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School on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications

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Inelastic x-ray scattering: principles

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Inelastic x-ray scattering: principles

Filippo Bencivenga

OUTLINE

Introduction

High resolution inelastic x-ray scattering (IXS)

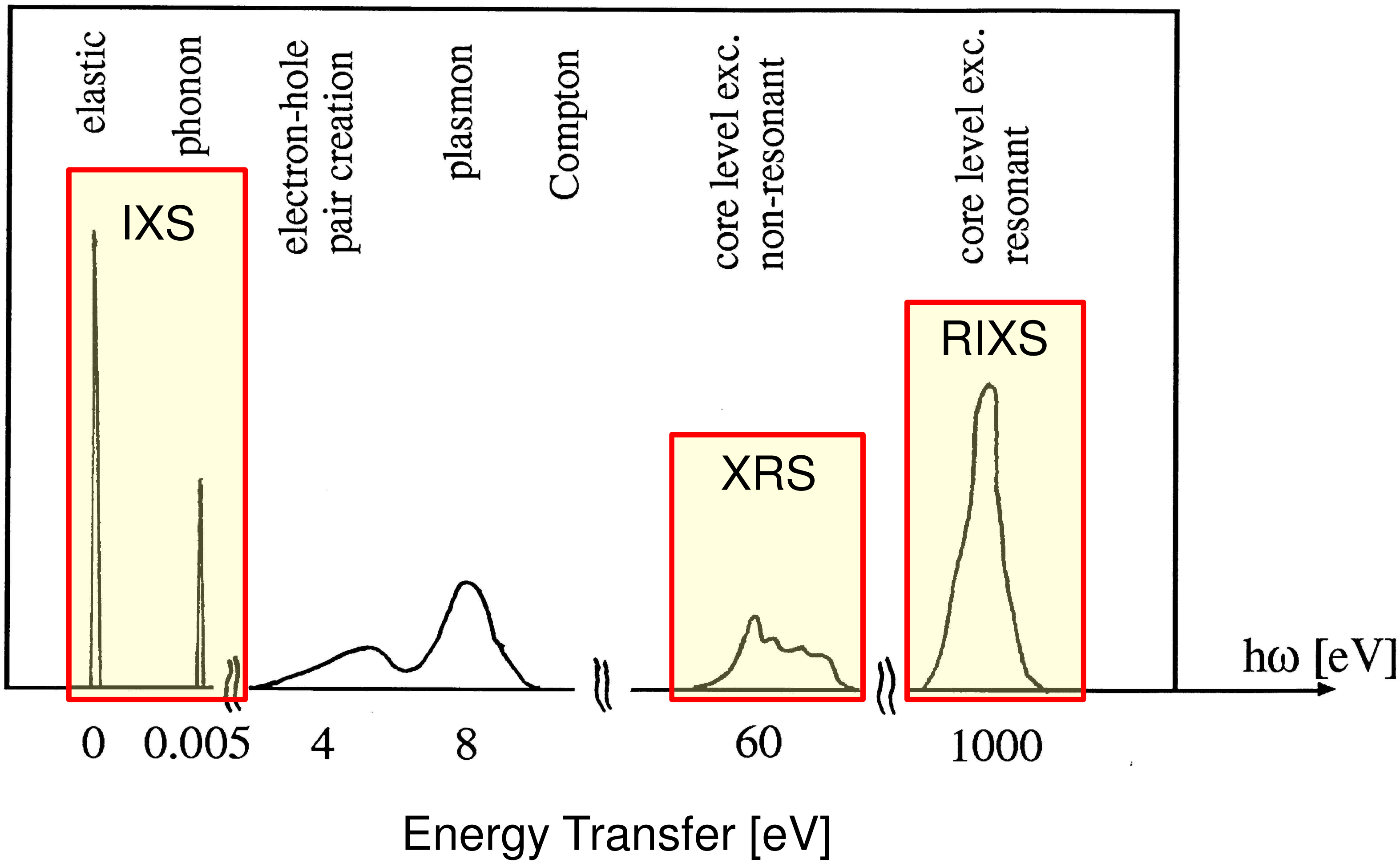
- Collective atomic dynamics
- Neutrons vs. X-rays
- Basic theory and instrumentation
- Experimental highlights

Inelastic x-ray “Raman” scattering (XRS)

- Experimental/theoretical aspects
- Scattering vs. absorption spectroscopy
- Experimental highlights

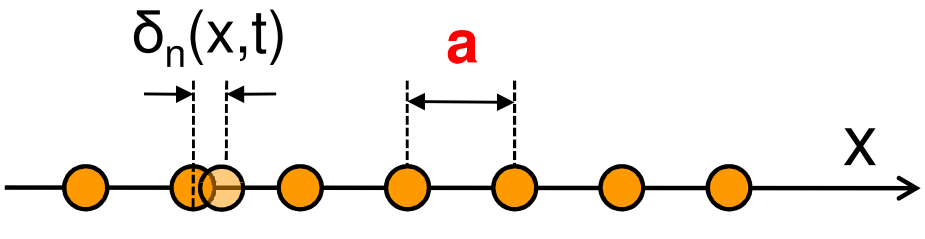
Resonant inelastic x-ray scattering (RIXS)

Introduction: inelastic X-ray spectrum



IXS: collective atomic dynamics

The simpler case



Information:

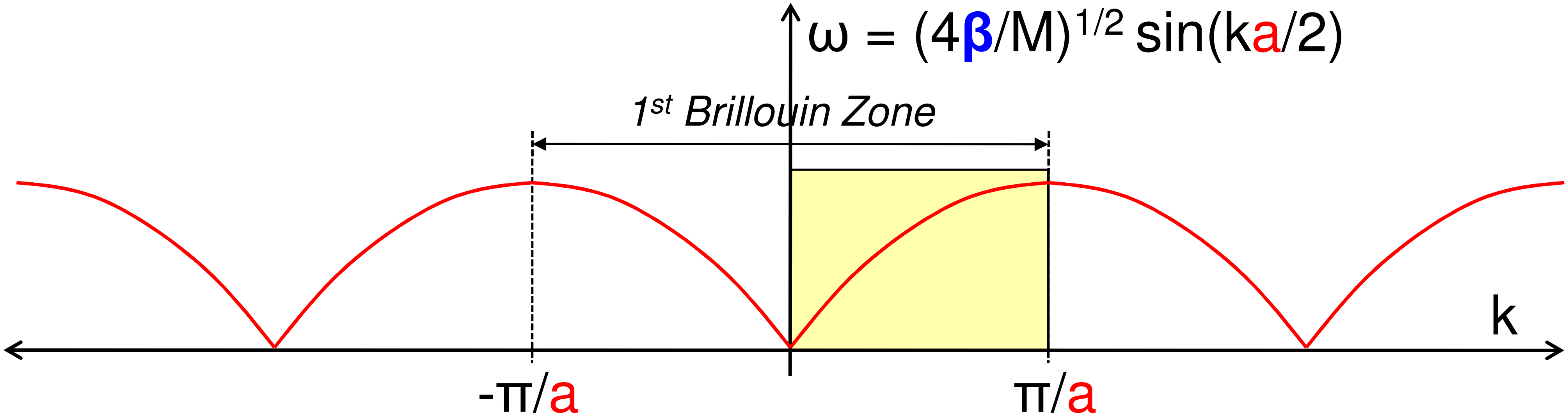
- Interatomic Structure (**a**)
- Interaction Potential (**β**)

$$U = -\beta x^2$$

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

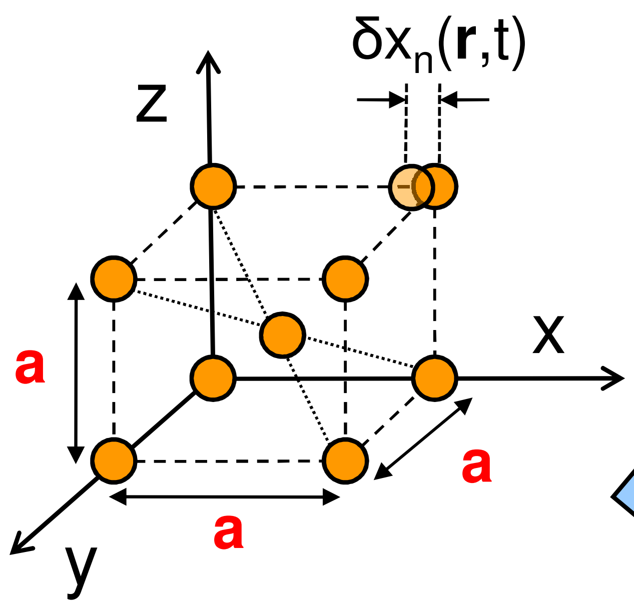
Phonons → Eigenstates of vibrational field

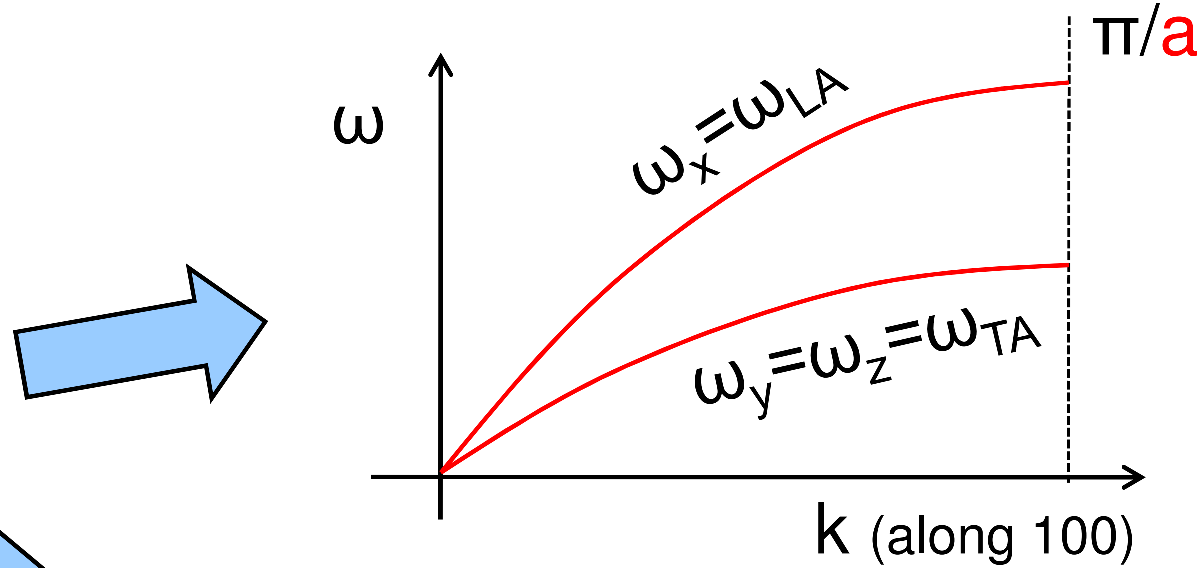
$\omega(k)$ → Dispersion relation



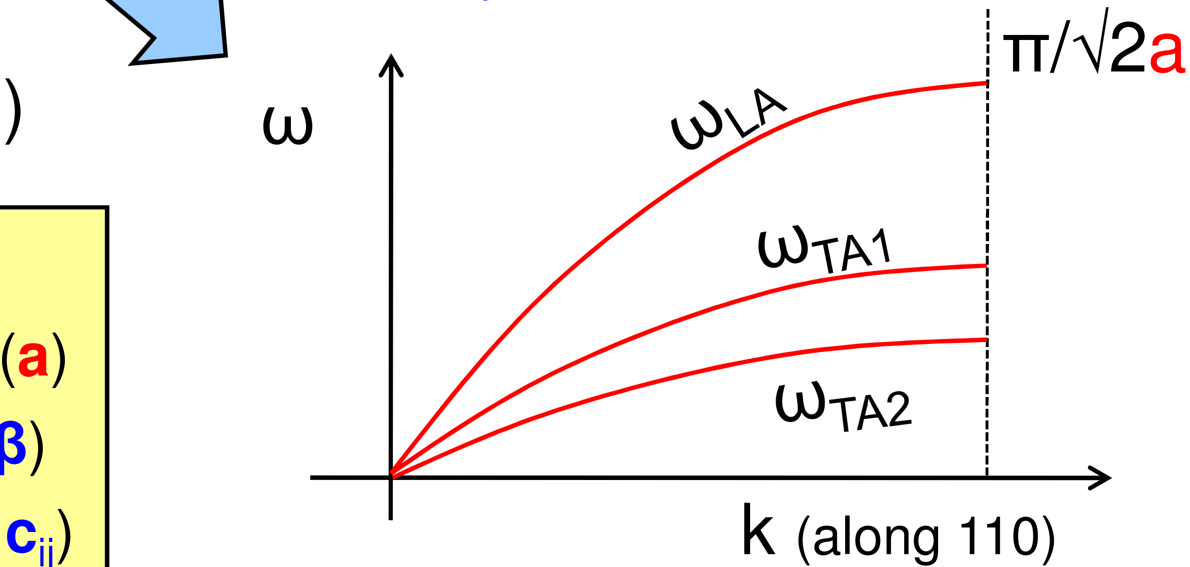
IXS: collective atomic dynamics

One step forward: 3D lattice





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

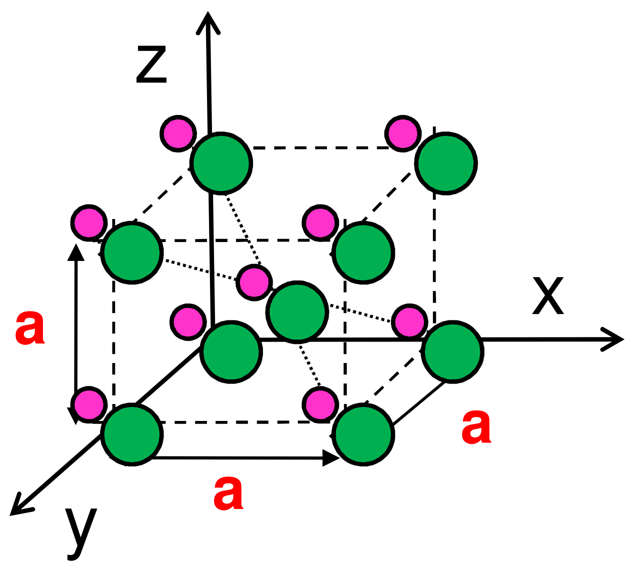


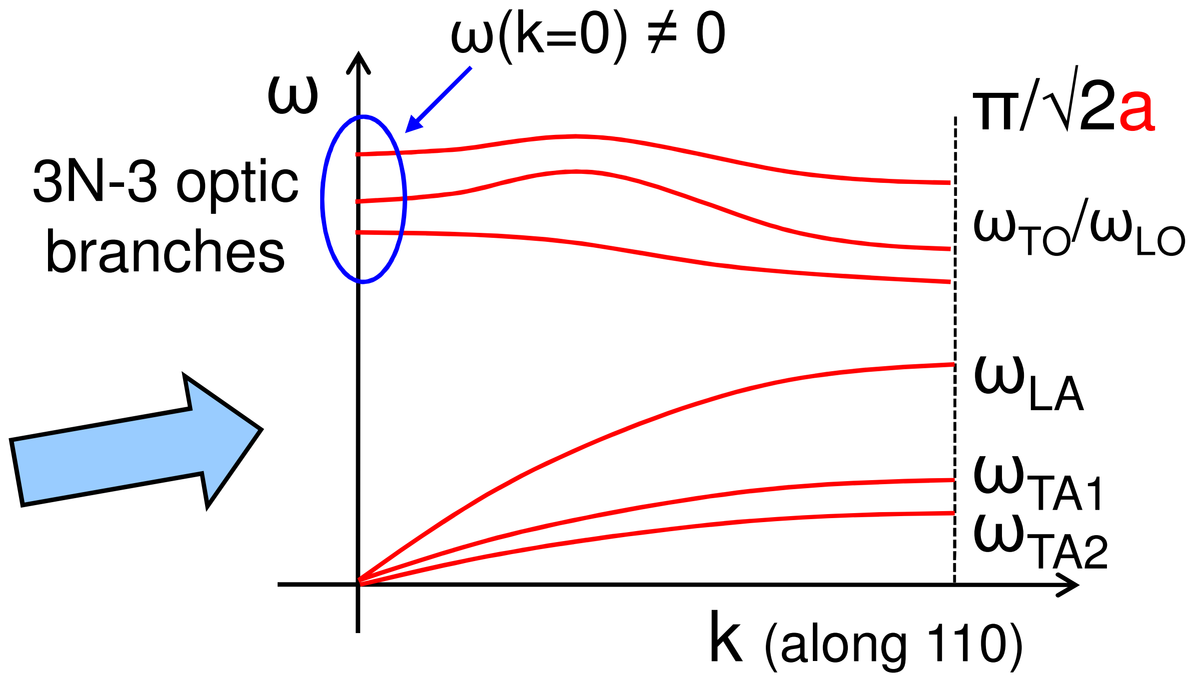
$U = -\boldsymbol{\beta}|\mathbf{r}|^2 \qquad \mathbf{r} = (x,y,z)$

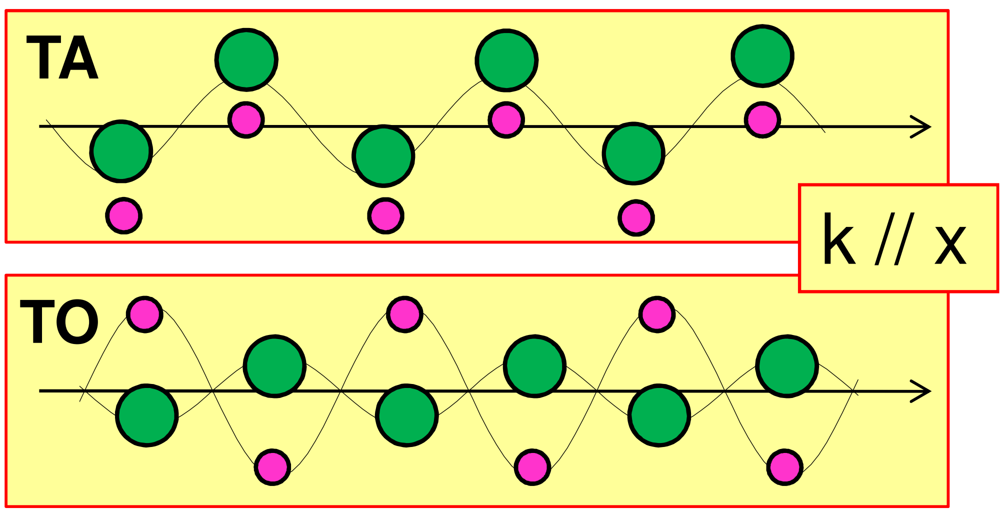
Information:

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

IXS: collective atomic dynamics





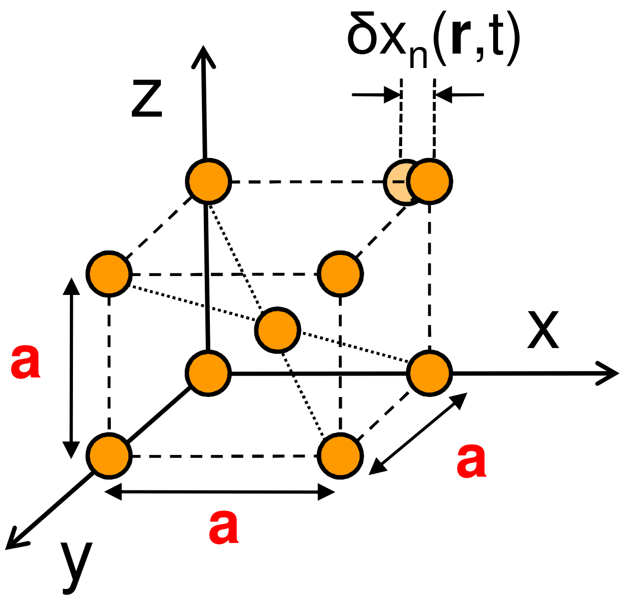


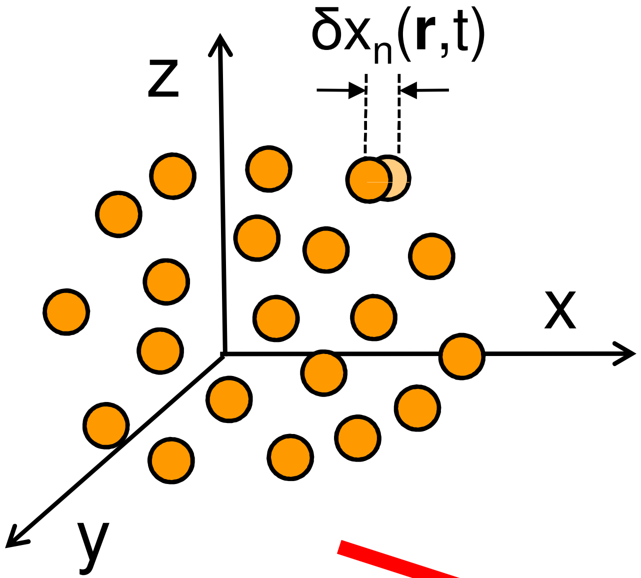
Information:

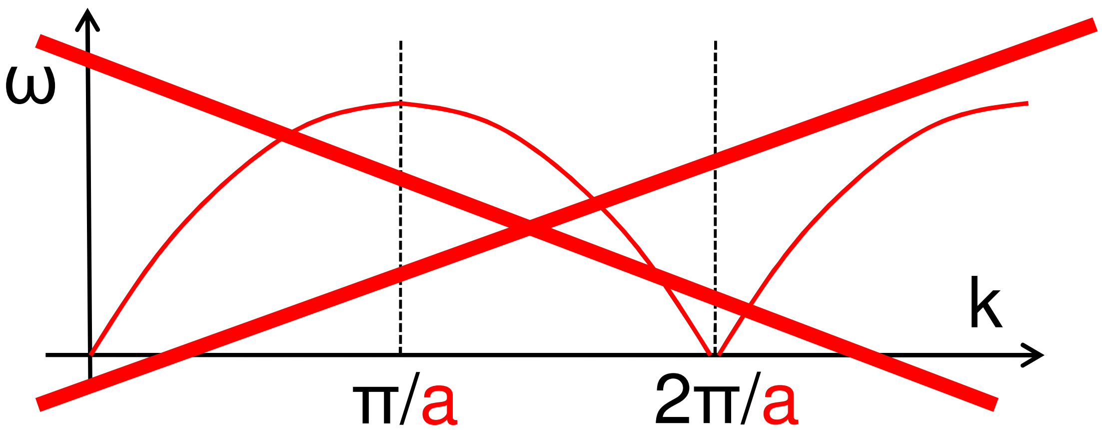
- Interatomic Structure (**a**)
- Interaction Potential (**β**)
- Anisotropy (elasticity: $\mathbf{c}_{ij}$)
- Intramolecular vibrations

IXS: collective atomic dynamics

The most complex case: disordered systems







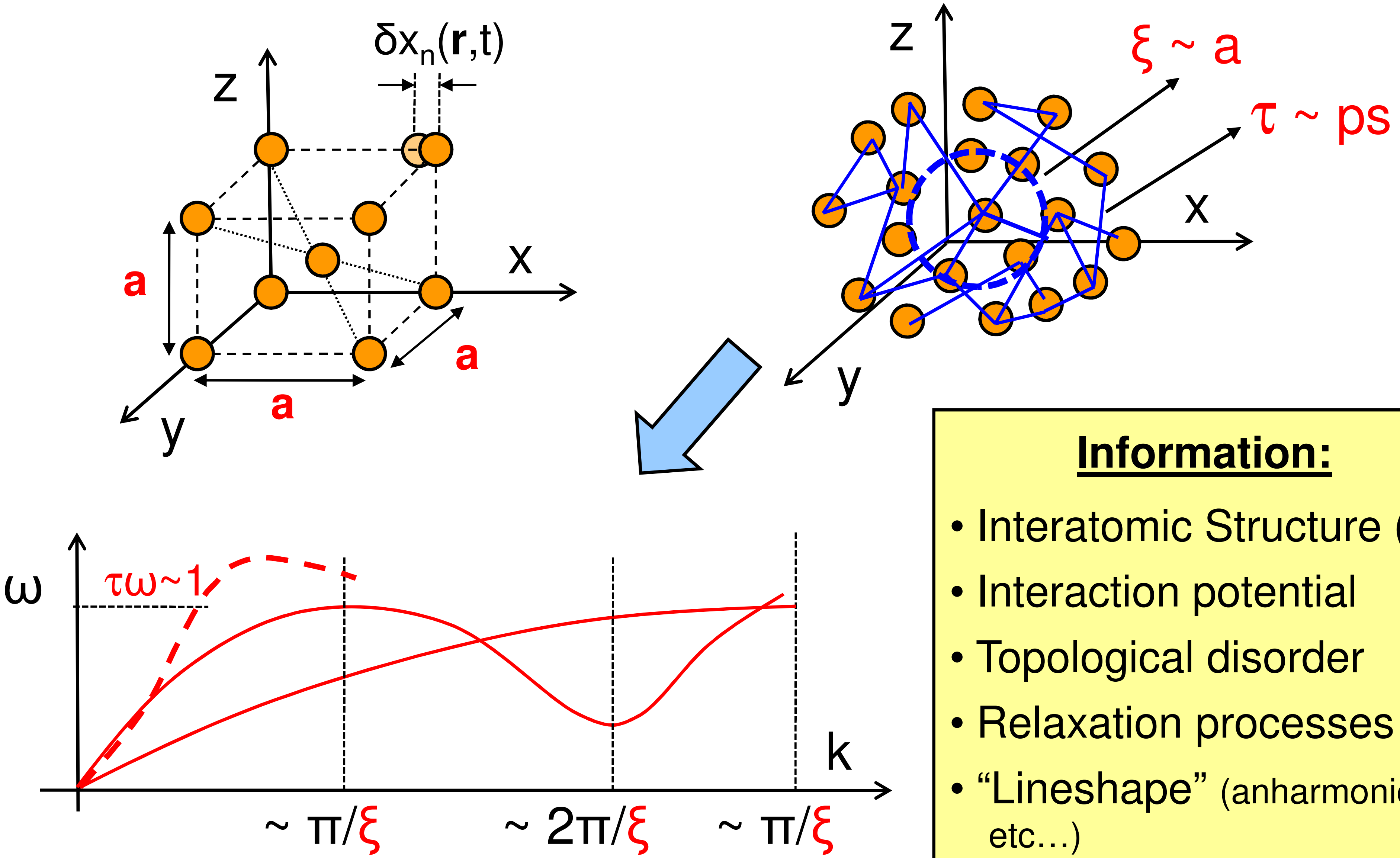
Translational periodicity (**a**)

Brillouin Zones

Eingenstates ∝ exp[i(kx-ωt)]

IXS: collective atomic dynamics

The most complex case: disordered systems

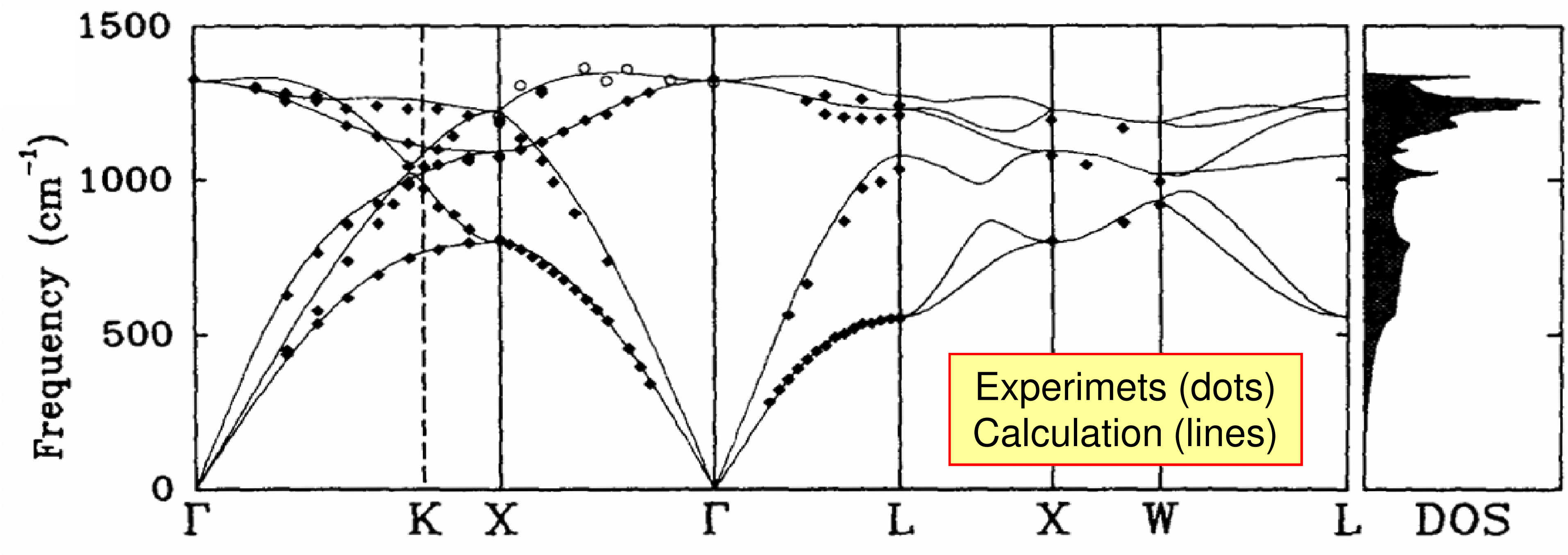


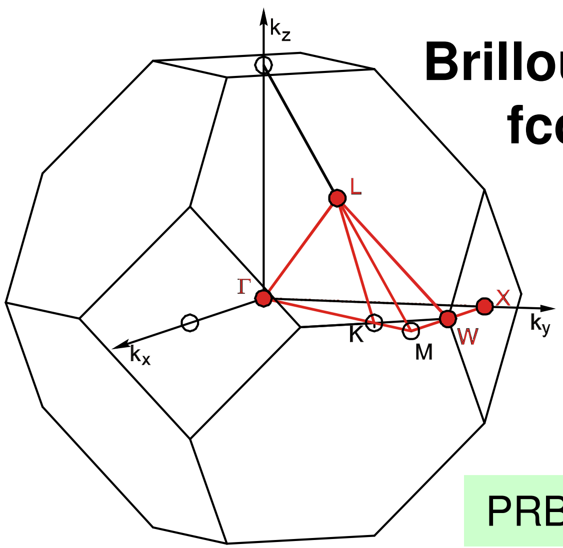
Information:

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

An example…

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





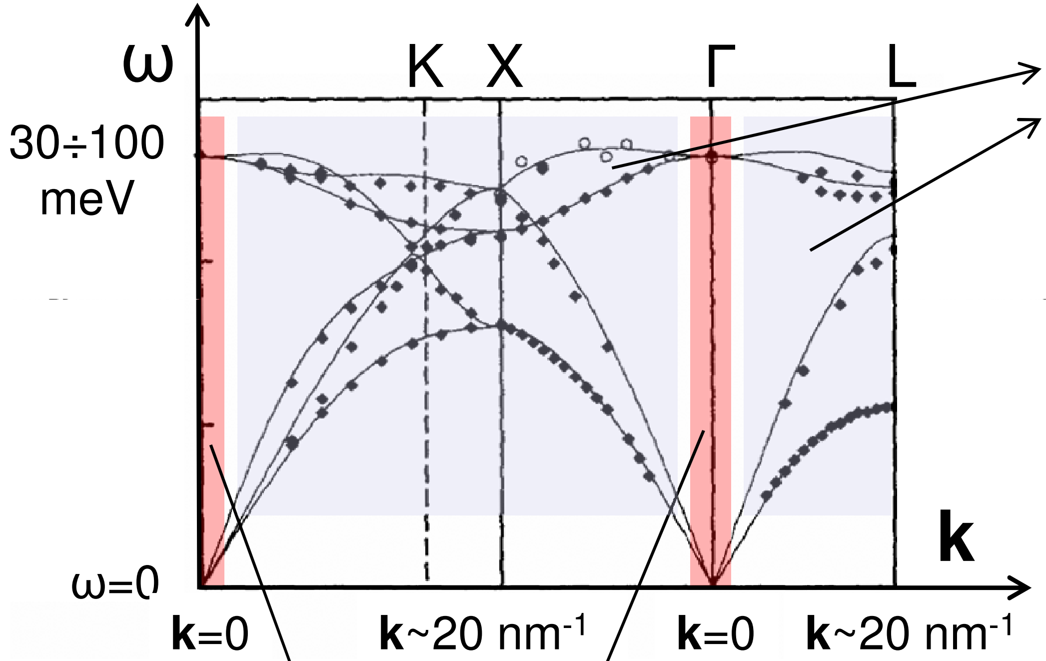
Brillouin zones for fcc symmetry

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?



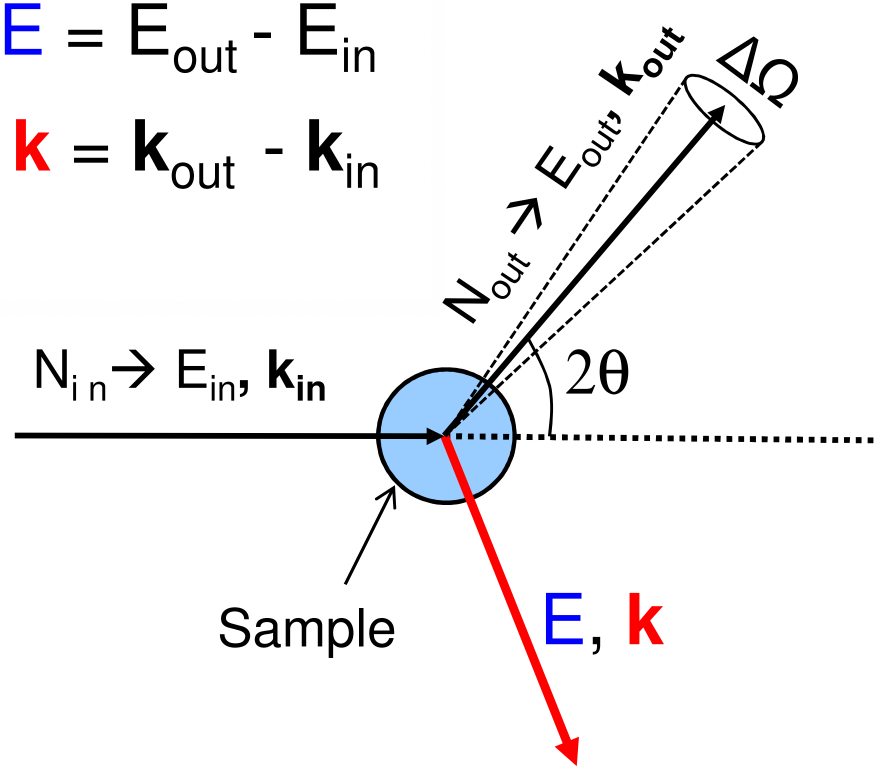
- Probe wavelenght (2π/|**k**|) < 0.1 nm
- Probe energy (E) > 30÷100 meV

- Inelastic Light Scattering (Brillouin & Raman)
- Ultrasonics
- 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
$\lambda_{in} = 1\text{Å} \Rightarrow E_{in} = 82\ \text{meV}$	$\lambda_{in} = 1\text{Å} \Rightarrow E_{in} = 12.4\ \text{keV}$
$E > 4\ \text{meV} \rightarrow \Delta E/E_{in} = 0.05$	$E > 4\ \text{meV} \rightarrow \Delta E/E_{in} = 3\cdot 10^{-7}$
Moderate energy resolution	Very high energy resolution
⇓	⇓
100 INS instruments	4 IXS instruments

\+

Spin sensitive

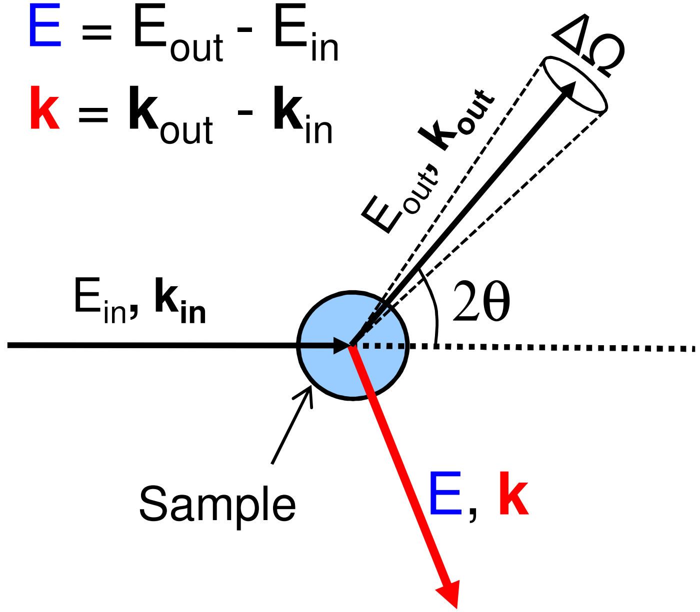
Better contrast

"Older" technique

Inelastic scattering:

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

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



Why X-rays?

Neutrons vs. X-rays

λ_{in} = 1Å ⇨ E_{in} = 82 meV

λ_{in} = 1Å ⇨ E_{in} = 12.4 keV

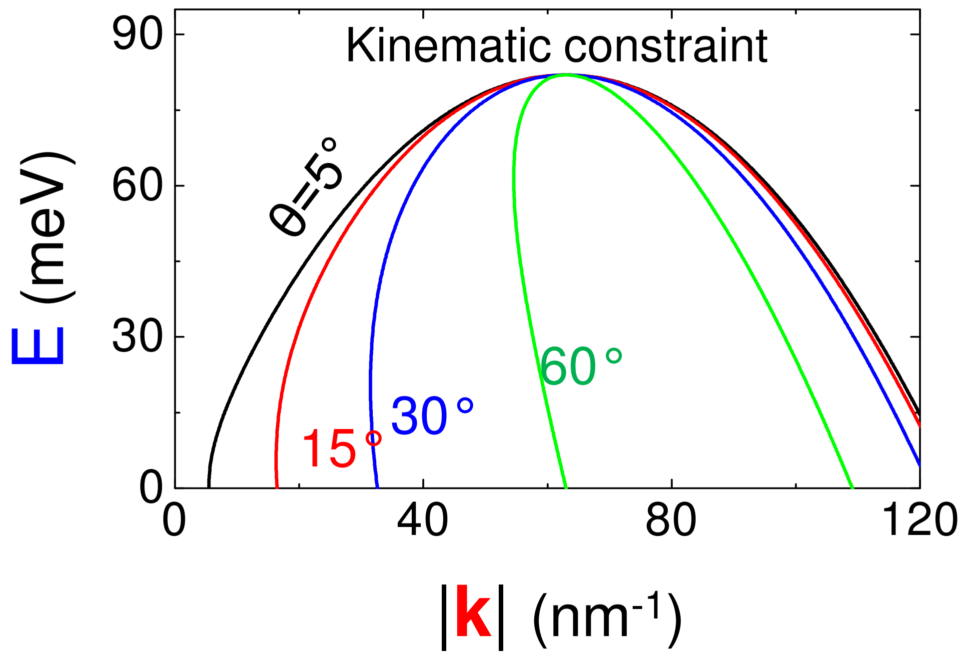
$E = E_{out} - E_{in}$ & $\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{in}$

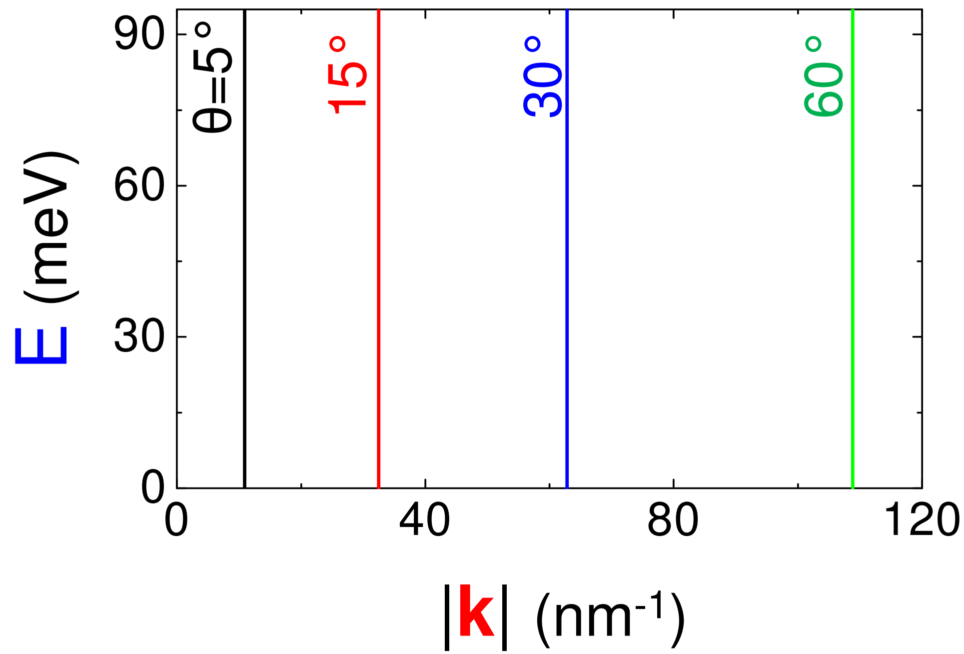
$E_{out} \neq E_{in}$

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

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

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





Neutrons vs. X-rays

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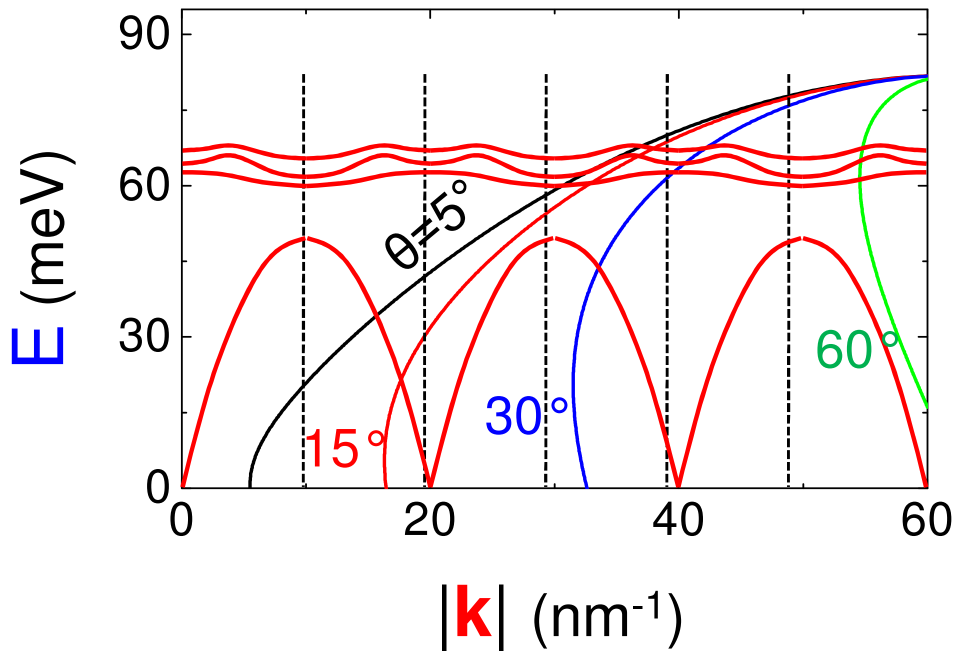
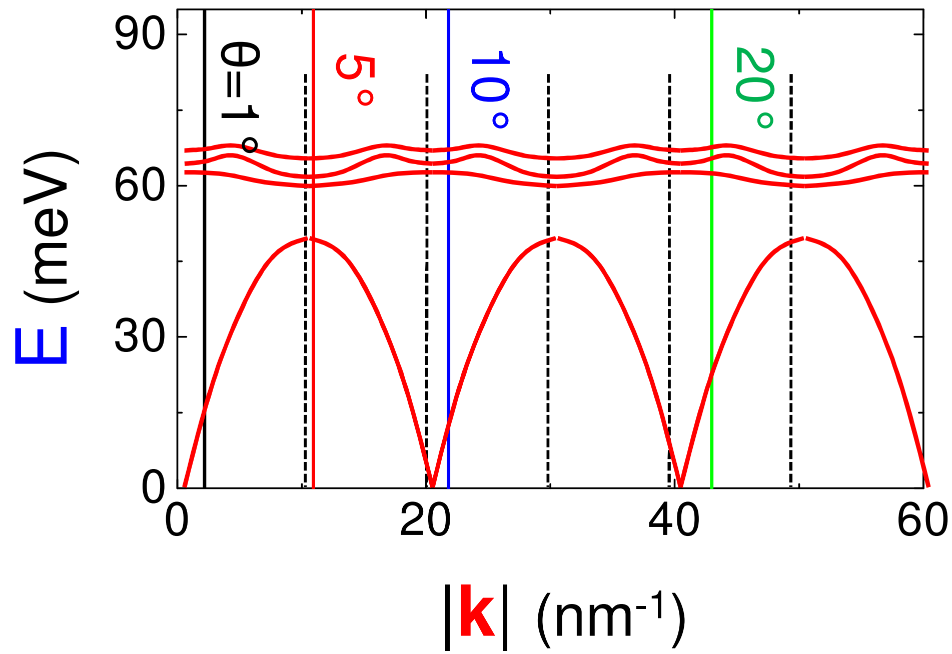
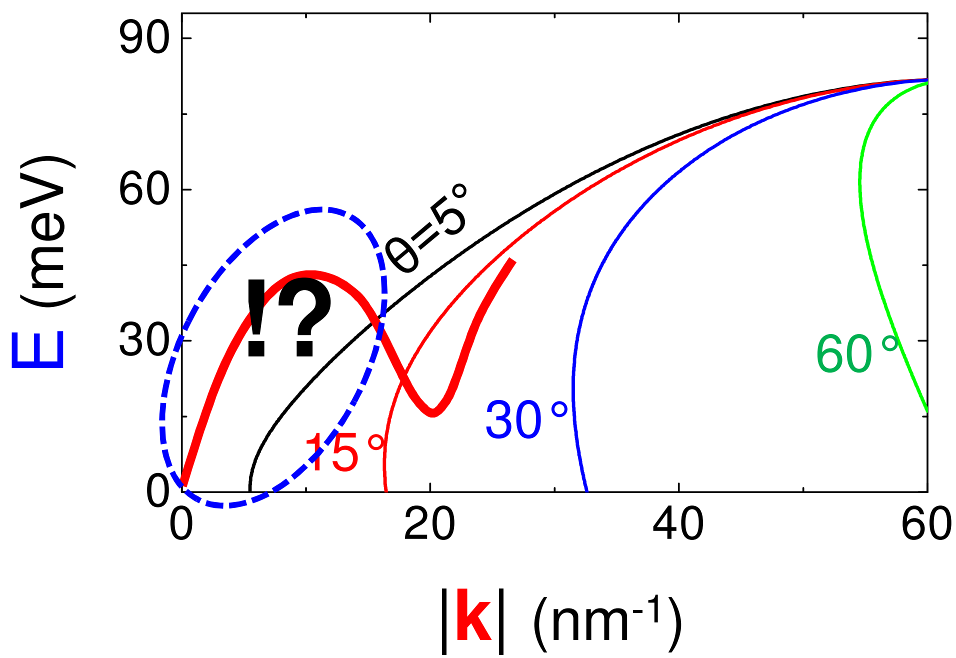


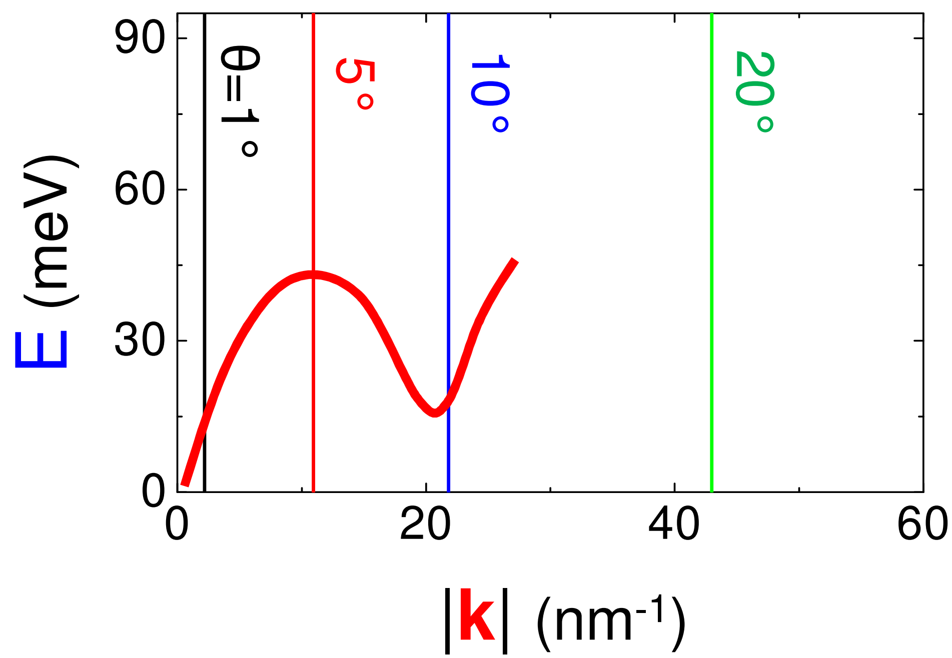


Neutrons vs. X-rays

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

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

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

E > 4 meV → $\Delta E/E_{in} = 0.05$

E > 4 meV → $\Delta E/E_{in} = 3 \cdot 10^{-7}$

Moderate energy resolution

⇩

100 INS instruments

+

Spin sensitive

Better contrast

"Older" technique

Very high energy resolution

⇩

3 IXS instruments

Why X-rays?

No kinematical constraints
(Disordered systems)

Small beams
(small samples: high pressure, exotic materials, etc…)

No incoherent cross section

Basic theoretical aspects

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

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

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

Basic theoretical aspects

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

The key assumption:

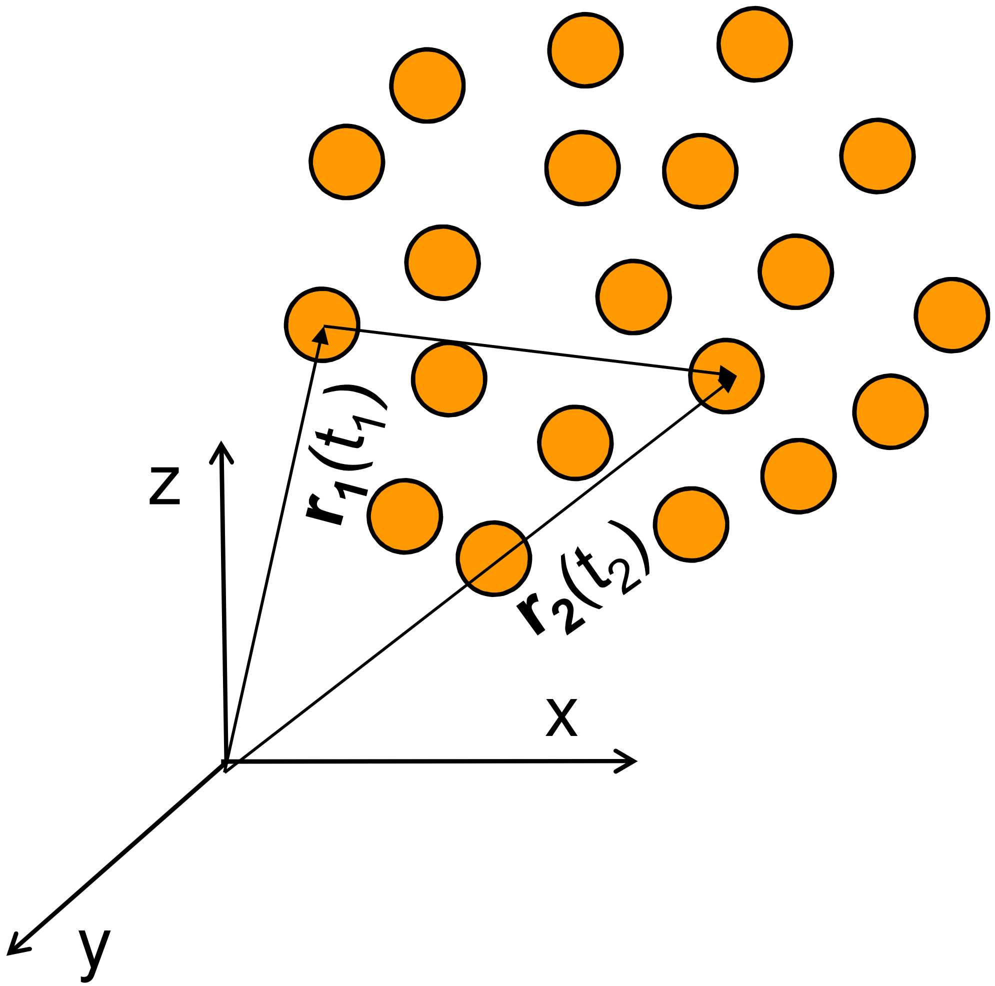
<u>Adiabatic approximation</u> → $|I>=|I_n>|I_e>$ and $|F>=|F_n>|F_e>$

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} = \underbrace{r_0^2(\varepsilon_{in}\cdot\varepsilon_{out})^2(k_{in}/k_{out})}\ \underbrace{F(|\mathbf{k}|)^2}\ \underbrace{S(\mathbf{k},E)}$$

- $r_0^2(\varepsilon_{in}\cdot\varepsilon_{out})^2(k_{in}/k_{out})$ → Thomson scattering cross section
- $F(|\mathbf{k}|)^2$ → Molecular form factor ($|I_e>$, $|F_e>$)
- $S(\mathbf{k},E)$ → **<u>Dynamic structure factor</u>**

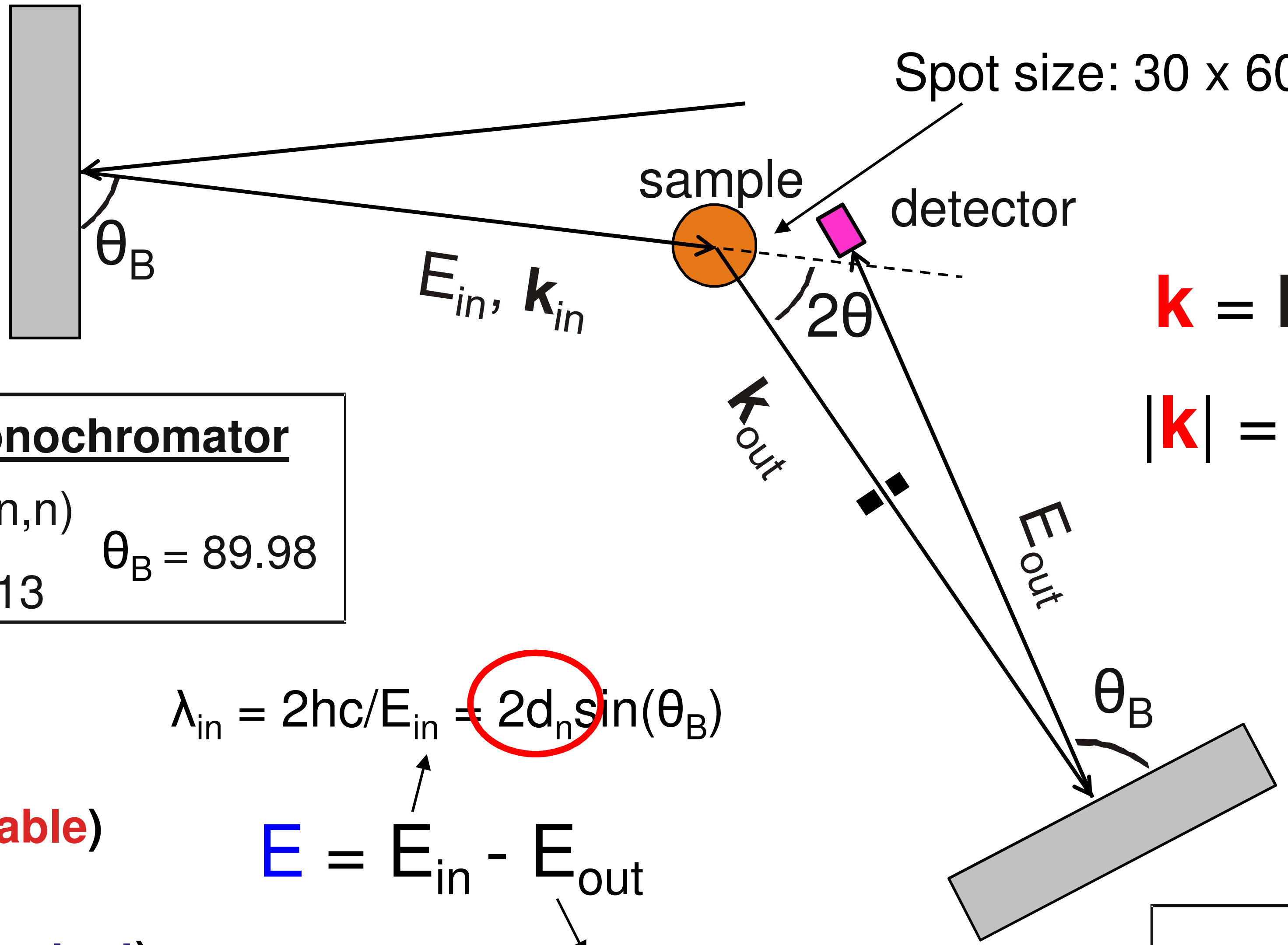
The dynamic structure factor

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) $\theta_B = 89.98$

n=7-13

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

λ_{in} (**tunable**)

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

λ_{out} (**constant**)

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

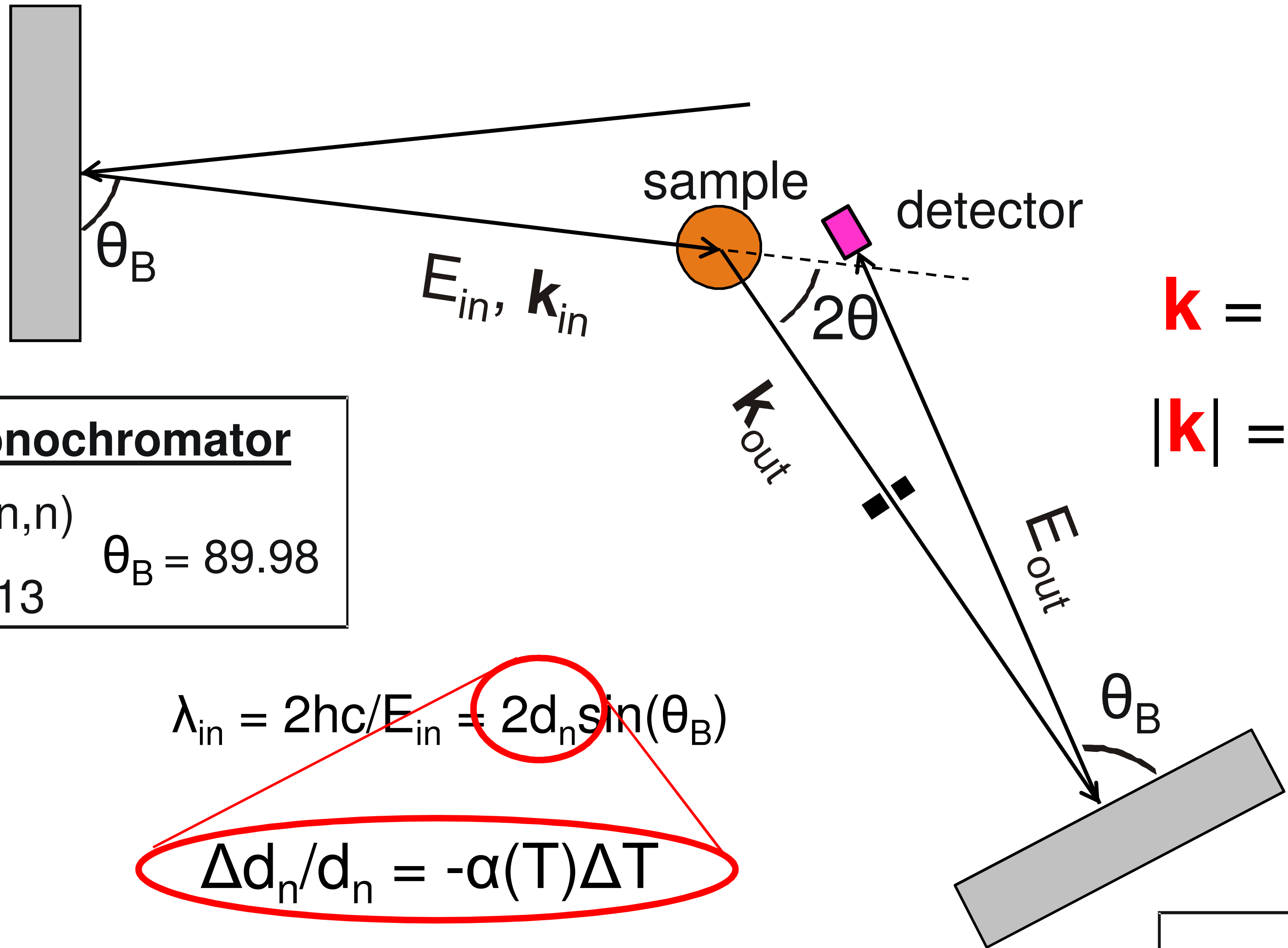
Analyser

Si(n,n,n) $\theta_B = 89.98$

n=7-13

$$\Delta E/E = \Delta\lambda_{in}/\lambda_{in} \sim \cot(\theta_B)$$

Basic IXS instrumentation



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

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

Monochromator

Si(n,n,n) $\theta_B = 89.98$

n=7-13

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

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

Analyser

Si(n,n,n) $\theta_B = 89.98$

n=7-13

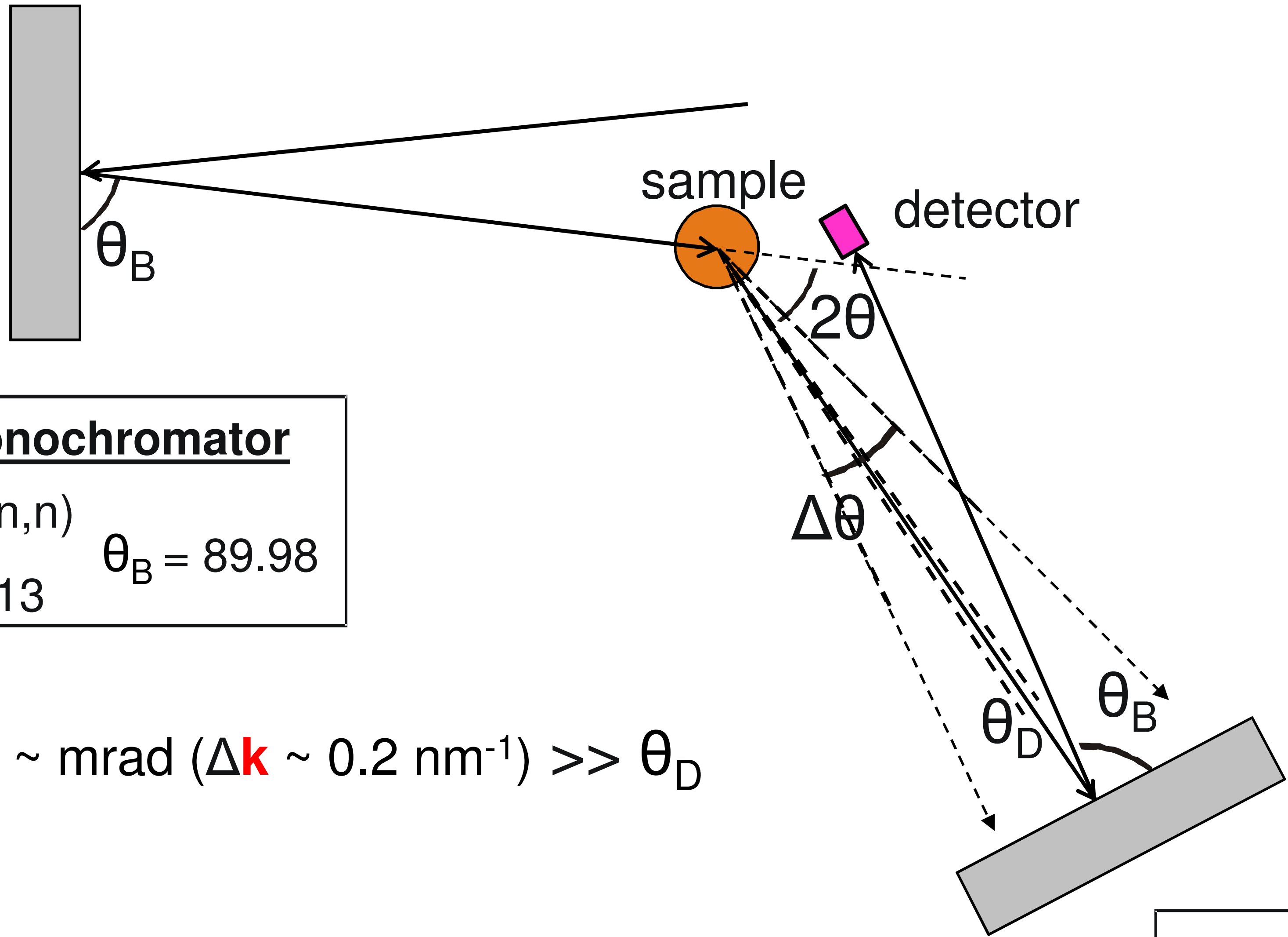
$\alpha \sim 2.58\cdot10^{-6}$

$\Delta T \sim$ mK

$(\Delta E/E)_{MAX} \sim 2\cdot10^{-8}$

→ < 1 meV @ 27 keV

Basic IXS instrumentation



Monochromator

Si(n,n,n) $\theta_B = 89.98$

n=7-13

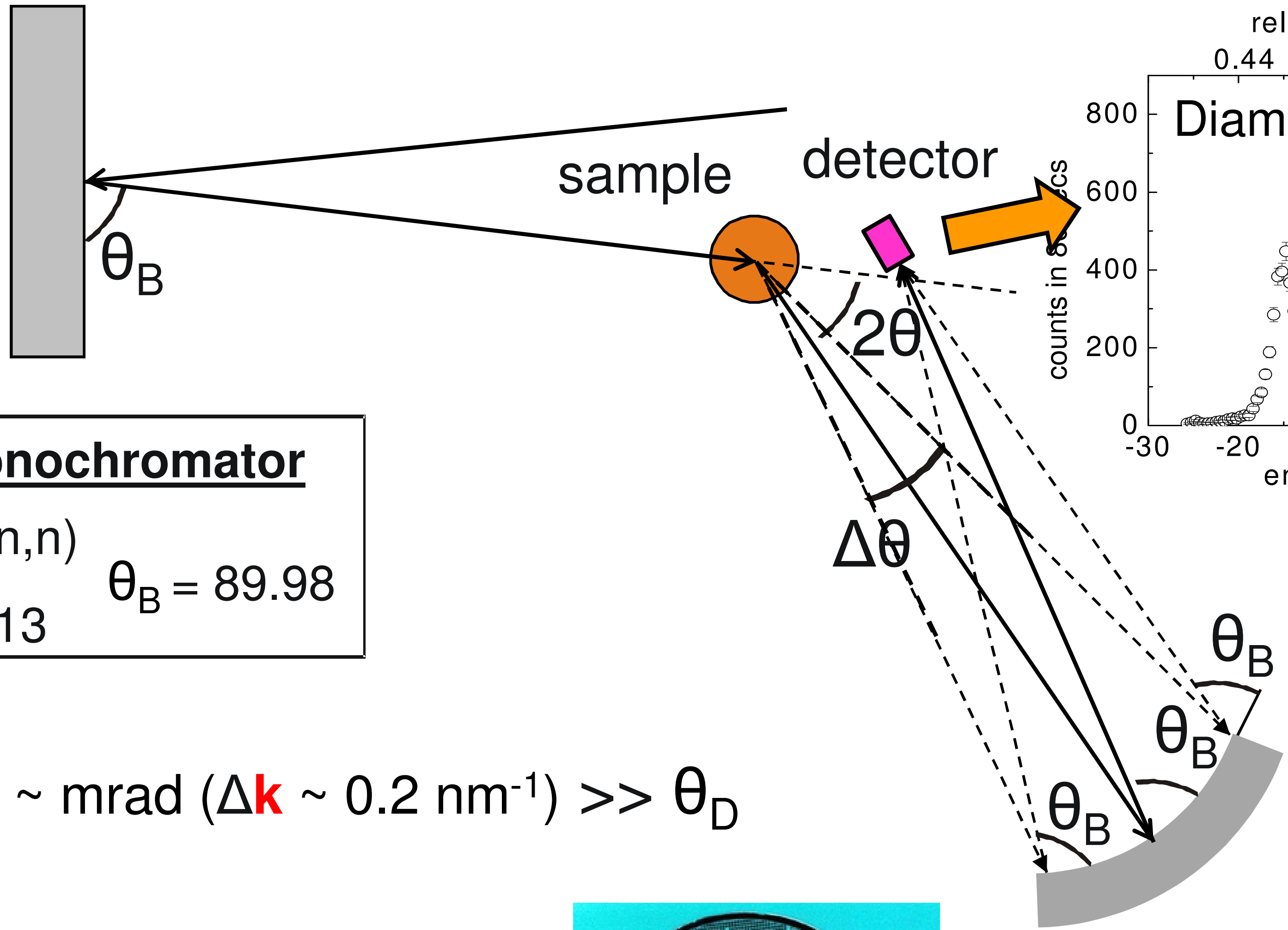
$\Delta\theta$ ~ mrad ($\Delta\mathbf{k}$ ~ 0.2 nm^{-1}) >> θ_D

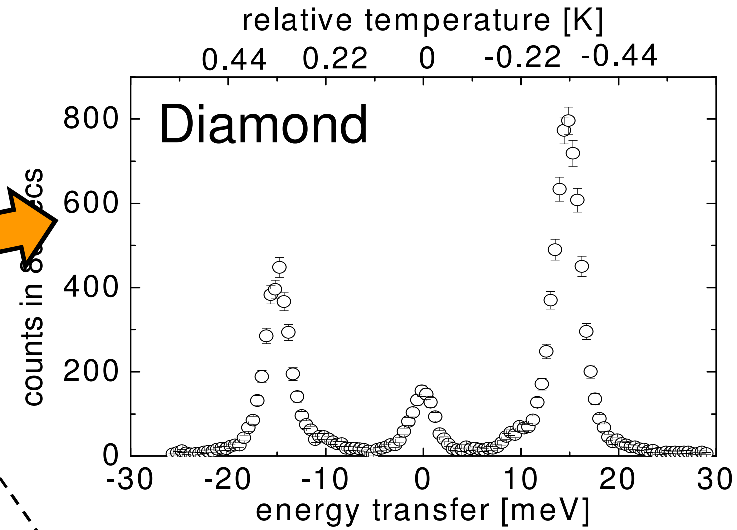
Analyser

Si(n,n,n) $\theta_B = 89.98$

n=7-13

Basic IXS instrumentation





Monochromator

Si(n,n,n)

n=7-13

$\theta_B = 89.98$

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

Analyser

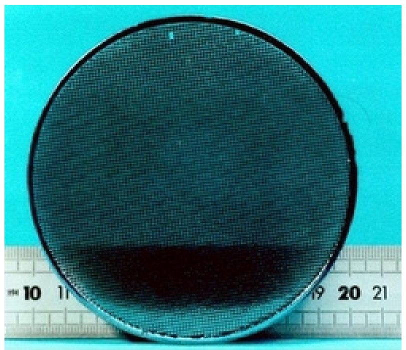
Si(n,n,n)

n=7-13

$\theta_B = 89.98$

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

NIM 111, 181 (1996)

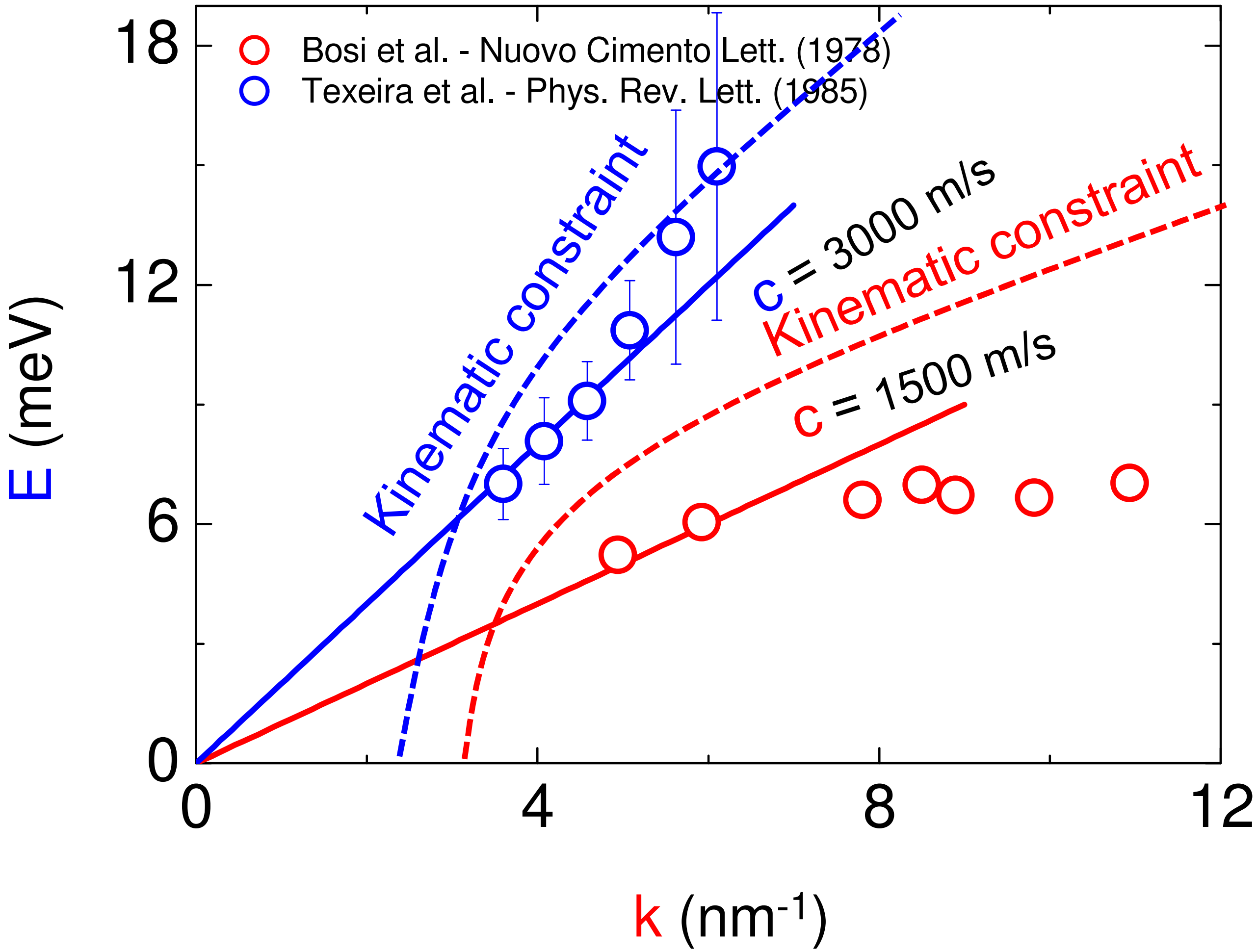


Experimental highlights (1)

Collective dynamics in water

Inelastic Neutron Scattering (D_2O):

2 experiments, 2 results: why?



A possible interpretation:

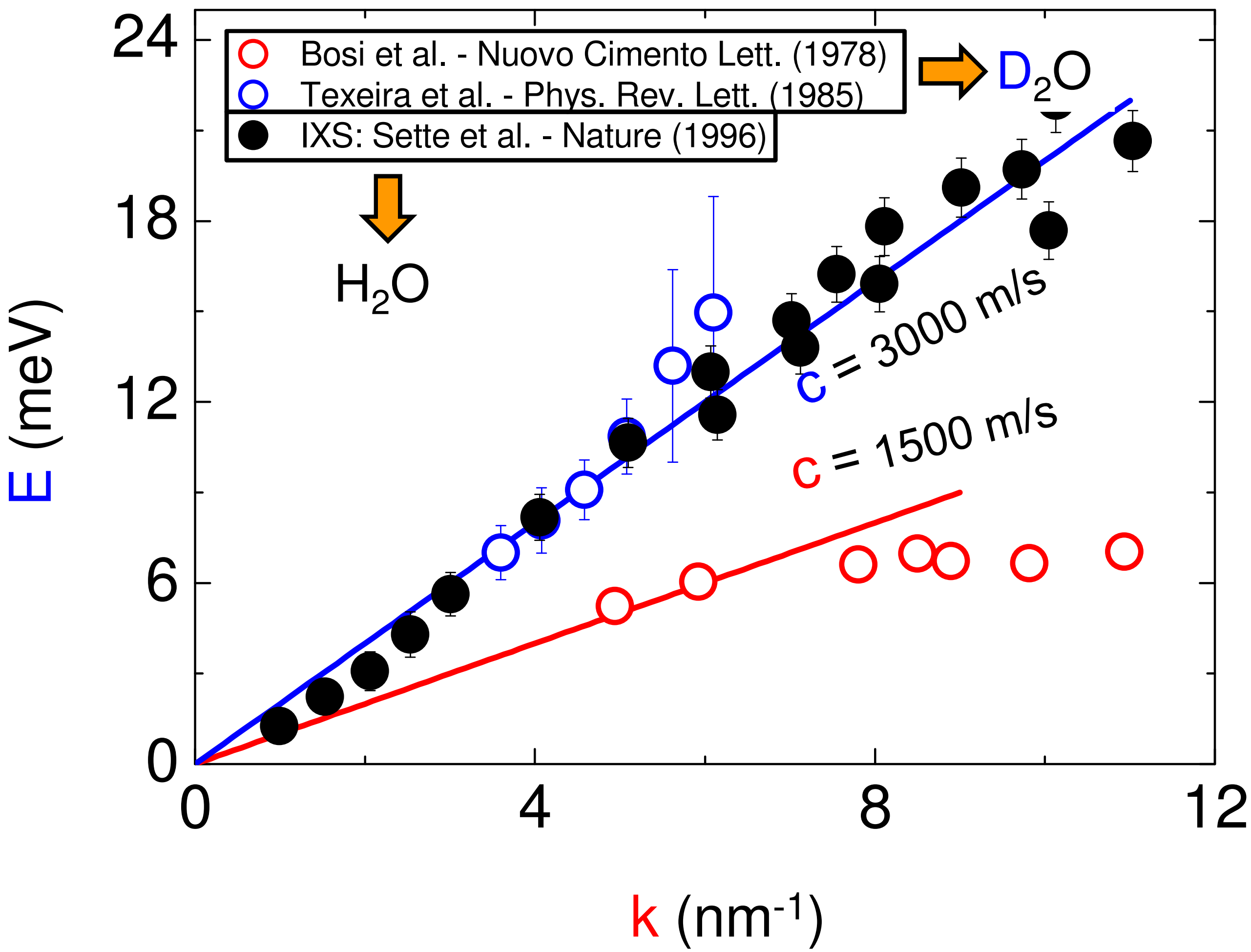
- High frequency mode → **D**
- Low frequency mode → **O**

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

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:

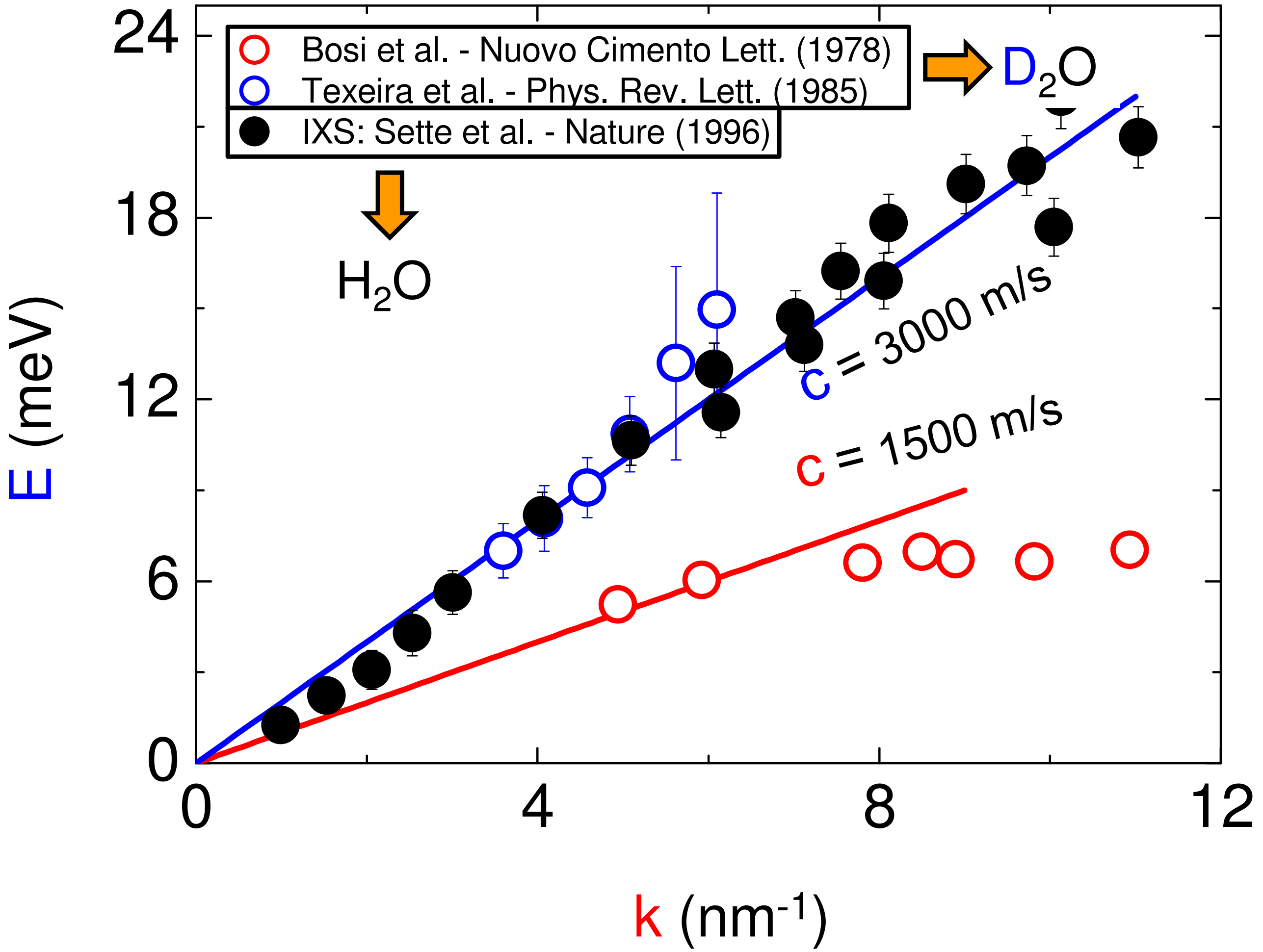
Expected for H_2O…
$\Omega_{IXS}/\Omega_{INS} \sim (m_H/m_D)^{1/2} \sim 1.4$

Experimental highlights (1)

Collective dynamics in water

Inelastic Neutron Scattering vs.

Inelastic X-ray Scattering (H_2O vs. D_2O)



A possible interpretation:

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

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

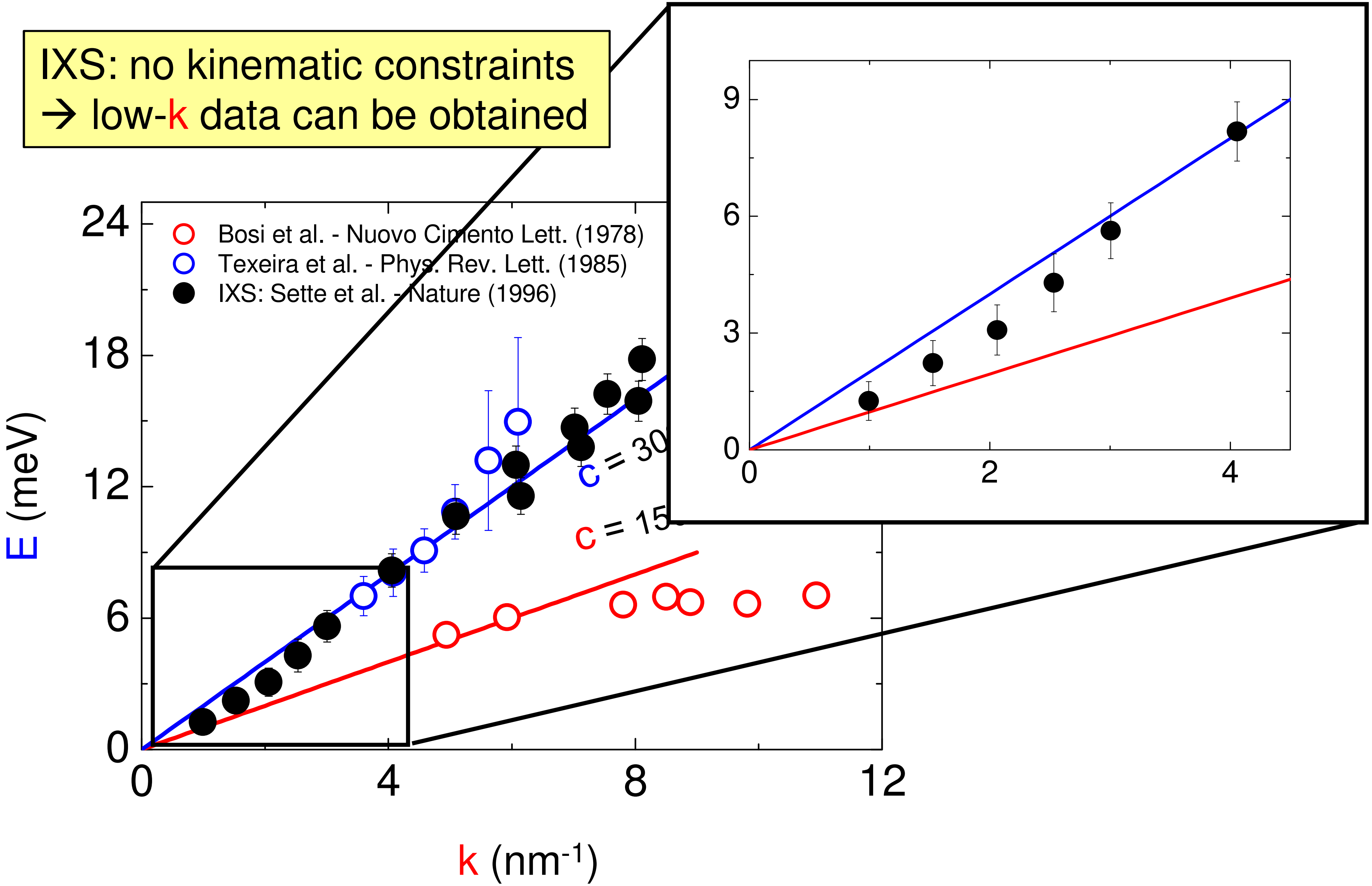
High frequency mode:

but… $\Omega_{IXS}=\Omega_{INS}$

Experimental highlights (1)

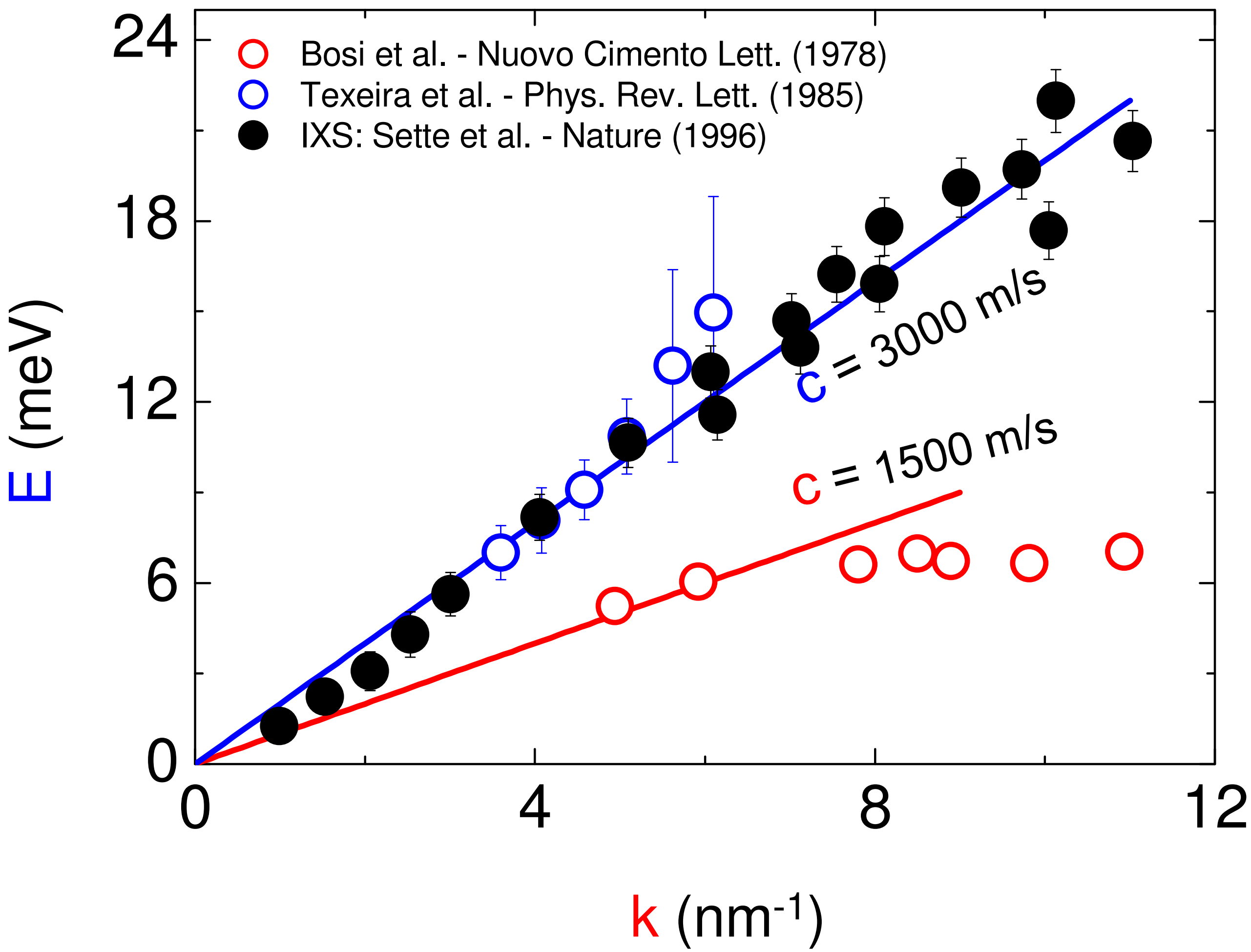
Collective dynamics in water

IXS: no kinematic constraints
→ low-k data can be obtained



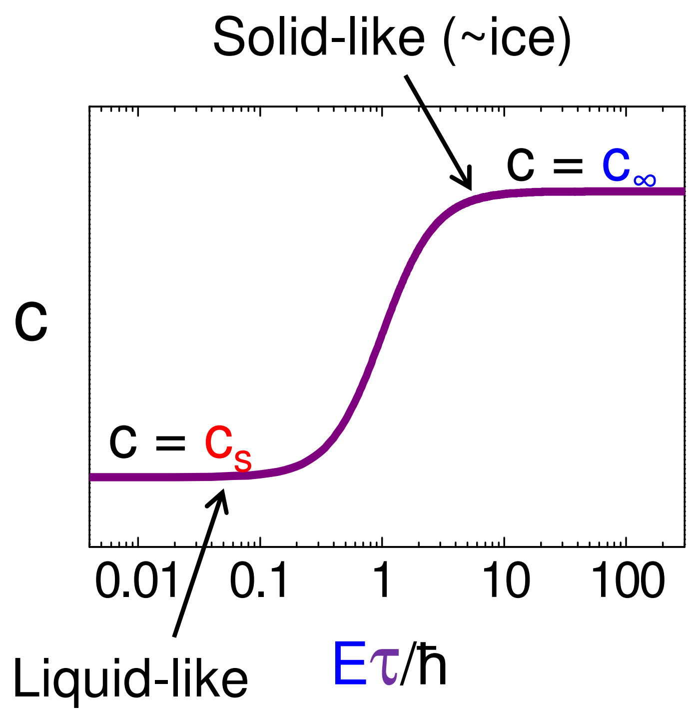
Experimental highlights (1)

Collective dynamics in water



Viscoelasticity:

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

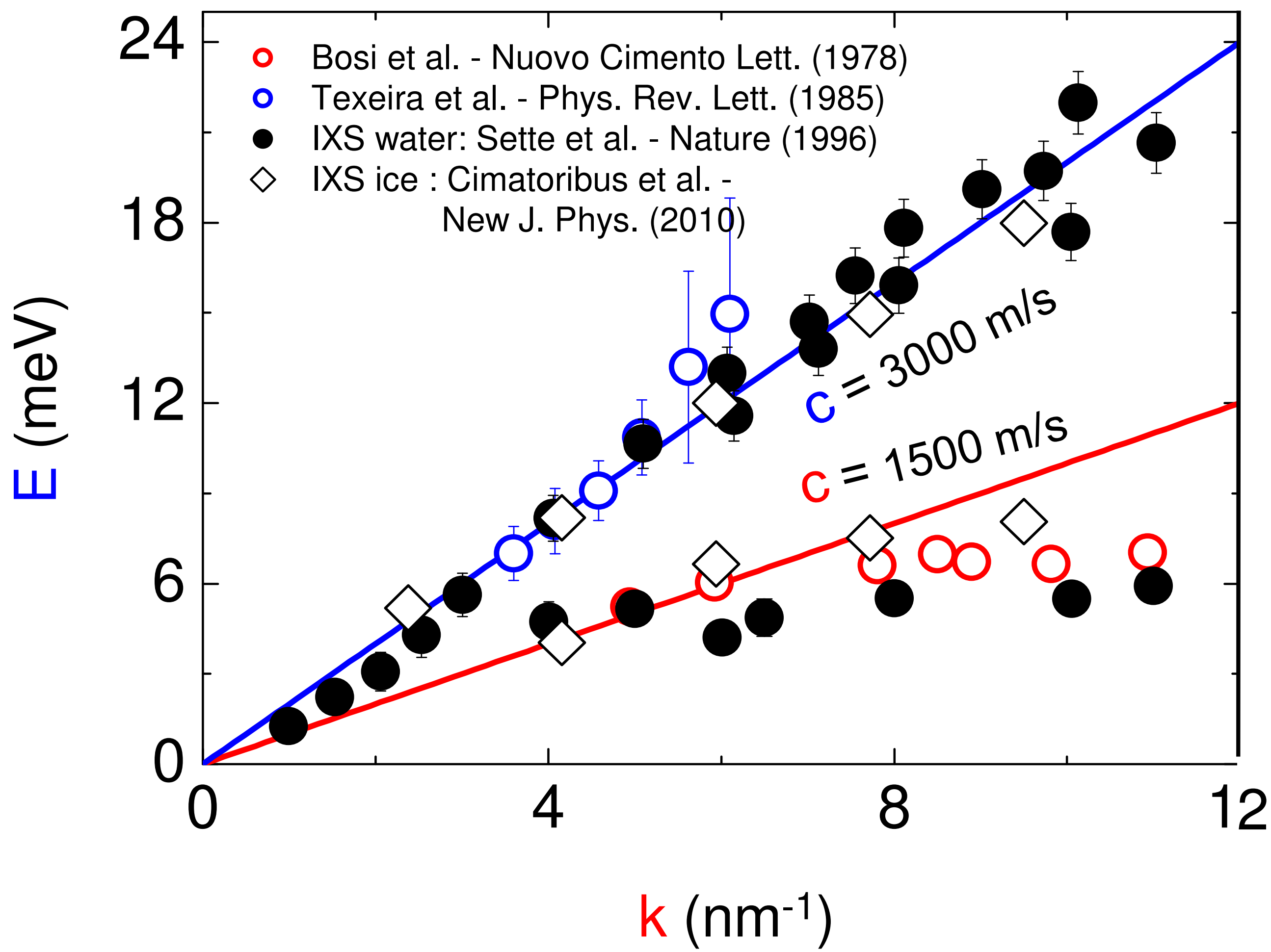


Experimental highlights (1)

Collective dynamics in water

Low frequency mode:

Transverse-like sound propagation in the elastic (solid-like) limit: $E\tau/\hbar >> 1$



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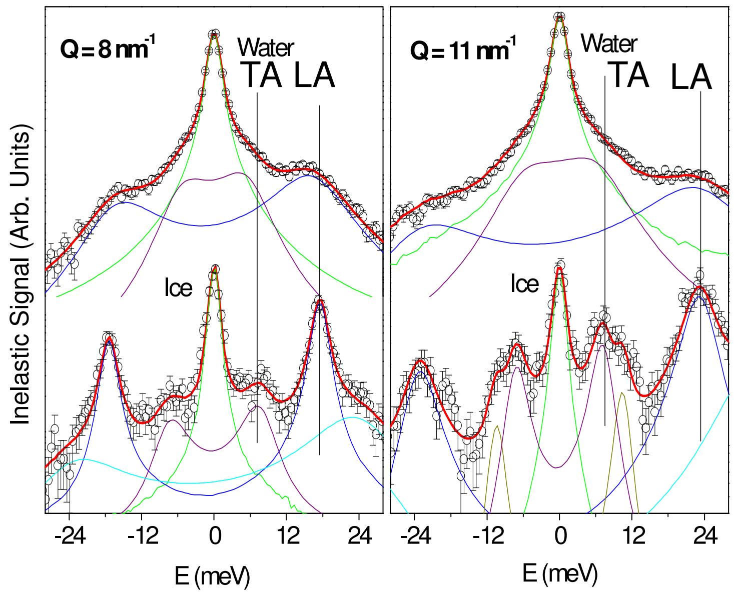


PRL 79, 1678 (1997)

PRE 71, 011501 (2005)

Experimental highlights (2)

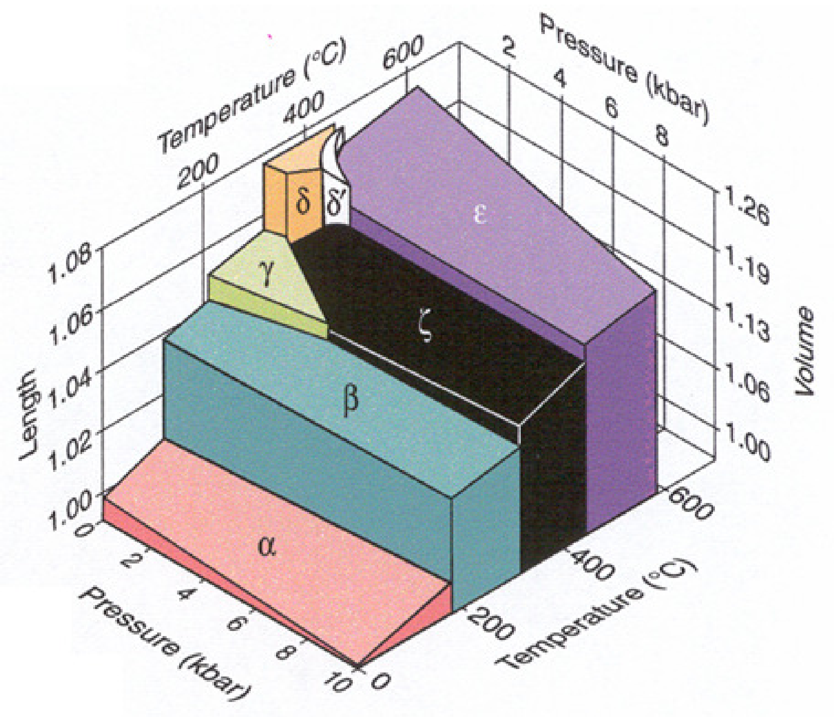
Phonon dispersions in plutonium

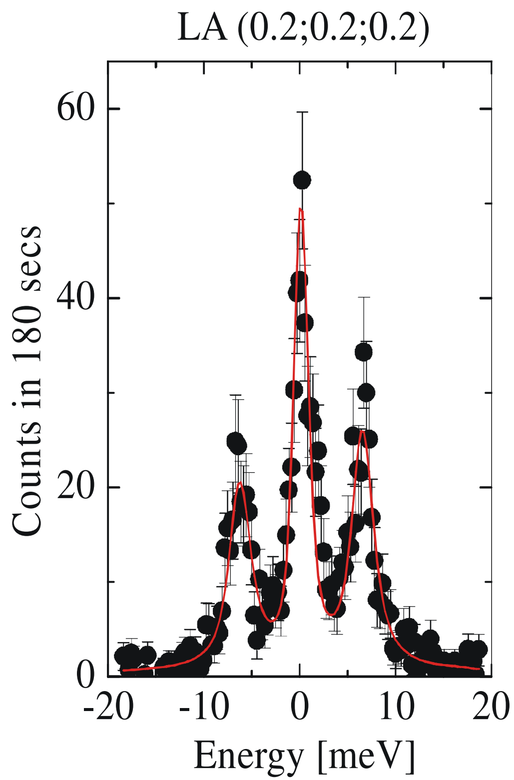
Putonium is one of the most fascinating and exotic element:

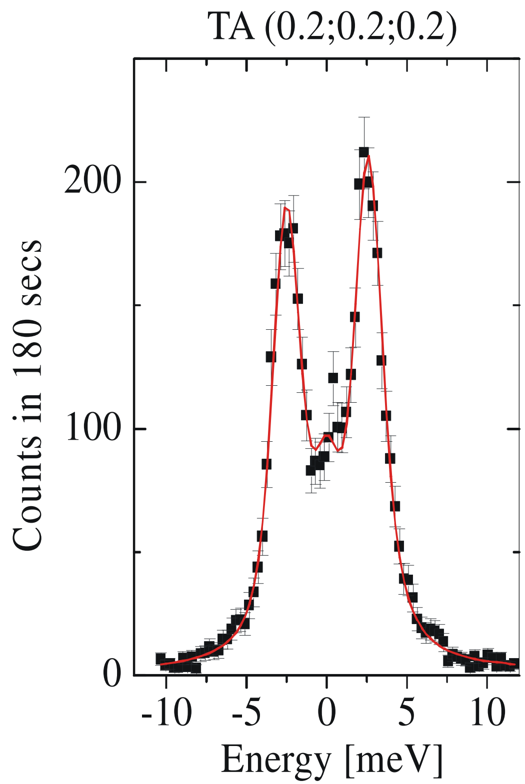
- Multitude of unusual properties
- Central role of 5f electrons

ID28 at ESRF

- Energy resolution: 1.8 meV
- Beam size: 20 x 60 μm² (HxV)
- Grain size: ~ 80 μm²
- On-line diffraction analysis



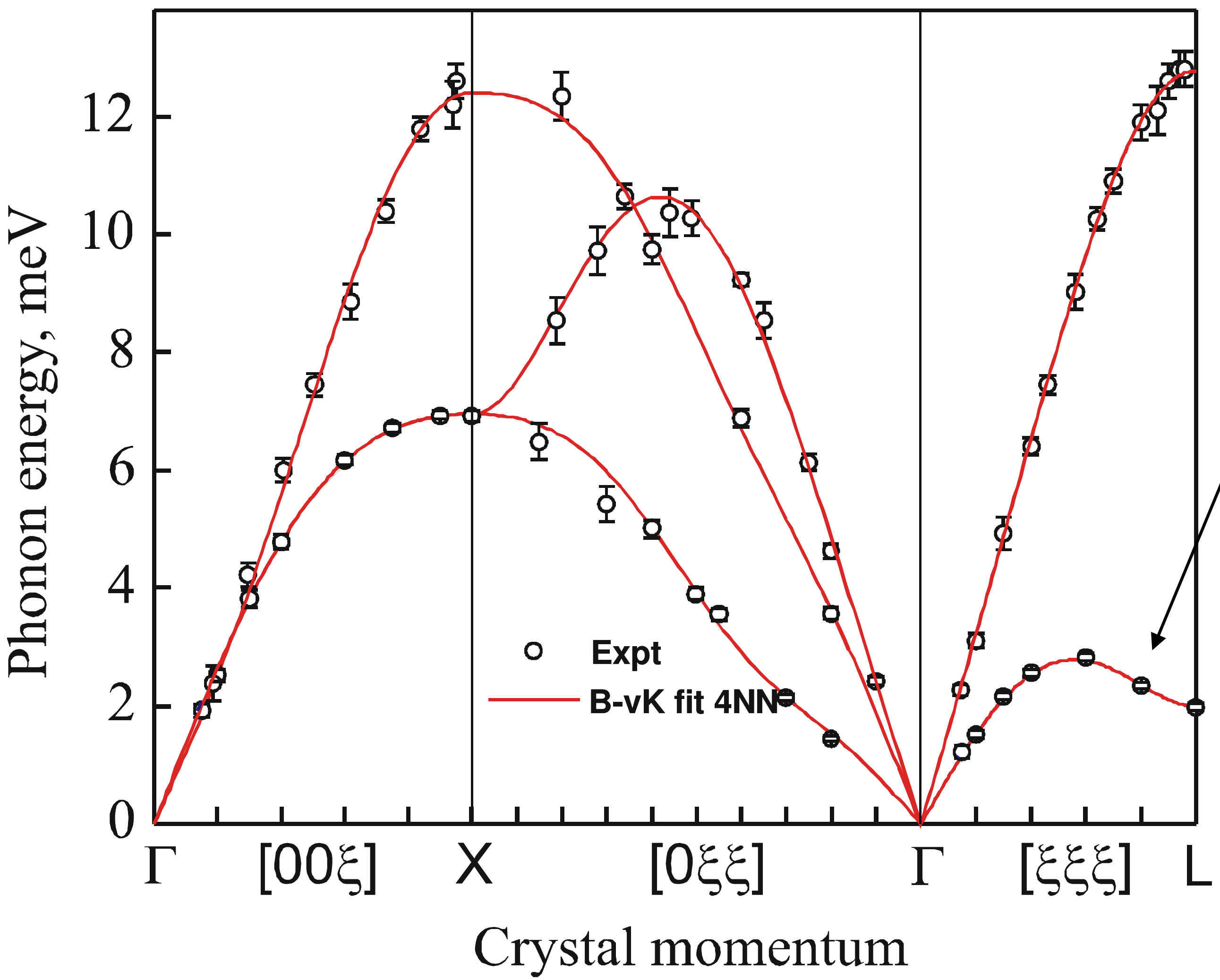




Science 301, 1078 (2003)

Experimental highlights (2)

Phonon dispersions in plutonium



soft-mode behavior 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: $E = Vq/\hbar$

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

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

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

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

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

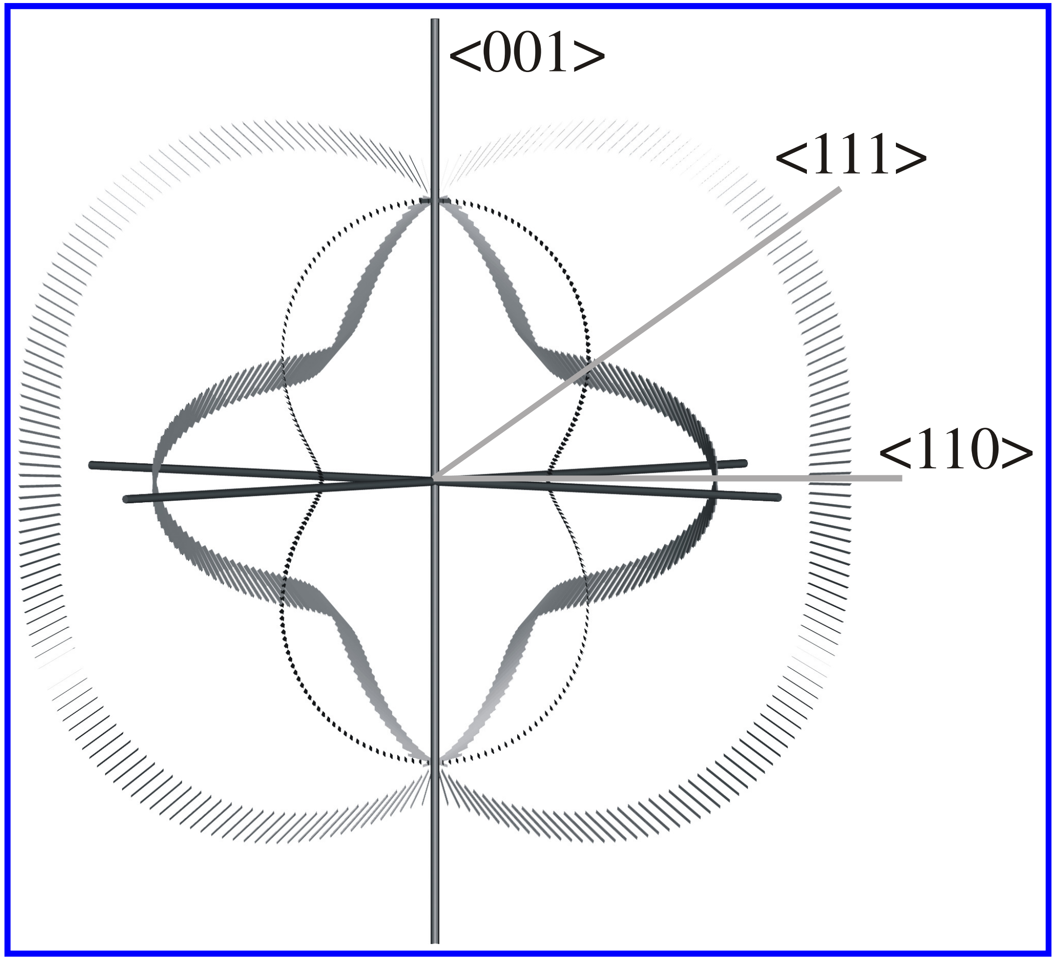
$V_L[111] = [C_{11}+2C_{12}+4C_{44}]/3\rho)^{1/2}$

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

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

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

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

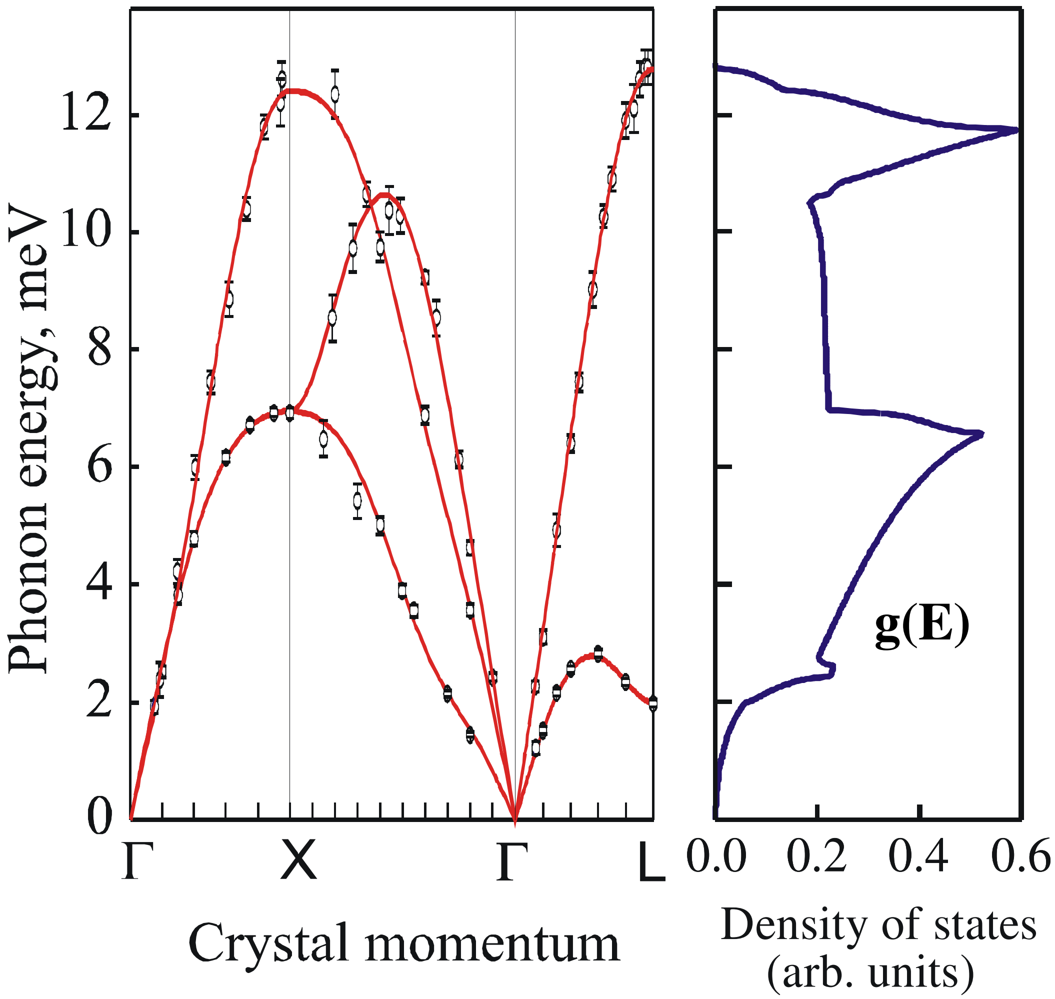


highest elastic anisotropy of all known fcc metals

Science 301, 1078 (2003)

Experimental highlights (2)

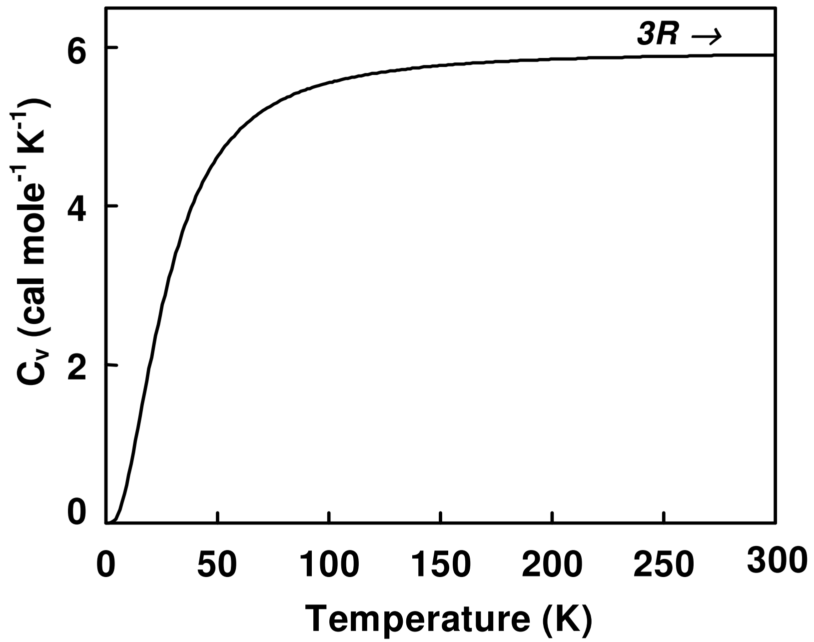
Phonon dispersions in plutonium



- **Born-von Karman fit**

Specific heat:

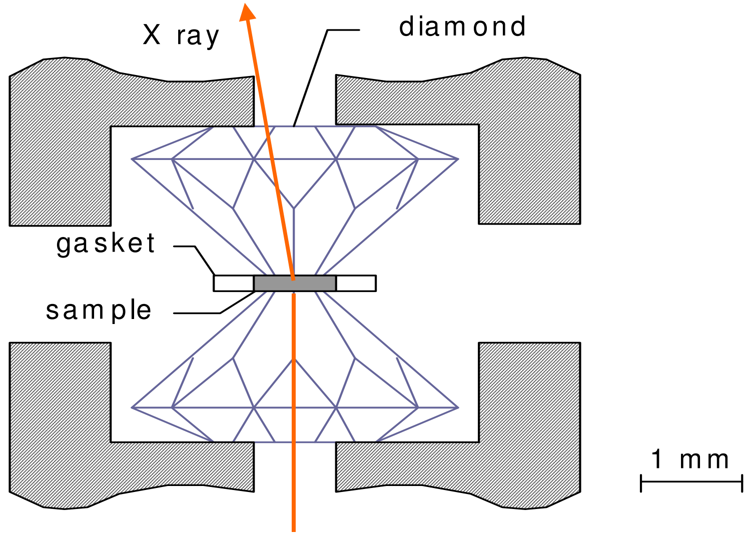
$$C_v = 3Nk_B \int_0^{E_{max}} \left(\frac{E}{k_B T}\right)^2 \frac{\exp(E/k_B T)\, g(E)\, dE}{(\exp(E/k_B T)-1)^2}$$



Science 301, 1078 (2003)

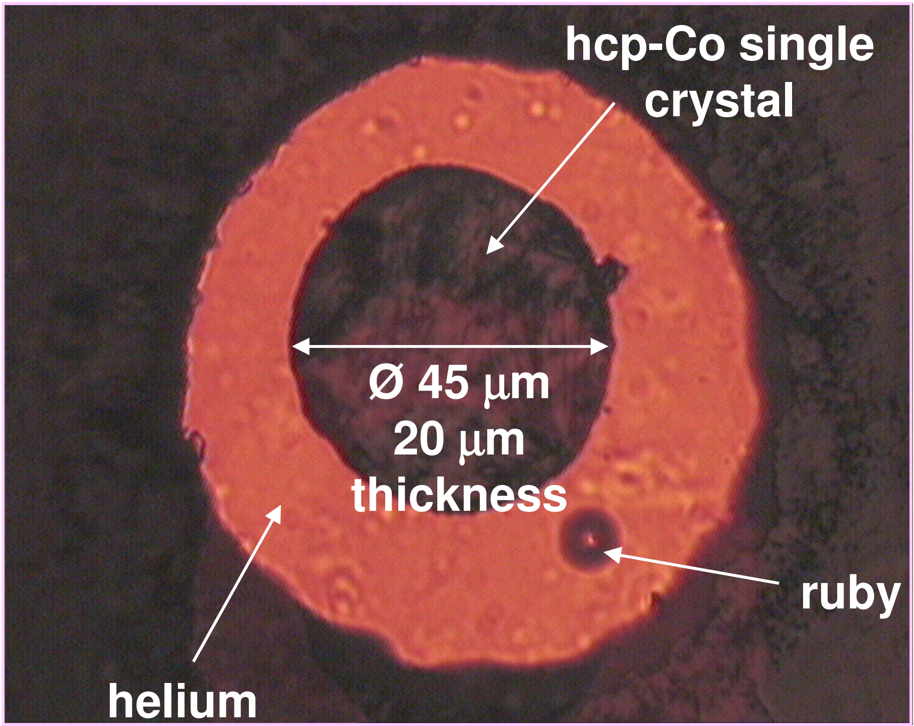
Experimental highlights (3)

Elasticity at high pressure



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

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



<u>hcp-structure:</u>

5 independent elastic moduli

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

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

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

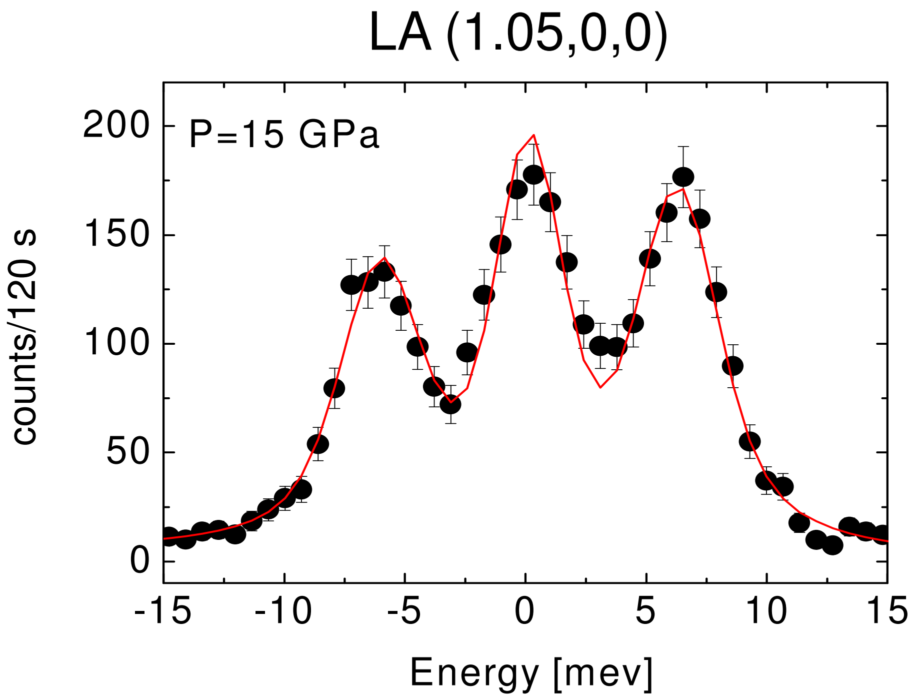
$V_{T2}[110] = (C_{44}/\rho)^{1/2}$

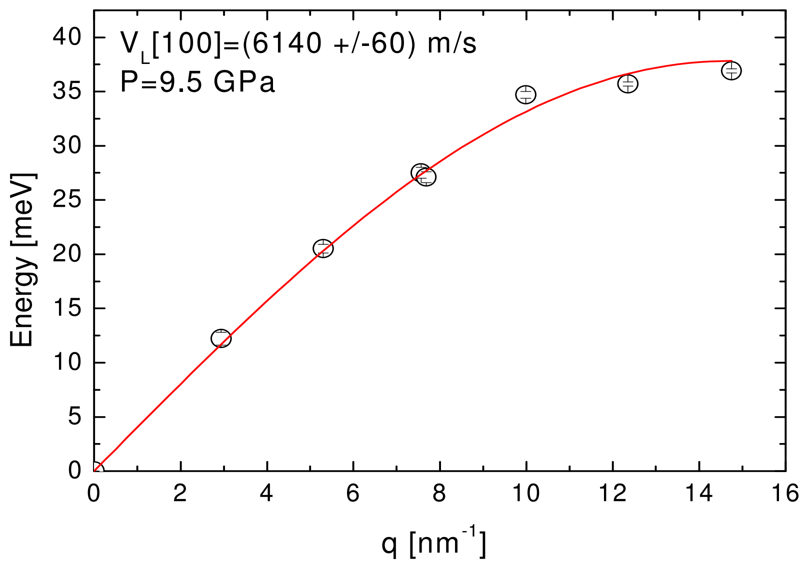
$V_{QL}[101] = f(C_{ij},\rho) \rightarrow C_{13}$

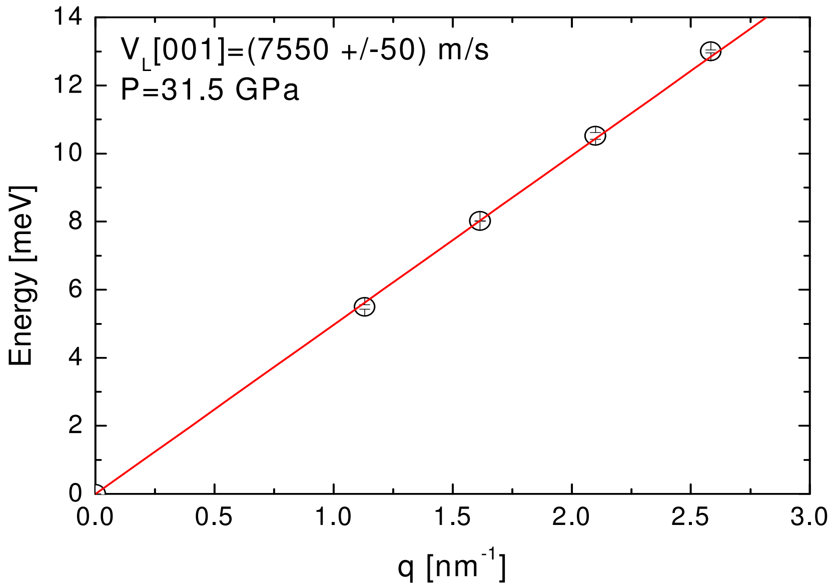
PRL 93, 215505 (2004)

Experimental highlights (3)

Elasticity at high pressure



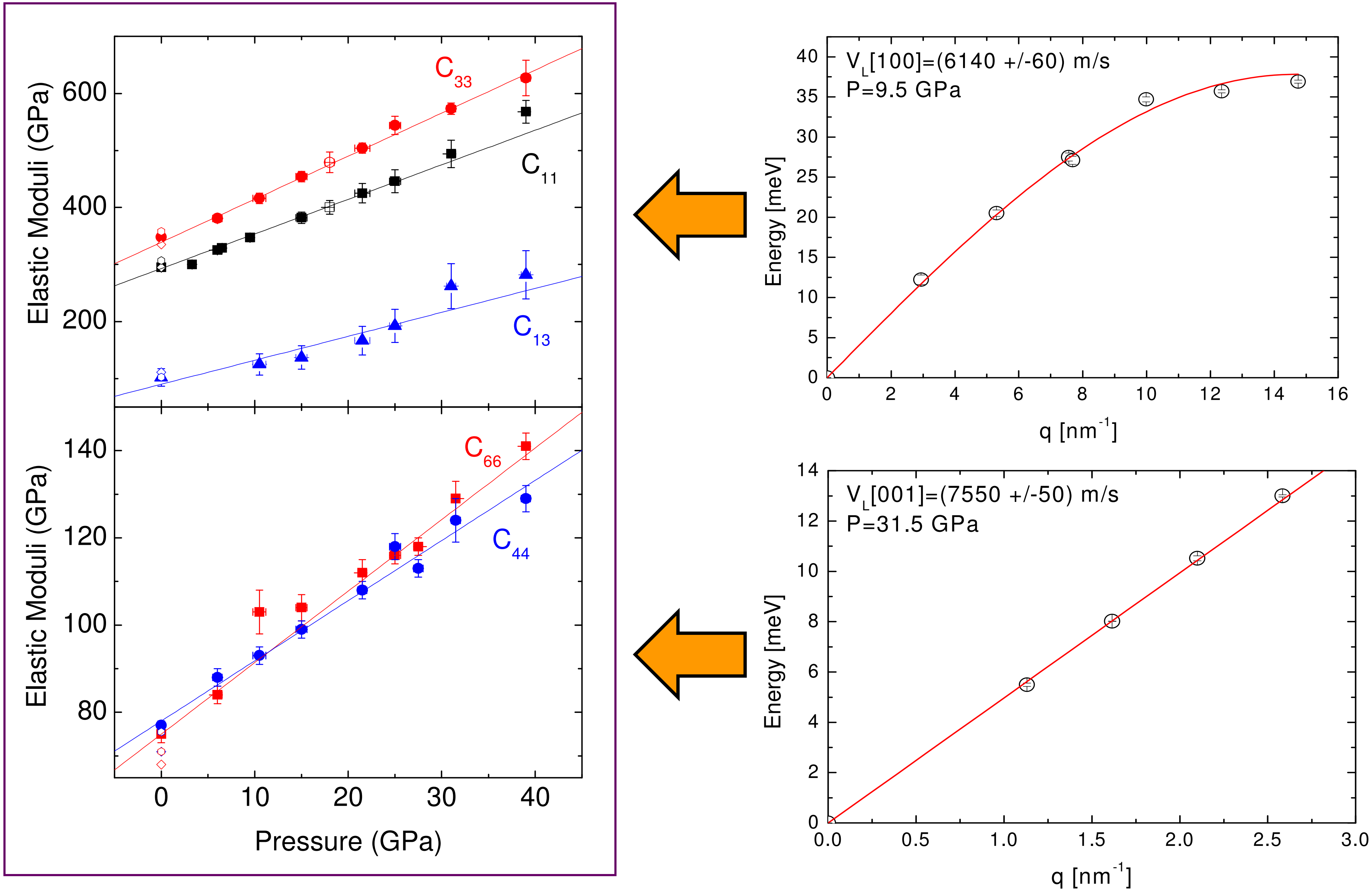




PRL 93, 215505 (2004)

Experimental highlights (3)

Elasticity at high pressure



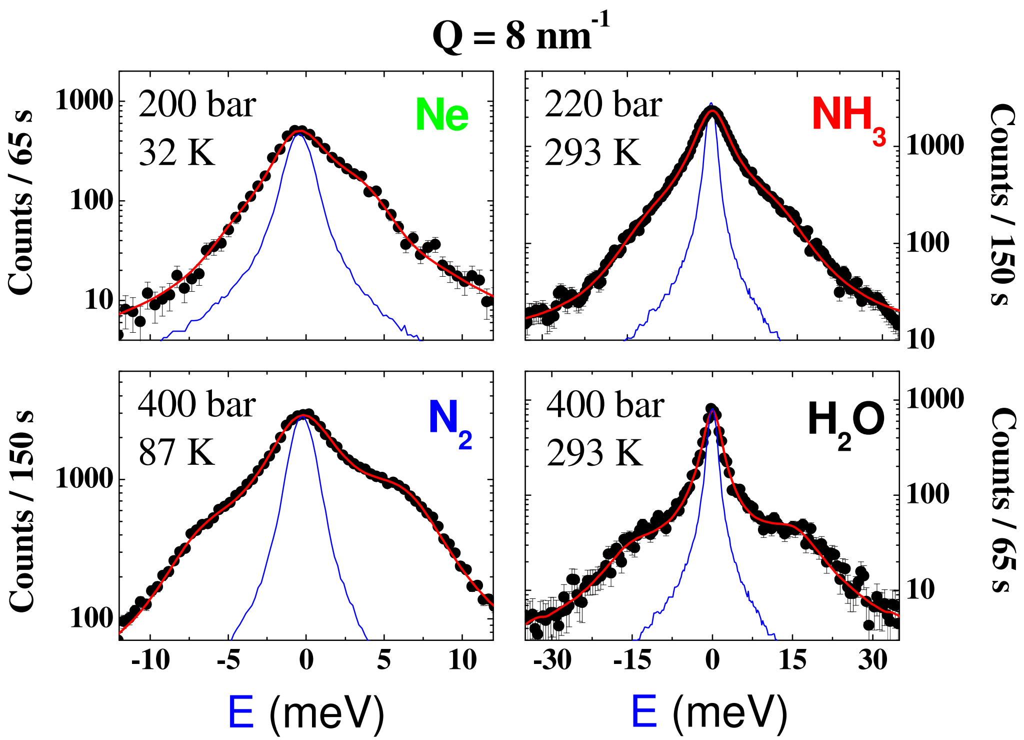
PRL 93, 215505 (2004)

Experimental highlights (4)

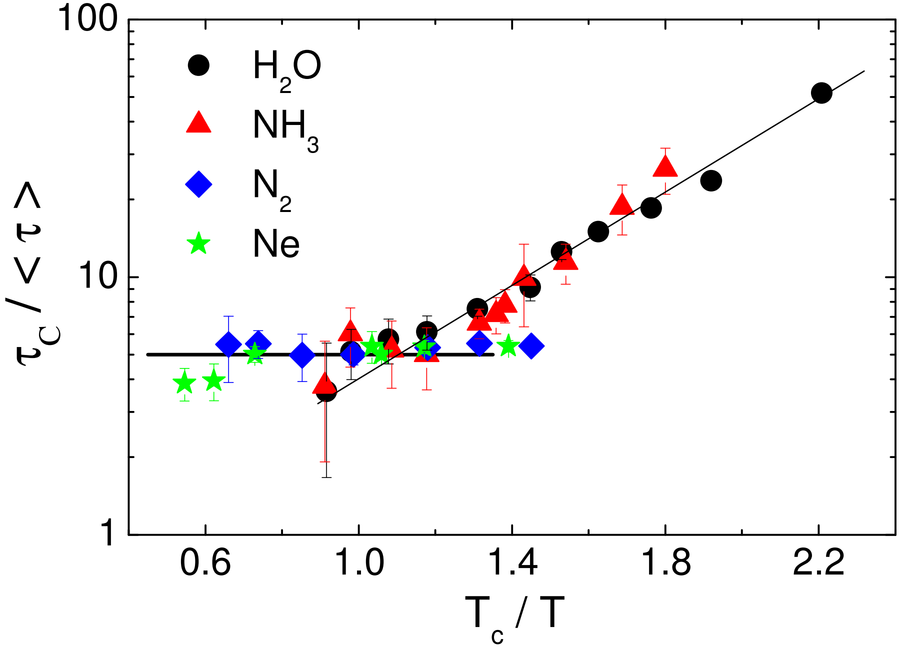
Liquids and supercritical fluids

<u>ID28 and ID16 at ESRF</u>

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



<u>Viscoelasic data analysis:</u>

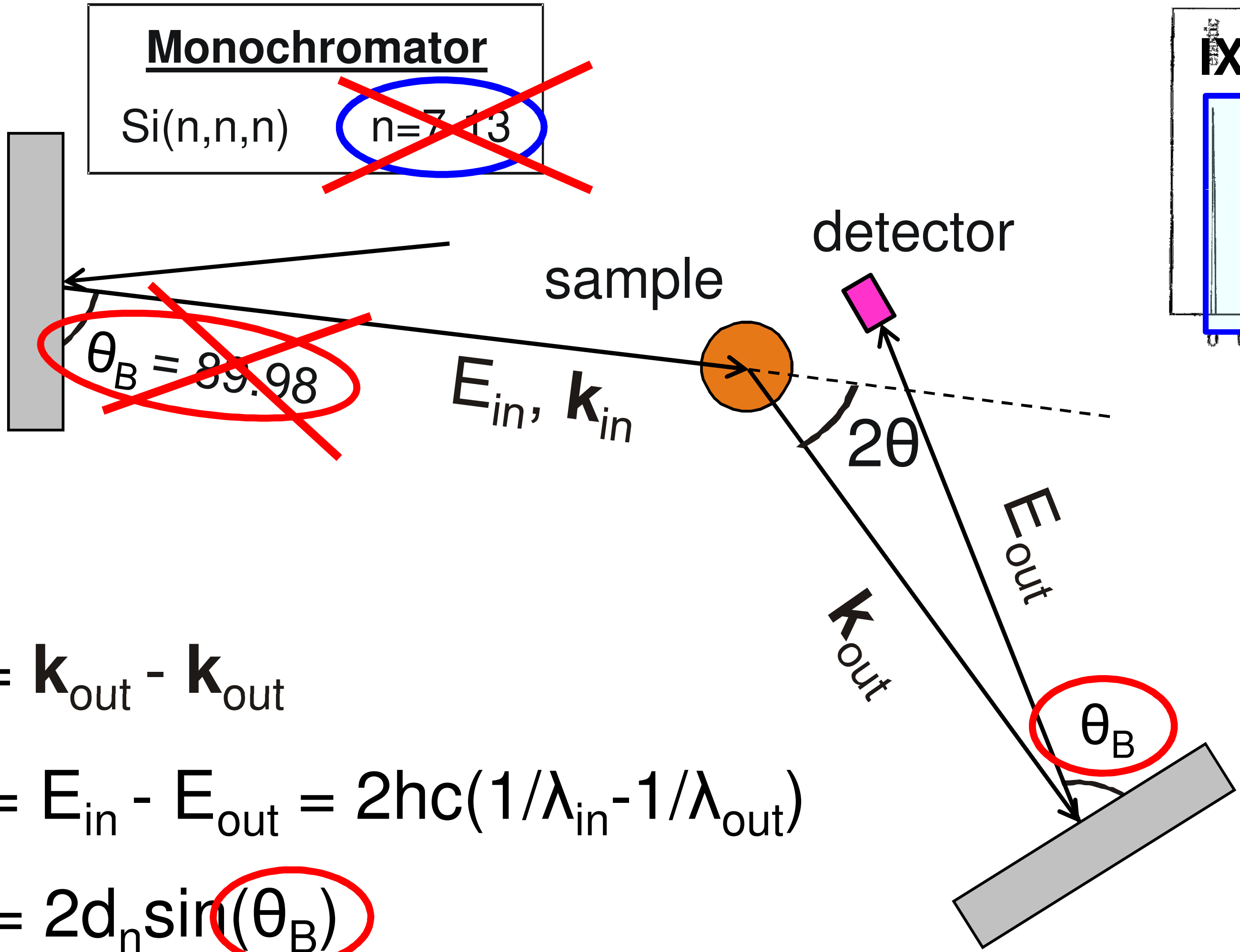


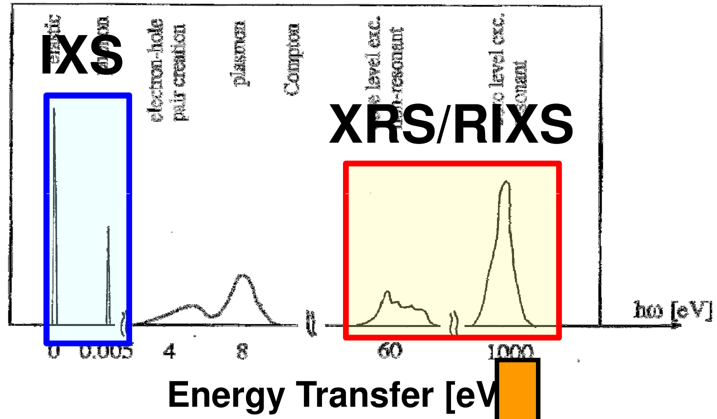
<u>Leading dynamics in fluids</u>:

- $T>T_c$ → collisions
- $T<T_c$ → bond's lifetime

PRL 98, 085501 (2007)

Basic instrumentation





ΔE ~ eV

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

$E = E_{in} - E_{out} = 2hc(1/\lambda_{in} - 1/\lambda_{out})$

$\lambda = 2d_n \sin(\theta_B)$

~~backscattering~~ + ~~high order reflections~~ = ~~ΔE ~ meV~~

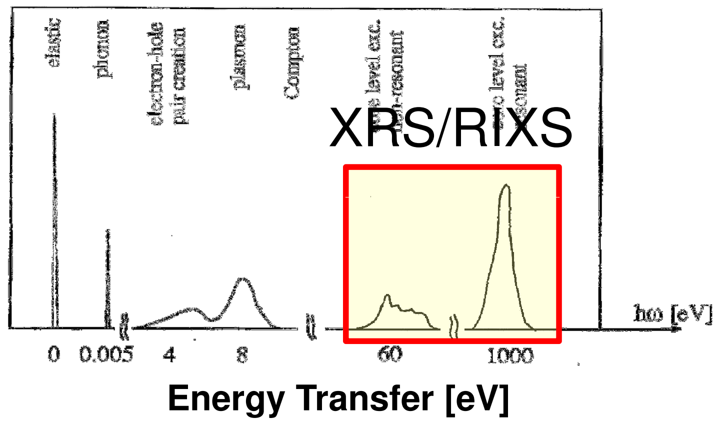
Basic instrumentation

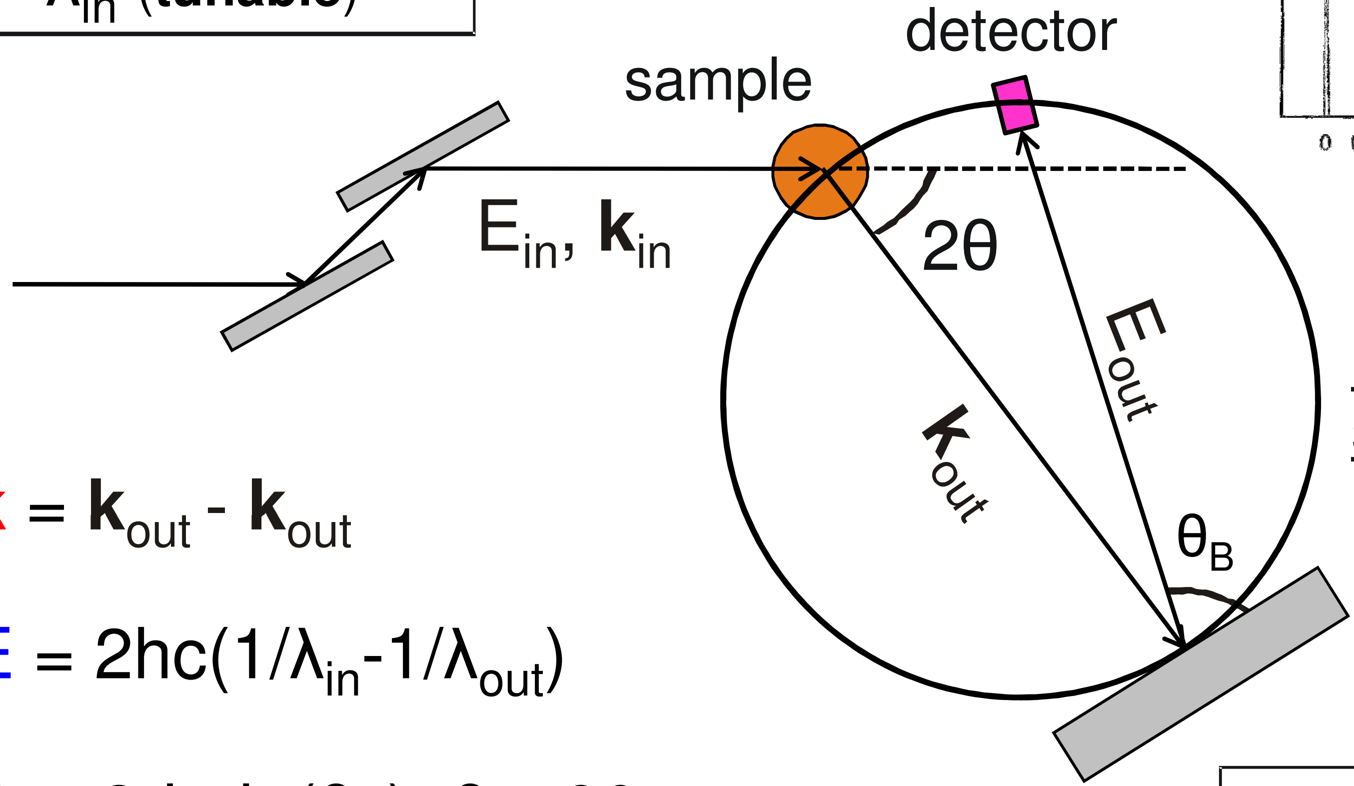
XRS / RIXS

Monochromator

Si(1,1,1); (2,2,0); …

λ_{in} (**tunable**)





Rowland circle spectrometer (1 m)

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

$E = 2hc(1/\lambda_{in} - 1/\lambda_{out})$

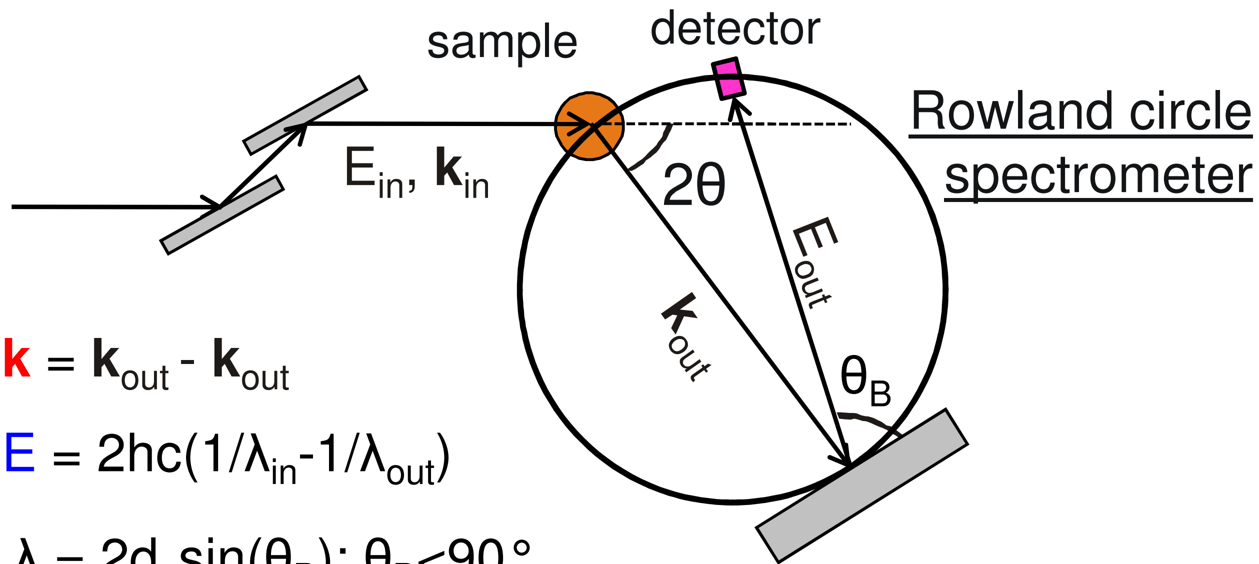
$\lambda = 2d_n \sin(\theta_B);\ \theta_B < 90°$

Analyser

Si(h,k,l) λ_{out} (**tunable**)

Basic instrumentation

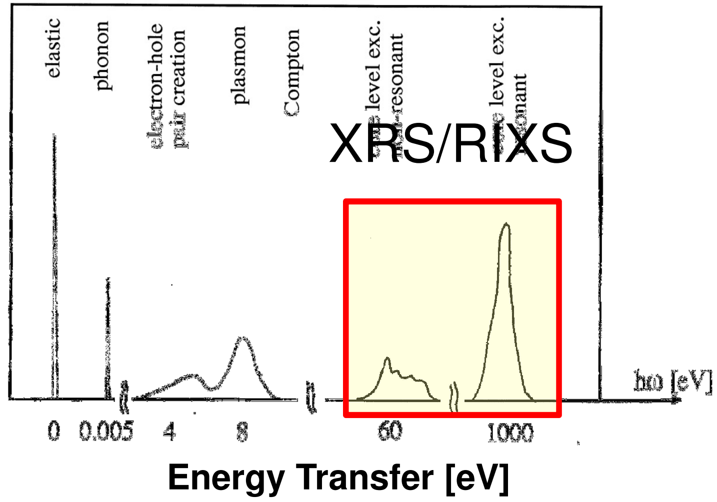
XRS / RIXS



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

$E = 2hc(1/\lambda_{in} - 1/\lambda_{out})$

$\lambda = 2d_n \sin(\theta_B);\ \theta_B < 90°$



Scanning strategy

1. E_{out} fixed, scanning E_{in}	IXS, XRS, RIXS
2. E_{in} fixed, scanning E_{out} (rotating crystal and follow with the detector)	RIXS
3. Scanning E_{in} and E_{out} keeping E constant	RIXS

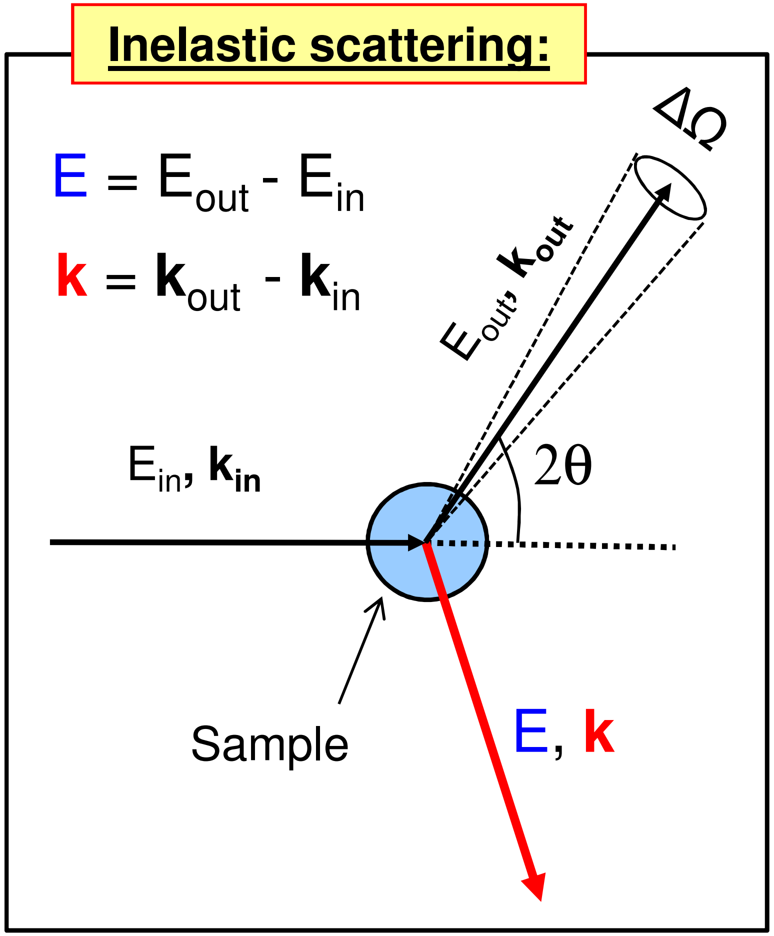
Basic theoretical aspects

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

A: vector potential of electromagnetic field

P: momentum operator of the electrons

j: summation over all electrons of the system



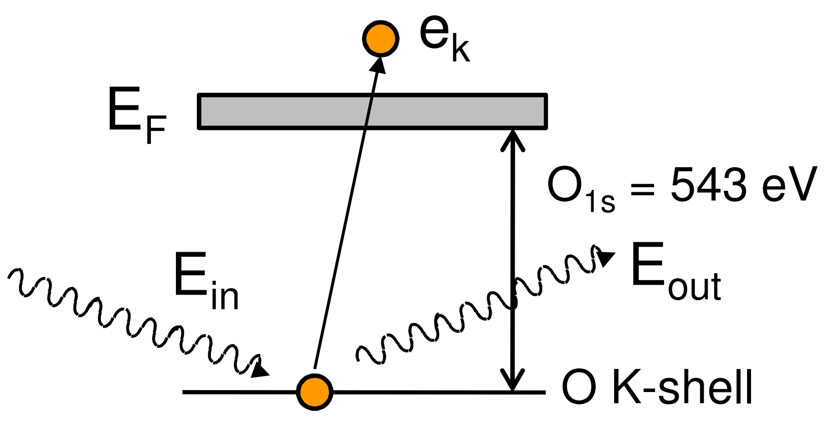
A·A → non-resonant scattering (example: IXS)

A·p → resonant scattering, absorption followed by emission

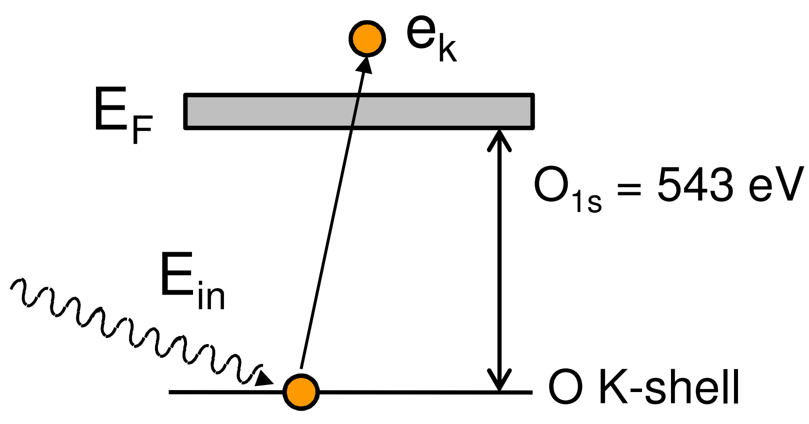
Basic theoretical aspects

Non resonant IXS cross section:

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



$$E_{1s}+e_k=E_{in}-E_{out}=E$$



$$E_{1s}+e_k=E_{in}$$

X-ray absorption cross section (dipolar approximation):

$$\frac{\partial\sigma}{\partial E_{in}} = 4\pi^2\alpha E_{in}\sum_I P_I|\langle I|\boldsymbol{\varepsilon}_{in}\cdot\mathbf{r}_j|F\rangle|^2\delta(E_{in}-E_F+E_I)$$

Basic theoretical aspects

Non resonant IXS cross section:

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

$$\mathbf{k}\cdot\mathbf{r}_j << 1 \rightarrow e^{i\mathbf{k}\cdot\mathbf{r}} \sim 1 + i\mathbf{k}\cdot\mathbf{r}_j$$

$\mathbf{k}\cdot\mathbf{r}_j <<1 \rightarrow$ Dipolar regime: identical to photon absorption, where:

i) The momentum transfer ($\mathbf{k}$) plays the role of the photon polarization vector ($\boldsymbol{\varepsilon}_{in}$)

ii) The energy transfer (E) plays the role of the incident energy (E_{in})

X-ray absorption cross section (dipolar approximation):

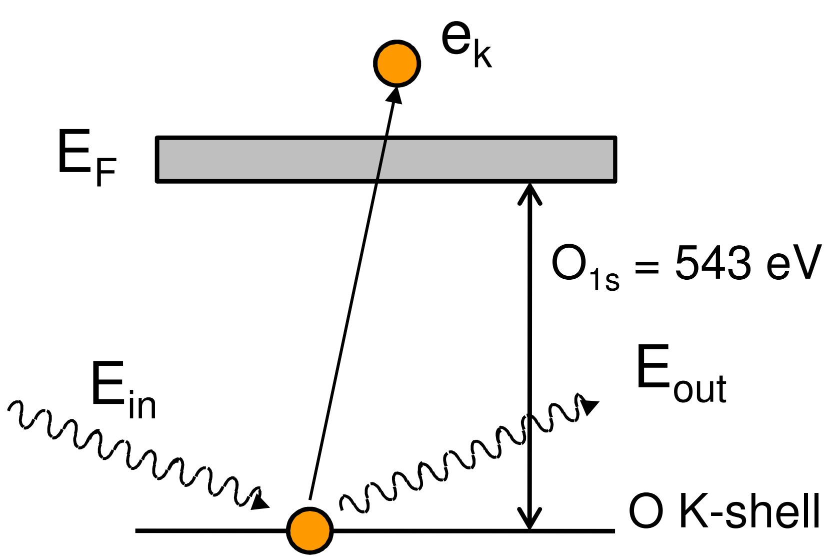
$$\frac{\partial\sigma}{\partial E_{in}} = 4\pi^2\alpha E_{in}\sum_I P_I|<I|\boldsymbol{\varepsilon}_{in}\cdot\mathbf{r}_j|F>|^2\delta(E_{in}-E_F+E_I)$$

Basic theoretical aspects

Non resonant IXS cross section:

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

X-ray Raman Scattering (XRS)



$E_{1s}+e_k=E_{in}-E_{out}=E$

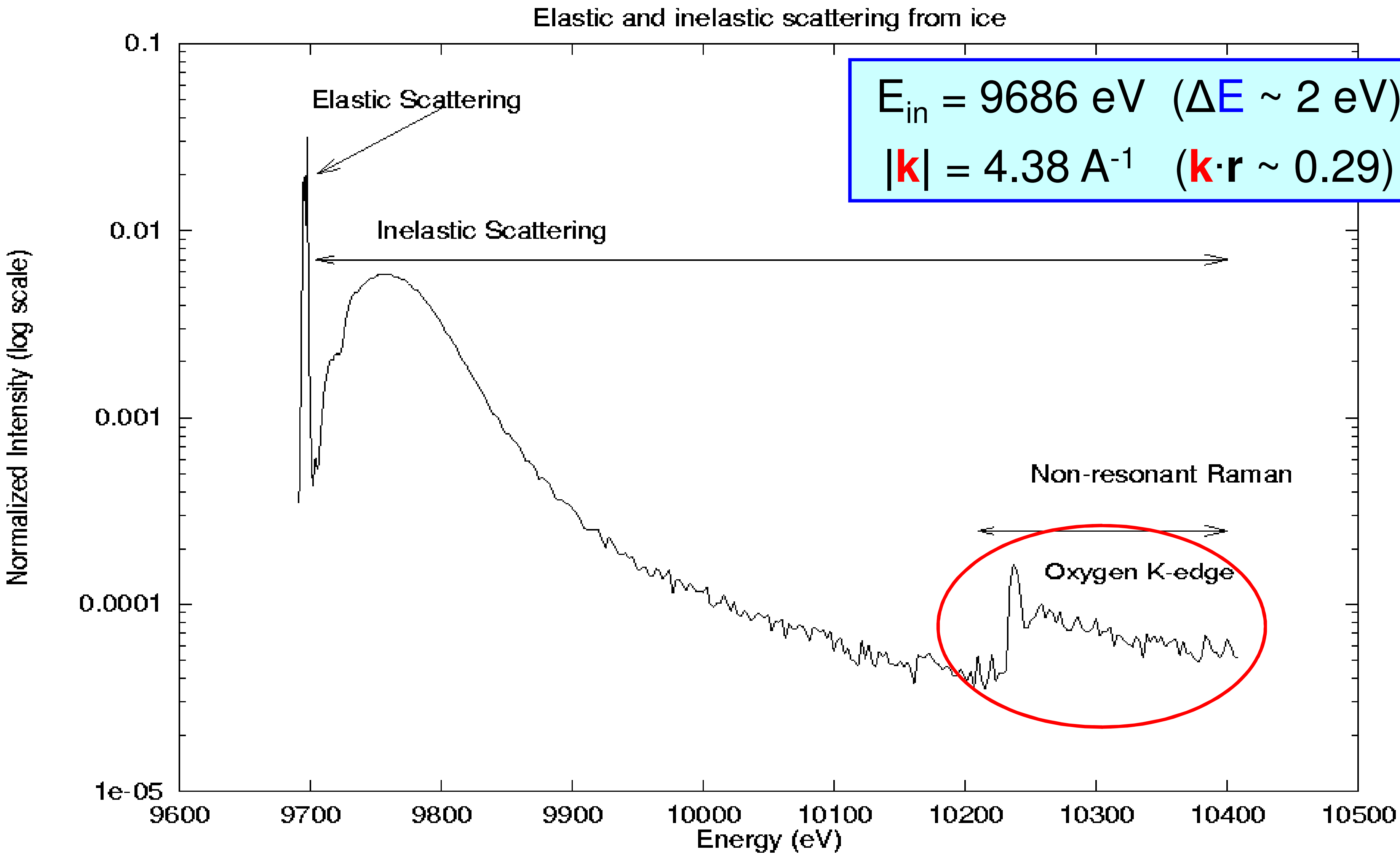
Motivation: element-selective probe for local atomic structure

XRS is alternative to:

- Neutron scattering (with isotopic substitution)
- X-ray (anomalous) scattering
- XANES and EXAFS

Experimental highlights (XRS)

XRS from O K-edge in water and ice

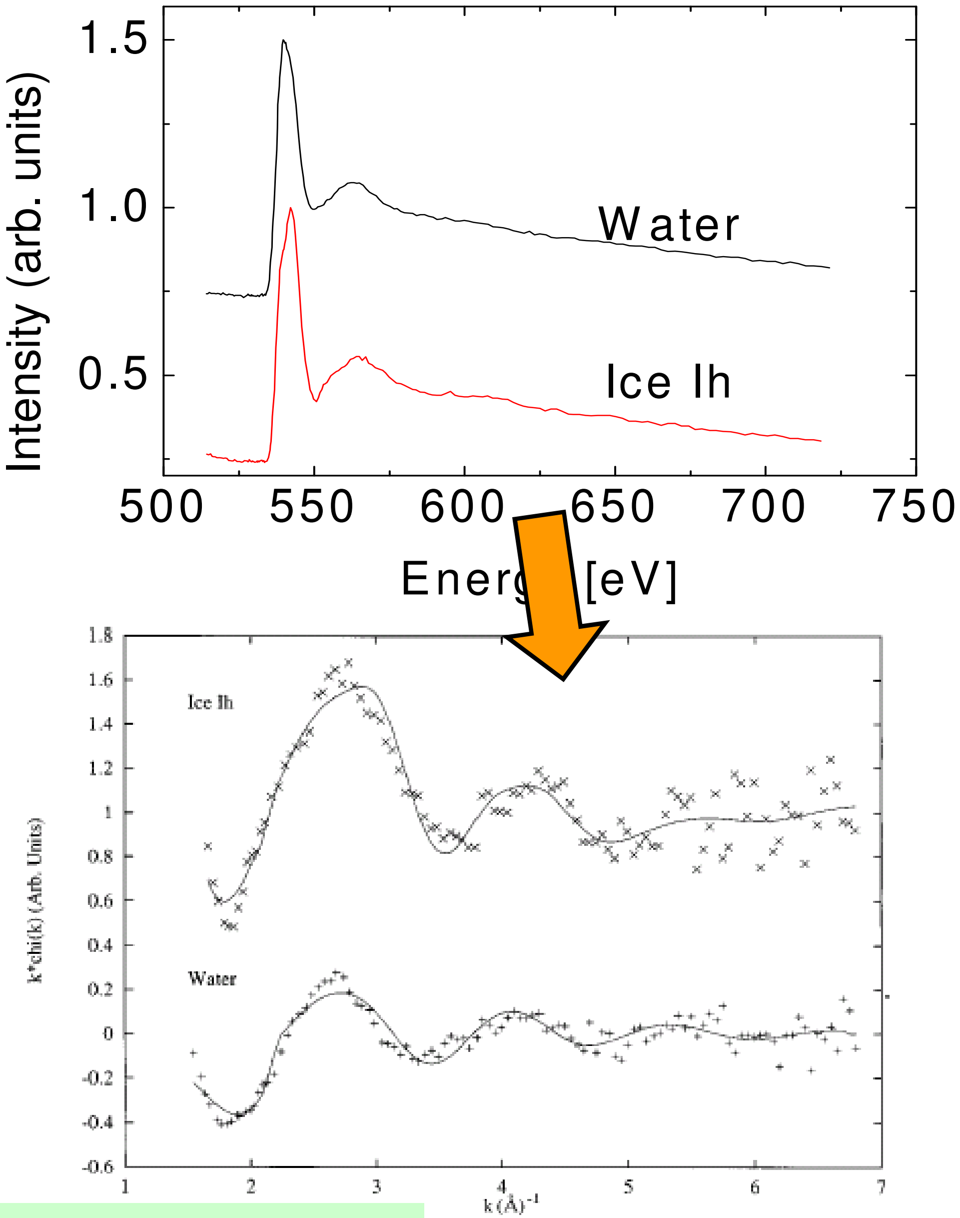


E_{in} = 9686 eV (ΔE ~ 2 eV)
$|\mathbf{k}|$ = 4.38 A^{-1} ($\mathbf{k}\cdot\mathbf{r}$ ~ 0.29)

PRB 62, R9223 (2000)

Experimental highlights (XRS)

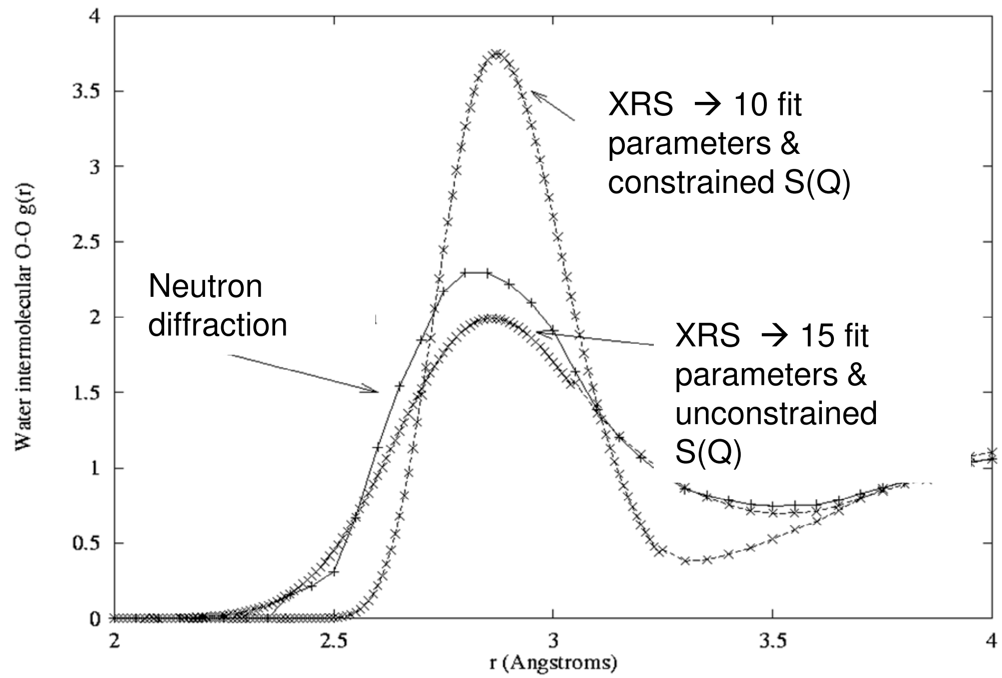
XRS from O K-edge in water and ice (EXAFS)

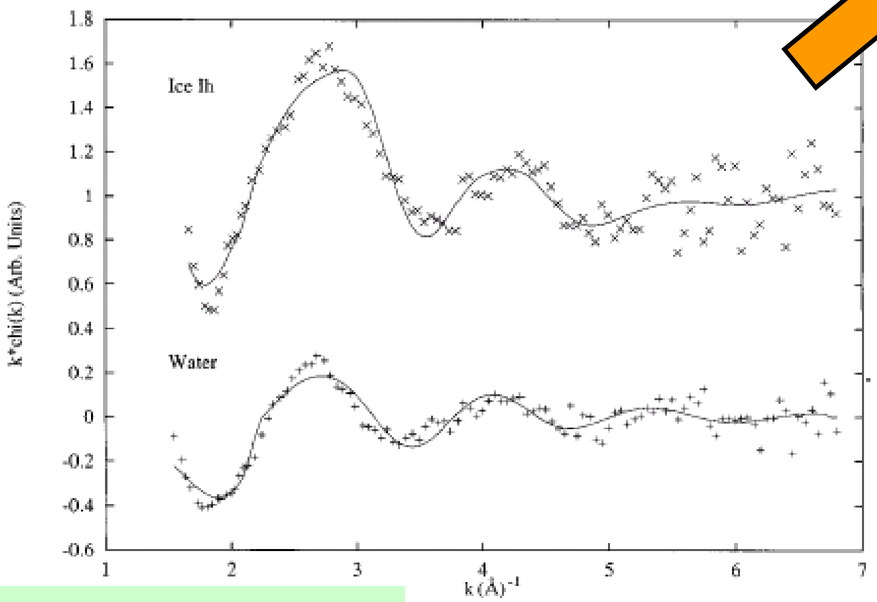


PRB 62, R9223 (2000)

Experimental highlights (XRS)

XRS from O K-edge in water and ice (EXAFS)





XRS:
O-O distance: 2.87 Å
Coordination: 4 - 7

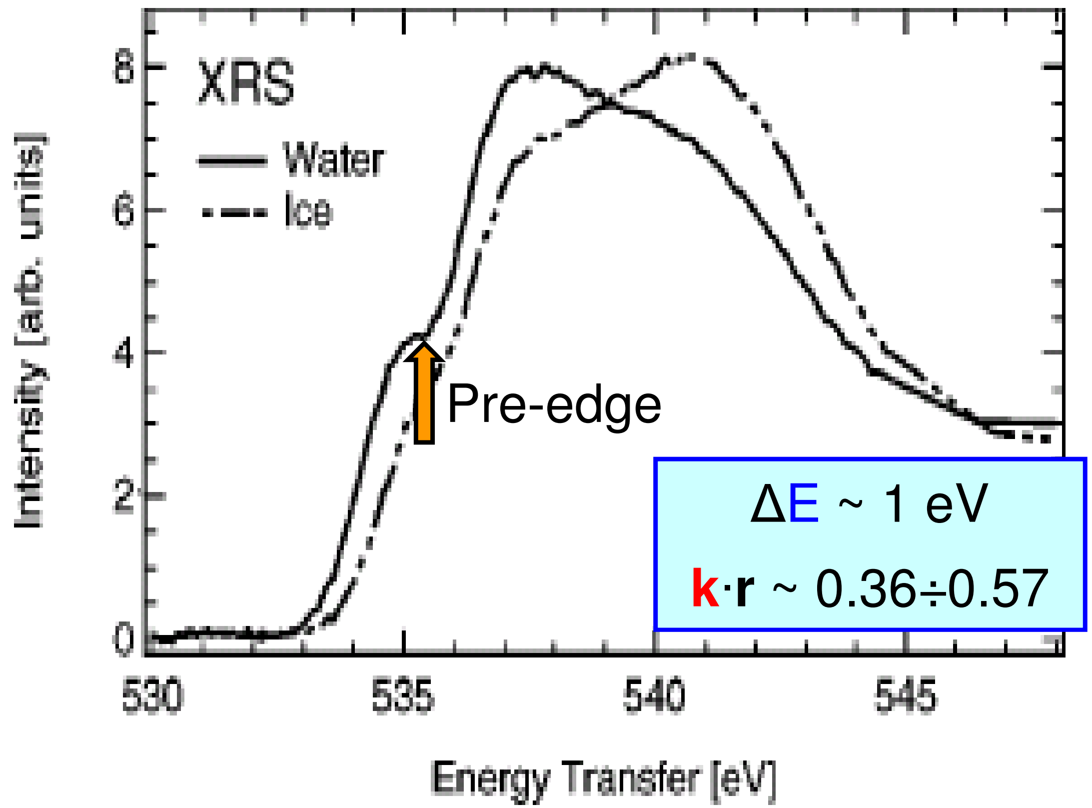
Neutrons:
O-O distance: 2.85 Å
Coordination: 4.4

PRB 62, R9223 (2000)

Experimental highlights (XRS)

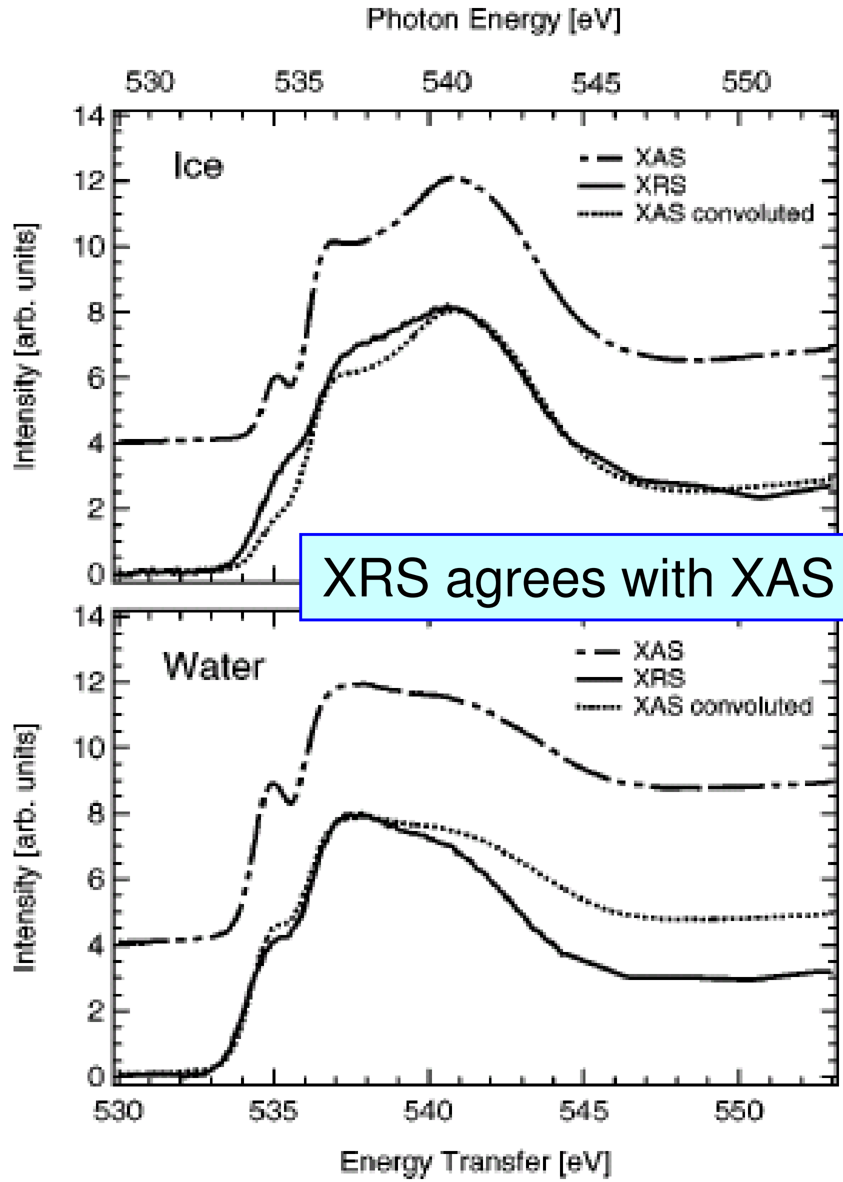
XRS from O K-edge in water and ice (XANES)

XANES sensitive to the number and “type” of hydrogen bonds (HB)



ΔE ~ 1 eV

k·**r** ~ 0.36÷0.57



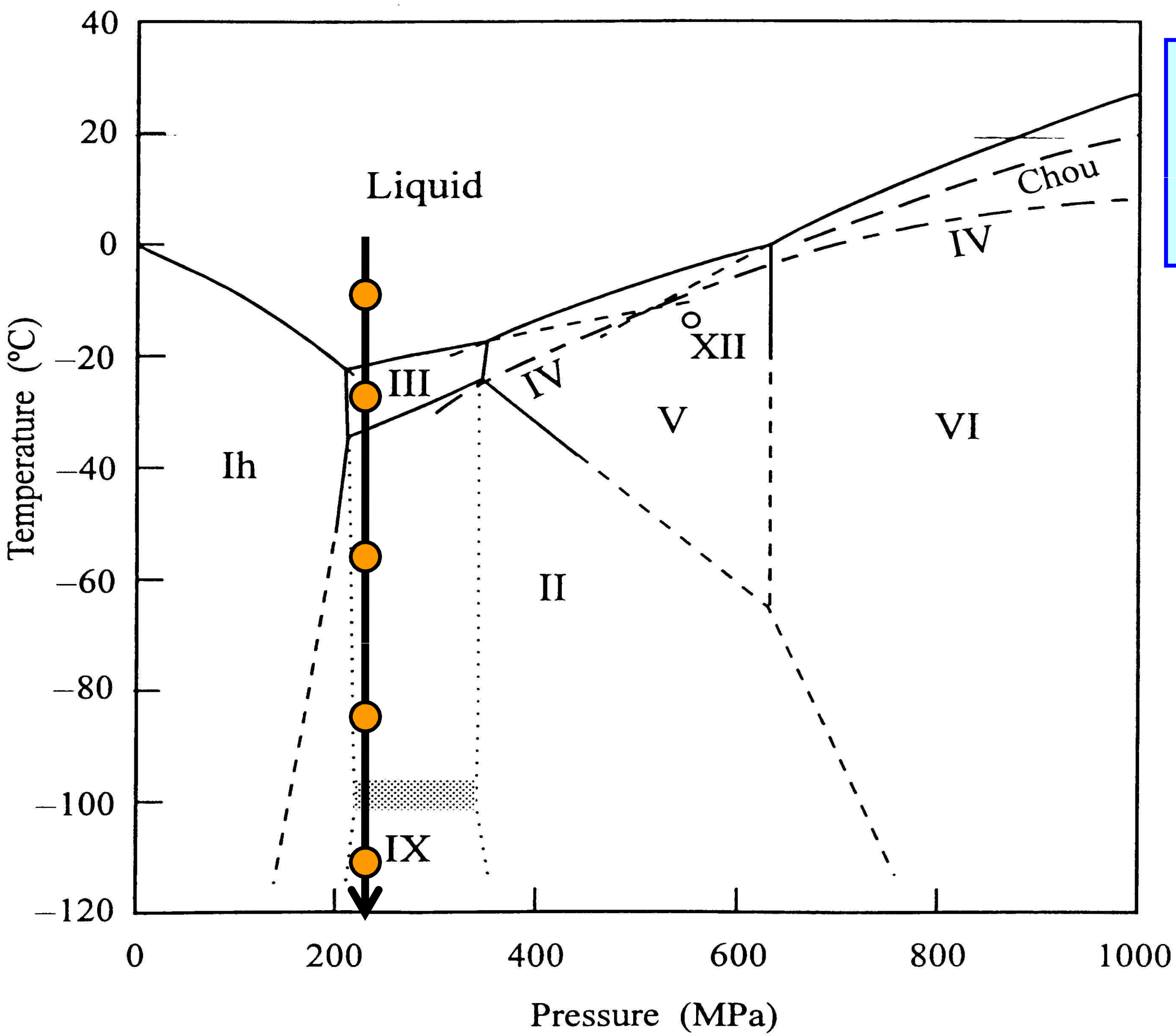
XRS agrees with XAS

• Pre-edge indicates a large number (~ 70%) of distorted or broken HB (supported by calculation)

PRB 66, 092107 (2002)

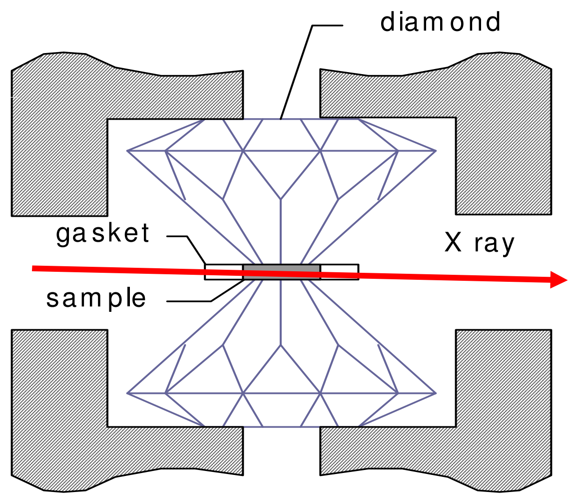
Experimental highlights (XRS)

XRS from O K-edge in ice under high pressure



E_{out} = 9885 eV
(ΔE ~ 0.2÷0.3 eV)
|**k**| ~ 3 A^{-1} (**k**·**r** ~ 0.2)

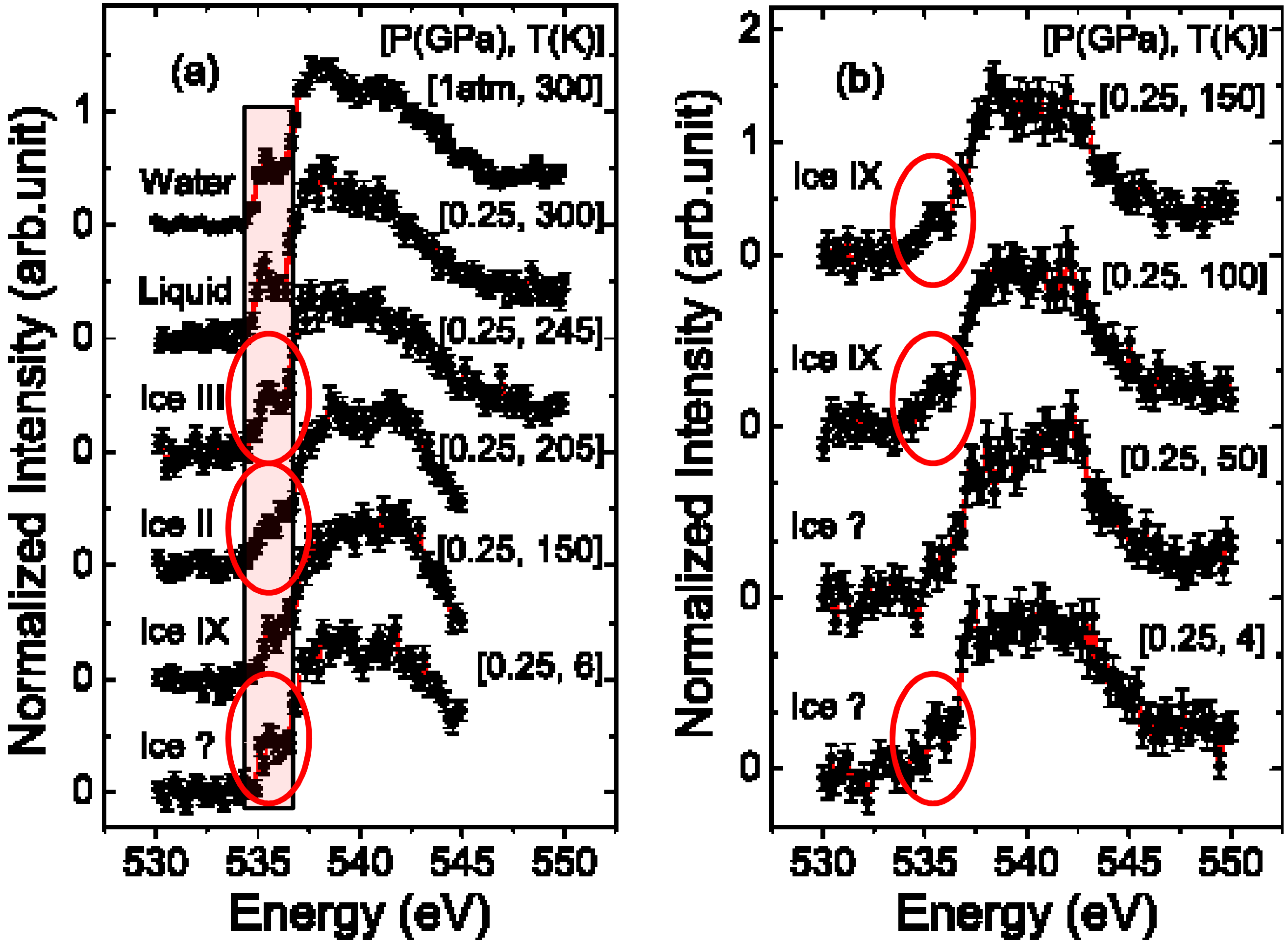
DAC sample environment: hard x-ray needed



PRL 94, 025502 (2005)

Experimental highlights (XRS)

XRS from O K-edge in ice under high pressure



- Slight increase of pre-edge with P (larger HB distortion)
- Increasing order of HB from liquid → Ice III (tetrahedral) → Ice II / IX
- New pre-edge increase @ low-T: new Ice phase?

<u>Observation of spectral changes:</u>

<u>Need of much better statistics and theory to extract quantitative information</u>

PRL 94, 025502 (2005)

XRS in summary

Soft x-ray spectroscopy in the hard x-ray regime

Advantages

- "simpler" sample environment (high pressure/temperature, etc…)
- bulk sensitive
- indicated for studying (bulk) Oxygen and Carbon

Drawbacks

- "weak probe" (practically limited to $Z < 14$)
- limited quality for structural analysis (EXAFS), reasonable quality in the XANES region

Exploit information in the near-edge region

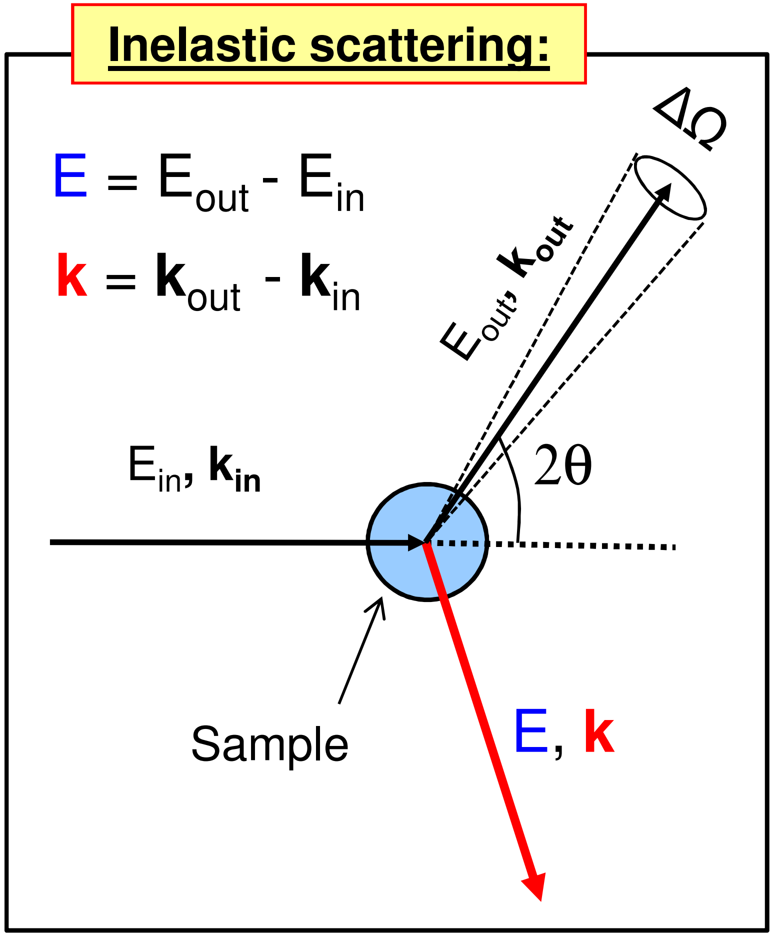
Basic theoretical aspects (RIXS)

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

A: vector potential of electromagnetic field

P: momentum operator of the electrons

j: summation over all electrons of the system



A·A → non-resonant scattering (IXS - XRS)

A·p → resonant scattering, absorption followed by emission

Basic theoretical aspects (RIXS)

Resonant IXS cross section:

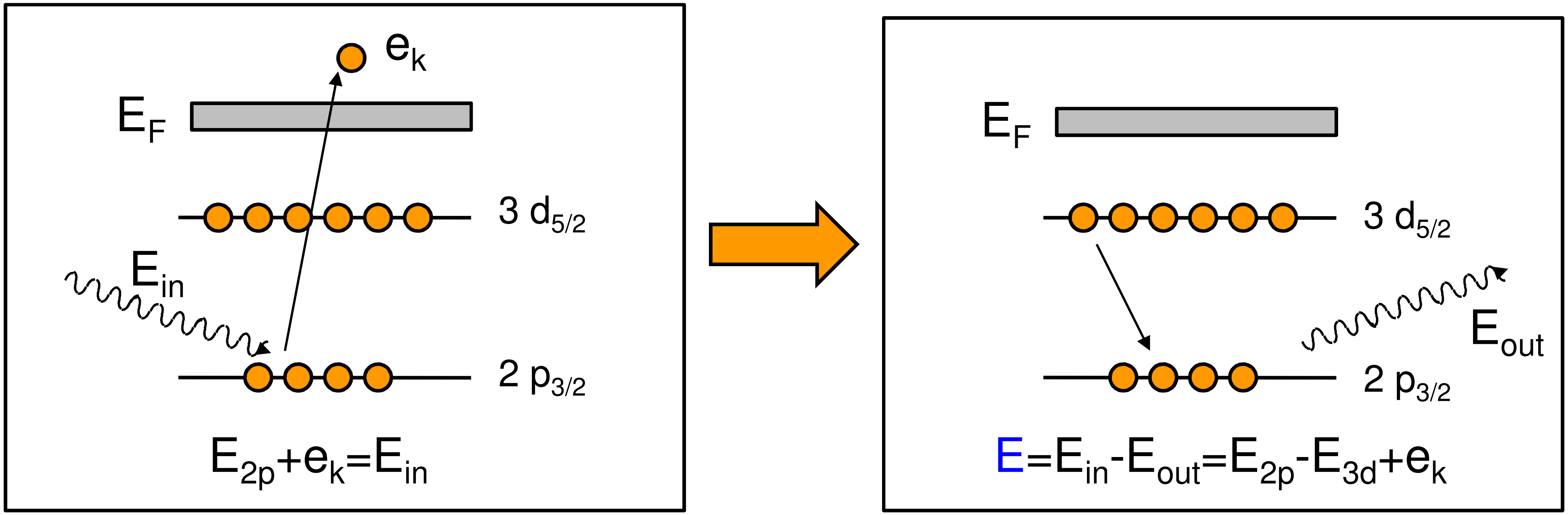
Absorption → $\langle I|C_k|N\rangle$

Emission → $\langle N|C_k^+|F\rangle$

Resonant denominator → $E_N - E_I - E_{in} - i\Gamma_N$

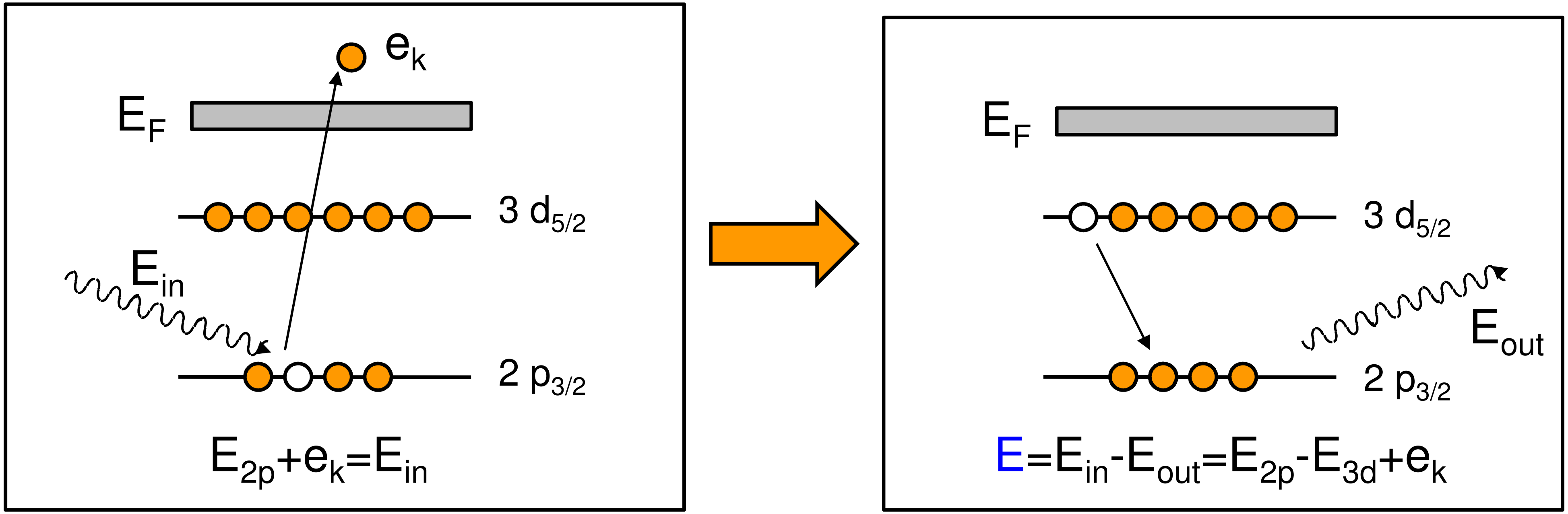
$$\frac{\partial^2\sigma}{\partial\Omega\partial E} \sim \sum_F \left| \sum_n \frac{\langle I|C_k|N\rangle \langle N|C_k^+|F\rangle}{E_N - E_I - E_{in} - i\Gamma_N} \right|^2 \delta(E - E_F + E_I)$$

$$C_k = \sum_j (\boldsymbol{\varepsilon}\cdot\mathbf{p}_j)\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}$$



Basic theoretical aspects (RIXS)

Final states for XAS are intermediate for RIXS (resolution ~ Γ_N)



Motivation: Final state core-hole lifetime < energy separation of the multiplet families

→ RIXS allows the separation of different excitation channels, which are obscured in XAS

Motivation: Keeping E fixed and tuning E_{in} through edge (CFS)

→ Resonant enhancement of intermediate states