NEUTRONS FOR SCIENCE

Исследования конденсированных сред с помощью «горячих» нейтронов

Institut Max von Laue - Paul Langevin
Grenoble

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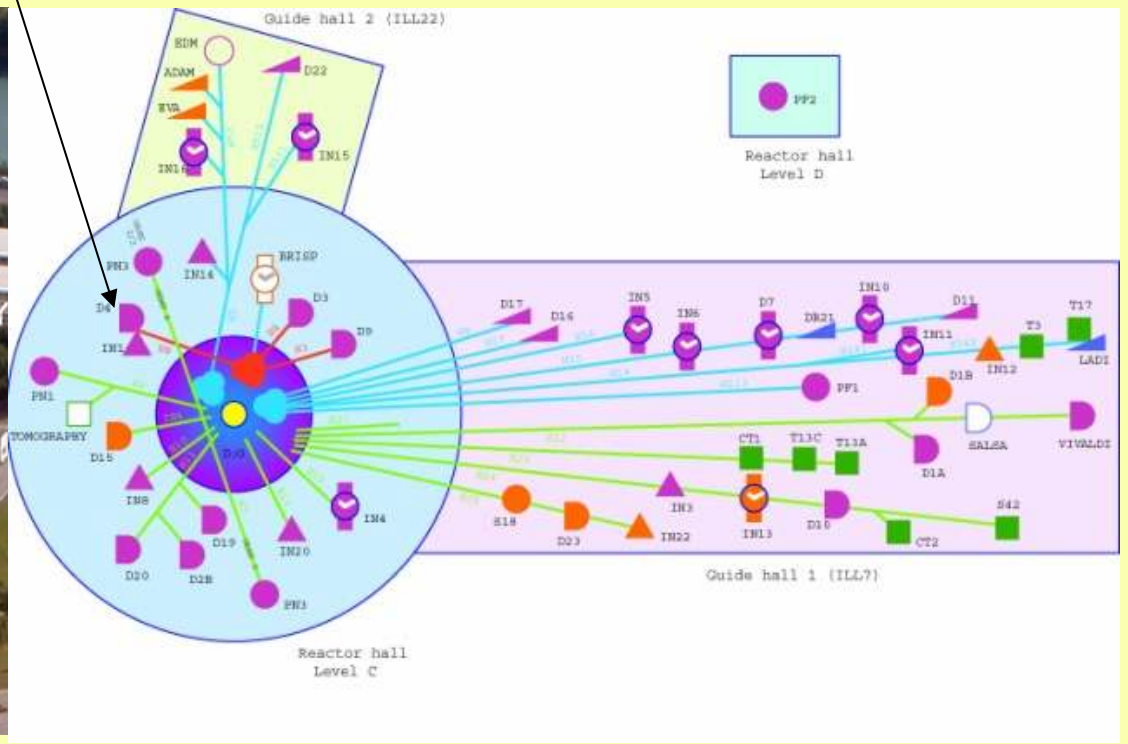
Three-Axis Spectrometers Group

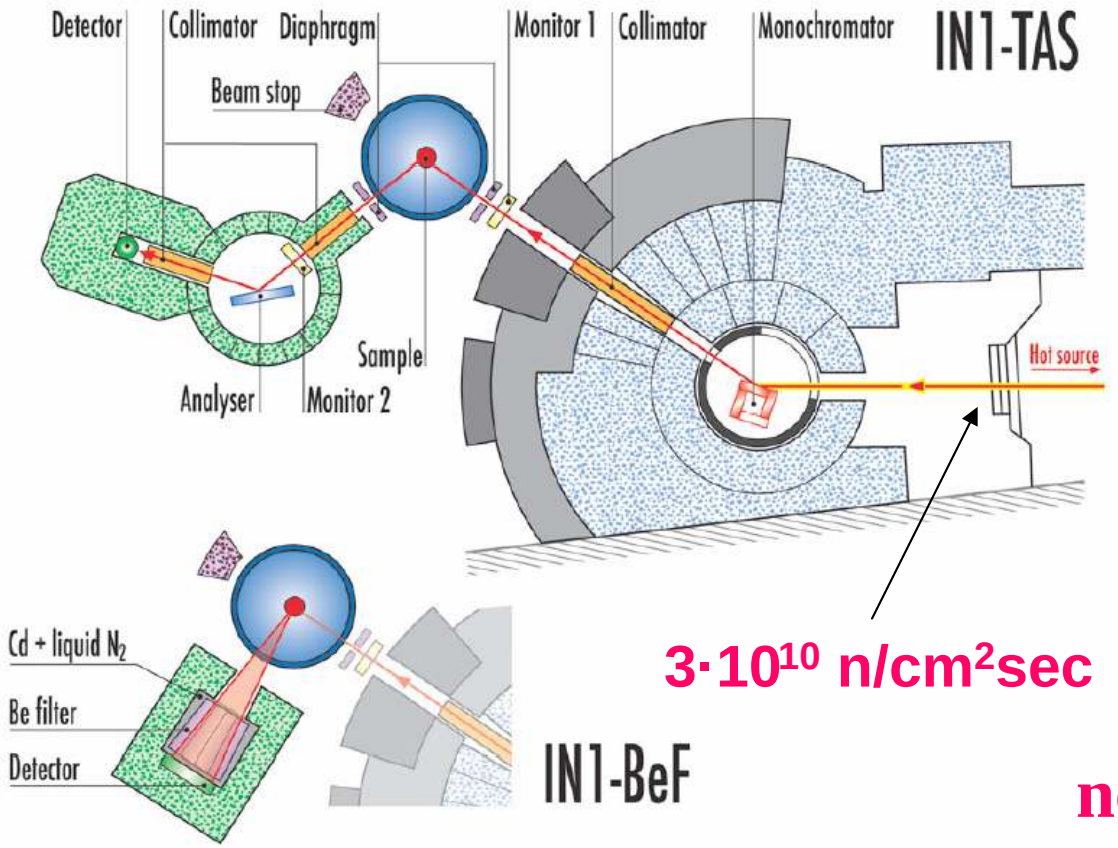
Исследования конденсированных сред с помощью «горячих» нейтронов

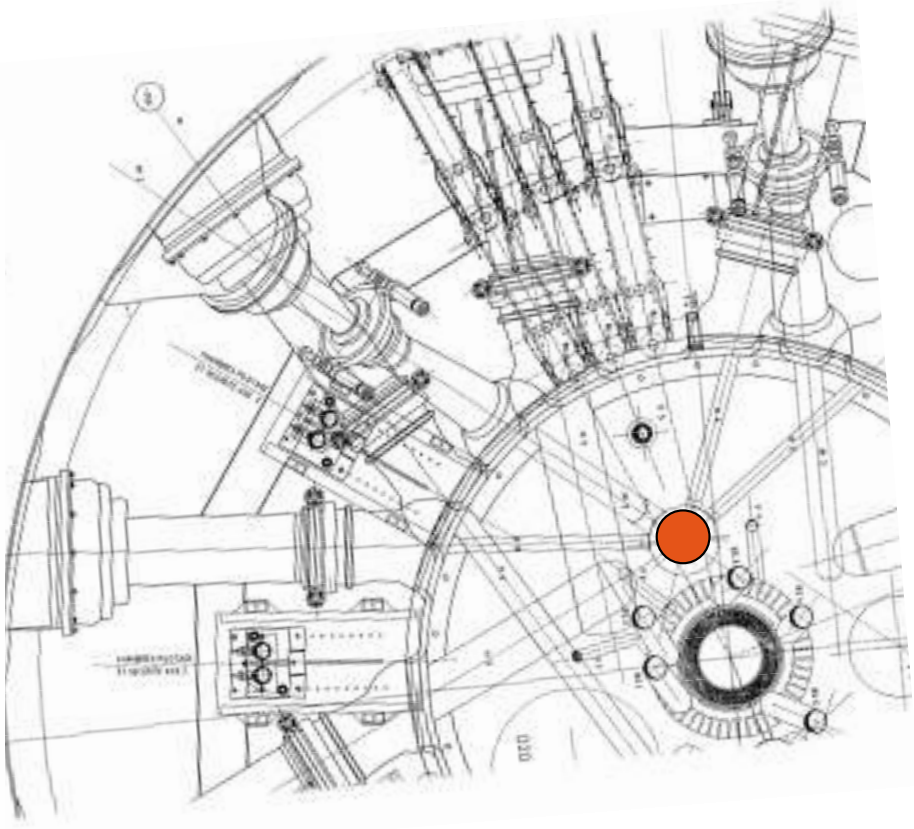
IN1: hot-neutron spectrometer



“Hot Source”: graphite at 2200 ºC

(heated by radiation from working fuel element)



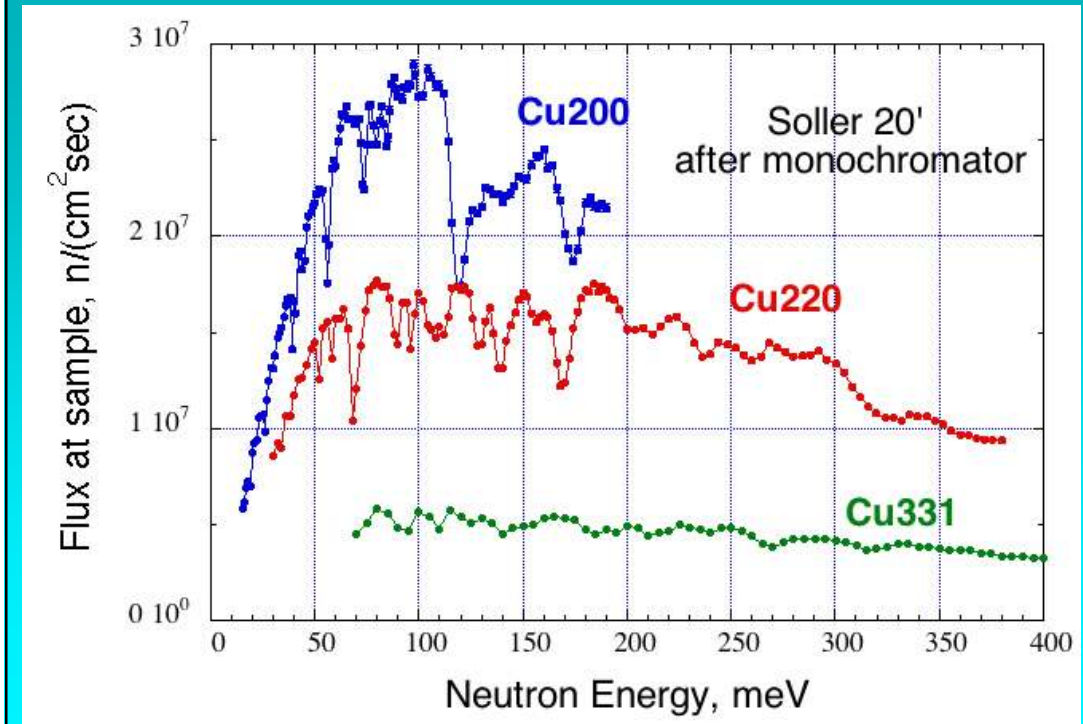


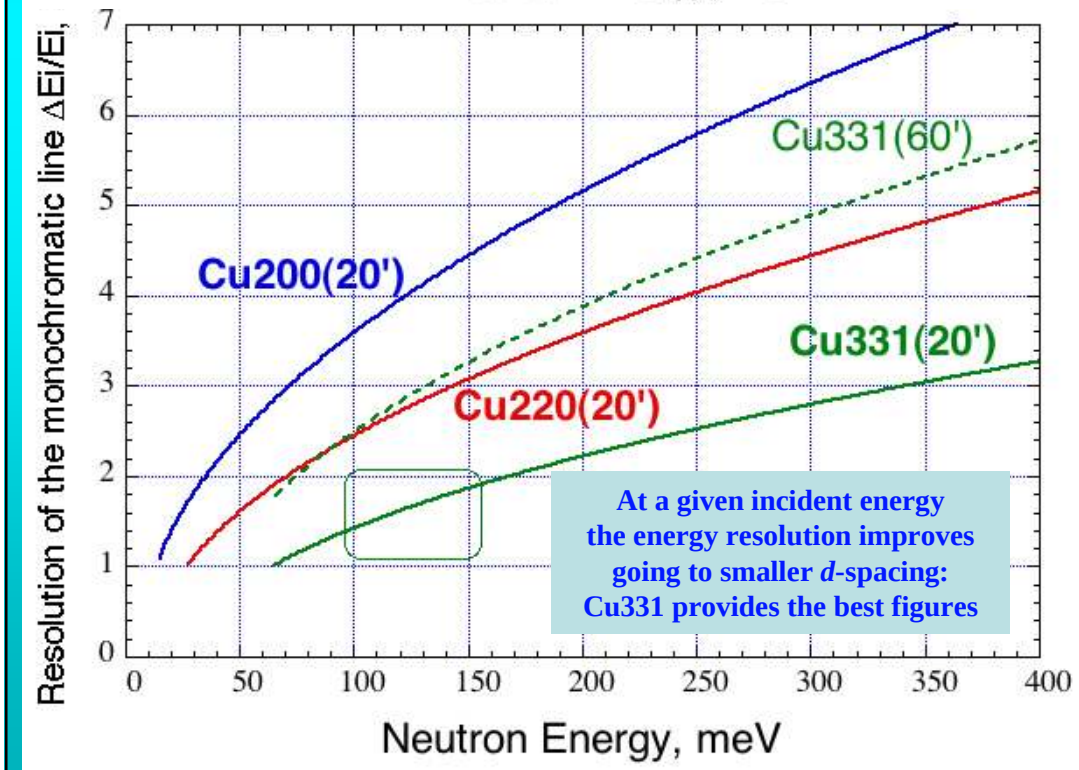
$3 \cdot 10^{10}$ n/cm^{2}sec

Spectrum enriched with neutron energies 100-500 meV

Three monochromators (all in *reflection*): **Cu200**, **Cu220**, **Cu331**

Slit collimators: 20’, 30’, 40’, 60’ ***Boron-coated blades***





Monochromatic flux is reduced for the reflecting crystal planes with high Miller indices:

d_{200}= 1.807 Å
d_{220}= 1.278 Å
d_{331}= 0.829 Å

$$\Delta E_i / E_i = 2 \cdot \cot(\theta_M) \cdot \Delta\theta_M$$

$$\cot(\theta_M) \approx 1/\sin(\theta_M) \sim d_{HKL} \cdot \sqrt{E_i}$$

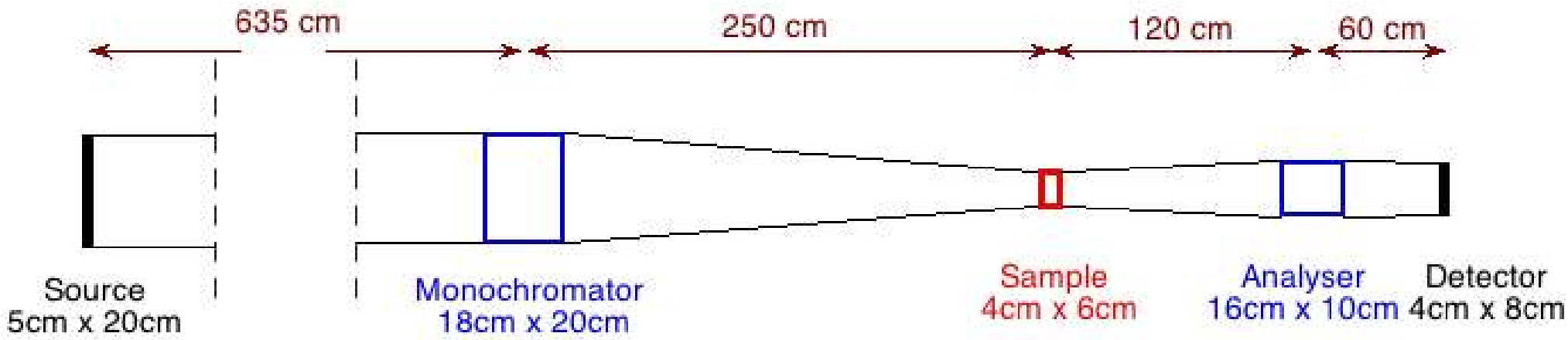
Neutron flux incident on the sample is given by ΔE_i modulated by the reactor spectrum ("thermalised to the source")

$$\Delta\theta_M = \sqrt{\frac{(\alpha_1\alpha_2)^2 + (\alpha_1\eta)^2 + (\alpha_2\eta)^2}{\alpha_1^2 + \alpha_2^2 + 4\eta^2}}$$

Angular dispersion scales approximately linearly with the beam collimations, *e.g.* for $\alpha_1 = \alpha_2 = \alpha$

$$\Delta\theta_M = \alpha/\sqrt{2}$$

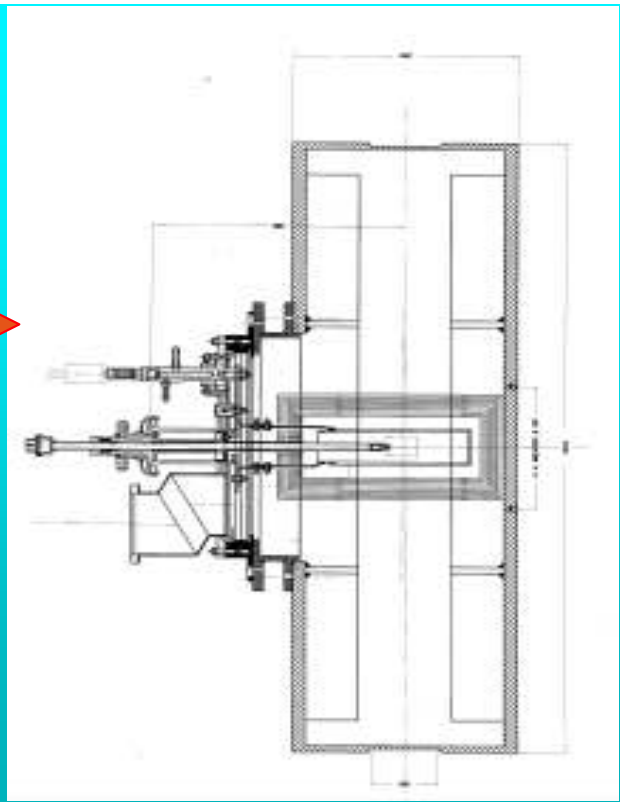
TAS secondary spectrometer



Both monochromator and analyser:

focusing vertically

flat horizontally



IN1-TAS

classical 3-axis scheme
variable incident and
scattered neutron energy

collective excitations
in single crystals

atomic dynamics in
liquids and glasses

IN1-BeF

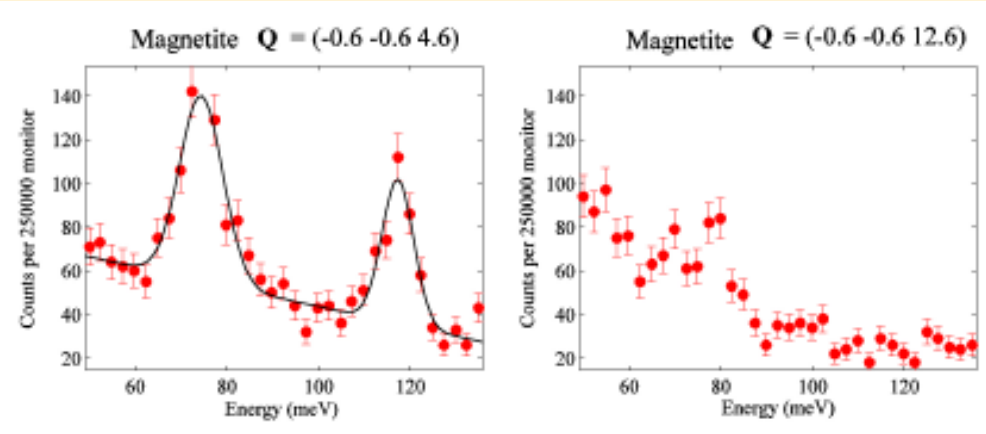
fixed scattered energy

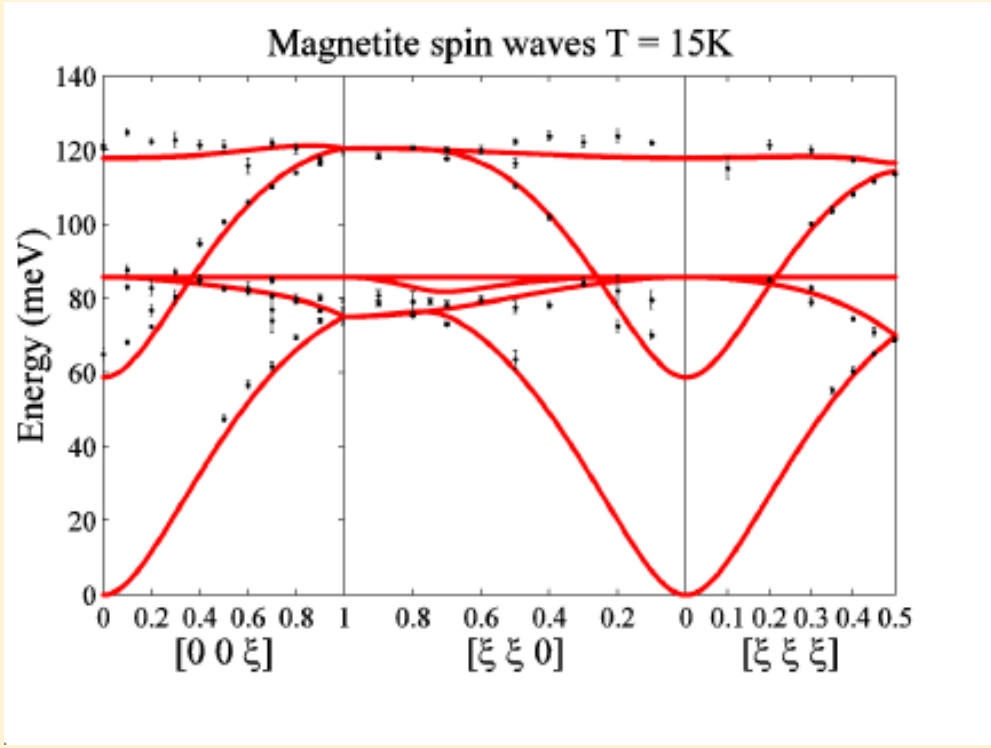
molecular dynamics
H-containing
compounds
Phonon DOS

Examples. TAS results.

Spin dynamics in magnetite Fe_3O_4

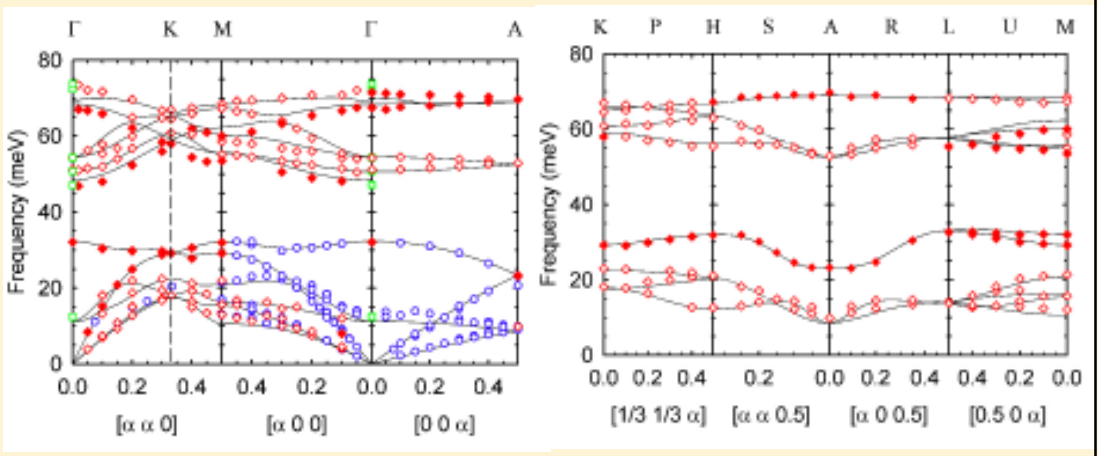
P.Mitchell *et al*





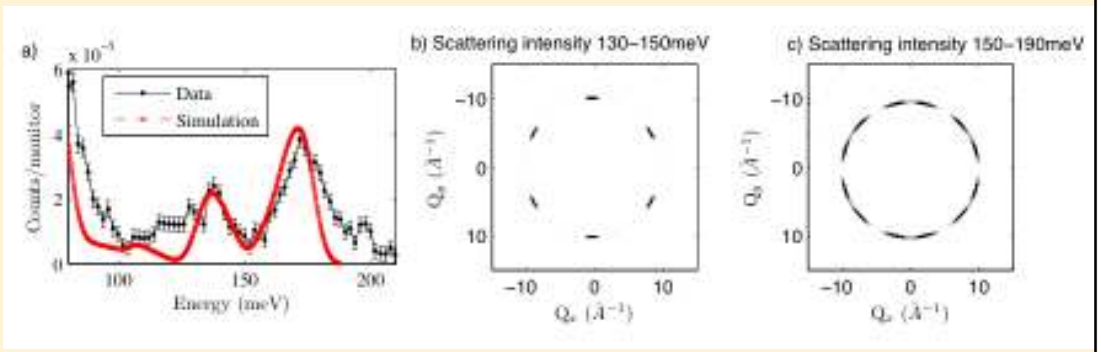
Phonon dispersion in ZnO

J.Serrano *et al*



Vibration spectrum of CaC_6

M.Dean *et al*



Brillouin scattering in liquids investigated with neutron TAS

Collective excitations: long wavelength phonons

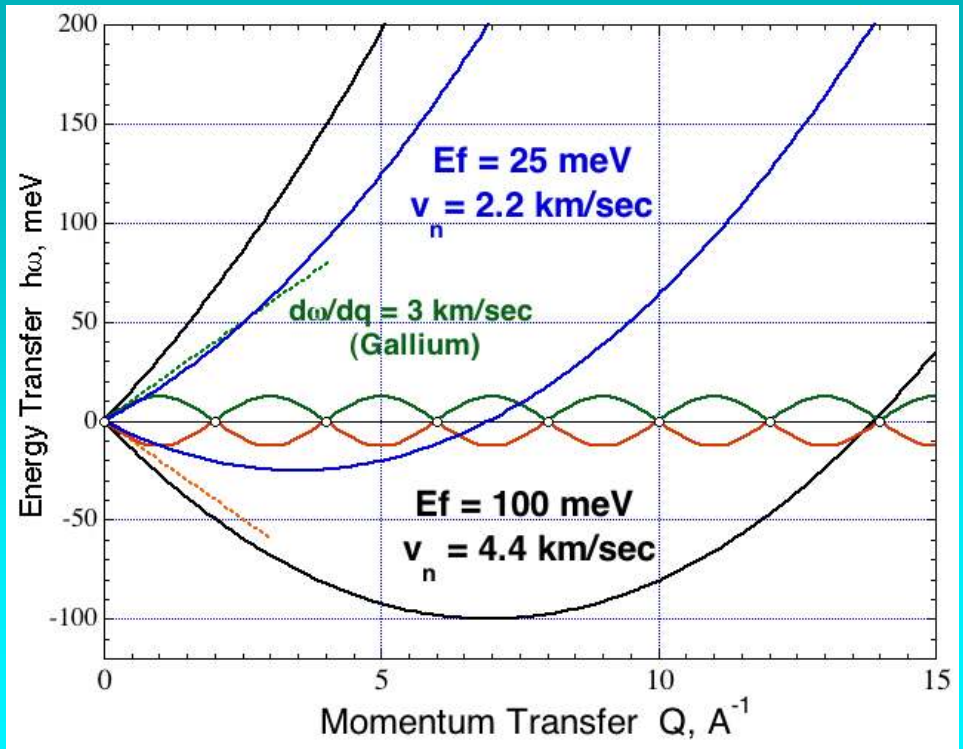
neutron-accessible typical $\boldsymbol{q}$ (0.1 - 1 A^{-1}) and $h\omega$ (1 - 10 meV) ranges are some 2 orders of magnitude higher than in the “classical” light-scattering technique

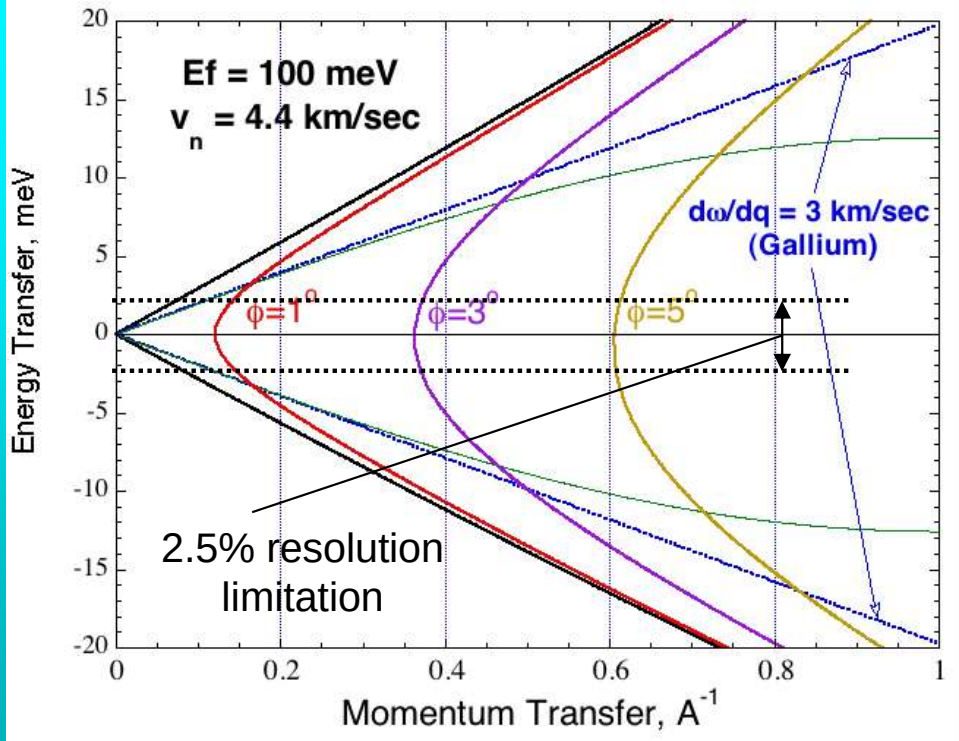
Low-Q experiments (neutron momentum transfer)

Need in very small scattering angles (down to 1 degree)

Restricted accessible (Q, ω) range

Use of “hot” neutrons makes accessible energy transfer range typical for *thermal* vibrations in the limit of low neutron momentum transfers.





For periodic structures (single crystals) neutron energy can be of the order of typical excitation energies $E_i \sim h\omega_{max}$: one can choose BZ ($Q = G + q$ with G≠0)

For liquids $G = 0$ and $Q = q$ is unavoidable

Brillouin scattering = life at small scattering angles: ~ 1 - 10 degrees

$V_n > V_{sound}$ is necessarily required

$V_n \sim 1.5\ V_{sound}$ is a reasonable minimum

as a result E_i (or E_f) >> $h\omega_{max}$ (at BZ/2)

Small scattering angles:

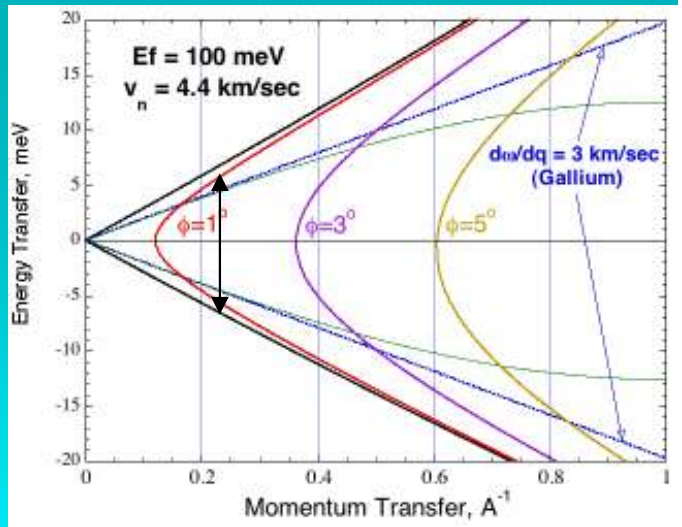
Need in *fine beam collimation* (α) before and after the sample

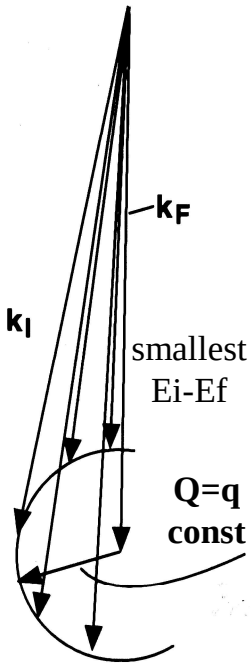
This demand is favorable as well for the energy resolution and maximization of the accessible energy transfer range

But severe decrease in luminosity: count rate ~ α^4

A typical experiment ~10-12 days (5-7 Q-values, 1-2 temperature points)

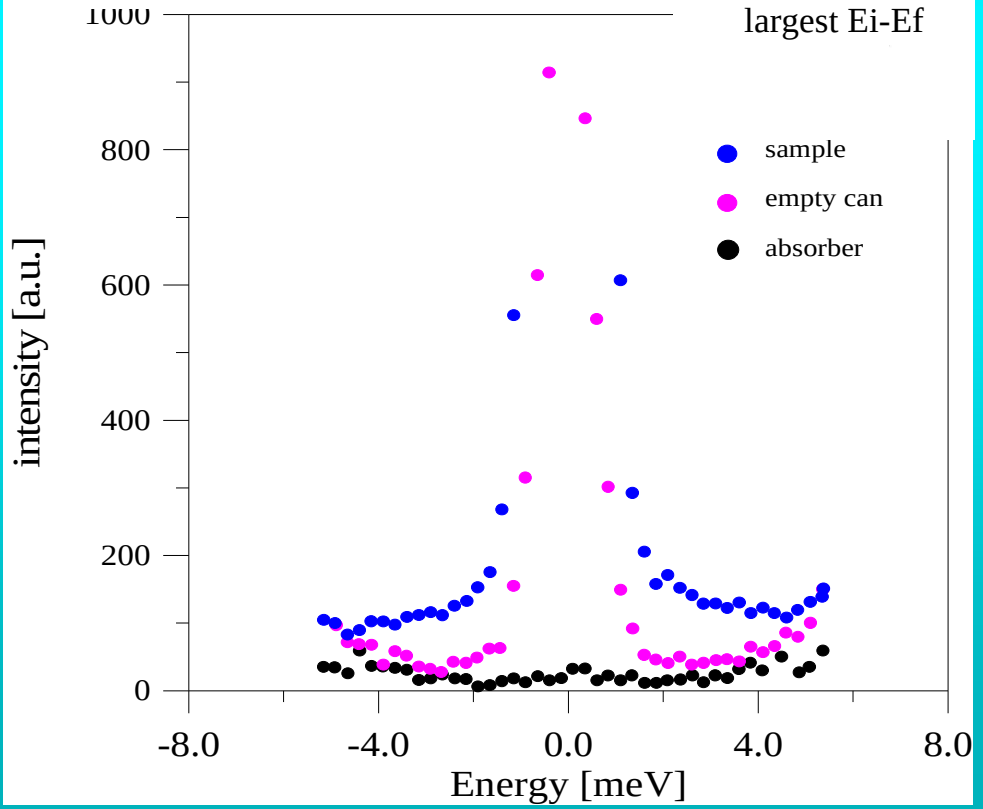
Instrument background is a key issue.



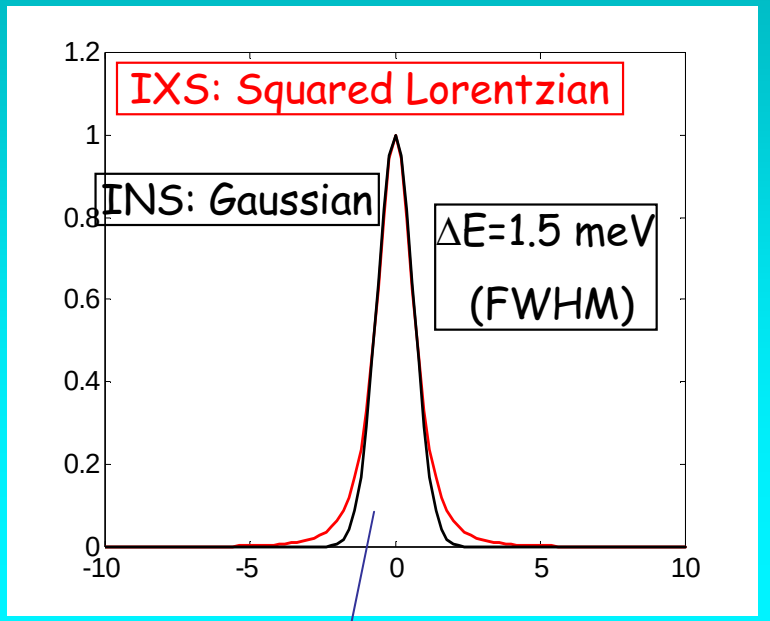


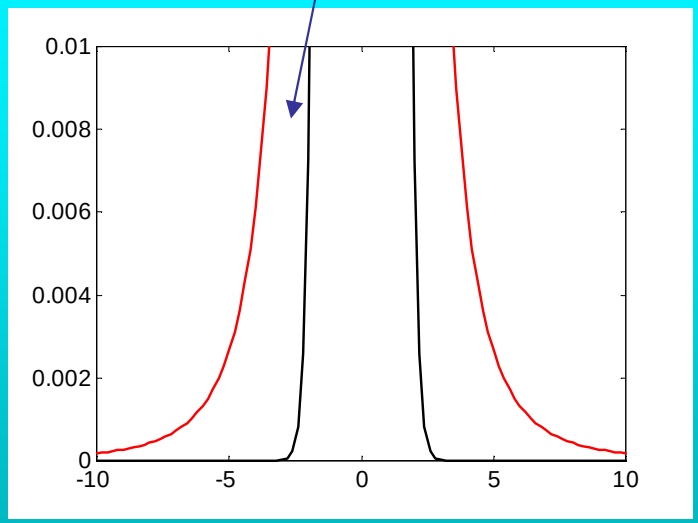
Q-const scan:

From small scattering angles through a larger angle back to small

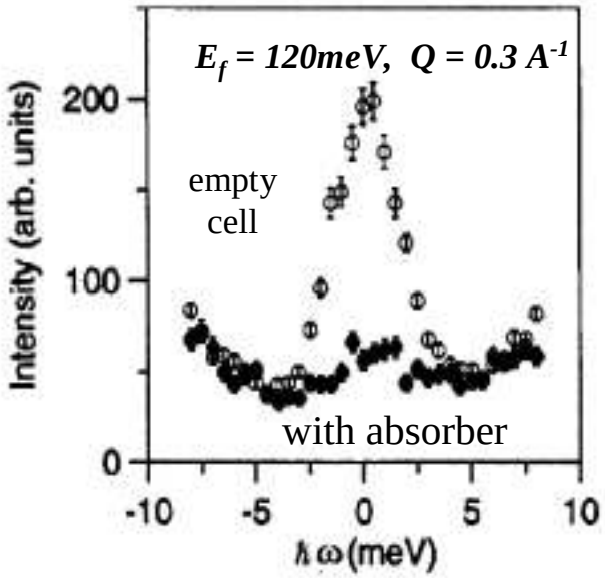


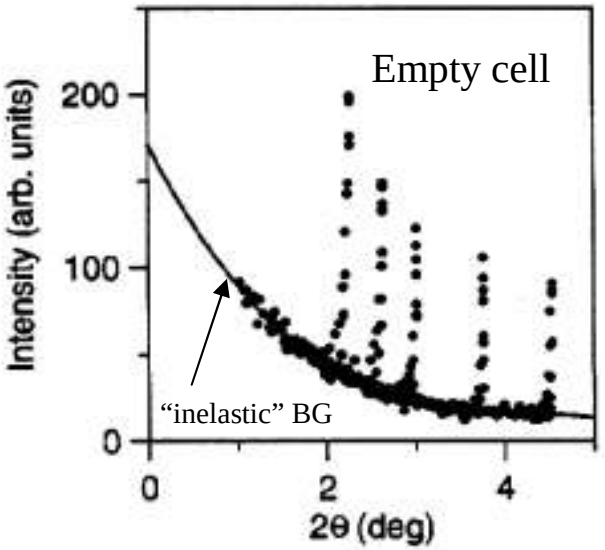
No long tails in resolution:





E [meV]





$$I_{BG} = I_{Cd} + T_S \cdot (I_{empty} - I_{Cd})$$

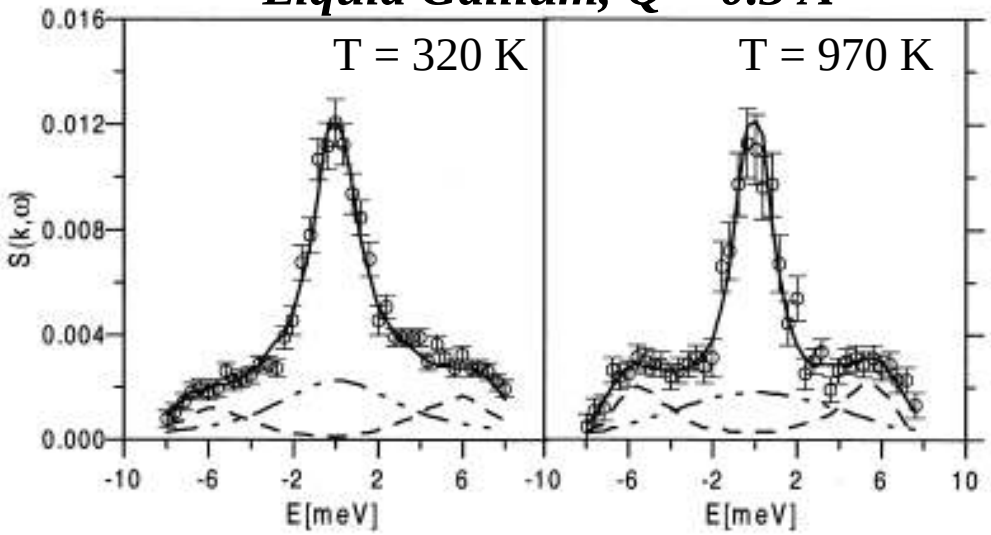
"Own" instrument background is low -

1-5 counts/minute

for an inelastic setting and at scattering angles > ~3 deg

Below these angles the BG is dependent practically on the scattering angle only.

Liquid Gallium, Q = 0.3 A^{-1}



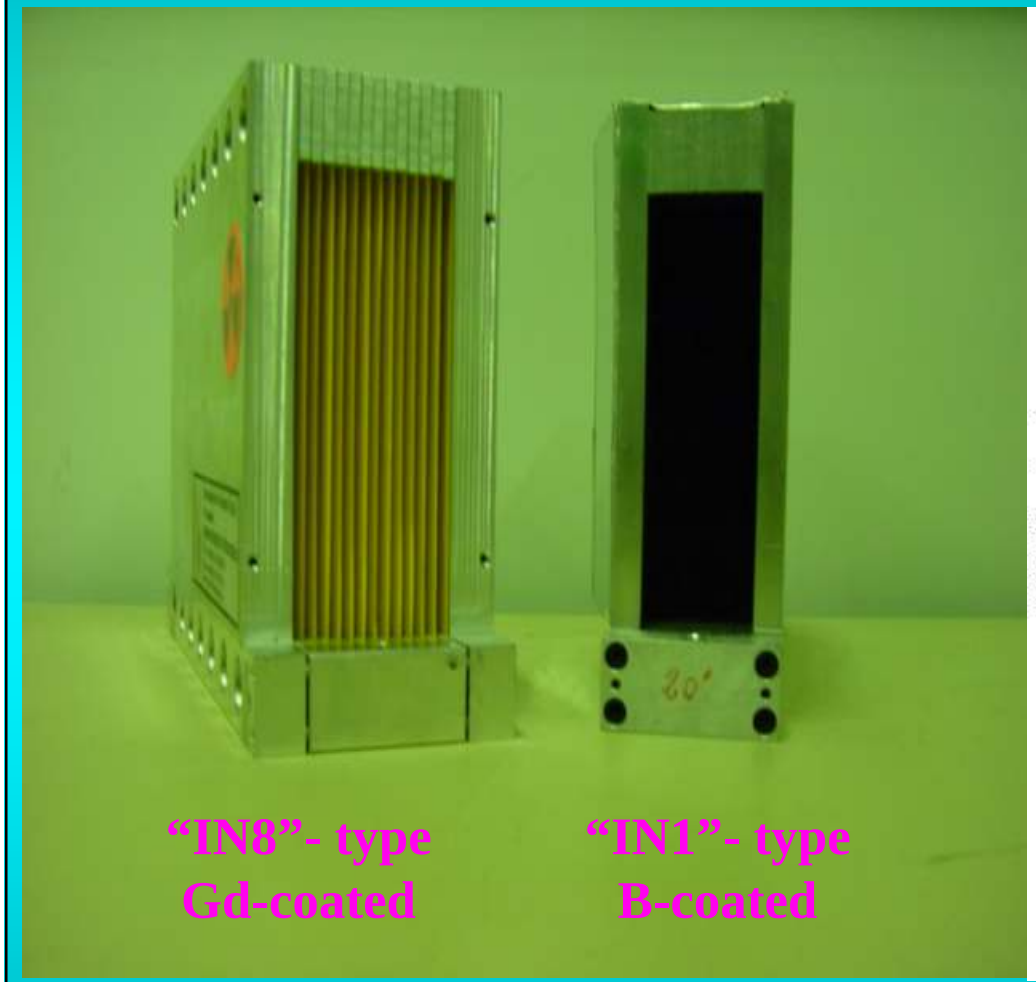
Other particularities of the small-angle experiment

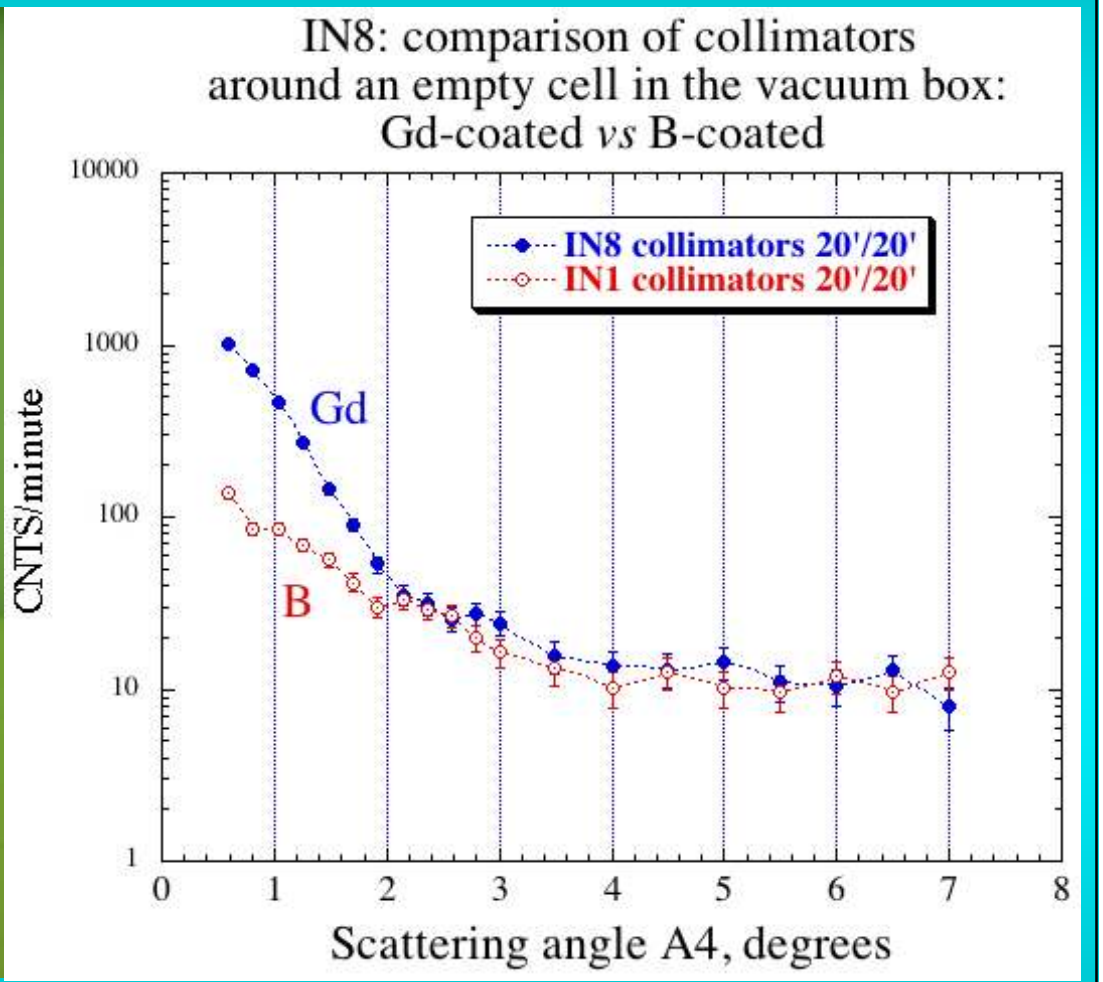
⇒ ***Resolution variation*** **along the scan is important, contrary to the case of "classical" large-Q phonons**

⇒ ***Multiple scattering*** **contribution is outlined - it stems from the (elastic) form-factor at large Q**

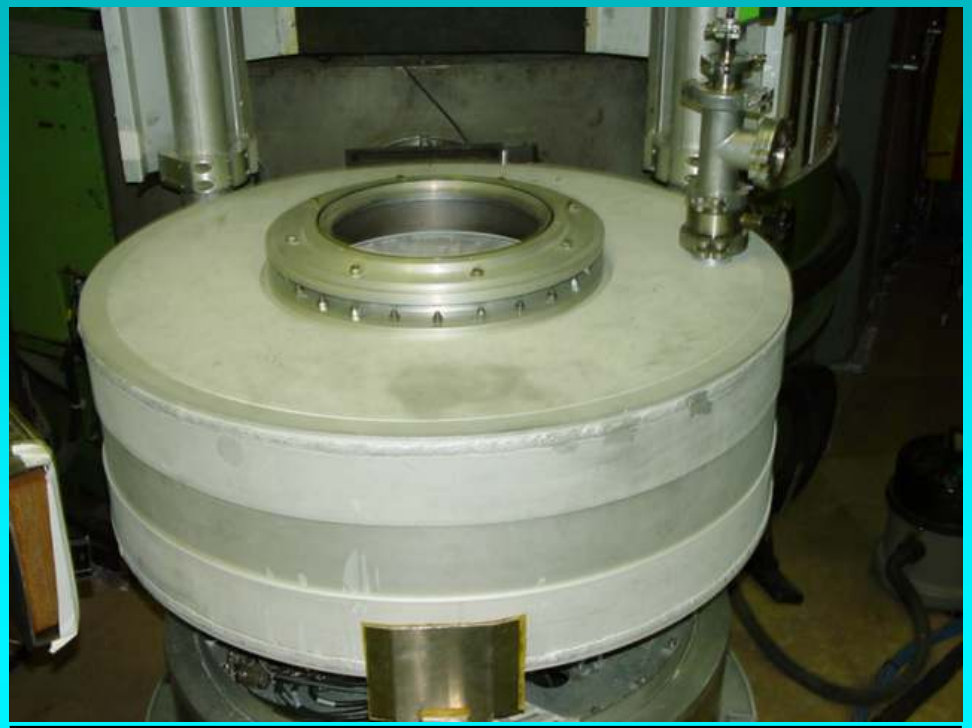
Components indispensable for reduction of Background

Boron coated slit collimators



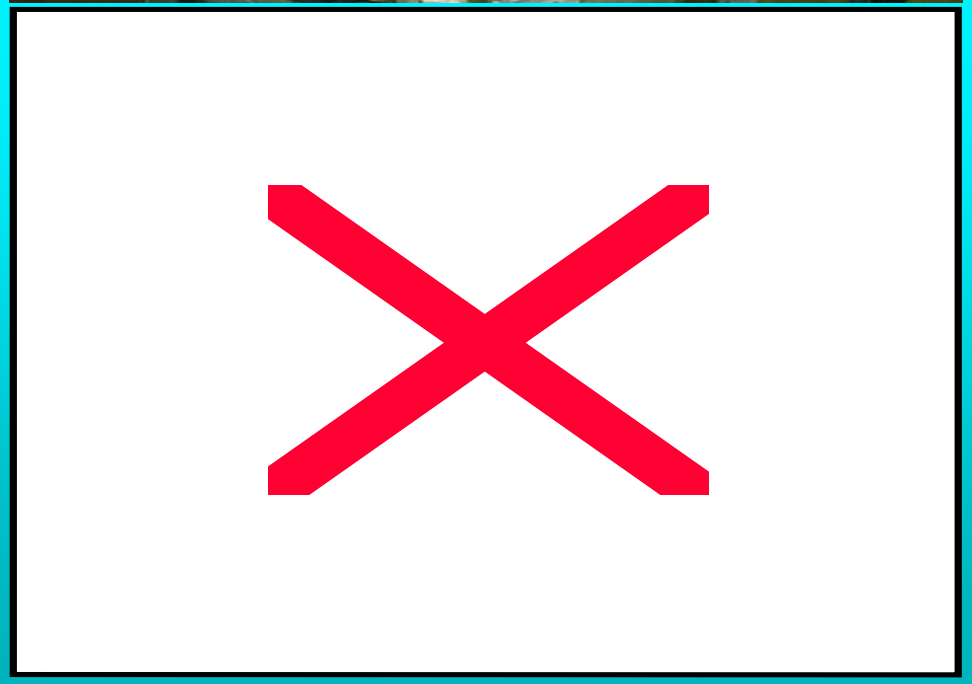


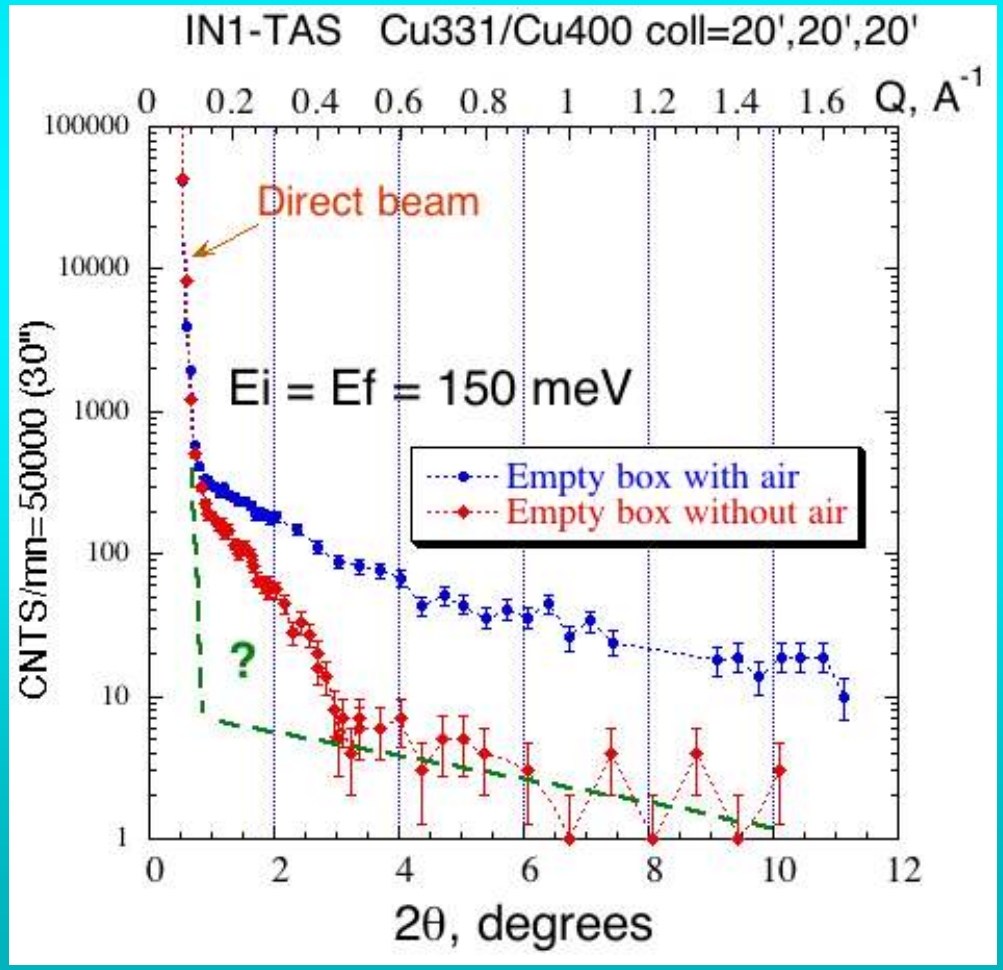
Components indispensable for reduction of Background



Vacuum beam path (1m) around the sample

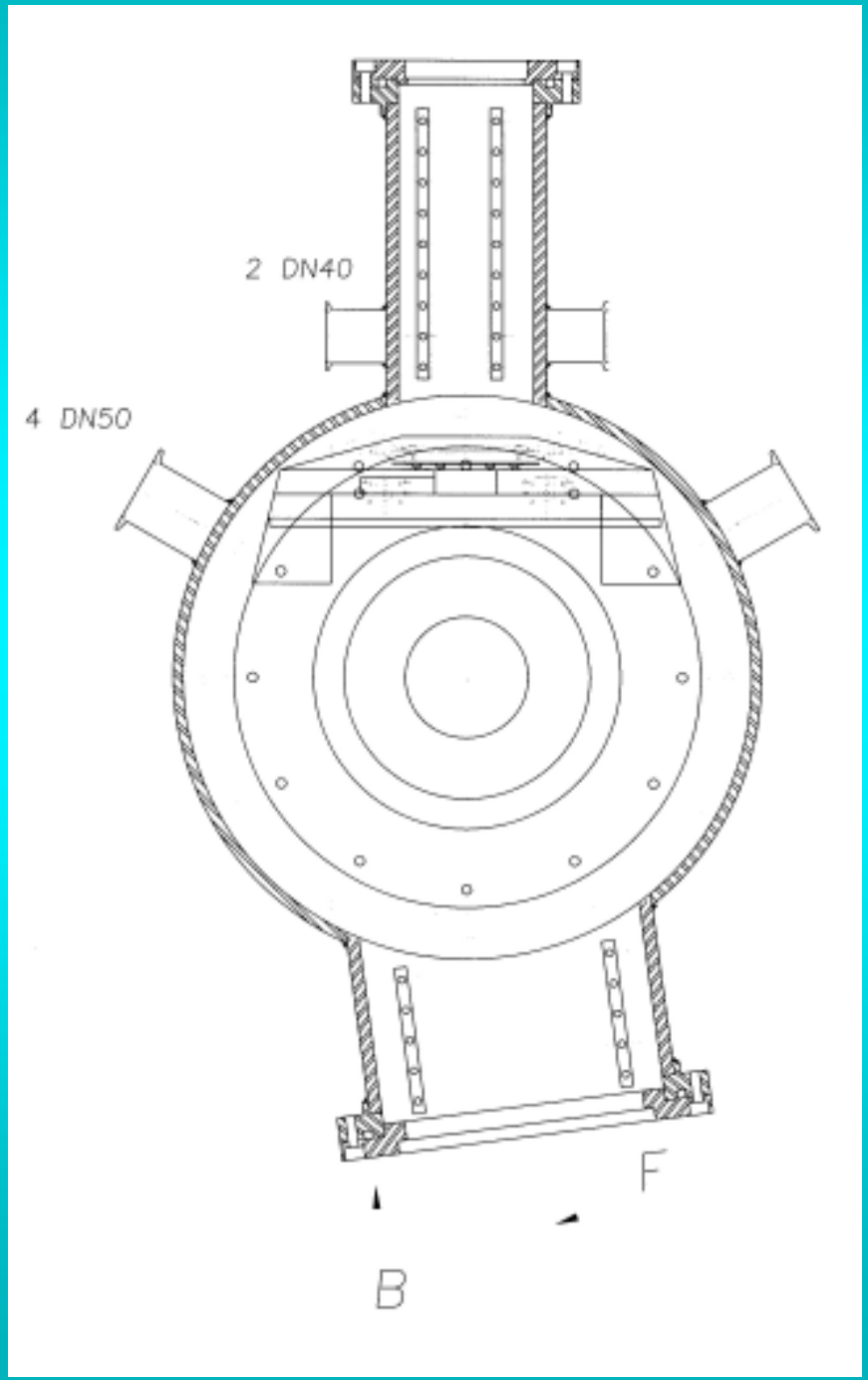
B_4C slits inside the box





A <u>new vacuum box</u> with *single-crystal Silicon* entrance and exit windows has been designed

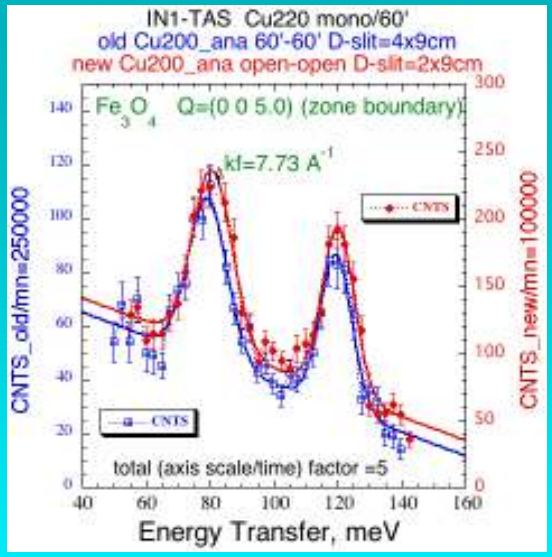
further *decrease in BG* and *lower scattering angles* are expected to be accessible

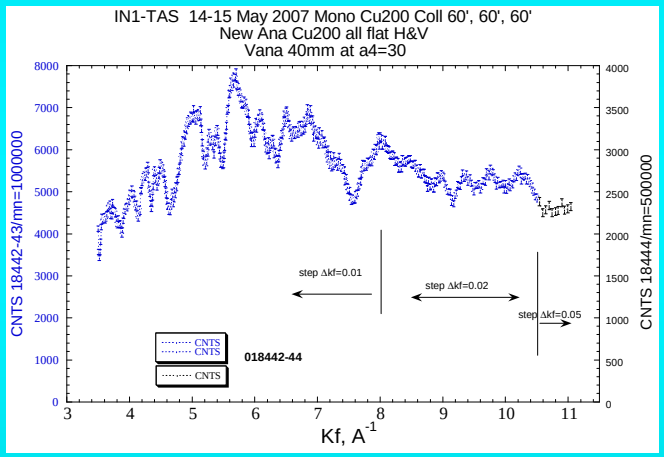


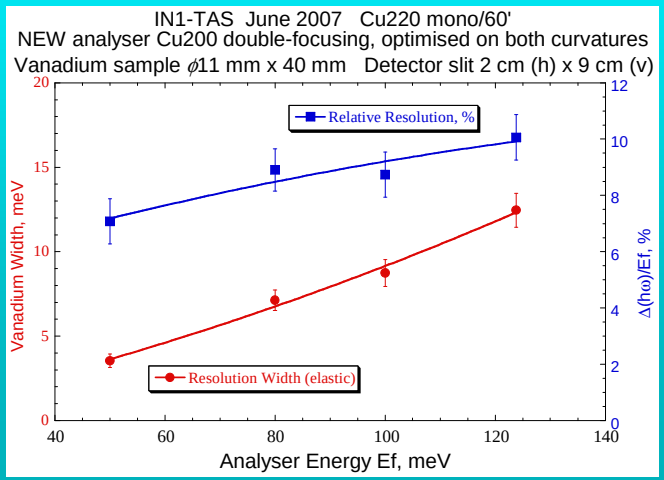
New double-focussing Cu200 analyser for IN1-TAS

The gain factor of ~2 for the Brillouin scattering experiments, when operated flat horizontally, due to: *crystal quality, reflectivity and mosaicity*

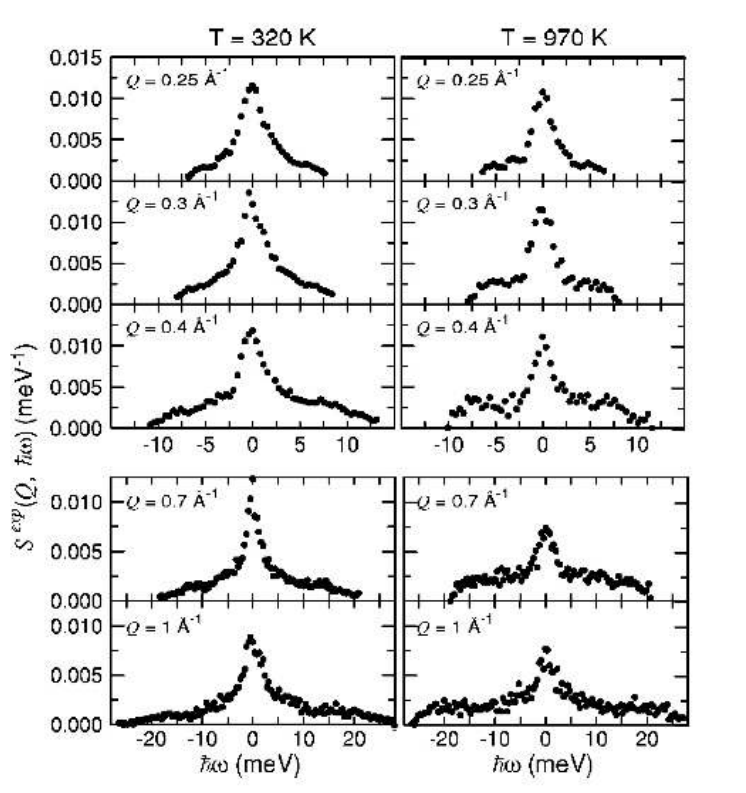
Supplementary gain due to horizontal focussing amounts to a factor of 2.5 -3.5 (total factor of 5 - 7)







Collective dynamics in liquid Ga

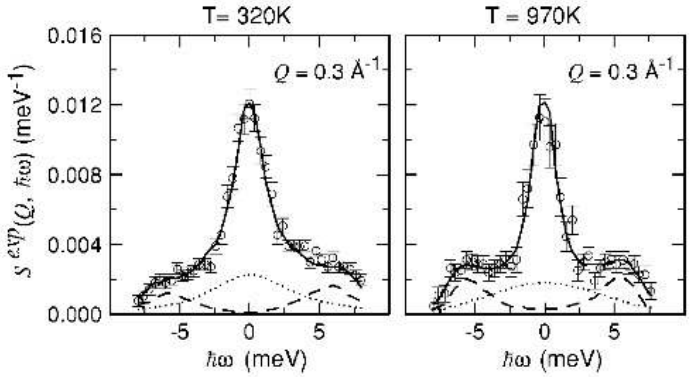


$$S_{qe}(Q,\omega) = \frac{\hbar\omega/k_B T}{1-\exp(-\hbar\omega/k_B T)}\left[\frac{a_0(Q)}{\pi}\frac{\Gamma_0(Q)}{\omega^2+\Gamma_0^2(Q)} + \frac{a_1(Q)}{\pi}\frac{\Gamma_1(Q)}{\omega^2+\Gamma_1^2(Q)}\right], \quad (2a)$$

$$S_{inel}(Q,\omega) = [n(\omega)+1]a_+(Q)\frac{\Gamma_+(Q,\omega)}{[\omega^2-\omega_+^2(Q)]^2+\Gamma_+^2(Q,\omega)}, \quad (2b)$$

slow (self) diffusion

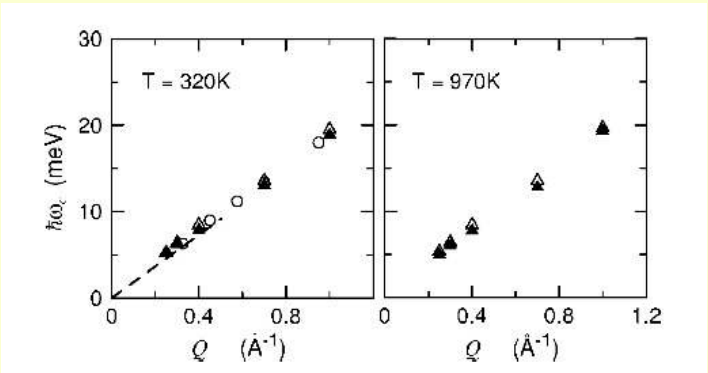
$$\Gamma_0(Q) = \frac{DQ^2}{1+\tau_0 DQ^2},$$

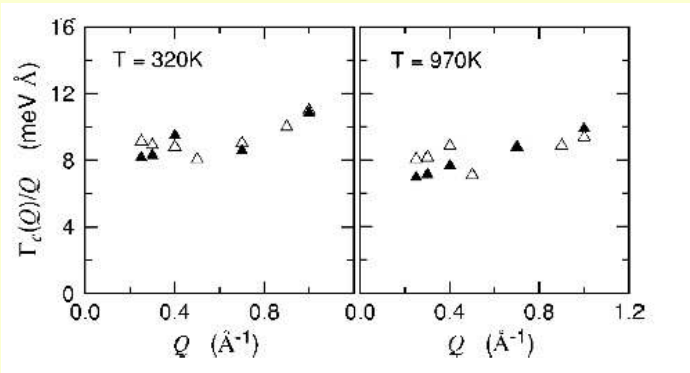


fast relaxation (cages)

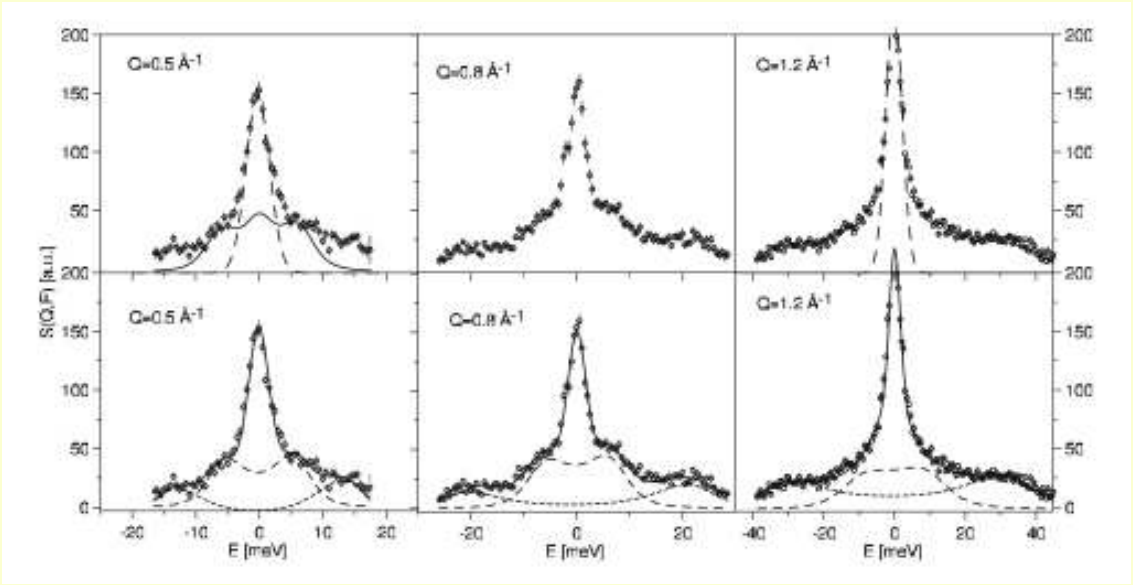
Γ_1 = const(T)
0.22 ps at 320K
0.13 ps at 970K

Collective vibrations: $\omega_c(Q) = c_0 \cdot Q$ ($c_0 > c_{sound}$) $\Gamma_c(\omega,Q) \sim const \cdot \omega \cdot Q$



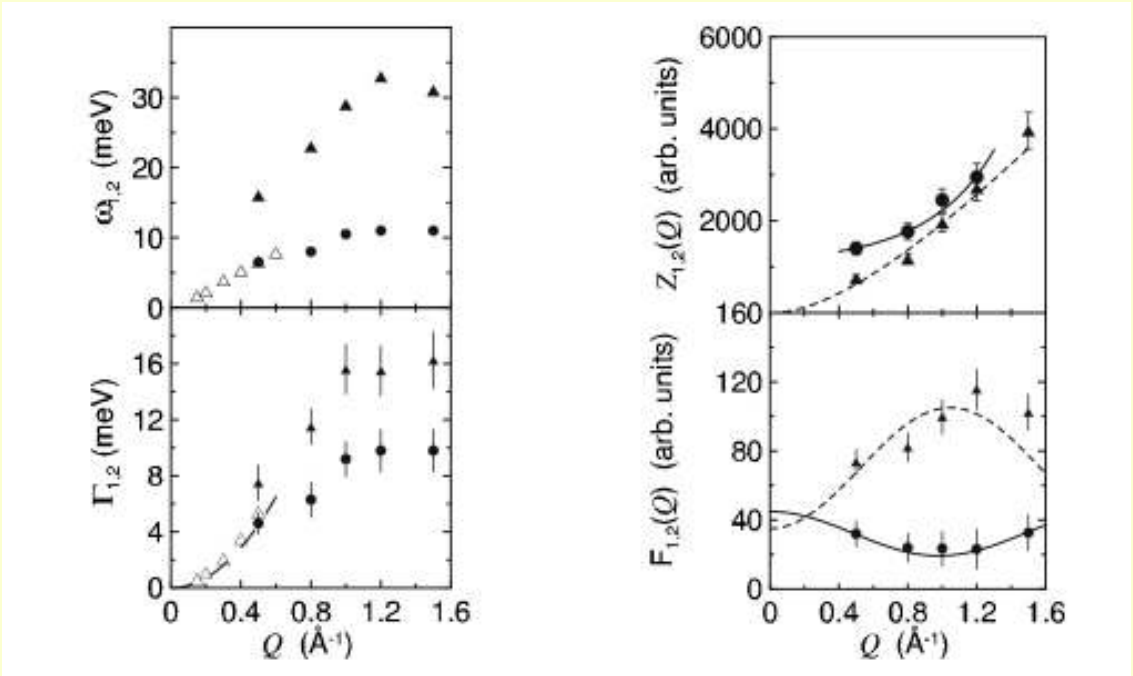


Collective dynamics in binary alloy Li-Bi



Two modes are observed simultaneously

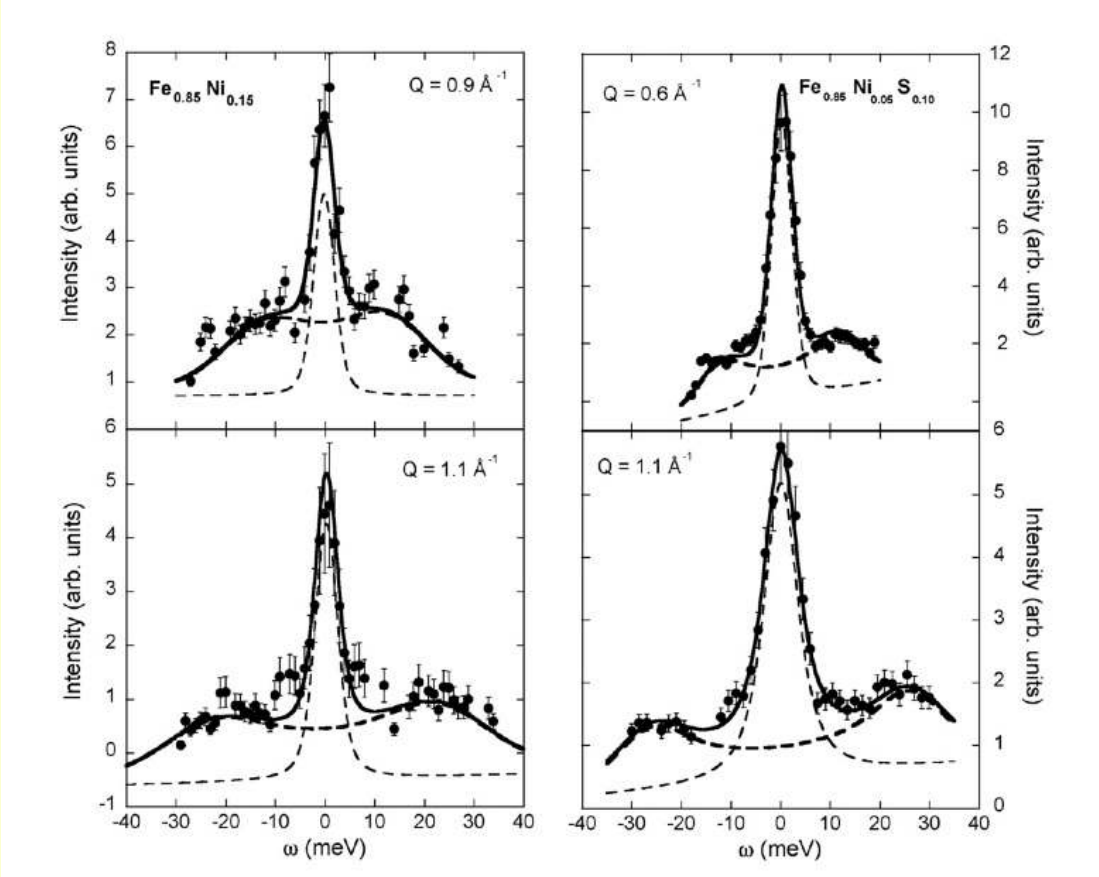
acoustic *vs* **optical**

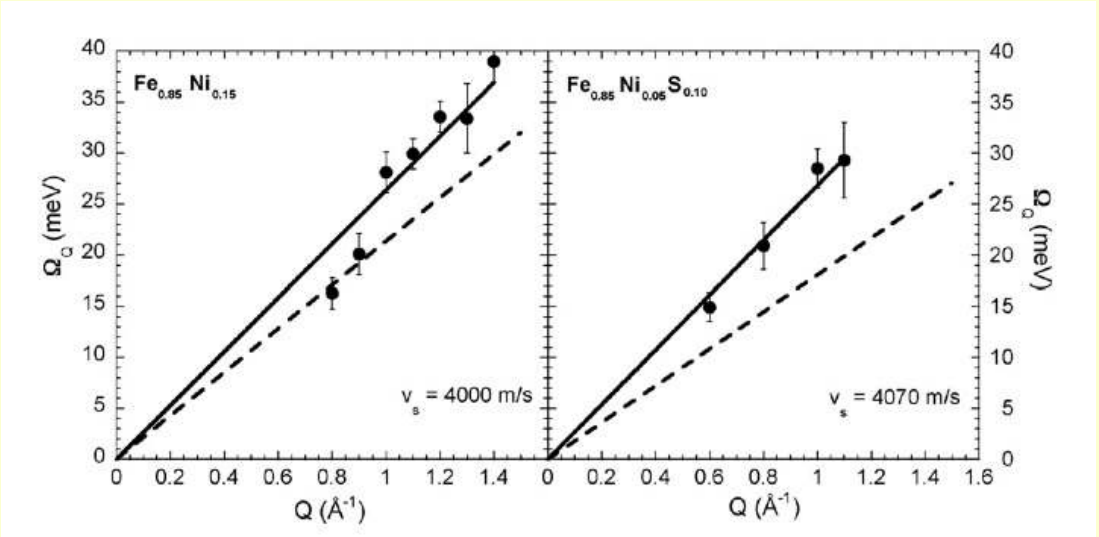


$$Z_{1,2}(Q) = \int_{-\infty}^{+\infty} I_{1,2}(Q,\omega)\mathrm{d}\omega$$

$$\sqrt{Z_{1,2}(Q)\omega_p(Q)/\{[2n(\omega_p(Q))+1]Q^2\}}$$

Molten alloys Fe-Ni and Fe-Ni-S (T ~ 1475ºC)





Only small differences
in the samples $Fe_{0.85}Ni_{0.15}$
and $Fe_{0.85}Ni_{0.05}S_{0.10}$

nano-clustering due to Sulfur
is not observed

IN1-TAS is a powerful instrument for studies of high-energy collective dynamics in condensed matter

For studies of atomic dynamics in liquids and glasses it offers a unique combination of

High Energy Resolution
Low instrument Background
Accessible scattering angles down to 1^{o}

in order to access typical dynamic range with scattering wave vectors Q above ~0.3 A^{-1} and characteristic times below ~10^{-12} s

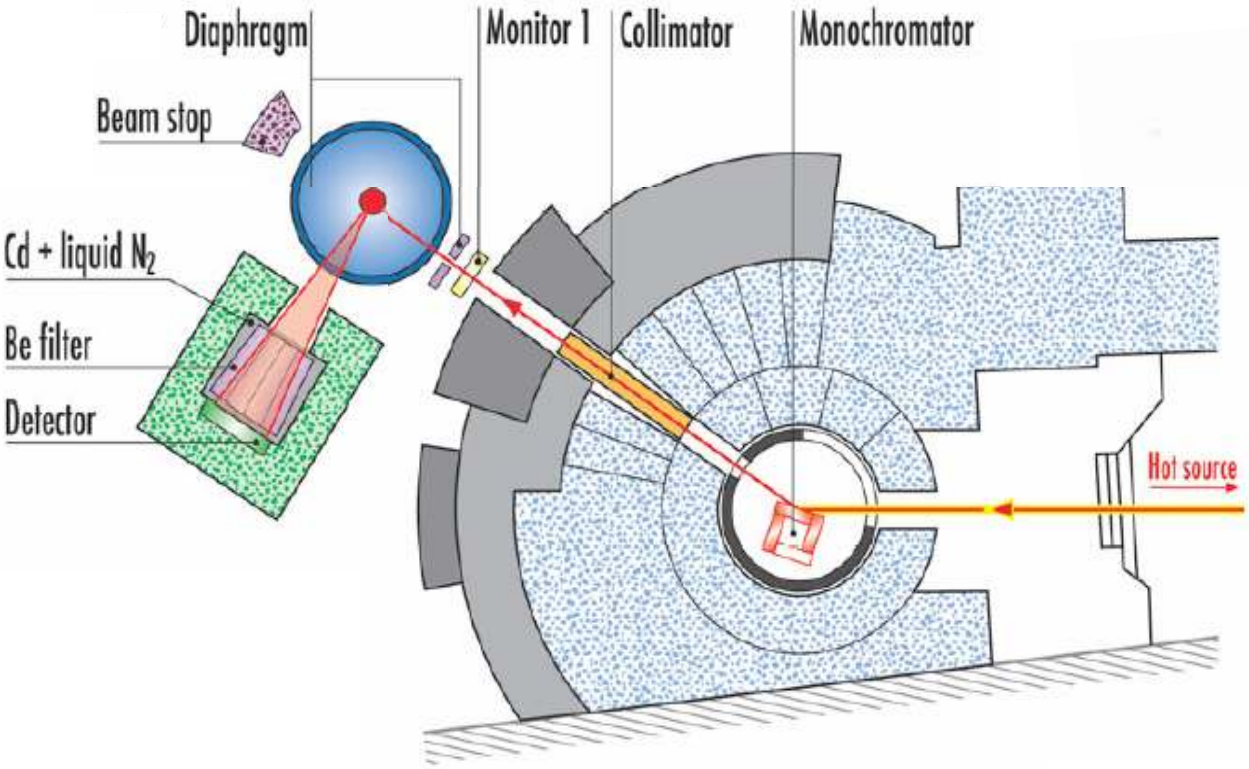
Molecular vibrations in complex compounds studied with Beryllium filter-analyser IN1-BeF

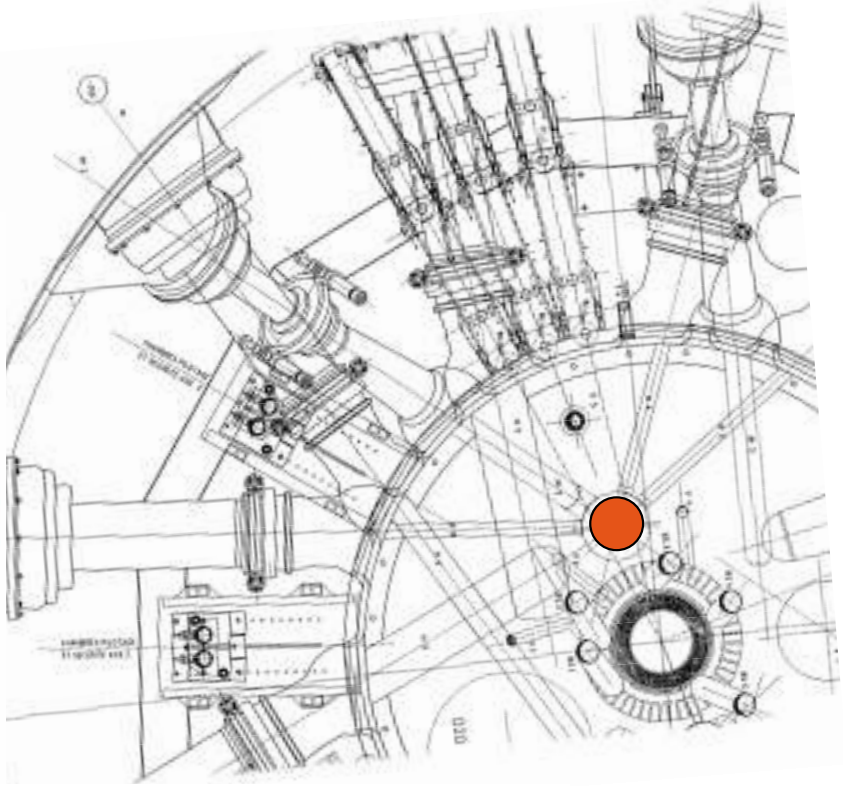
Almost infinite list of materials which can be investigated because *polycrystals* are sufficient to obtain integral characteristics of vibration spectra such as Phonon DOS

however a few experiments with single crystal or oriented (textured) samples brought in an important insight to their lattice dynamics

Recent examples include*: metal hydrides, hydrogen absorbers, compounds with hydrogen bonds, catalysts (Pt-based, Raney Co), molecular zieves (zeolites), nanocrystalline oxides, biological matter, minerals (kaolinite), water in hydrates, amorphous materials *etc.

10 publications in the year 2009





Beryllium-Filter analyser

(fixed energy window for scattered neutrons)

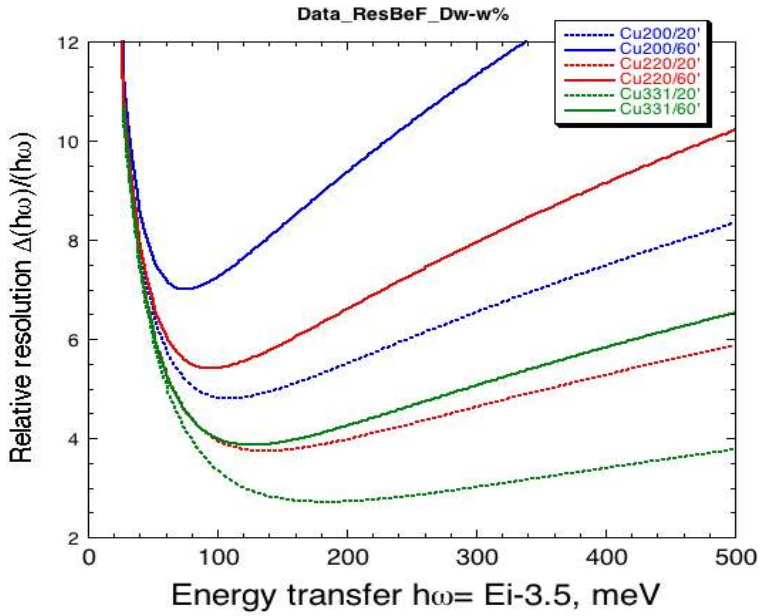
Constant scattered energy E_f = 3.5 meV
Constant resolution ΔE_f = 3 meV

Incident energy E_i varies "step-by-step"
(E_i = 14 - 1000 meV)

Monochromatic line resolution
ΔE_i = 1 meV -> (20-40 meV)
as a function of incident energy, selected monochromator plane and beam collimation

Flexible variation of the energy resolution permits gains in intensity for small or poorly scattering samples

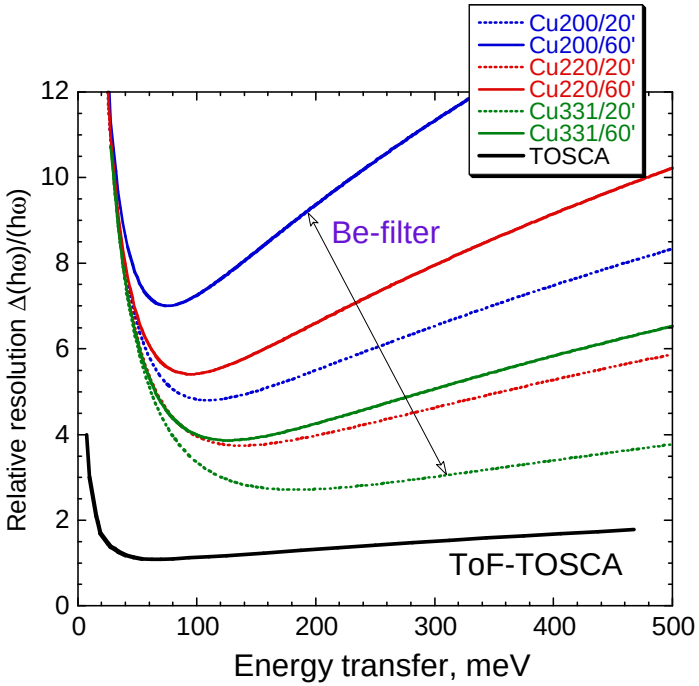
The full energy resolution is a combination of variable ΔE_i and constant ΔE_f

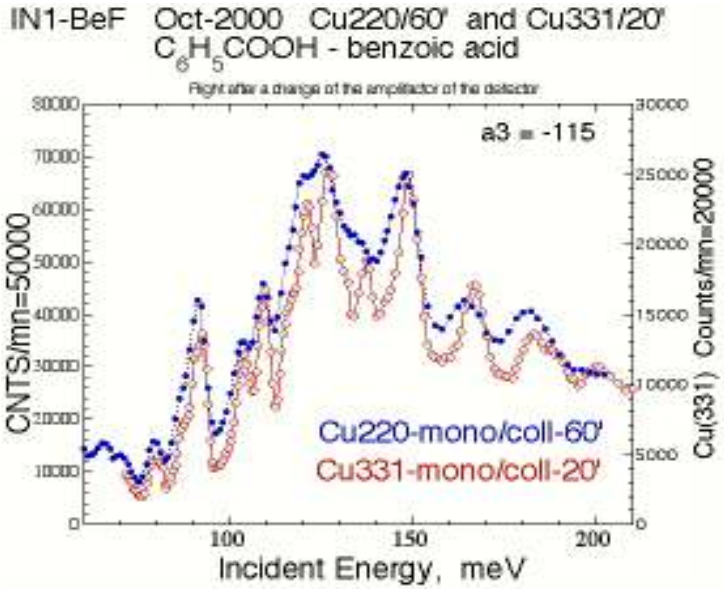


the monochromator contributes to the resolution at high energy transfers

while

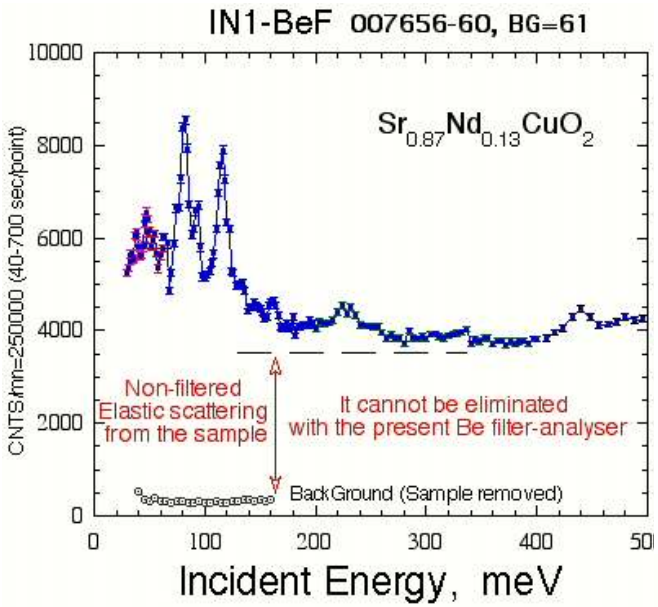
the analyser energy window is important below ~150-200 meV

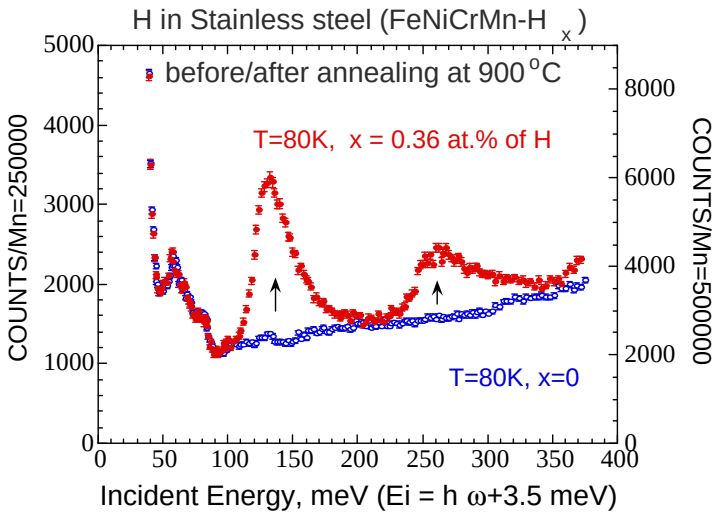




BackGround is not a serious problem for hydrogenated samples:

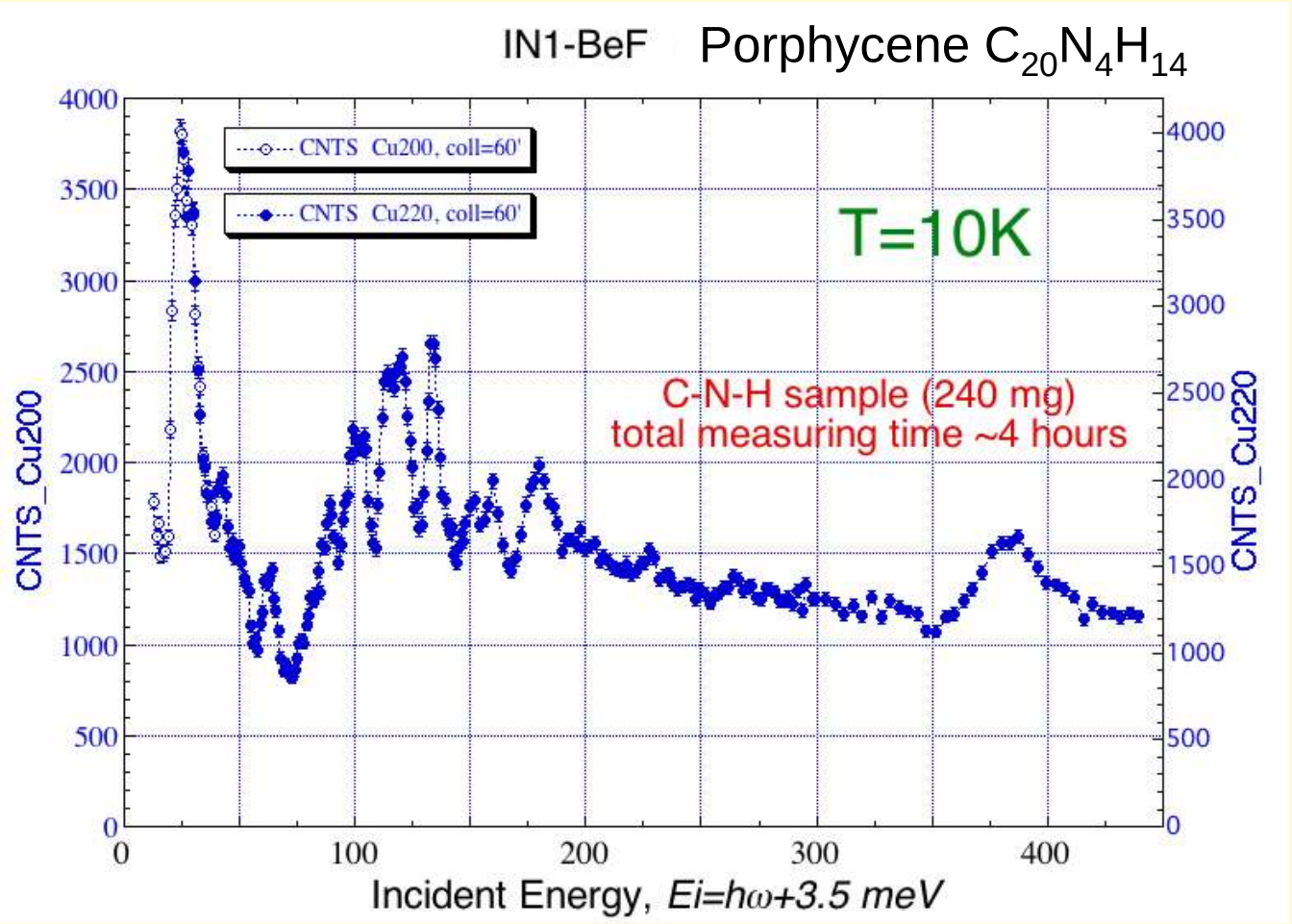
signal = inelastic ~ σ_{sc} /M
BG = elastic ~ σ_{sc}





as many H-atoms as in 50 mm3 of water

Examples of studies with Beryllium-Filter spectrometer



Inelastic spectra in complex compounds serve to refine or resolve structure

High luminosity: *small samples are possible*

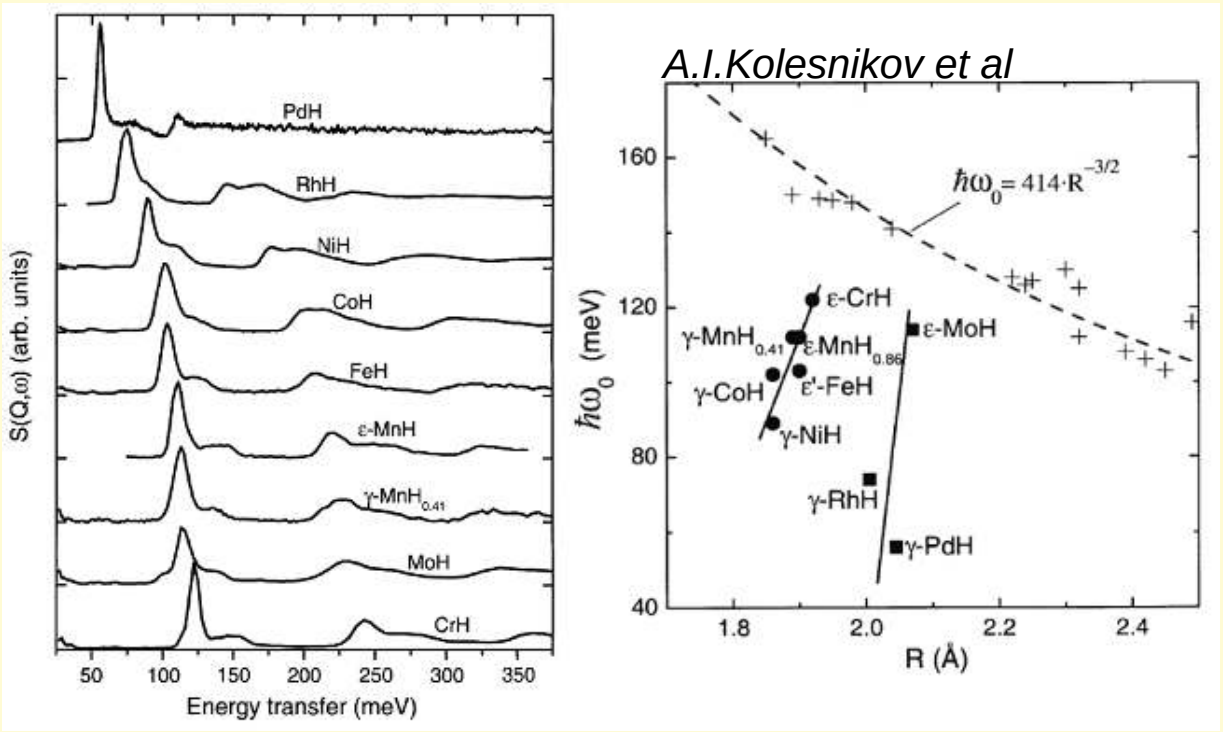
Examples of studies with Beryllium-Filter spectrometer

High luminosity: *small samples are possible*

An example - mono-hydrides of transition metals
prepared at extreme conditions
and metastable at ambient Temperature and Pressure
(V.E.Antonov et al, ISSP Chernogolovka)

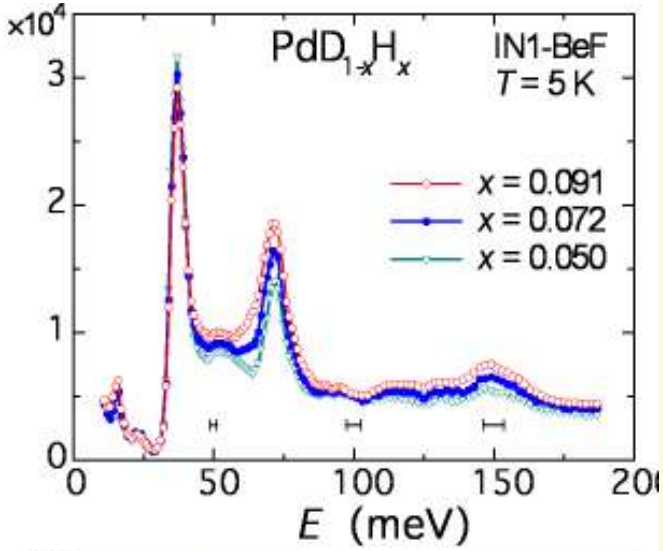
Typical weight of the samples - a few hundred milligrams
they contain a *few milligrams* of Hydrogen

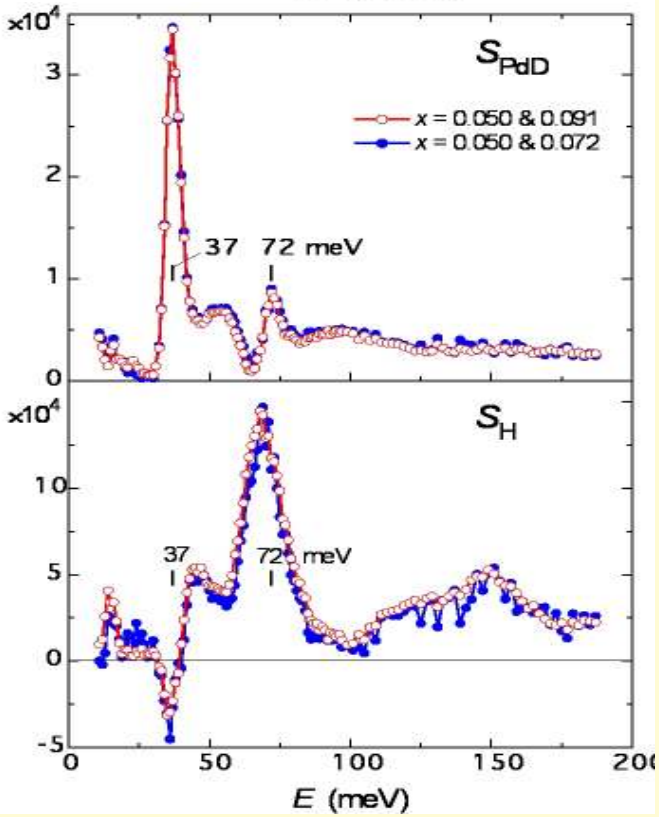
Examples of studies with Beryllium-Filter spectrometer



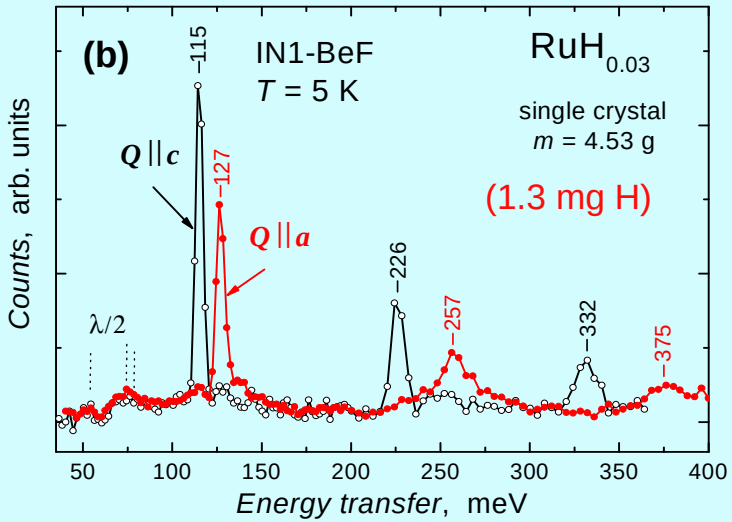
A.I.Kolesnikov et al

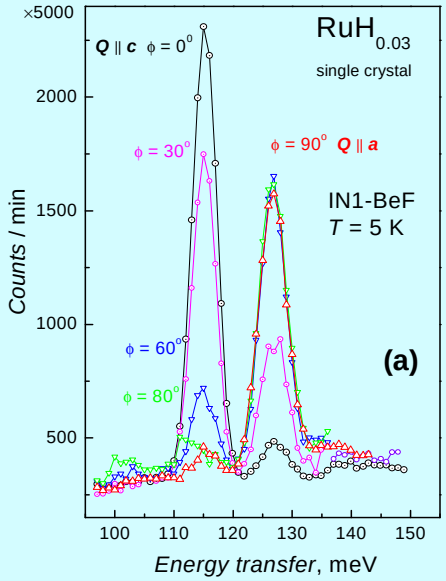
M.A.Kuzovnikov et al





V.E.Antonov et al





Examples of studies with Beryllium-Filter spectrometer

Carbon (nano-)phases

from the neutron scattering point of view
much more material is needed than for hydrides:

the integral characteristics of scattering power is

$$\frac{\text{Scattering cross-section}}{\text{atomic mass}}$$

by a factor of 100

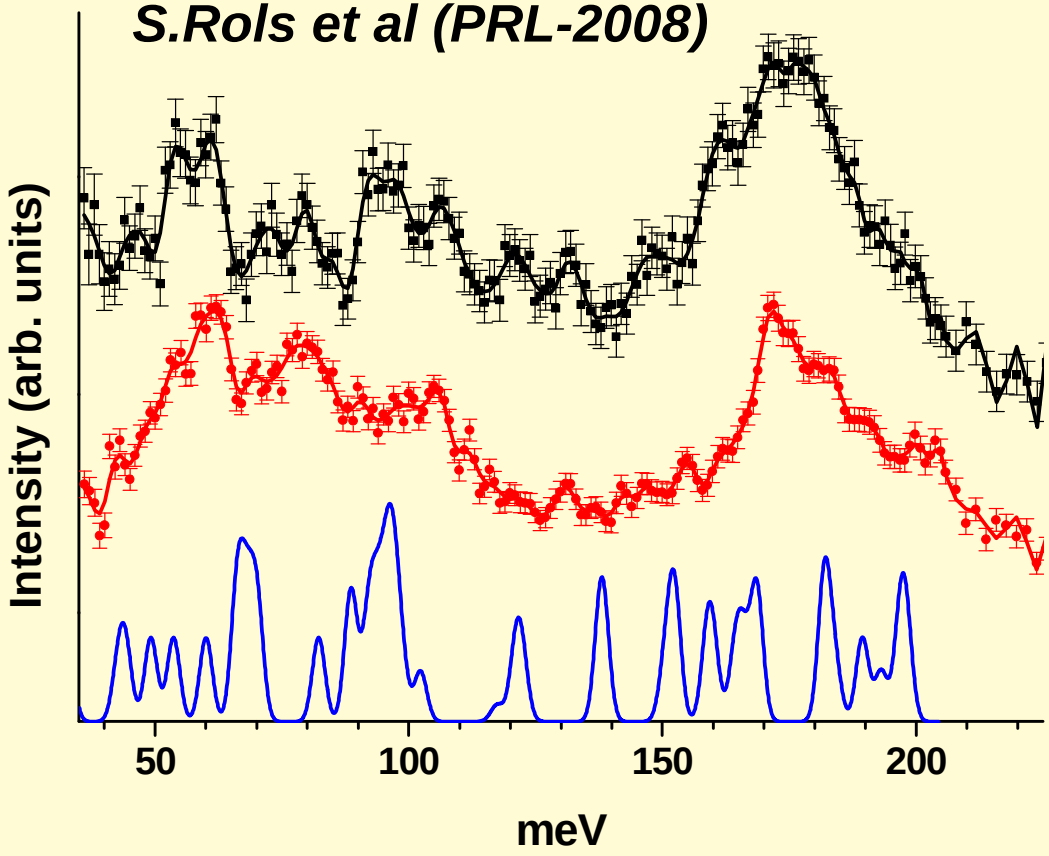
Carbon is "worse" than Hydrogen
in an inelastic neutron scattering experiment

taking into account larger energy spread of vibration spectrum in C-phases,
a few-hundred-milligram samples are required

Examples of studies with Beryllium-Filter spectrometer

Peapods: 1D C_{60} chains inserted inside SWNT

IN1BeF monomer peapods T=10K
S.Rols et al (PRL-2008)



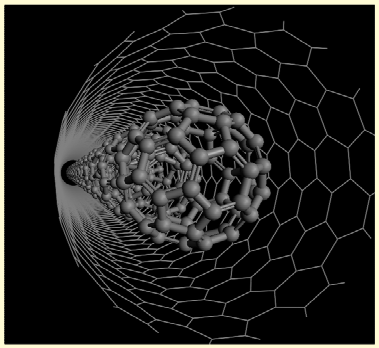
Sample : monomer peapods
Source : H. Kataura (Japan)
Cost : 20000€ (1 month to make and prepare the nanotubes)
650 - 700 mg in the beam

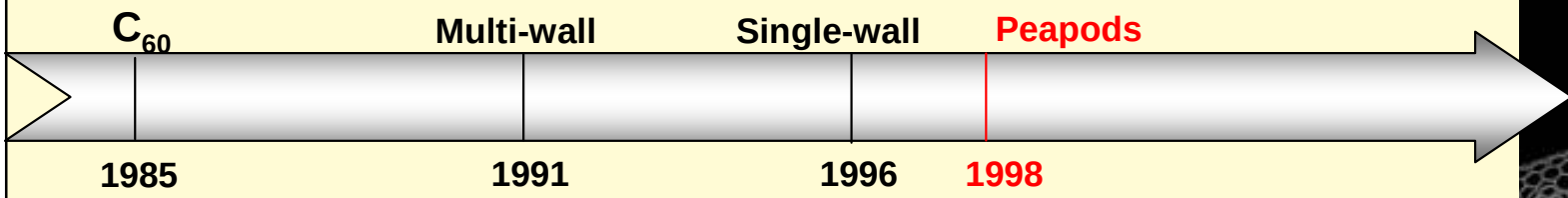
Acquisition time ~ 24h

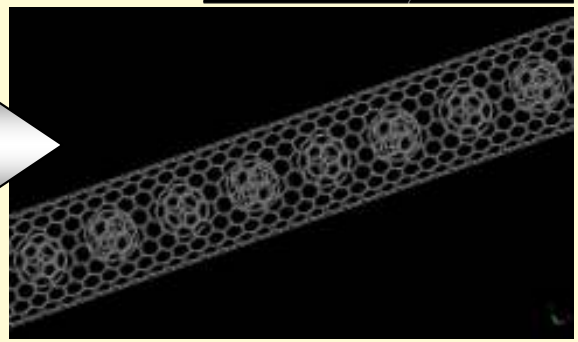
Carbon Nano-Peapods

Single-Wall C-Nanotubes

Simulation C_{60} alone







The instrument sensitivity in a standard experiment can be estimated as
~10^{20} Hydrogen atoms or ~150μg in the sample

As "many" as
in ~2cm^3 of hydrogen gas or
in ~1.5mm^3 of water

For Carbon samples (fullerenes or nano-tubes) the minimal required quantity will be at some 10^{22} C-atoms or 200mg of sample

This is a very good performance not achieved elsewhere

why IN1-BeF is such an exceptional instrument and whether further improvements are possible?

Two main techniques are applied in practice for neutron energy determination:

***Bragg diffraction* in use on TAS (three-axes) spectrometers**
and neutron *time-of-flight* on TOF spectrometers

TAS: continuous beam and a small solid angle (0.1-10·10^{-3} Steradian)

TOF: chopped beam but large solid angle (0.1-0.5 Steradian)

***Actual IN1-BeF*: continuous beam (TAS-like)**
and an intermediate solid angle (0.06 Sterad)

while the outcome (Phonon DOS) is "TOF-like"

This combination gives a key for understanding high luminosity of IN1-BeFilter and a hint to further improvements of the instrument performance

Such improvements are requested because
samples of *novel materials* appear first in small quantities,
moreover in certain applications the *energy resolution* may be not
sufficient and/or the sample-dependent *background* will reduce
the precision of measured spectral intensities

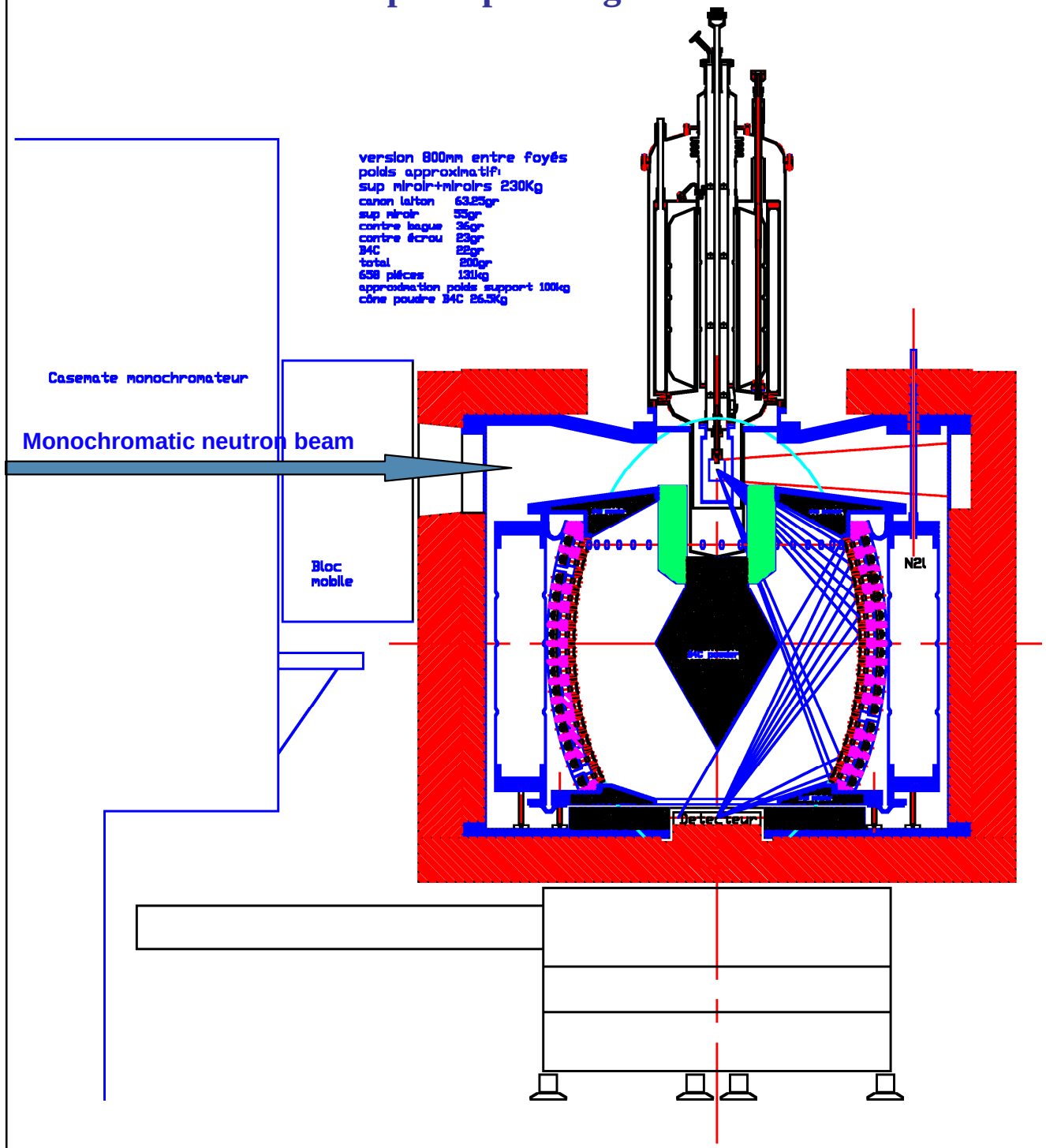
In order to improve the IN1-BeF instrument capabilities for the Phonon DOS studies we have started construction of the new spectrometer called

IN1-LAGRANGE

(LArge GRaphite ANalyzer for Genuine Excitations)

with a different principle of analyzing scattered neutron energy

A vertical cut of the principal design



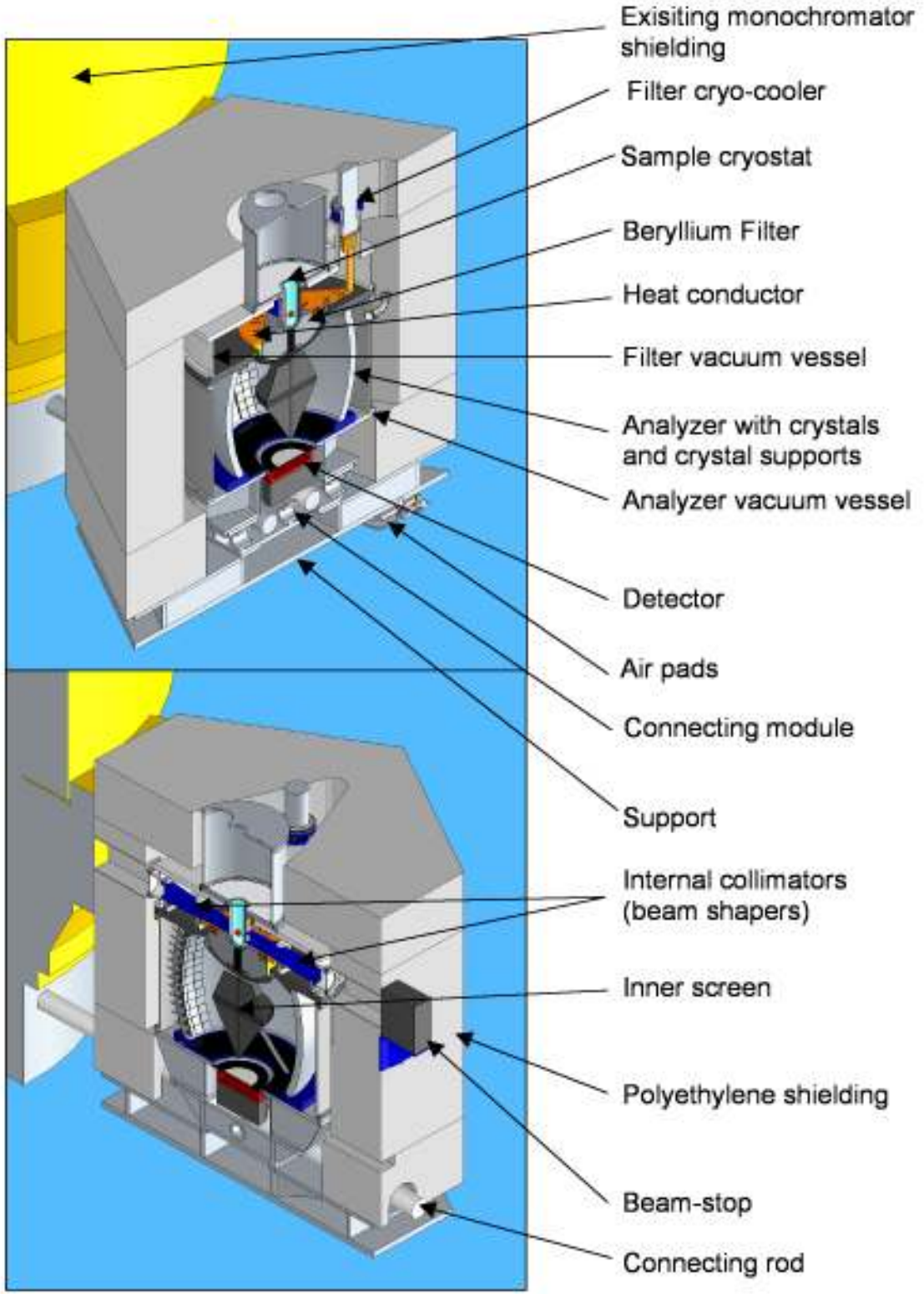
Advantages of the LAGRANGE

combining the best properties of TAS and TOF techniques: continuous beam and very large solid angle

using space focussing: a small single counter - increase in solid angle (up to 2.5 Sterad) but without multiplying counting volume

typical instrument volume ~1 m^3

low and sample–independent BG: protection on the sample-counter path



Currently accepted design of the IN1-LAGRANGE spectrometer

The budget sources are defined and the execution phase has commenced

We aim to have the instrument commissioned in the year 2011

In comparison with the present set-up the performance will be improved in three respects:

count rate in detector

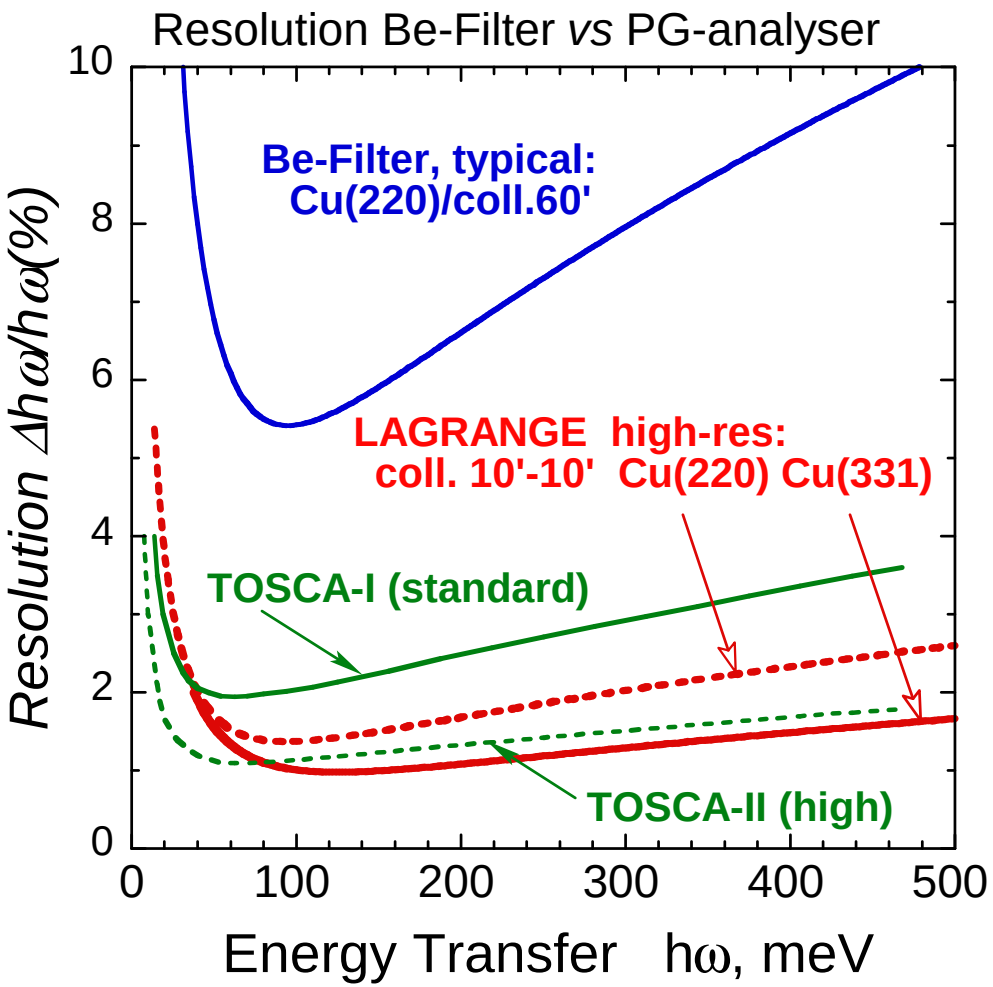
energy ***resolution***

level of ***background***

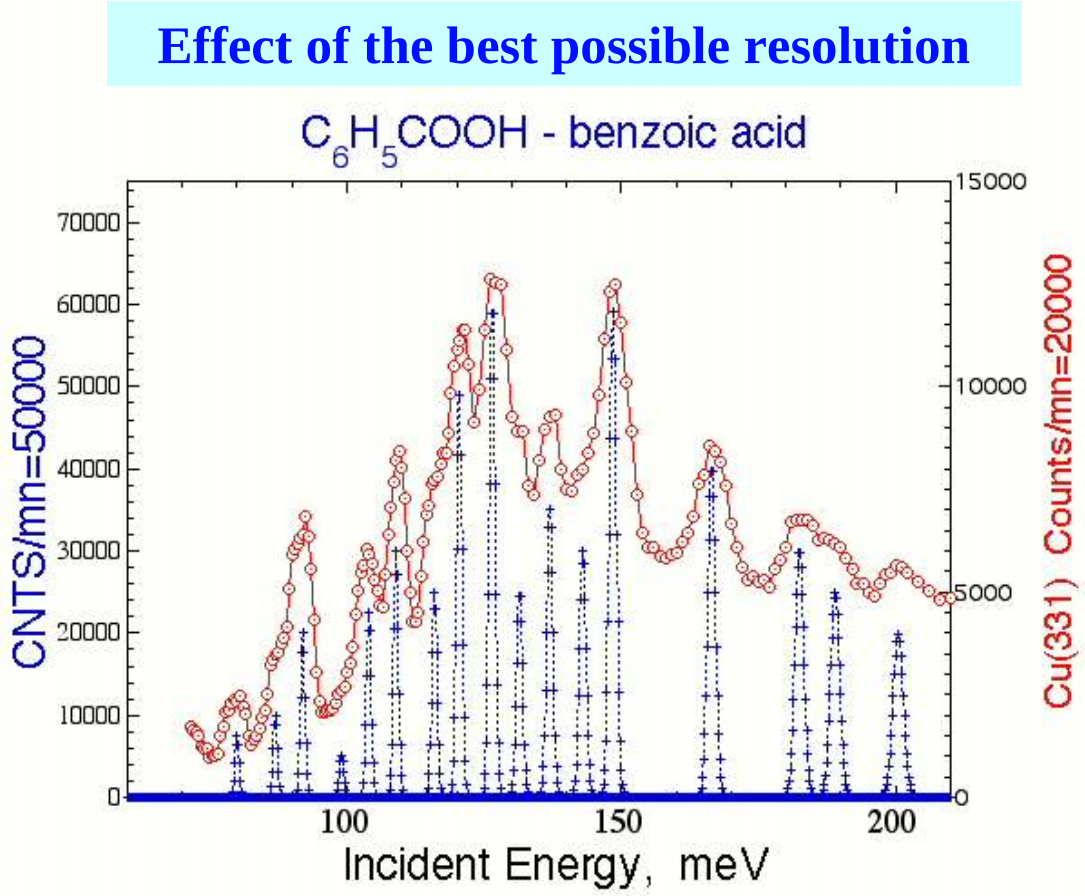
	BeF at present	LAGRANGE	Gain
$\Delta\Omega_f$	0.06 Sr	2.5 Sr	40
ΔE_f	3 meV	0.75 meV	1/4
Transmission	0.7	0.5	0.7
Total peak intensity gain ($\Delta\Omega_f$*ΔE_f*Transm):			5 - 7 fold
Background	1	1/10 - 1/30	
Signal-to-noise gain			50-100 fold

Resolution *vs* Intensity

trading the intensity gain for the best resolution



Effect of the best possible resolution



The the intensity gain by a factor of 5 (a conservative estimate) can be "paid" in order to leave behind the highest presently known level of the energy resolution in neutron spectroscopy of molecular excitations and to attain the level of ~1%.

The new spectrometer LAGRANGE
for the hot-source IN1 will be
a versatile, highly sensitive and high-resolution instrument

Maintaining the flexibility in optimisation on resolution/intensity
the LAGRANGE spectrometer will become a unique tool
for studies in the energy range of excitations
of molecules containing light atoms.

By combination of its parameters the new spectrometer will be superior
to the existing instruments of similar destination elsewhere

The new instrument will permit:

- **investigation of much smaller samples, inherent in novel materials studies,**
- **recording well-resolved vibration spectra,**
- **more detailed probing of external parameters like T, P, x, H**
- **access to time dependent processes**
- ***etc.***

Spectrometer of IN1

cusing (vertical and horizontal)

ensity at the sample position up to

ntly used energy range

Perspectives of high-energy spectrometry on steady-state sources

Due to upgrades both primary and secondary spectrometers
the total count rate in detectors of IN1 instruments
will be up to
30 times higher

for the LAGRANGE set-up
sensitivity will attain levels of ~10 μg of Hydrogen
(10 mg of Carbon) in the samples

Approaching spallation sources (ISIS, SNS, ESS)
by energy resolution (down to ~1%)

their spectral characteristics are less favourable
in the domain of "hot neurons":
keep being competitive in the future