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Collective Atomic Dynamics: Inelastic X-ray Scattering

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Collective Atomic Dynamics: Inelastic X-ray Scattering

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Trieste 2008

OUTLINE

Introduction:

- Collective atomic dynamics
- Inelastic scattering (neutrons vs. X-rays)

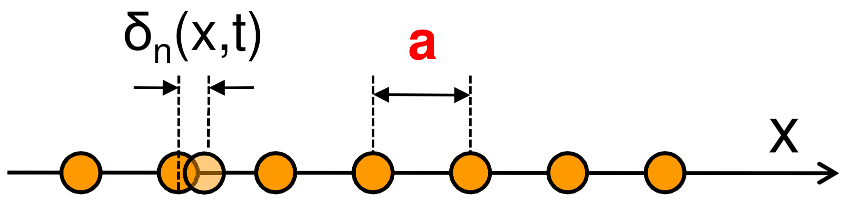
IXS Instrumentation

Experimental highlights:

- Collective dynamics in water
- Phonon dispersion in plutonium
- Elasticity at high-pressure
- Etc …

Introduction: collective atomic dynamics

The simpler case



Information:

- Interatomic Structure (**a**)
- Interaction Potential (**β**)

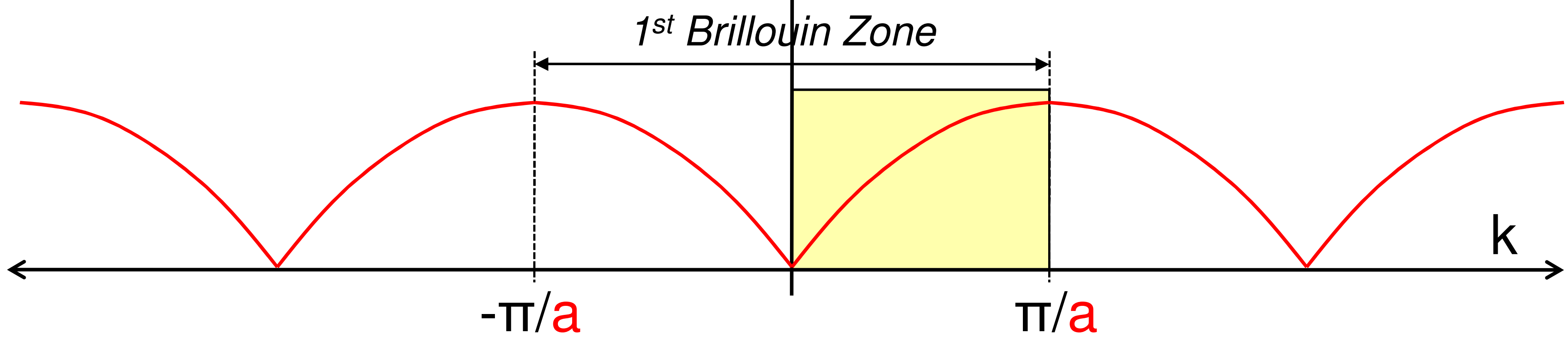
$U = -\beta x^2$

$\delta_n(x,t) = \delta_{n,0}\exp[i(kx-\omega t)]$

Phonons → Eigenstates of vibrational field

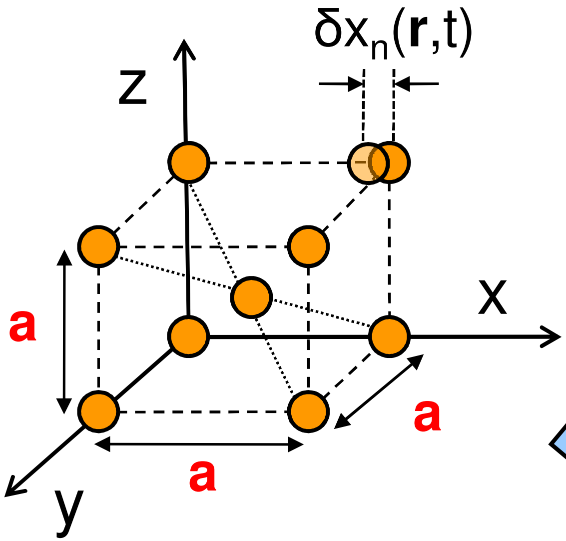
$\omega(k)$ → Spectrum of eigenvalues

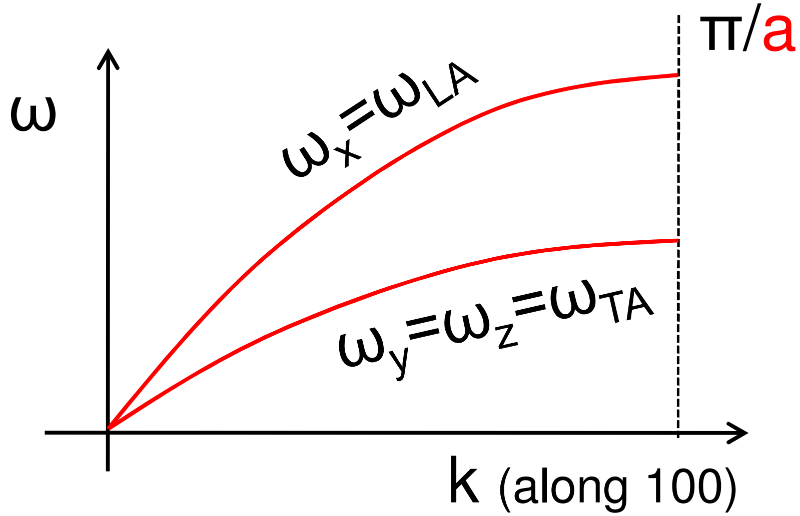
$\omega = (4\beta/M)^{1/2}\sin(ka/2)$



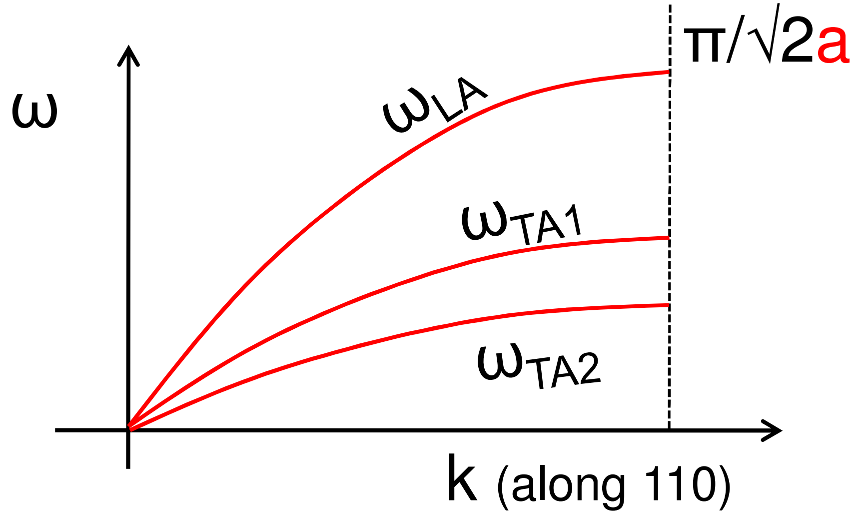
Introduction: collective atomic dynamics

One step forward: 3D lattice





$\omega = (\mathbf{c}_{ij}/\rho)^{1/2} \sin(ka^*)$

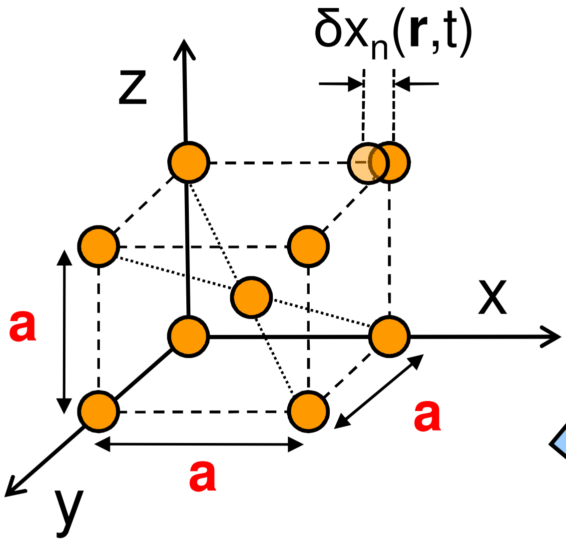


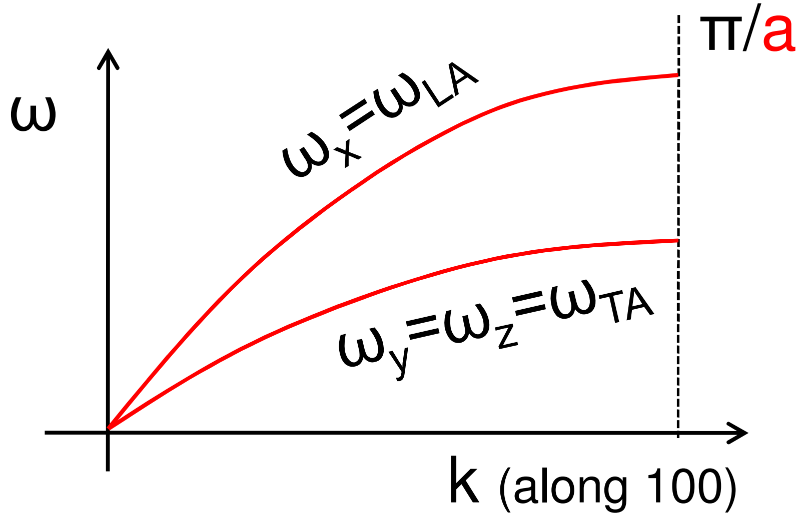
$U = -\boldsymbol{\beta}|\mathbf{r}|^2 \qquad \mathbf{r} = (x,y,z)$

$$\delta x_n(\mathbf{r},t) = \delta x_{n,0} \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega_x t)]$$
$$\delta y_n(\mathbf{r},t) = \delta y_{n,0} \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega_y t)]$$
$$\delta z_n(\mathbf{r},t) = \delta z_{n,0} \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega_z t)]$$

Introduction: collective atomic dynamics

One step forward: 3D lattice





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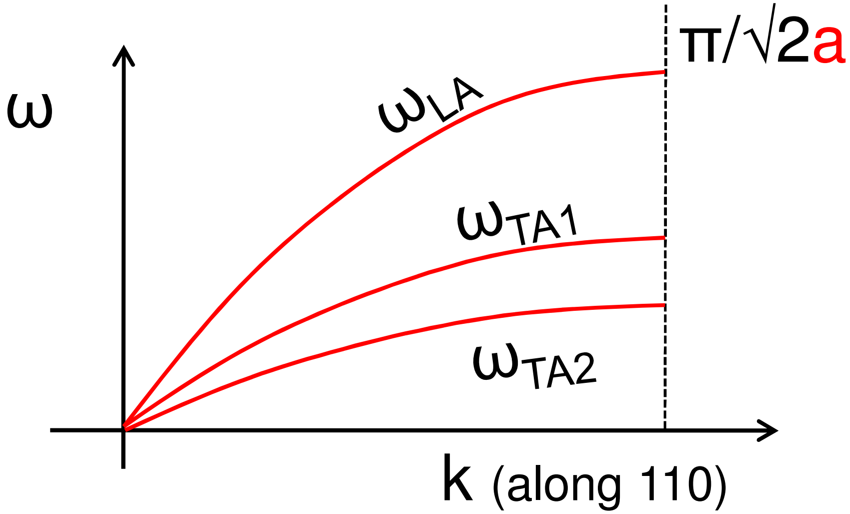
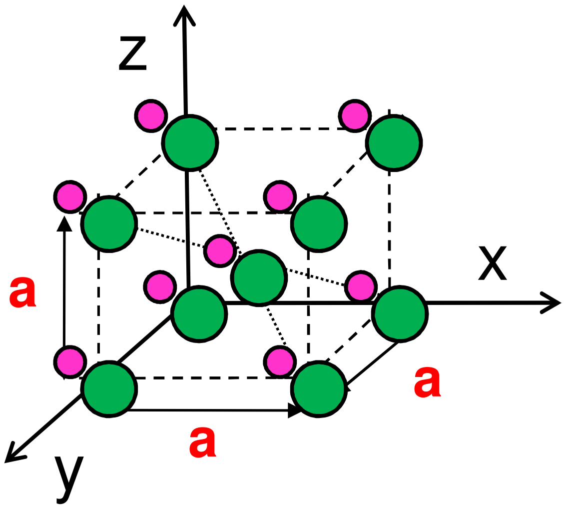


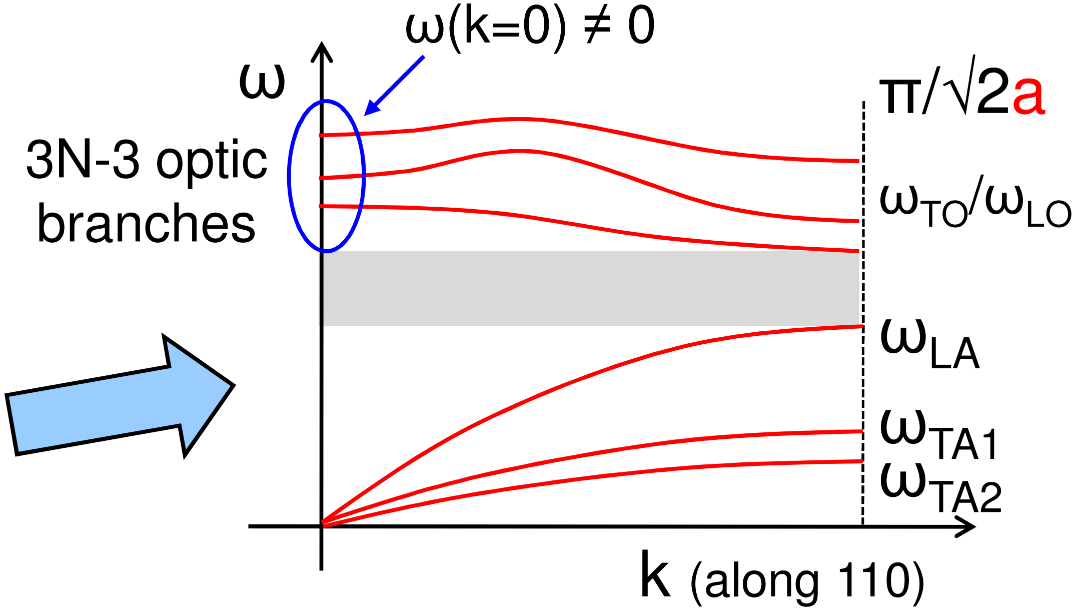
$U = -\boldsymbol{\beta}|\mathbf{r}|^2 \qquad \mathbf{r} = (x,y,z)$

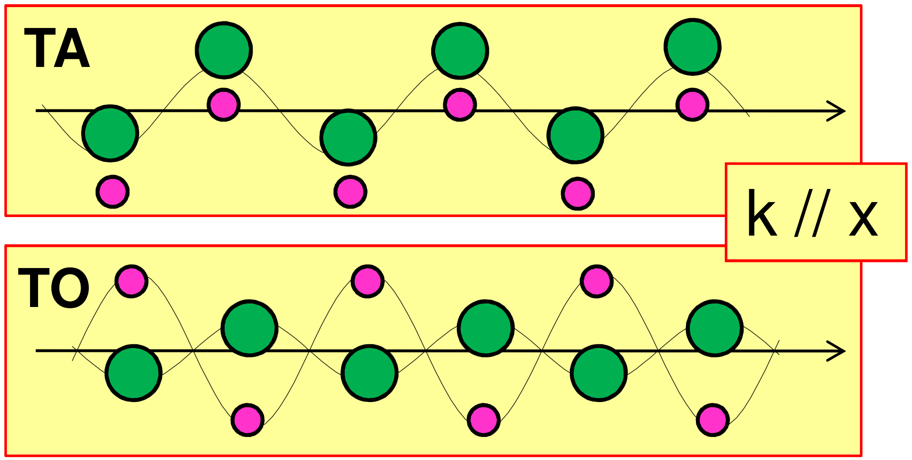
Information:

- Interatomic Structure (**a**)
- Interaction Potential (**β**)
- Anisotropy (elasticity: $\mathbf{c}_{ij}$)

Introduction: collective atomic dynamics





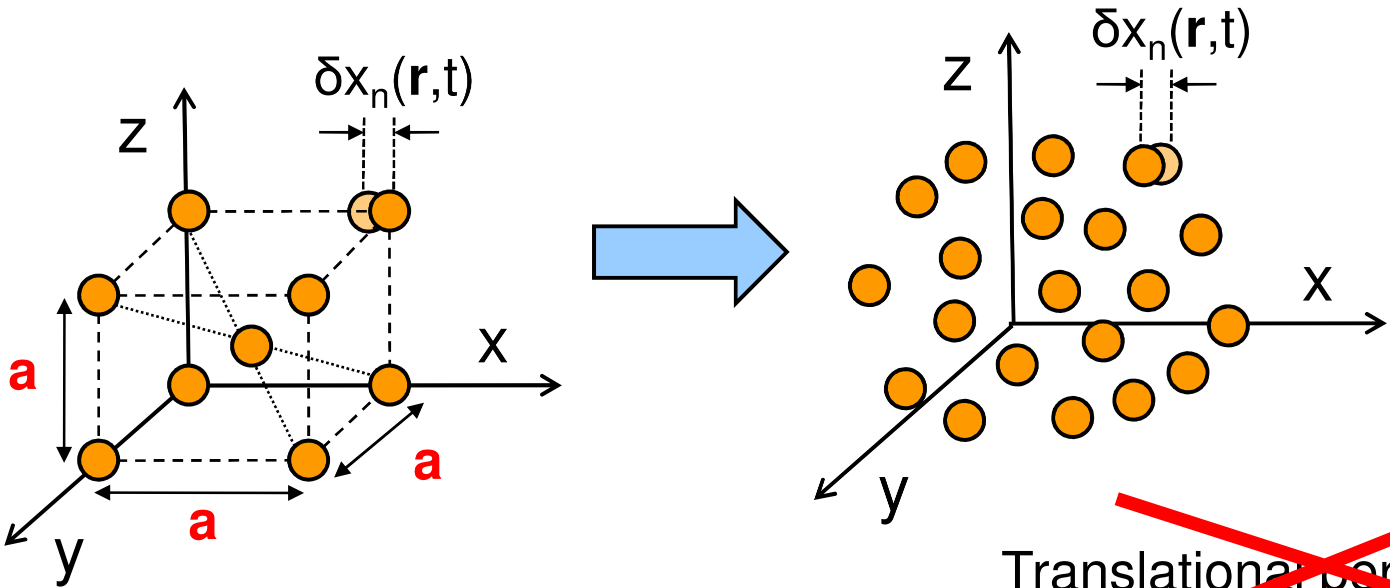


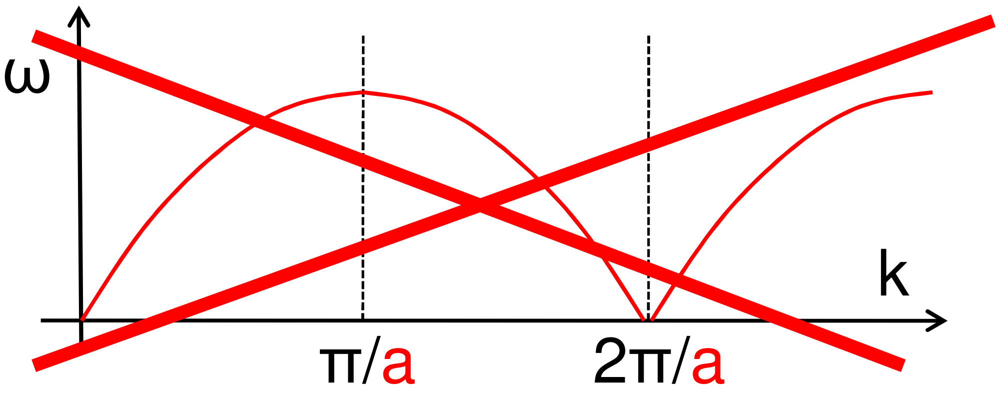
Information:

- Interatomic Structure (**a**)
- Interaction Potential (**β**)
- Anisotropy (elasticity: $\mathbf{c}_{ij}$)
- Intramolecular vibrations
- Propagation gap

Introduction: collective atomic dynamics

The most complex case: disordered systems





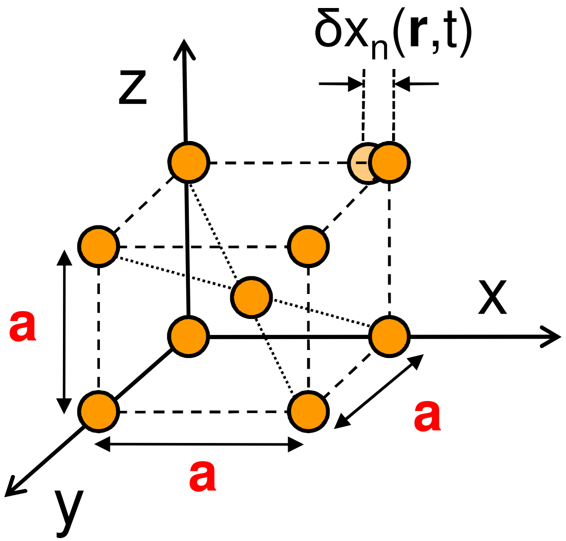
Translational periodicity (**a**)

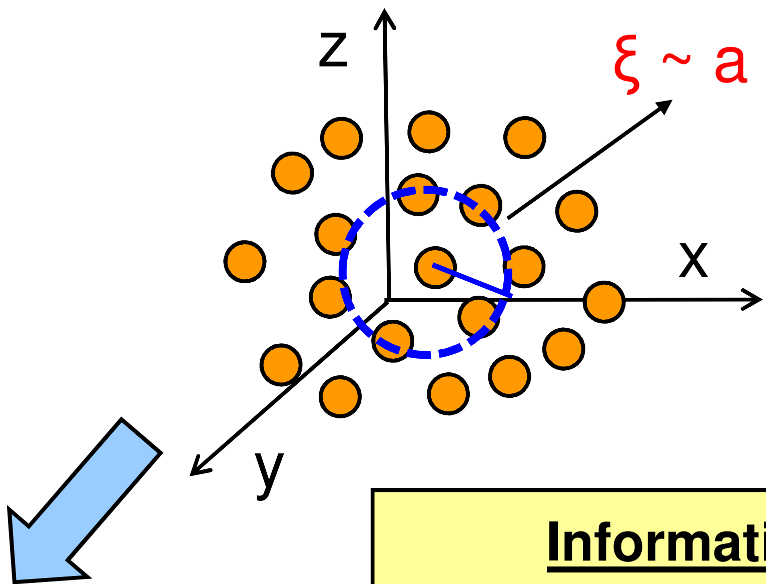
Brillouin Zones

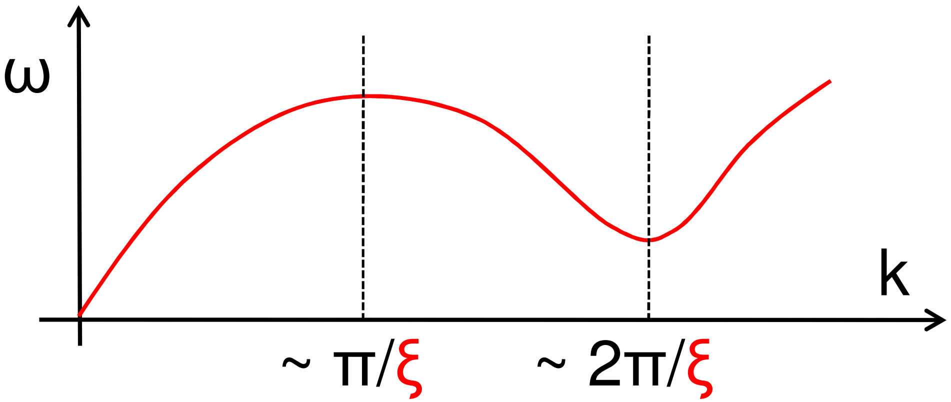
Eingenstates ~ exp[i(kx-ωt)]

Introduction: collective atomic dynamics

The most complex case: disordered systems





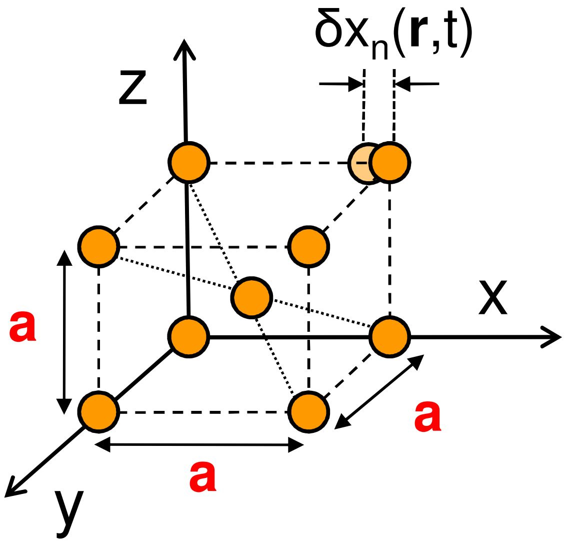


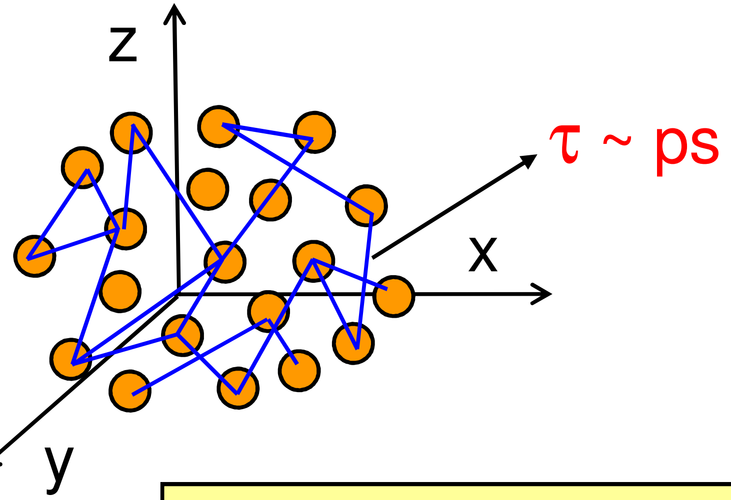
Information:

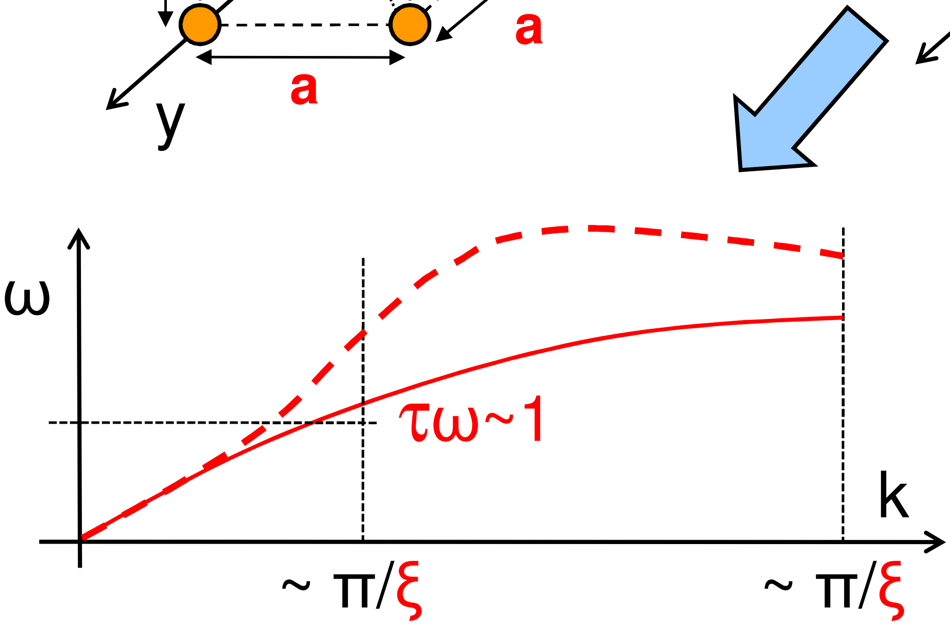
- Interatomic Structure (**ξ**)
- Interaction potential
- Topological disorder
- Relaxation processes
- "Lineshape" (anharmonicity, etc…)

Introduction: collective atomic dynamics

The most complex case: disordered systems







Information:

- Interatomic Structure (**ξ**)
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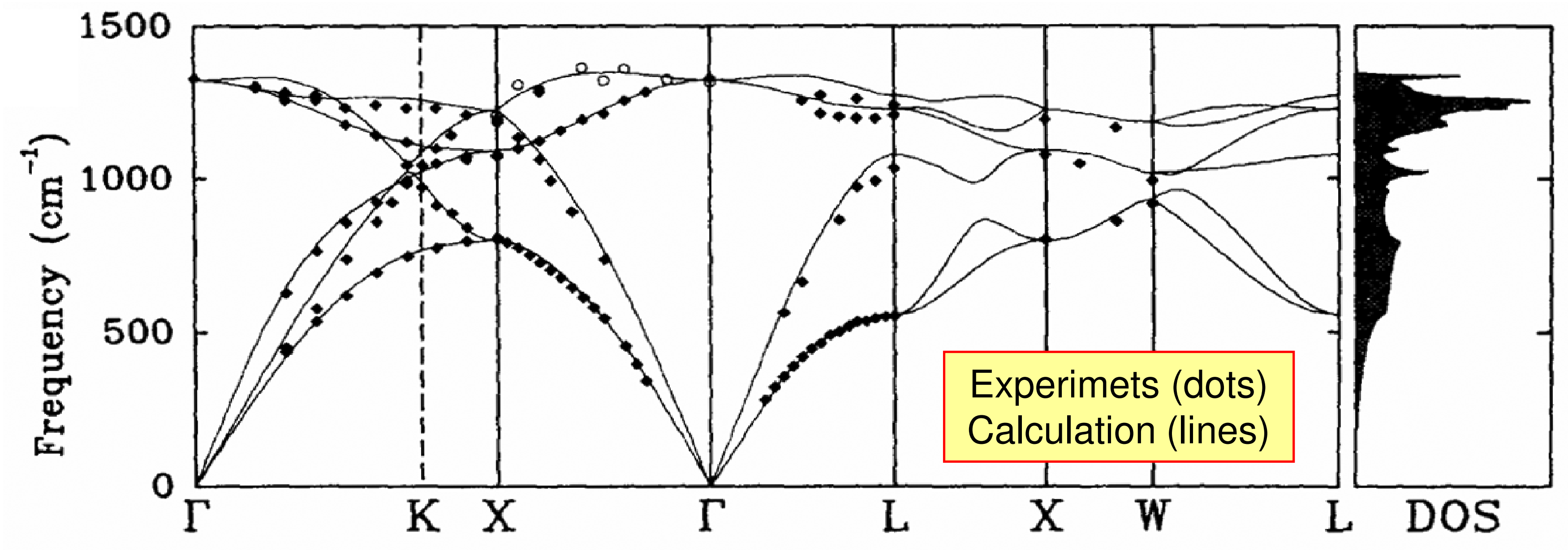
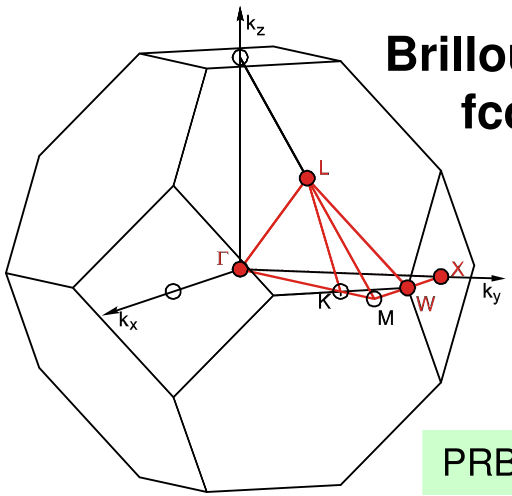
An example…

Diamond: fcc symmetry + 2 C atoms each lattice site @ (¼,¼,¼)





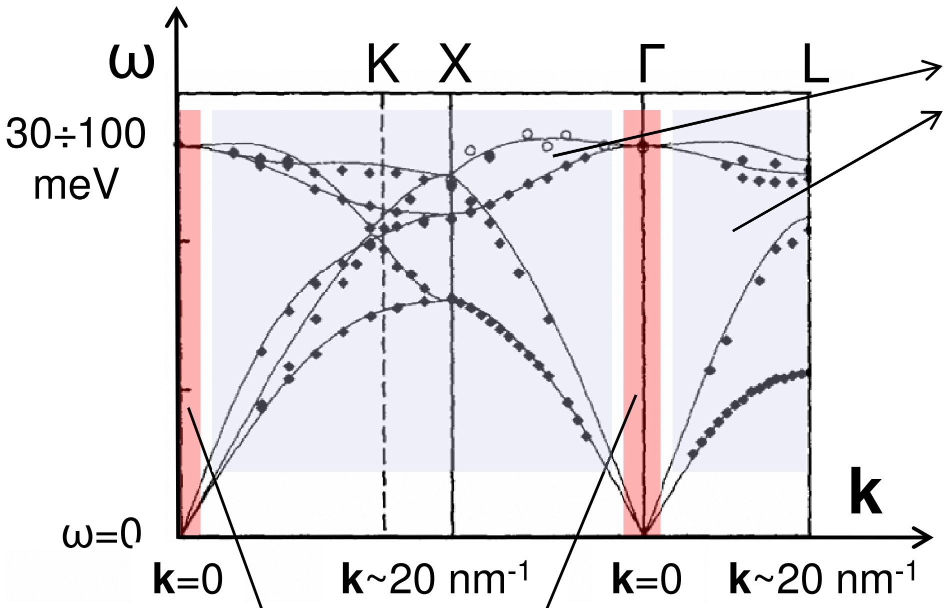
Brillouin zones for fcc symmetry

PRB 48, 3156 (1993)

Information:

- **Structure** and **Elasticity** (sound velocities)
- **Interaction Potential** and **Anharmonicity**
- **Dynamical Istabilities** (phonon softening)
- **Phonon-Electron coupling**
- **Thermodynamics** (c_V, λ, Θ_D, S_D, etc …)

How can we measure Atomic Dynamics?



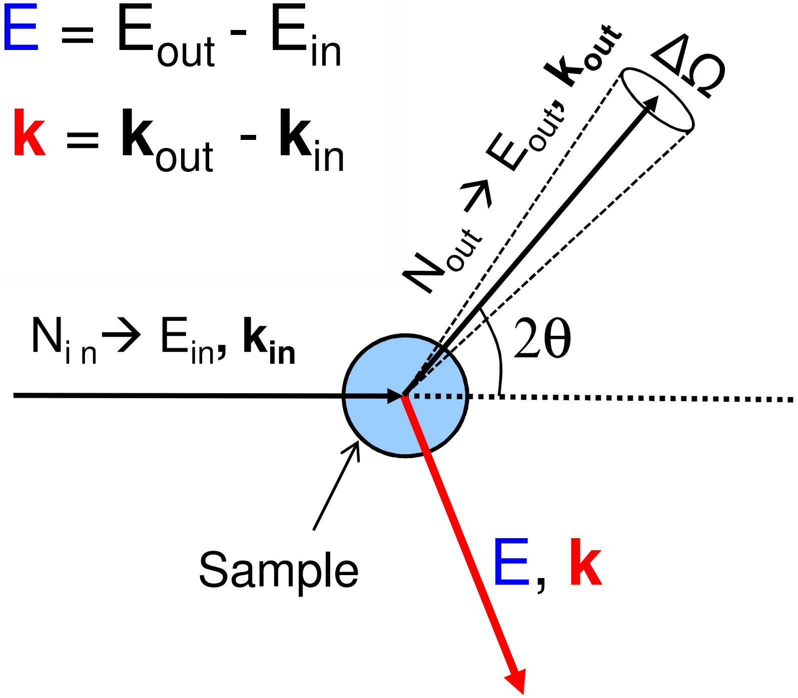
- Probe wavelenght ($2\pi/|\mathbf{k}|$) < 0.1 nm
- Probe energy (E) > 30÷100 meV

- Inelastic Light Scattering (Brillouin & Raman)
- Ultrasounics
- Transient Grating
- Etc …

Inelastic scattering:

$E = E_{out} - E_{in}$

$\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{in}$



Cross section: $\frac{\partial^2 \sigma}{\partial \Omega \partial E} \sim N_{out}/N_{in}$

Neutrons vs. X-rays

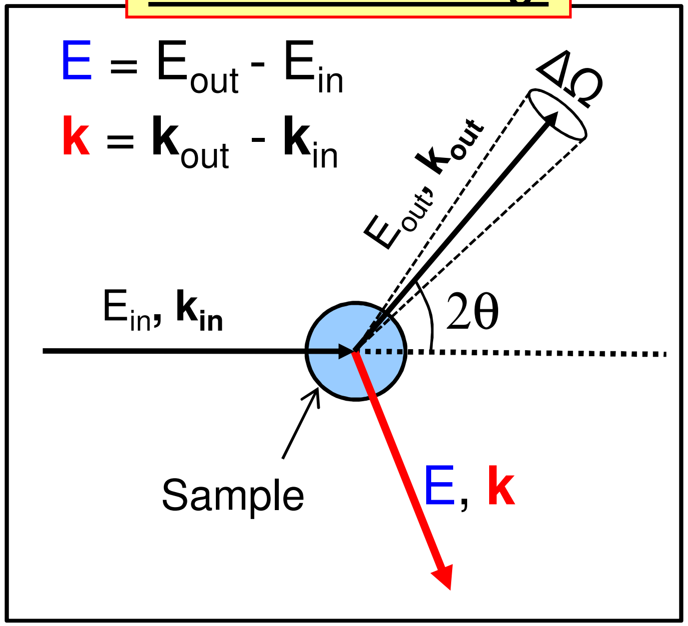
Neutrons	X-rays
λ_{in} = 1Å ⇨ E_{in} = 82 meV	λ_{in} = 1Å ⇨ E_{in} = 12.4 keV
E > 4 meV → $\Delta E/E_{in} = 0.05$	E > 4 meV → $\Delta E/E_{in} = 3 \cdot 10^{-7}$
Moderate energy resolution	Very high energy resolution
⇩	⇩
50 INS instruments	3 IXS instruments

Spin sensitive

Better contrast

"Older" technique

Inelastic scattering:



Why X-rays?

Neutrons vs. X-rays

λ_{in} = 1Å ⇒ E_{in} = 82 meV

λ_{in} = 1Å ⇒ E_{in} = 12.4 keV

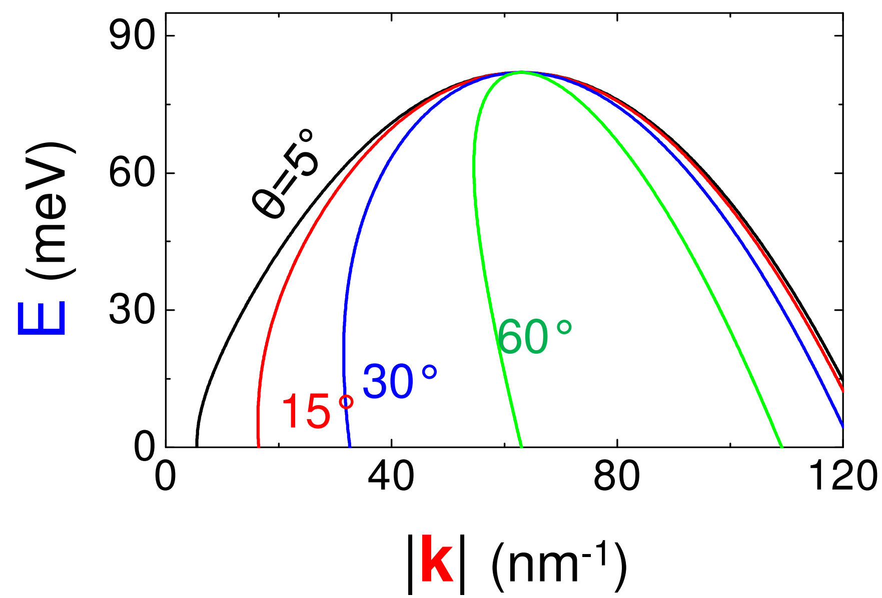
$E = E_{out} - E_{in}$ & $\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{in}$

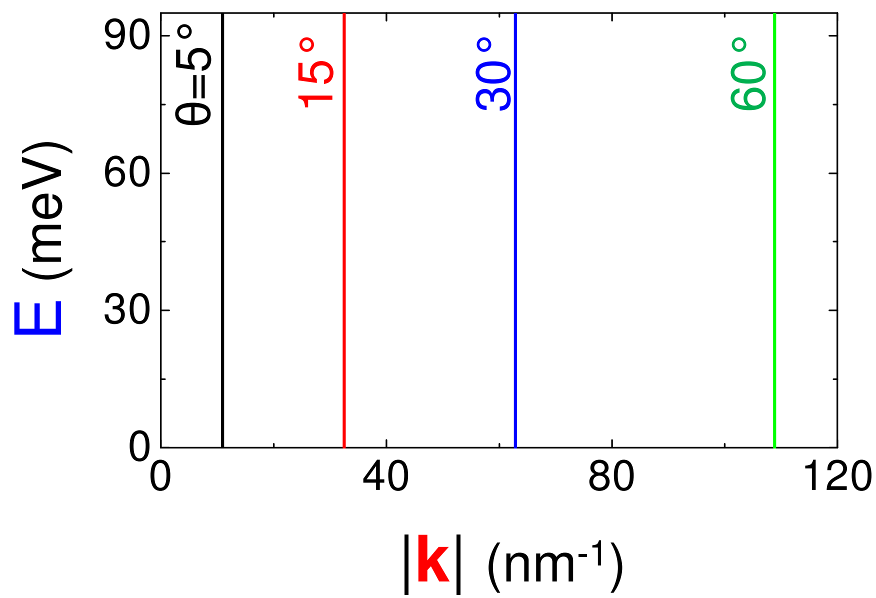
$E_{out} \neq E_{in}$

$$\frac{|\mathbf{k}|^2}{2|\mathbf{k}_{in}|^2} = 1 - E/E_{in} + \cos(2\theta)(1-2E/E_{in})^{1/2}$$

$E_{out} \approx E_{in}$

$$|\mathbf{k}| = 2|\mathbf{k}_{in}|\sin(\theta)$$





Neutrons vs. X-rays

$\lambda_{in} = 1Å$ ⇨ $E_{in} = 82\ meV$

$\lambda_{in} = 1Å$ ⇨ $E_{in} = 12.4\ keV$

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Neutrons: $E_{out} \neq E_{in}$

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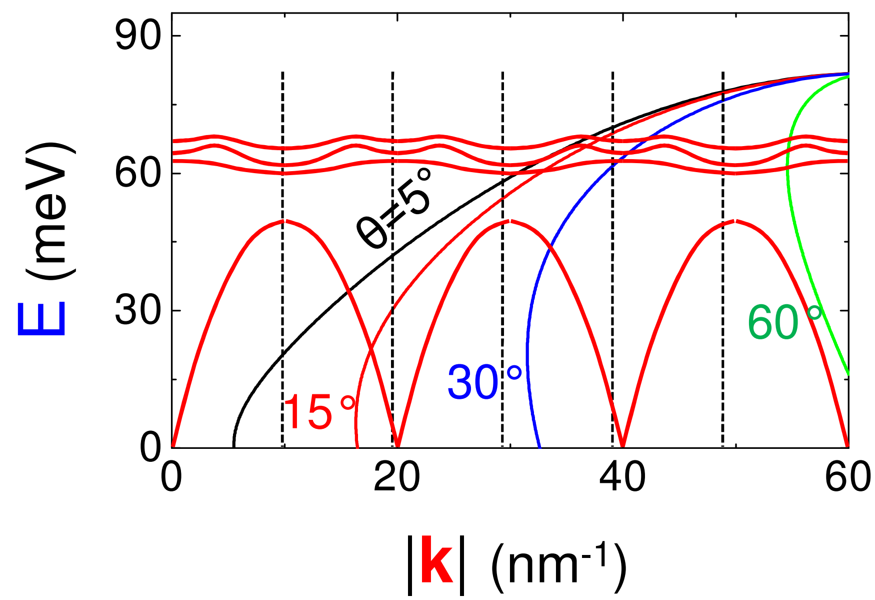
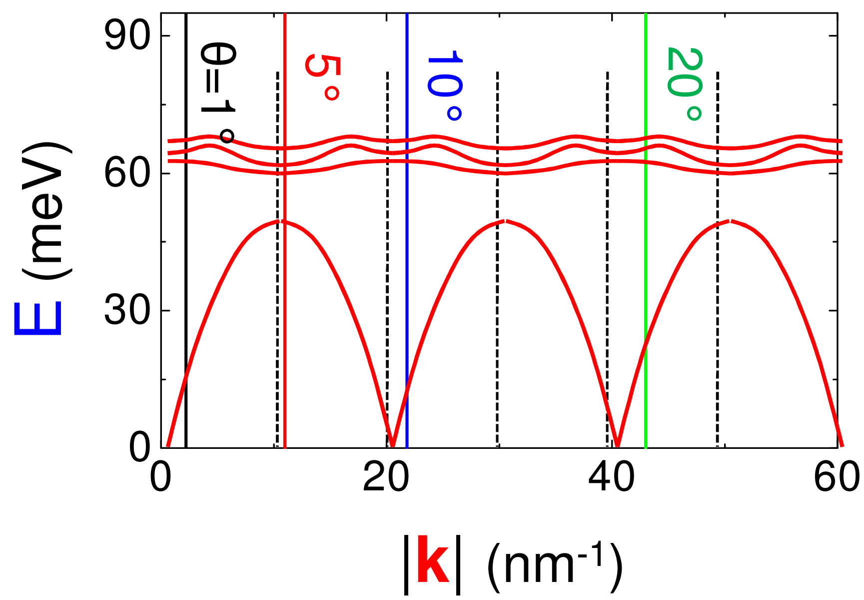
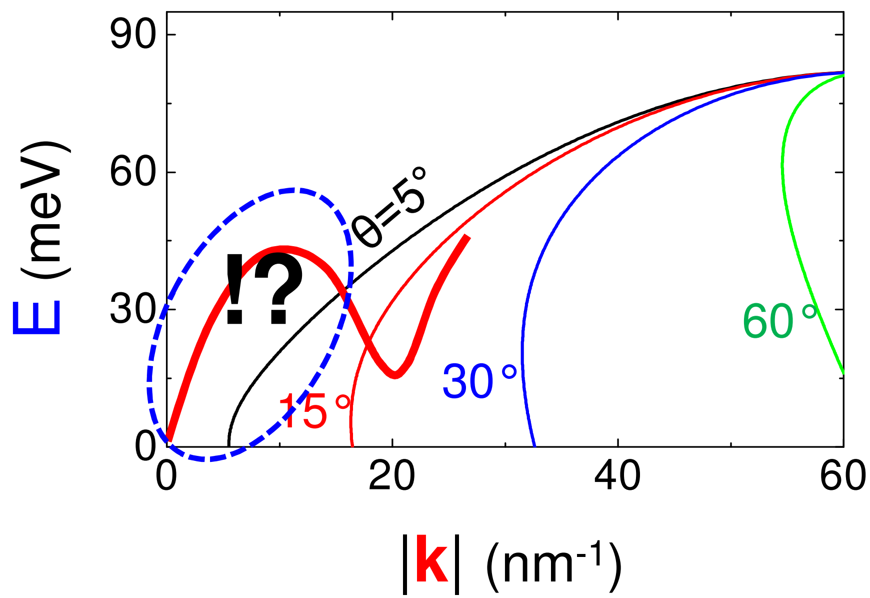


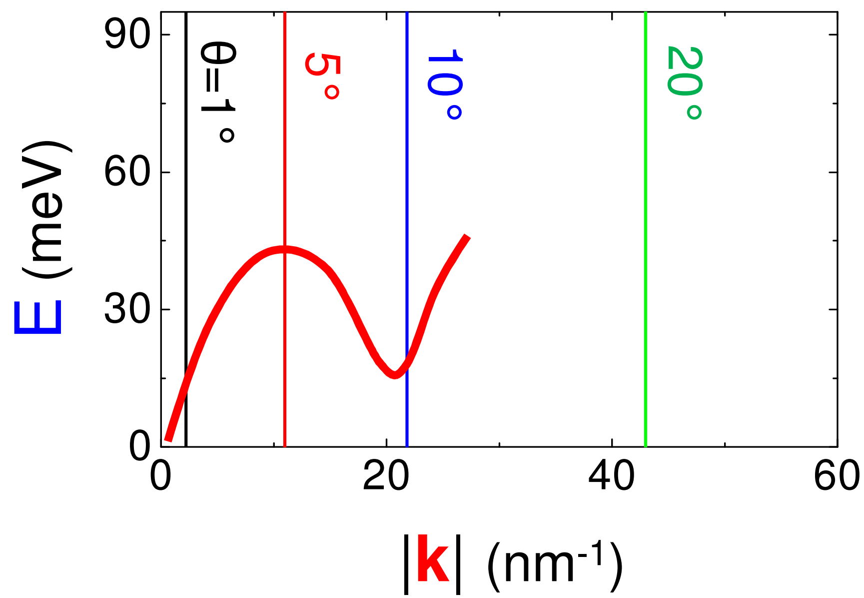


Neutrons vs. X-rays

Inelastic excitations in disordered systems

Neutrons	X-rays
λ_{in} = 1Å E_{in} = 82 meV	λ_{in} = 1Å E_{in} = 12.4 keV





Neutrons vs. X-rays

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$E > 4$ meV → $\Delta E/E_{in} = 0.05$	$E > 4$ meV → $\Delta E/E_{in} = 3 \cdot 10^{-7}$
Moderate energy resolution	Very high energy resolution
↓	↓
?? INS instruments	3 IXS instruments

Spin sensitive

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Why X-rays?

- **No kinematical constraints** (Disordered systems)
- **Small beams** (small samples: high pressure, exotic materials, etc…)
- **No incoherent cross section**

Basic theoretical aspects

$$H_{int}=(e/m_e c)\sum_j[(e/2c)\mathbf{A}_j\cdot\mathbf{A}_j+\mathbf{A}_j\cdot\mathbf{p}_j+\text{magnetic}]$$

A is the vector potential of electromagnetic field

p is the momentum operator of the electrons

j is the summation over all electrons of the system

1st order perturbation theory

A·A term → one photon (non-resonant) scattering

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} = r_0^2(\varepsilon_{in}\cdot\varepsilon_{out})^2(k_{in}/k_{out})\sum_{I,F}P_I|\langle I|\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}|F\rangle|^2\delta(E-E_{out}+E_{in})$$

Basic theoretical aspects

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} = r_0^2(\boldsymbol{\varepsilon}_{in}\cdot\boldsymbol{\varepsilon}_{out})^2(k_{in}/k_{out})\sum_F P_F|\langle I|\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}|F\rangle|^2\delta(E-E_F+E_I)$$

The key assumption:

<u>Adiabatic approximation</u> → $|I\rangle=|I_n\rangle|I_e\rangle$ and $|F\rangle=|F_n\rangle|F_e\rangle$

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} = \underbrace{r_0^2(\varepsilon_{in}\cdot\varepsilon_{out})^2(k_{in}/k_{out})}_{\text{Thomson scattering cross section}}\ \underbrace{F(|\mathbf{k}|)^2}_{\text{Molecular form factor}}\ \underbrace{S(\mathbf{k},E)}_{\text{Dynamical structure factor}}$$

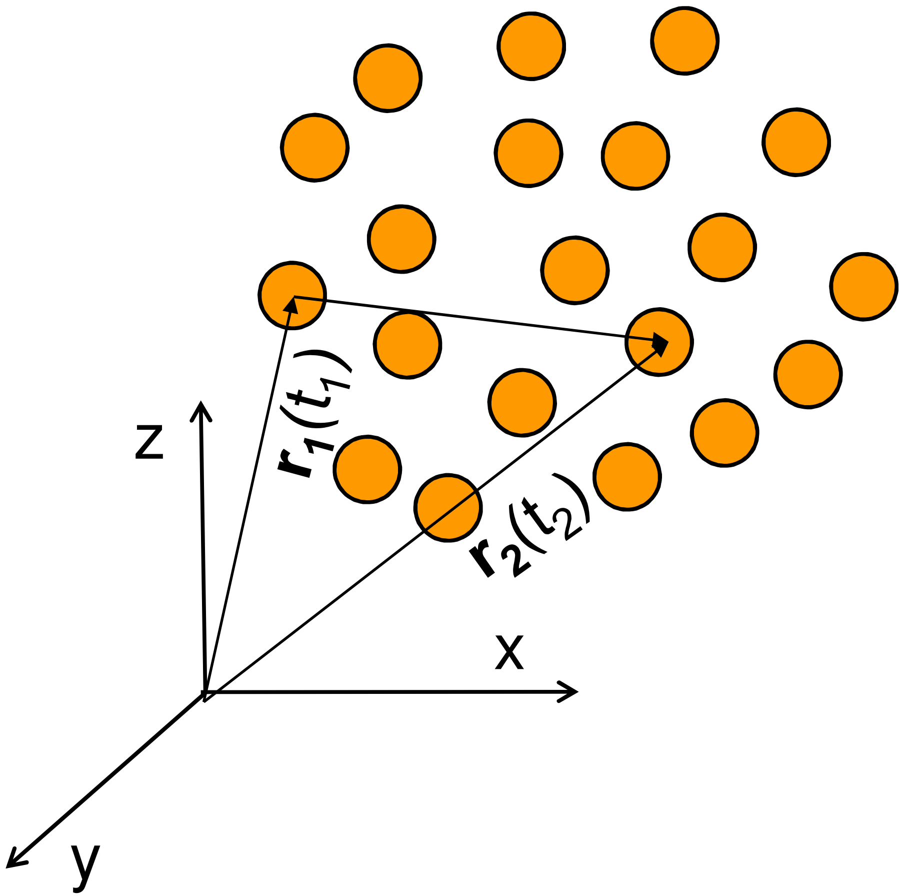
Thomson scattering cross section

Molecular form factor

<u>Dynamical structure factor</u>

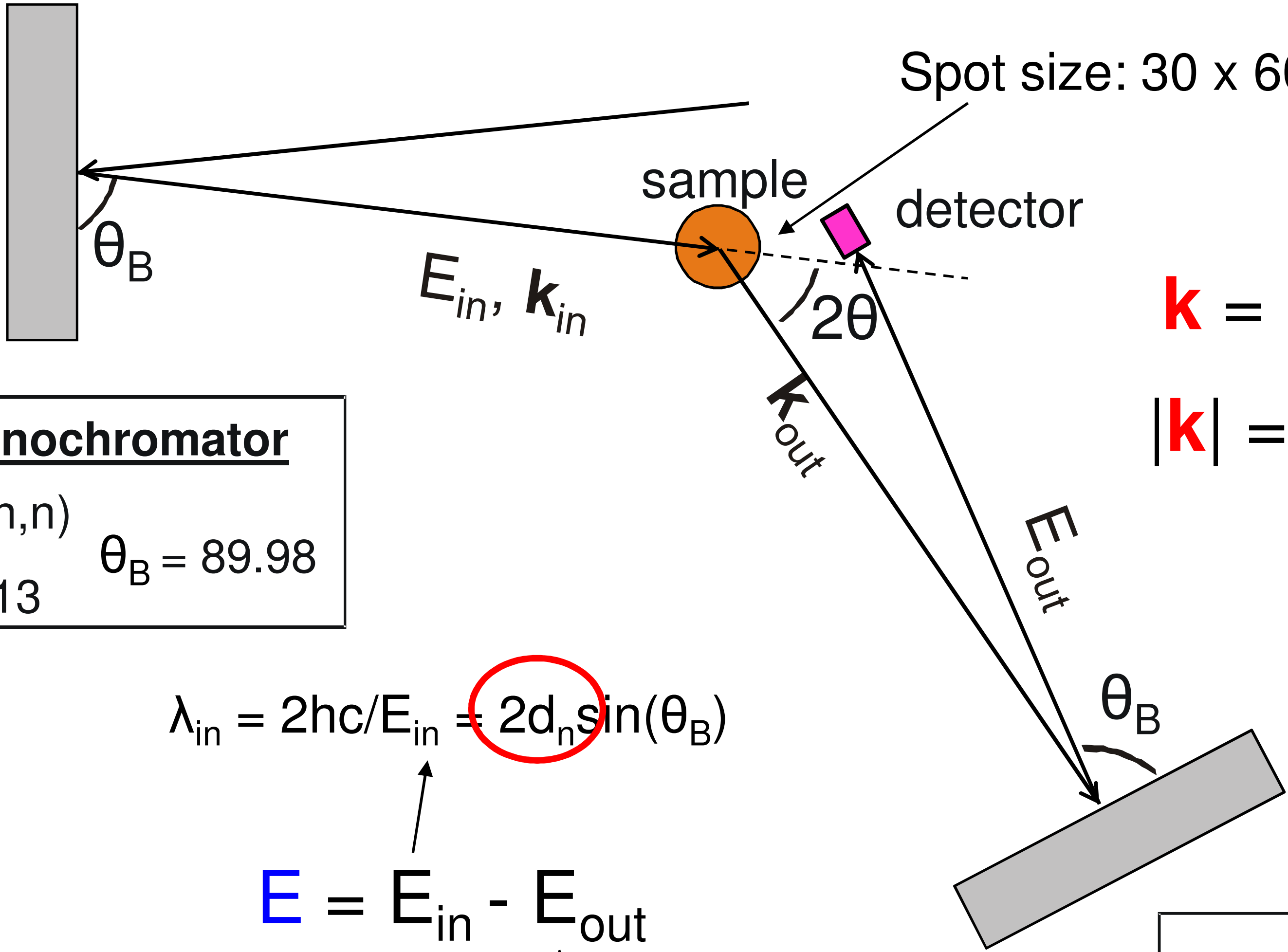
The dynamical structure factor

S(**k**,E) is the **SPACE** and **TIME** Fourier transform of G(**r**,t)



G(**r**,t) is the probability to find two distinct particles at positions $\mathbf{r}_1(t_1)$ and $\mathbf{r}_2(t_2)$, separated by the distance $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$ and the time interval $t=t_2-t_1$.

Basic IXS instrumentation



$\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{out}$

$|\mathbf{k}| = 4\pi\sin(\theta)$

Monochromator

Si(n,n,n)

n=7-13

$\theta_B = 89.98$

$\lambda_{in} = 2hc/E_{in} = 2d_n\sin(\theta_B)$

$E = E_{in} - E_{out}$

$\lambda_{out} = 2hc/E_{out} = 2d_n\sin(\theta_B)$

λ_{in} (**tunable**)

λ_{out} (**constant**)

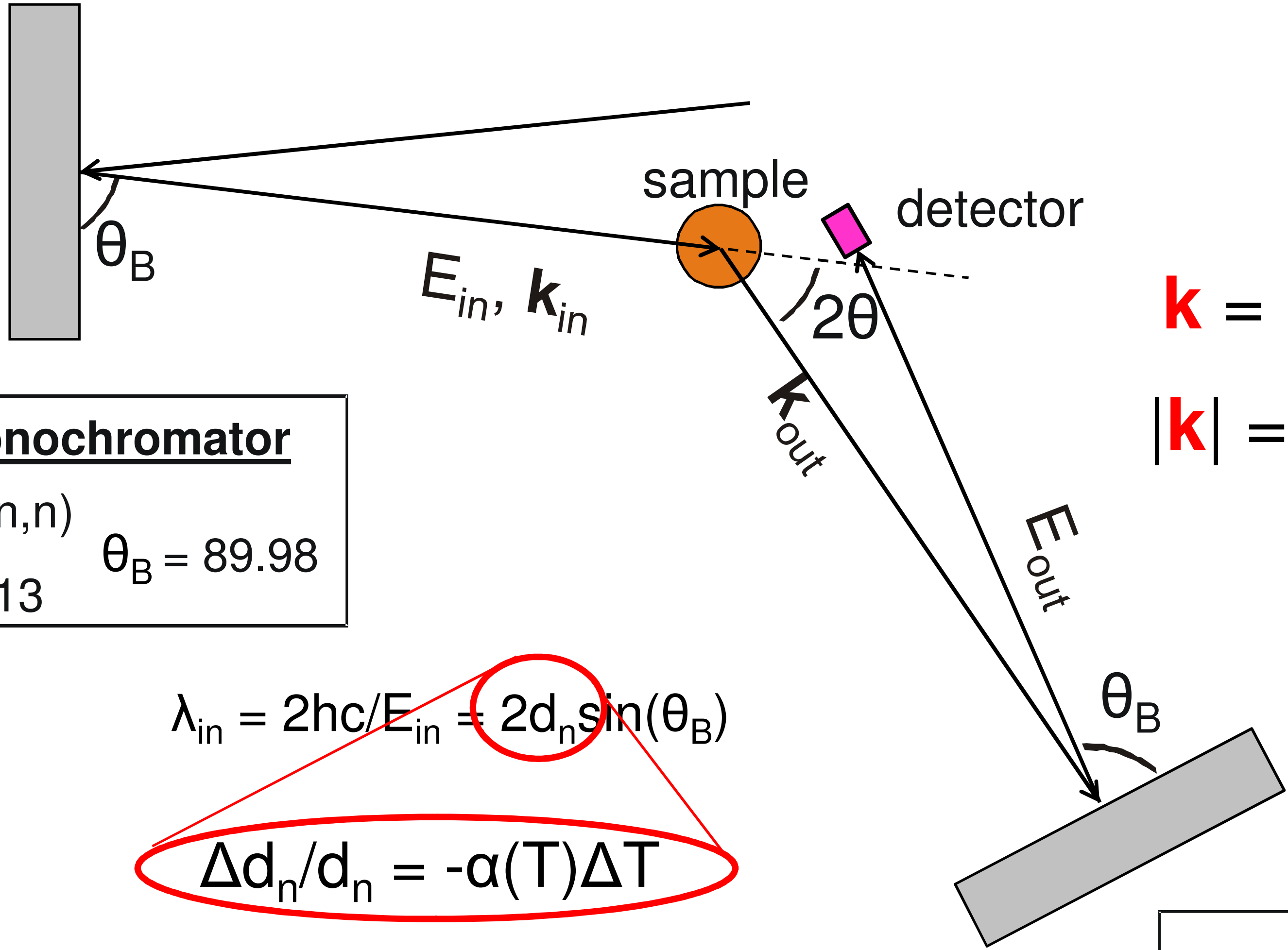
Analyser

Si(n,n,n)

n=7-13

$\theta_B = 89.98$

Basic IXS instrumentation



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n=7-13

$\theta_B = 89.98$

$$\lambda_{in} = 2hc/E_{in} = 2d_n \sin(\theta_B)$$

$$\Delta d_n/d_n = -\alpha(T)\Delta T$$

Analyser

Si(n,n,n)

n=7-13

$\theta_B = 89.98$

$\alpha \sim 2.58 \cdot 10^{-6}$

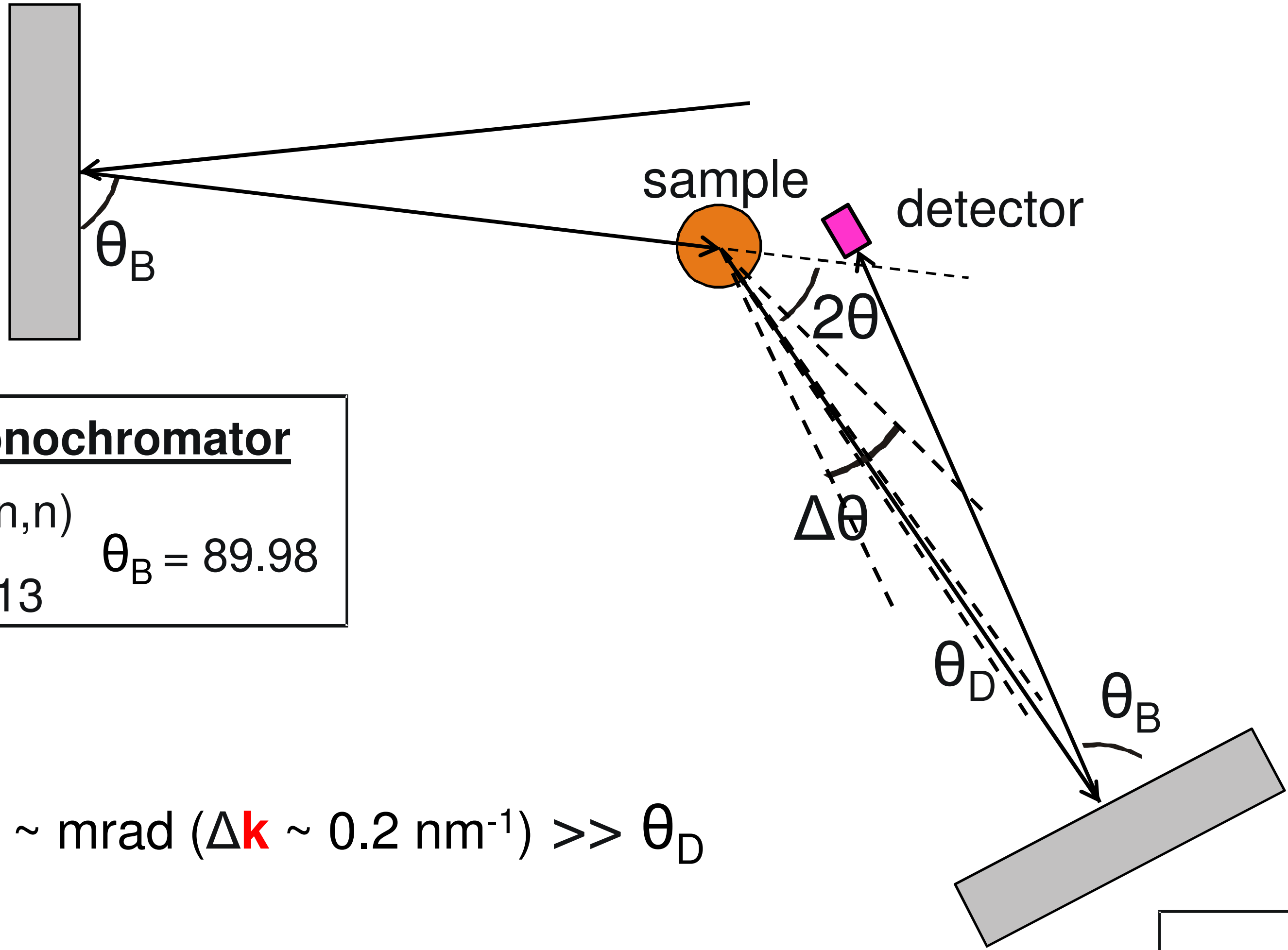
$\Delta T \sim$ mK

→

$(\delta E/E)_{MAX} \sim 3 \cdot 10^{-8}$

→ 1 meV @ 27 keV

Basic IXS instrumentation



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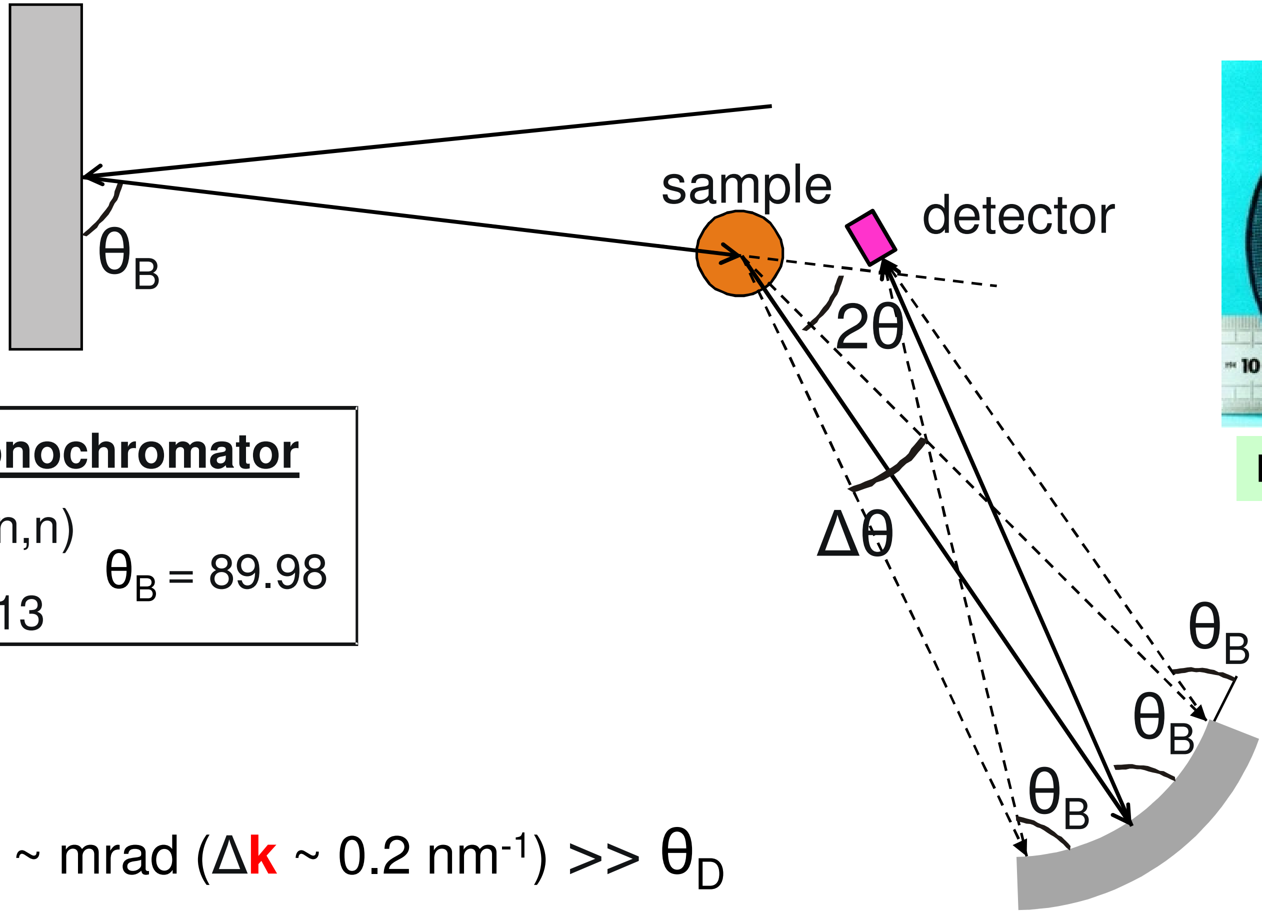
$\Delta\theta$ ~ mrad (Δ**k** ~ 0.2 nm^{-1}) >> θ_D

Basic IXS instrumentation



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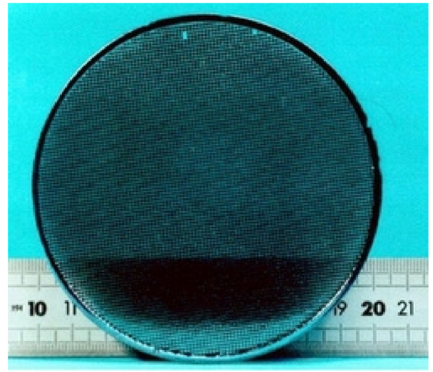


NIM 111, 181 (1996)

$\Delta\theta$ ~ mrad (Δ**k** ~ 0.2 nm^{-1}) >> θ_D

≈ 12000 flat Si “perfect” single crystals (0.6x0.6 mm^2) that approximate a spherical surface

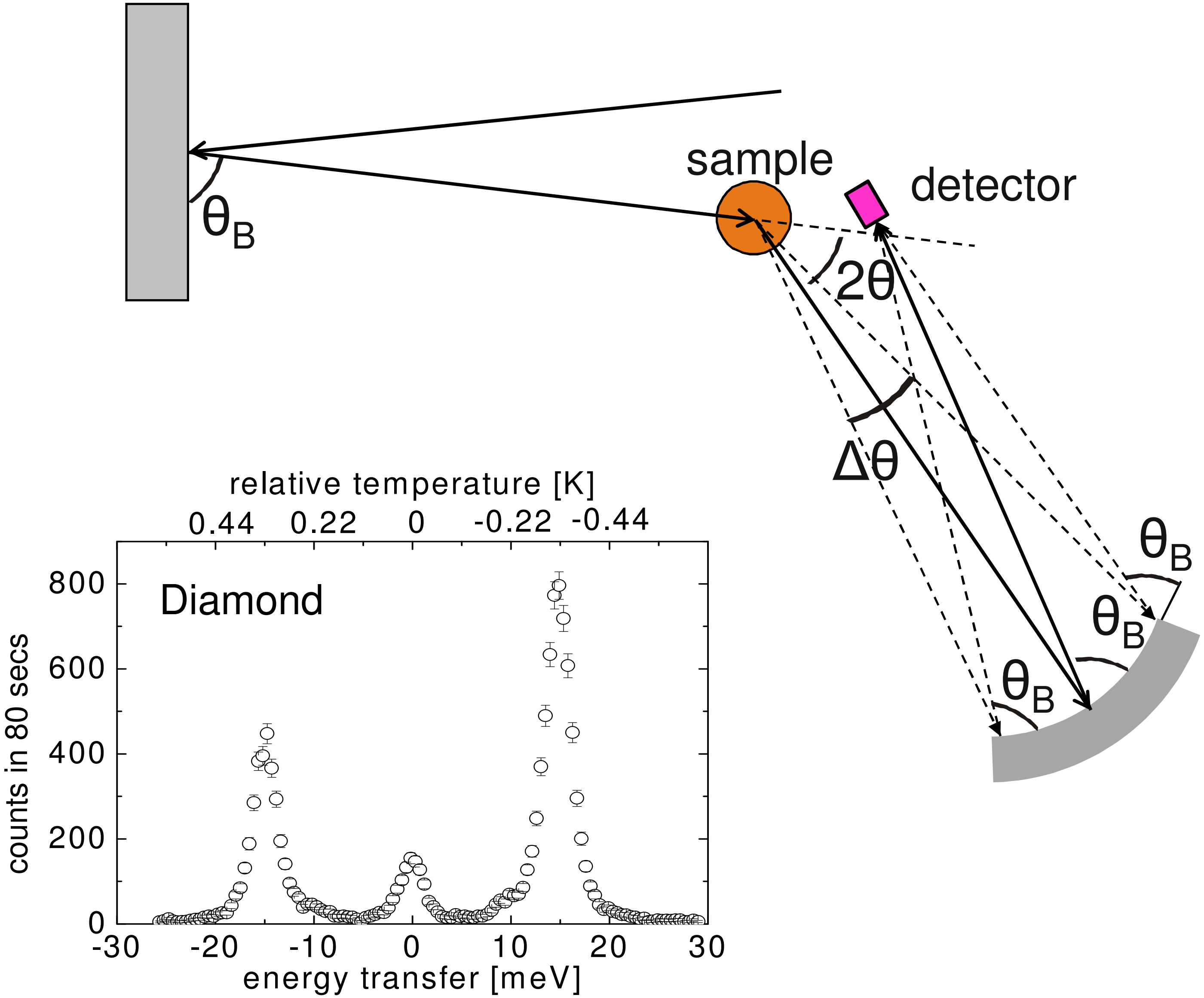
Analyser

Si(n,n,n)

n=7-13

$\theta_B = 89.98$

Basic IXS instrumentation

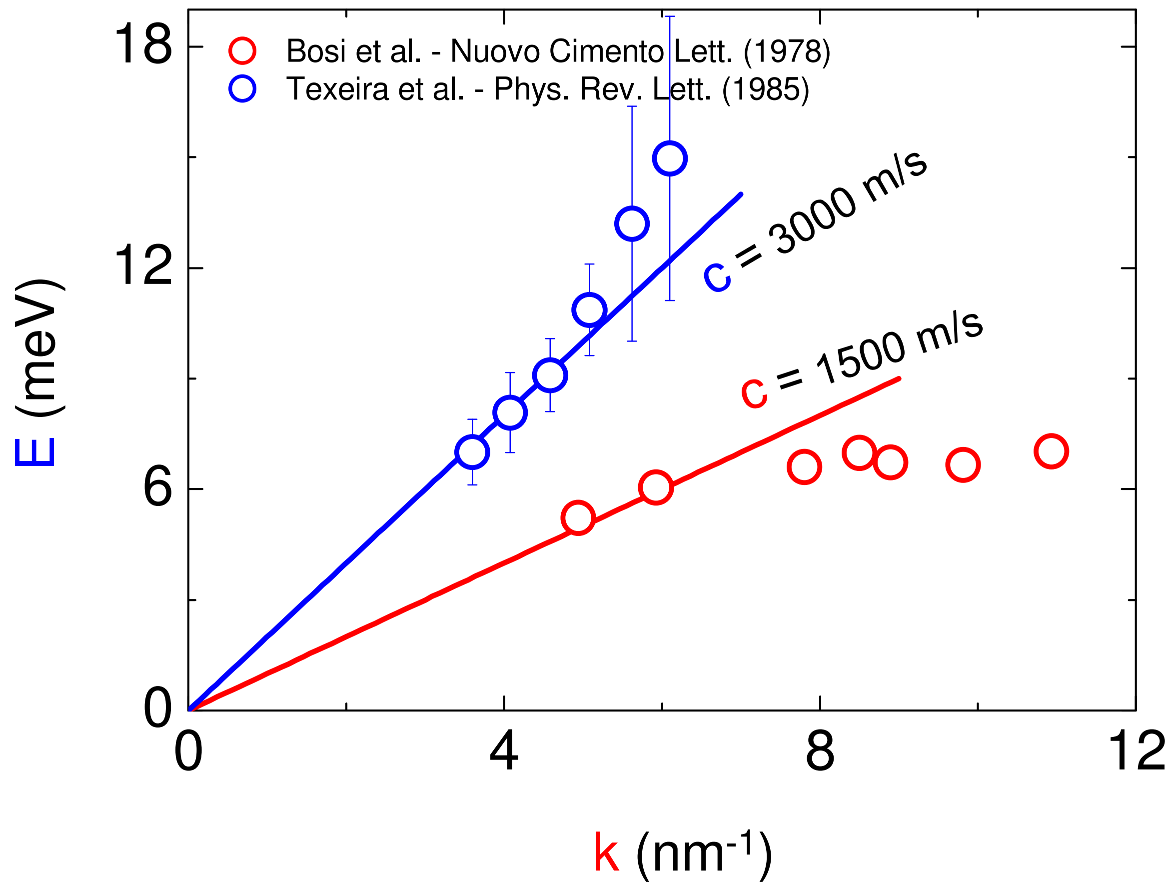


Experimental highlights (1)

Collective dynamics in water

Inelastic Neutron Scattering (D_2O):

2 experiments, 2 results: why?



Experimental highlights (1)

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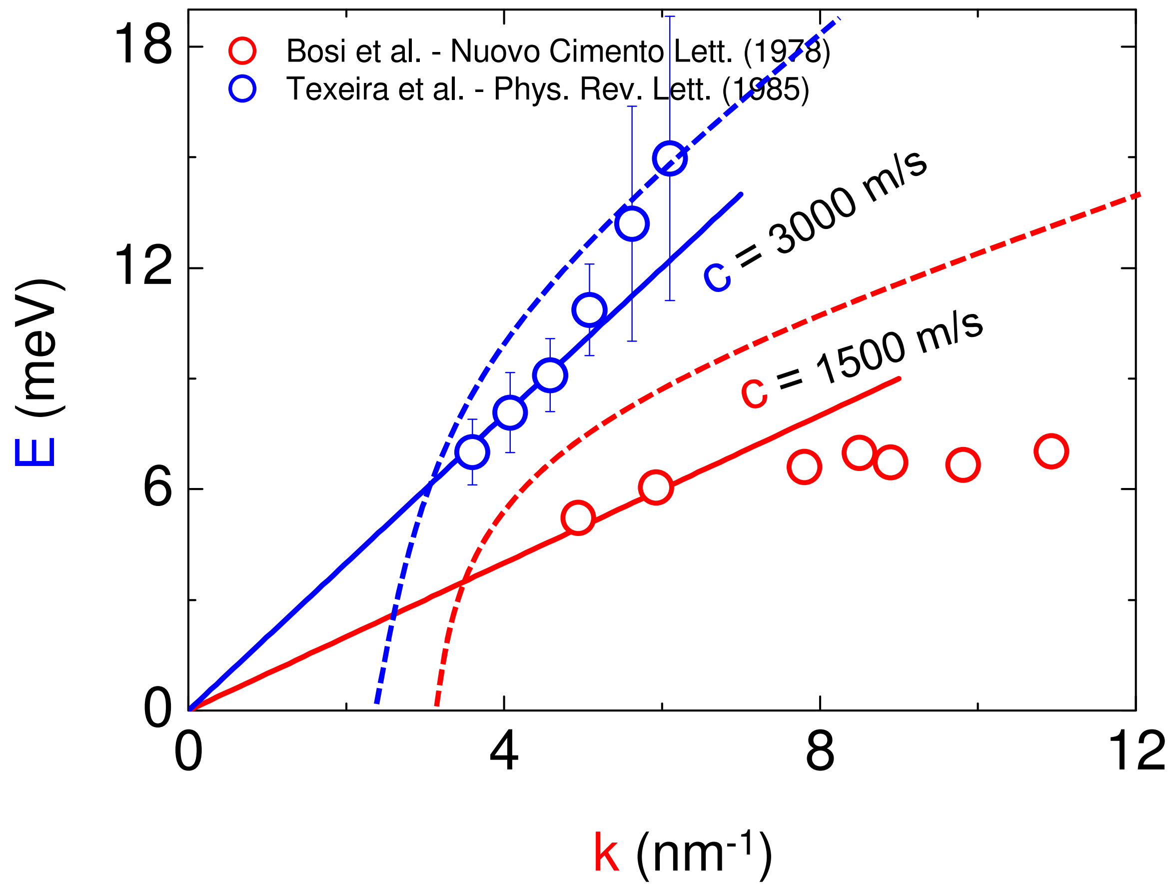
<u>Inelastic Neutron Scattering (D_2O):</u>

2 experiments, 2 results: <u>where is the rub?</u>



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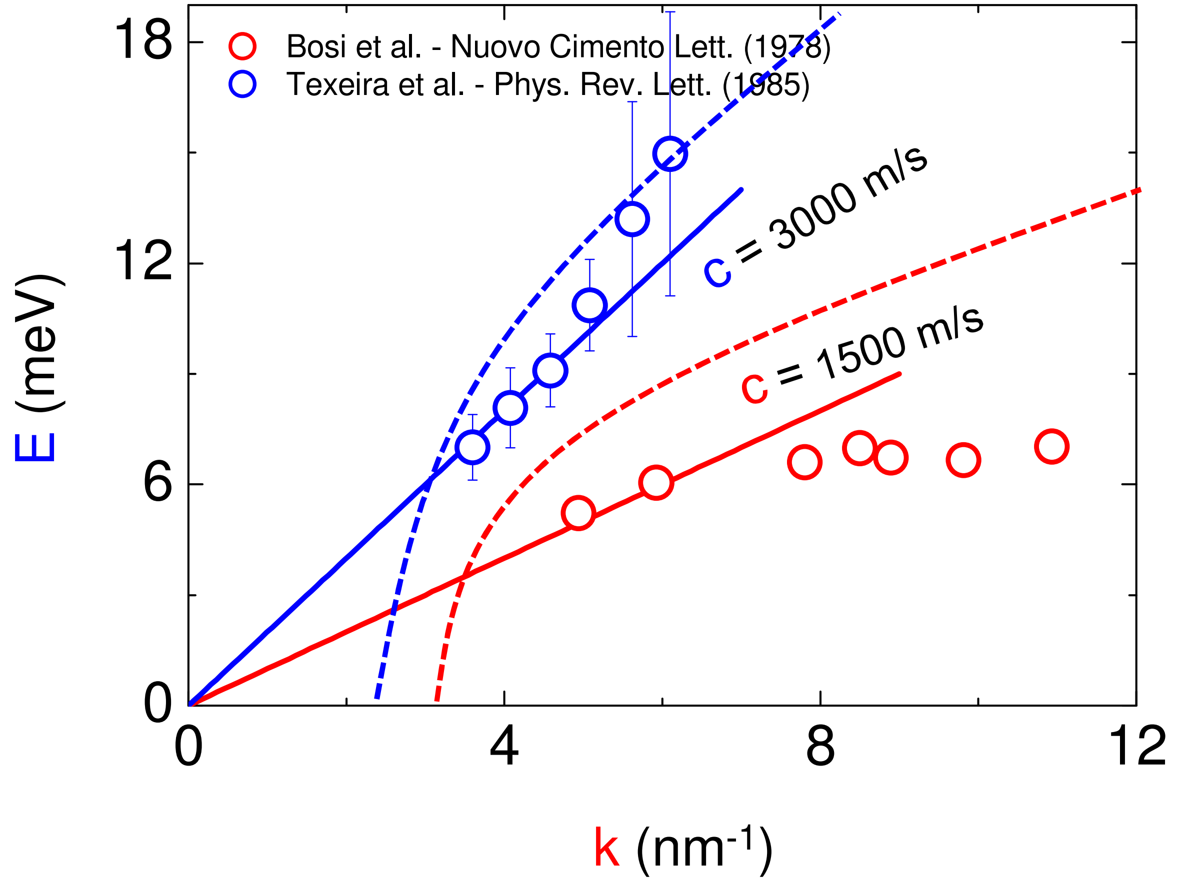


A possible interpretation:

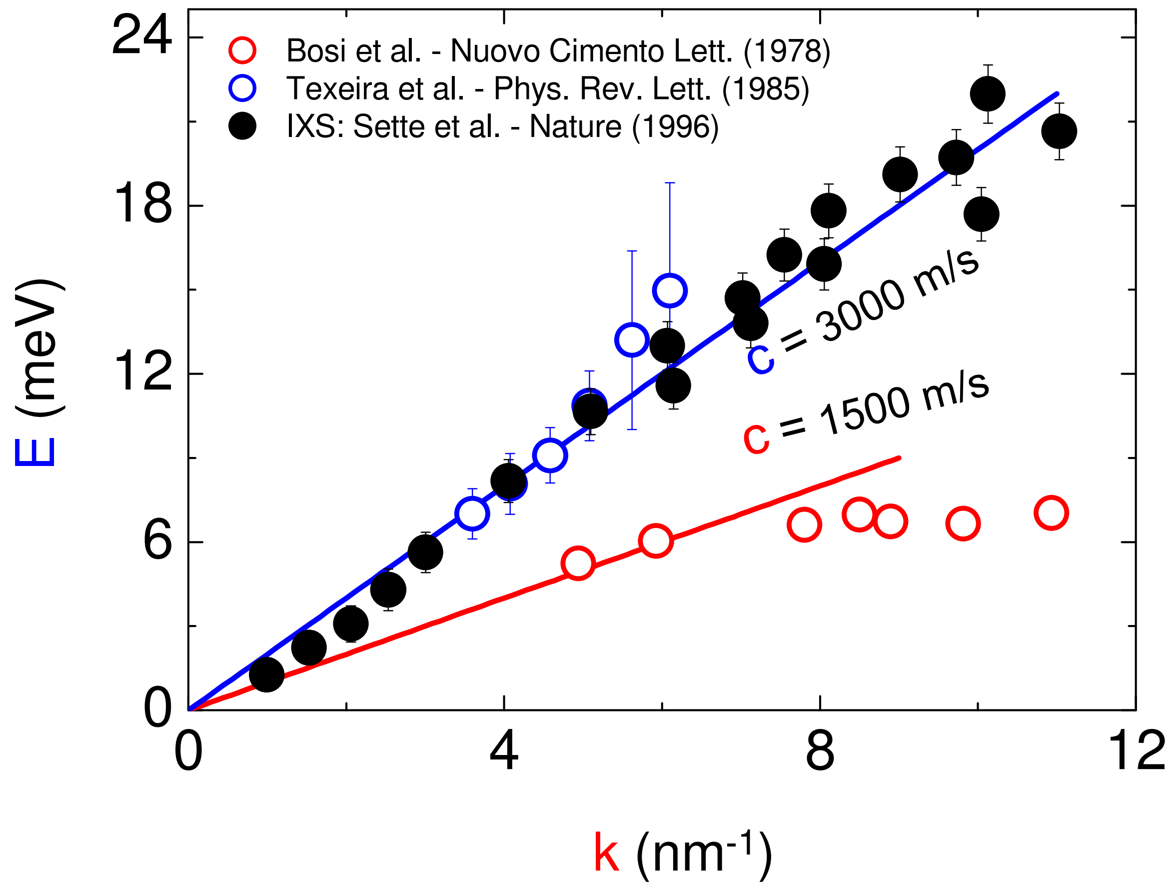
- High frequency mode → **D**
- Low frequency mode → **O**

$\Omega_{HF}/\Omega_{LF} \sim (m_O/m_D)^{1/2} \sim 2$

Experimental highlights (1)

Collective dynamics in water

Inelastic Neutron Scattering vs.
Inelastic X-ray Scattering (H_2O vs. D_2O)



A possible interpretation:

- High frequency mode → **D**
- Low frequency mode → **O**

$\Omega_{HF}/\Omega_{LF} \sim (m_O/m_D)^{1/2} \sim 2$

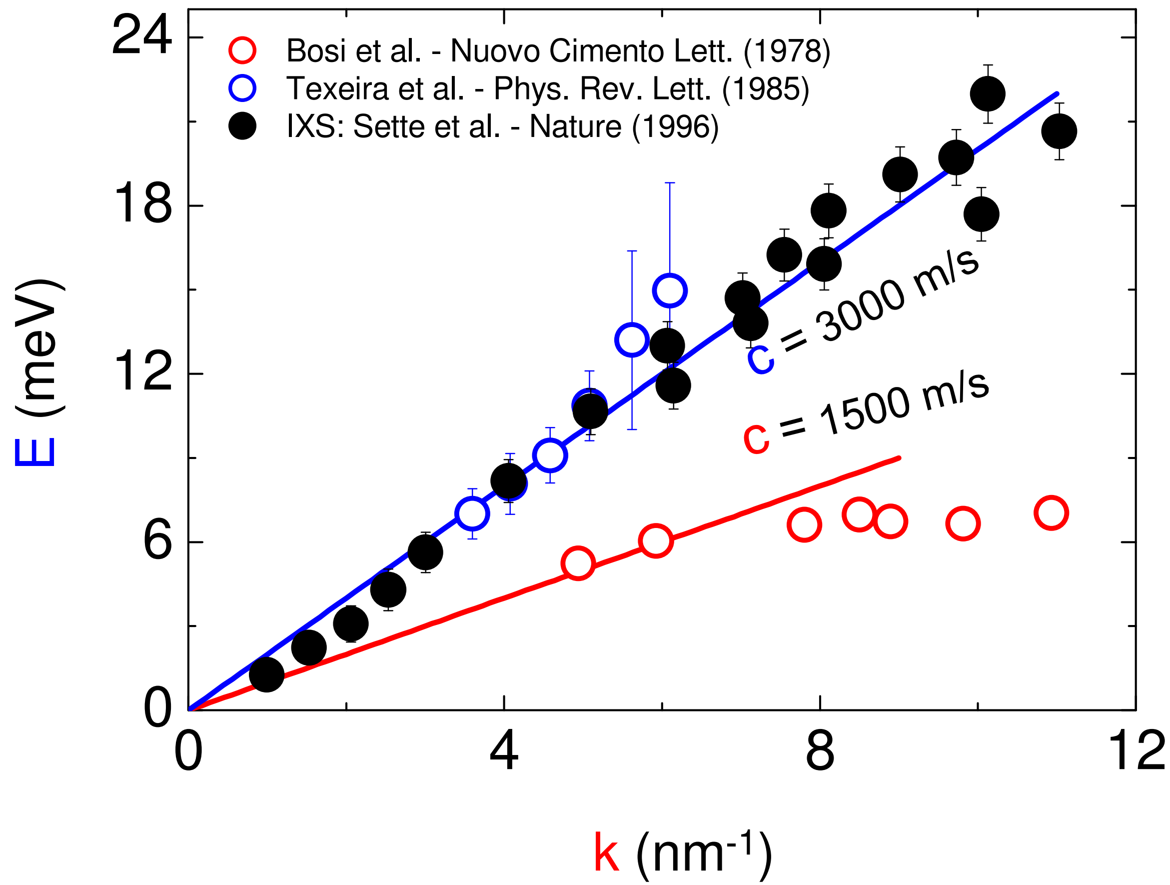
High frequency mode:

$\Omega_{IXS}/\Omega_{INS} \sim (m_H/m_D)^{1/2} \sim 1.4$

Experimental highlights (1)

Collective dynamics in water

Inelastic Neutron Scattering vs.
Inelastic X-ray Scattering (H_2O vs. D_2O)



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- ~~High frequency mode → **D**~~
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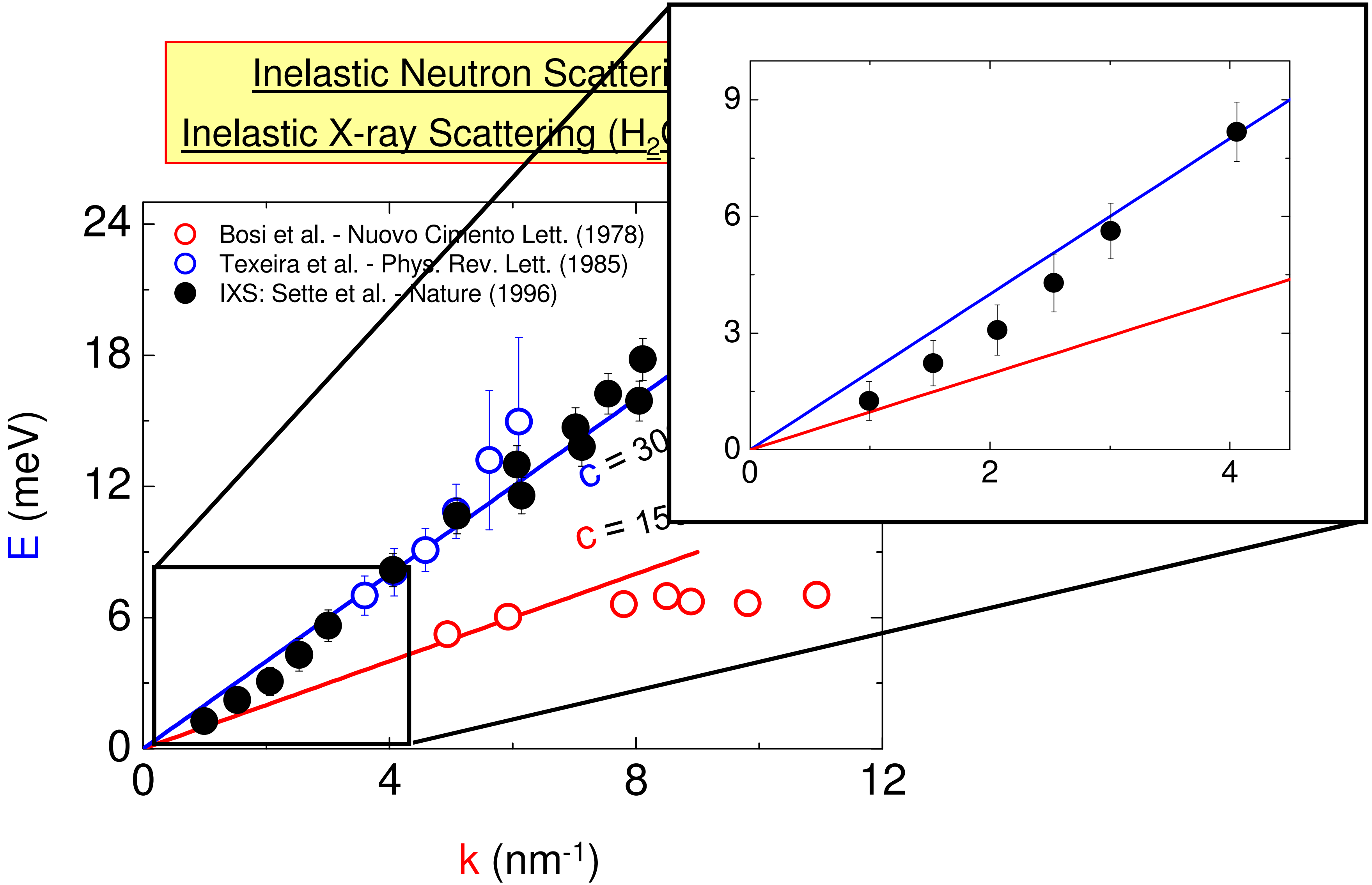
~~**High frequency mode:**~~

~~$\Omega_{IXS}/\Omega_{INS} \sim (m_H/m_D)^{1/2} \sim 1.4$~~

Experimental highlights (1)

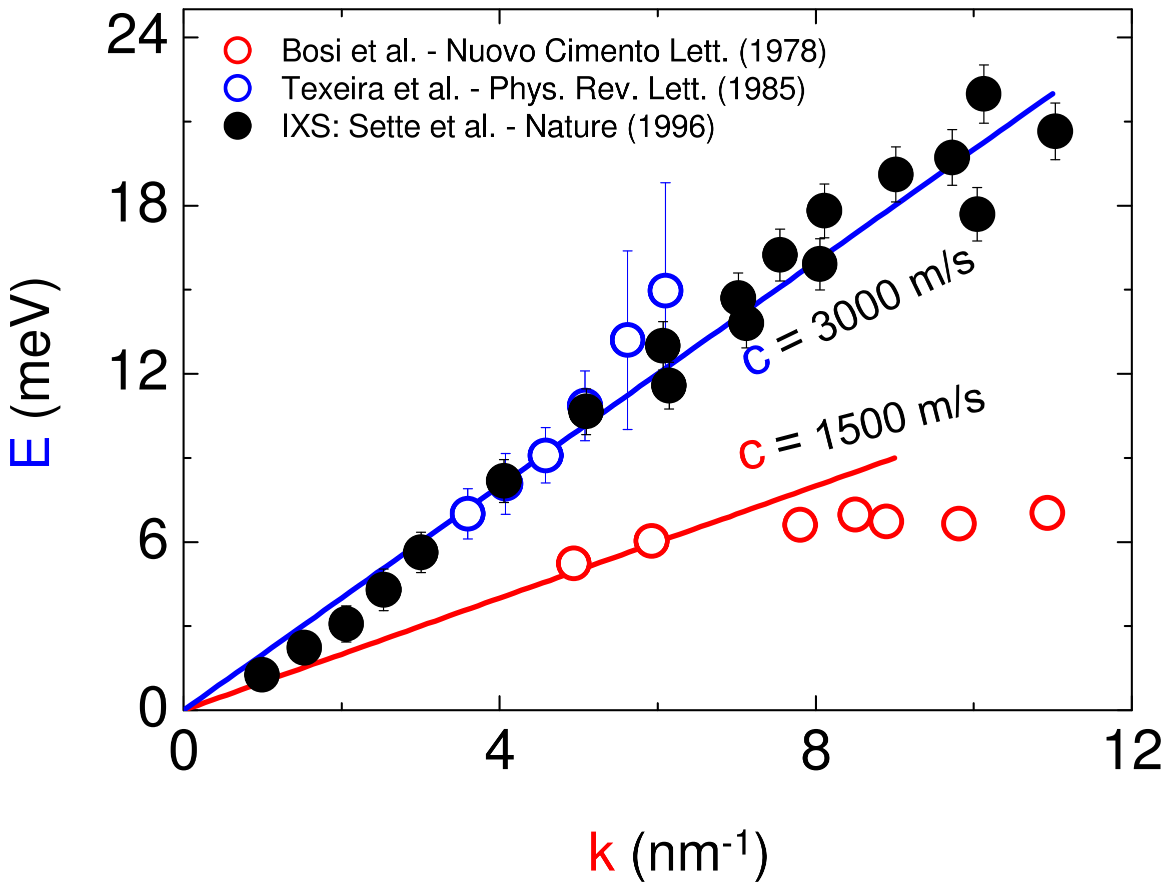
Collective dynamics in water



Experimental highlights (1)

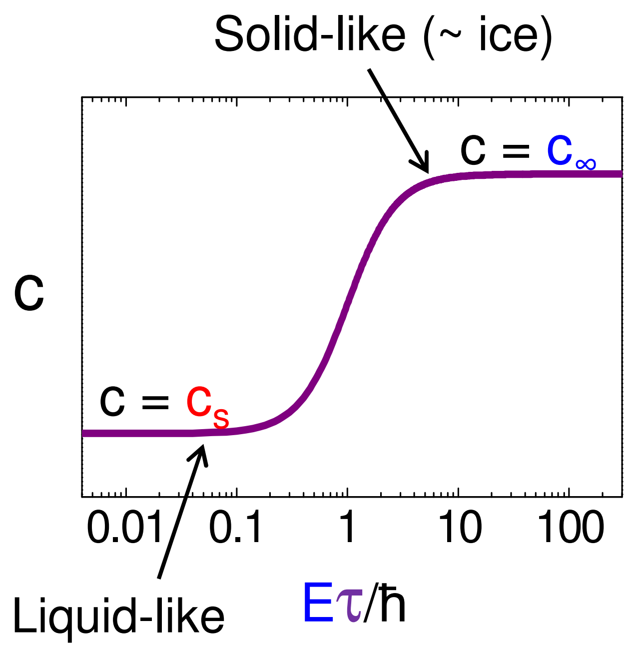
Collective dynamics in water

<u>Inelastic Neutron Scattering vs.</u>
<u>Inelastic X-ray Scattering (H_2O vs. D_2O)</u>



Viscoelasticity:

The sound velocity ($c=E/\hbar k$) is not constant but depends on $E\tau/\hbar$



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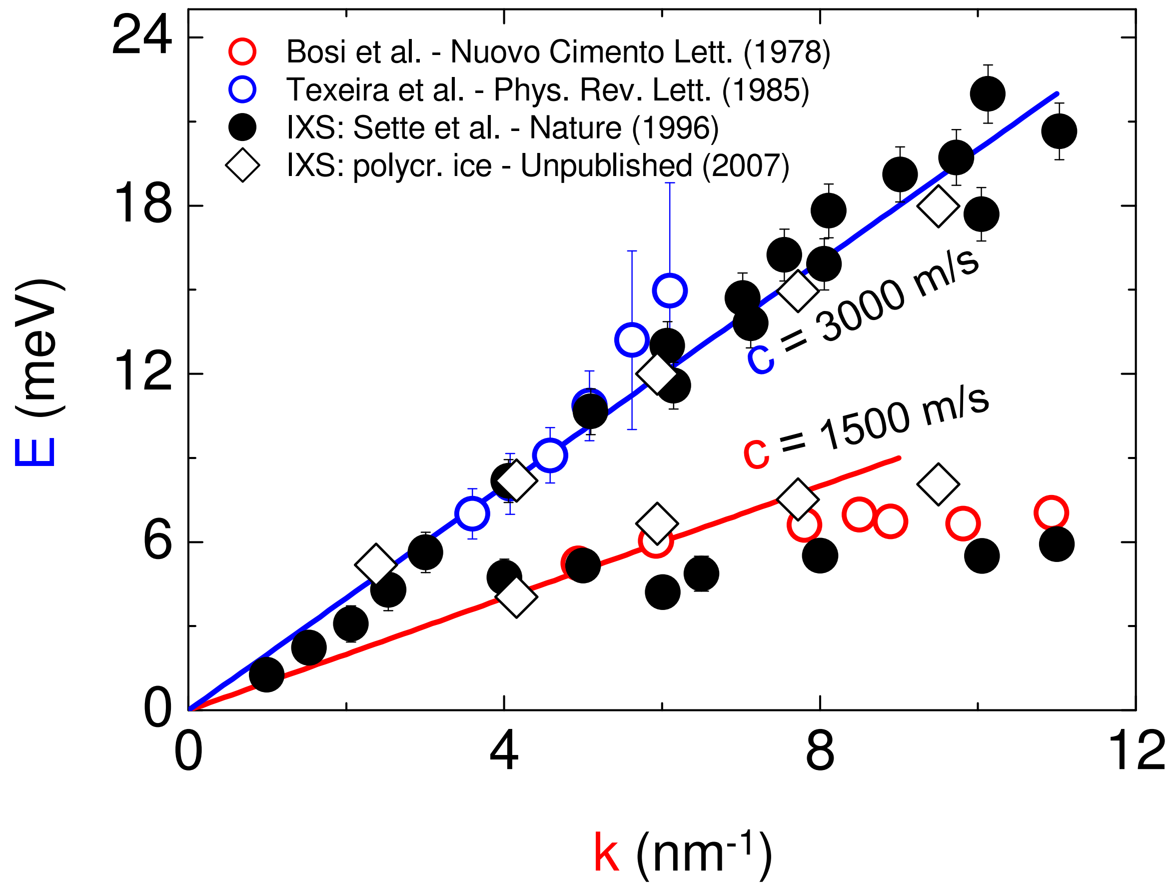
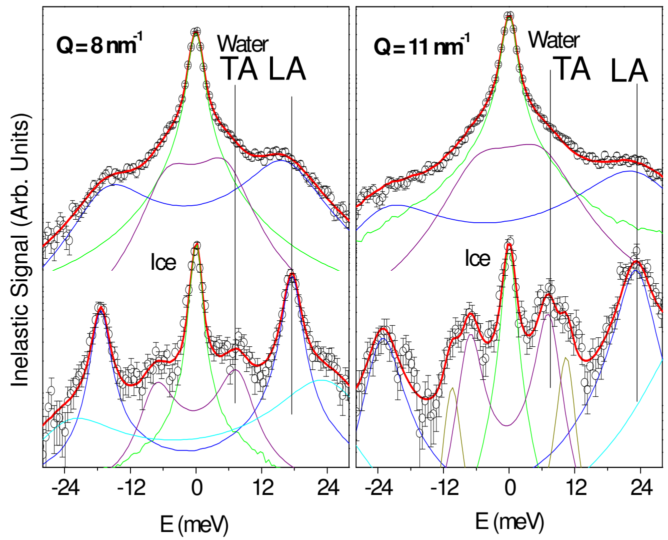


Low frequency mode:

Transverse-like sound propagation in the elastic, solid-like, limit:

$E\tau/\hbar >> 1$



PRL 79, 1678 (1997)

PRE 71, 011501 (2005)

Experimental highlights (2)

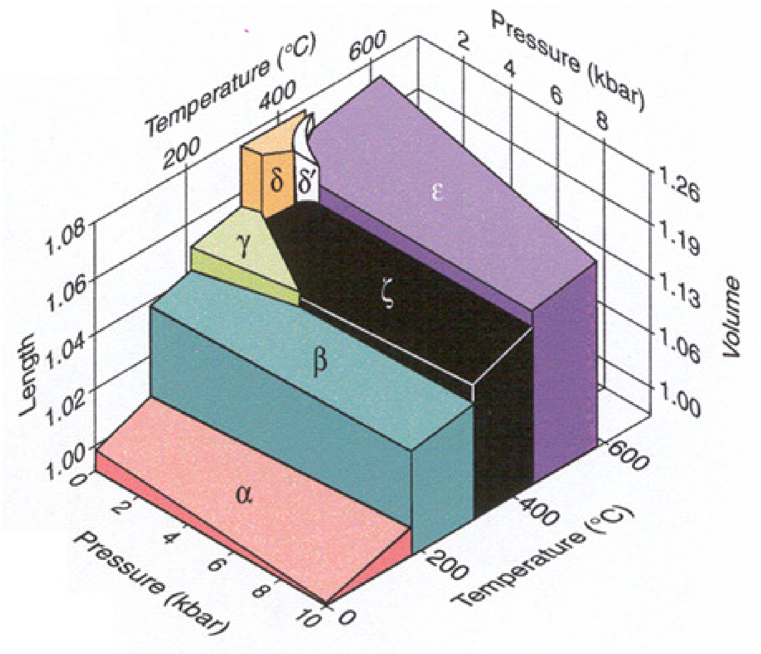
Phonon dispersions in plutonium

<u>Putonium is one of the most fascinating and exotic element:</u>

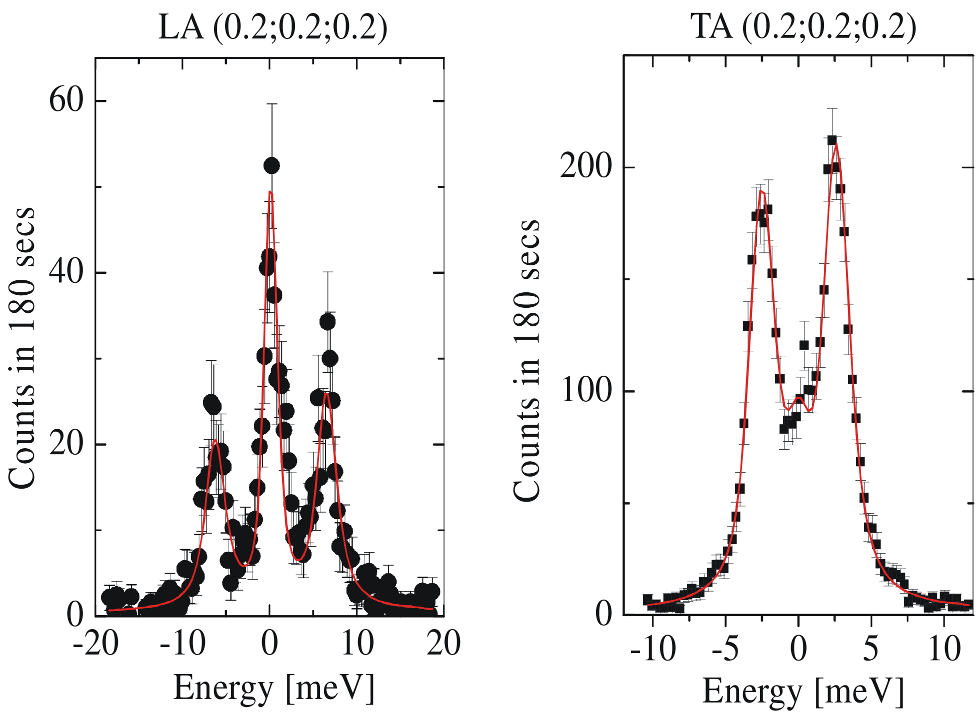
- Multitude of unusual properties
- Central role of 5f electrons

<u>ID28 at ESRF</u>

- Energy resolution: 1.8 meV
- Beam size: 20 x 60 μm^2 (HxV)
- Grain size: ~ 80 μm^2
- On-line diffraction analysis

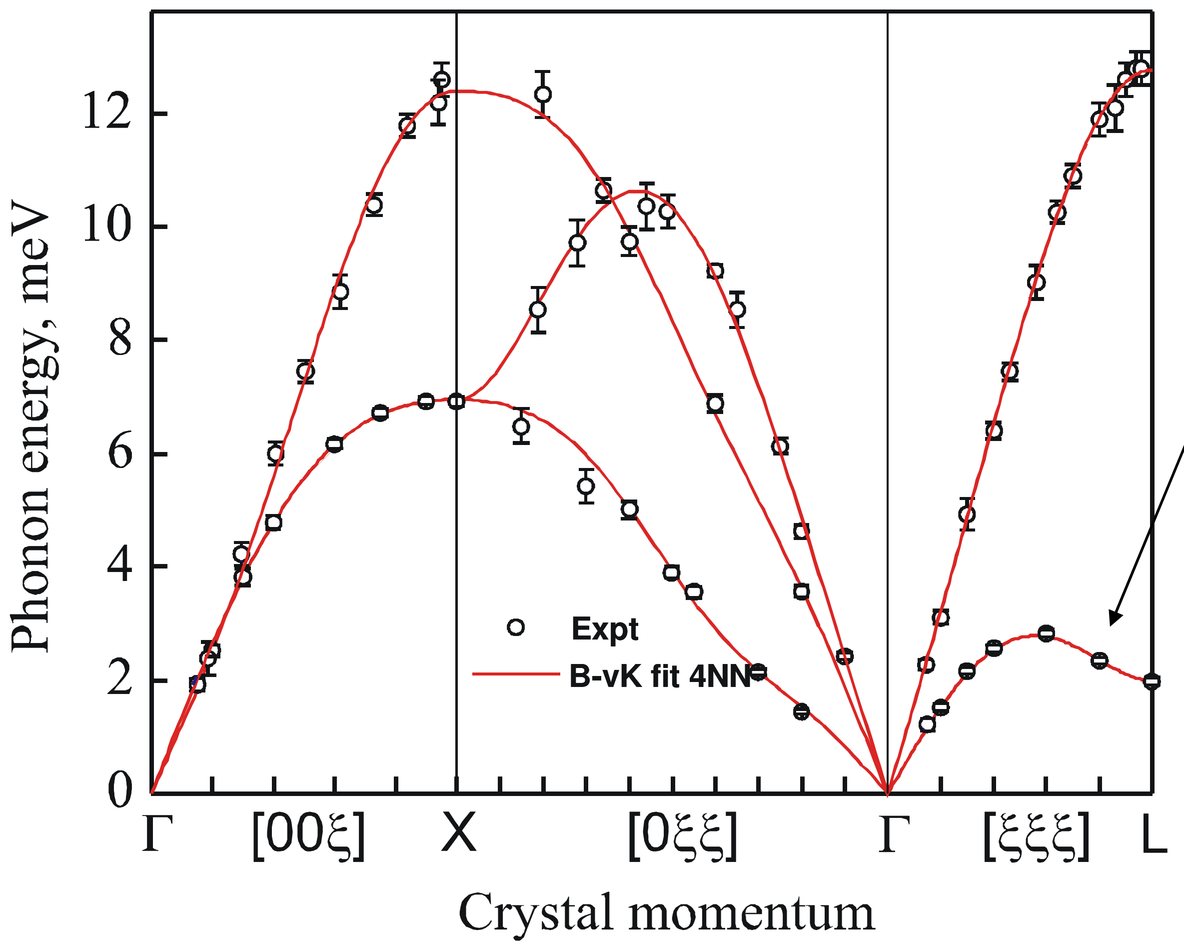


Science 301, 1078 (2003)



Experimental highlights (2)

Phonon dispersions in plutonium



soft-mode behaviour of T[111] branch

Onset of phase transitions (here to monoclinic α' phase at 163 K)

- **Born-von Karman force constant model fit** (fourth nearest neighbors)

Science 301, 1078 (2003)

Experimental highlights (2)

Phonon dispersions in plutonium

Close to Γ-point: **E** = **V**q/ħ

$\mathbf{V}_L[100] = (C_{11}/\rho)^{1/2}$

$\mathbf{V}_T[100] = (C_{44}/\rho)^{1/2}$

$\mathbf{V}_L[110] = ([C_{11}+C_{12}+2C_{44}]/\rho)^{1/2}$

$\mathbf{V}_{T1}[110] = ([C_{11} - C_{12}] /2\rho)^{1/2}$

$\mathbf{V}_{T2}[110] = (C_{44}/\rho)^{1/2}$

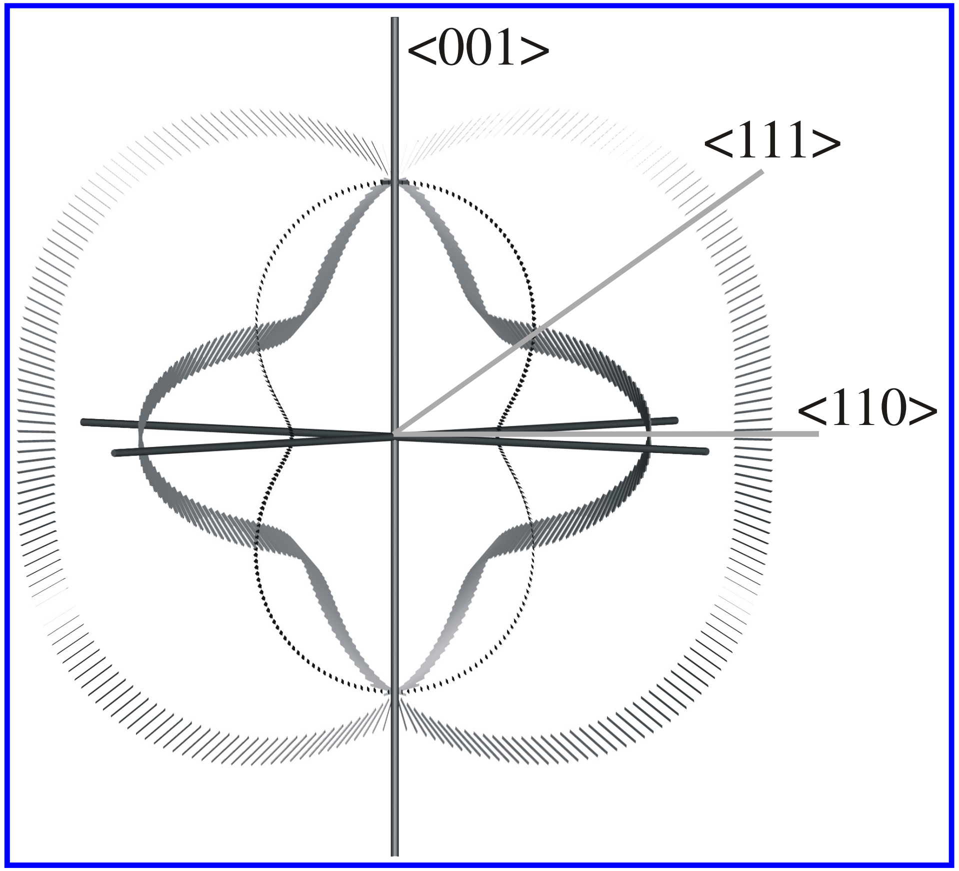
$\mathbf{V}_L[111] = [C_{11}+2C_{12}+4C_{44}]/3\rho)^{1/2}$

$\mathbf{V}_T[111] = ([C_{11}-C_{12}+C_{44}]/3\rho)^{1/2}$

$C_{11} = 35.3 \pm 1.4$ GPa

$C_{12} = 25.5 \pm 1.5$ GPa

$C_{44} = 30.5 \pm 1.1$ GPa

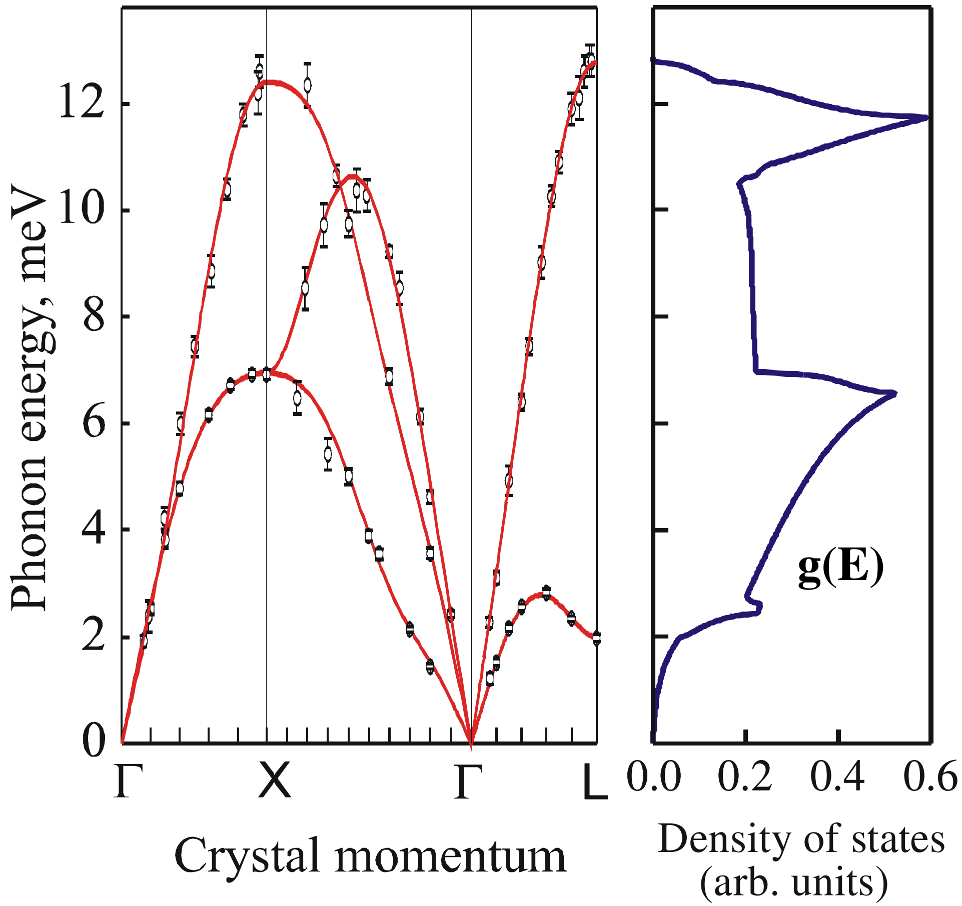


highest elastic anisotropy of all known fcc metals

Science 301, 1078 (2003)

Experimental highlights (2)

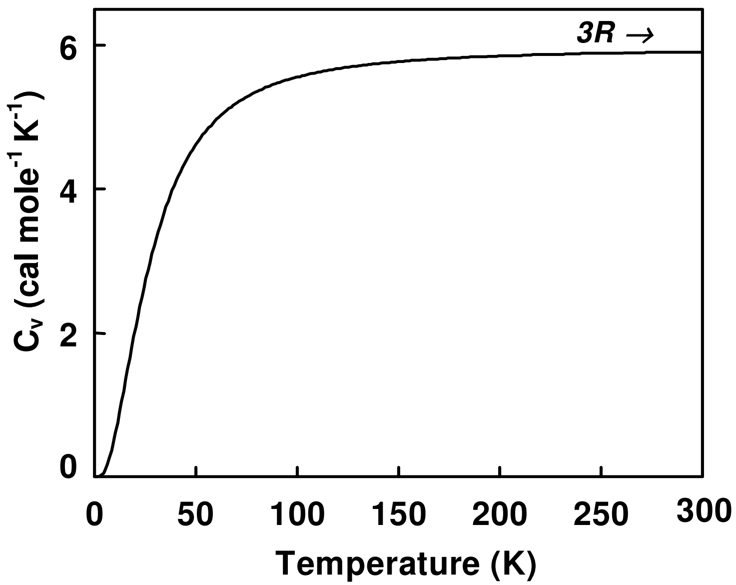
Phonon dispersions in plutonium



- **Born-von Karman fit**

Specific heat:

$$C_v = 3Nk_B \int_0^{E_{max}} \left(\frac{E}{k_B T}\right)^2 \frac{\exp(E/k_B T)\, g(E)\, dE}{(\exp(E/k_B T)-1)^2}$$



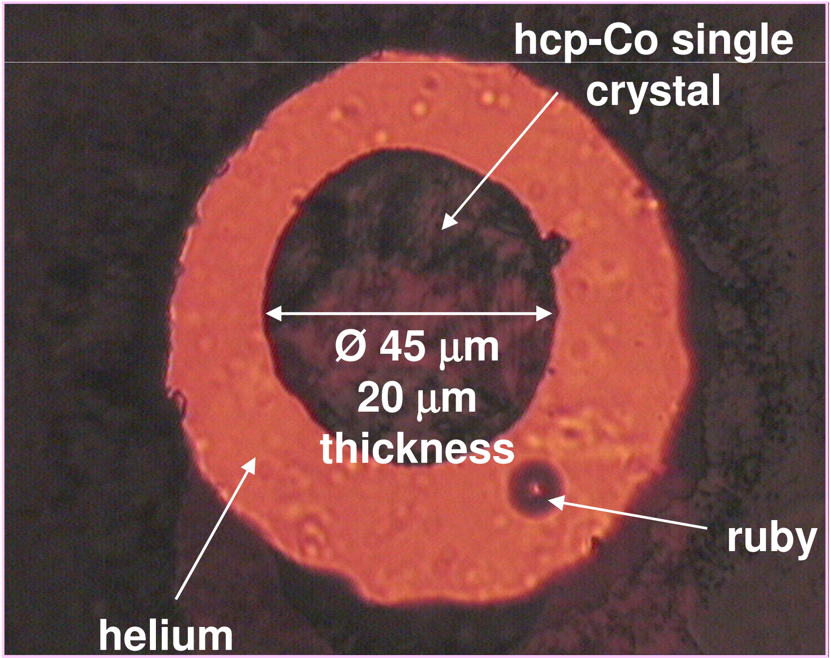
Science 301, 1078 (2003)

Experimental highlights (3)

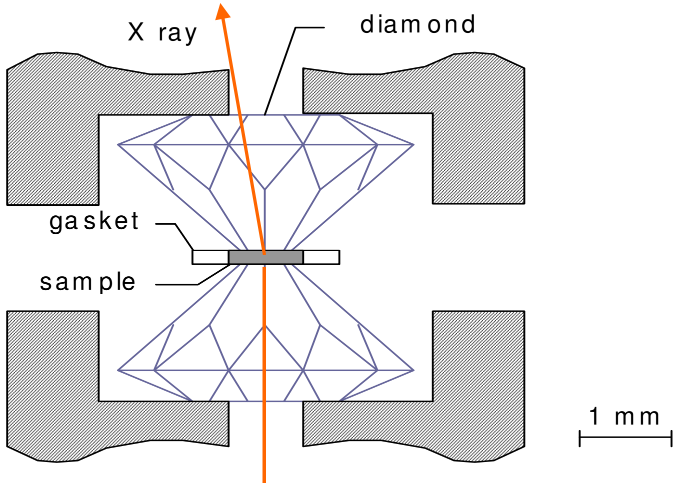
Elasticity at high pressure

Elasticity of hcp-metals under very high pressure (up to 1 Mbar):

- Geophysical interest (Earth core)
- DAC sample environment + IXS



PRL 93, 215505 (2004)



hcp-structure:

5 independent elastic moduli

$\mathbf{V}_L[001] = (C_{33}/\rho)^{1/2}$

$\mathbf{V}_L[100] = (C_{11}/\rho)^{1/2}$

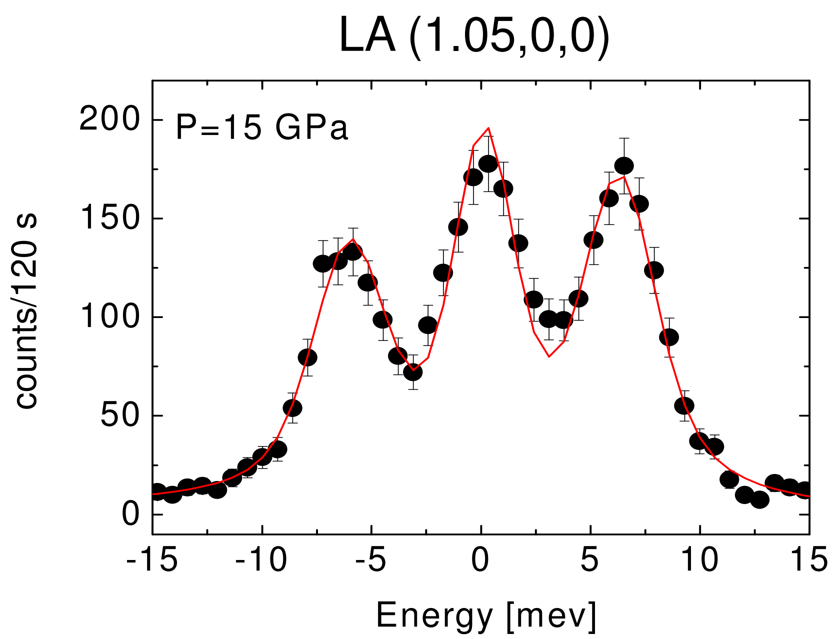
$\mathbf{V}_{T1}[110] = ([C_{11} - C_{12}] /2\rho)^{1/2}$

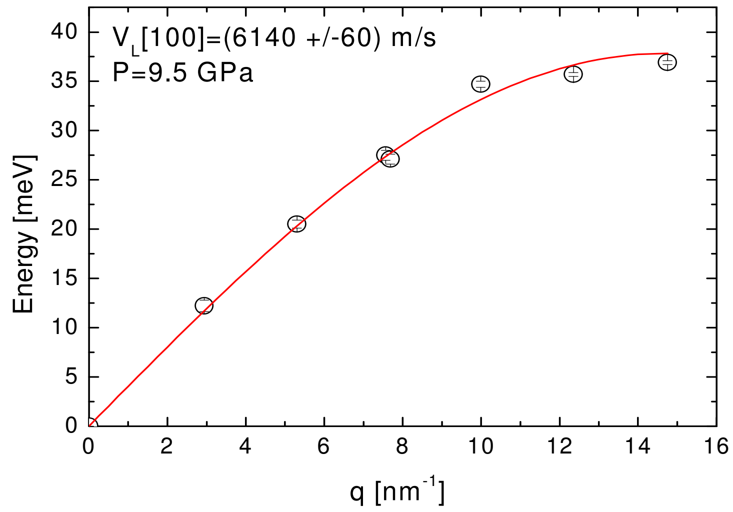
$\mathbf{V}_{T2}[110] = (C_{44}/\rho)^{1/2}$

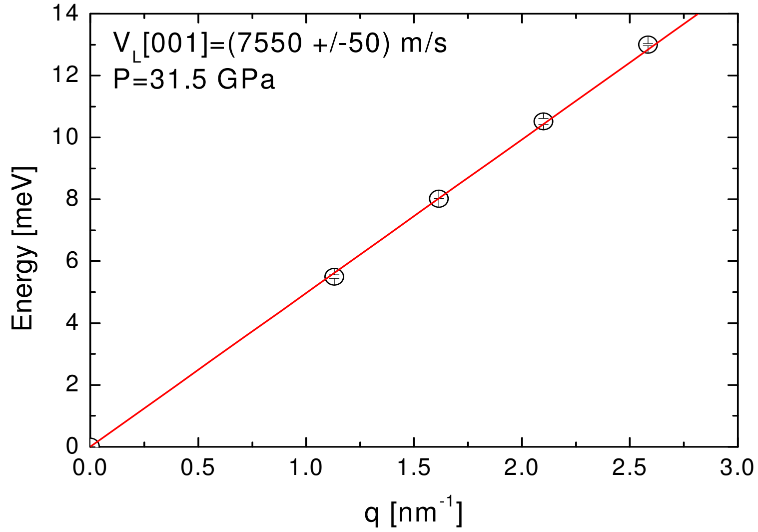
$\mathbf{V}_{QL}[101] = f(C_{ij},\rho) \rightarrow C_{13}$

Experimental highlights (3)

Elasticity at high pressure



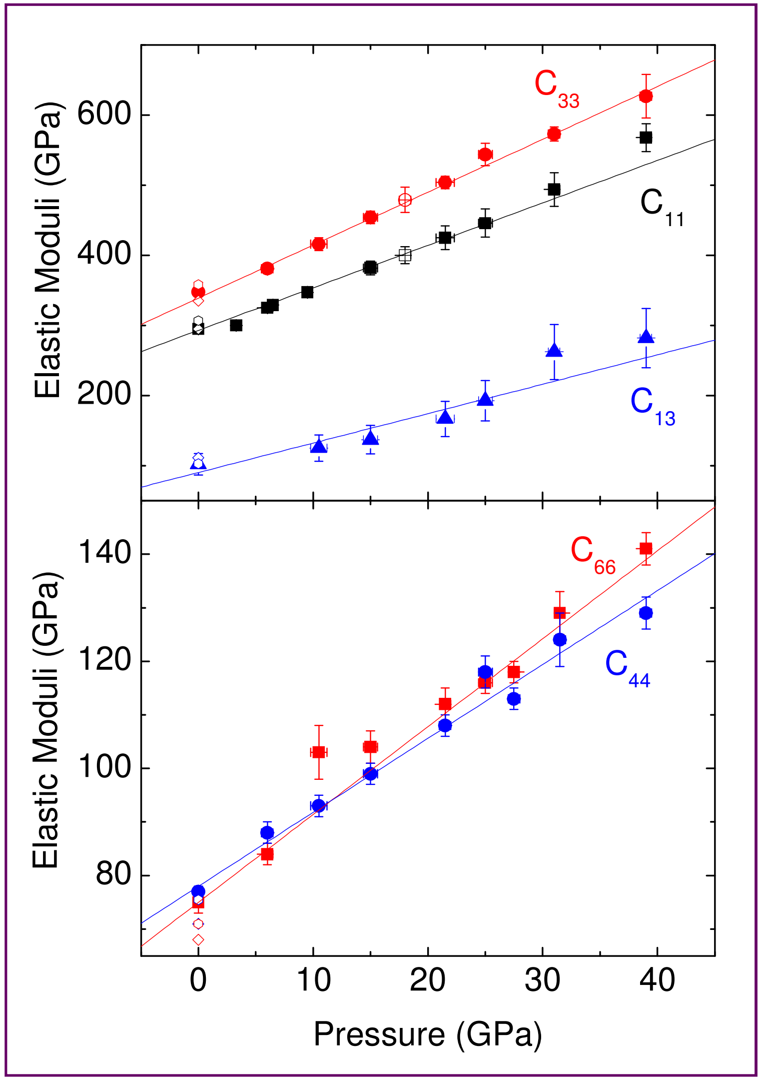


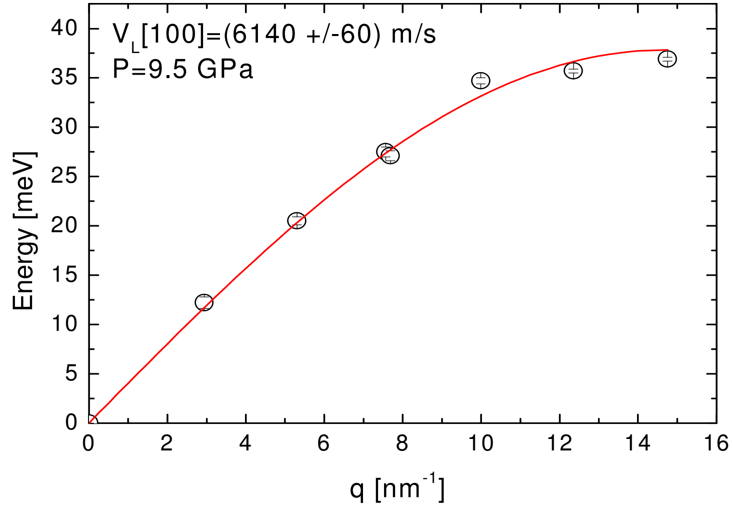


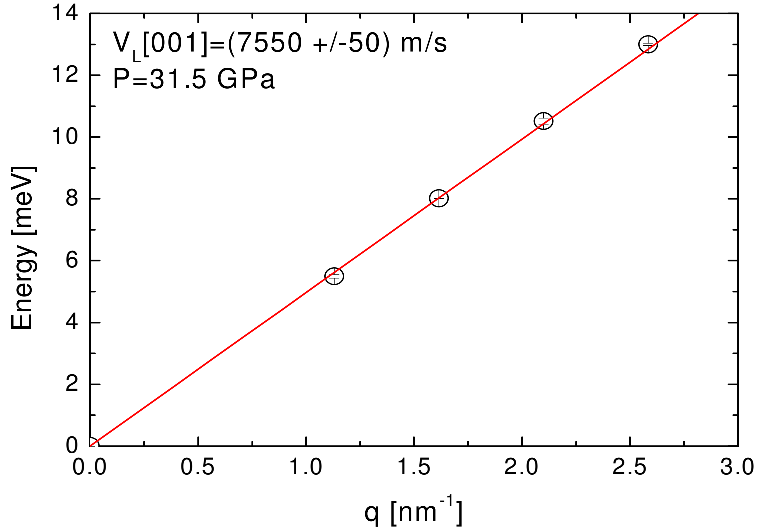
PRL 93, 215505 (2004)

Experimental highlights (3)

Elasticity at high pressure

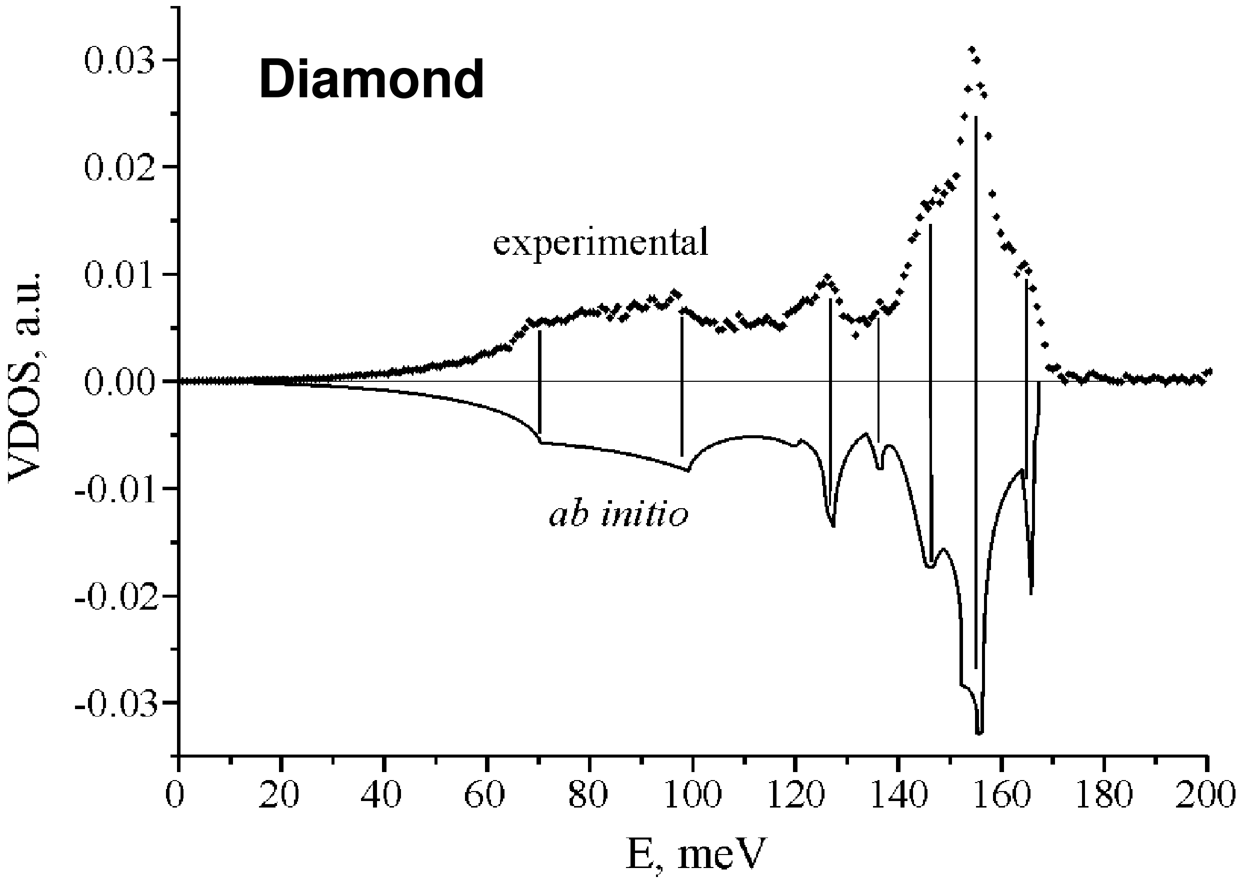






PRL 93, 215505 (2004)

Other examples (VDOS)



Alternative to:

Incoherent Inelastic Neutron Scattering
(but no large volume)

Nuclear Inelastic X-ray Scattering
(but no Mössbauer isotope needed)

Perspectives

High pressures

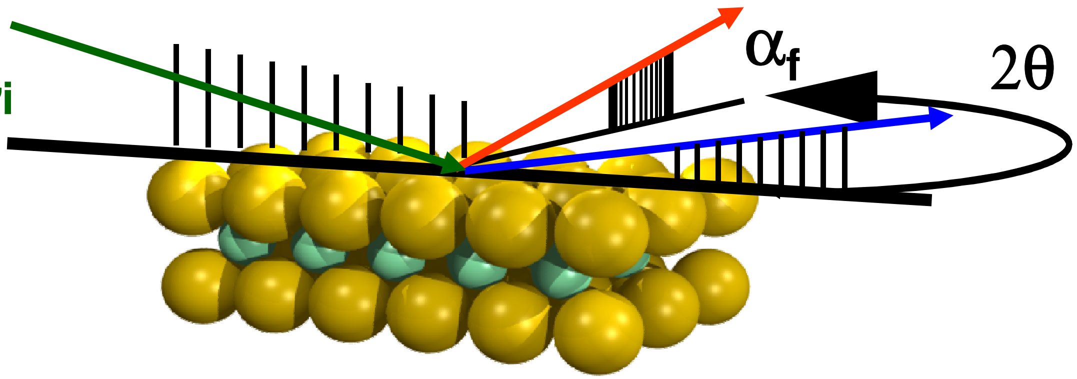
single crystal elastic constants
(VDOS + IXS + Diffraction)

partial VDOS in multi-component systems
(VDOS, INS and NIS)

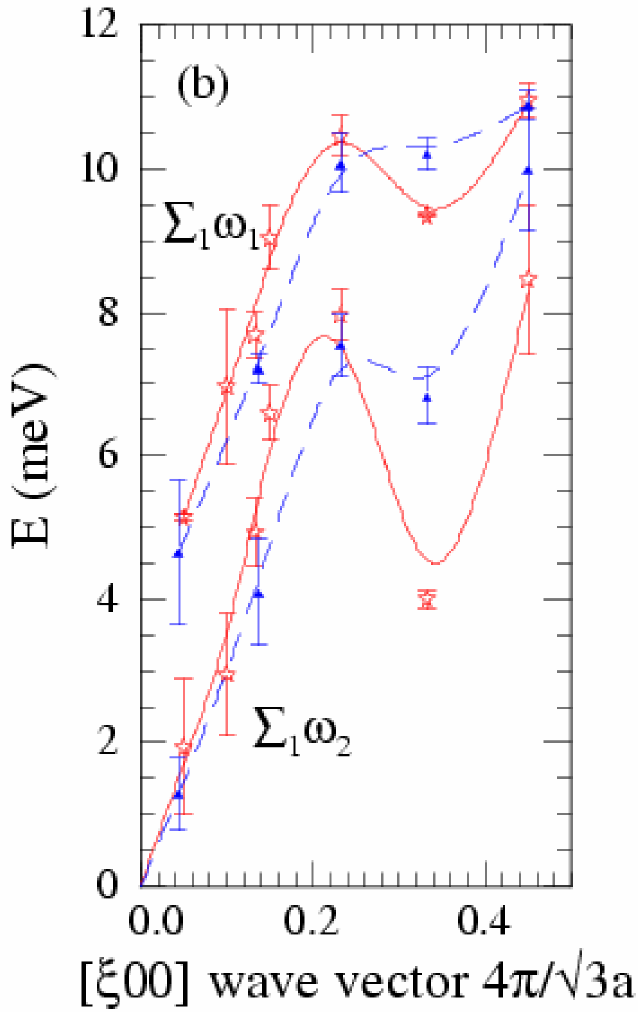
- ΔE = 3 meV
- Sum of 10 IXS spectra (45 nm^{-1}<k<60 nm^{-1})

Ab initio calculations: P. Pavone et al.; Phys. Rev. B 48, 3156 (1993)

Other examples (crystalline surfaces)



2H-NbSe$_2$



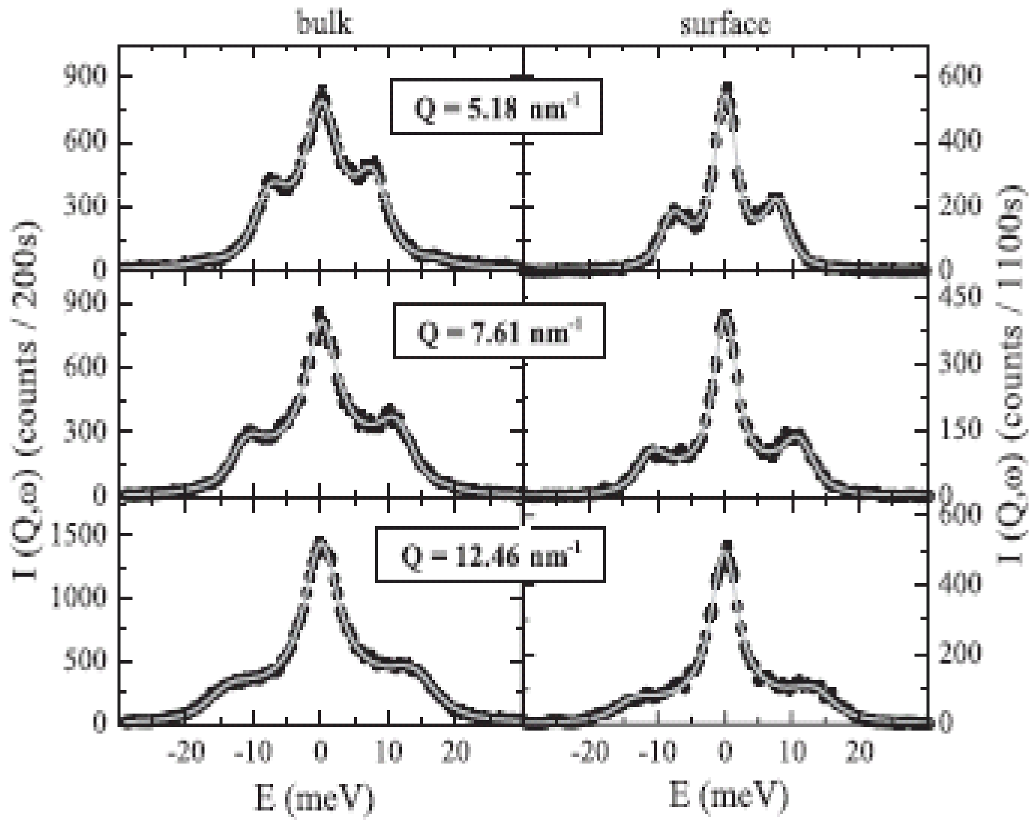
α_i = 0.18°– 0.03°, penetration depth: ~30 Å
Energy resolution: 3 meV

PRL 95, 256104 (2005)

Other examples (liquid surfaces)

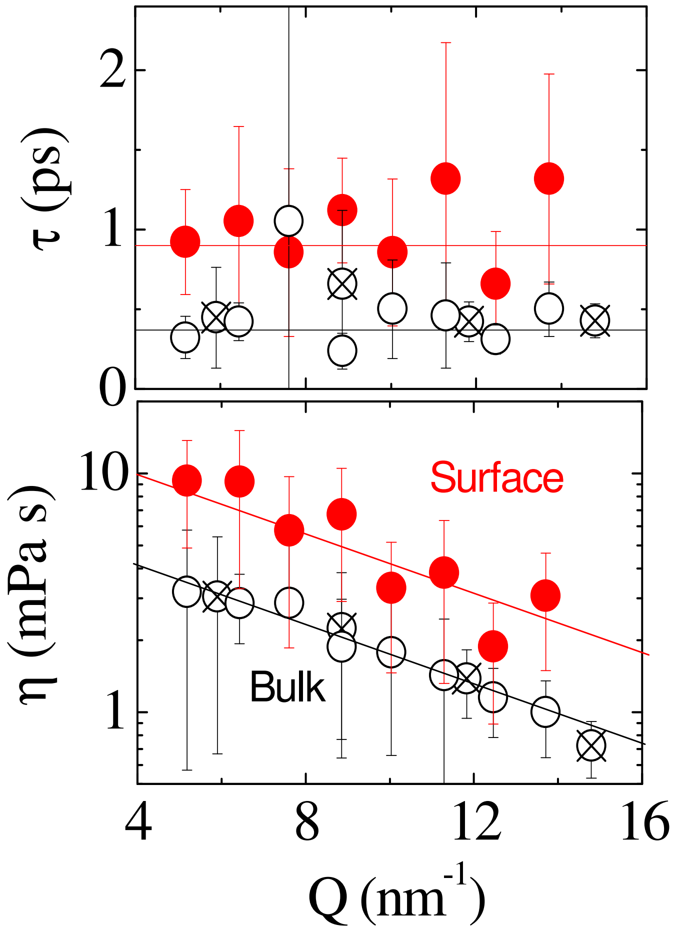
Liquid indium: ID28 at ESRF

- Energy resolution: 1.5 (3) meV
- Beam size: 250 x 30 μm^2 (HxV)
- Penetration depth: 46 Å



PRL 98, 096104 (2007)

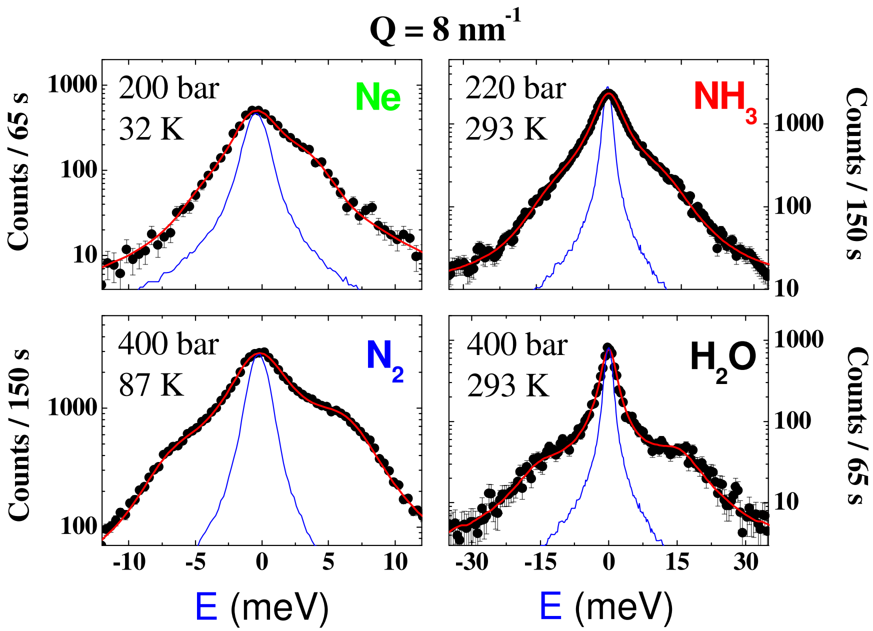
Viscoelasic data analysis:



Other examples (liquids & supercritical fluids)

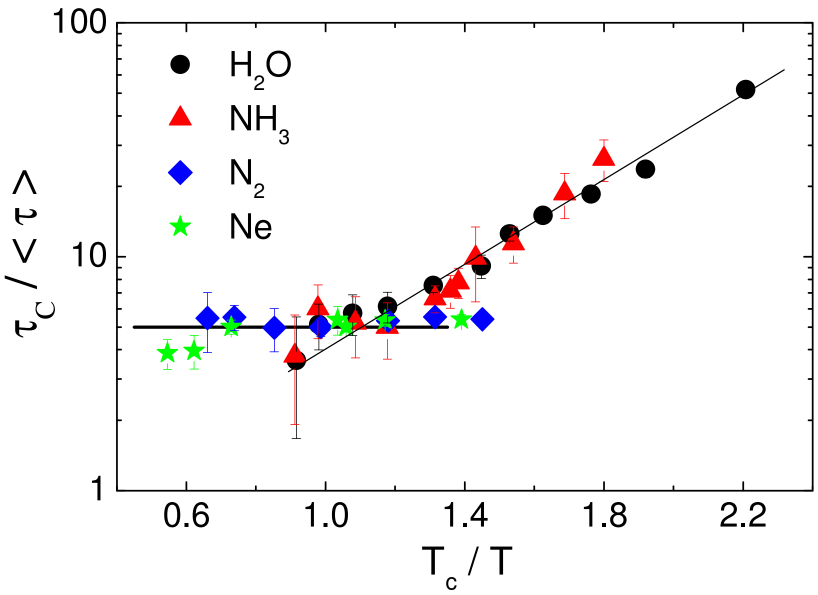
ID28 and ID16 at ESRF

- Energy resolution: 1.5 meV
- Moderate pressure (< 500 bar)
- Various temperatures (20÷800 K)



PRL 98, 085501 (2007)

Viscoelasic data analysis:



Leading dynamics in fluids:

- T>Tc → collisions
- T<Tc → bond's lifetime