Inelastic X-ray Scattering from Collective Atom Dynamics

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Introduction and Motivation

INS and IXS

IXS Instrumentation

High frequency collective dynamics of liquid water

Sound velocities in hcp-iron to 110 GPa

Perspectives

(Trieste, 10 May 2002)

Aim of IXS (INS) Experiments

Study of phonon(-like) excitations in condensed matter.

- interatomic force constants
- sound velocities
- thermodynamical properties
- dynamical instabilities (phonon softening)
- electron-phonon coupling
- relaxation phenomena

….etc., etc.

X-rays and phonon studies ?

Two citations from standard text books

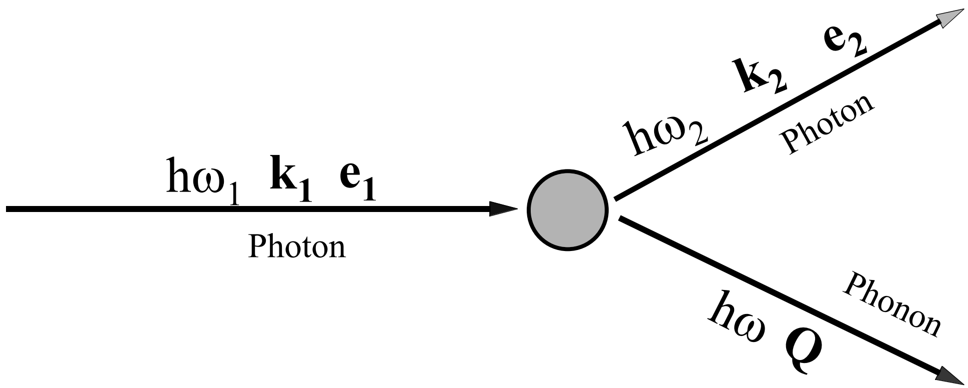
“When a crystal is irradiated with X-rays, the processes of photoelectric absorption and fluorescence are no doubt accompanied by absorption and emission of phonons. The energy changes involved are however so large compared with phonon energies that information about the phonon spectrum of the crystal cannot be obtained in this way.”

W. Cochran in Dynamics of atoms in crystals, (1973)

“…In general the resolution of such minute photon frequency is so difficult that one can only measure the total scattered radiation of all frequencies, … As a result of these considerations x-ray scattering is a far less powerful probe of the phonon spectrum than neutron scattering. ”

Ashcroft and Mermin in Solid State Physics, (1975)

Scattering kinematics



- Energy analysis of the scattered phonons: E_1 - E_2 = E
- Directional analysis of the scattered phonons: $\mathbf{k_1}$ **-** $\mathbf{k_2}$ **= Q**

IXS versus INS: scattering kinematics

Energy Transfer:

Neutrons:

λ_1 = 1 Å => E_1 = 82 meV   E = some meV $E_1 \neq E_2$

=>   moderate energy resolution: $E/E_1 = 0.05$

X-rays:

λ_1 = 1 Å => E_1 = 12398 eV   E = some meV $E_1 \approx E_2$

=>   extremely high energy resolution: $E/E_1 = 10^{-7}$

IXS versus INS: scattering kinematics

MomentumTransfer:

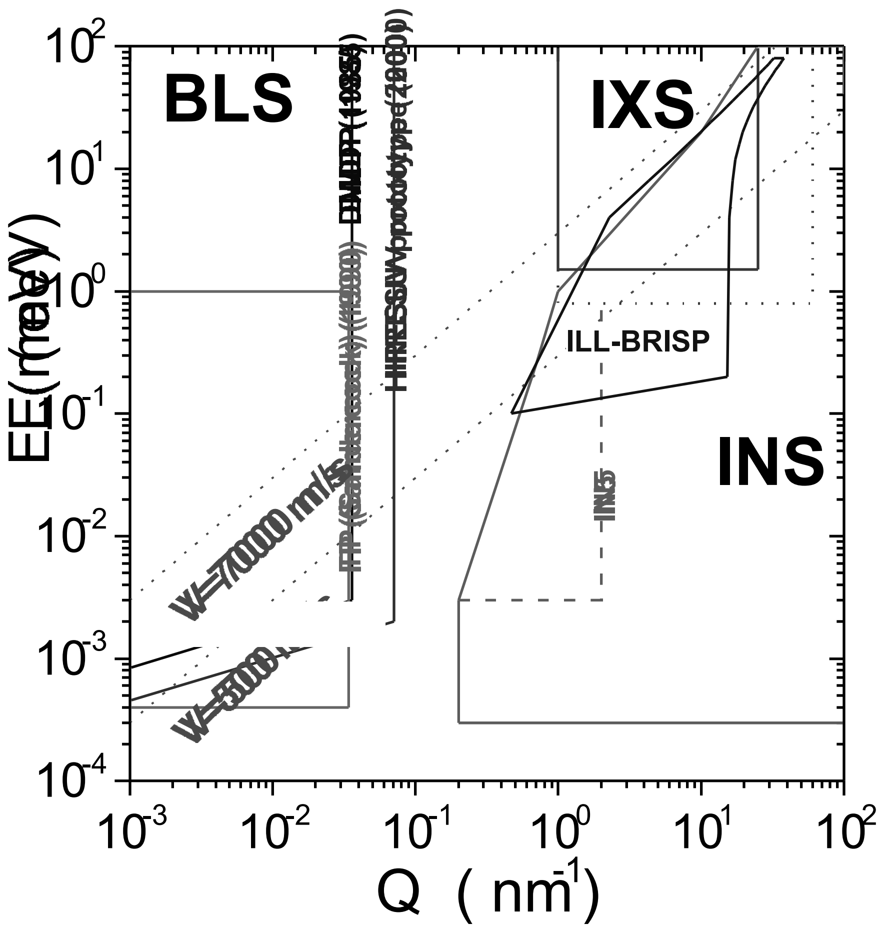
Neutrons: $$Q = \sqrt{k_1^2 + k_2^2 - 2k_1k_2\cos(\vartheta)}$$

=> strong coupling between E and Q
inaccessible E-Q region

X-rays: $$Q = 2k_1 \sin(\vartheta/2)$$

=> Q only controlled by scattering angle ϑ

The Q-E Space of phonon spectroscopies



IXS has advantages in disordered systems with a high speed of sound (v_g = E/Q)

IXS versus INS

IXS

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} = r_0^2\,\frac{k_1}{k_2}\left(\vec{\varepsilon}_1 \cdot \vec{\varepsilon}_2\right) f(Q)^2\; S\left(\vec{Q},E\right)$$

- no correlation between momentum- and energy transfer
- $\Delta E/E = 10^{-7}$ to 10^{-8}
- Cross section ~ Z^2 (for small Q)
- Cross section is dominated by photoelectric absorption (~ $\lambda^3 Z^4$)
- no incoherent scattering
- small beams: 100 μm or smaller

INS

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} = b^2\,\frac{k_1}{k_2}\,S\left(\vec{Q},E\right)$$

- strong correlation between momentum- and energy transfer
- $\Delta E/E = 10^{-1}$ to 10^{-2}
- Cross section ~ b^2
- Weak absorption => multiple scattering
- incoherent scattering contributions
- large beams: several cm

here do have X-rays an advantage with respect to neutron

- In disordered systems with a high speed of sound (v_g = E/Q).

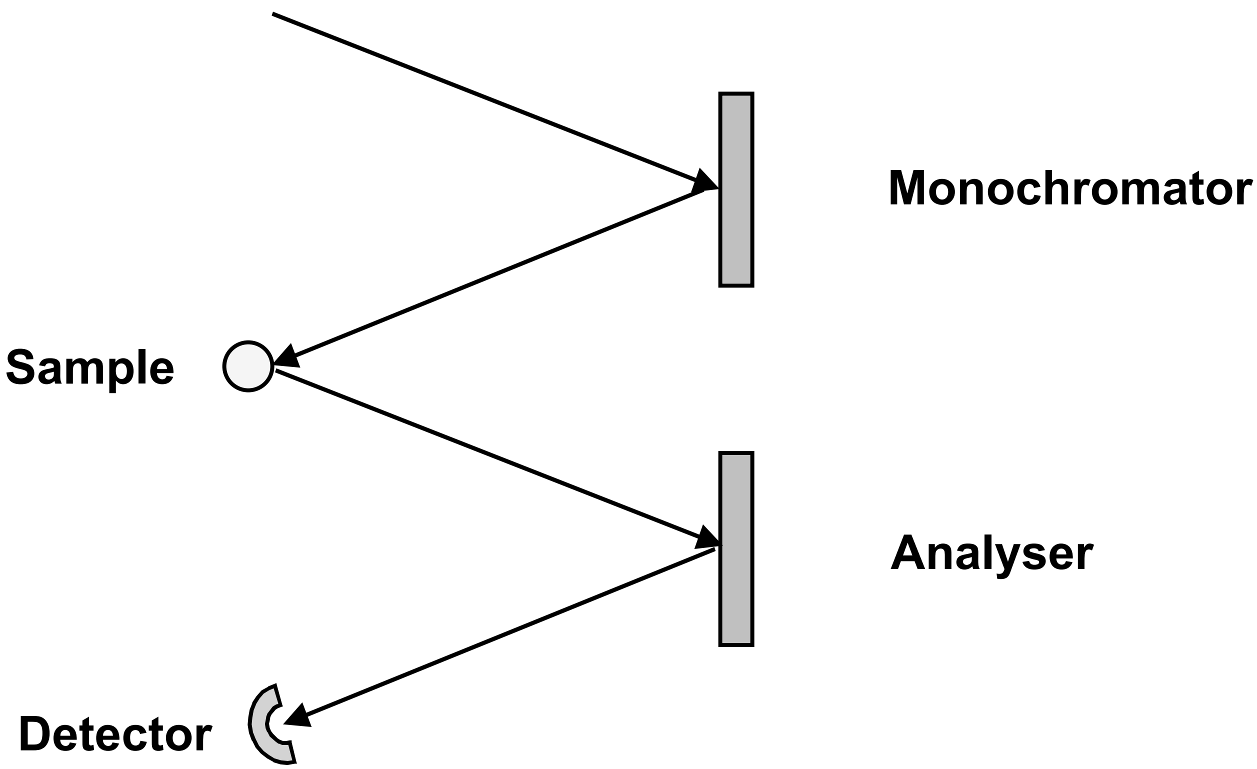
Kinematic limitations for INS

- Samples (only available) in small quantities.
  - novel (exotic) materials (MgB_2, …..)
  - samples under very high pressures

Neutron beams: several cm => signal loss
SR beams: 10 - 100 μm, t_μ = 10 -100 μm

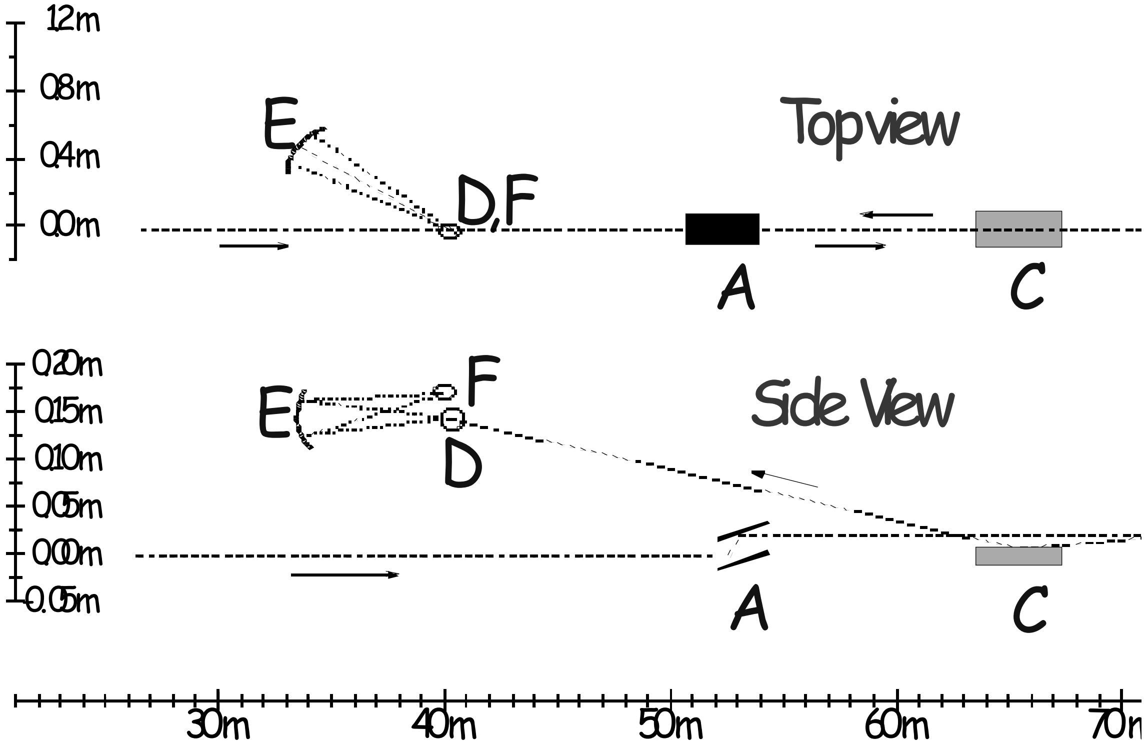
large high pressure cell => P < 100 kbar
Diamond anvil cell => P > 1 Mbar

Experimental principle



Beamline Layout ID16 and ID28 at the ESRF

• The x-ray source	
• High heatload premonochromator	(A)
• Main monochromator	(B)
• Focusing mirror	(C)
• Sample	(D)
• Analyser	(E)
• Detector	(F)



High Energy Resolution Monochromator

- Silicon (n,n,n) at θ_B = 89.98°
- $\omega_D = \Delta E/E \tan(\theta_B) > s_z', s_x'$

Reflection	Energy [eV]	DE [meV]	D
(7 7 7)	13840	5.3	3.8
(8 8 8)	15817	4.4	2.8
(9 9 9)	17794	2.2	1.2
(11 11 11)	21747	1.02	4.7
(12 12 12)	23725	0.73	3.0
(13 13 13)	25703	0.5	2.0

Energy Analysis: The Crystal Analyser

Requirements:

- Perfect single crystal properties (as HR mono)
- Collect some solid angle (ΔQ_{app}; flux)

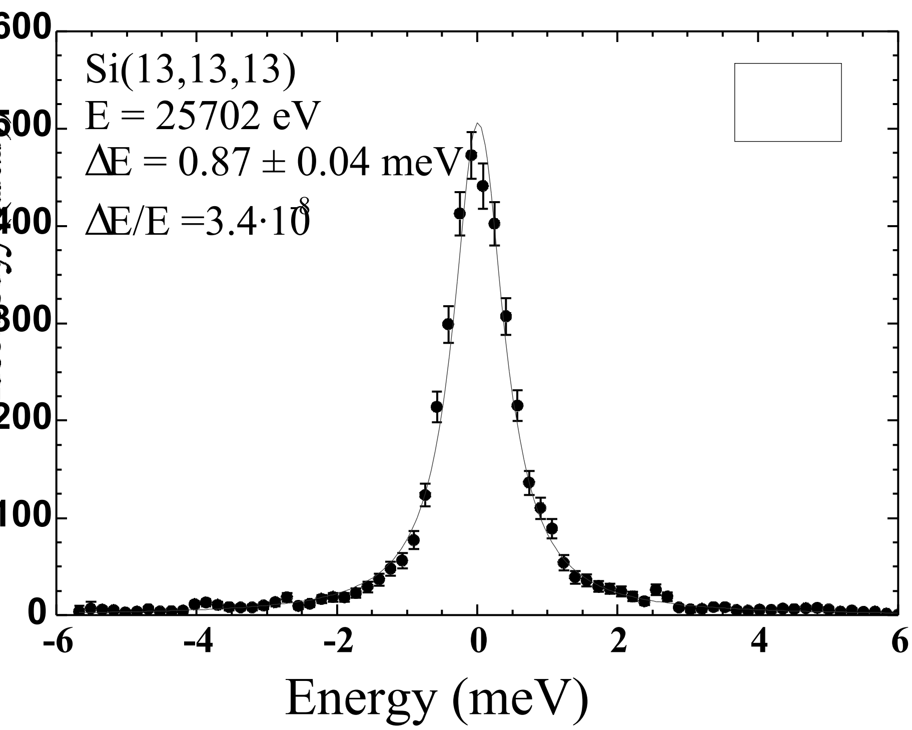
Solution:

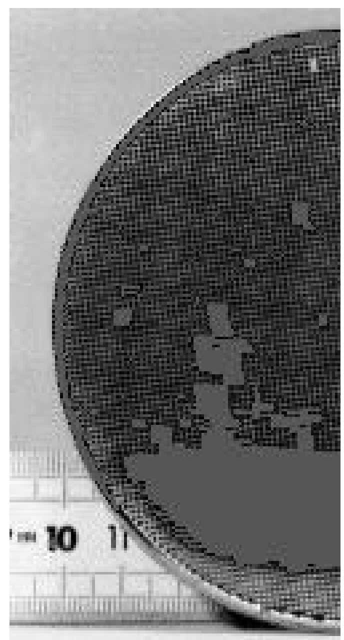
- Spherical crystal in Rowland Geometry ($\Delta\theta = 0$)
  - R = 2.5 (6.5; 11.5) m
  - elastic deformation => $\Delta E/E$ =

- Approximation to sphere by 10000 0.6x0.6x3 mm^3 cubes
  - preservation single crystal properties
  - $\theta_B = 89.98°$ to minimise cube size contribution to $\Delta E/E$

The Analyser in real life

Best Resolution so far obtained:



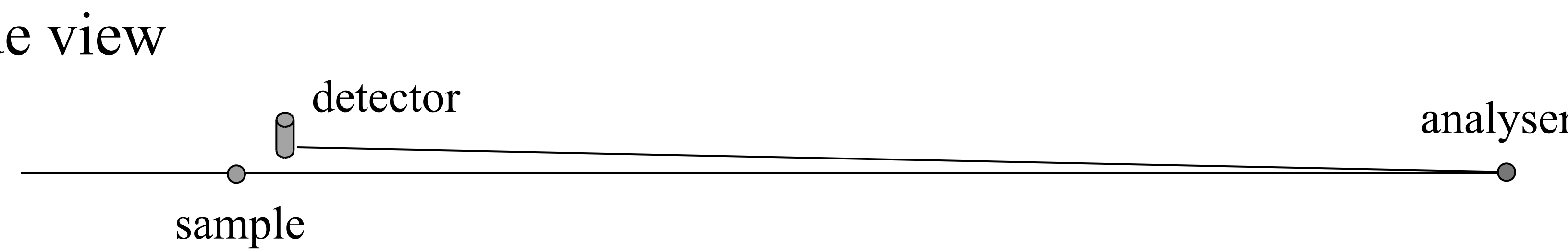


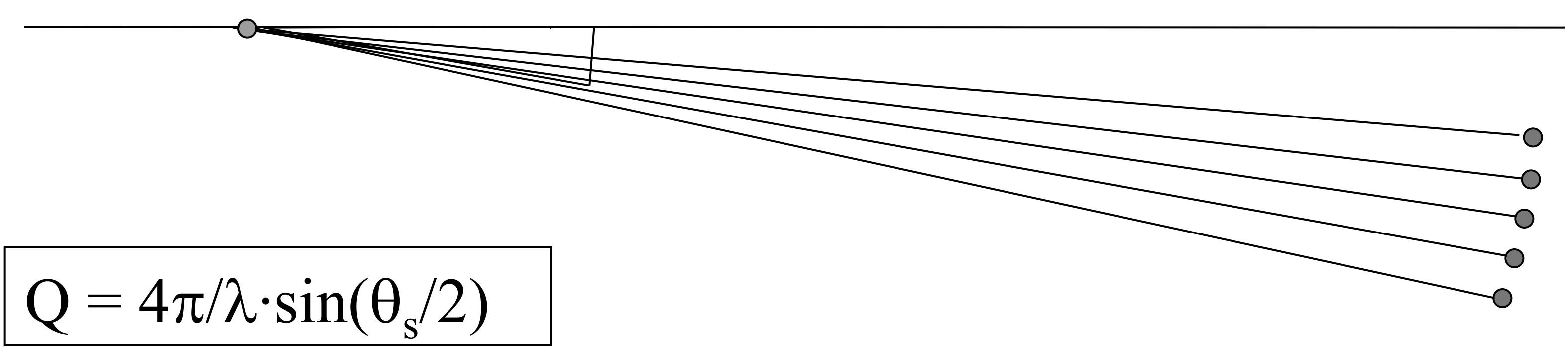
HR Mono: Energy Scans via Temperature Scans

$\lambda = 2 \cdot d(T) \sin\theta_B$
$\Delta d/d = -\alpha(T) \cdot \Delta T$ ($\alpha = 2.58 \cdot 10^{-6}$ at RT)

- Temperature controlled by Thermometer bridge
  $\Delta T_{min} = 0.25$ mK
  $\Delta T_{typ} = 3, 5, 10, 15$ mK/minute

The IXS spectrometers (schematics)

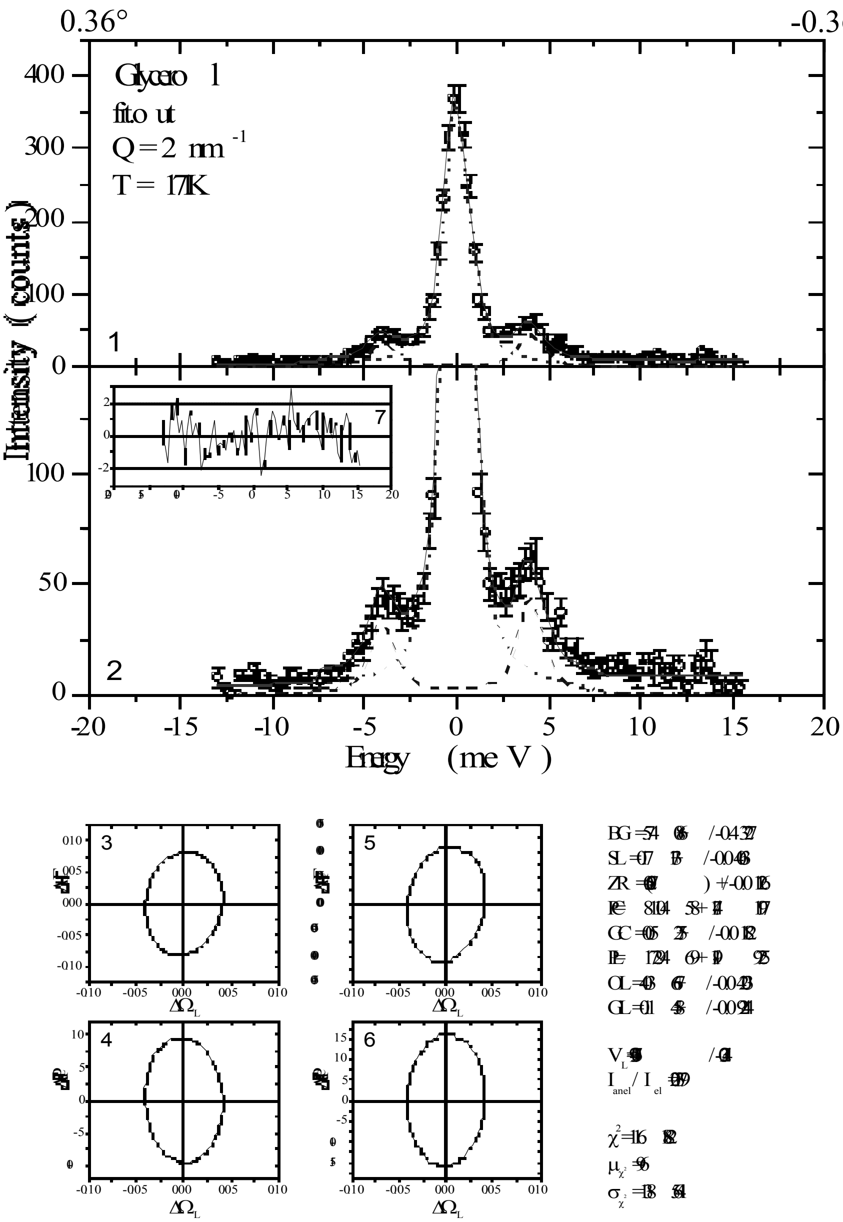




$$Q = 4\pi/\lambda \cdot \sin(\theta_s/2)$$

3 mm

Example of IXS spectrum and of data analysis



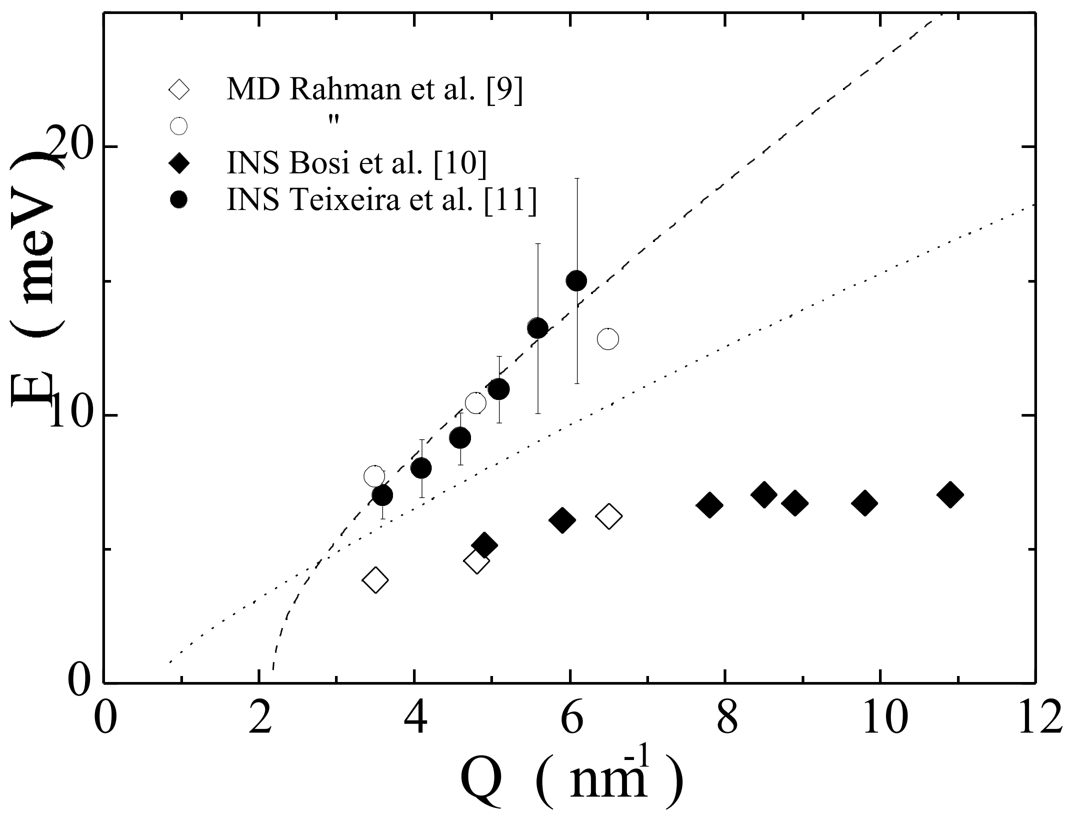
Si(11,11,11)
ΔE = 1.5 meV at 21747 eV
8 hours accumulation

Data Analysis:
Damped Harmonic Oscillator

The high-frequency dynamics of liquid water

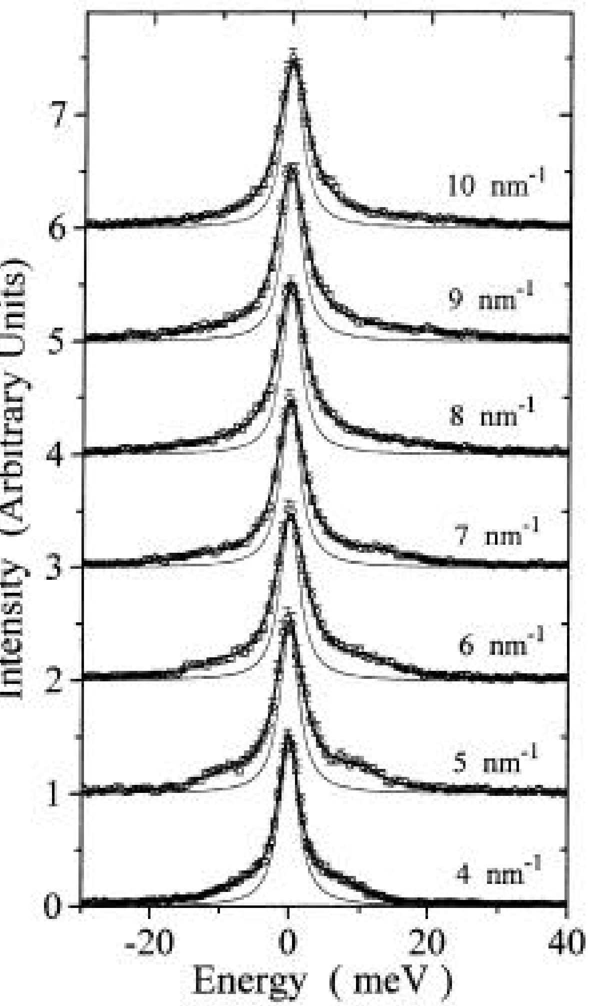
1993 - 200?

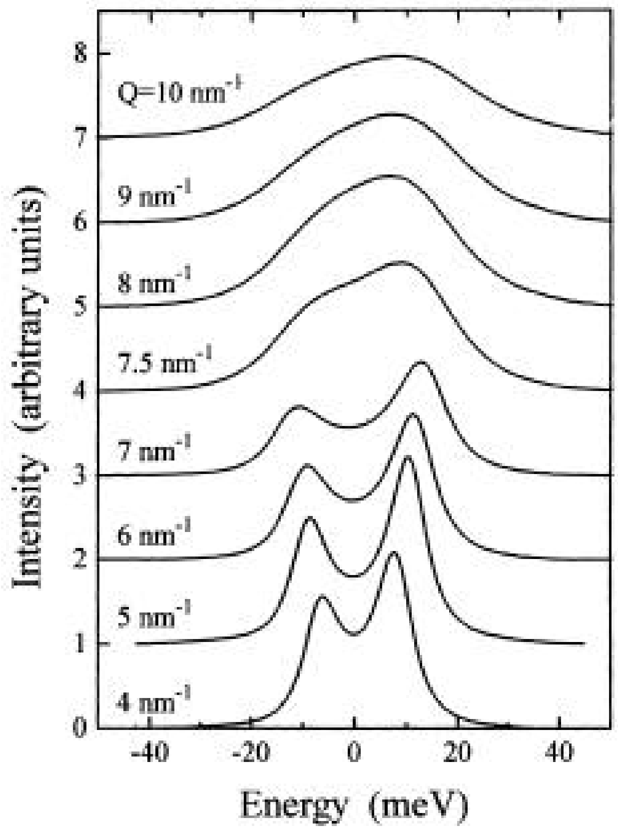
INS and Molecular Dynamics Results (as of 1993)



Origin and nature of these two excitations?

IXS results with ΔE = 5 meV

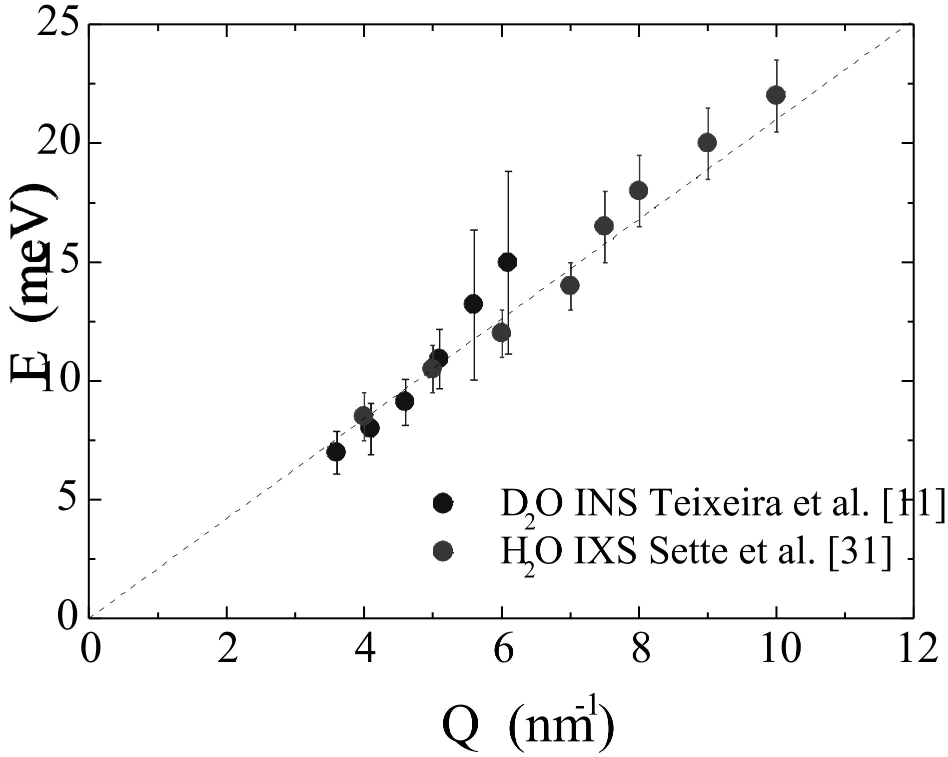




Damped harmonic oscillator

$$F(Q,\omega)=\left[n(\omega)+1\right]I(Q)\frac{\alpha}{\left[\Omega(Q)^2\right.}$$

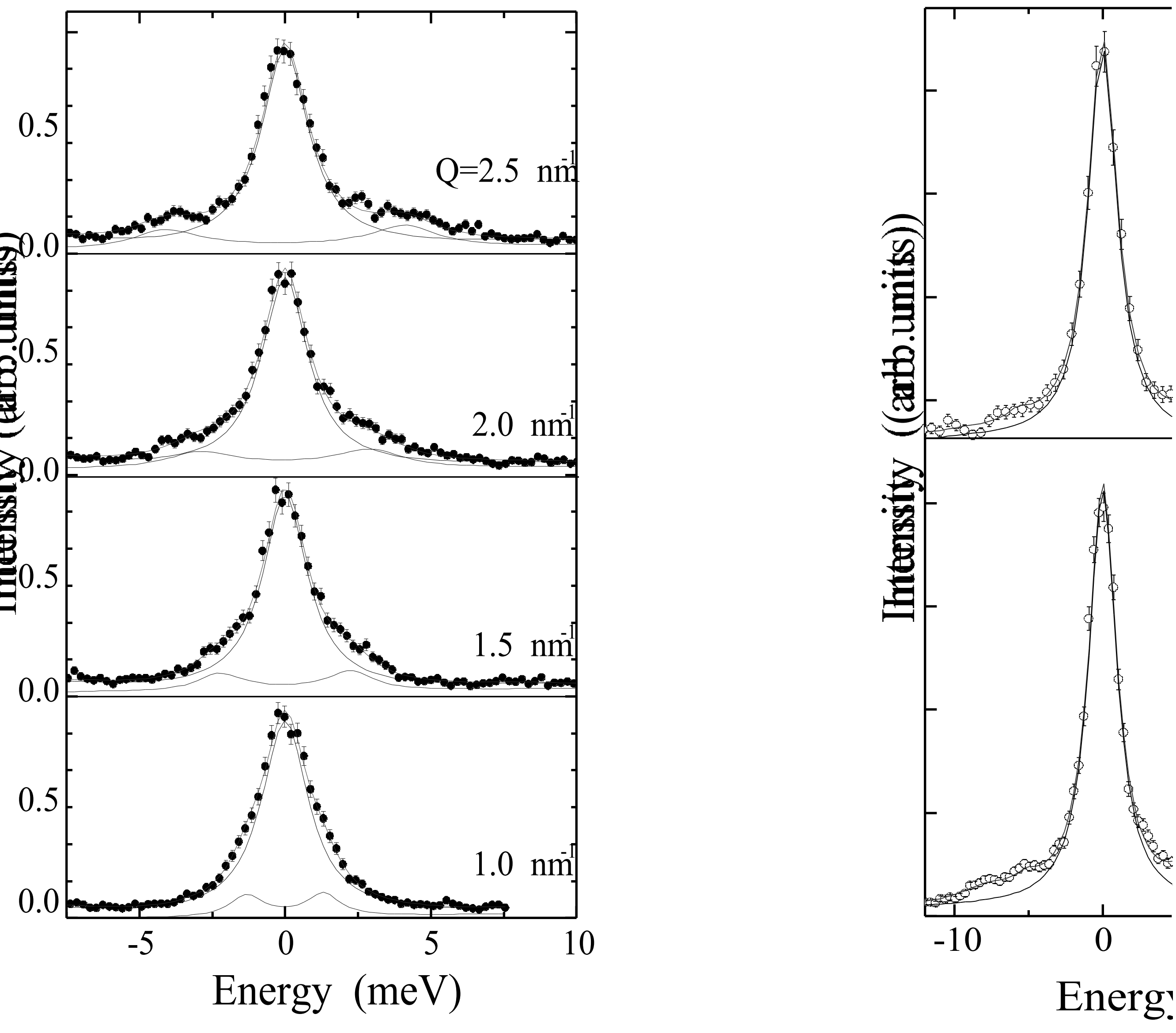
Dispersion relation for water at 5º C



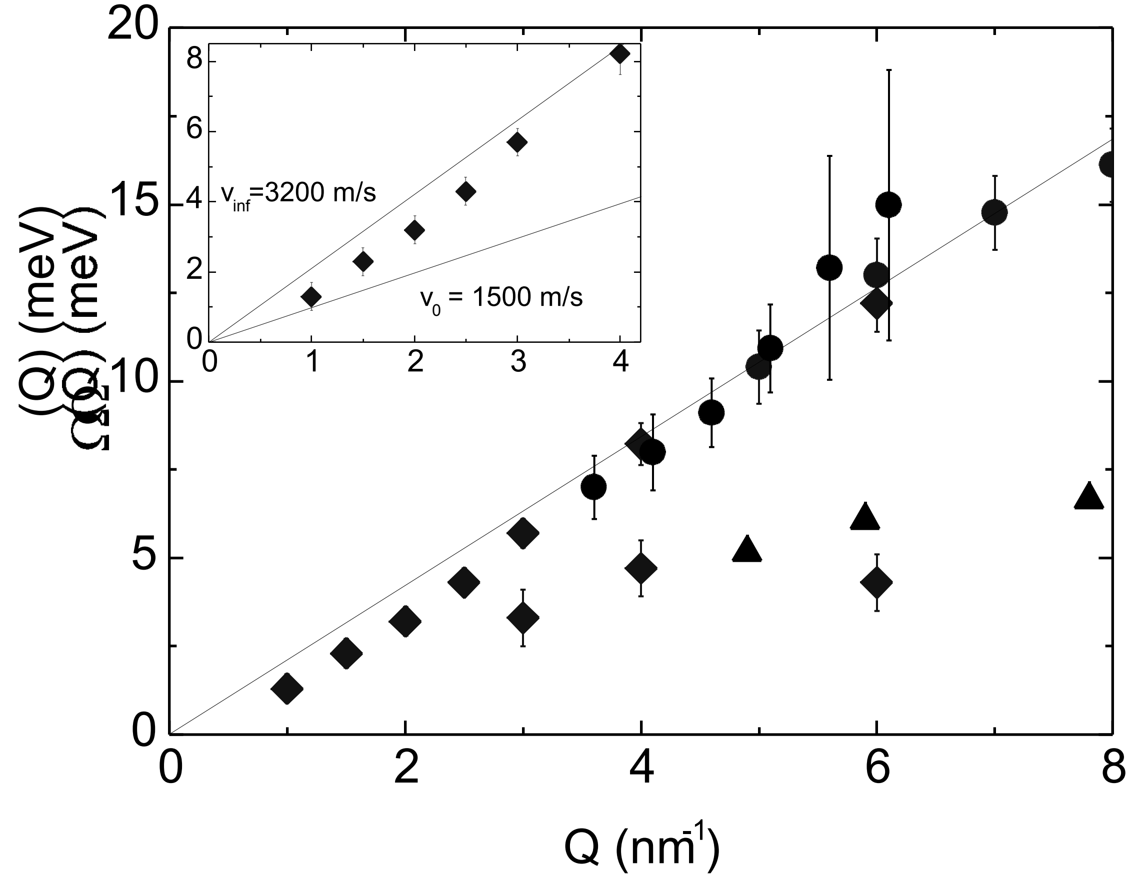
• Confirmation of the existence of the “fast sound”.
• Excitation involves the center of mass of the molecule.

No clear evidence for low energy excitations!

IXS results with ΔE = 1.5 meV



Complete dispersion relation for water at 5º C



Existence of two sounds: v_0 = 1500 m/s and v_∞ = 3200 m/s
The “fast sound” is the continuation of the “hydrodynamic” sound.
The low energy mode only visible once the “fast sound” value is reach

Signature of a structural relaxation process ("fast" α-relaxation)

Low-frequency viscous regime ($\Omega\tau \ll 1$): liquid-like response
high-frequency elastic regime ($\Omega\tau \gg 1$): solid-like response

$\Omega\tau \approx 1$: Coupling of the phonon-like excitations with structural rearrangement

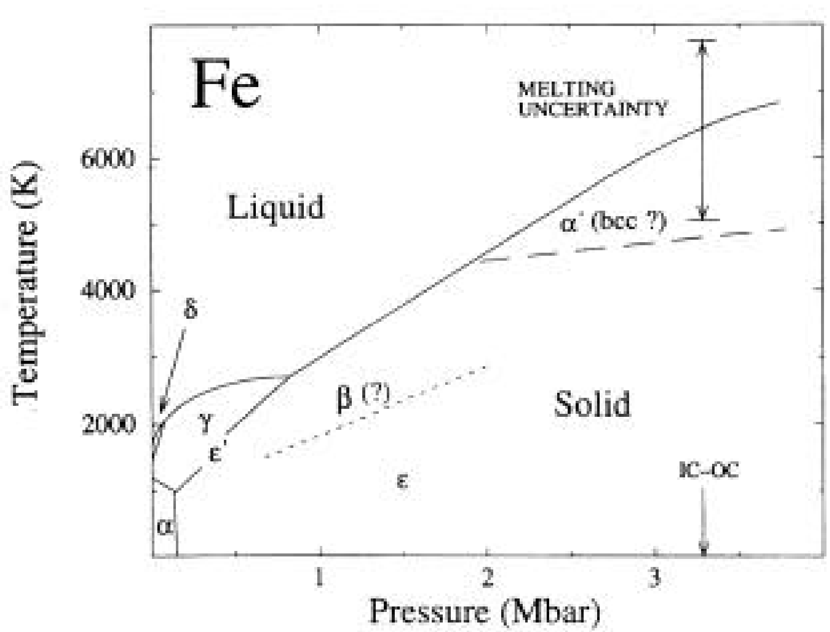
$E \approx 3.3$ meV $\quad\quad \tau = h/E = 1.3$ ps
$Q = 2\ \mathrm{nm}^{-1}$ $\quad\quad \xi = 3.1$ nm

Time and length scale can be associated with the formation and breaking of hydrogen bonds.

Sound velocities in hcp-iron to 110 GPa

Determination of sound velocities in iron is essential for:

- elastic properties
- comparison with seismological observations
- understanding the composition of Earth's inner core



- α (bcc) -> ε (hcp) at 13.4 GPa
- study of polycrystalline samples
- averaged longitudinal sound velocity

Alternative techniques

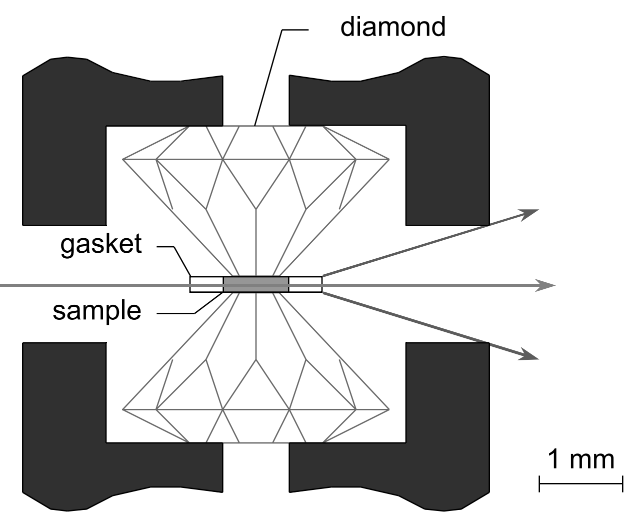
rect

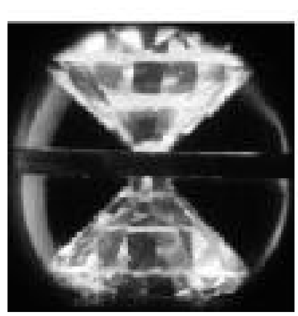
Inelastic neutron scattering	< 10 GPa
Ultrasound measurements	< 16.5 GPa
Brillouin light scattering	signal too weak

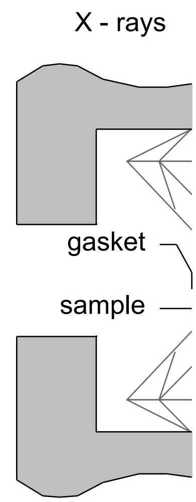
ndirect

ray diffraction	uniaxial stress, elasticity tensor c_{ij} $\rho v^2 \sim f(c_{ij})$
clear resonant inelastic x-ray scattering	Debye law for low energy phonon DOS $3v_D^{-3} = v_p^{-3} + 2v_s^{-3}$ K and ρ from diffraction measuremen
ock wave measurements	T-P correlation

X-ray studies at high pressure using diamond anvil cel







Mega-bar Pressures

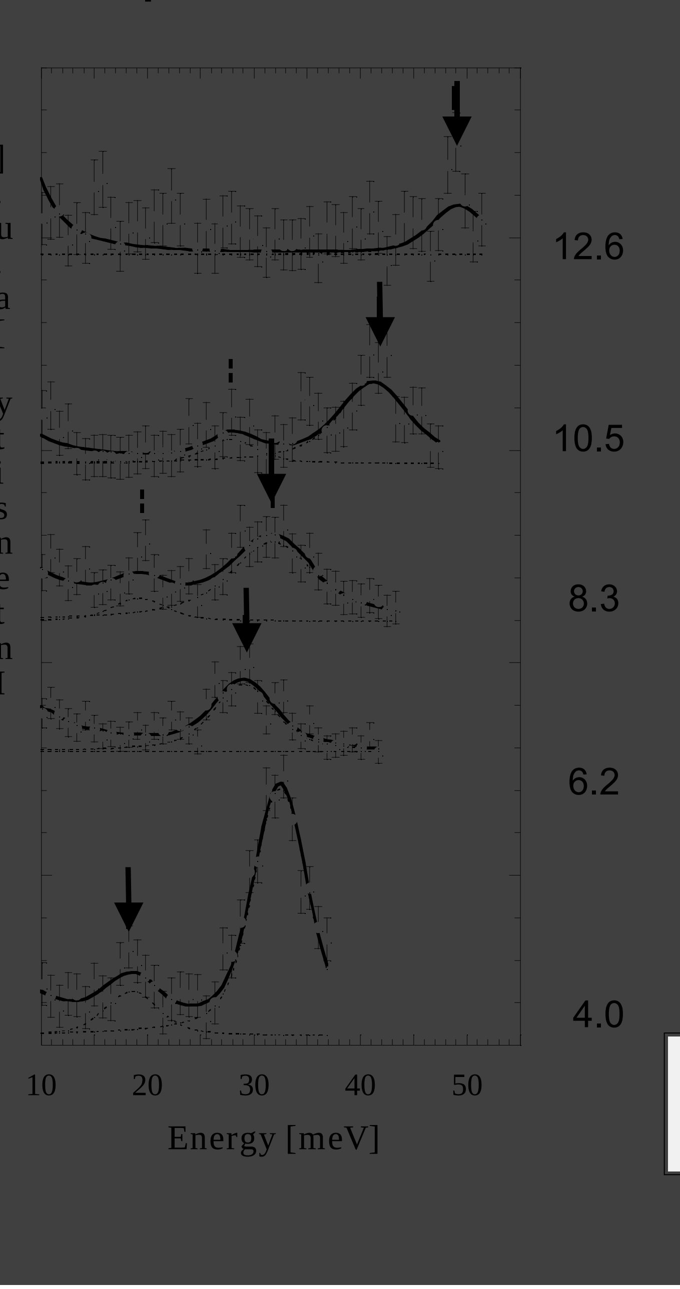
pical sample dimensions:
- 200 μm diameter
- 40 μm thickness

(Reasonably) well matched with:

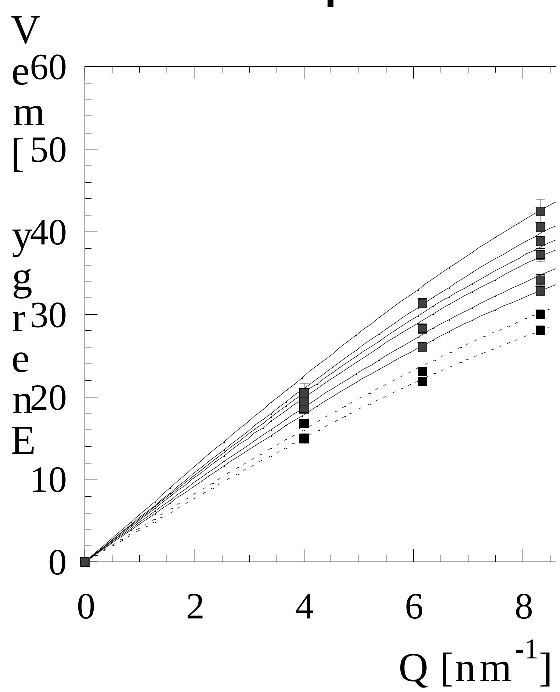
- typical x-ray spot sizes

- x-ray absorption length (for Z=30 - 50)

hcp iron at 28 GPa



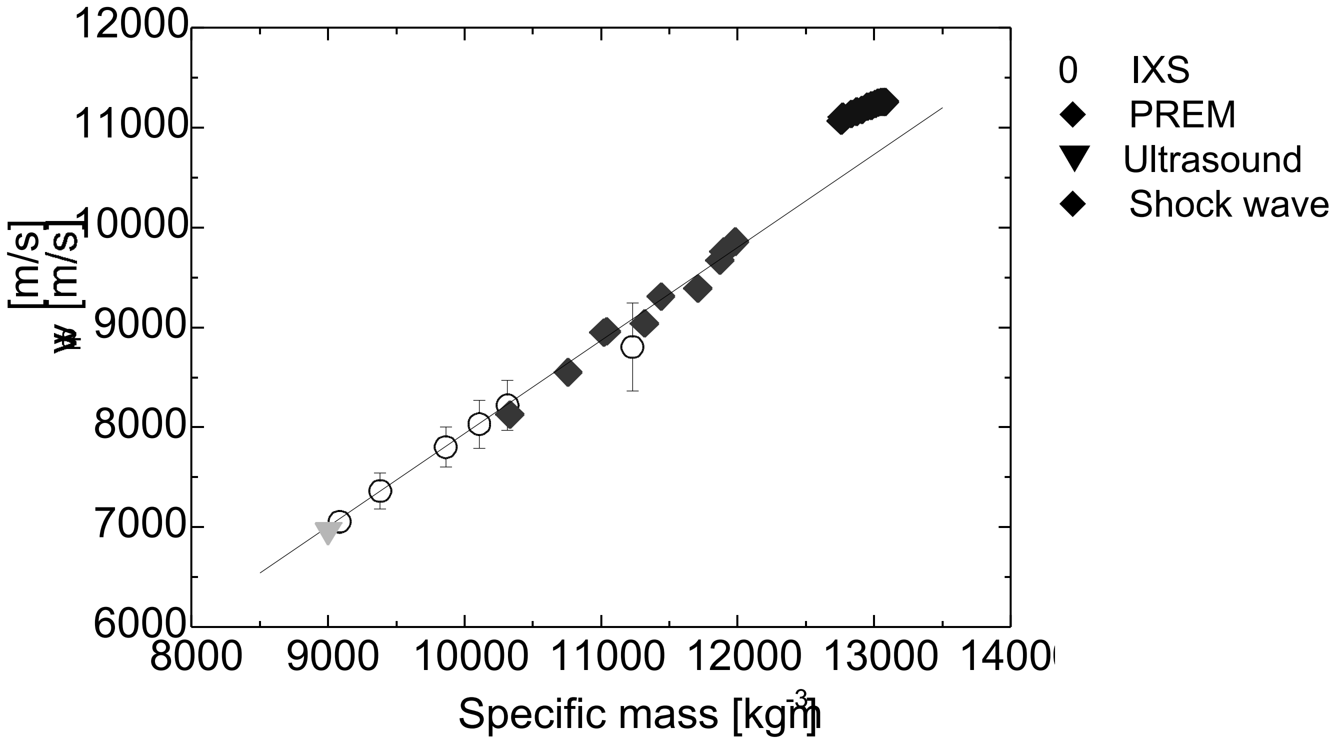
Pressure dependent dispersion curves



bcc-iron: 0 - 7 GPa
hcp-iron: 19 - 110 GPa

- Sine fit to the data
- obtain sound velocities from initial slope

Density dependence of sound velocity



- Good agreement with ultrasound and shock wave data.
- hcp iron follows a Birch law for v_p
  $dv_p/dT = -9 \cdot 10^{-5}$ km/s/K
- Indication that the inner core is slightly lighter than pure iron.

A selection of other investigated Systems

Liquids and glasses

- Teflon, Polyethylene	(high presssure)
- Na, Si, Ge, Sn	(high temperature)
- SiO_2, aSi	
- H_2, D_2	
- glycerol, polybutadiene, salol	
- water	

Polycrystals

- Ice IX, XII	
- **Fe**, FeS, FeO, FeSi	(high pressure)

Single crystals

- Ice VI,VII	(high pressure)
- Co, Zn,Ta	(high pressure)
- $SrTiO_3$	(high pressure)
- SmS	(high pressure)
- C^{12},C^{13},GaN, SiC (ZB), ZnMgY	
- $NbSe_3$	
- $Nd_{1.86}Ce_{0.14}CuO_{4+\delta}$	