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ICTP 40th Anniversary

SCHOOL ON SYNCHROTRON RADIATION AND APPLICATIONS
In memory of J.C. Fuggle & L. Fonda

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Inelastic X-ray Scattering from Collective Atom Dynamics

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Inelastic X-ray Scattering from Collective Atom Dynamics

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Introduction and Motivation

Inelastic neutron and x-ray scattering

IXS Instrumentation

High frequency collective dynamics of liquid water

Sound velocities in hcp-iron to 110 GPa

Elastic moduli in hcp-cobalt to 25 Gpa

Phonon dispersion in superconductors

Aim of IXS (INS) Experiments

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

Breakdown of the static lattice model

- specific heat
- thermal expansion
- melting

- T-dependence of DC conductivity
- thermal conductivity of insulators
- sound transmission
- superconductivity

↓

dynamical lattice model

Information obtained from IXS (INS) Experiments

• inter-atomic force constants
• sound velocities
• thermodynamic properties
• dynamical instabilities (phonon softening)
• electron-phonon coupling
• relaxation phenomena
….etc., etc.

X-rays and phonon studies ?

"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. "

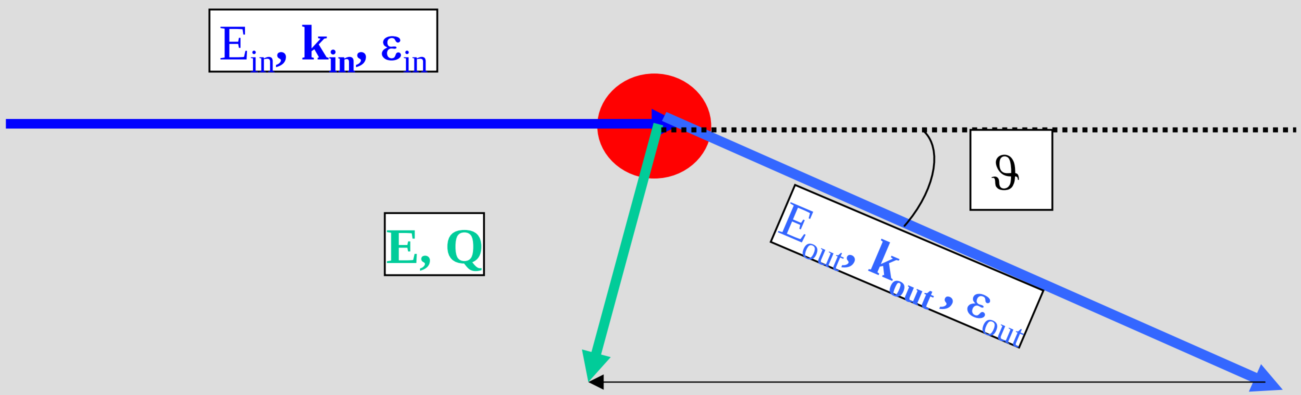
Ashcroft and Mermin in Solid State Physics, (1975)

$\Delta E \approx$ meV !!!

$E_{inc} > 10$ keV !!!

Photon flux ???

Scattering kinematics



- Energy transfer $E = E_{out} - E_{in}$ $(E \ll E_{in})$ ⬇
- Momentum transfer $\mathbf{Q} = \mathbf{k}_{out} - \mathbf{k}_{in} = 2k \sin(\vartheta/2)$ $(k_{out} \approx k_{in} \equiv k)$

♦ Directional analysis of the scattered photons → **Q**

♦ Energy analysis of the scattered photons → E

X-ray inelastic cross section

Electron-photon interaction Hamiltonian

$$H_{X-Th} = \frac{1}{2} r_0 \sum_j A^2\left(r_j, t\right)$$

Double-differential cross section

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = r_0^2 \left(\vec{\varepsilon}_1 \cdot \vec{\varepsilon}_2\right)^2 \frac{k_1}{k_2} \sum_{I,F} P_I \left| \left\langle F \left| \sum_j e^{i\vec{Q}\vec{r}_j} \right| I \right\rangle \right|^2 \delta\left(E - E_f - E_i\right)$$

Thomson scattering cross section

The central approximations

(i) Adiabatic approximation: $|S\rangle = |S_e\rangle |S_n\rangle$

(ii) $|I\rangle = |I_e\rangle |I_n\rangle$ $\qquad |F\rangle = |I_e\rangle |F_n\rangle$

For a mono-atomic system:

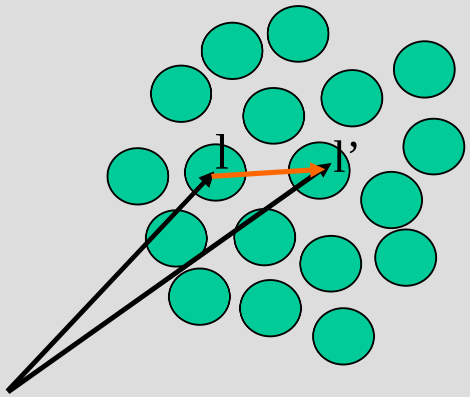
$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = r_0^2 \, (\vec{\varepsilon}_1 \cdot \vec{\varepsilon}_2)^2 \, \frac{k_1}{k_2} \left| f(Q) \right|^2 \, S(\vec{Q}, E)$$

Thomson scattering cross section

Atomic form factor

Dynamical structure factor

The dynamical structure factor



Dynamical structure factor S(**Q**,ω):

Space and **time** Fourier transform of $G_P(\mathbf{r},t)$.

Pair correlation function $G_P(\mathbf{r},t)$**:**

$G_P(\mathbf{r},t)$ is the probability to find two different particles at positions $\mathbf{R}_{l'}(t=0)$ and $\mathbf{R}_{l'}(t)$, separated by the **distance r** and the **time intervall t.**

The dynamical structure factor

The pair correlation function

$$G(\vec{r},t) = \frac{1}{N} \sum_{l.l'} \int d^3\vec{r}' \left\langle \delta\left(\vec{r}' - \vec{R}_{l'}(0)\right) \delta\left(\vec{r}' + \vec{r} - \vec{R}_l(t)\right) \right\rangle$$

G(r,t) is the probability to find two different particles at positions $R_{l'}$(t=0) and R_l(t), and separated by the distance r and the time intervall t.

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar} \int dt \exp(-i\omega t) \int d^3 r \exp\left(i\vec{Q}\vec{r}\right) G(\vec{r},t)$$

S(Q,ω) is the space and time Fourier transform of the pair correlation function G(r,t).

Q ≈ 2π/ξ	ξ is a characteristic length
ω = E/h ≈ 2π/τ	τ is a characteristic (relaxation) time

IXS versus INS

IXS

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

- 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

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

- 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

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:

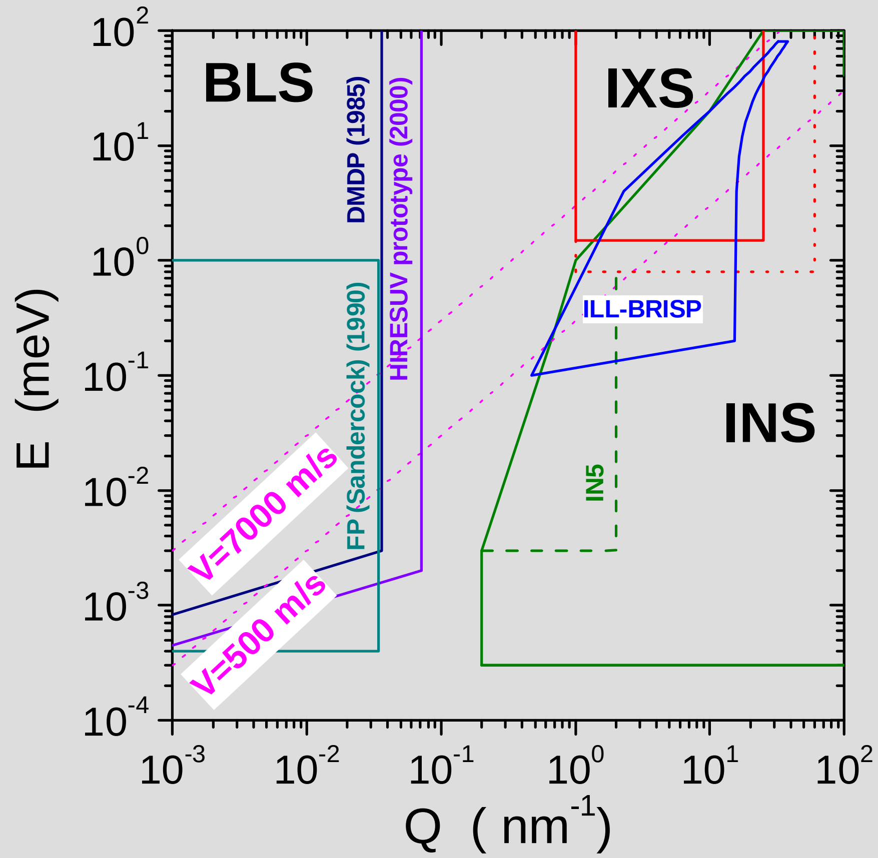
Neutrons: $Q = \sqrt{k_1^2 + k_2^2 - 2k_1k_2\cos(\vartheta)}$

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

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

=> Q only controlled by scattering angle ϑ

The Q-E Space of phonon spectroscopies



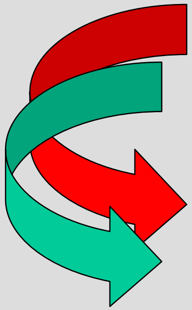
IXS has advantages in disordered systems with a high speed of sound (v_g = E/Q)

Where do X-rays complement neutrons?

- 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

Z. Phys. B – Condensed Matter 69, 179–183 (1987)

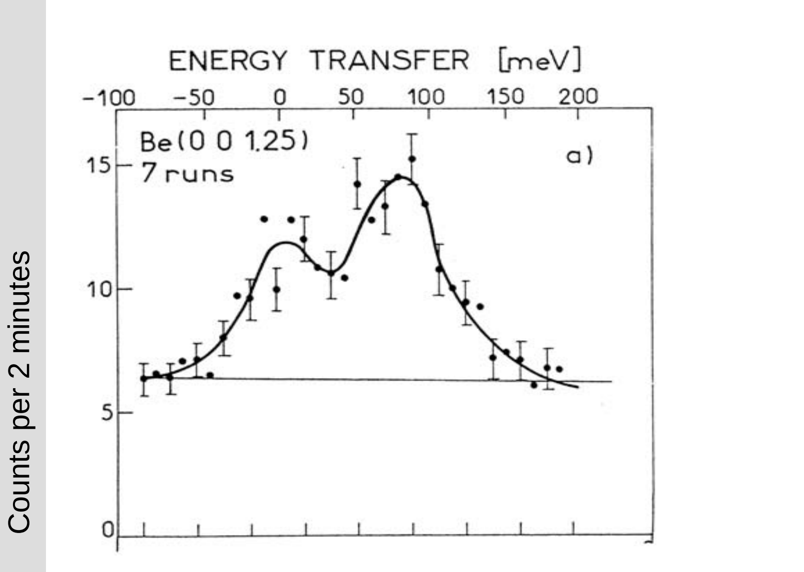
Condensed Matter
Zeitschrift für Physik B

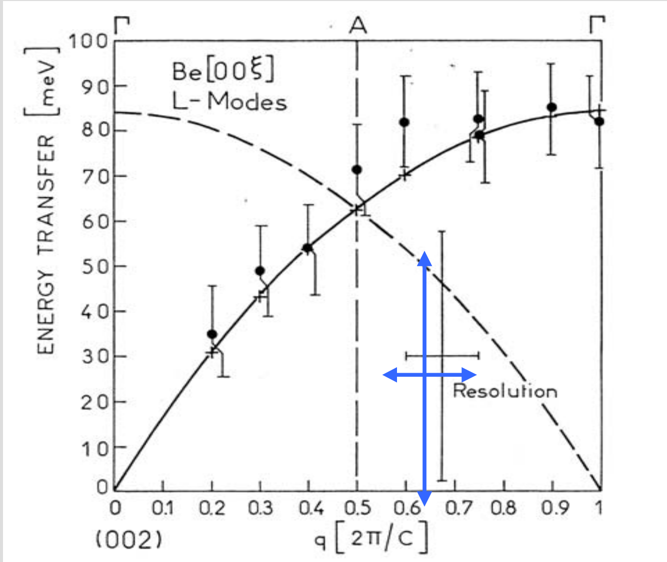
First Measurement of a Phonon Dispersion Curve by Inelastic X-ray Scattering

B. Dorner*, E. Burkel, Th. Illini, and J. Peisl
Sektion Physik der Ludwig Maximilians Universität, München, Federal Republic of Germany

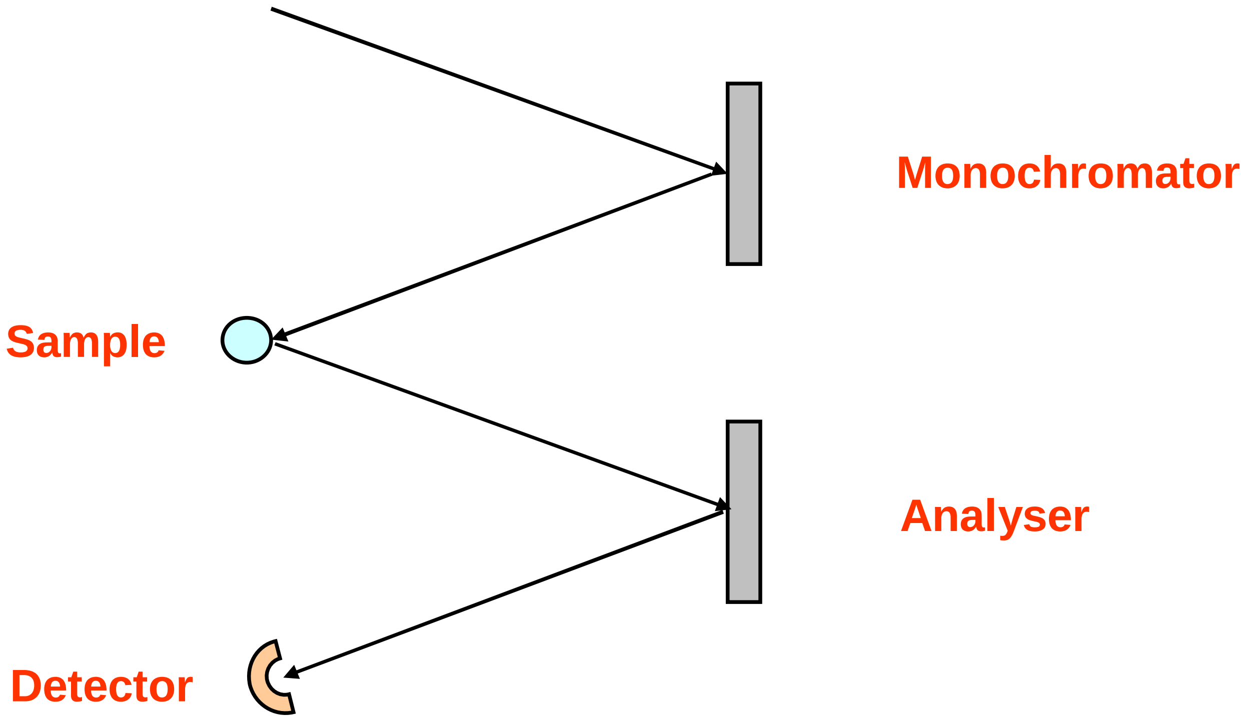
Received July 6, 1987

Inelastic scattering of 13.8 keV X-rays with very high energy resolution of $\Delta E = 55$ meV was used to measure the phonon dispersion curves for the LA and LO modes in the [00ξ] direction in Be. The results agree with inelastic neutron scattering data known from the literature. The X-ray scattering intensities of the phonon excitations for different momentum transfers are in very good agreement with the prediction from the scattering law.



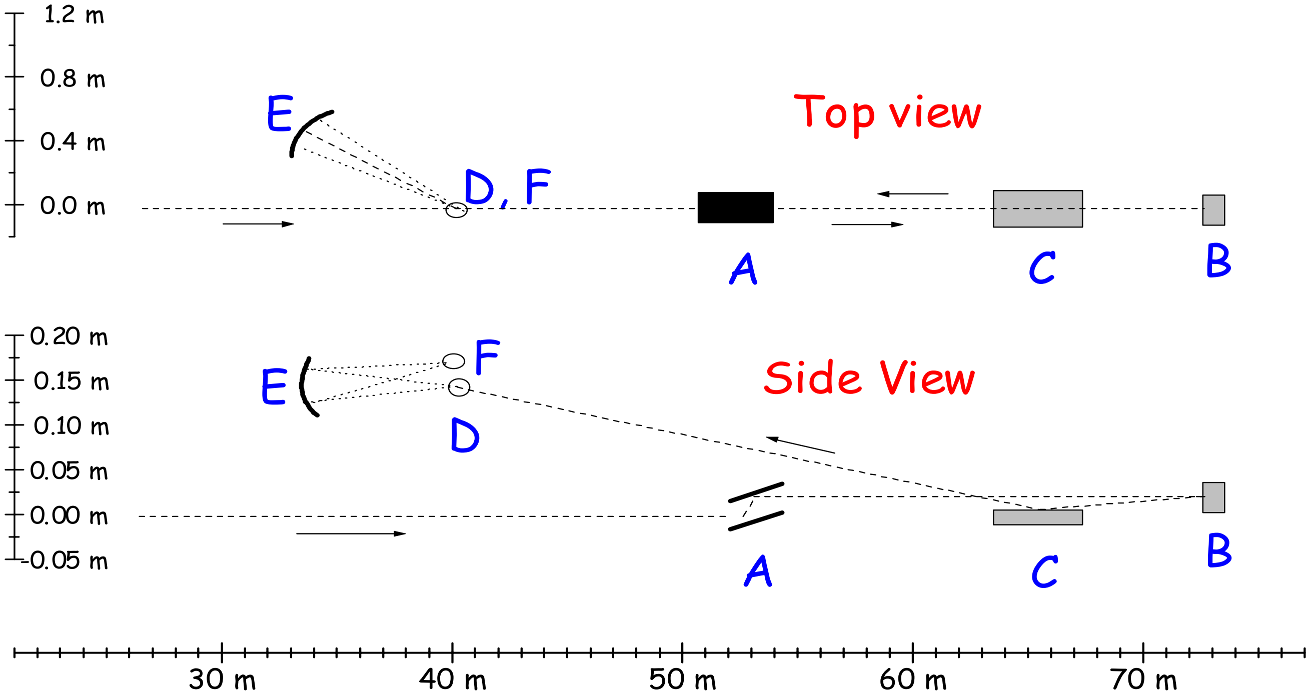


Experimental principle



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]	DE/E
(7 7 7)	13840	5.3	$3.8 \cdot 10^{-7}$
(8 8 8)	15817	4.4	$2.8 \cdot 10^{-7}$
(9 9 9)	17794	2.2	$1.2 \cdot 10^{-7}$
(11 11 11)	21747	1.02	$4.7 \cdot 10^{-8}$
(12 12 12)	23725	0.73	$3.0 \cdot 10^{-8}$
(13 13 13)	25703	0.5	$2.0 \cdot 10^{-8}$

Energy Analysis: The Crystal Analyser

Requirements:

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

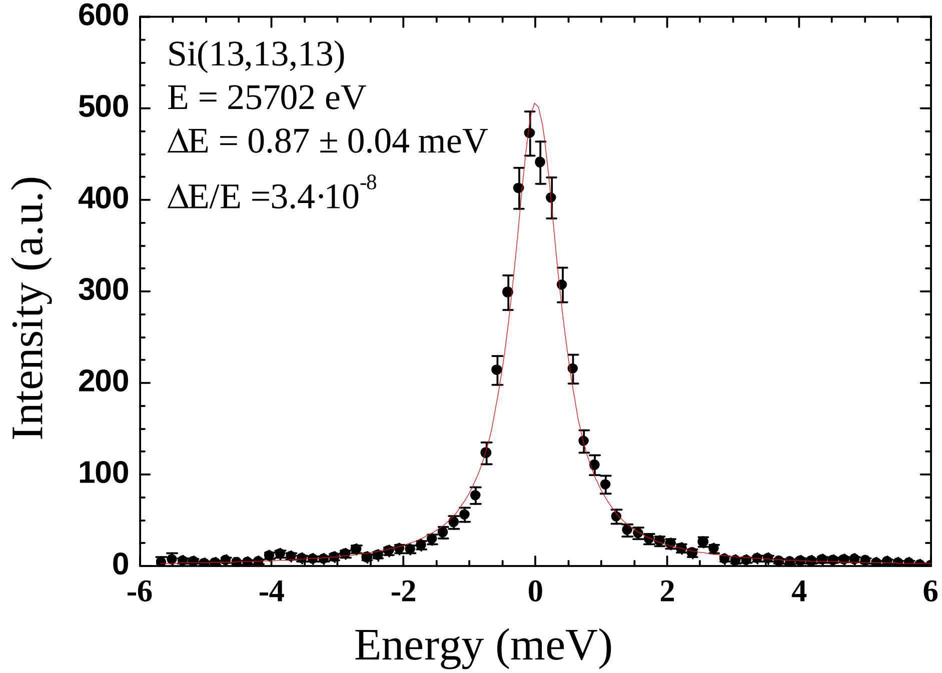
Solution:

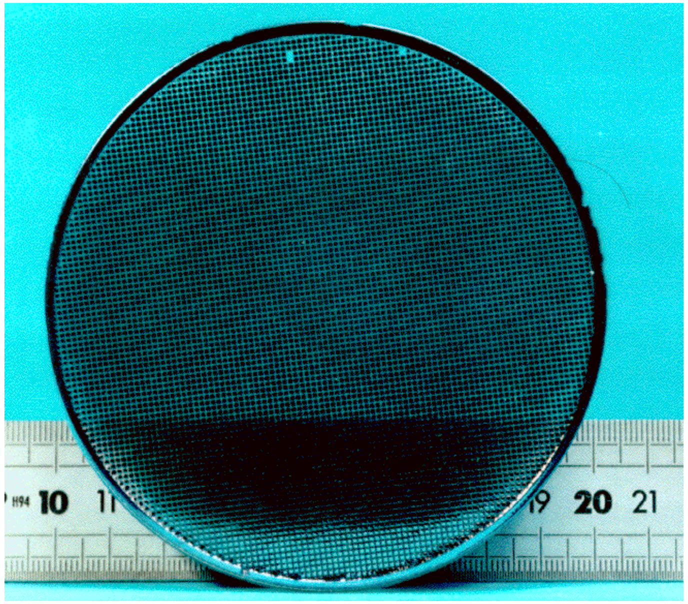
- Spherical crystal in Rowland Geometry ($\Delta\theta = 0$)
  - R = 2.5 (6.5; 11.5) m
  - elastic deformation => $\Delta E/E$ = ☹

- 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)

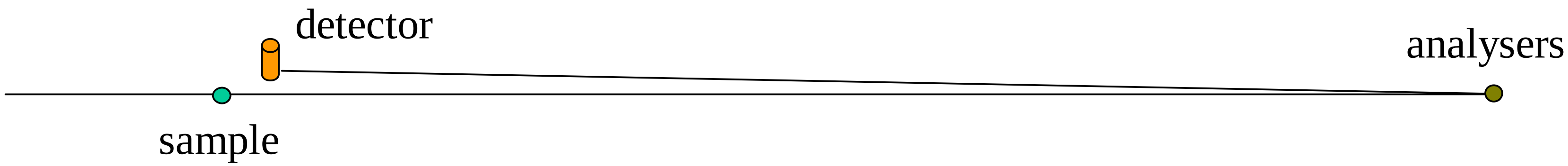
- Temperature controlled by AC Thermometer bridge

  $\Delta T_{min} = 0.25$ mK

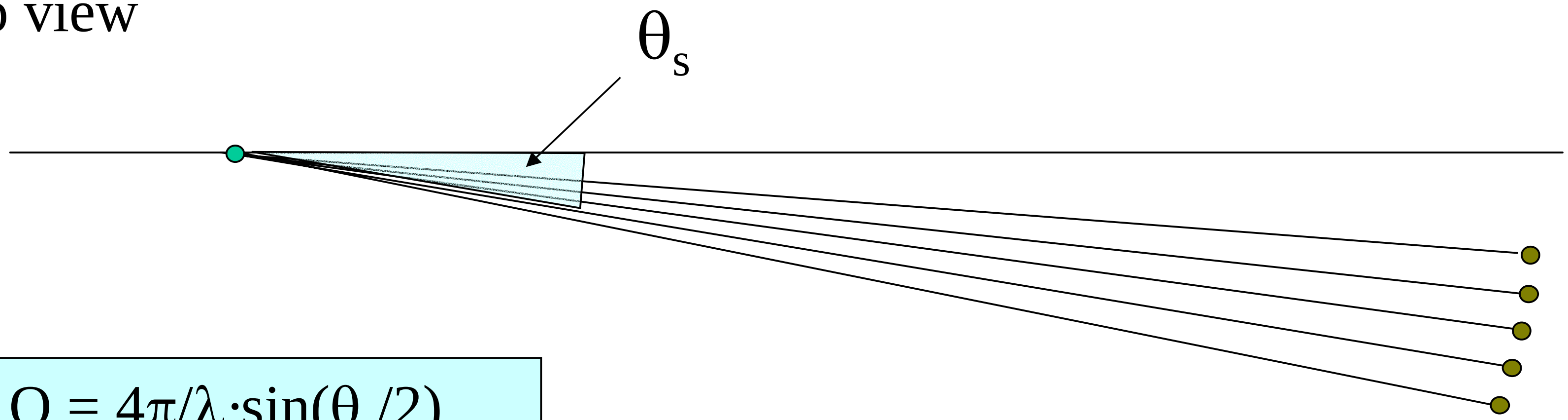
  $\Delta T_{typ} = 3, 5, 10, 15$ mK/minute

The IXS spectrometers (schematics)

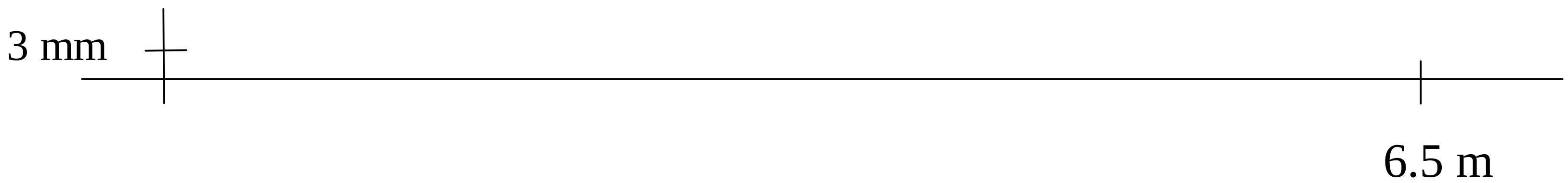
Side view



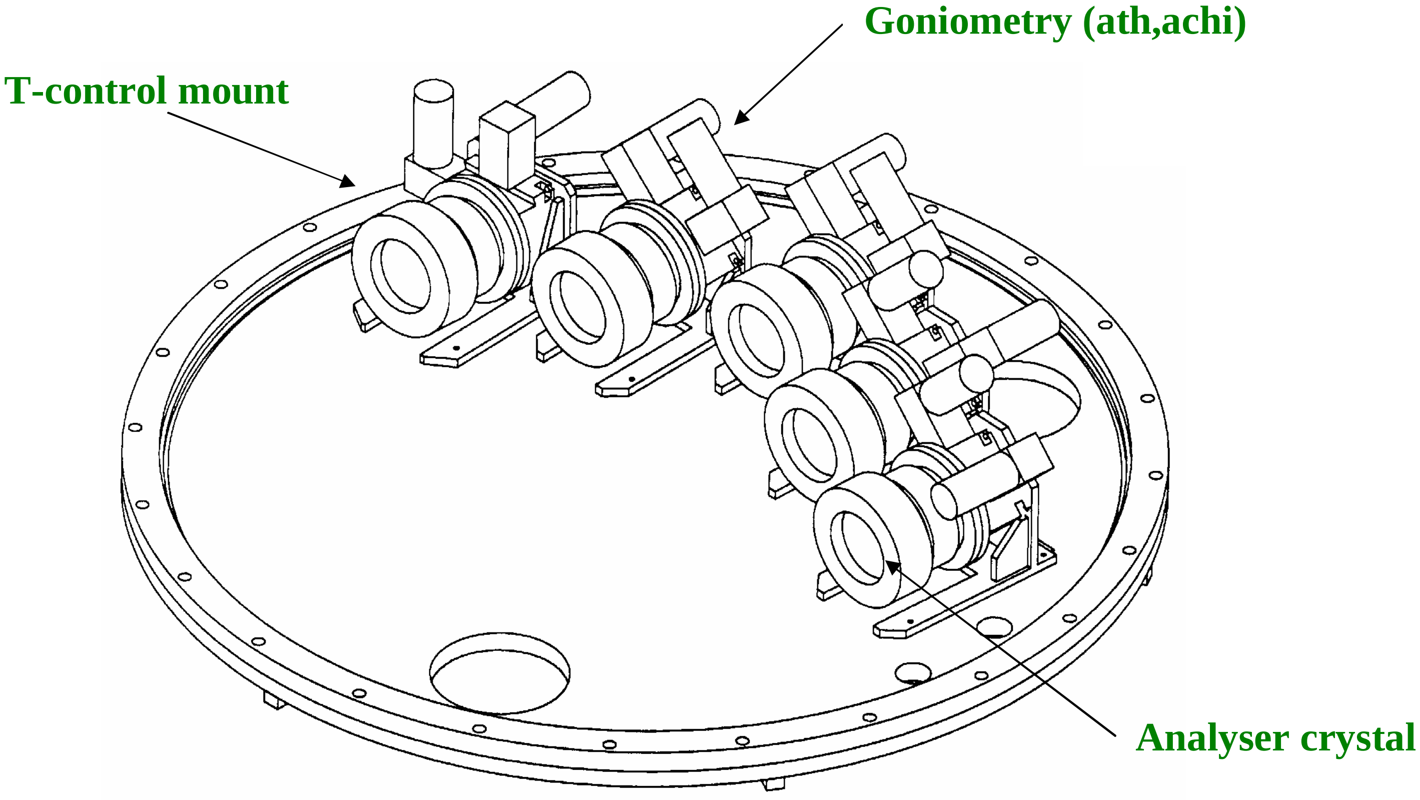
Top view



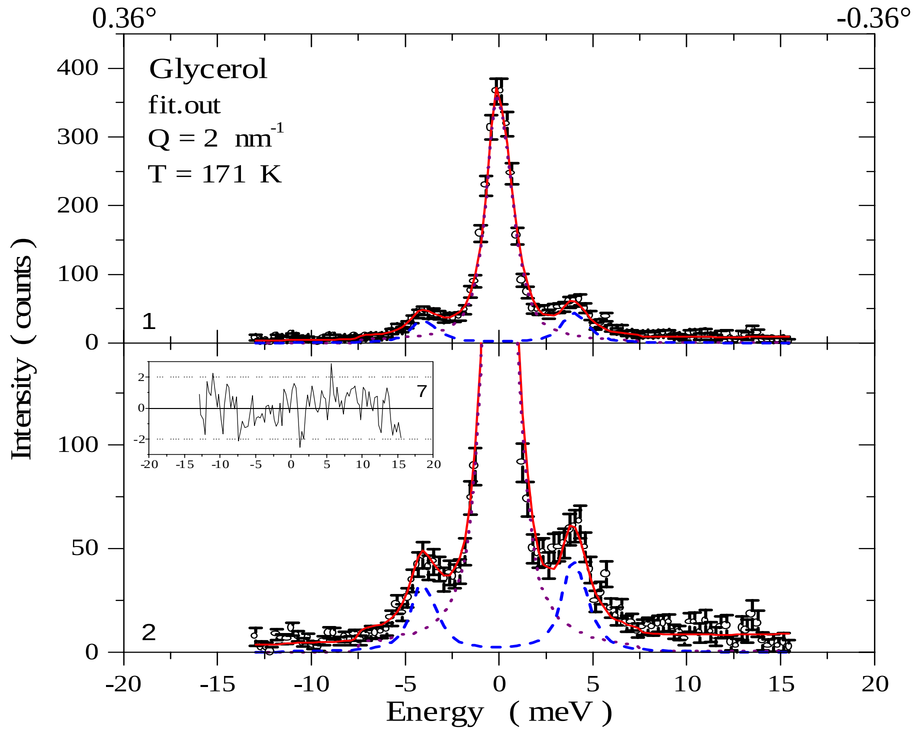
$Q = 4\pi/\lambda \cdot \sin(\theta_s/2)$

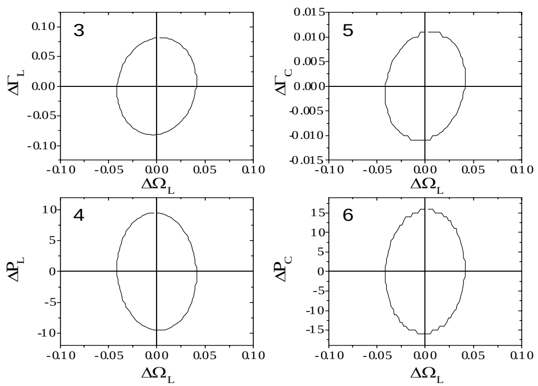


5-Analyser Assembly



Example of IXS spectrum and of data analysis





BG = 5.74086 +/- 0.43727
SL = 0.17173 +/- 0.04063
ZR = (-0.05627) +/- 0.01126
PC = 811.0458 +/- 17.41197
GC = 0.05275 +/- 0.01182
PL = 172.9469 +/- 11.99725
OL = 4.03667 +/- 0.04203
GL = 0.11458 +/- 0.09244

V_L = 3075.943 +/- 32.0274
I_{anel}/ I_{el} = 0.21379

χ^2 = 116.1882
μ_{χ^2} = 96
σ_{χ^2} = 13.85641

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

Data Analysis:
Damped Harmonic Oscillator

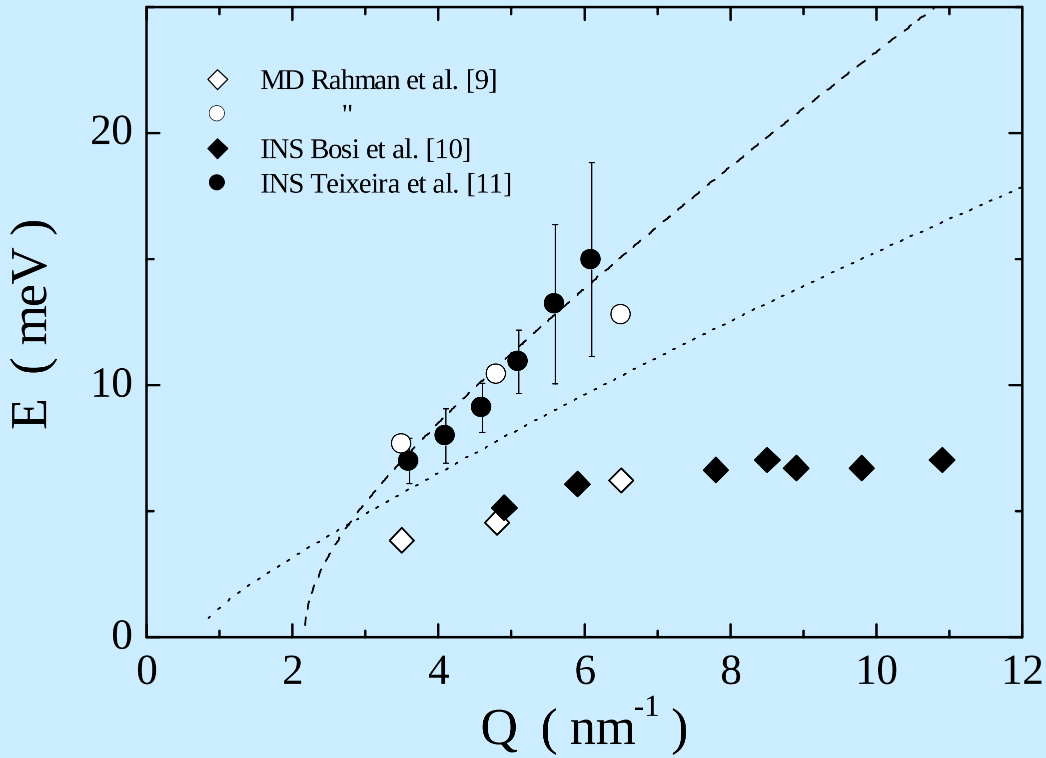
The high-frequency dynamics of liquid water

1993 - 2004

Some key references:

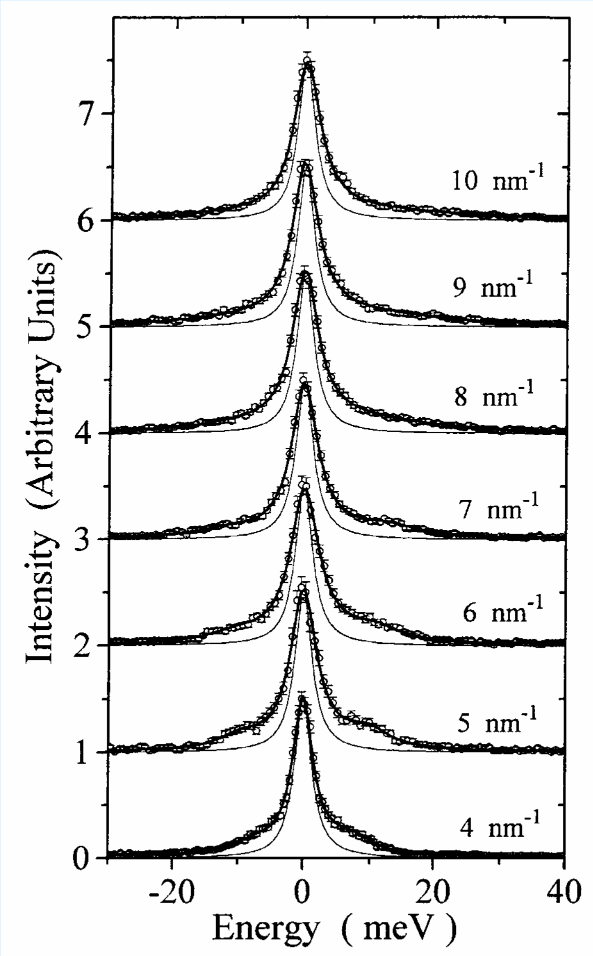
J. Teixeira et al.; Phys. Rev. Lett. 54, 2681 (1985)
G. Ruocco and F. Sette; J.Phys.: Condens.Matter 11, R259 (1999)
M. Krisch et al.; Phys. Rev. Lett. 89, 125502 (2002)

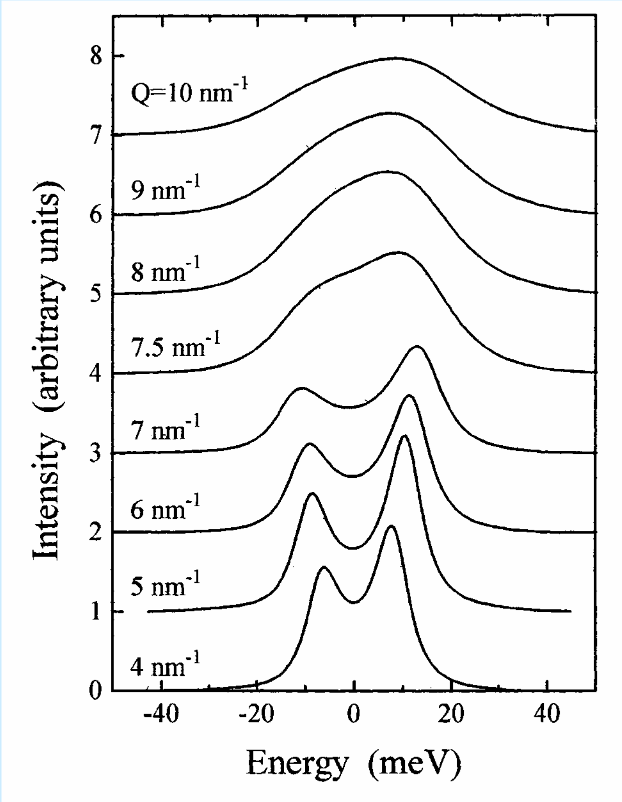
INS and Molecular Dynamics Results (as of 1993)



Origin and nature of these two excitations?

IXS results with ΔE = 5 meV

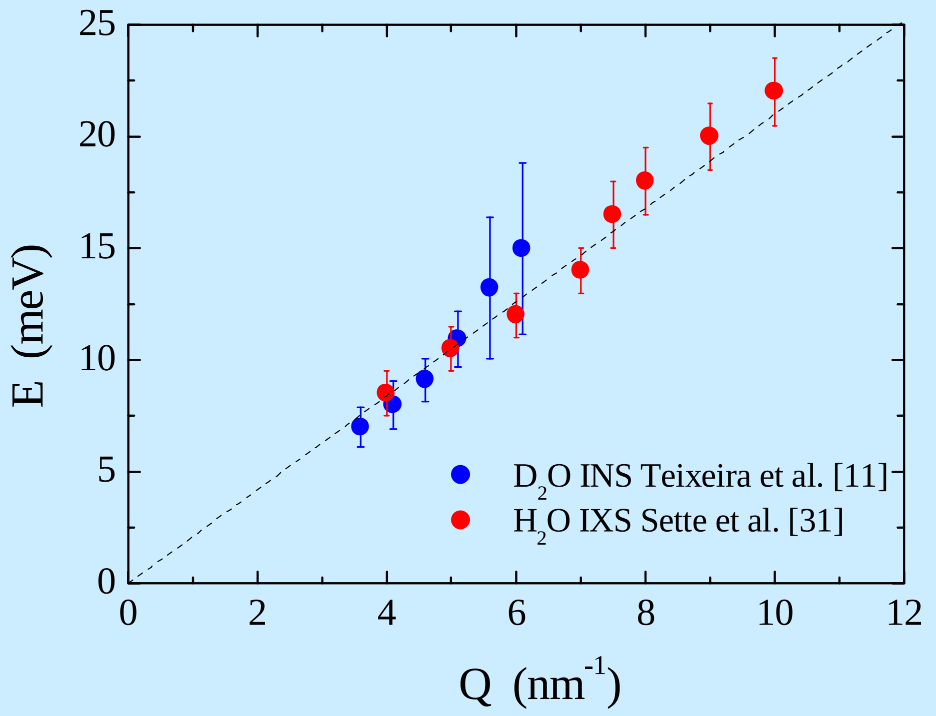




Damped harmonic oscillator

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

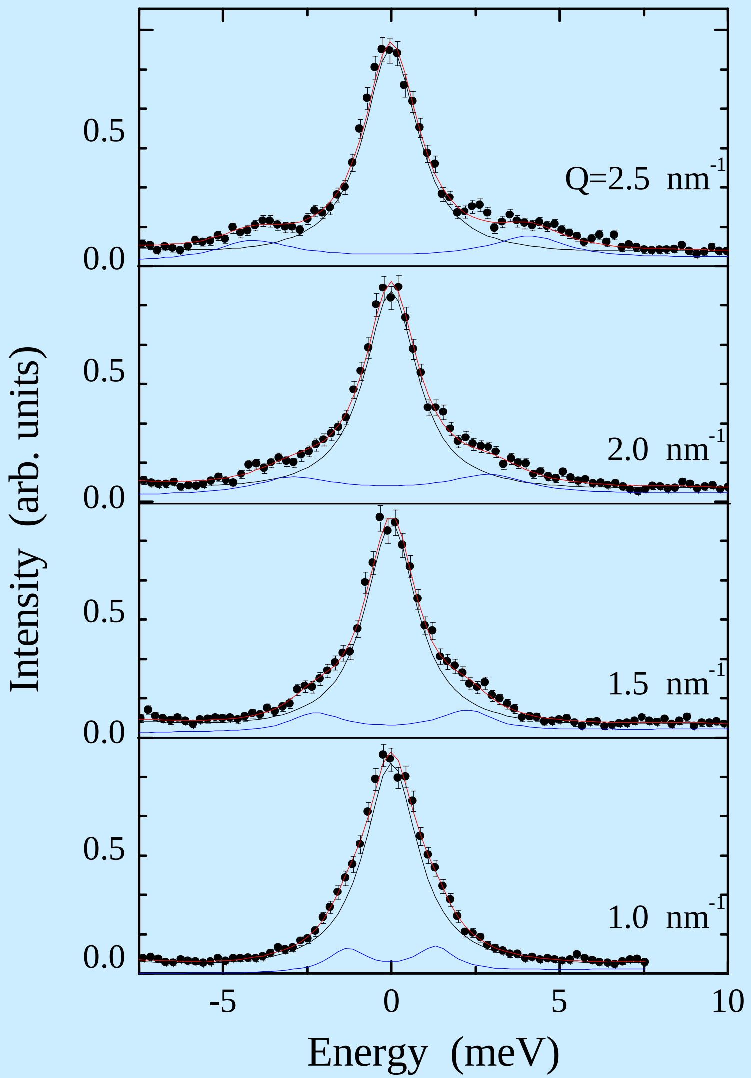
Dispersion relation for water at 5º C

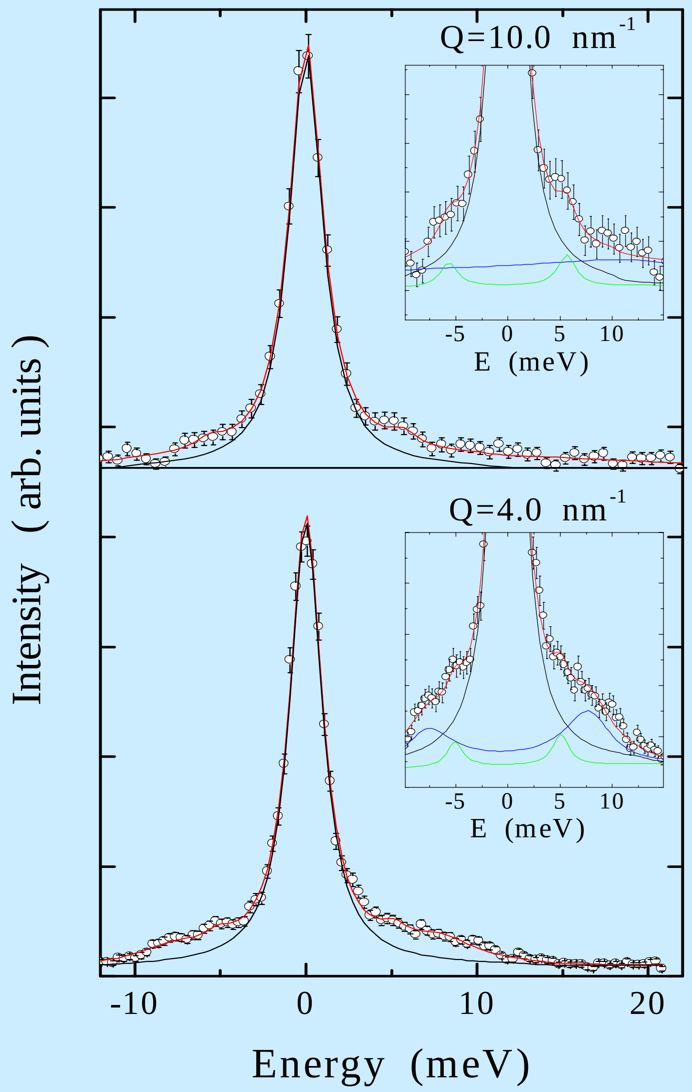


• Confirmation of the existence of the "fast sound".
• Excitation involves the center of mass of the molecule.

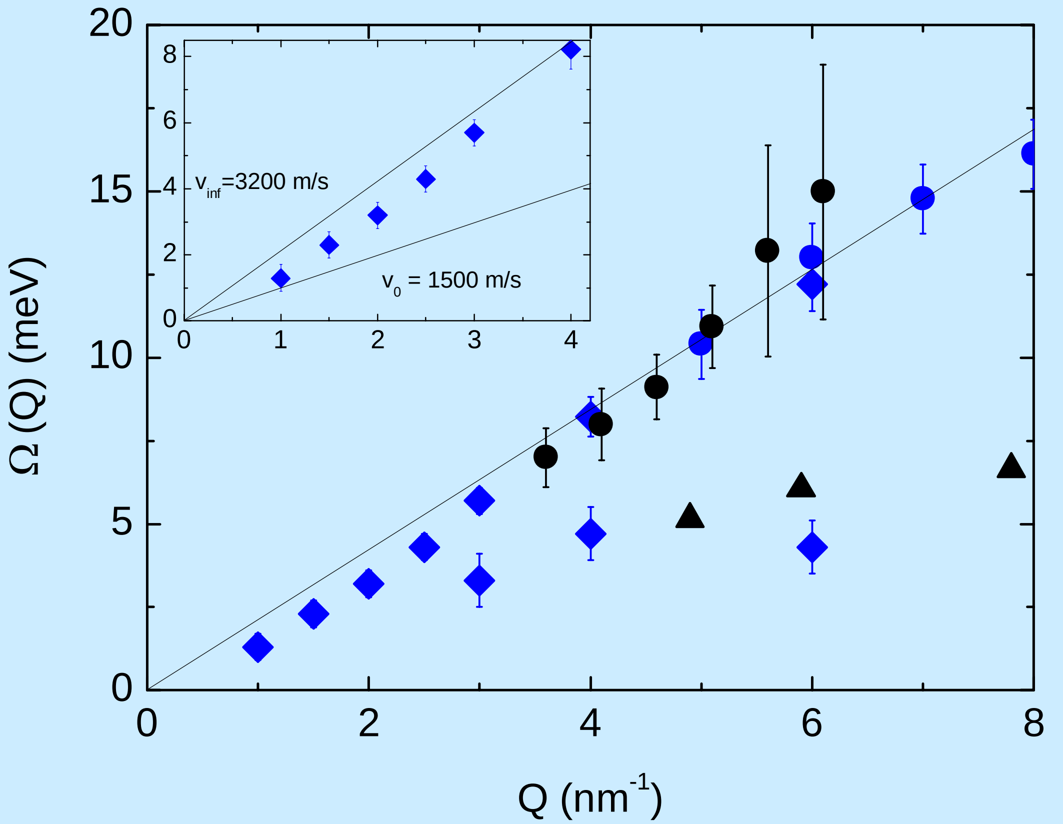
No clear evidence for low energy excitations!

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 reached.

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

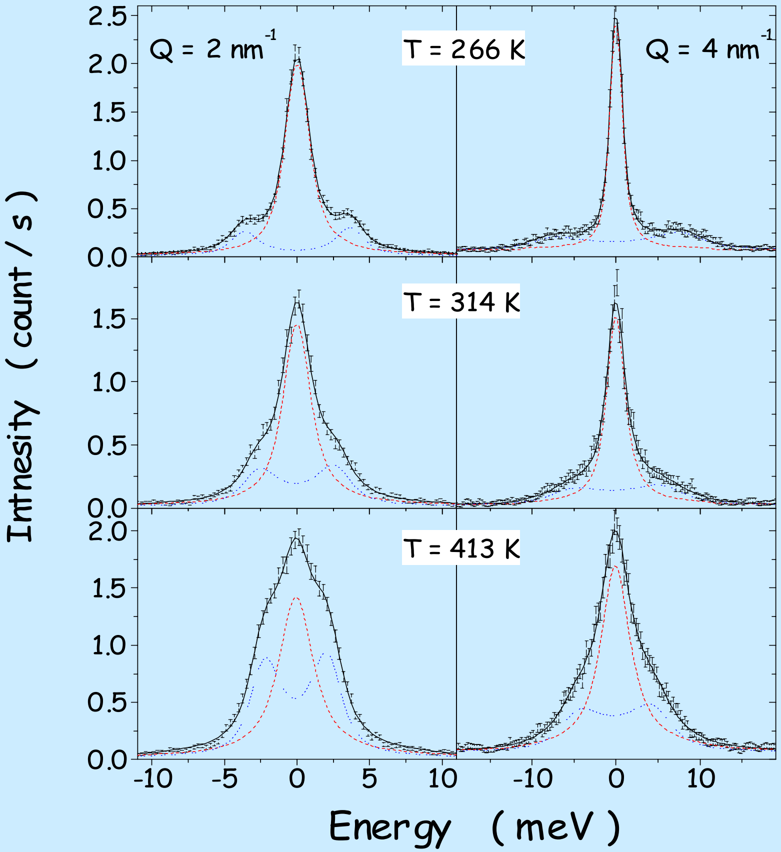
Low-frequency viscous regime ($\Omega\tau << 1$): liquid-like response
high-frequency elastic regime ($\Omega\tau >> 1$): solid-like response

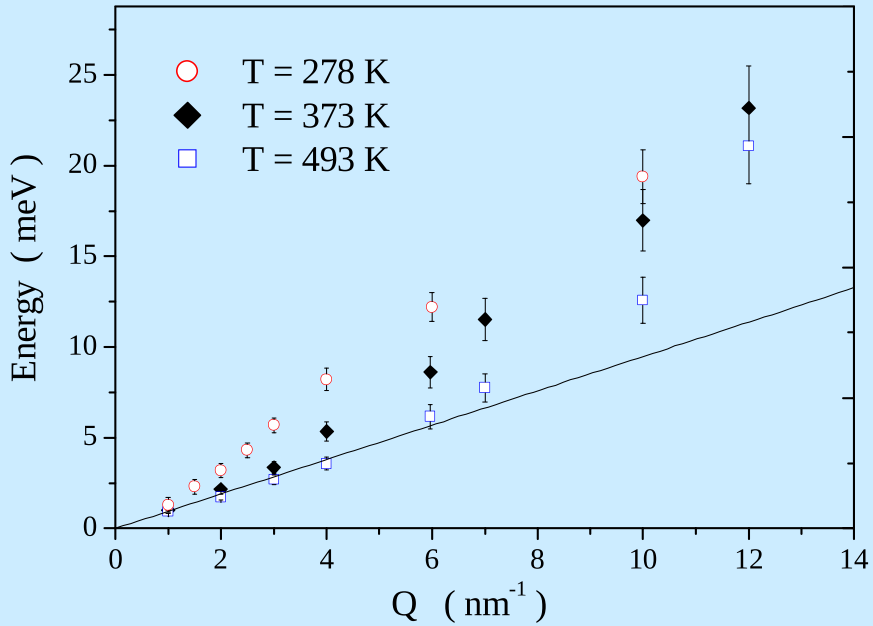
$\Omega\tau \approx 1$: Coupling of the phonon-like excitations with structural rearrangements.

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

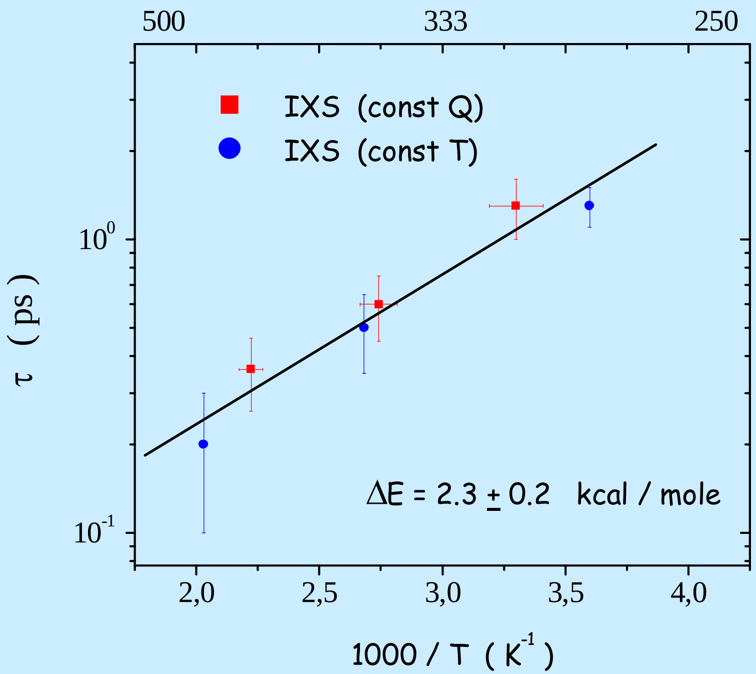
Time and length scale can be associated with the formation and breaking of hydrogen bond networks.

Fast sound transition as a function of T





Relaxation time $\tau(T)$ from: $\Omega_{trans}(T)\ \tau=1$



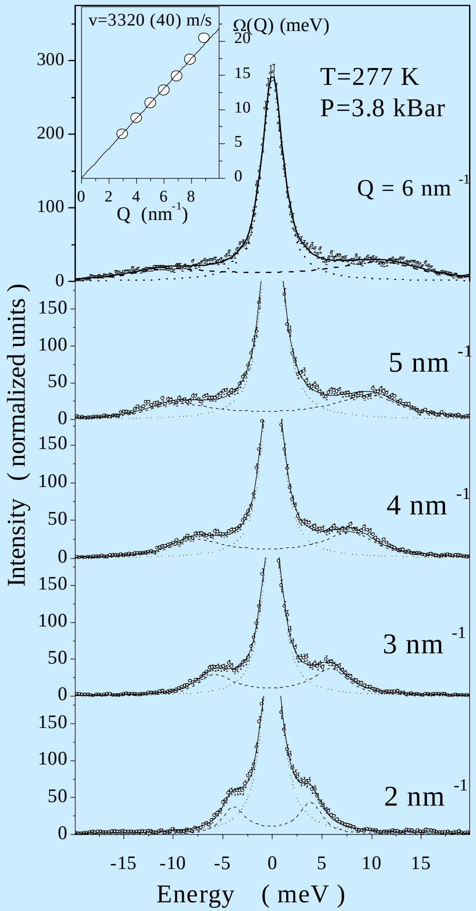
- Arrhenius behavior: $\Delta E = 2.3 \pm 0.2$ kcal / mole
- Hydrogen bond in water : $E_{HB} = 5$ kcal / mole

Water under pressure

Large volume cell

V = 20 mm^3

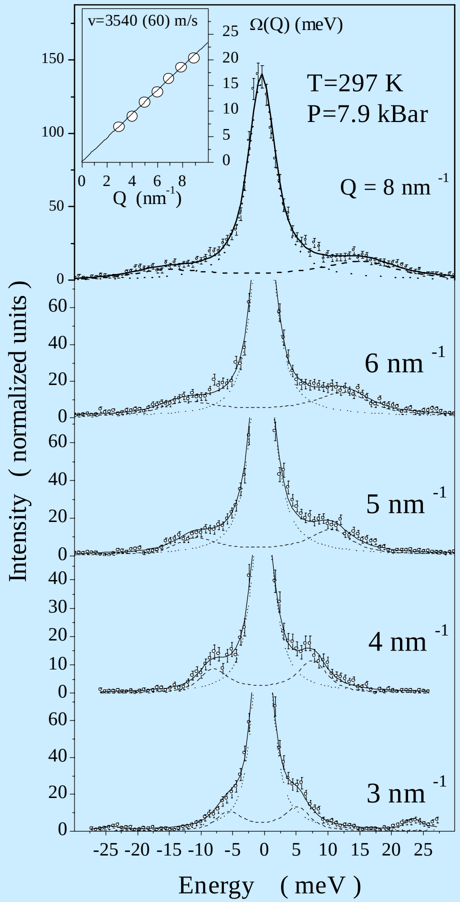
ΔE=1.5 meV, Si (11,11,11)



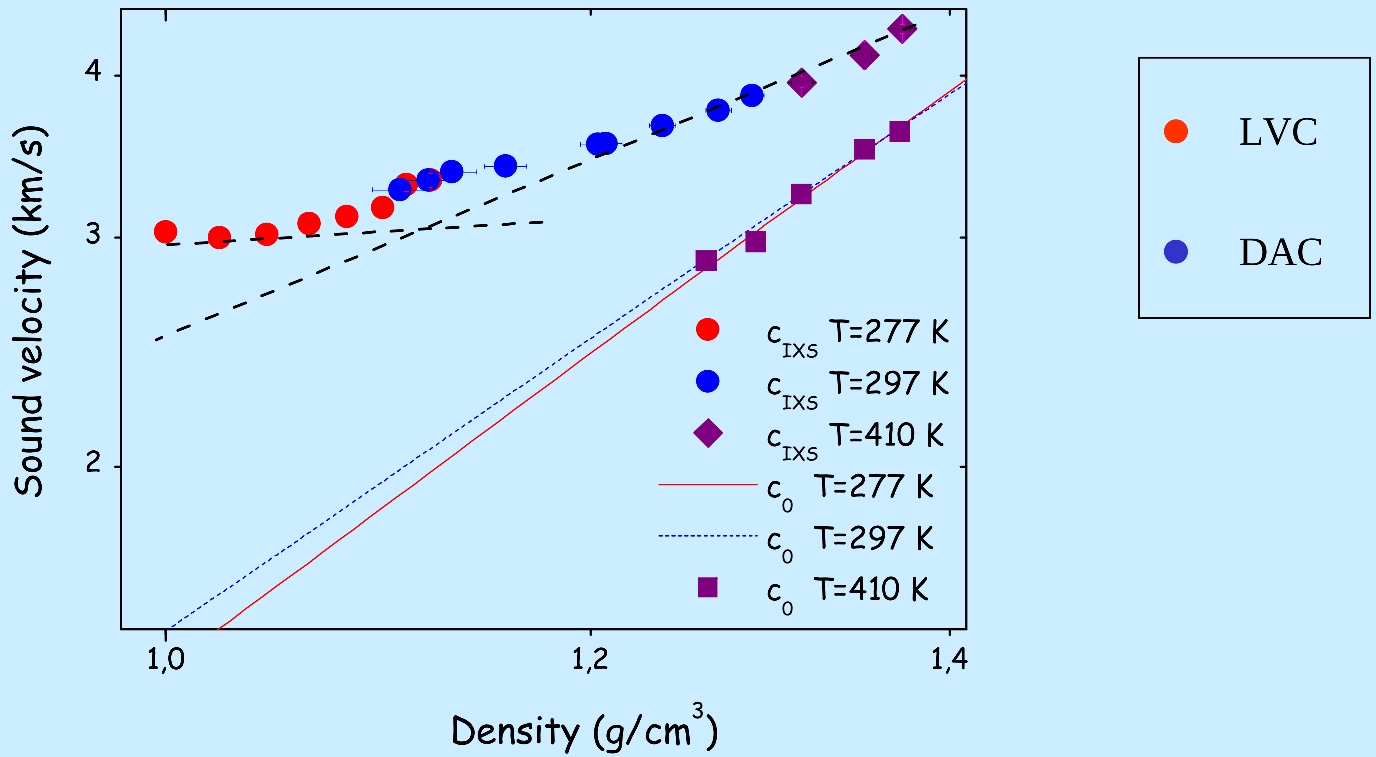
Diamond anvil cell

V = 0.04 mm^3

ΔE=3.0 meV, Si (9,9,9)

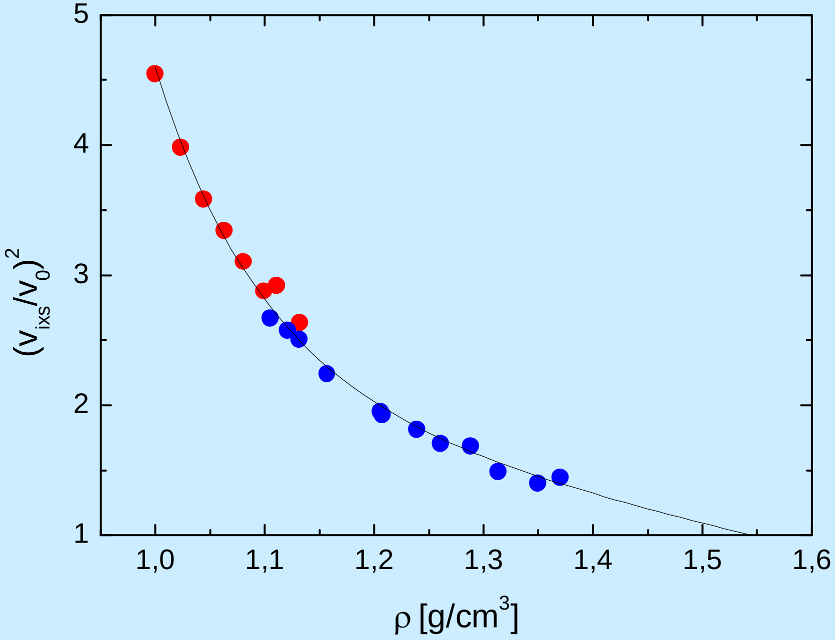


Density dependence of sound velocity



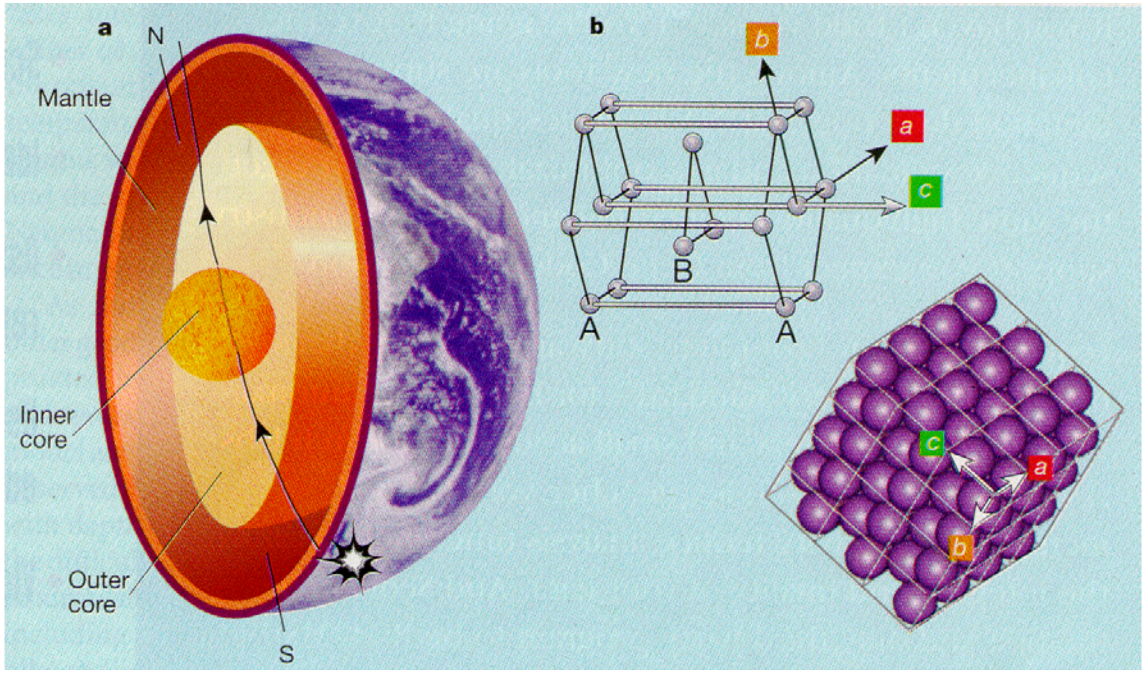
- c_{IXS} and c_0 approach each other.
- c_{IXS} shows anomalous behavior at density, ρ~1.12 gcm^{-3}

Pressure dependence of v_{IXS}/v_0



- **Decreasing role of H-bond network for water dynamics.**
- **Water becomes a simple liquid.**
- **ρ = 1.12 g/cm^3 seems to mark transition region.**

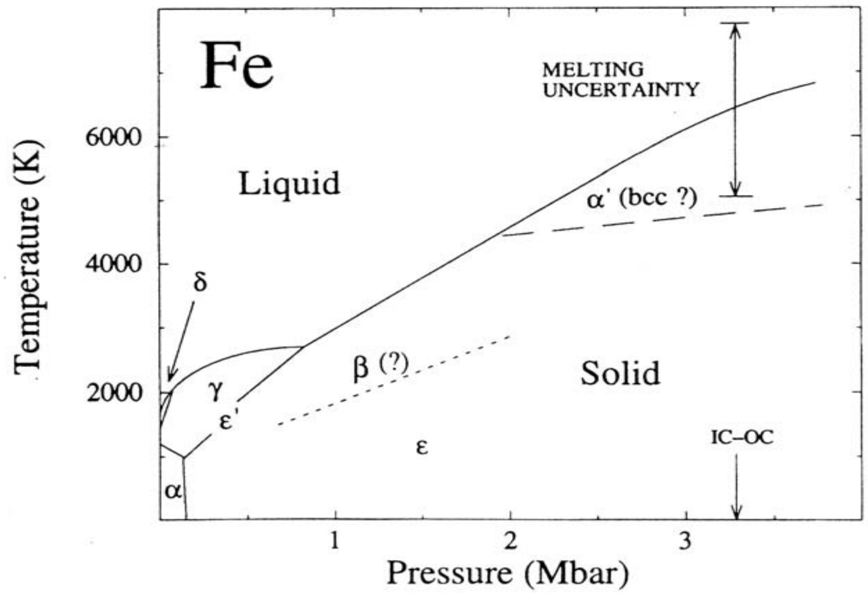
Geophysical applications of IXS



Jephcoat/Refson
Nature 413,28 (2001)

- Earth's shells
- Earth's composition
- Earth's dynamics

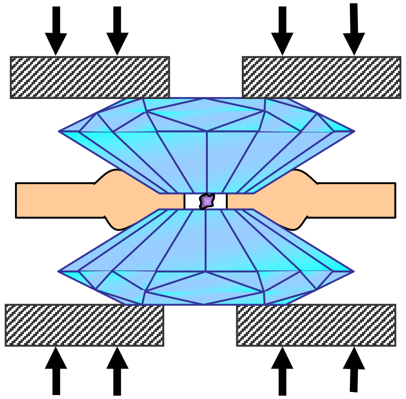
hcp –iron: the main constituent of Earth's inner core

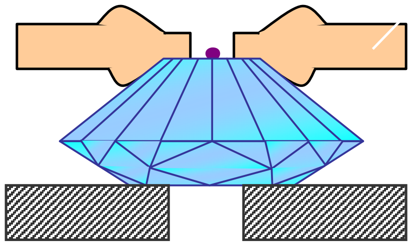


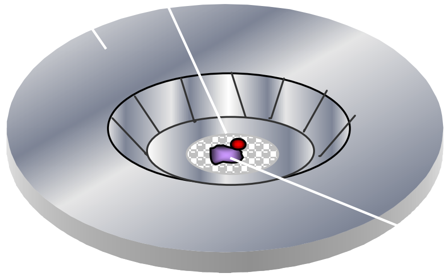
Determination of sound velocities

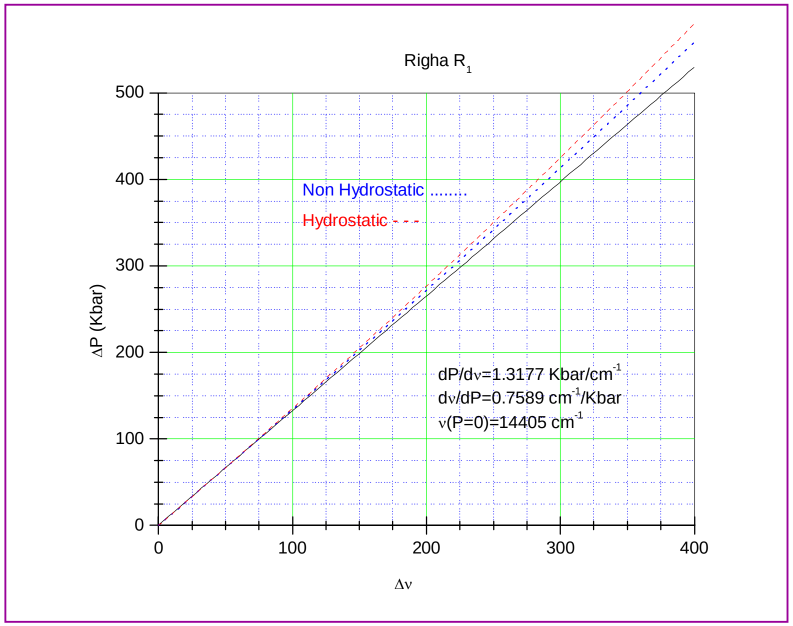
- Comparison with seismic results
- constraining compositional models
- texturing mechanisms

Diamond anvil cell (DAC) techniques

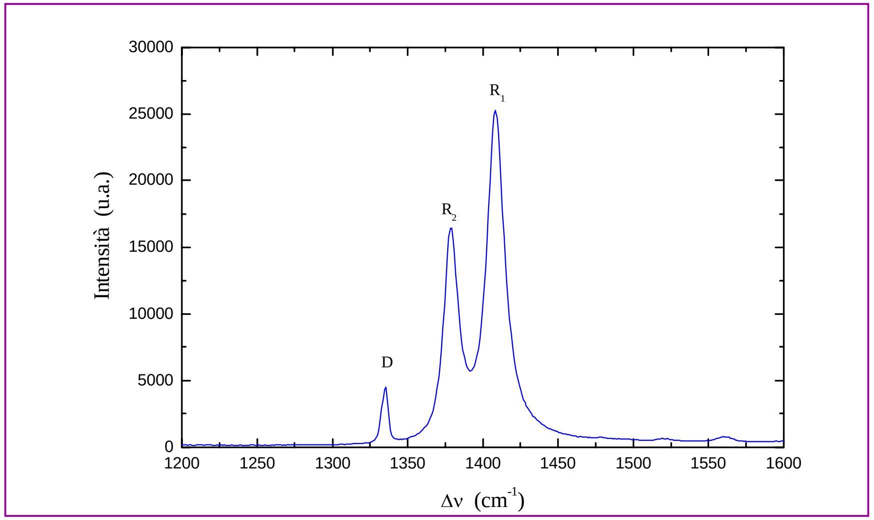






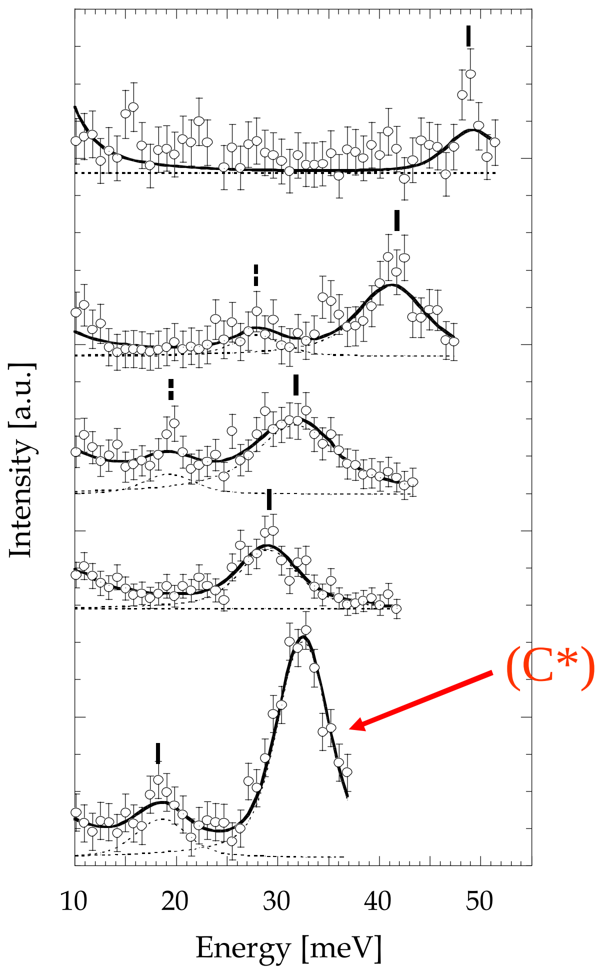


Pressure measurement by frequency shift of ruby fluorescence



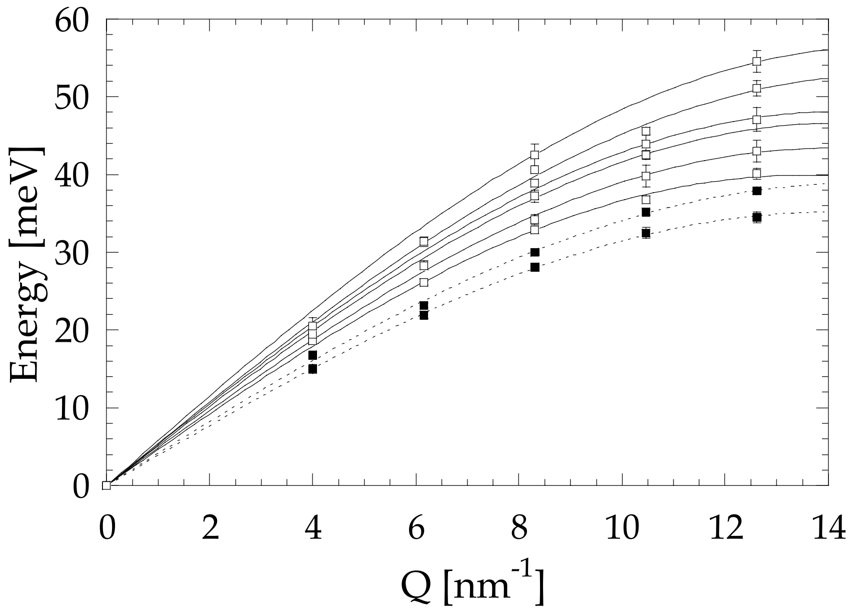
polycrystalline ε (hcp)-iron

hcp iron at 28 GPa



ID 28

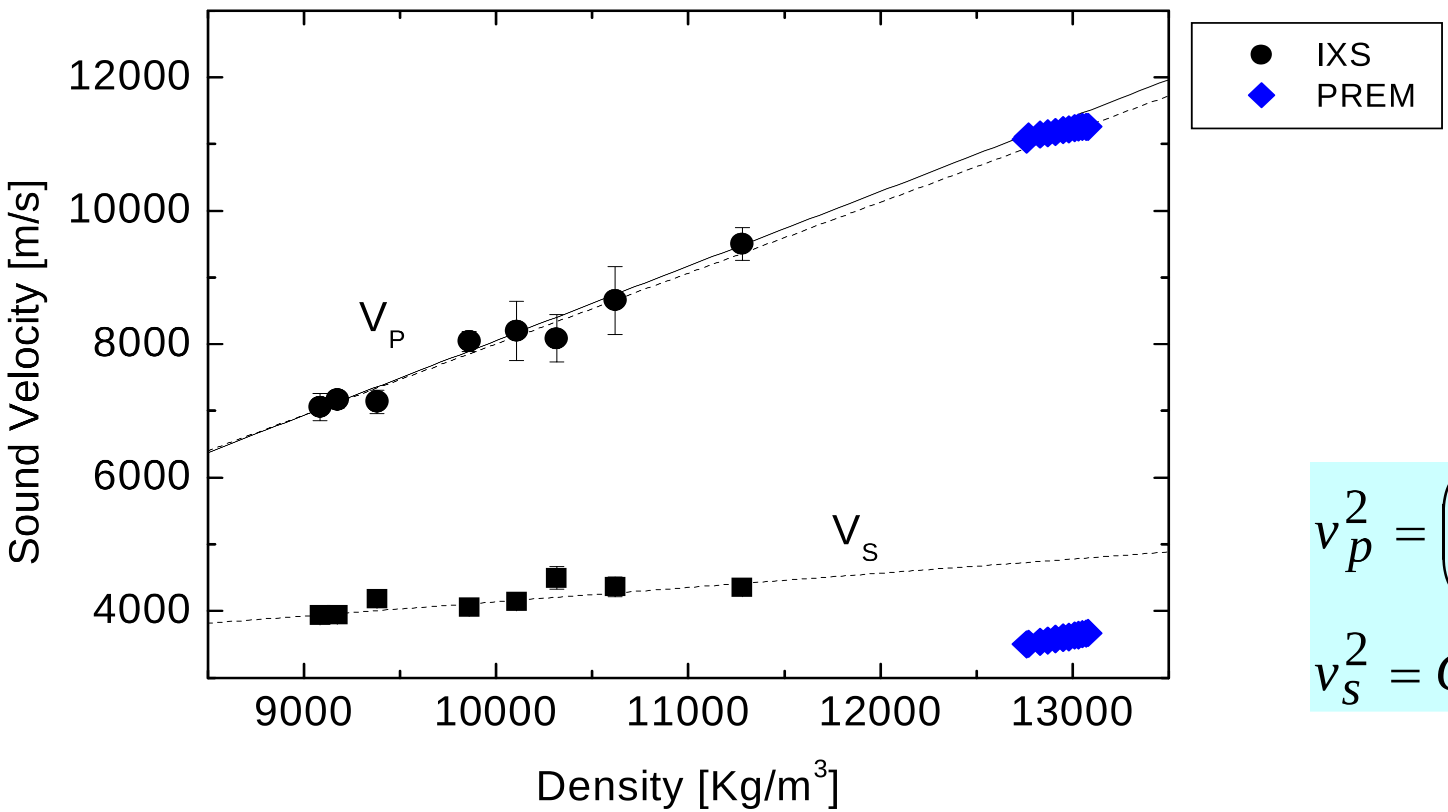
- ΔE = 5.5 meV at 15816 eV
- focal size: 250 x 70 μm^2 (FWHM)



$$E(Q) = I \cdot \left[\sum_n \left(1 - \cos\left(\frac{n\pi Q}{Q_{max}} \right) \right) \right]^{1/2}$$

G. Fiquet, J. Badro, F. Guyot, H. Requardt and M. Krisch; Science 291, 468 (2001)

V_P and V_S as a function of density

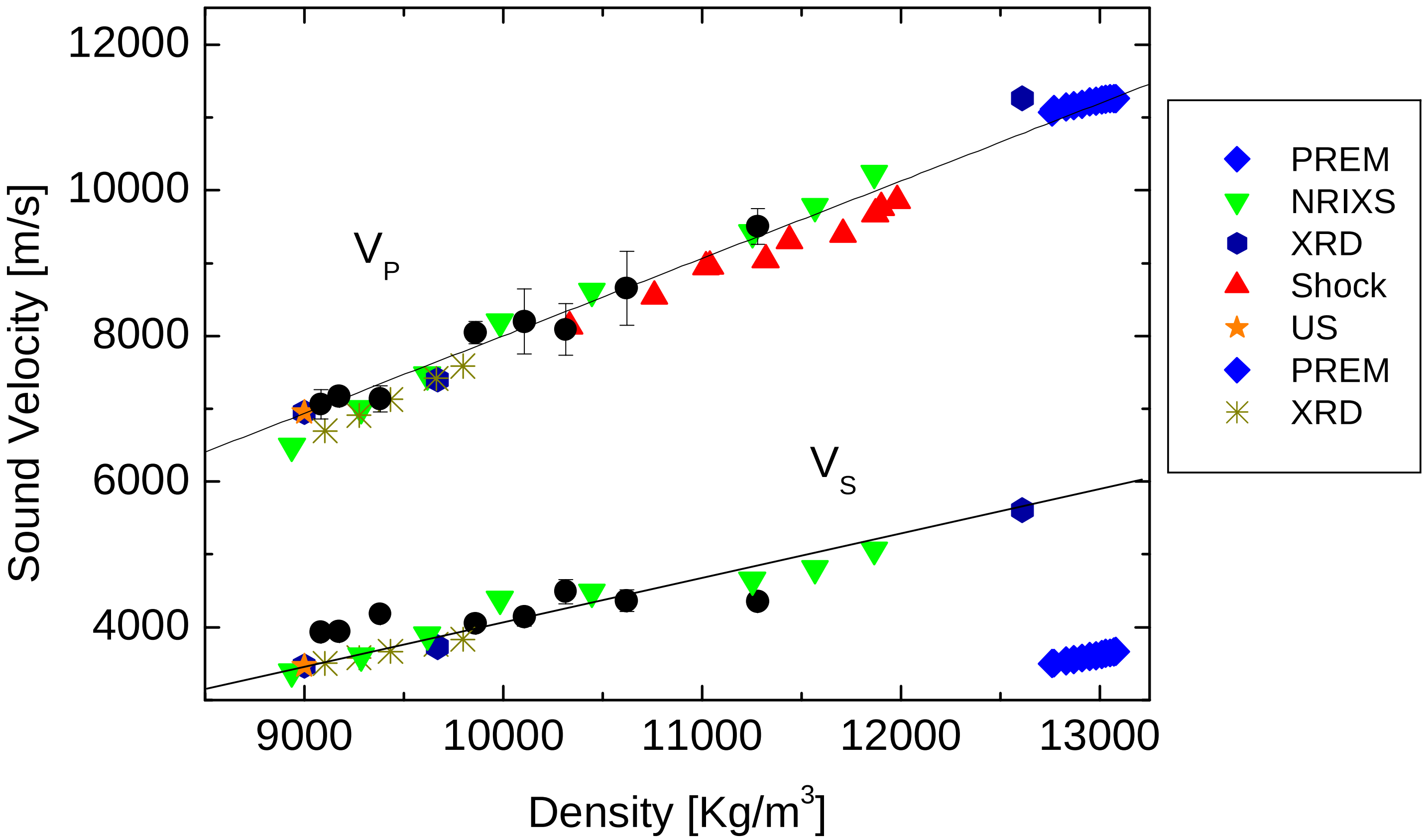


$$v_p^2 = \left(K + \frac{4}{3} G \right) / \rho$$

$$v_s^2 = G / \rho$$

D. Antonangeli et al; submitted to Earth and Planetary Science Letters (2004)

Comparison with other experimental techniques



Conclusions

- Good agreement between very different experimental techniques.
  - stringent test for theoretical approaches

- Shock results yield systematically lower V_P's.
  - $V_P(\rho, \mathbf{T})$
  - Evidence that ε-iron V_P too low w/r to PREM
    - different iron phase?
    - presence of light elements?

- Strong temperature effect on V_S
  - partial melting of the core?
  - strong T-dependence of shear modulus G close to melting

  (confirmed by calculations: Laio et al.; Science 287, 1027, 2000)

Limitations of polycrystals

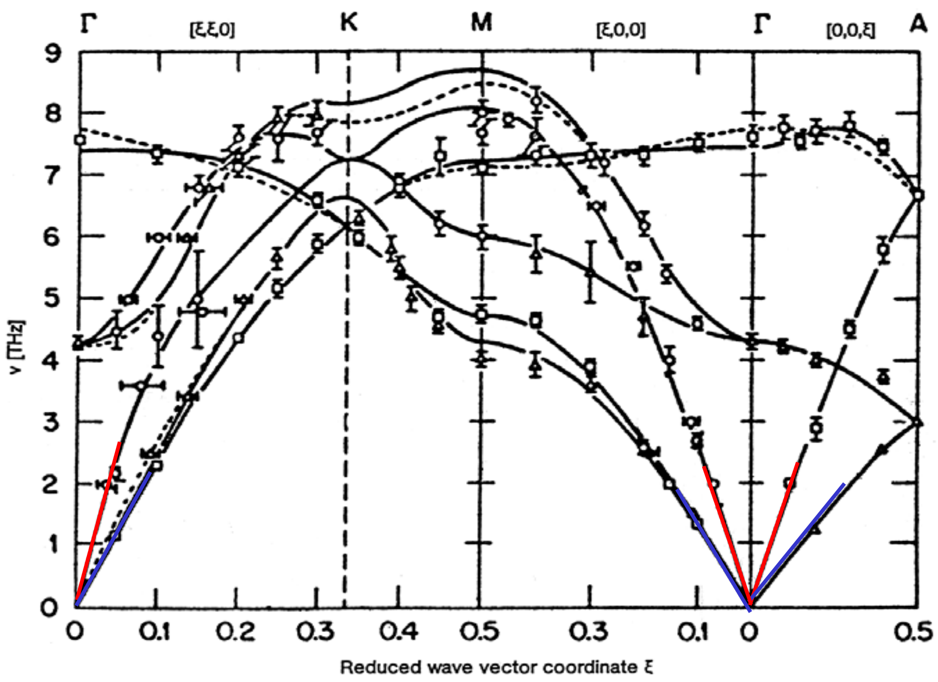
- orientationally averaged sound velocities

- no transverse modes

single crystals:

- all elastic moduli (constants)

hcp-Co



hcp-cobalt as an analogue to hcp-iron

Thesis work of Daniele Antonangeli

hcp-Co five independent elastic moduli: C_{11}, C_{33}, C_{44}, C_{12}, C_{13}

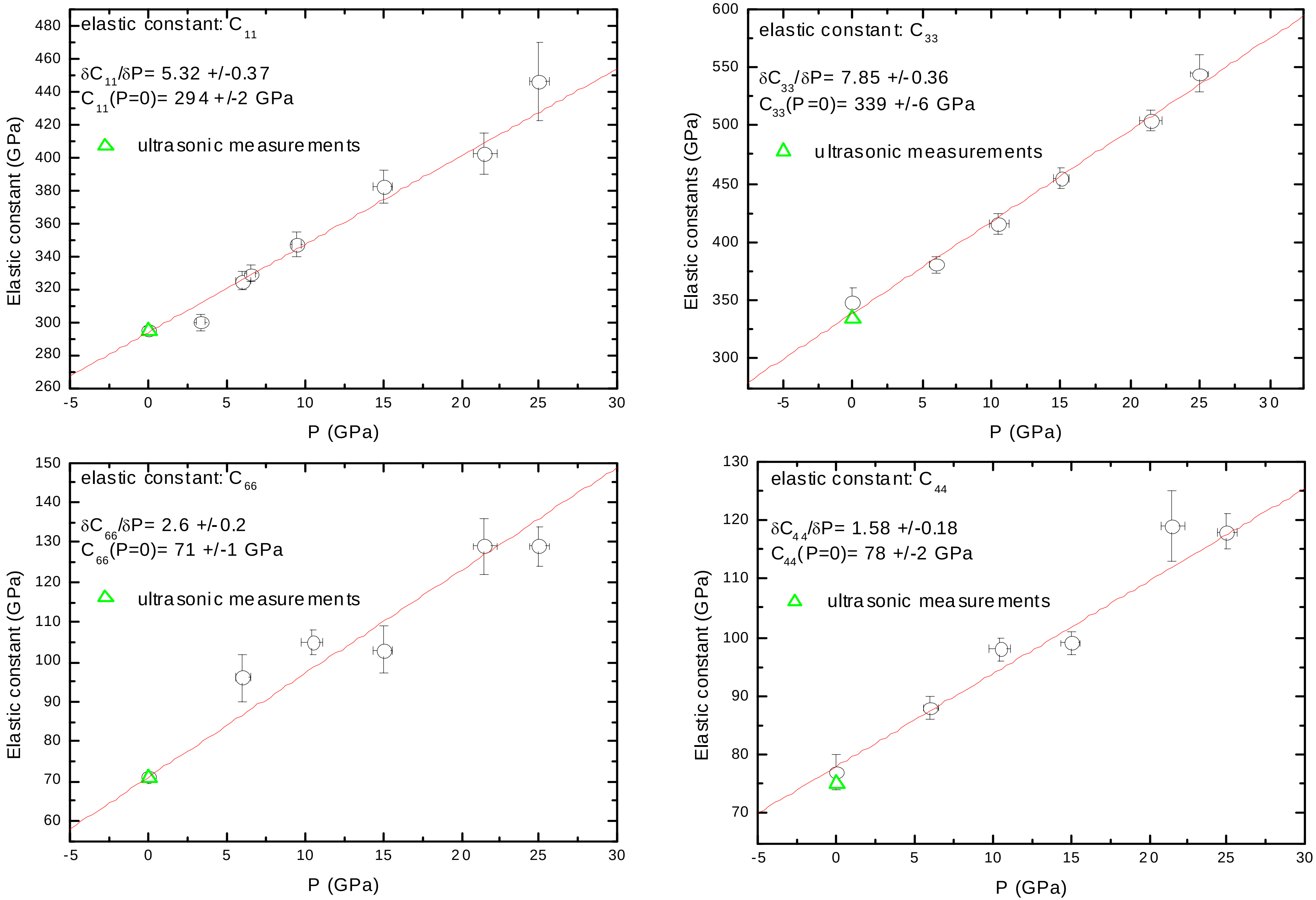
$$LA\,(001) \rightarrow \frac{1}{V} = \left(\frac{\rho}{C_{33}}\right)^{\frac{1}{2}} \rightarrow C_{33}$$

$$LA\,(100) \rightarrow \frac{1}{V} = \left(\frac{\rho}{C_{11}}\right)^{\frac{1}{2}} \rightarrow C_{11}$$

$$LA\,(110)_{\langle 100\rangle} \rightarrow \frac{1}{V} = \left(\frac{\rho}{C_{66}}\right)^{\frac{1}{2}} \rightarrow C_{66} = \frac{1}{2}(C_{11} - C_{12})$$

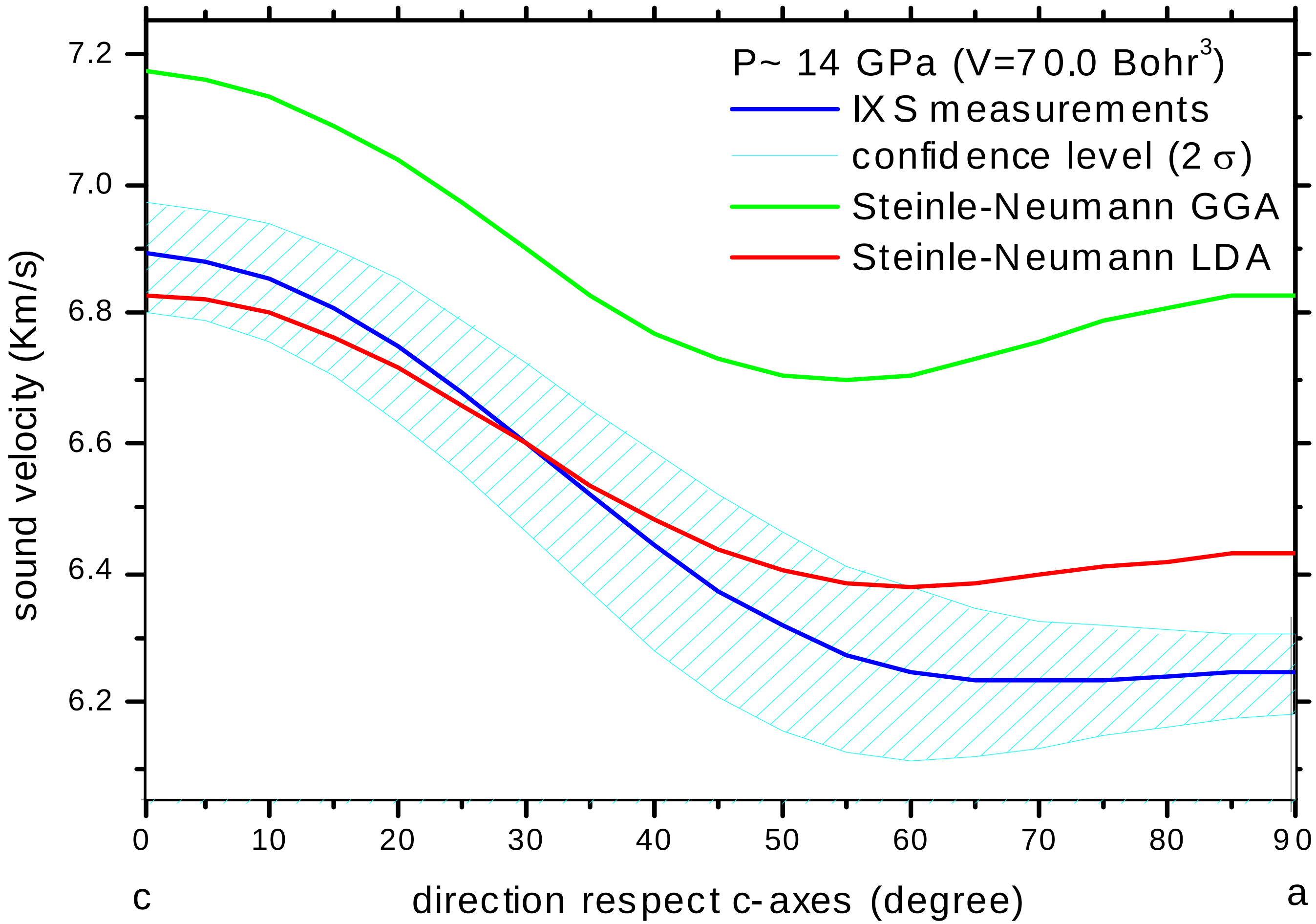
$$TA\,(110)_{\langle 001\rangle} \rightarrow \frac{1}{V} = \left(\frac{\rho}{C_{44}}\right)^{\frac{1}{2}} \rightarrow C_{44}$$

$$LA\,(101) \rightarrow \mathrm{f}\left(C_{11}, C_{33}, C_{44}, C_{12}, C_{13}\right) \rightarrow C_{13}$$



elastic constant: C11
δC11/δP= 5.32 +/-0.37
C11(P=0)= 294 +/-2 GPa
ultrasonic measurements
Elastic constant (GPa)
P (GPa)
elastic constant: C33
δC33/δP= 7.85 +/-0.36
C33(P=0)= 339 +/-6 GPa
ultrasonic measurements
Elastic constants (GPa)
P (GPa)
elastic constant: C66
δC66/δP= 2.6 +/-0.2
C66(P=0)= 71 +/-1 GPa
ultrasonic measurements
Elastic constant (GPa)
P (GPa)
elastic constant: C44
δC44/δP= 1.58 +/-0.18
C44(P=0)= 78 +/-2 GPa
ultrasonic measurements
Elastic constant (GPa)
P (GPa)

Comparison of IXS with theory

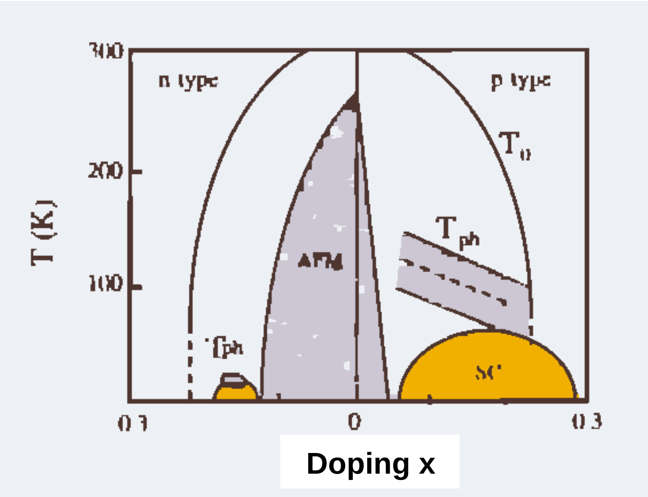


Ref.:Steinle-Neumann et al., *Phys. Rev. B*, **60**, 791, (1999)

Phonon dispersion in $Nd_{1.86}Ce_{0.14}CuO_{4+\delta}$

M. D'Astuto et al.; Phys. Rev. Lett. 88, 167002 (2002)

Electron-phonon coupling in electron-doped high Tc superconducting cuprates?

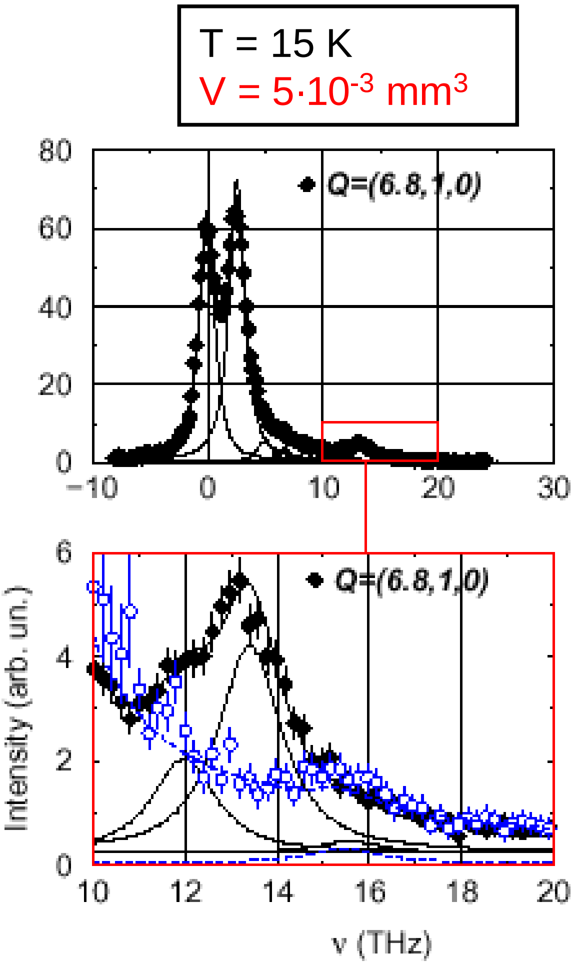


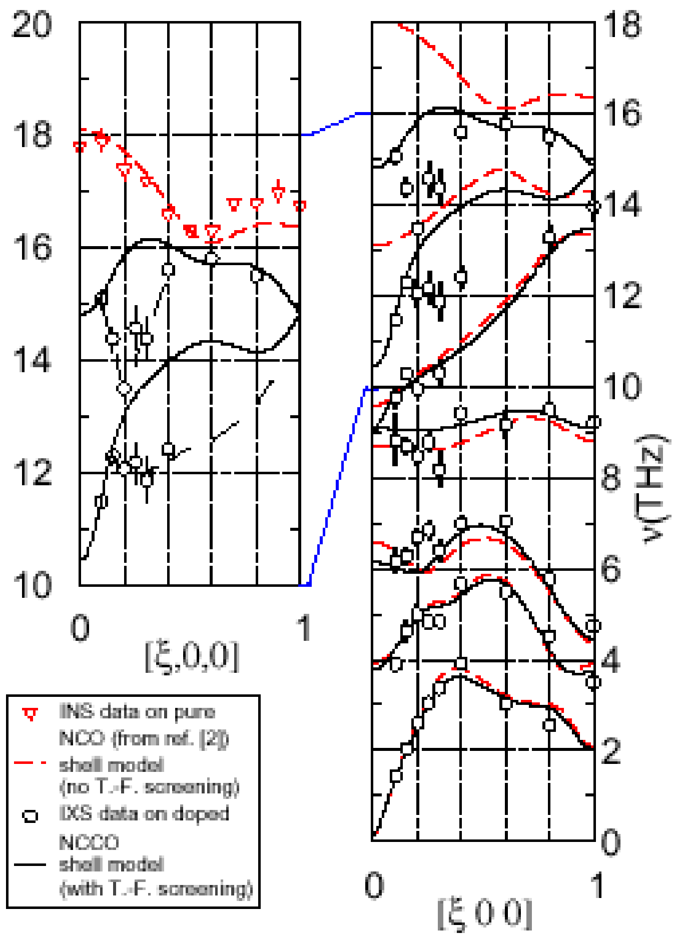
Z.-X. Shen (2001)

Explanation of particle-hole asymmetry

Angle-resolved photoemission studies: Discontinuity in the quasi-particle dispersion.

INS on hole-doped systems ($La_{1.85}Sr_{0.15}CuO_4$): Anomalous softening of LO phonons.





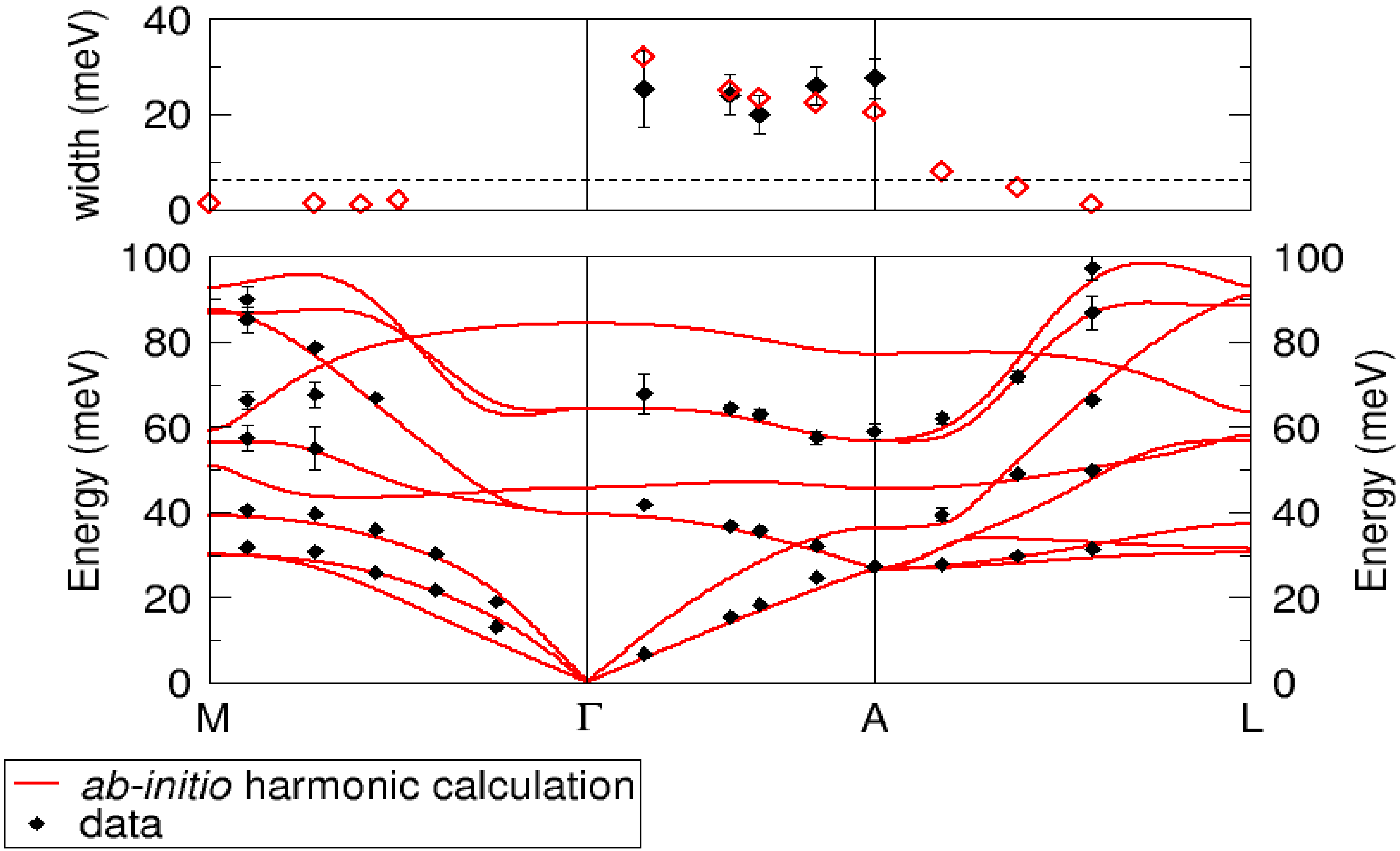
- Renormalisation of the highest LO branch with respect to undoped compound.
- Anomalous softening of the highest LO branch.

=>

Strong evidence for e-ph coupling as well in electron doped cuprates.

Phonon dispersion in MgB_2

A. Shukla et al.; Phys. Rev. Lett. 90, 095506 (2003)



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; CH_4-H_2O (high pressure)
- **Co**, Zn,Ta,Mo (high pressure)
- $SrTiO_3$ (high pressure)
- SmS (high pressure)
- C^{12},C^{13},GaN, SiC (ZB), ZnMgY
- $NbSe_3$, **Pu**
- $Nd_{1.86}Ce_{0.14}CuO_{4+\delta}$, $LaSrCuO_4$, $HgBa_2CuO_4$