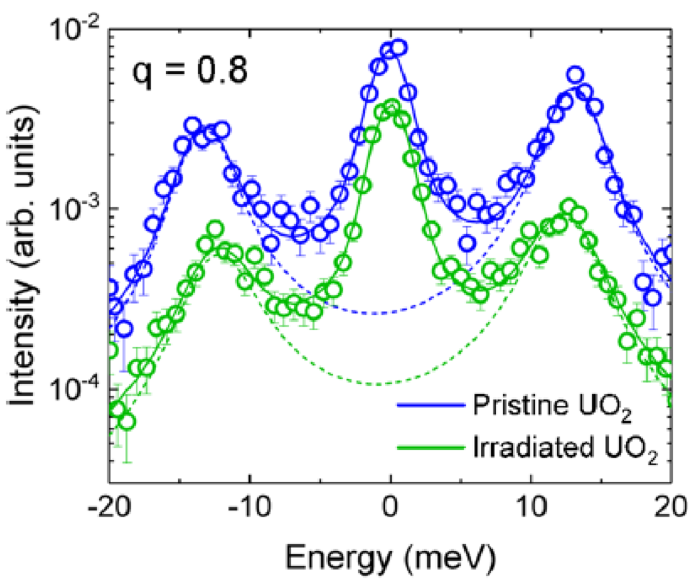


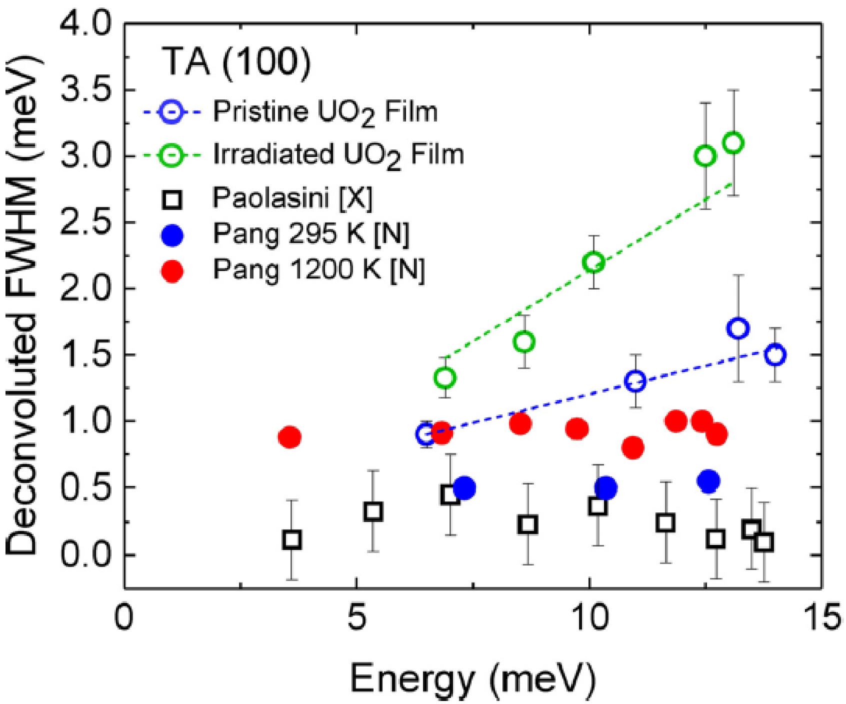
Thin films can be irradiated to make uniform damage up to a thickness of ~ 4 microns. Radiation using accelerated particles to simulate fission damage cannot penetrate > 20 microns

Experiments to compare phonons in pristine and irradiated UO_2 films of 300 nm

Phonons measured from 300 **μg** of material

Phonon *energies* same as measured in bulk and no change with irradiation, however extra diffuse scattering, and broader phonons, and some E or ***q*** dependence of broadening. Consistent with 50% drop in thermal conductivity, κ. Cannot measure optic modes.





Rennie *et al.* Phys. Rev. B 97, 224303 (2018)

Summary of phonon experiments

Neutrons are the probe of choice for phonons.

Many instruments at both reactors and pulsed sources are designed for such experiments and they can be used with both single crystals and polycrystalline samples.
Be sure you know what you are looking for!

The crystals will have to be at least 100 mm^3

For exceptionally small samples (i.e. thin films) or high pressure, then you may want to consider inelastic x-ray scattering. (No magnetic excitations! RIXS?)