Neutron Spectroscopy

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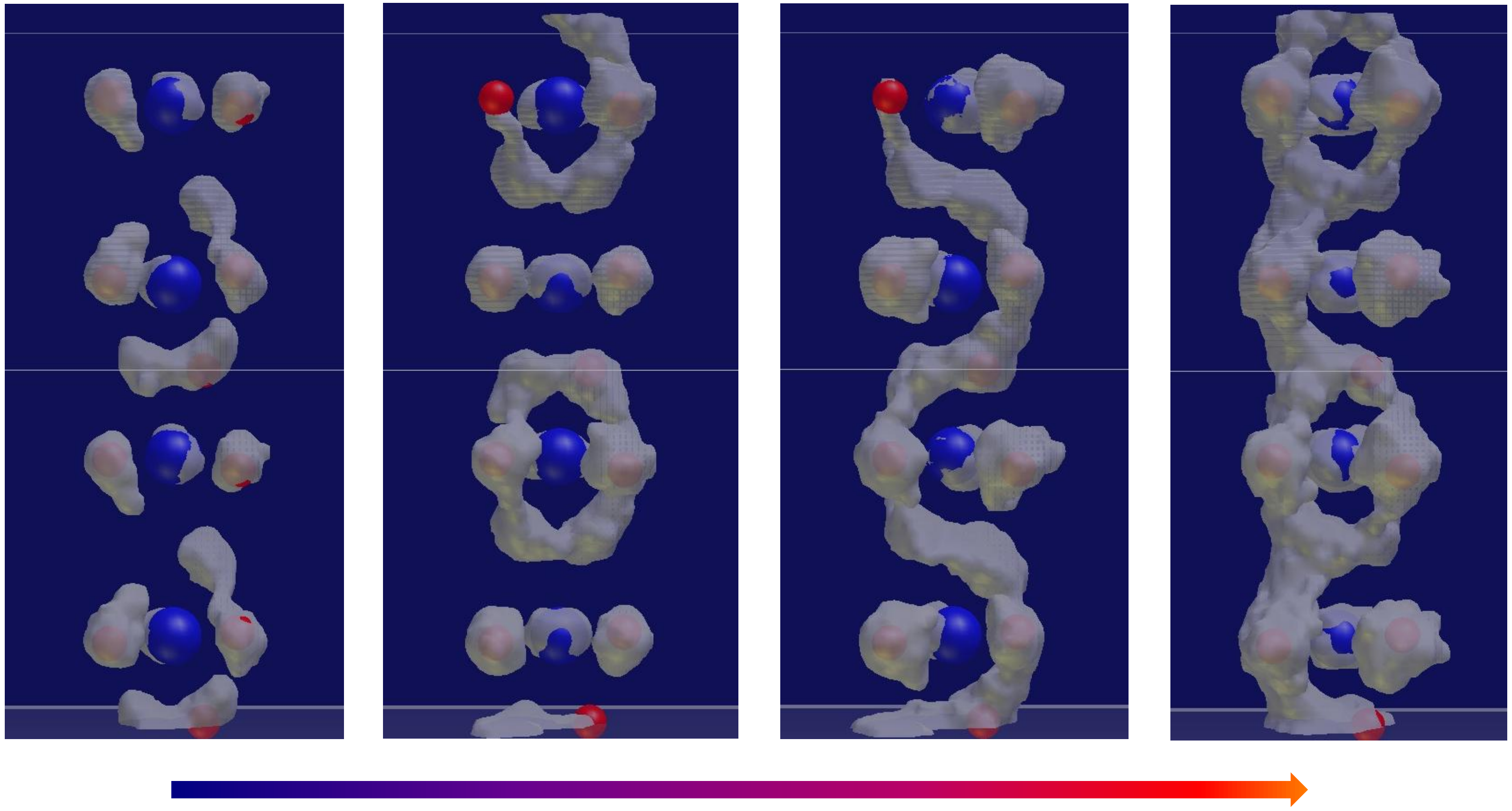
Institut Laue-Langevin, Spectroscopy Group

Introduction and Motivation



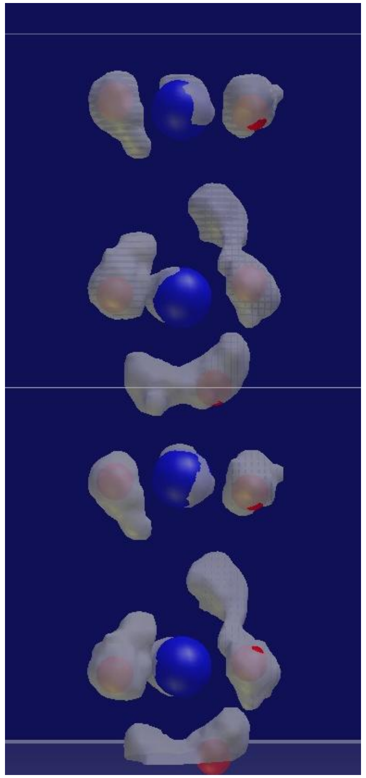
Oxide Ion Dynamics in Solid Electrolytes : $La_2Mo_2O_9$

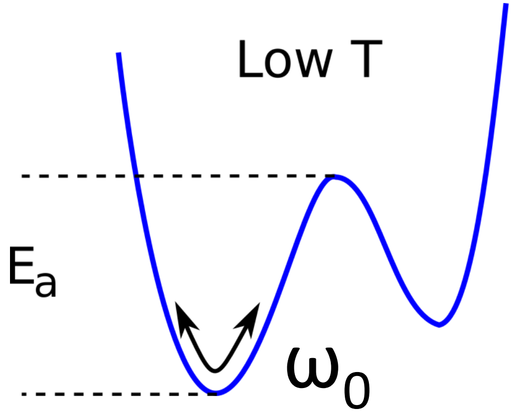
Joseph R Peet et al., *Chem. Mater.* 29 (2017)

Results from ab initio Molecular Dynamics simulation

- Details of the bonding potential, characteristic frequencies, amplitudes, anharmonic effects, i.e., frequency changes as a response to T, p, E, B, ... variation, life time of vibrations, ...
- Potential wells, activation energies, time scales
- Mechanism of displacive dynamics, hopping, continuous, translational, rotational
- Pathways for displacive dynamics, dimensionality, symmetry, isotropy, confinement effects
- Diffusion constants, mean-square displacements

Introduction and Motivation

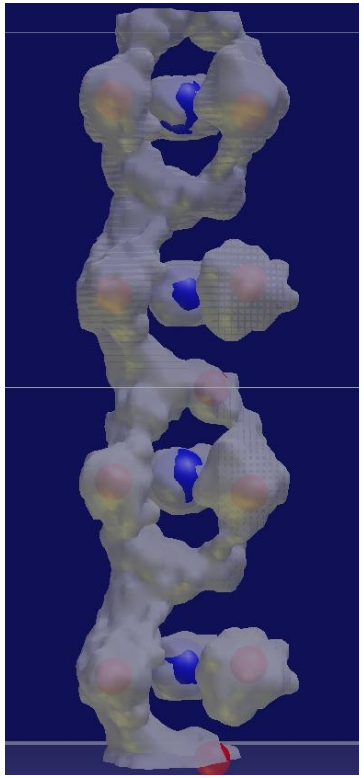


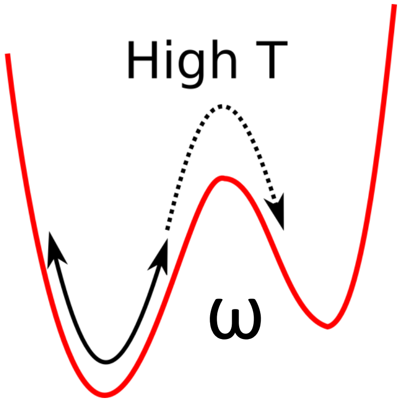


Hook's law :

$\omega_0 = (K/m)^{1/2}$

	cm^{-1}	meV	THz
O-H	3700	450	110
C-H	3000	370	90
C=O	1700	210	50
C-C	1250	150	36





Arrhenius' law :

$\omega = \omega_0 \exp(-E_a/k_B T)$

Gedankenexperiment :

Activation energy : E_A = 200 meV

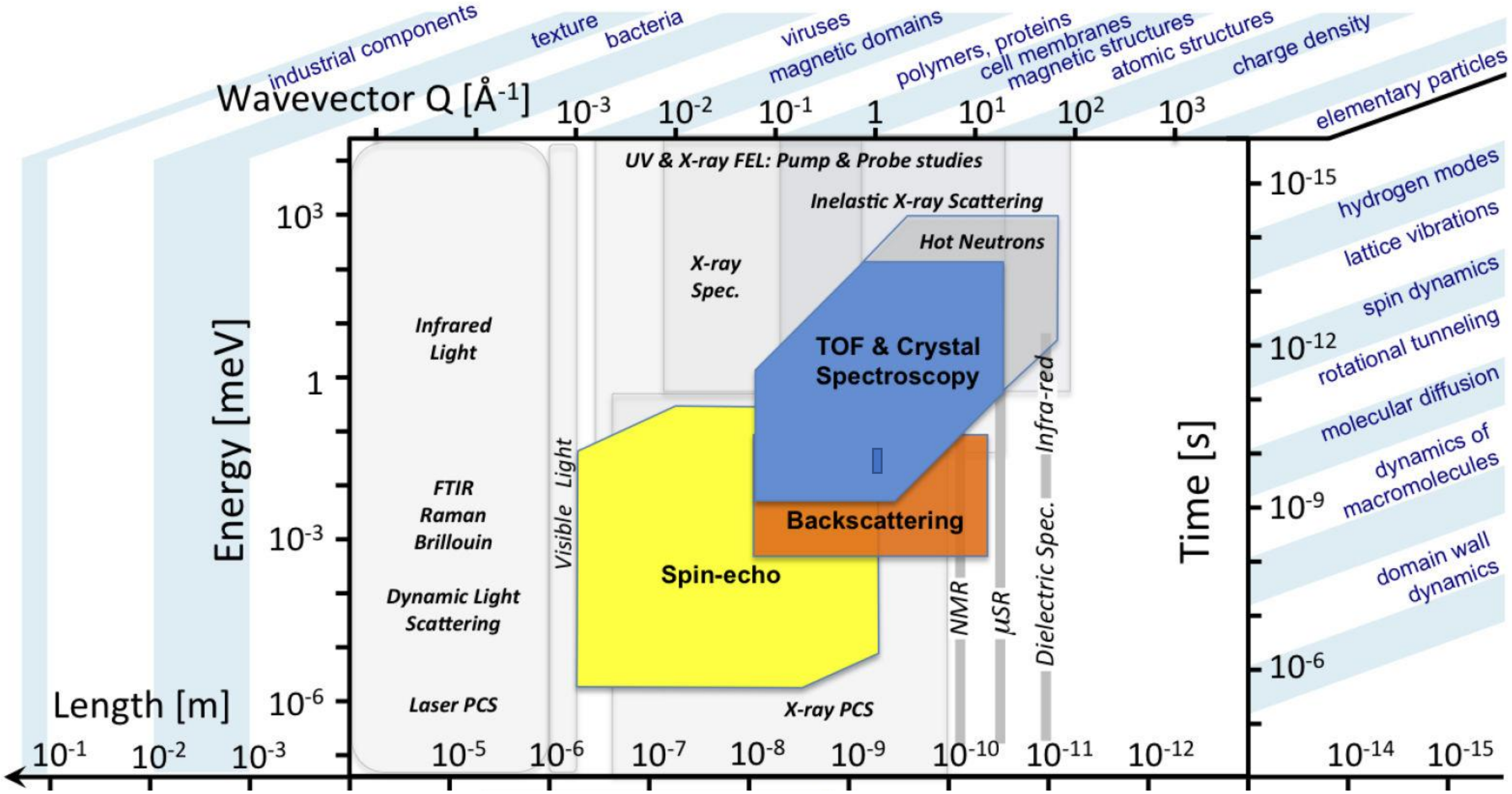
Trial frequency : v_0 = 1-100 THz

Temperature : T = 300 K

→ 0.002 – 0.2 meV

→ 0.1 nsec – 1 psec

Energy – Time – Wavevector – Length Phase Space



ESS Technical Design Report 2013

Neutron Energy Range

λ [Å]	1	2	4	6	10
E [meV]	80	20	5	2	1
T [K]	960	240	60	24	12
v [m/s]	3911	1956	978	620	437

Cold neutrons :	0.1-10 meV	D_2 at 25 K
Thermal neutrons :	10-100 meV	D_2O at room T
Hot neutrons :	100-500 meV	Graphite at 2400 K

Neutron Energy Range

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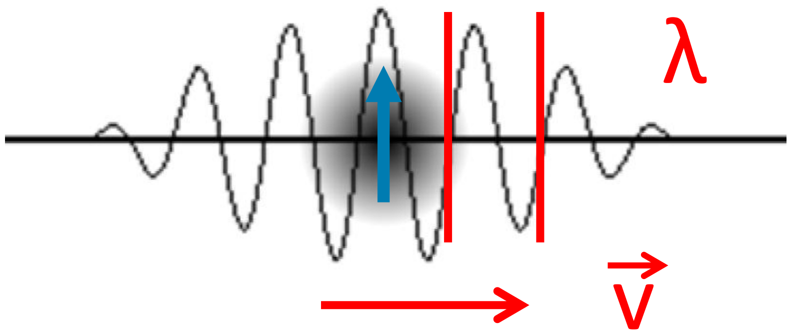
E [meV]	80	20	5	2	1
T [K]	960	240	60	24	12
v [m/s]	3911	1956	978	620	437

- Mass = 1.675 10^{-27} kg
- Electrical Charge = 0
- Spin = ½
- Magnetic Moment = -1.913 μ_n

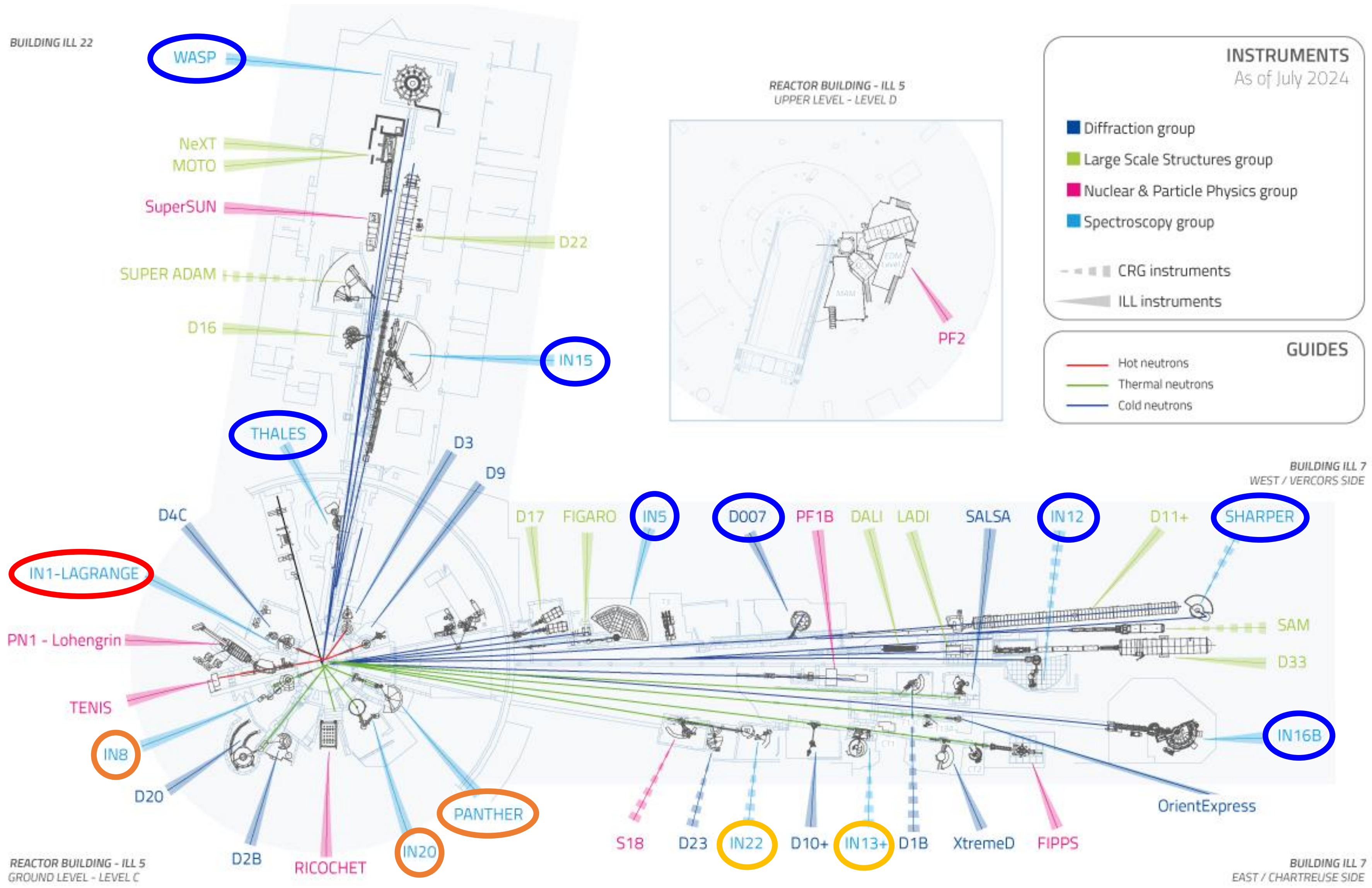


$$\boldsymbol{E = 81.81 \cdot \lambda^{-2} = 2.07 \cdot k^2 = 5.23 \cdot v^2}$$

$[E]$ = meV ; $[\lambda]$ = Å ; $[k]$ = Å^{-1} ; $[v]$ = km/sec

1 meV = ¼ THz = 8.1 cm^{-1} = 11.6 K = 10.4 kJ/mol

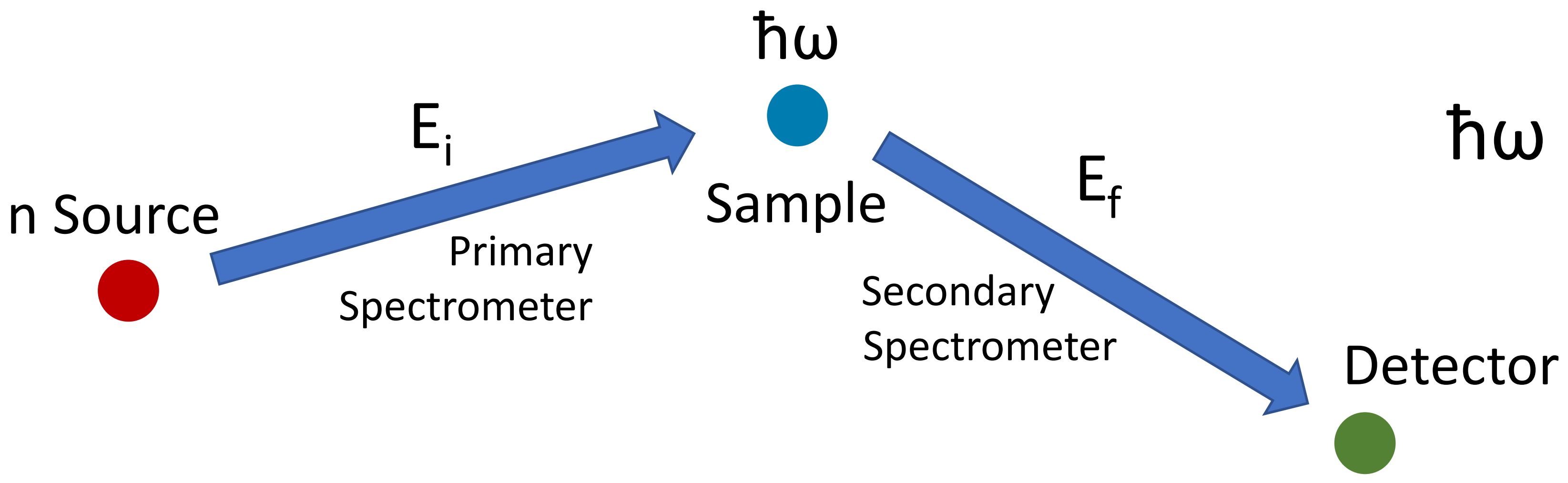
Instrument Map of the ILL



- Cold neutrons
- Thermal neutrons
- Hot neutrons

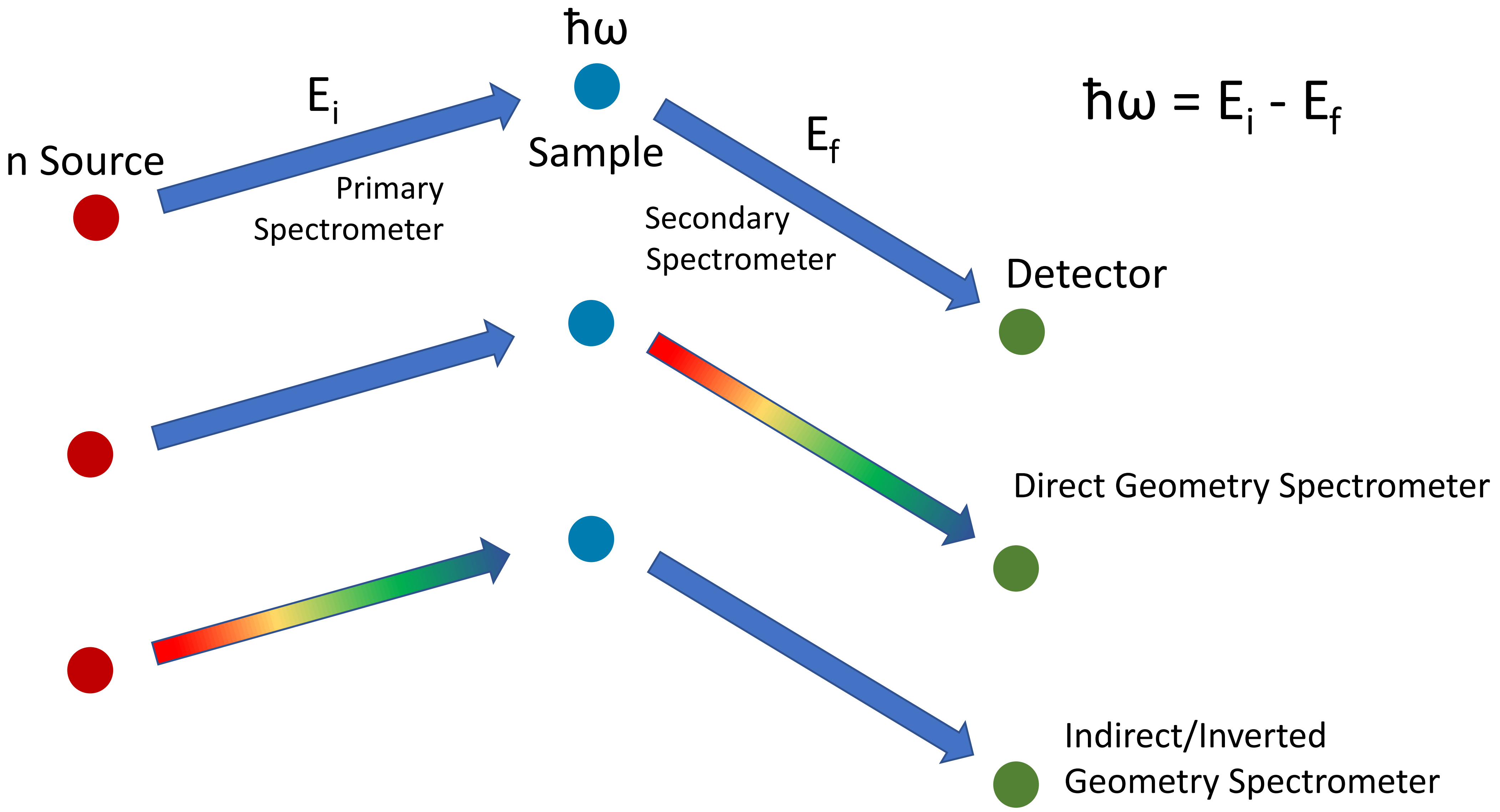
ToF – Time of Flight
TAS – Three Axis Spectro
NSE – Neutron Spin Echo
BS – Back-Scattering

Basic Spectrometer Concepts



$$\hbar\omega = E_i - E_f$$

Basic Spectrometer Concepts



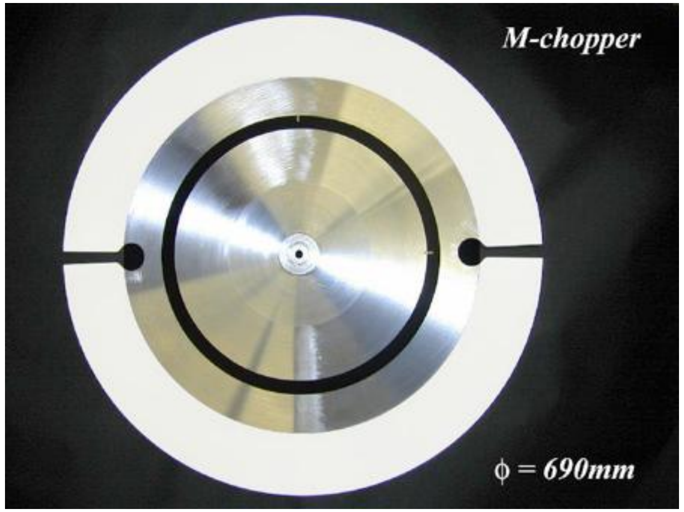
$$\hbar\omega = E_i - E_f$$

Essential Spectrometer Components

NEUTRONS
FOR SOCIETY

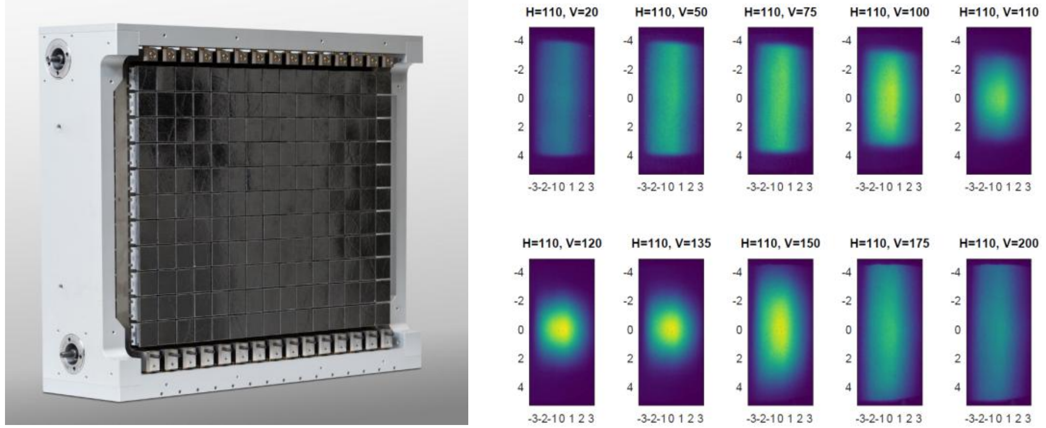
Primary	Secondary	Instruments	
v	v	IN5b	ToF
λ	v	SHARPER, PANTHER, D007	ToF
λ/v	λ	IN16b/BATS, IN13+	BS
λ	λ	IN8, IN12, IN20, IN22, Thales, IN1-Lagrange	TAS
↑	↑	WASP, IN15	NSE
λ/↑	λ/↑	ZETA@IN22	TAS-NSE

Chopper disc of IN5b



Ferenc Mezei first NSE prototype coils

Double focusing monochromator of PANTHER`/ TAS



Resolution Considerations

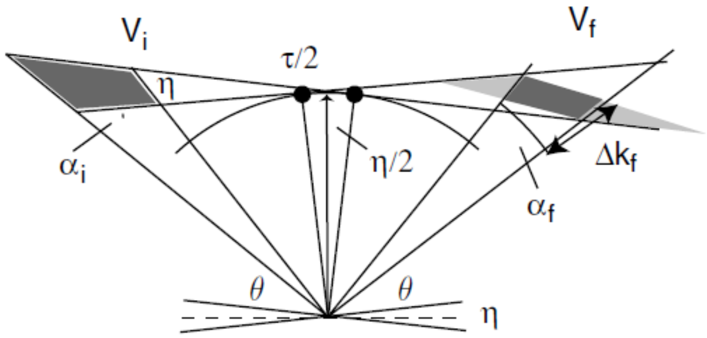
NEUTRONS FOR SOCIETY

For the ToF energy resolution :

$$E = \frac{\hbar^2 (2\pi)^2}{2m_\mathrm{n}} \frac{1}{\lambda^2} = \frac{1}{2} m_\mathrm{n} \left(\frac{L}{t}\right)^2 \rightarrow \Delta E = \frac{\hbar^3 (2\pi)^3}{m_\mathrm{n}} \frac{\Delta t}{L\lambda^3}$$

- Use long wavelength
- Use long flightpath
- Use short chopper pulses

For the monochromator energy resolution :

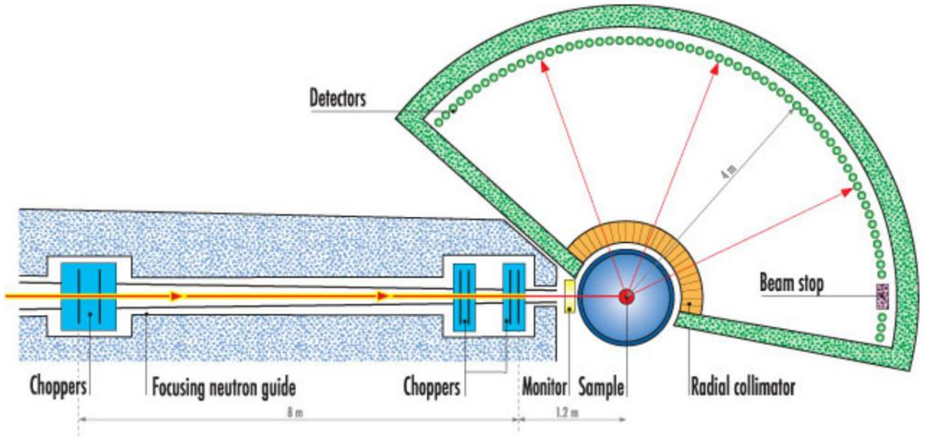


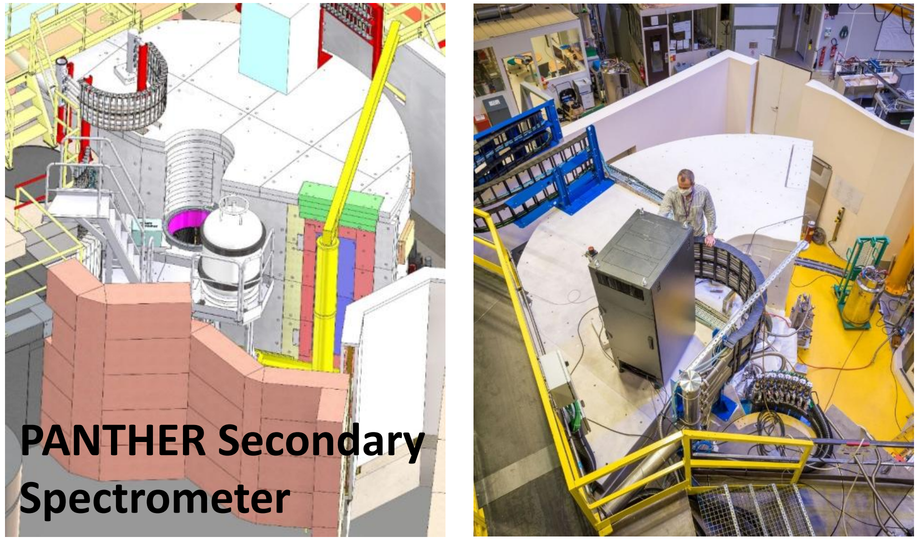
$$\lambda = 2d\sin(\theta) \rightarrow \frac{\Delta\lambda}{\lambda} = \cot(\theta)\Delta\theta + \frac{\Delta d}{d}$$

- Work in backscattering geometry 2θ = 180°
- Use high quality crystals

Time of Flight Spectrometers

IN5b –Disc Chopper Instrument





IN5b

Chopper	E_i [meV]
33 – 280 Hz	2 - 20

SHARPER-CRG

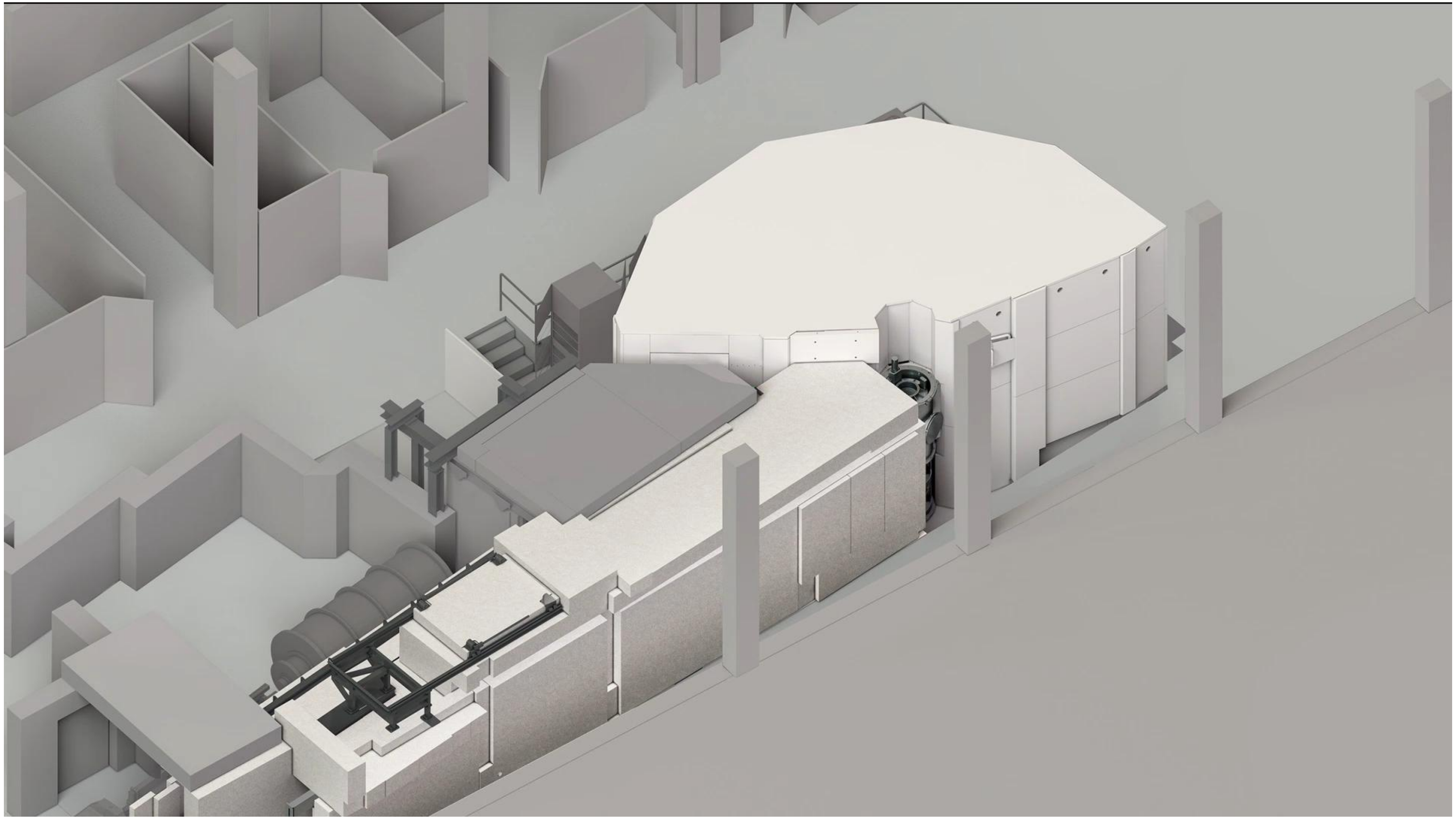
Monochr.	E_i [meV]
PG(002)	2 - 20

PANTHER

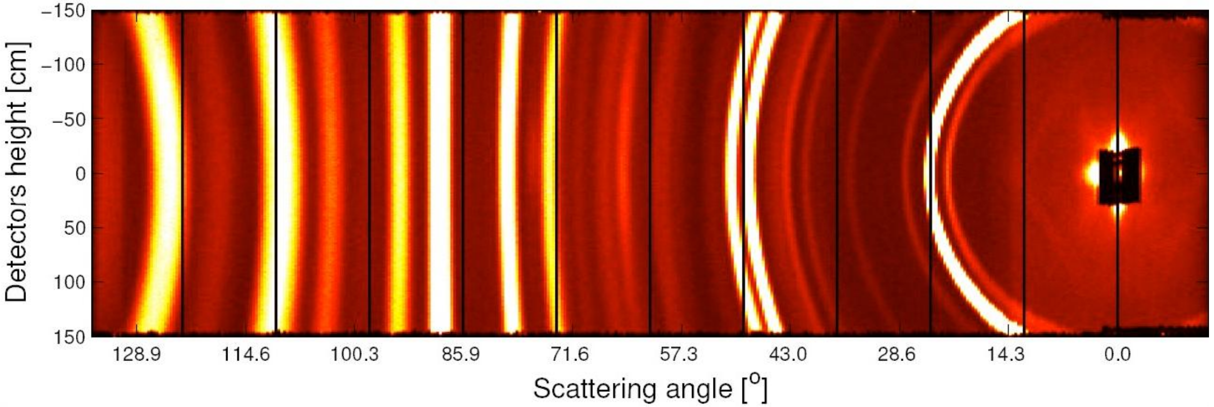
Monochr.	E_i [meV]
PG(002)	7.5 - 19
PG(004)	30 - 76
PG(006)	68 - 171
Cu(220)	52 - 130
Cu(331)	123 – 150

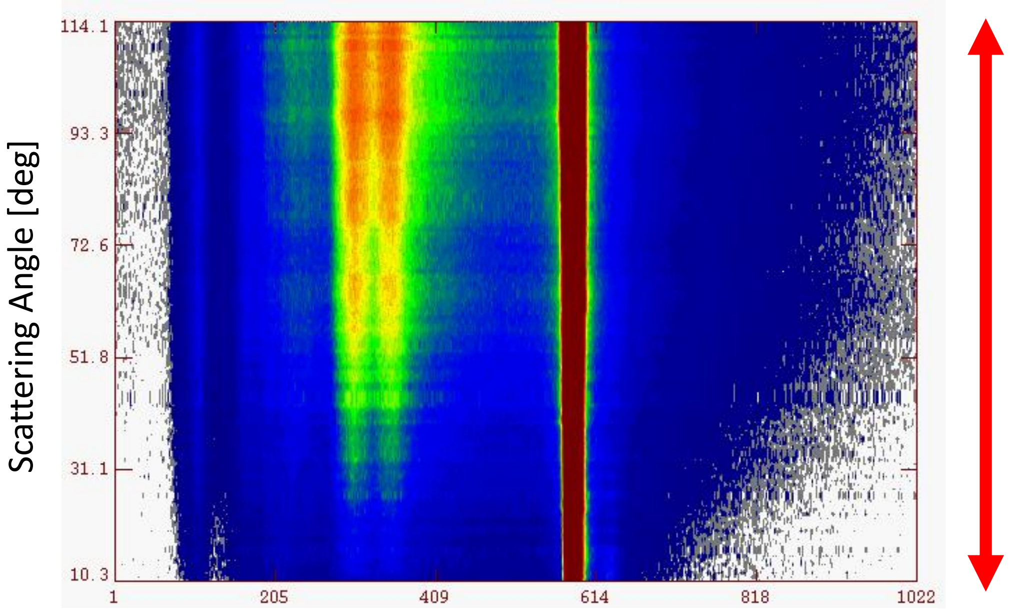
IN5b – Cold Neutron Disc Chopper Spectrometer

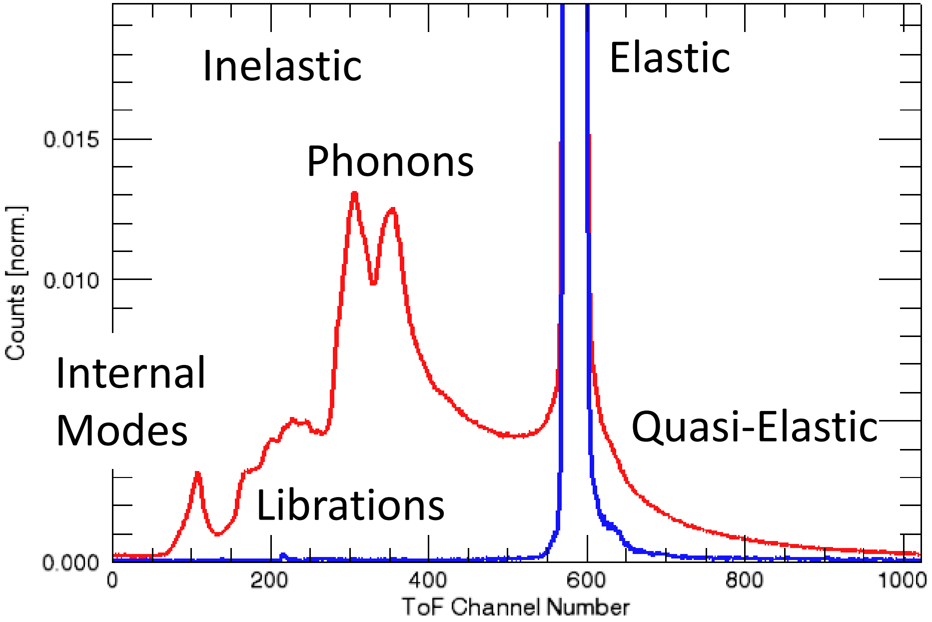
To watch the explanatory IN5b video, go to :
https://www.ill.eu/fileadmin/user_upload/ILL/3_Users/Instruments/Instruments_list/00_-_SPECTROSCOPY/00_-_TIME_OF_FLIGHT/IN5/html5/IN5B-principle/IN5-2025.html

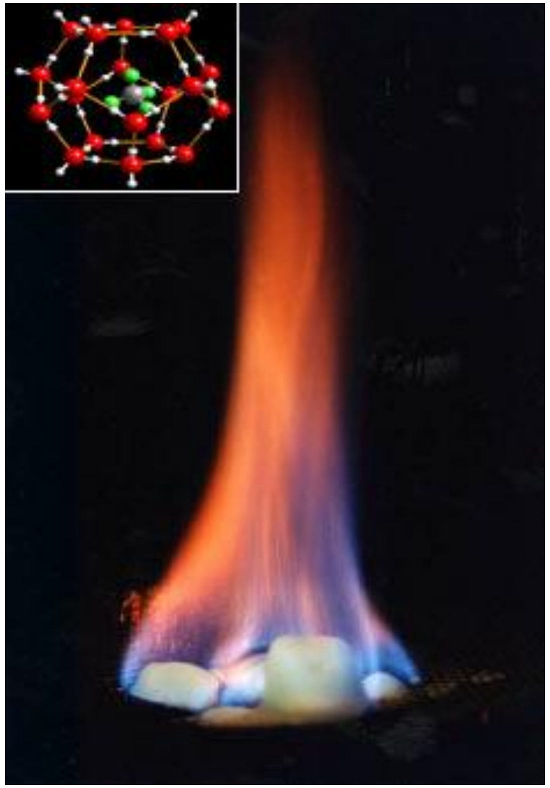


Powders, Polycrystals, Liquids, Amorphous Compounds









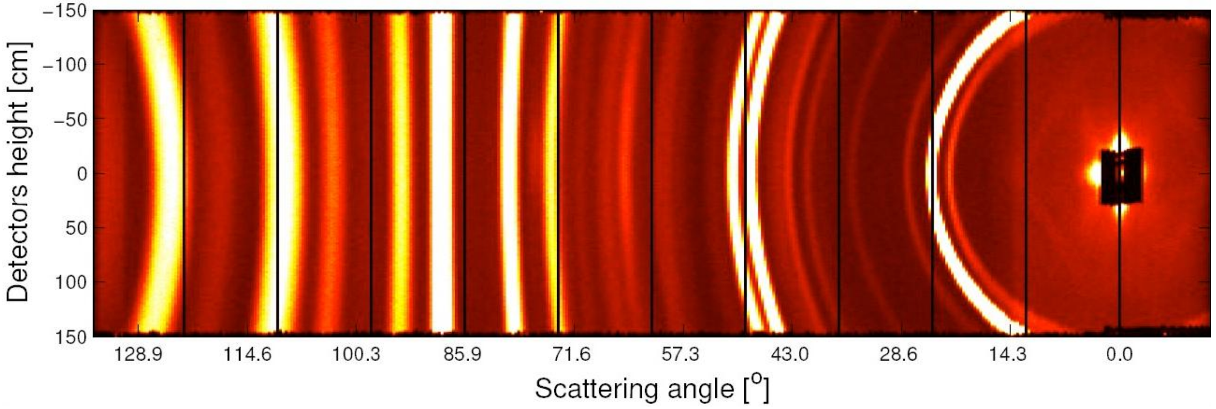
CH_4 in H_2O-clathrate :
Large amounts trapped in perma-frost soils and deep-sea sediments!
Environmental risk through global warming!

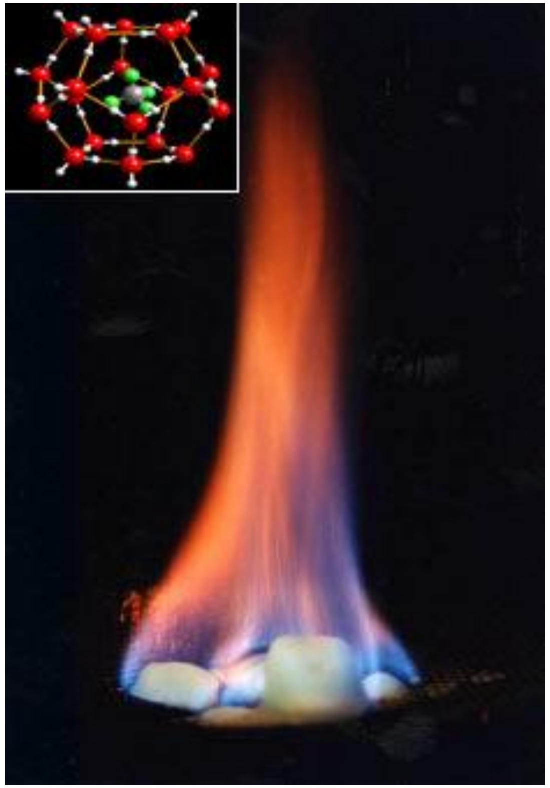
CO_2 in H_2O-clathrate :
For CO_2 sequestration in deep-sea sediments.

H_2 in H_2O-clathrate :
Co-hosted with e.g. THF as hydrogen storage medium.

H_2O-clathrate as moderator material for very cold neutrons.

Powders, Polycrystals, Liquids, Amorphous Compounds





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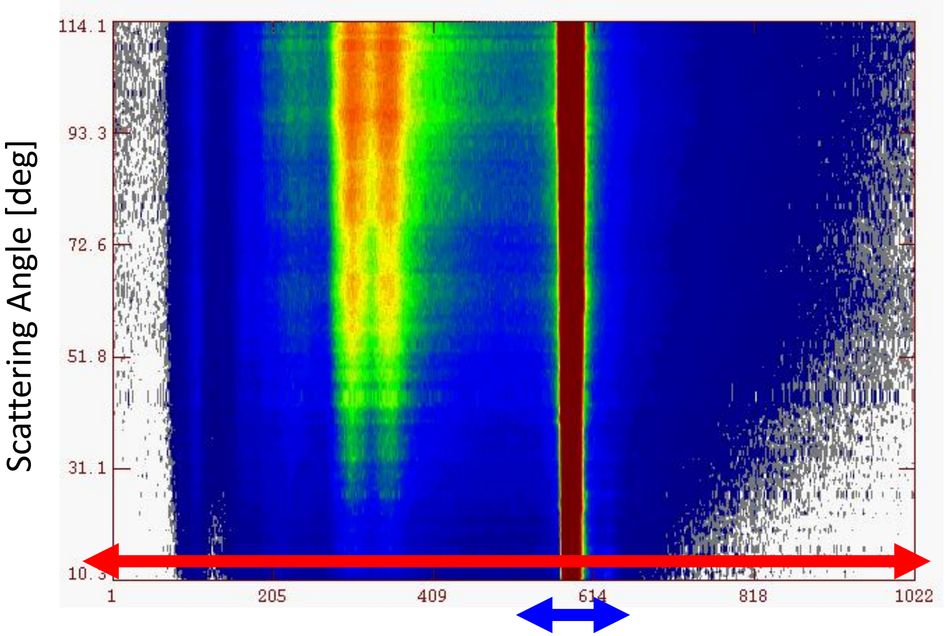
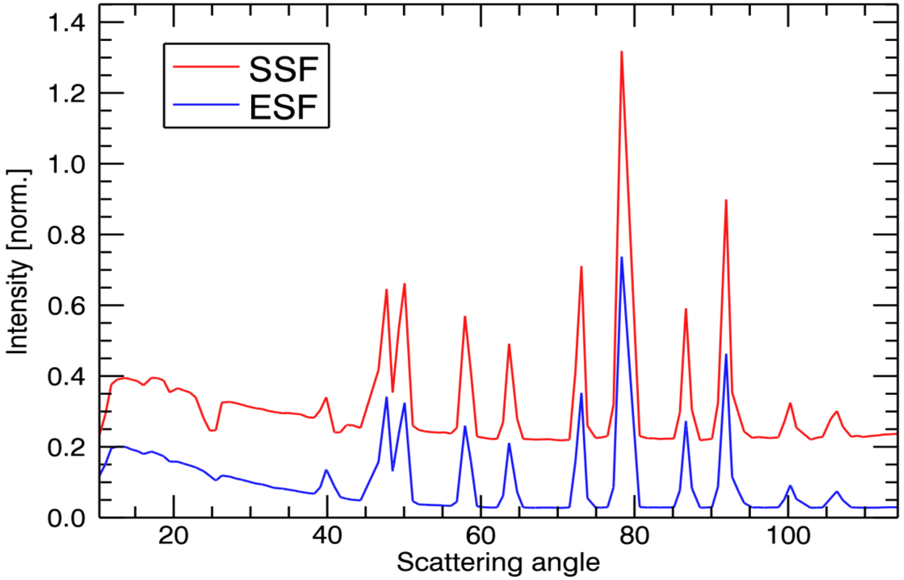
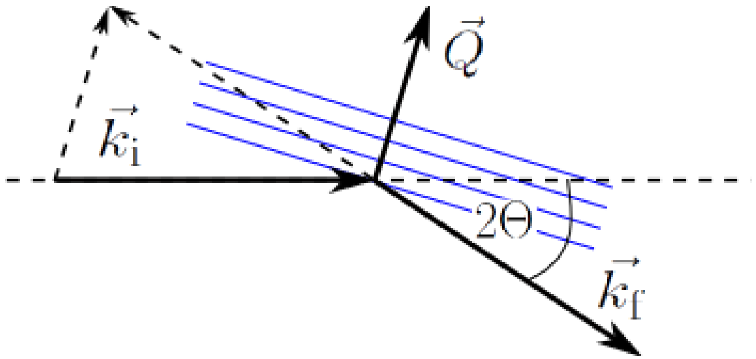
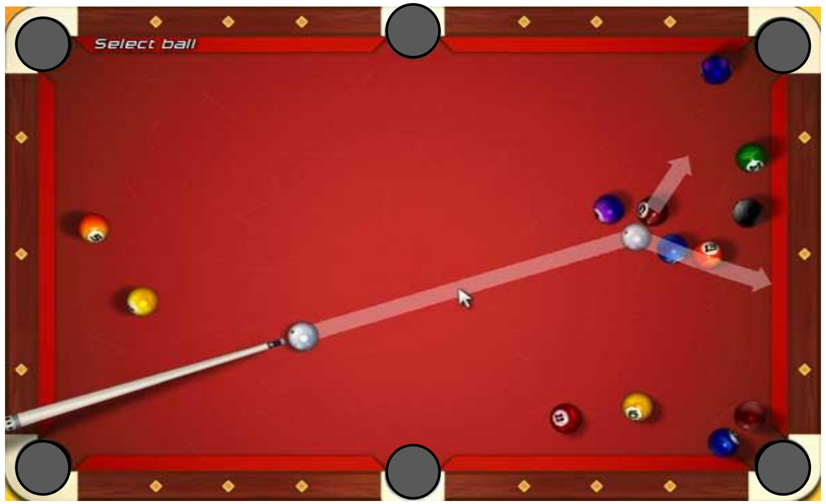




Energy and Momentum Conservation





Conservation Laws :

Momentum : $$\hbar\vec{Q} = \hbar(\vec{k}_{\mathrm{i}} - \vec{k}_{\mathrm{f}})$$

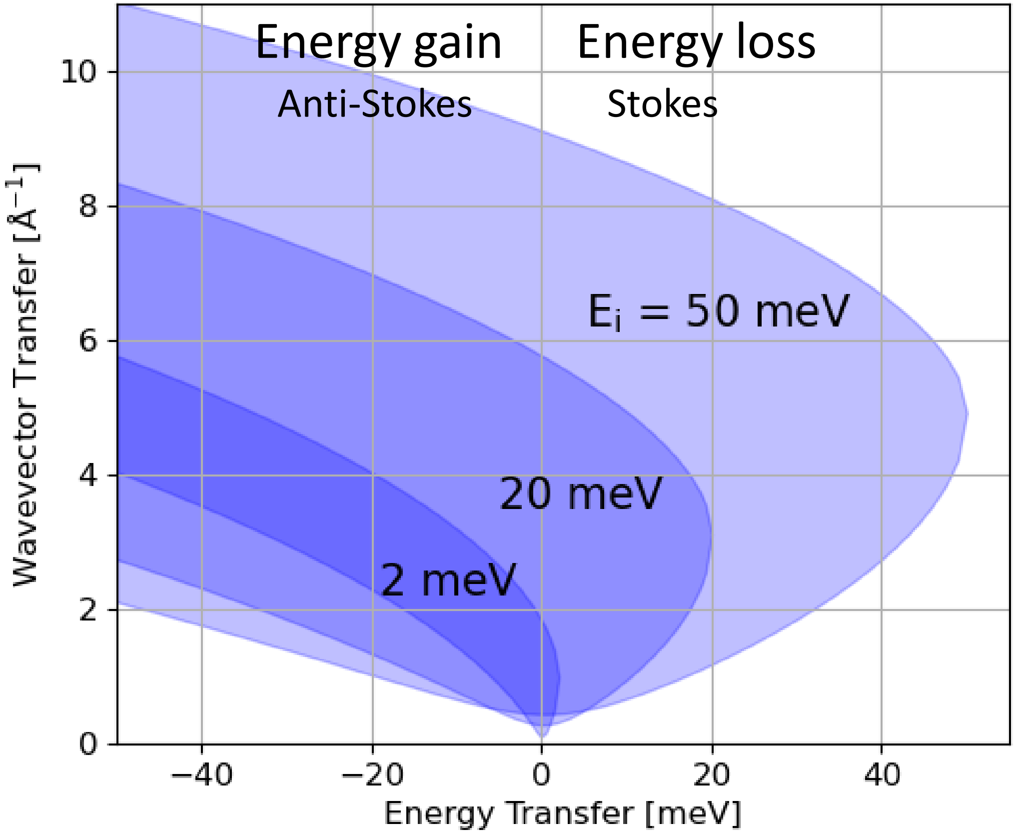
Its modulus : $$\vec{Q}^2 = \vec{k}_{\mathrm{i}}^{\,2} + \vec{k}_{\mathrm{f}}^{\,2} - 2|\vec{k}_{\mathrm{i}}||\vec{k}_{\mathrm{f}}|\cos(2\Theta)$$

Energy : $$\hbar\omega = E_{\mathrm{i}} - E_{\mathrm{f}} = \frac{\hbar^2}{2m_{\mathrm{n}}}(\vec{k}_{\mathrm{i}}^{\,2} - \vec{k}_{\mathrm{f}}^{\,2})$$

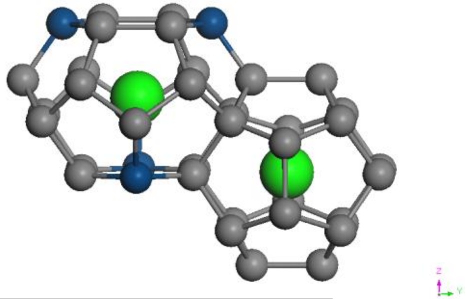
Kinematics of Neutrons and Thermal Occupation

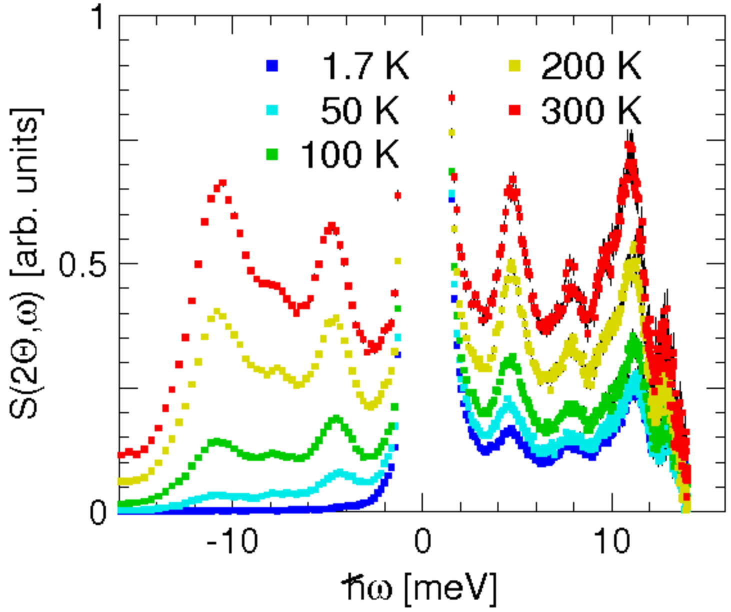
$$\vec{Q}^2 = \vec{k_\mathrm{i}}^2 + \vec{k_\mathrm{f}}^2 - 2|\vec{k_\mathrm{i}}||\vec{k_\mathrm{f}}|\cos(2\Theta)$$

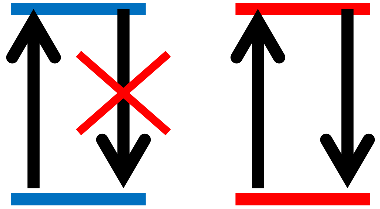
$$\hbar\omega = E_\mathrm{i} - E_\mathrm{f} = \frac{\hbar^2}{2m_\mathrm{n}}(\vec{k_\mathrm{i}}^2 - \vec{k_\mathrm{f}}^2)$$



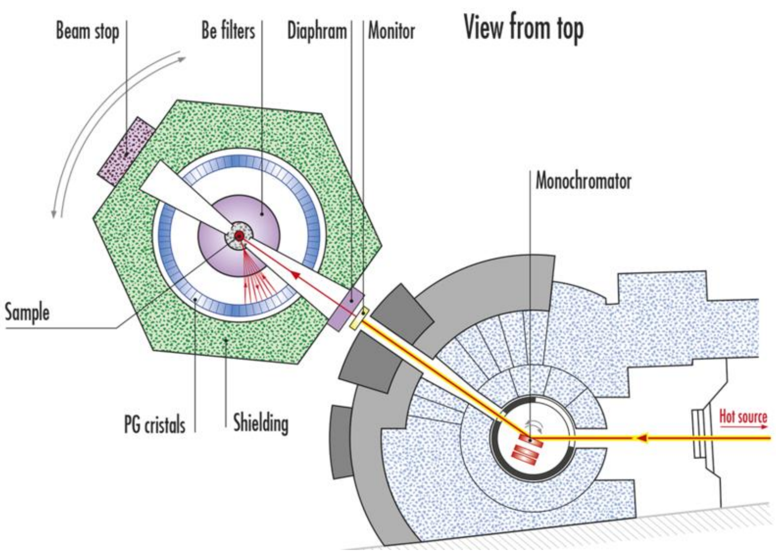
Thermolelectric Clathrate : $Ba_8Zn_xGe_{46-x}$





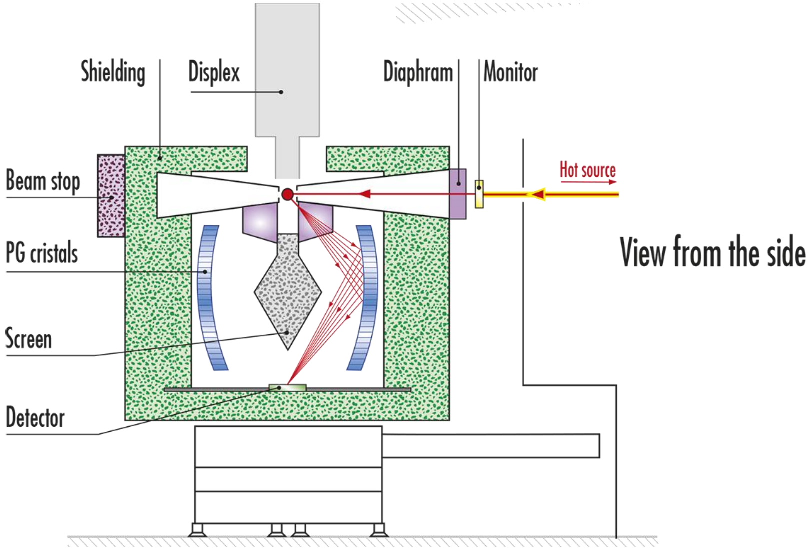


IN1-Lagrange : Vibrational Spectroscopy



Monochr.	Ei range (meV)	ΔEi (meV)
Cu(220)	[26-500]	2-3% Ei
Cu(331)	[67-500]	1.5-2% Ei
Si(311)	[16.5-60]	0.8
Si(111)	[4.5-20]	0.8

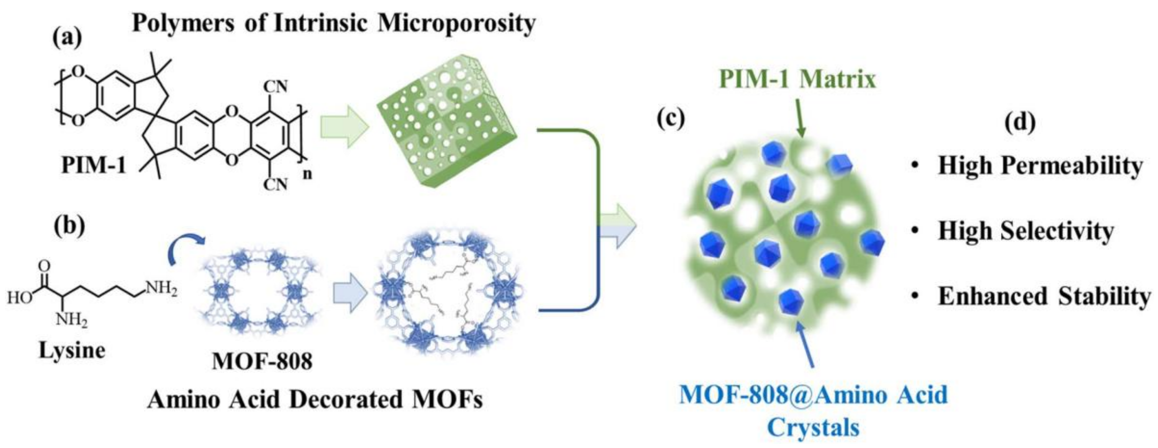
Analyser: PG(002) of 1m^2 surface with E_f = 4.5 meV

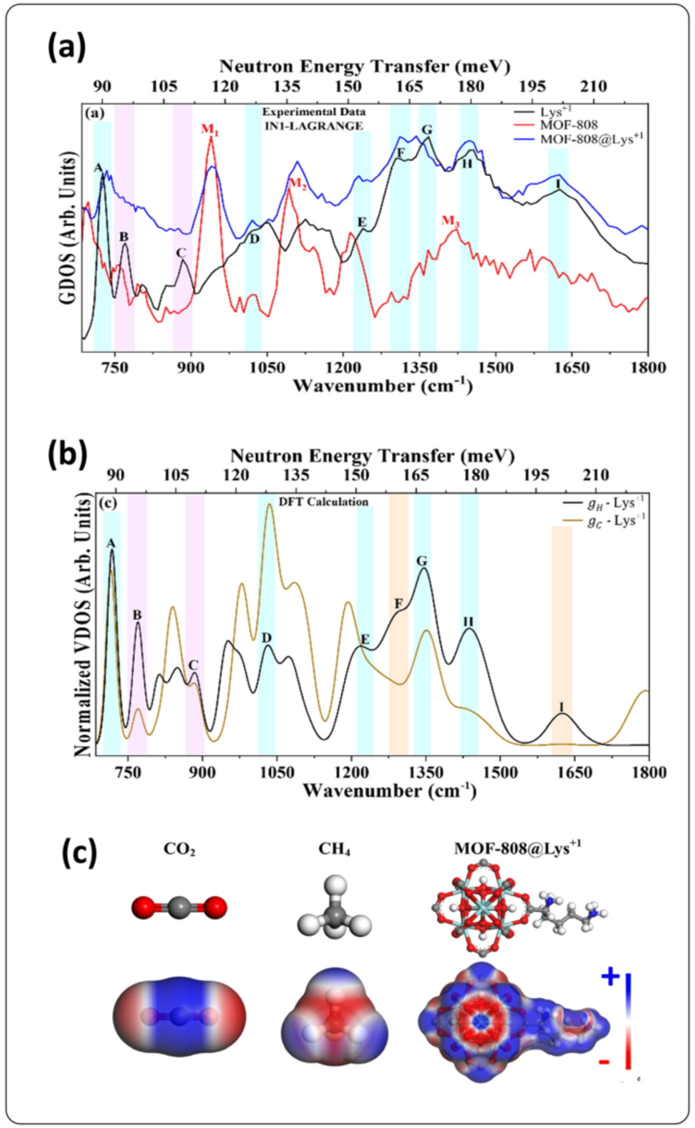


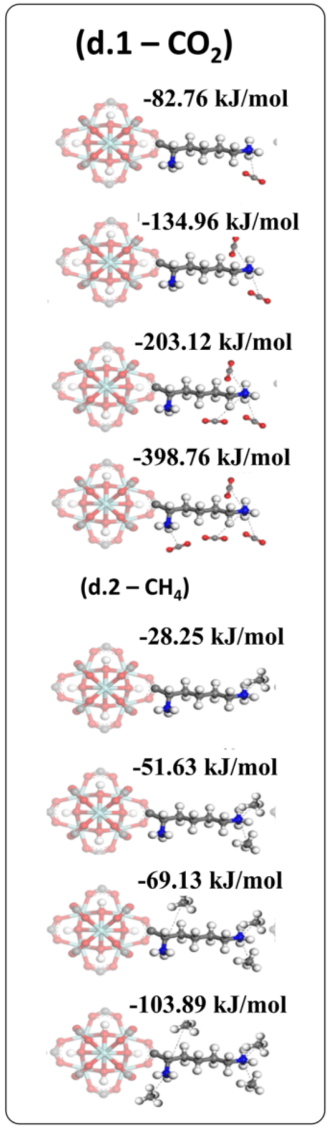
- H_2 cycle, energy storage, solid oxide fuel cells, …
- Materials for catalysis
- H-bonding and its role in geological and biological systems
- Dynamics and bonding: functional abilities of materials
- Structure of complex molecular compounds
- Gas separation in porous media
- Location in the host matrix of molecular groups active in selectivity processes

Membranes with Functionalized MOF-808 for CO_2 / CH_4 Separation

D. Refaat et al., J. *Mater. Chem. A* 13 (2025)







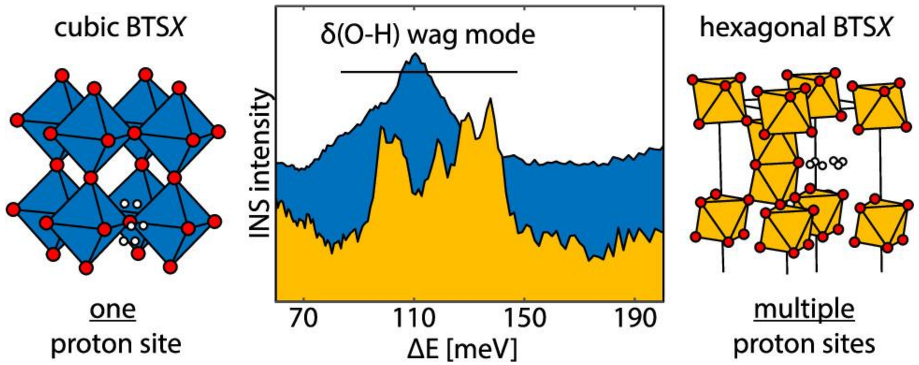
Scientific Interest :

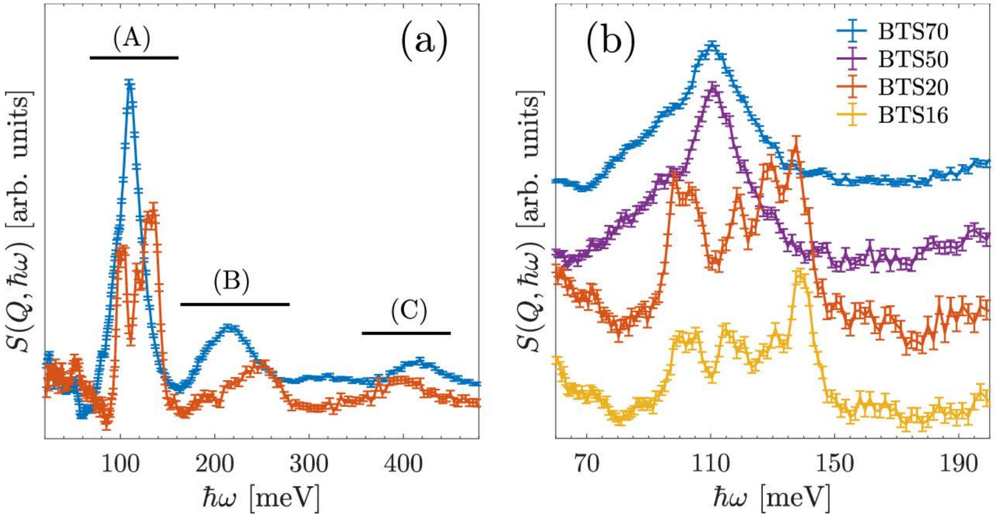
- Filtering and cleaning of biogas (CH_4) from CO_2
- Polymeric membranes production is cheap and easy to scale up but miss efficiency
- Composite materials (polymer matrix with metalo-organic frameworks (MOF) functionalized with amino acids) achieve superior permeability and selectivity values
- CO_2 and CH_4 access similar docking sites but CO_2 bonding energies are up to 3 times stronger

Proton Positions and Dynamics in Sc-doped $BaTiO_3$ and Ca_3CrN_3H

A. Perrichon et al., J. *Phys. Chem. C* 124 (2020)

- Potential electrolyte material for solid state fuel cells
- H conductivity in cubic structure 2 orders of magnitude higher



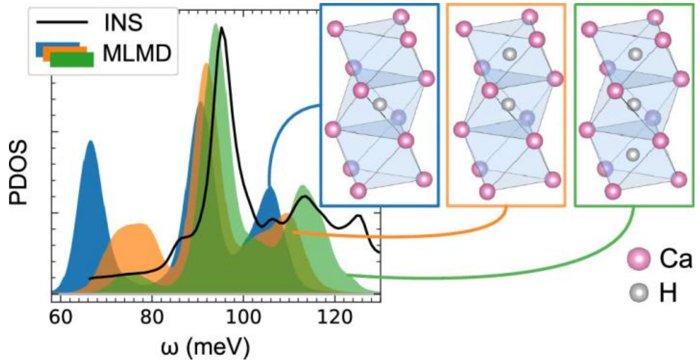


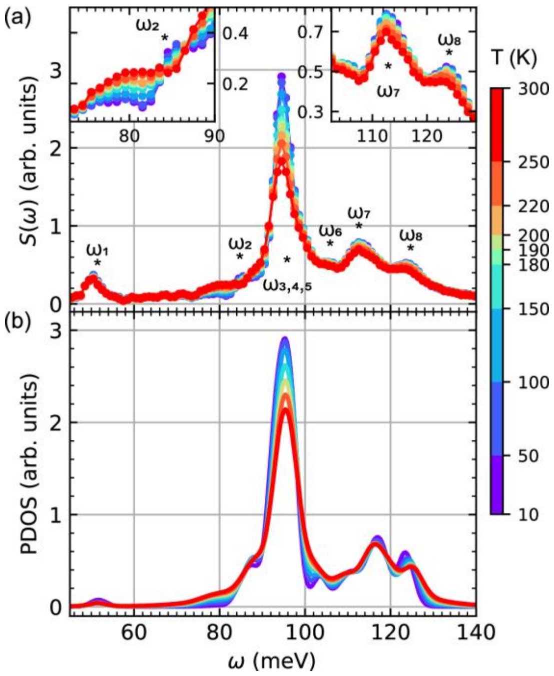
IN1-Lagrange

TOSCA@ISIS

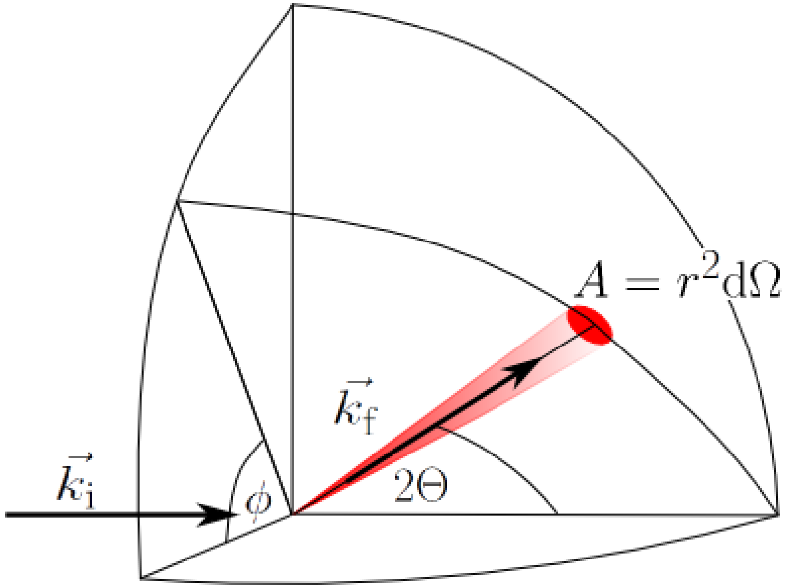
L. Fine et al., *Chem. Mater.* 37 (2025)

- Potential catalytic material for ammonia (NH_3) synthesis





Double Differential Scattering Cross Section



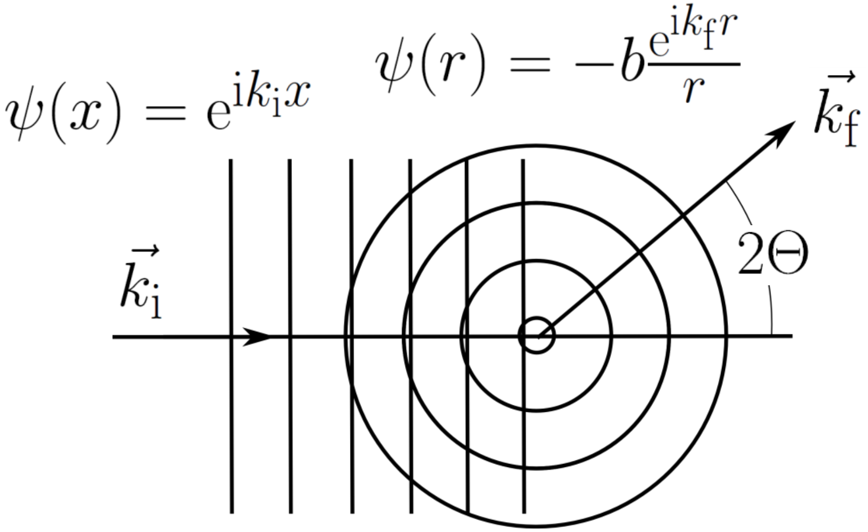
$d\Omega$: segment of solid angle

A : area at distance r from sample

k_i : initial wavevector of a neutron

k_f : final wavevector of a scattered neutrons

2θ, ϕ : polar coordinates characterizing the direction of scattered neutrons



Incident neutrons are characterized by plane waves, scattered neutrons by spherical waves. Justified as long as neutron source is far away and neutron wavelength larger than size of nuclei !

b = nuclear scattering length, amplitude of the scattering process.

b is a complex number, accounting as well for neutron absorption.

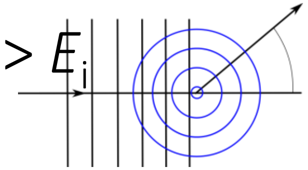
Double Differential Scattering Cross Section

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i}\left[\frac{\sigma_{inc}}{4\pi} S_{inc}(\vec{Q},\omega) + \frac{\sigma_{coh}}{4\pi} S_{coh}(\vec{Q},\omega)\right]$$

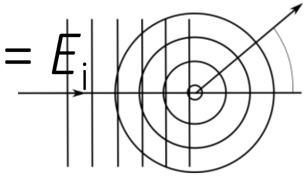
Phase space factor, property of initial (i) and final (f) neutron state (wavelength, wave vector, energy, ...)

Dynamic Structure Factor - DSF, comprises information on the physics of the material

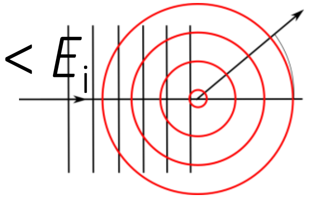
$E_f > E_i$



$E_f = E_i$



$E_f < E_i$



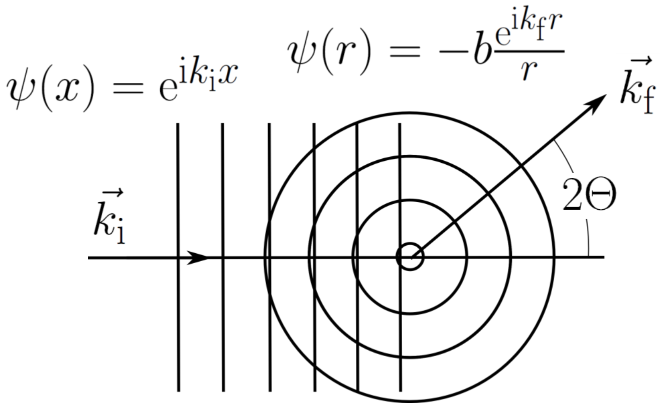
Scattering cross sections, effective areas of nuclei seen by the neutron

Common and

$$\sigma_{coh} = 4\pi \langle b \rangle^2$$

Individual character

$$\sigma_{inc} = 4\pi(\langle b^2 \rangle - \langle b \rangle^2)$$



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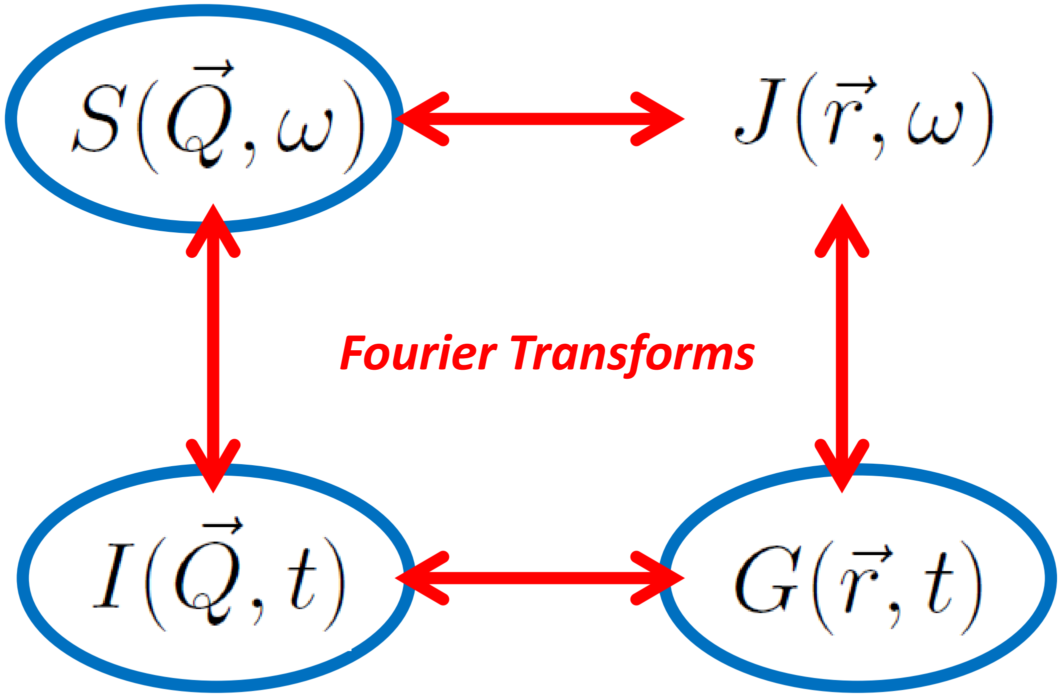
Observables in Neutron Spectroscopy

NEUTRONS
FOR SOCIETY

Observable in
ToF, TAS, BS

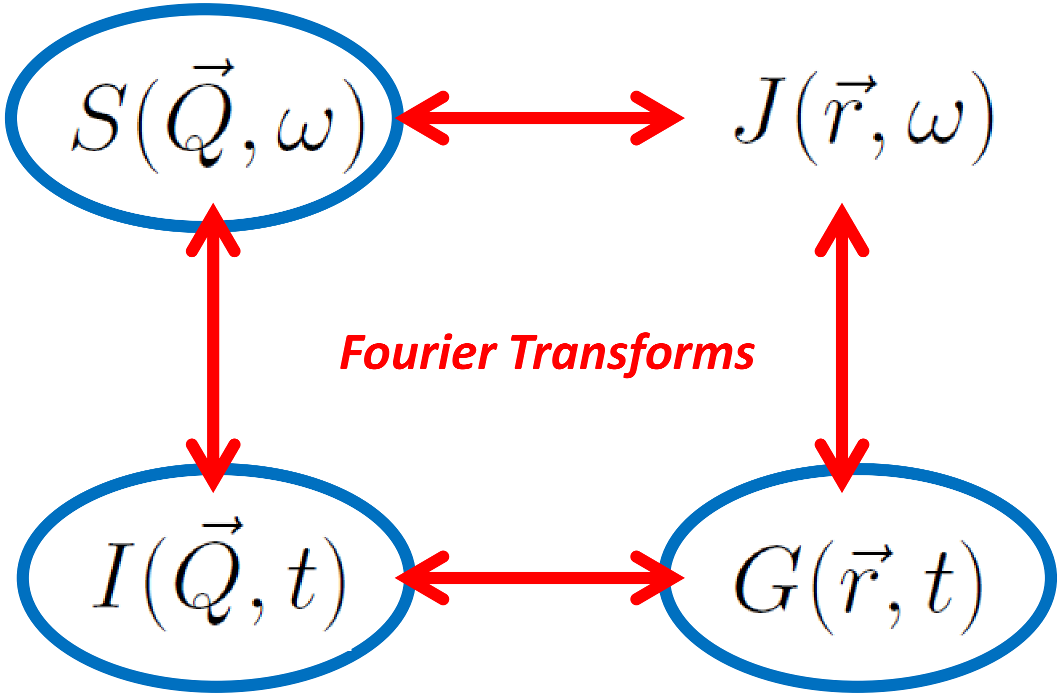


Observable in NSE,
basic models

Basic models,
computer simulations

Observables in Neutron Spectroscopy

Observable in
ToF, TAS, BS



Observable in NSE,
basic models

Basic models,
computer simulations

Dynamic Structure Factor

$$S_{\text{coh}}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int I(\vec{Q},t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t$$

$$S_{\text{inc}}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int I_{\text{s}}(\vec{Q},t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t$$

Intermediate Scattering Function :

$$I(\vec{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle \mathrm{e}^{-\mathrm{i}\vec{Q}\vec{r}_i(0)}\mathrm{e}^{\mathrm{i}\vec{Q}\vec{r}_j(t)}\right\rangle$$

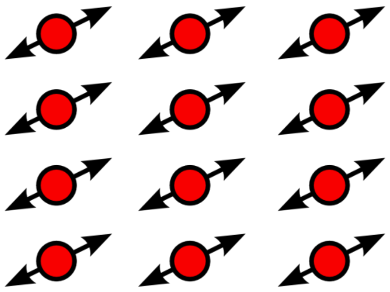
$$I_{\text{s}}(\vec{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\left\langle \mathrm{e}^{-\mathrm{i}\vec{Q}\vec{r}_i(0)}\mathrm{e}^{\mathrm{i}\vec{Q}\vec{r}_i(t)}\right\rangle$$

Van Hove Correlation Function :

$$S_{\text{coh}}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int\int G(\vec{r},t)\mathrm{e}^{\mathrm{i}(\vec{Q}\vec{r}-\omega t)}\mathrm{d}\vec{r}\mathrm{d}t$$

$$S_{\text{inc}}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int\int G_{\text{s}}(\vec{r},t)\mathrm{e}^{\mathrm{i}(\vec{Q}\vec{r}-\omega t)}\mathrm{d}\vec{r}\mathrm{d}t$$

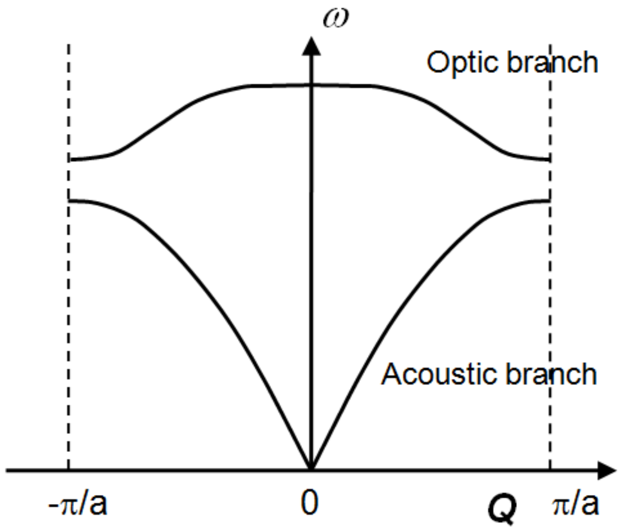
Phonons, Collective Vibrations

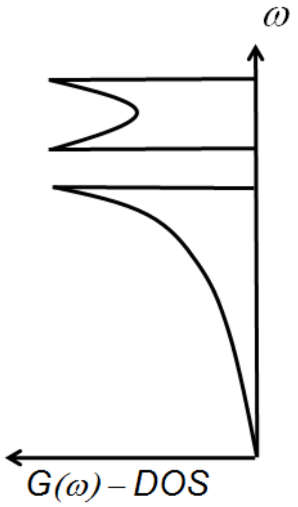


$$\vec{r}_i(t) = \vec{R}_i + \vec{u}_i(t)$$

$$I(\vec{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle e^{-i\vec{Q}\vec{r}_i(0)} e^{i\vec{Q}\vec{r}_j(t)}\right\rangle$$

$$I_s(\vec{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\left\langle e^{-i\vec{Q}\vec{r}_i(0)} e^{i\vec{Q}\vec{r}_i(t)}\right\rangle$$





Phonon Dispersion

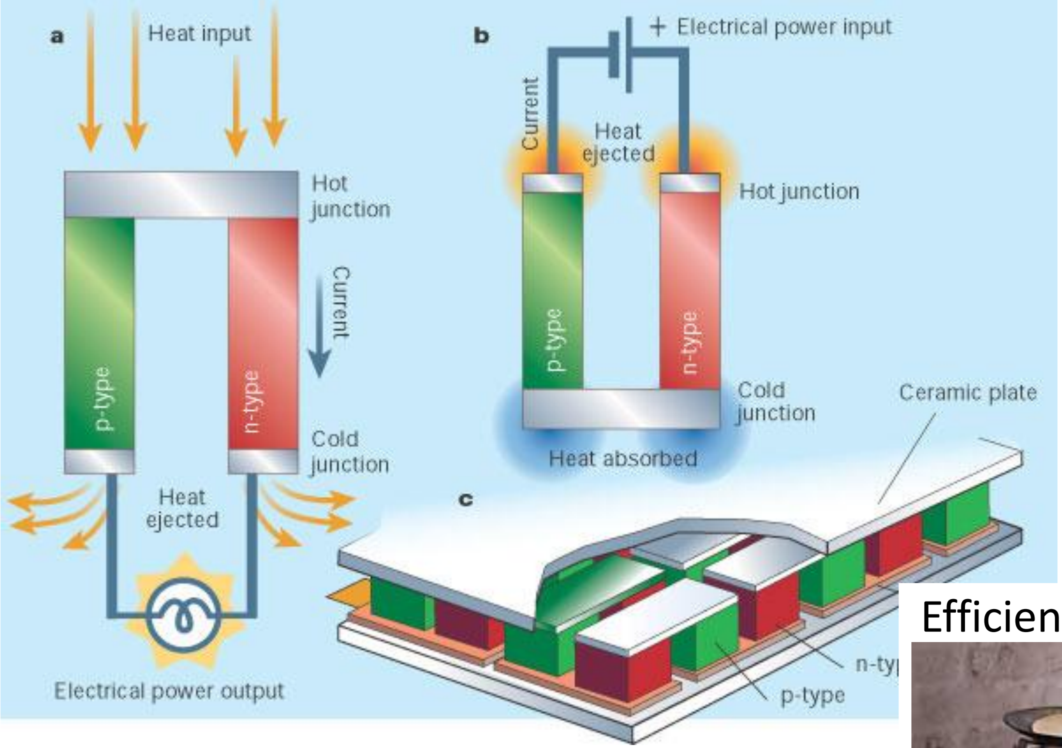
$$S^{(1)}_{\text{coh}}(Q,\omega) \sim \frac{n(\omega,T)}{\omega} e^{-W(Q,T)} \times \sum_{i,j,l} e^{i\vec{Q}(\vec{R}_i - \vec{R}_j)} \frac{(\vec{Q}\cdot\vec{\epsilon}^{\,l}_i)(\vec{Q}\cdot\vec{\epsilon}^{\,l}_j)}{M}\delta(\omega \pm \omega_{i,l})$$

Phonon Density of States

$$S^{(1)}_{\text{inc}}(Q,\omega) \sim \frac{n(\omega,T)}{\omega}\frac{Q^2}{M} e^{-W(Q,T)} \sum_{i,l}\delta(\omega \pm \omega_{i,l})$$

Thermoelectric Power Management

Cronin B. Vining, Nature 413 (2001)



Cooling Power Supply

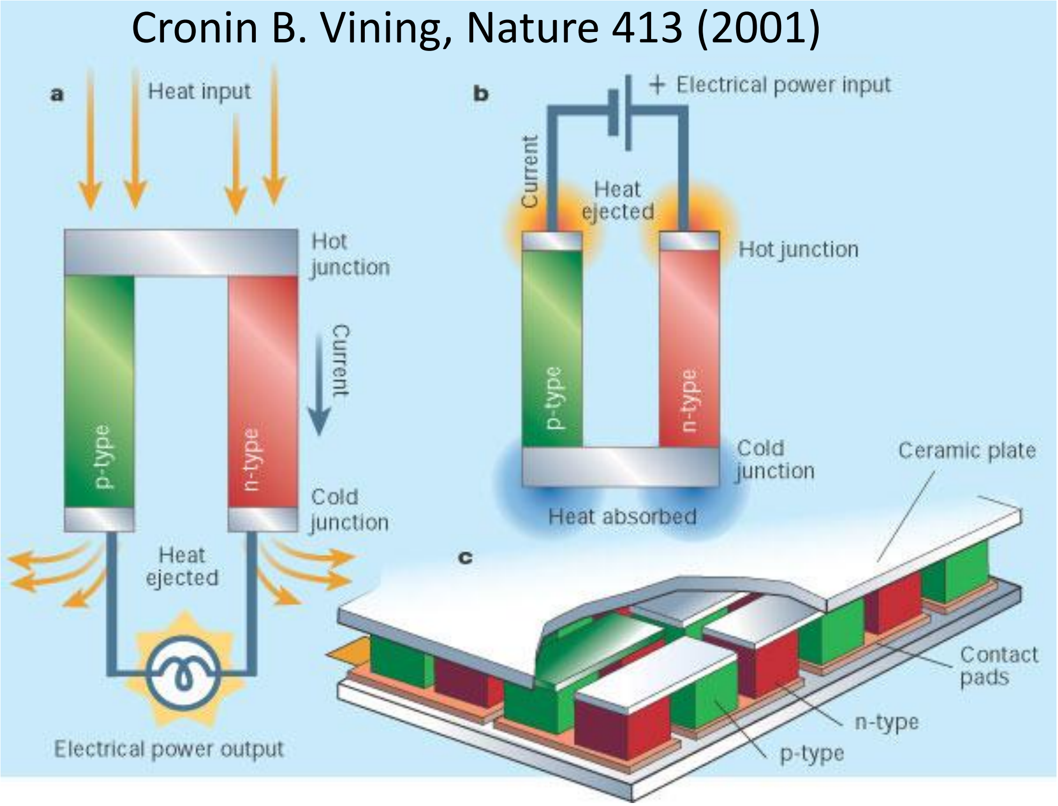
Electrical Power Supply

Efficiency Gains

Waste Heat Recovery

Thermoelectric Power Management

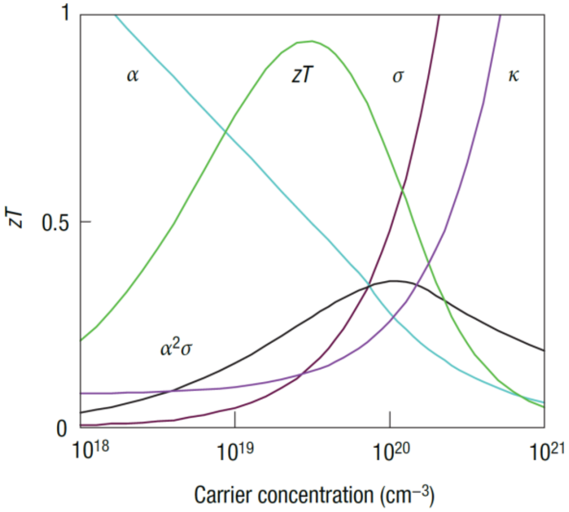
Cronin B. Vining, Nature 413 (2001)



Thermoelectric Figure of Merit ZT :

$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_l} T$$

S = Seebeck coefficient (dV/dT)
σ = electrical conductivity
κ_e = electronic thermal conductivity
κ_l = lattice thermal conductivity



Snyder G.J. et al., Nature Materials 7 (2008)

Lattice Thermal Conductivity and Peierls – Boltzmann Theory

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$$\kappa_l = \frac{1}{3} C_V v l = \frac{1}{3} C_V v^2 \tau = \frac{1}{3} C_V v^2 \frac{1}{\Gamma}$$

C_V heat capacity, v sound velocity, l mean free path

Phonon Density of States

ToF on Polycrystals, Powders

Phonon Dispersion

ToF + TAS with Single Crystals

Phonon Lifetime

TAS-NSE
with Single Crystals

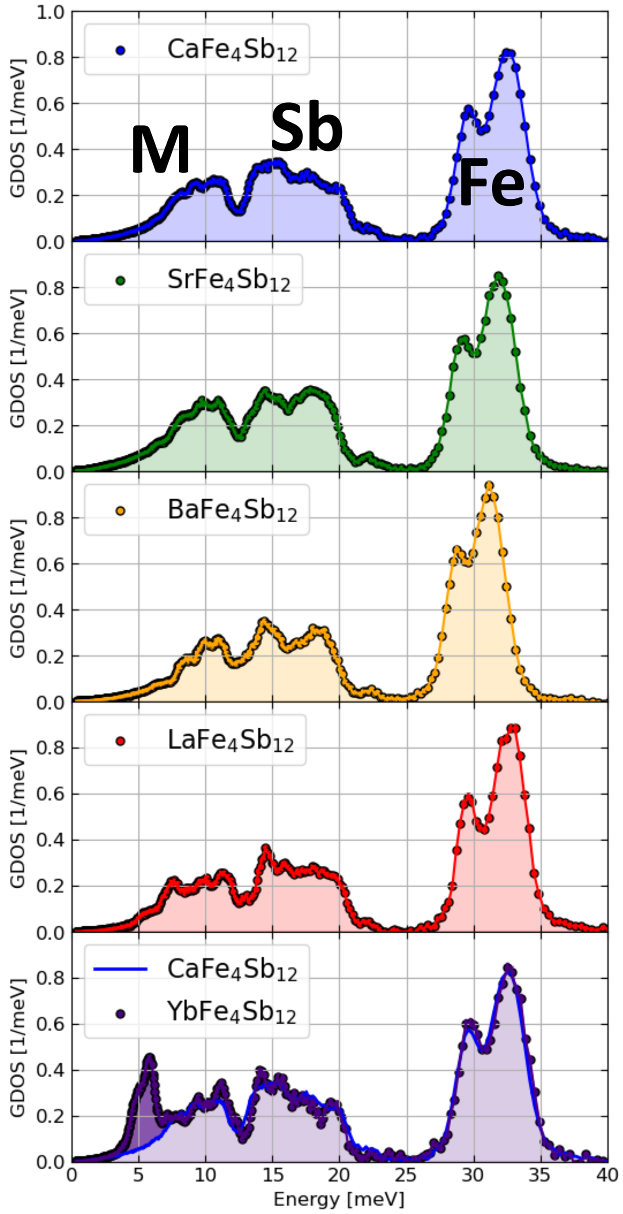
Phonon Linewidth

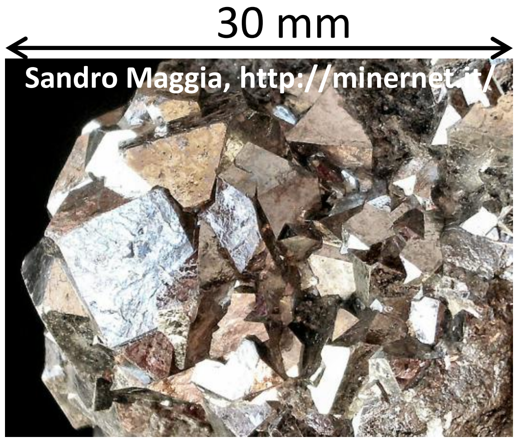
ToF + TAS
with Single Crystals

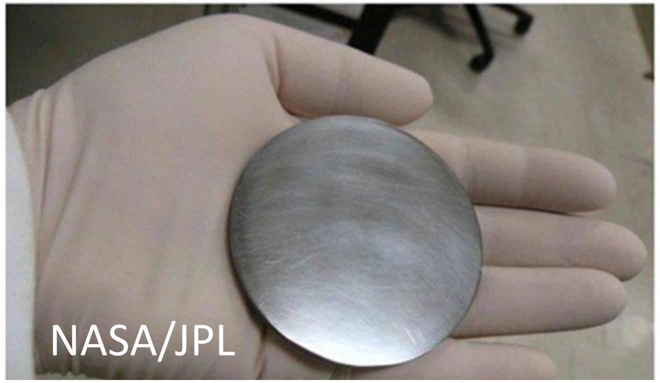
Solid State Diffusion

ToF + BS and NSE

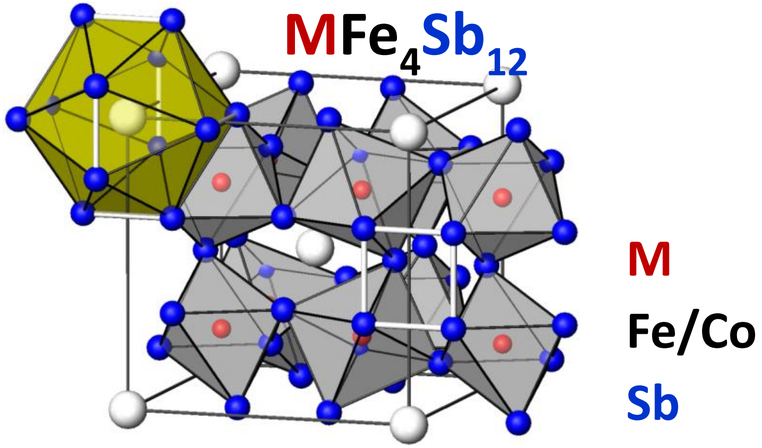
Phonons in Skutterudites

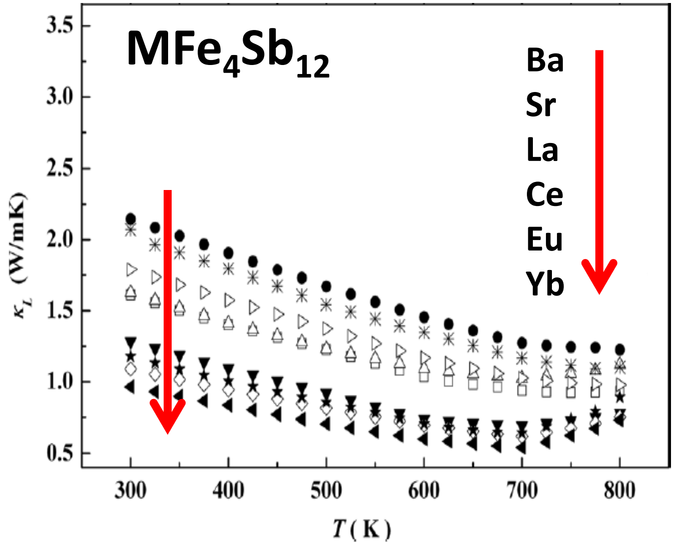






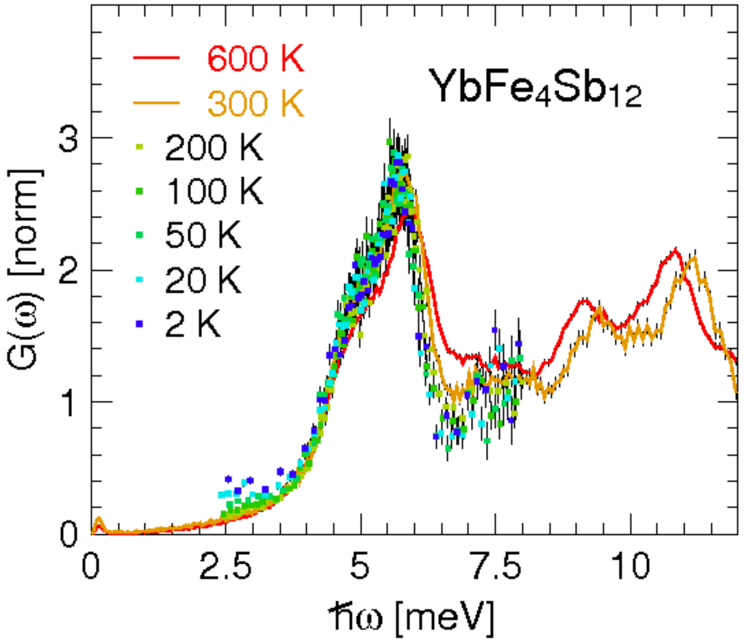
NASA/JPL/DoE :
Since 2016 development of new thermoelectric modules based on Skutterudite materials with increased efficiency (+25%) and durability than present devices.

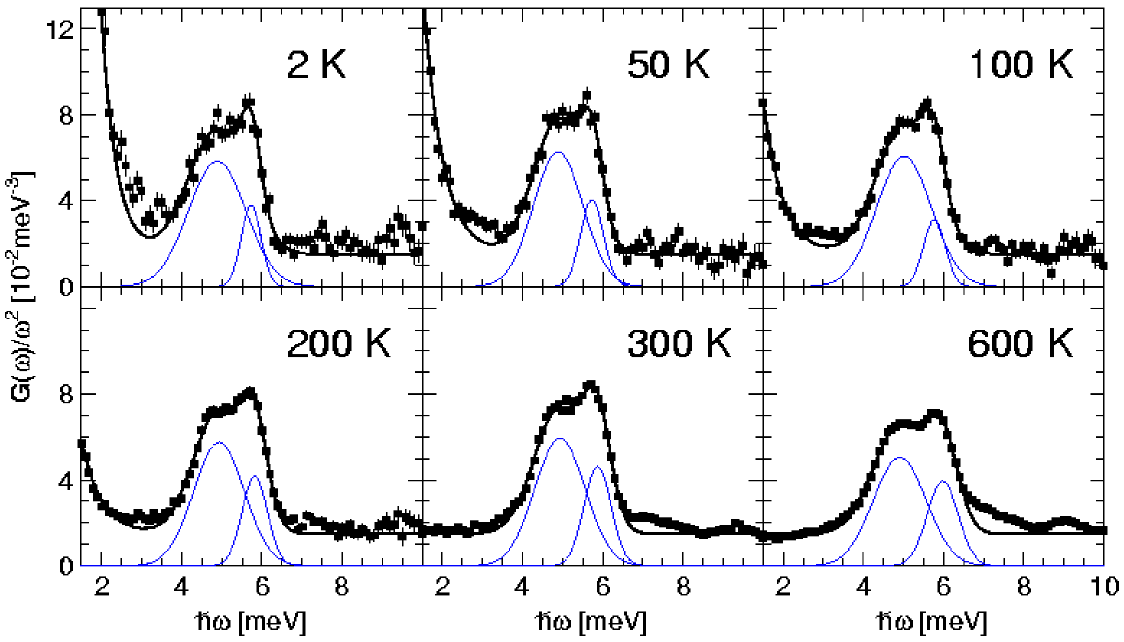




P.F. Qiu et al., J.Appl.Phys. 109 (2011)

Phonon Response to Temperature and Pressure Changes



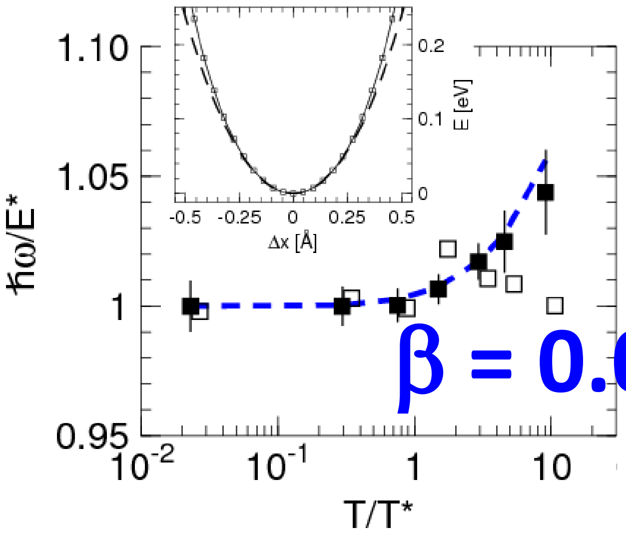


Single Isolated Particle in a Quartic Potential :

T. Dahm & K. Ueda, Phys. Rev. Lett. 99, 187003 (2007)

$$U(x) \approx A \cdot \Delta x^2 + B \cdot \Delta x^4$$

$$\beta \propto B/amu^2/\omega_o^3$$



$\beta = 0.013(3)$

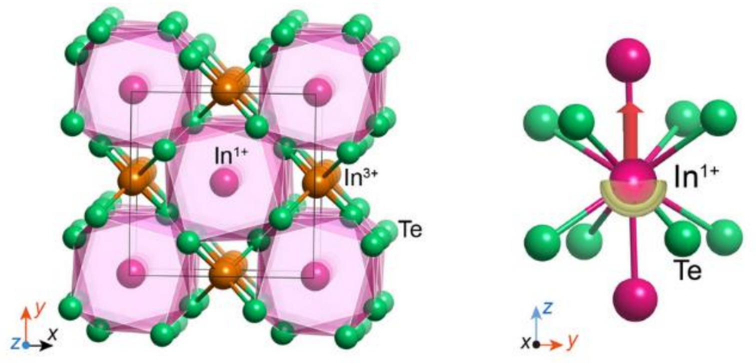
Lone Pair Expression as Origin of Giant Phonon Anharmonicity

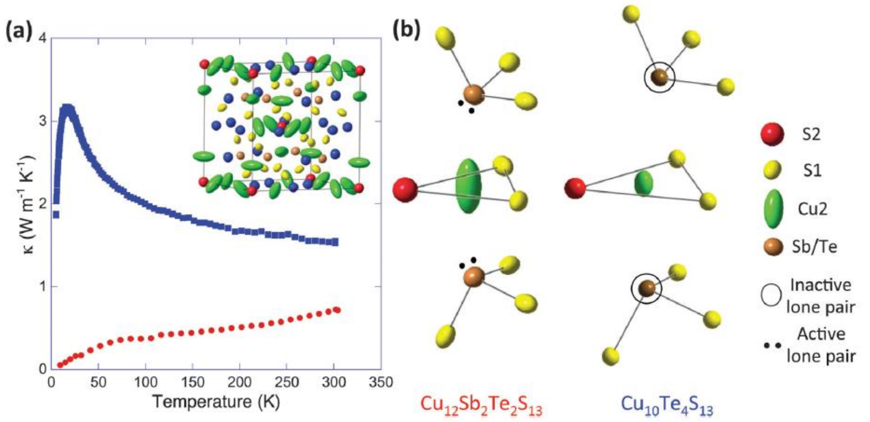
NEUTRONS FOR SOCIETY

J. Zhang et al., *Angew.Chem.Int.Ed.* 62 (2023)

Y. Bourie et al., *Phys.Chem.Chem.Phys*. 17 (2015)

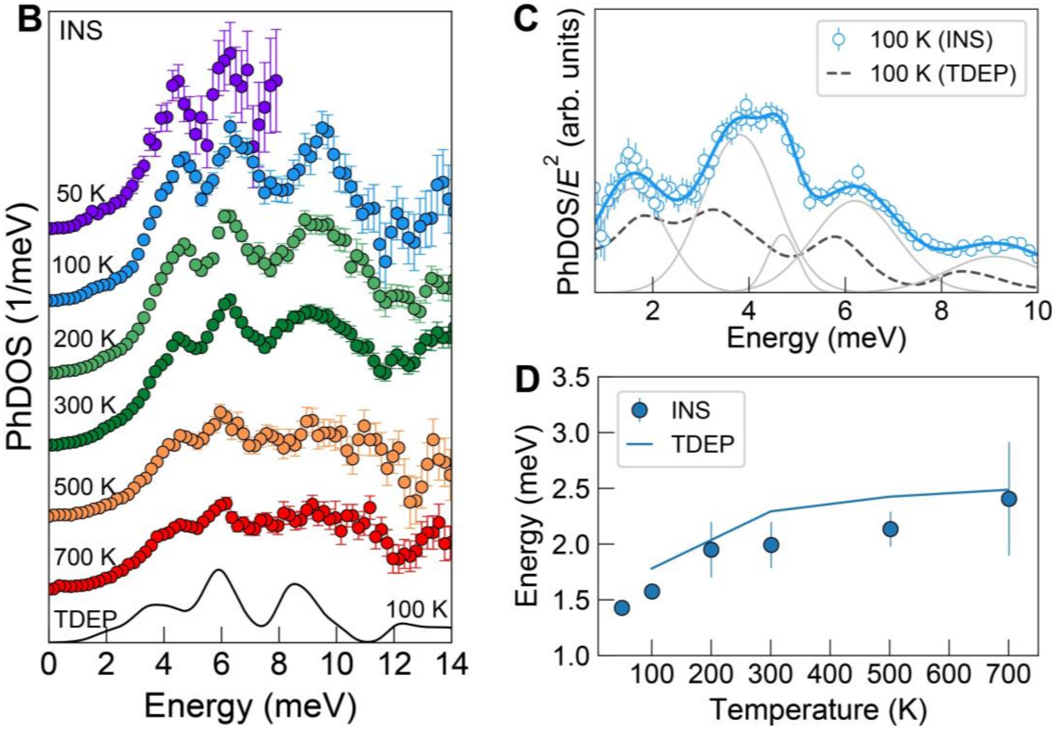
InTe

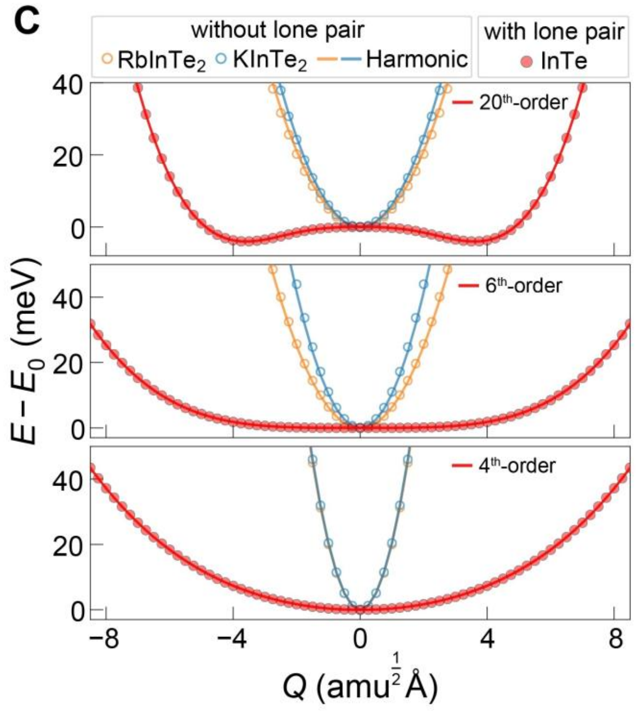


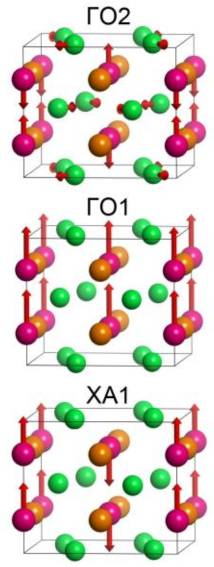


$Cu_{10}Te_4S_{13}$

$Cu_{12}Sb_2Te_2S_{13}$



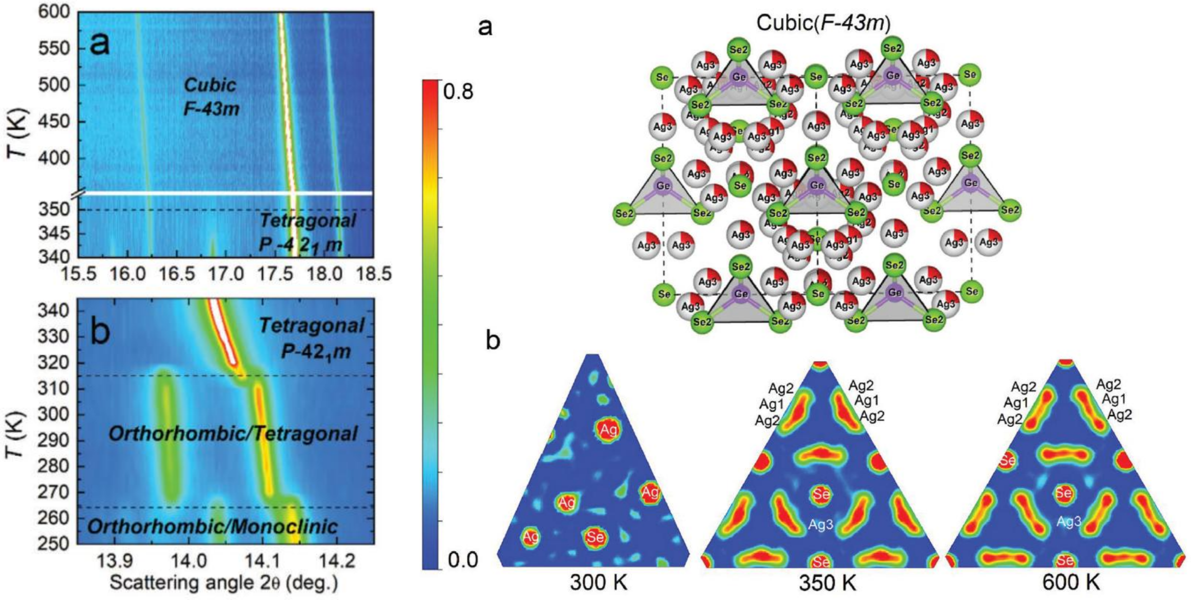


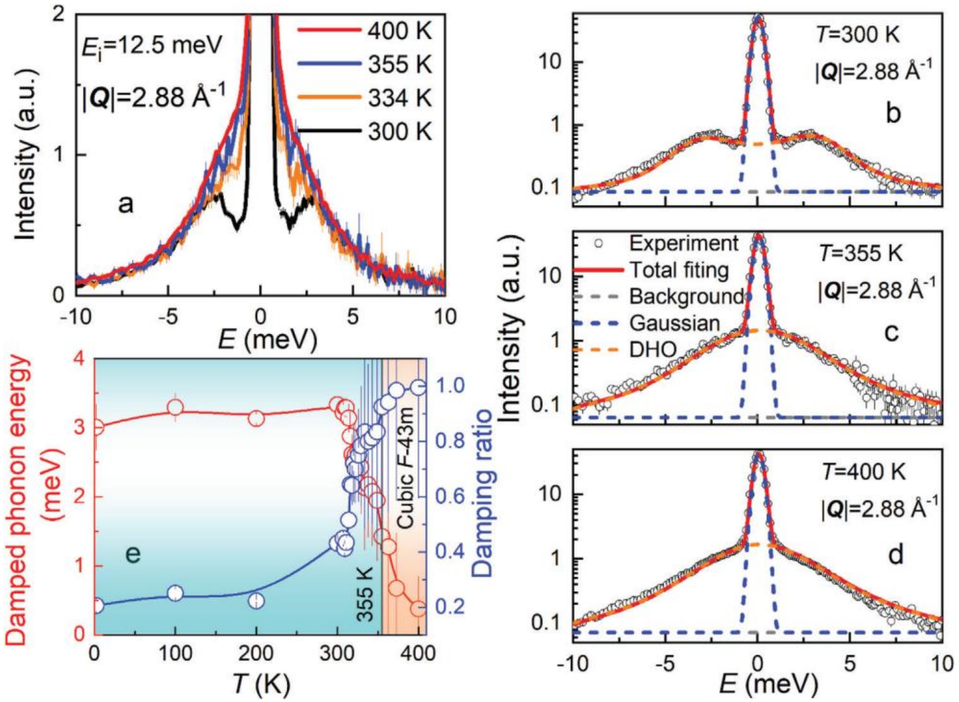


From Thermoelectrics to Super-Ionic Conductors

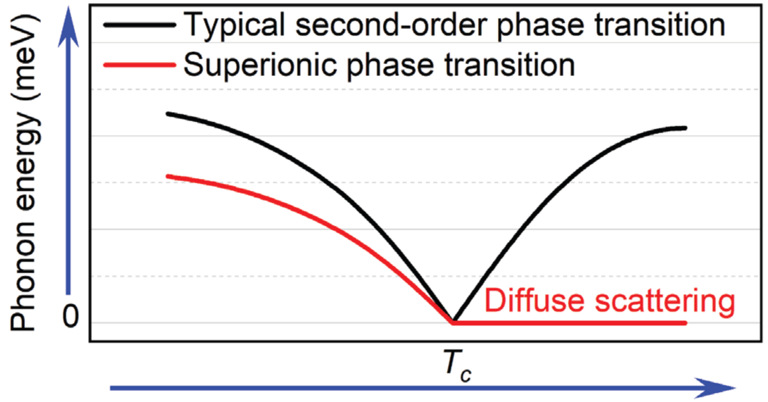
NEUTRONS FOR SOCIETY

Ag8GeSe6, X. Shen et al. *SMALL2023* 19 (2023)



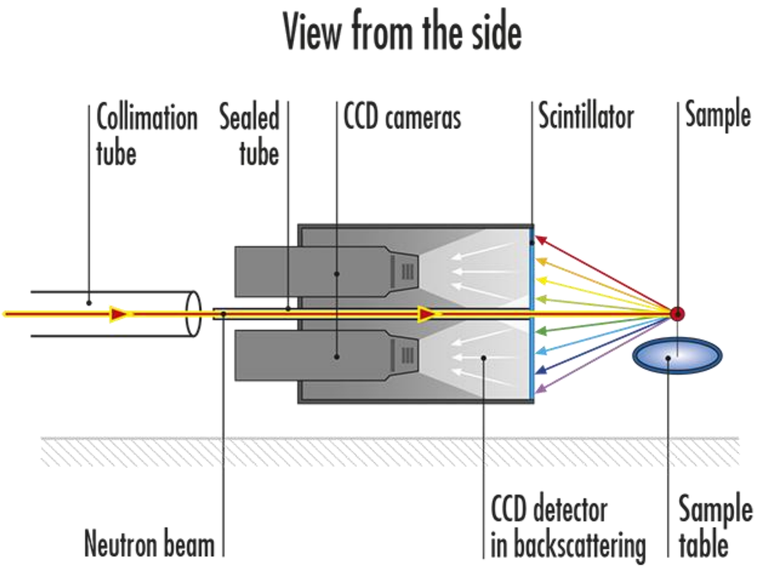


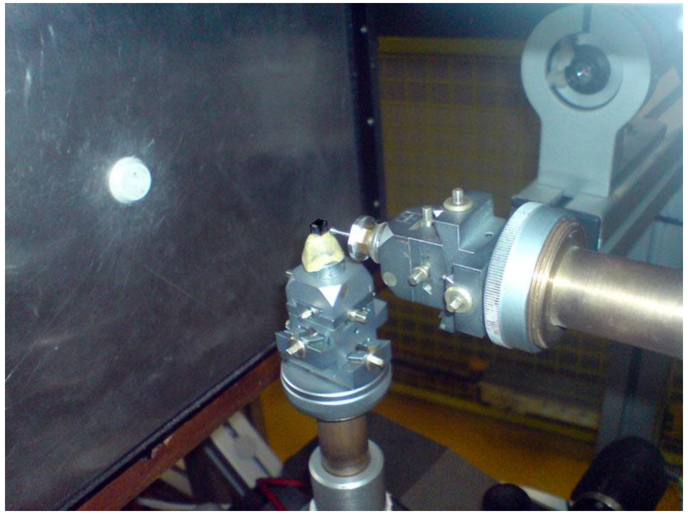
Cu_2Se, Liu H. et al., *Nature Materials* 11 (2012)
Cu_2Se, Voneshen D.J. et al., *Phys.Rev.Lett.* 118 (2017)
Ag_8SnSe_6, Q.Ren et al., *Nature Materials* (2023)

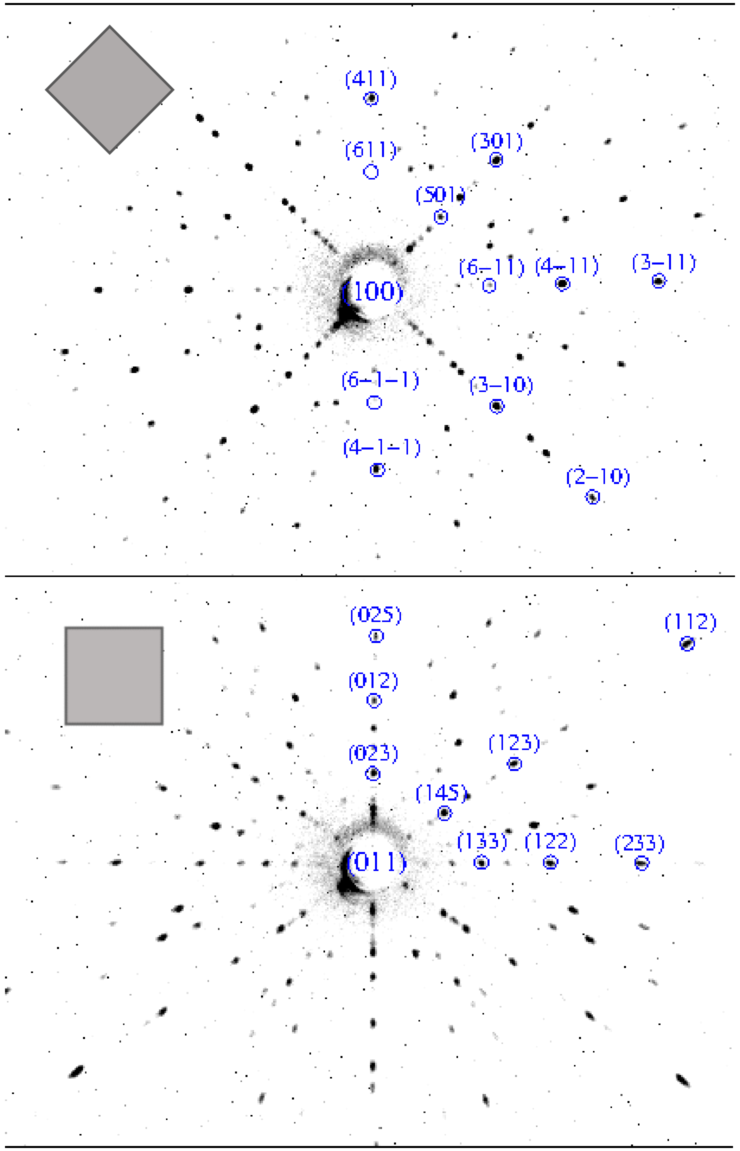


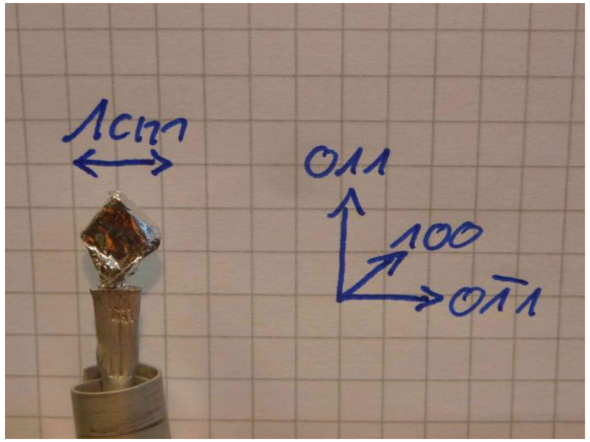
Single Crystal Experiments

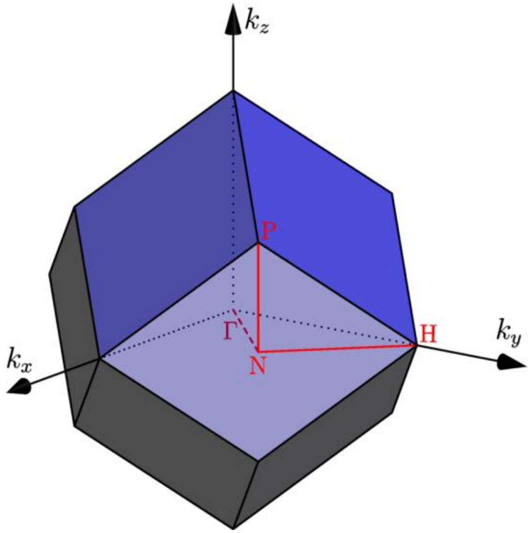
OrientExpress : Neutron Laue Camera





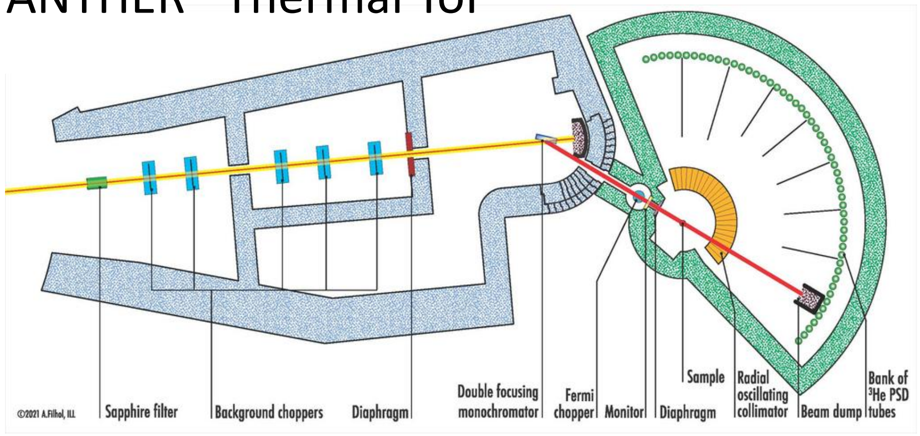




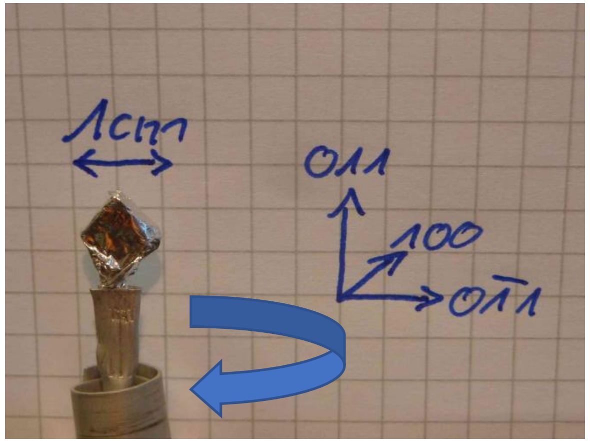


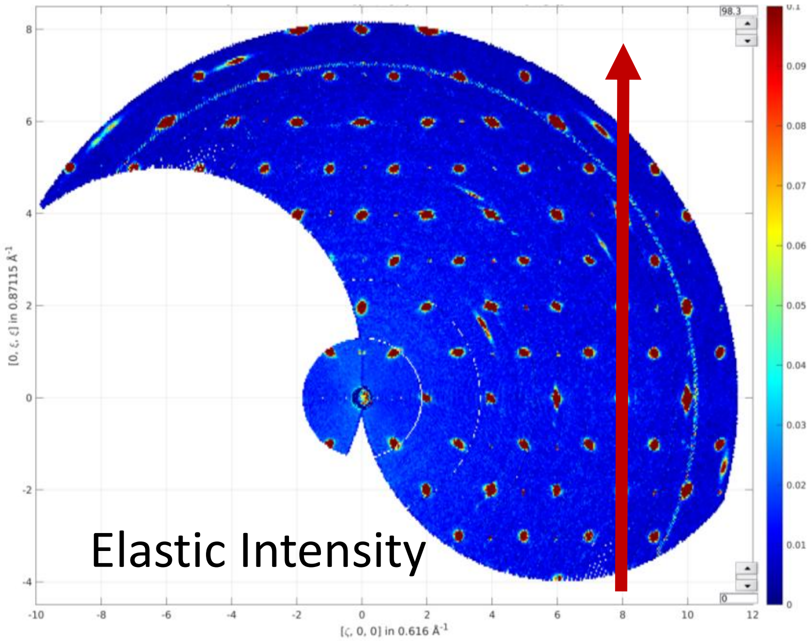
Single Crystal Experiments

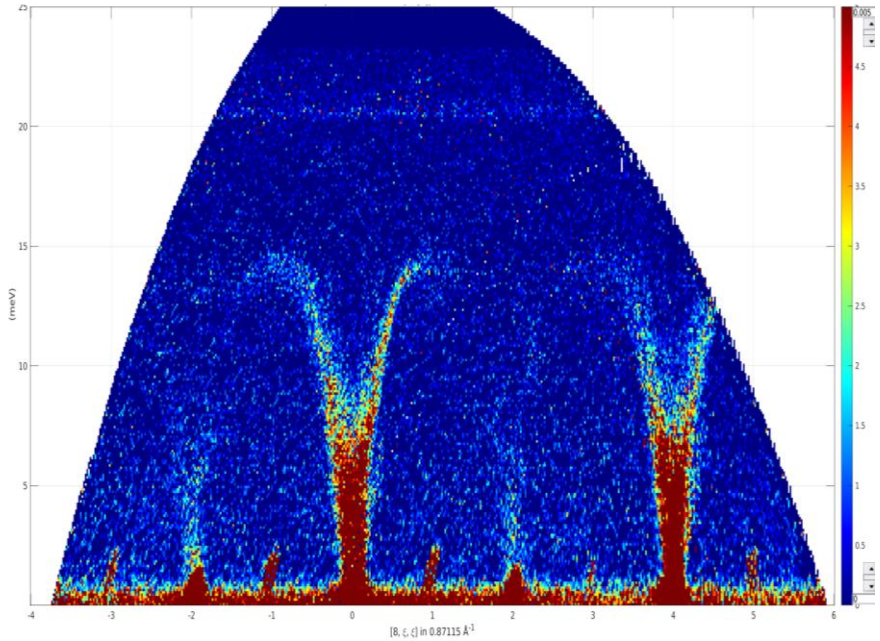
PANTHER –Thermal ToF

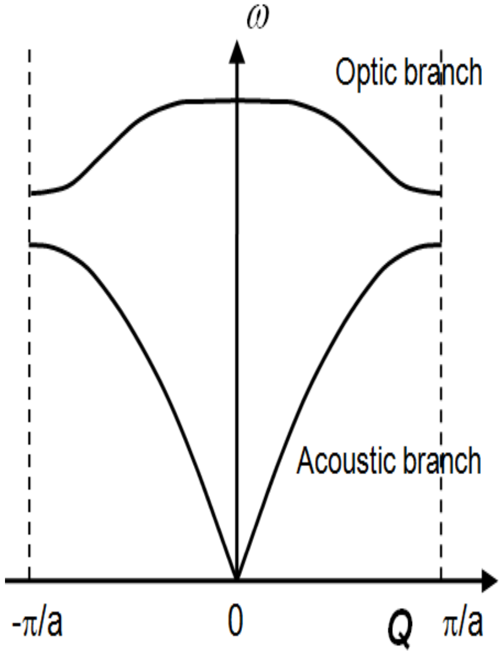


ToF measurement of successive sample orientations, such as Δα = 120° total rotation angle with 1° increment and 1-5 min. acquisition time.





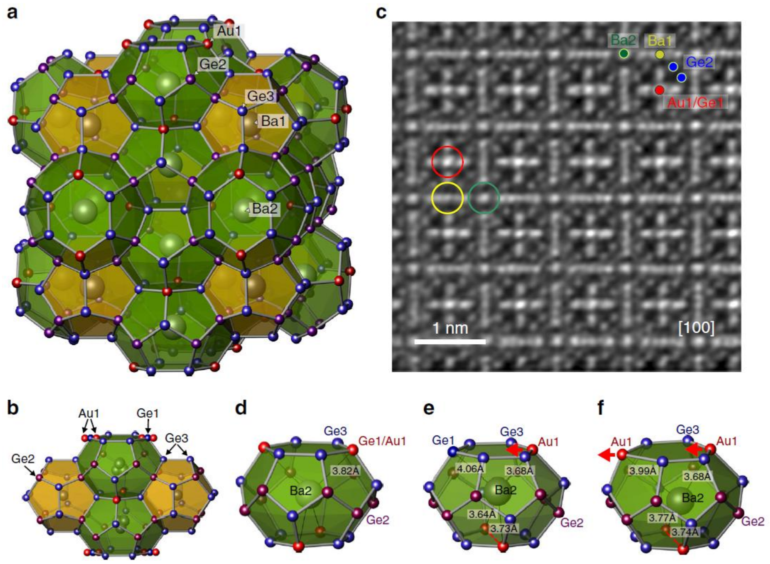


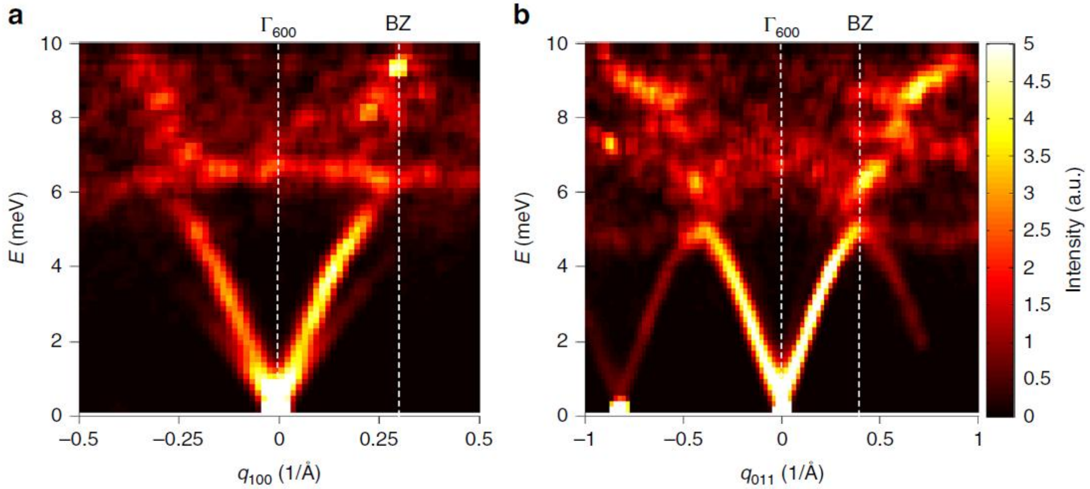


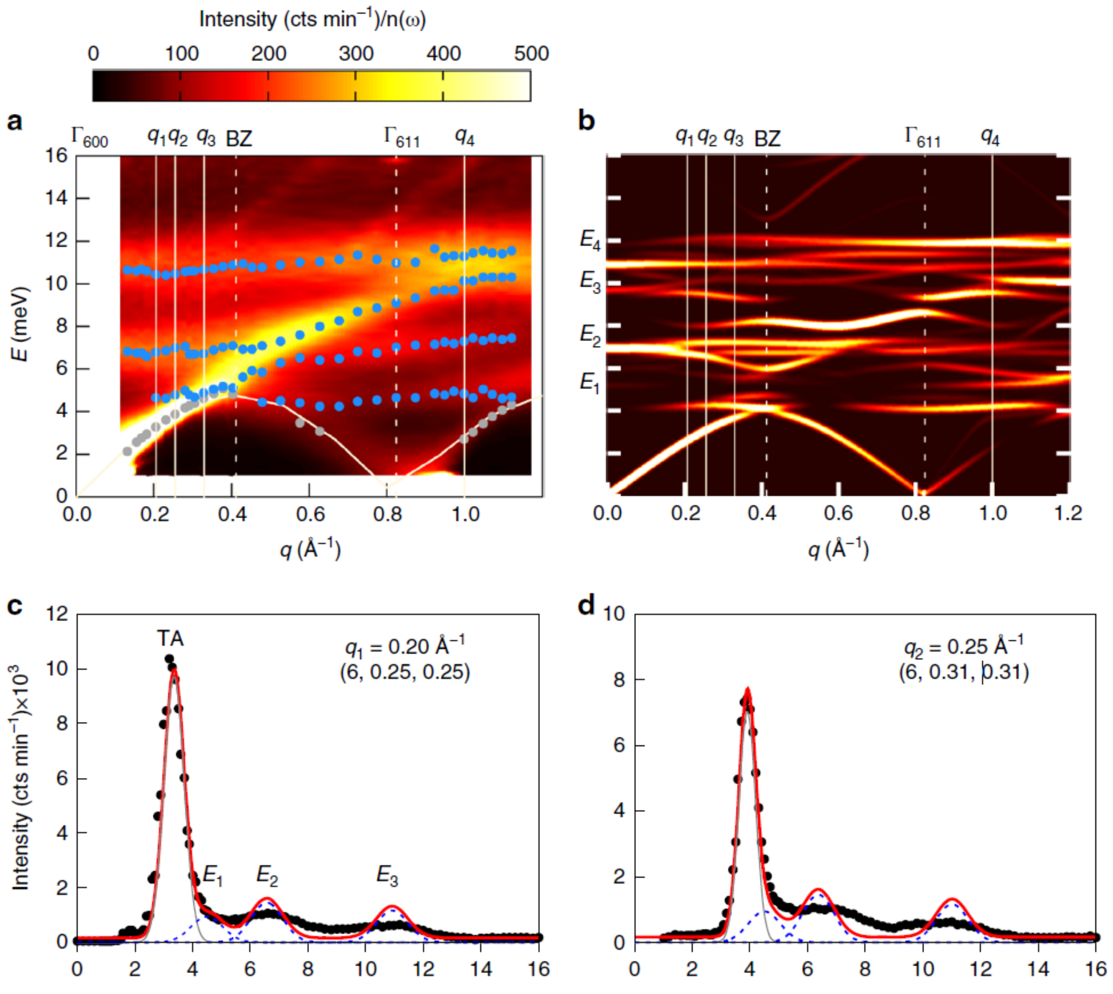
Phonons in Thermoelectric Clathrates

P.F. Lory et al., *Nature Comm.* 8 (2017)

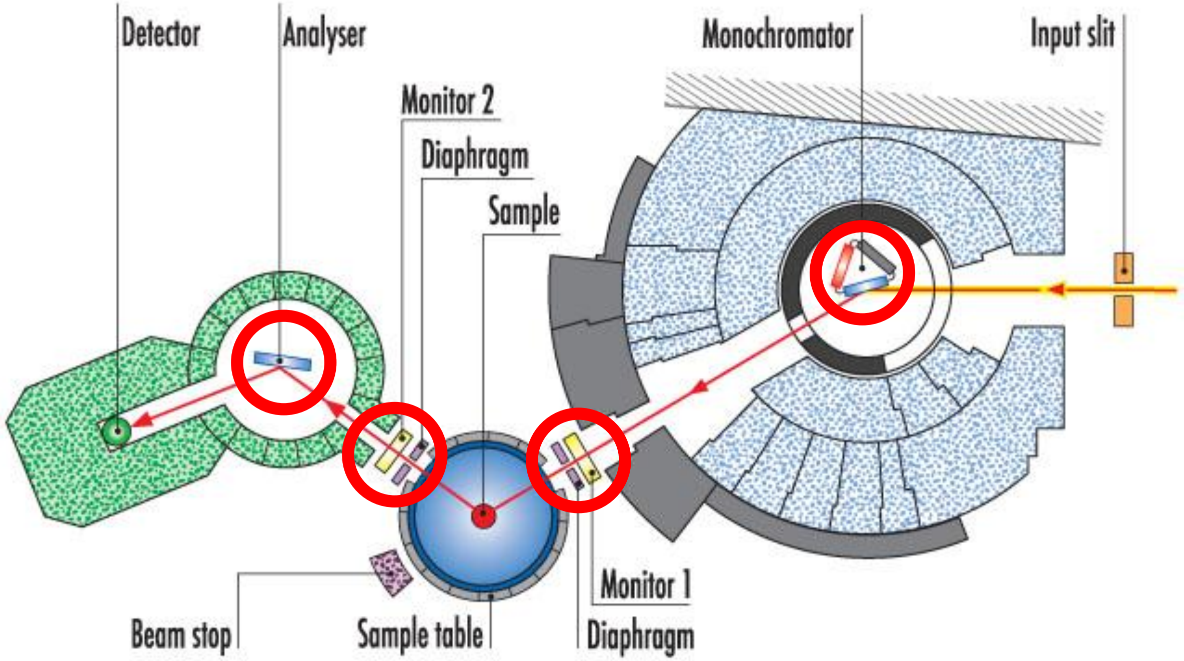
Phonon dispersion and lifetimes in $Ba_{7.81}Ge_{40.67}Au_{5.33}$





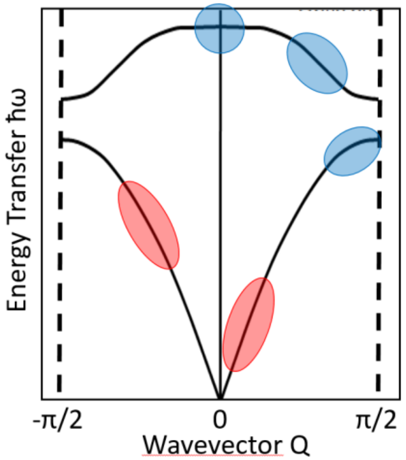


Three Axis Spectrometers



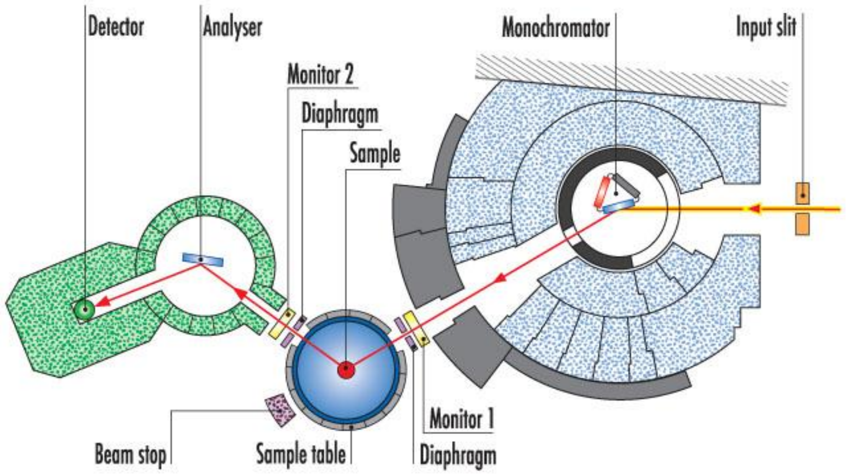
IN8 Thermal Neutron TAS

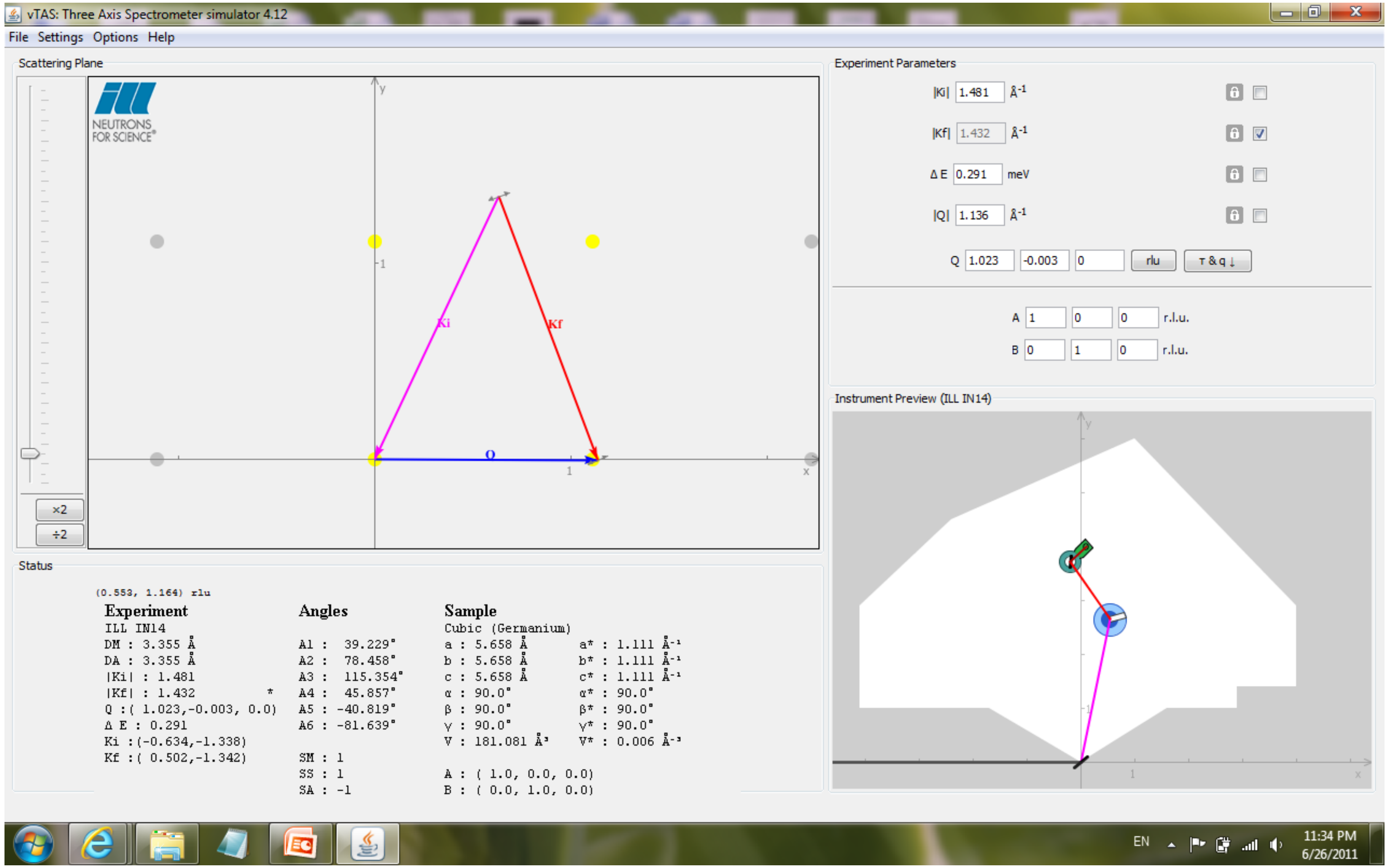
Exchangeable and variable optic components



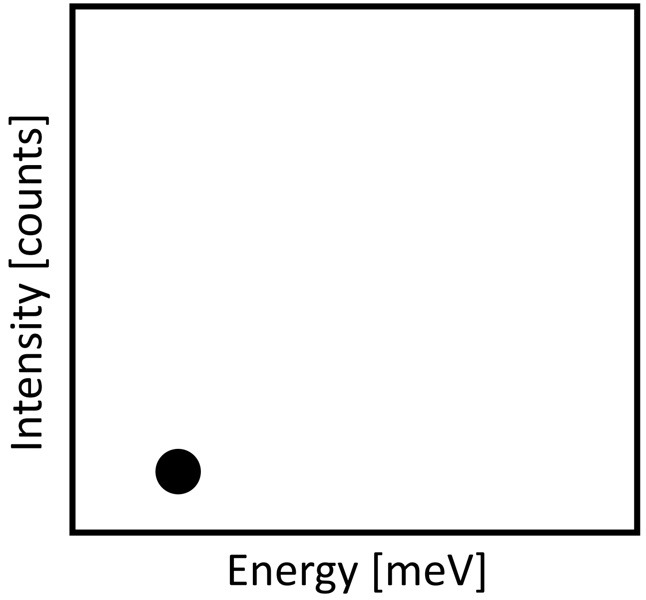
Instrument	unpolarized	polarized
IN12 CRG	2-42 meV	2-42 meV
THALES	2-20 meV	2-20 meV
IN8	15-100 meV	
IN20	18-42 meV	15-130 meV
IN22	15-35 meV	15-35 meV

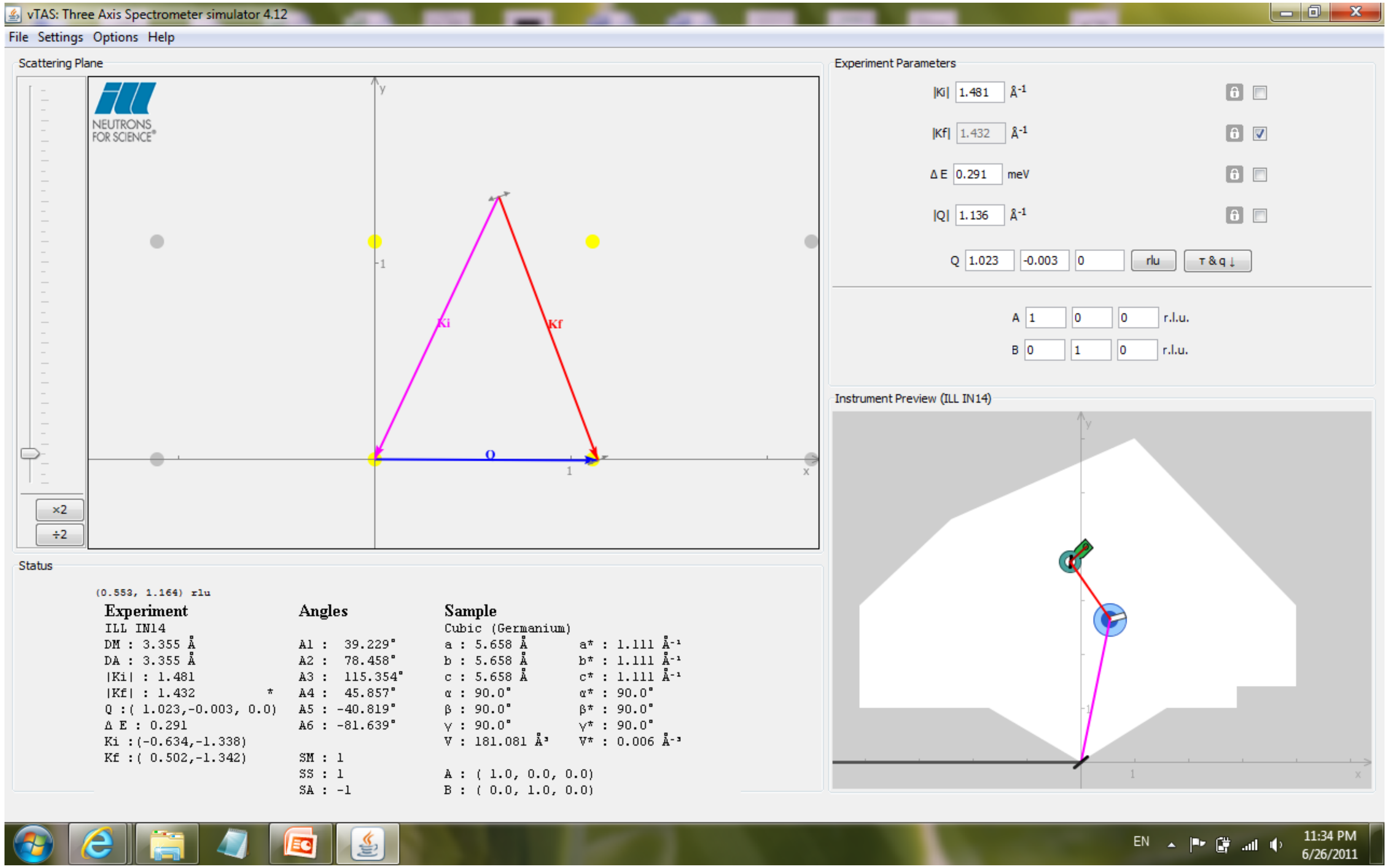
Three Axis Experiment





Three Axis Experiment





Three Axis Experiment

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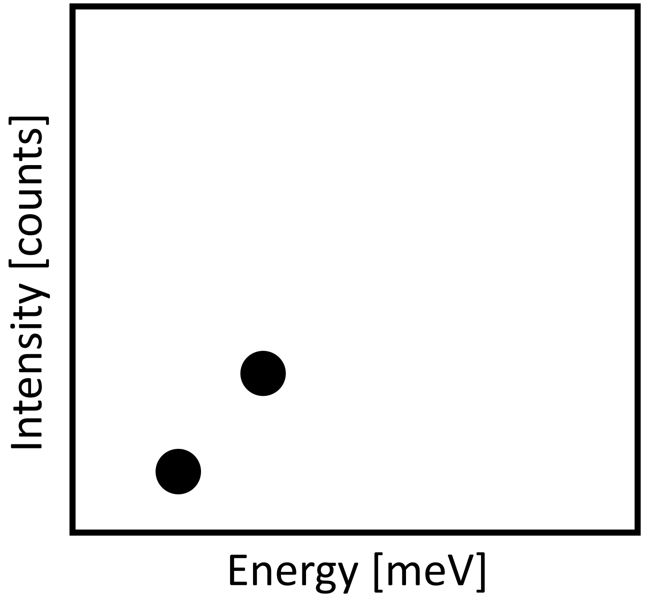
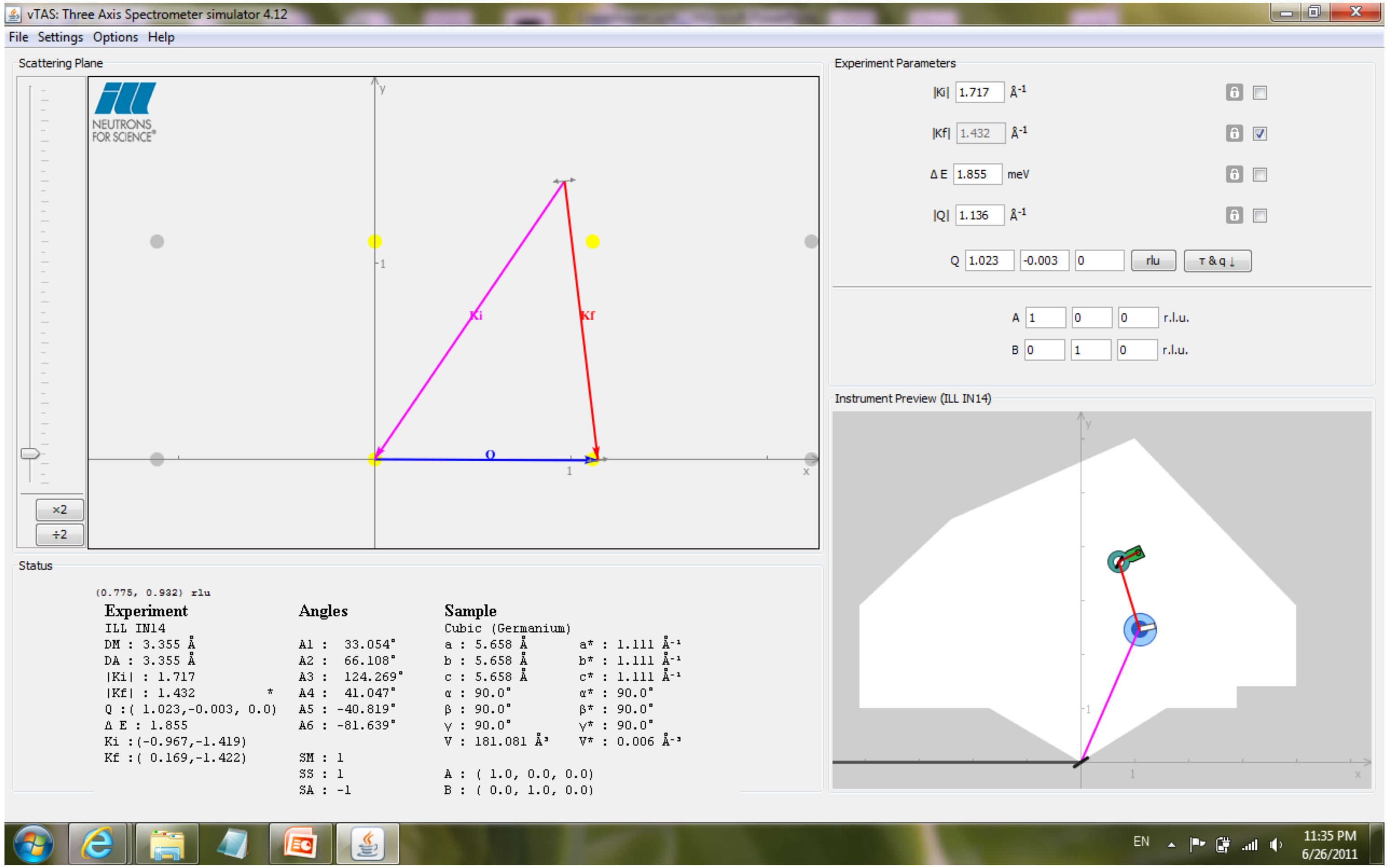
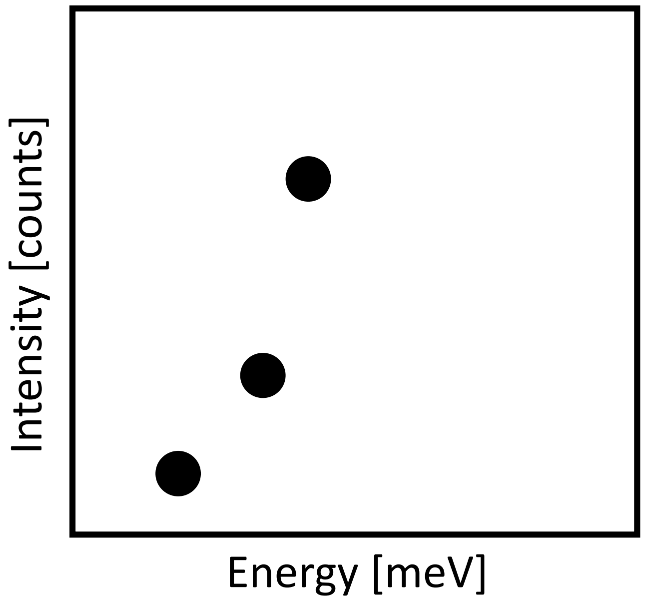
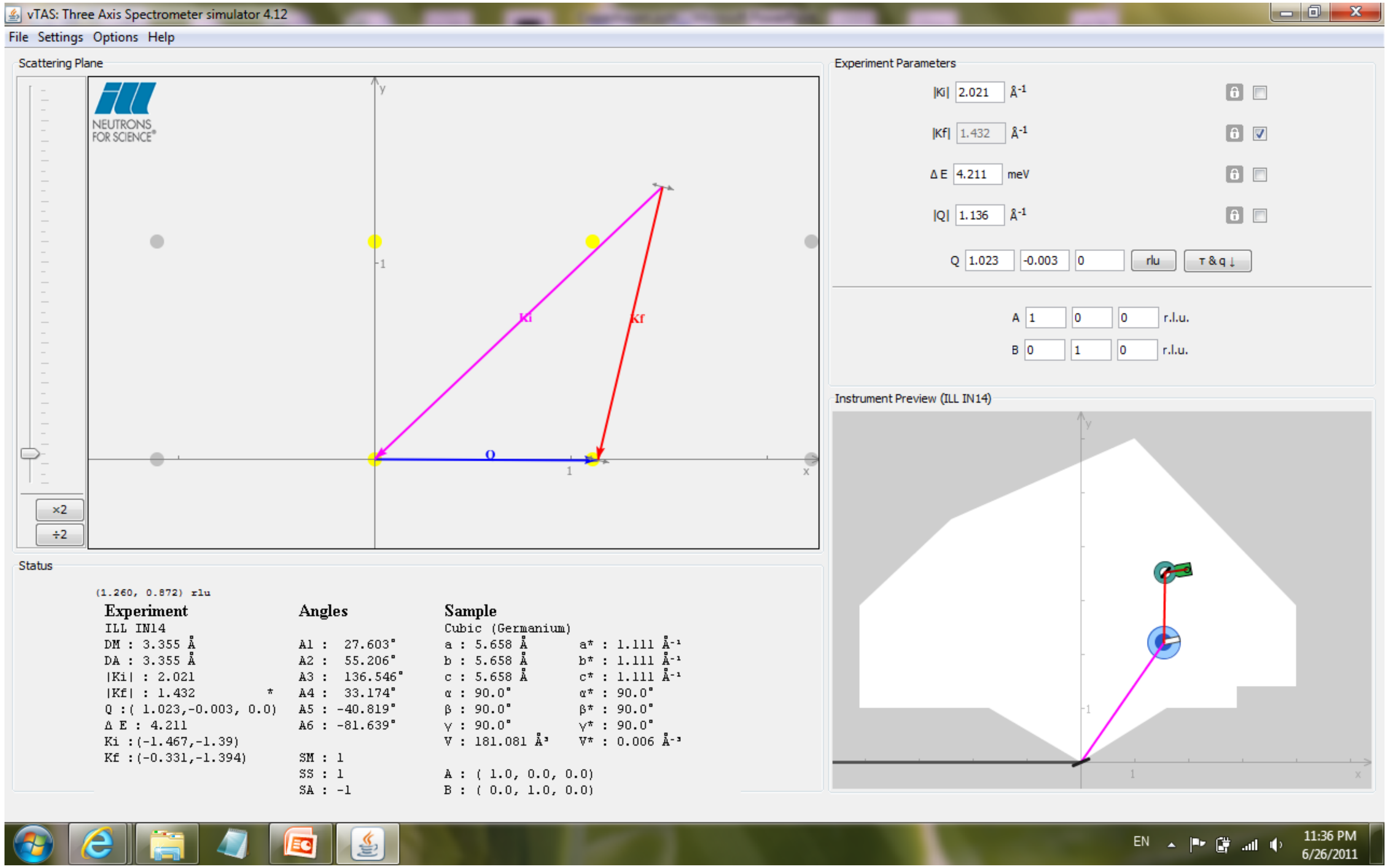




Three Axis Experiment





Three Axis Experiment

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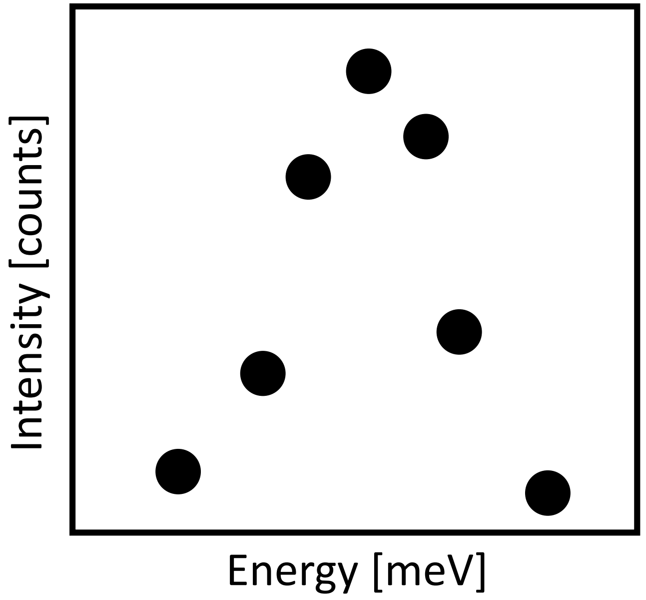
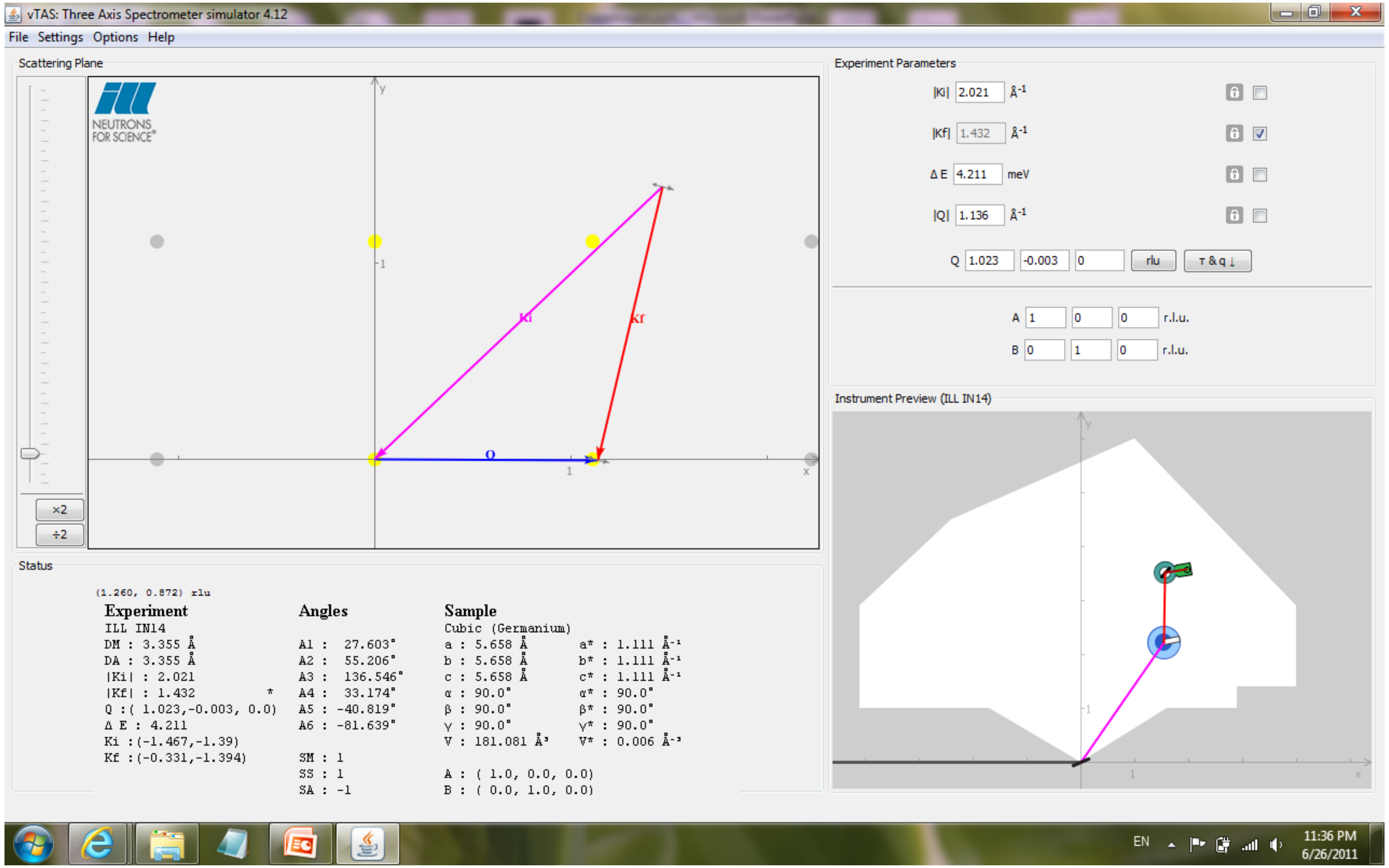
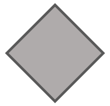
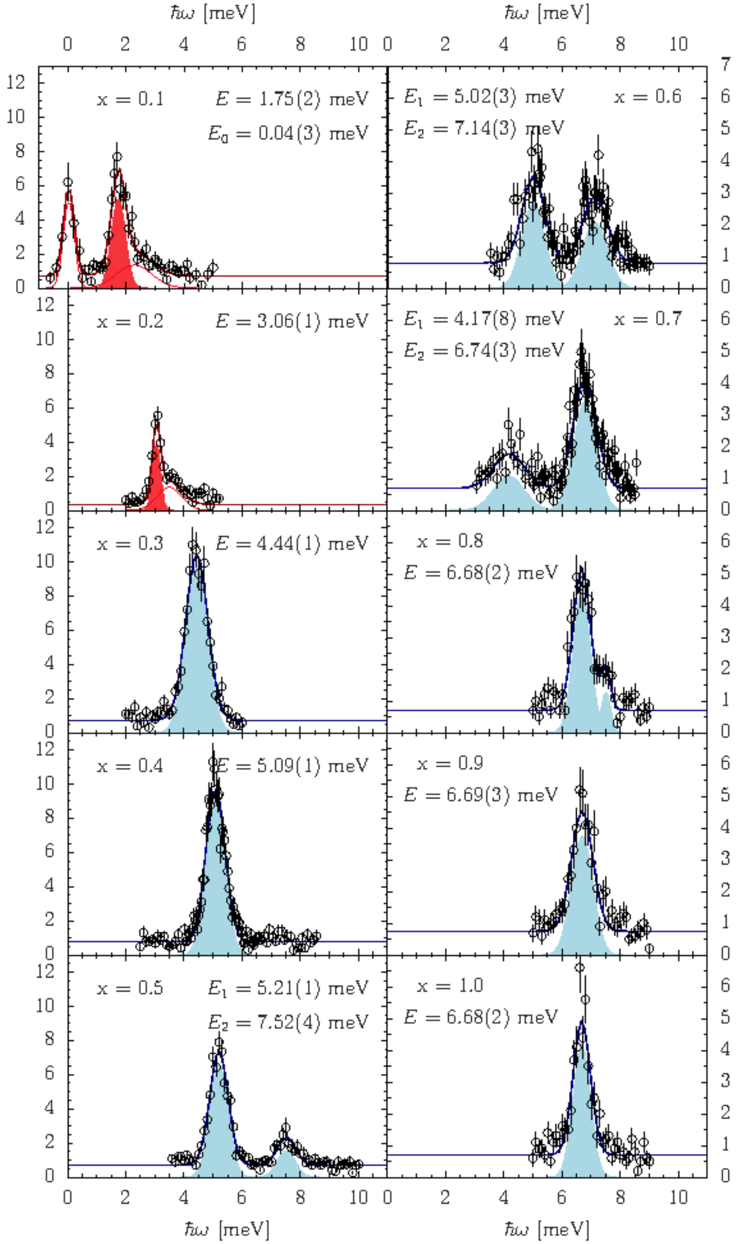
FOR SOCIETY



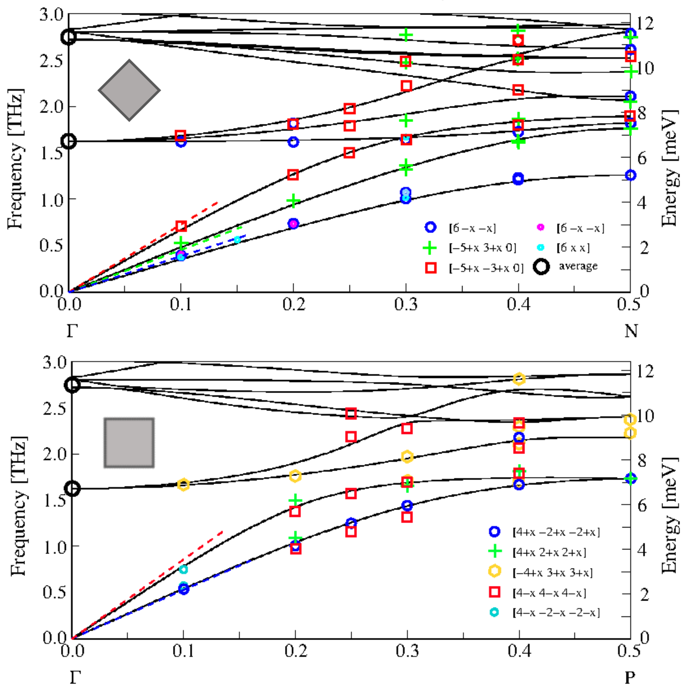


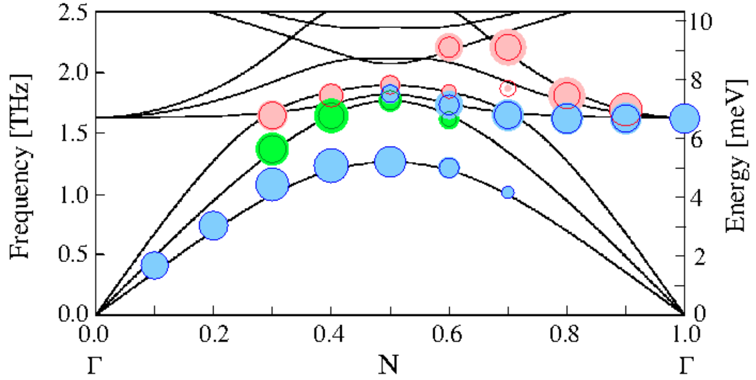
Phonon Dispersion in Thermoelectric Skutterudites





IN8 and DFT-LD Dispersion





Elastic Constants in GPa

	IN8@ILL	Ishii *et al.*
ta1 [xx0]	49(1)	49.4
ta2 [xx0]	94(2)	68.2
la [xx0]	169(2)	175.7
ta [xxx]	60(1)	61.9
la [xxx]	122(5)	163.9
la [x00]	186(10)	189.1 194.5

Computed from symmetry relations

la [x00] = C_{11} and ta1 [xx0] = C_{44}

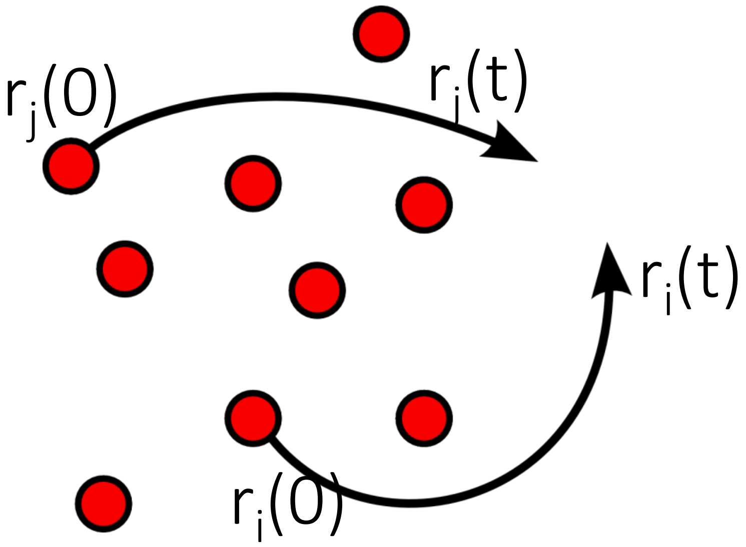
I. Ishii et al., J.Phys.Soc.Jpn. 78 (2009) at 140 K.

DFT-LD computed intensity

Measured intensity

Van Hove Correlation Function and Quasielastic Scattering

NEUTRONS FOR SOCIETY



Van Hove correlation functions = density-density correlation functions

In the classical limit :

$$G(r,t) = \frac{1}{N}\sum_{i,j}\delta(r - r_i(t) + r_j(0))$$

$$G_s(r,t) = \frac{1}{N}\sum_{i}\delta(r - r_i(t) + r_i(0))$$

1. t = 0 : *G(r,0)* pair distribution → Static structure factor
   : $G_s(r,0)$ self count of particles in the sample
2. t → ∞ or r → ∞ : $G(r,\infty) = \rho_o$ density of sample
3. $r_i(t)-r_i(0) = \Delta r_i(t)$ → $\mathbf{I_s(Q,t) = \exp(-Q^2 \langle \Delta r_i^2(t)\rangle/6)}$

   (ideal gas, harmonic crystals, diffusion in liquids at large times, …)

Fickian diffusion, random walk :
$\langle \Delta r_i^2(t)\rangle = D_s * t$

Ballistic process :
$\Delta r_i(t) = v * t$ → $\langle \Delta r_i^2(t)\rangle \sim t^2$

Van Hove Correlation Function and Quasielastic Scattering

Long range self diffusion :

Self correlation function obeys Fick's law
Spatial and temporal invariance holds and each particle starts at r=0 for t=0

$$I_s(Q,t) = \exp\left(-Q^2 D_s t\right)$$

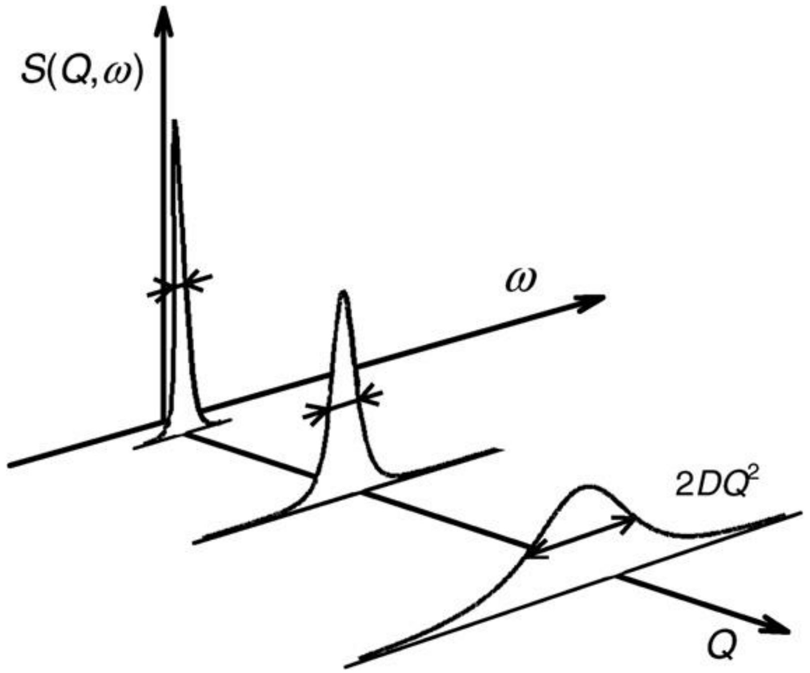
Lorentzian function in *Q* and ω

$$S_{\rm inc}(Q,\omega) = \frac{1}{\pi} \frac{\hbar D_s Q^2}{(\hbar D_s Q^2)^2 + (\hbar\omega)^2}$$

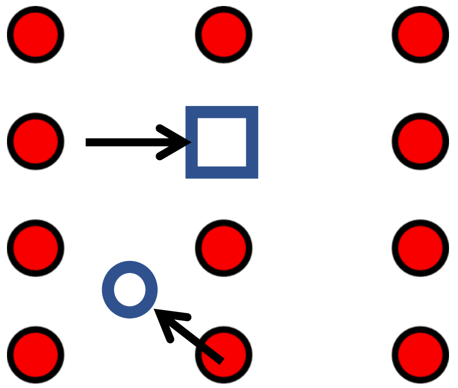
with Half Width at Half Maximum Γ(*Q*)

$$\Gamma(Q) = \hbar D_s Q^2$$

H.Jobic & D.N.Theodorou, Microporous and Mesoporous Materials 102 (2007) 21–50



Van Hove Correlation Function and Quasielastic Scattering



Jump diffusion models : Diffusion via successive jumps

Between successive jumps of distance *r*, atoms stop for a residence time *t*

Chudley + Elliot : *r* = constant

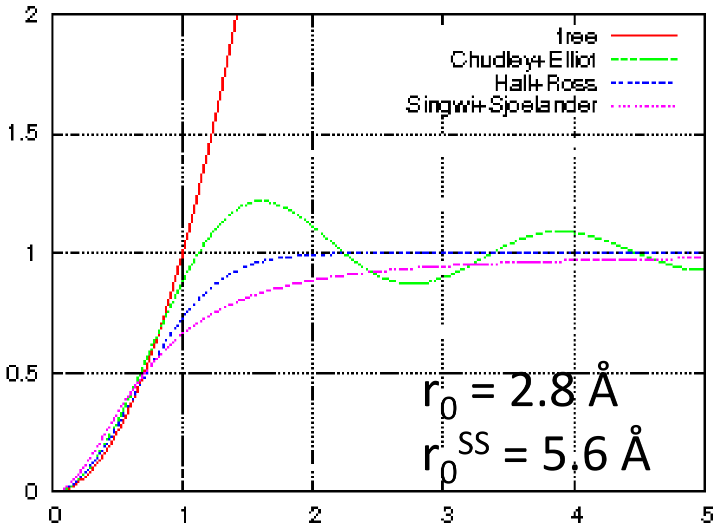
$$\Gamma(Q) = \frac{\hbar}{\tau}\left(1 - \frac{\sin(Qr)}{Qr}\right)$$

Hall + Ross : Gaussian distribution of jump lengths

$$\Gamma(Q) = \frac{\hbar}{\tau}\left(1 - \mathrm{e}^{-Q^2 r_o^2/6}\right)$$

Singwi + Sjoelander : Exponential distribution of jump lengths

$$\Gamma(Q) = \frac{\hbar}{\tau}\frac{Q^2 r_o^2}{1 + Q^2 r_o^2}$$

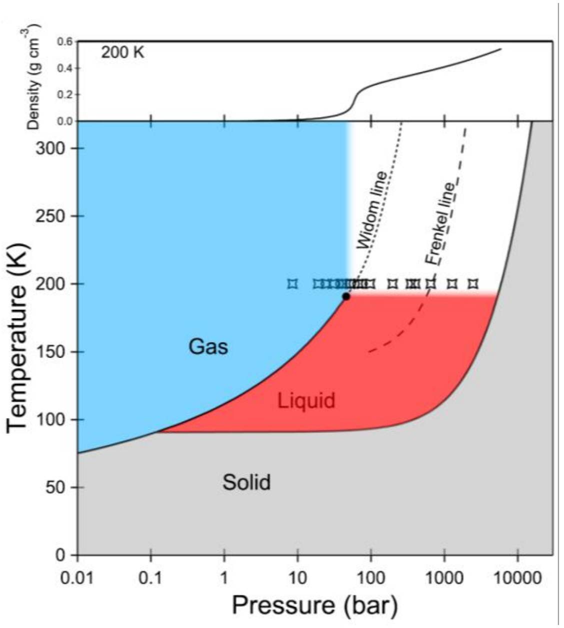


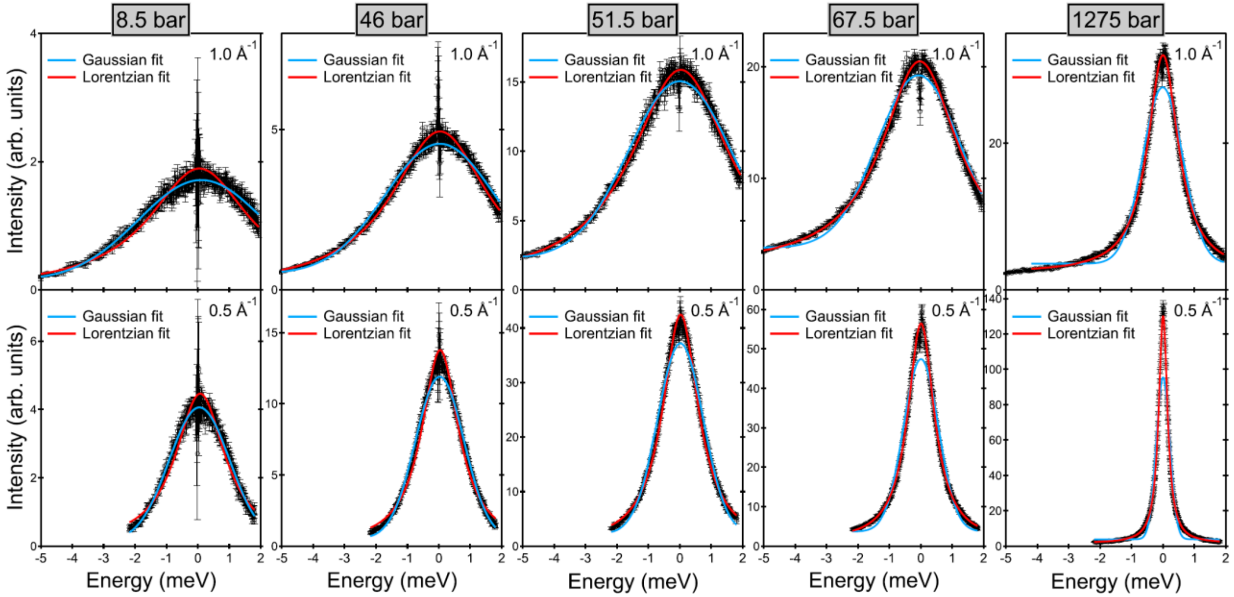
$$\lim_{Q\to 0} \Gamma(Q) = \hbar D Q^2$$

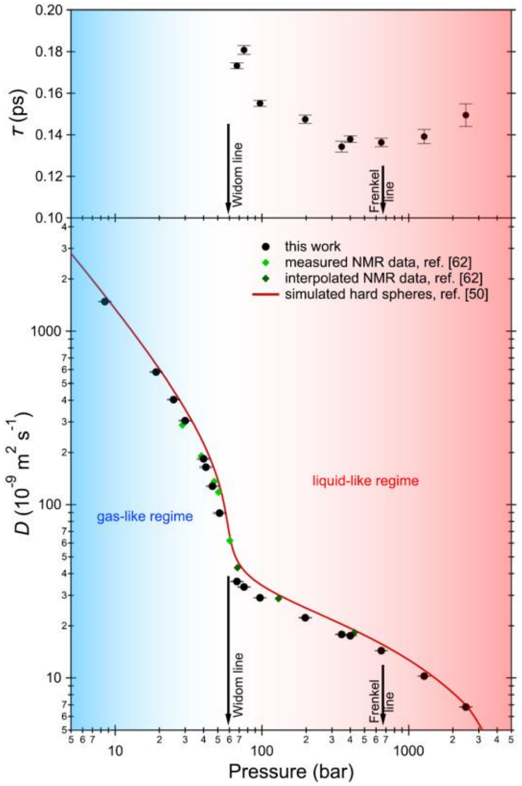
Crossover from Gas-like to Liquid-like Diffusion

NEUTRONS FOR SOCIETY

Supercritical Methane : U. Ranieri et al., *Nature Communications* 15 (2024)

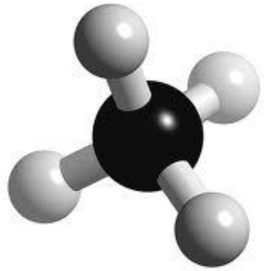




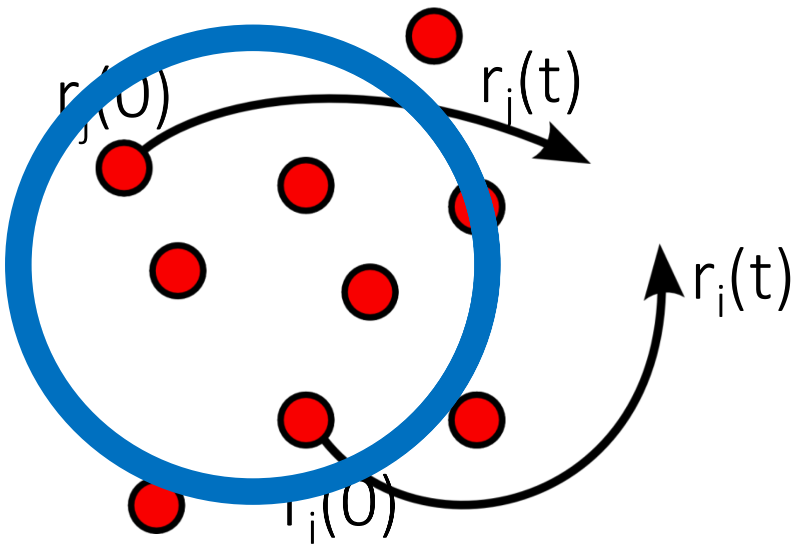


Scientific Interest :

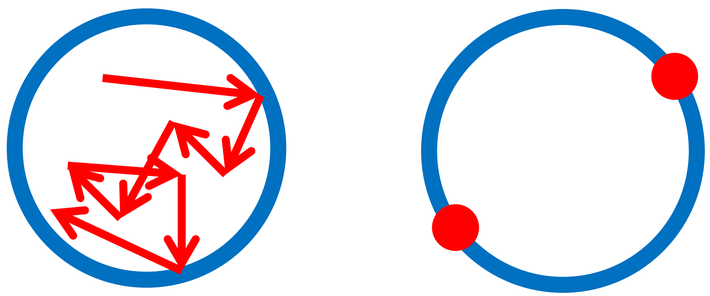
- Textbook scenario : Above critical point liquid and gas behave the same
- Challenged by Benjamin Widom and Yacov Frenkel
- Widom from critical point minima/maxima in thermophysical properties exist
- Frenkel continuous to solid-like diffusion, no transverse to transverse excitations

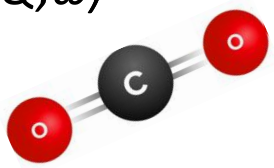


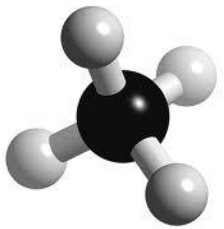
Van Hove Correlation Function and Quasielastic Scattering



What if the diffusing particles are confined in space ?
Correlation functions remain finite for infinite time
An elastic signal will be always present in *S(Q,ω)*







Consider Van Hove's correlation function as a superposition :

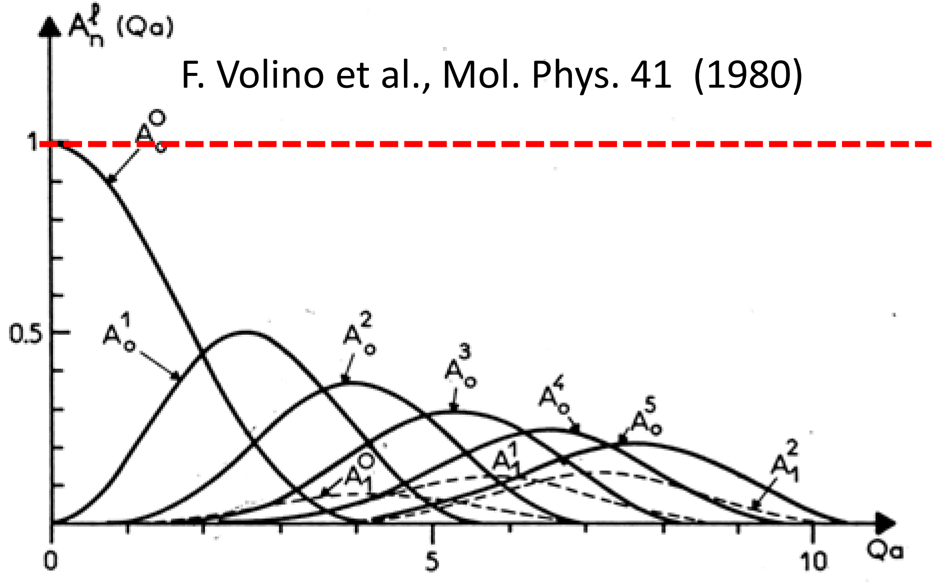
$$G_s(r,t) = G_s(r,\infty) + G'_s(r,t) \quad \rightarrow \quad S_{inc}(Q,\omega) = S_{inc}^{el.}(Q) + S_{inc}^{inel.}(Q,\omega)$$

Elastic contribution is defined as the Elastic Incoherent Structure Factor EISF

$$EISF = \frac{I^{el.}}{I^{el.} + I^{inel.}}$$

Van Hove Correlation Function and Quasielastic Scattering

F. Volino et al., Mol. Phys. 41 (1980)



Sum over spherical Besselfunctions

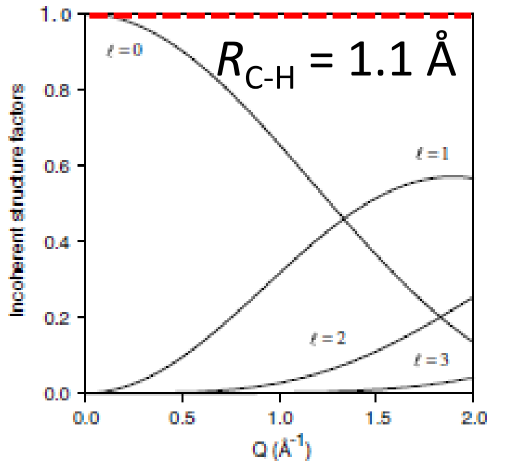
$$S_{\text{inc}}(Q,\omega) = A_\circ(Q)\delta(\omega) + \frac{1}{\pi}\sum_{l,n}(2l+1)A_n^l(Q)\cdot L(D,R,\omega)$$

with the EISF

$$A_\circ(Q) = \left(\frac{3j_1(Qa)}{Qa}\right)^2$$

$$j_1(x) = \frac{\sin(x)}{x^2} - \frac{\cos(x)}{x}$$

H. Jobic et al. Micro.& Mesoporous Materials 102 (2007)

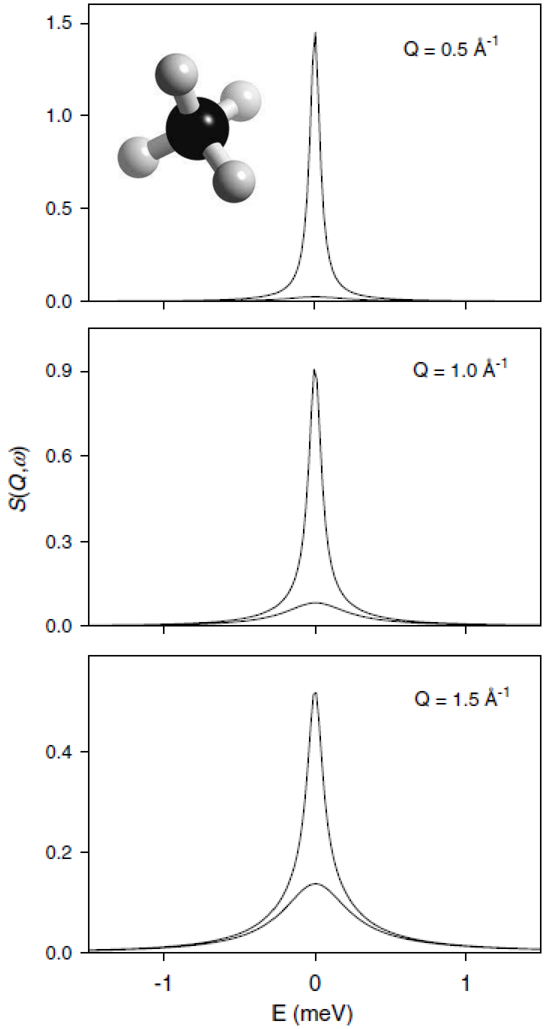


Rotational diffusion of CH_4 :

Spectra simulated for

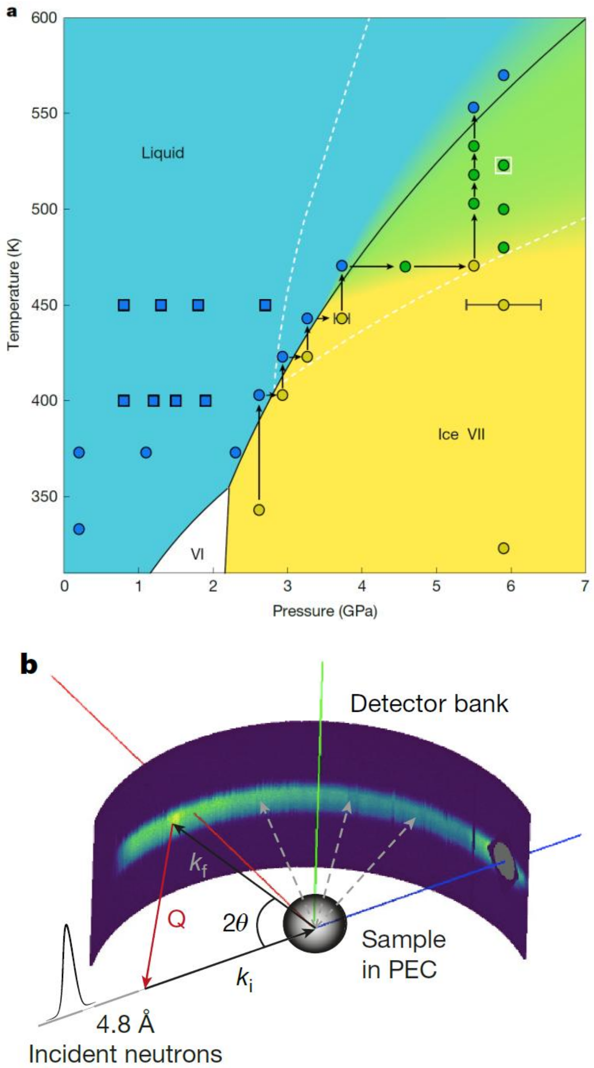
$D_{trans} = 6\cdot10^{-10}$ m^2/s

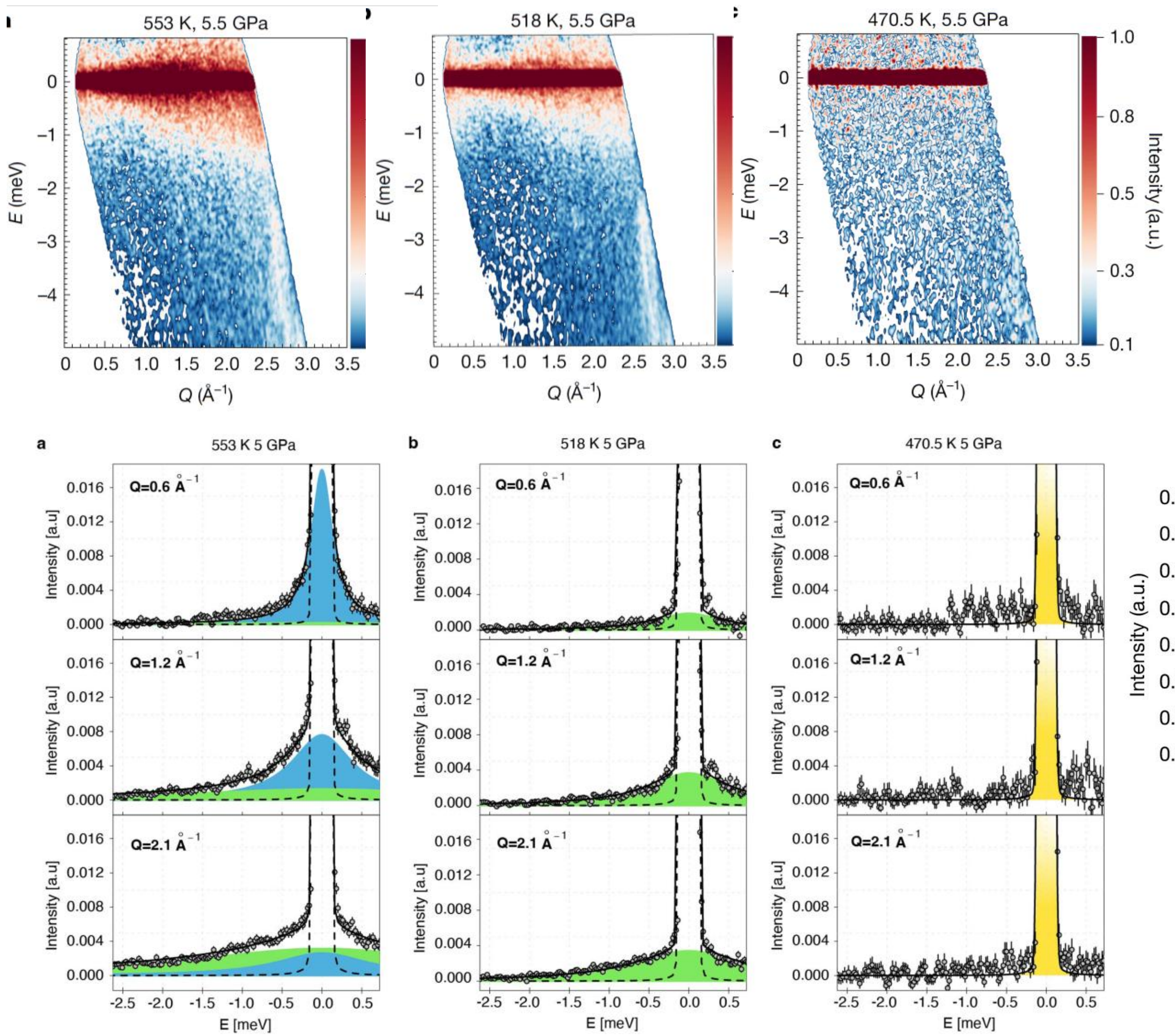
$D_{rot} = 8\cdot10^{10}$ 1/s

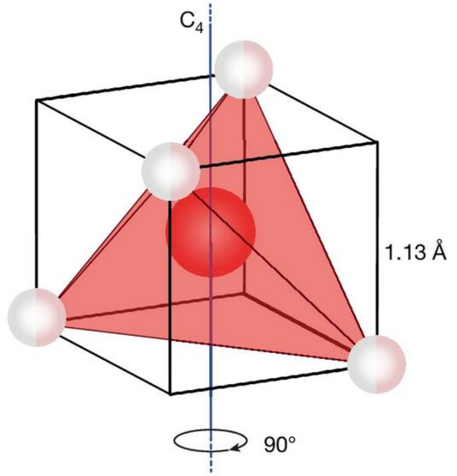


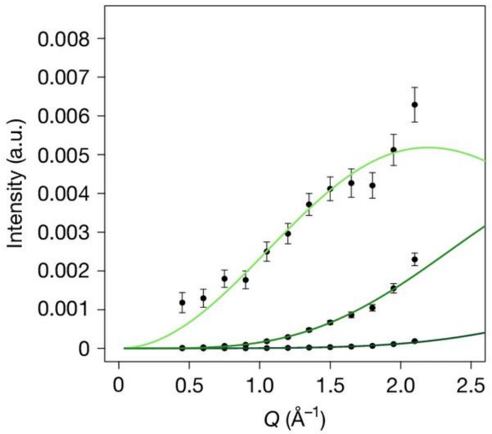
Rotational Degrees of Freedom in Ice VII – Plastic Ice

M. Rescigno et al., *Nature* 640 (2025)



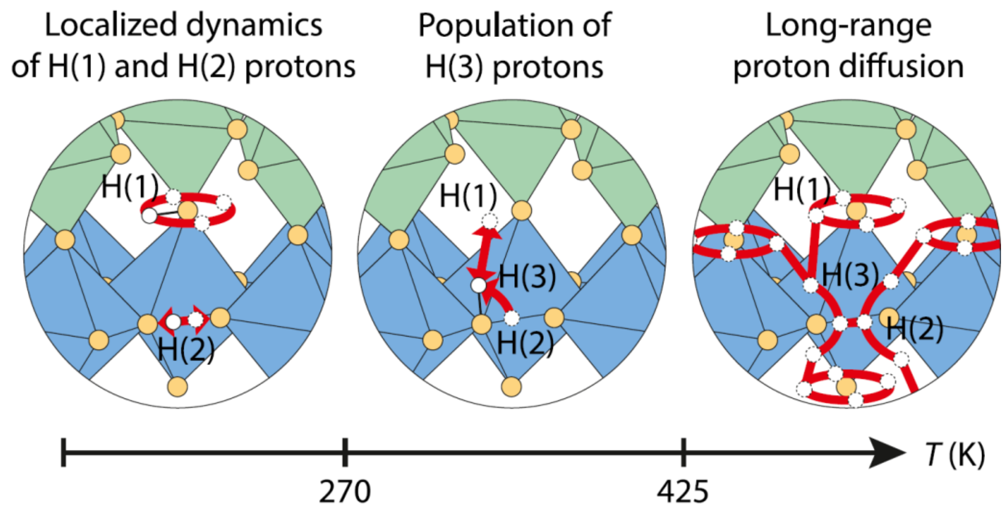


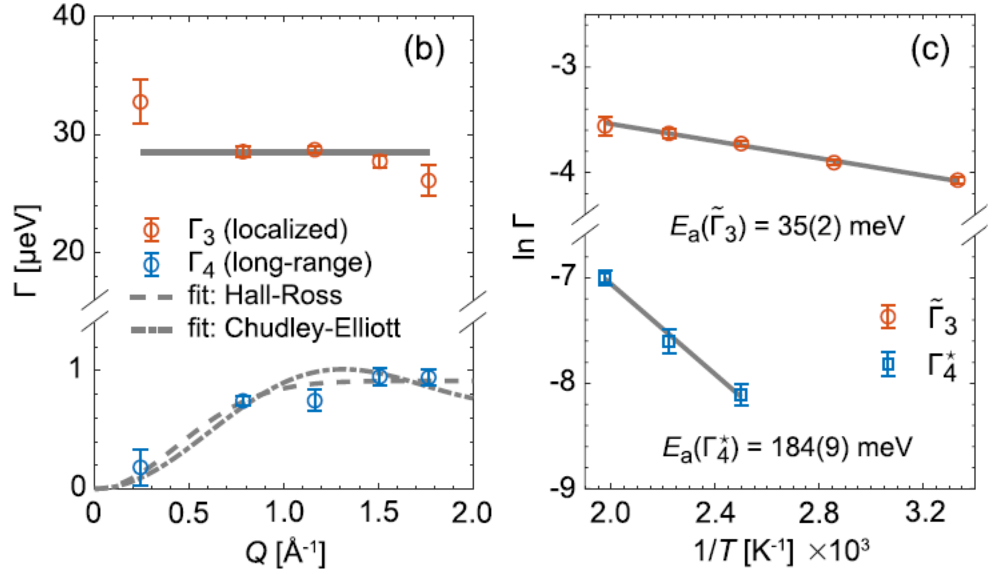


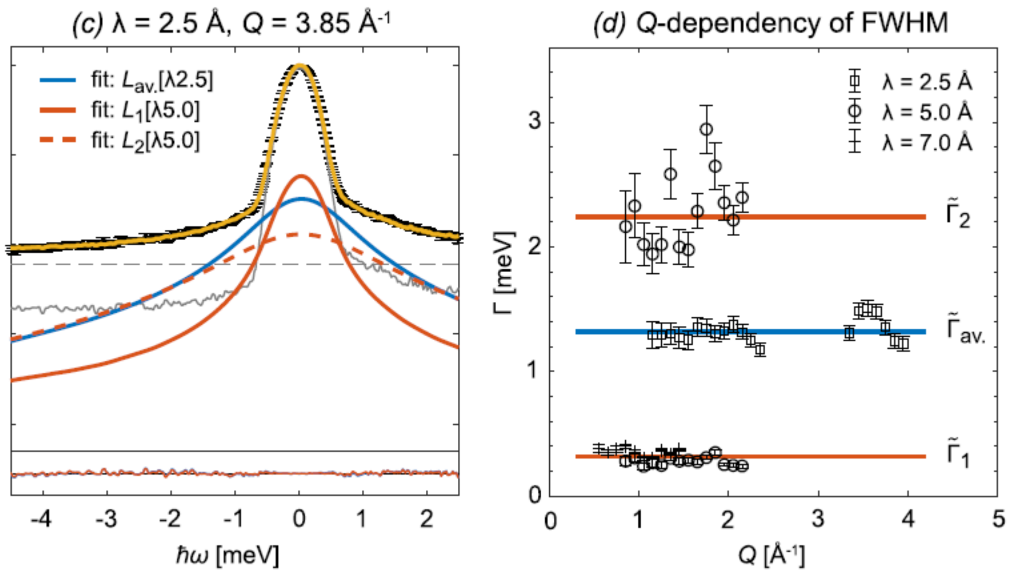


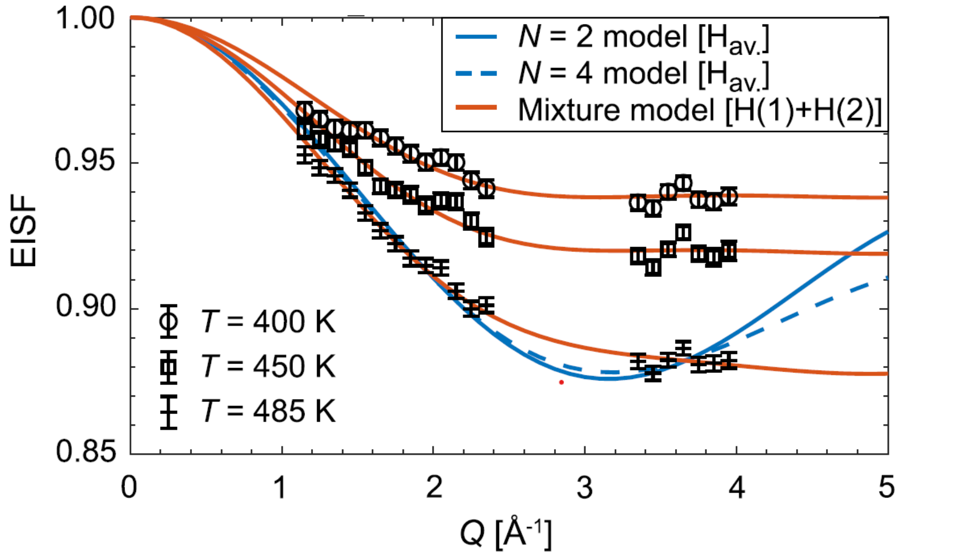
Proton Diffusion in Solid Oxide Fuel Cells

A. Perrichon et al., *Chem. Mater.* 35 (2023)



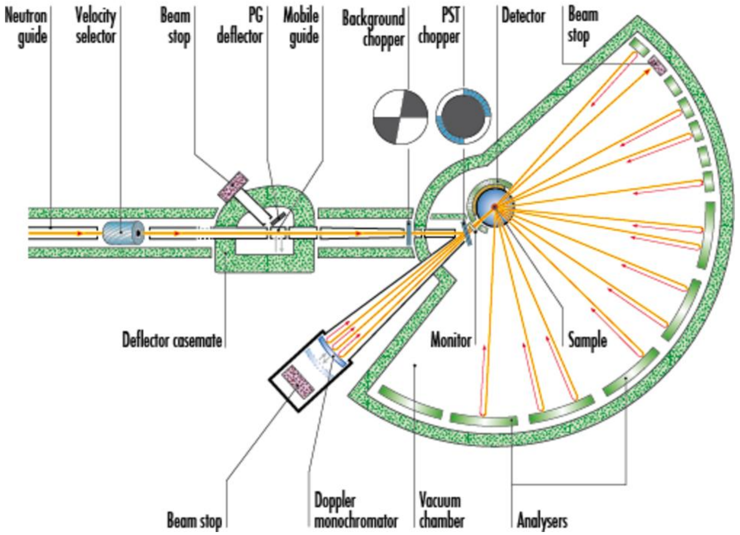


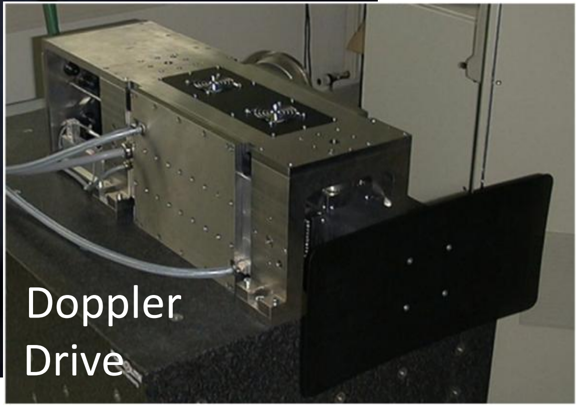


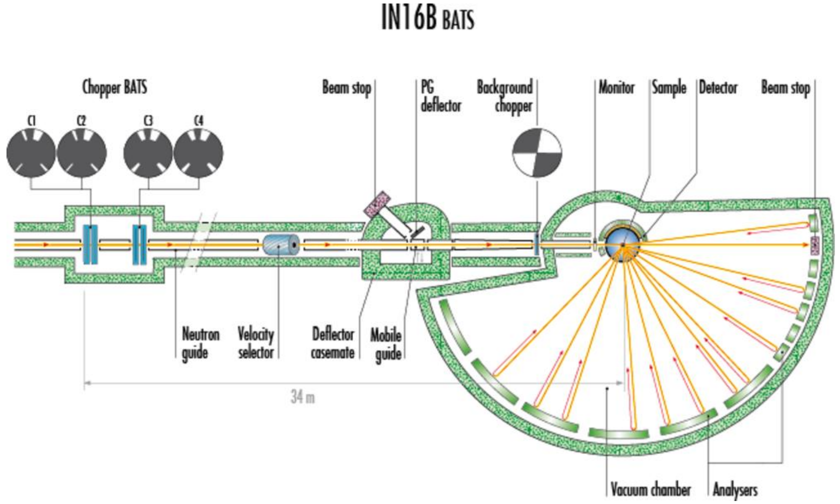


TOFTOF@MLZ cold neutron disc chopper spectrometer

Backscattering Spectrometer IN16b / BATS





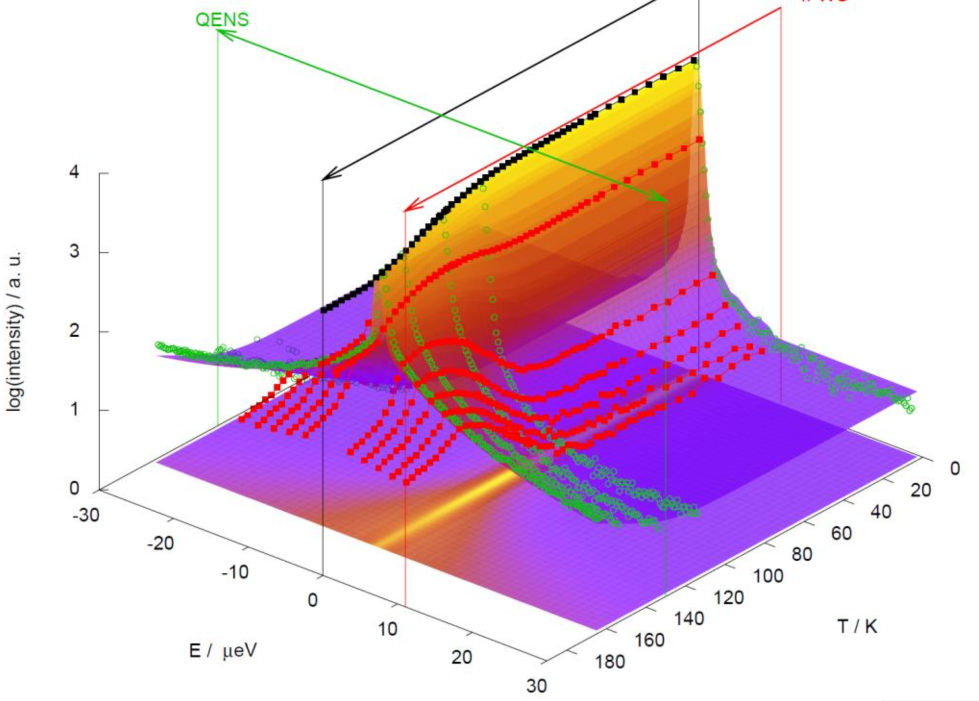


IN16b	Si(111)	Si(311)
λ_i [Å]	6.3	3.3
dE [μeV]	0.8	2.0
ΔE [μeV]	±30	±30

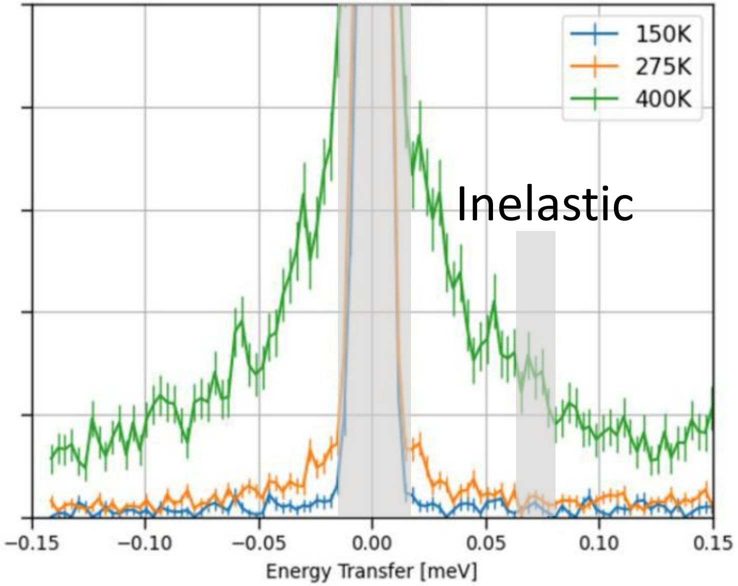
BATS	Si(111)	Si(311)
dE [μeV]	1.5 - 8	
ΔE [μeV]	±250	±800

Backscattering Spectrometer IN16b / BATS

Markus Appel, PhD Thesis



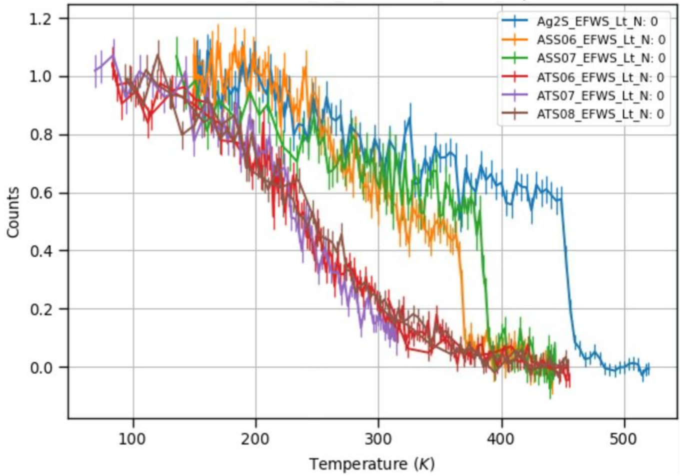
Elastic



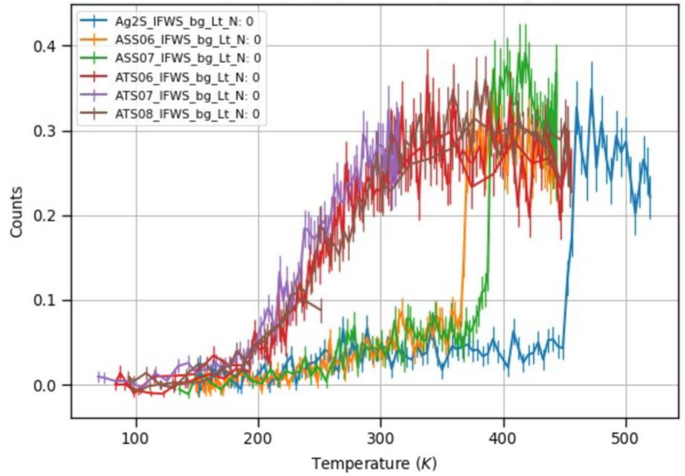
Operational Modes :

- Elastic fixed window scan EFWS
- Inelastic qfixed widow scan IFWS
- Energy-resolved QENS

Elastic Intensity

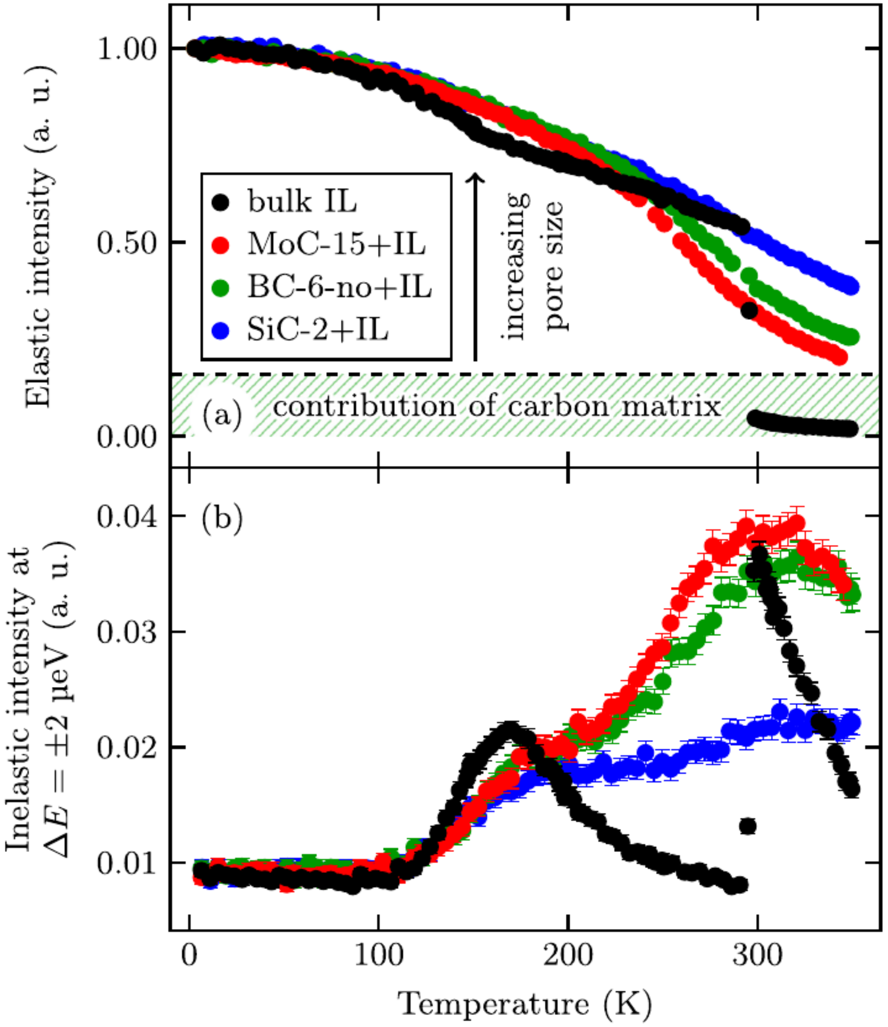


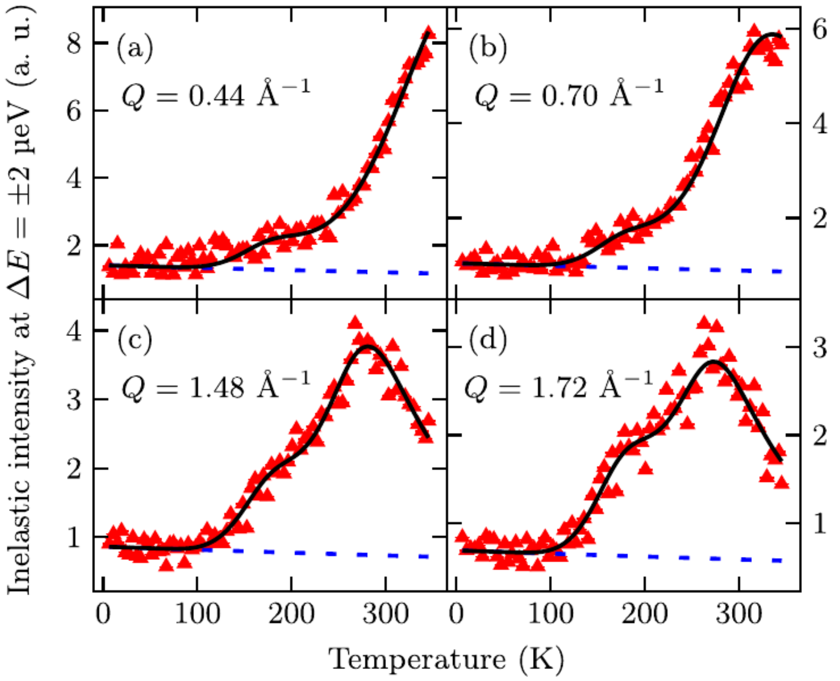
Inelastic Intensity



Ionic Liquid Dynamics in Nanoporous Carbon

S. Busch et al., *Phys. Rev. Mater*. 4 (2020)



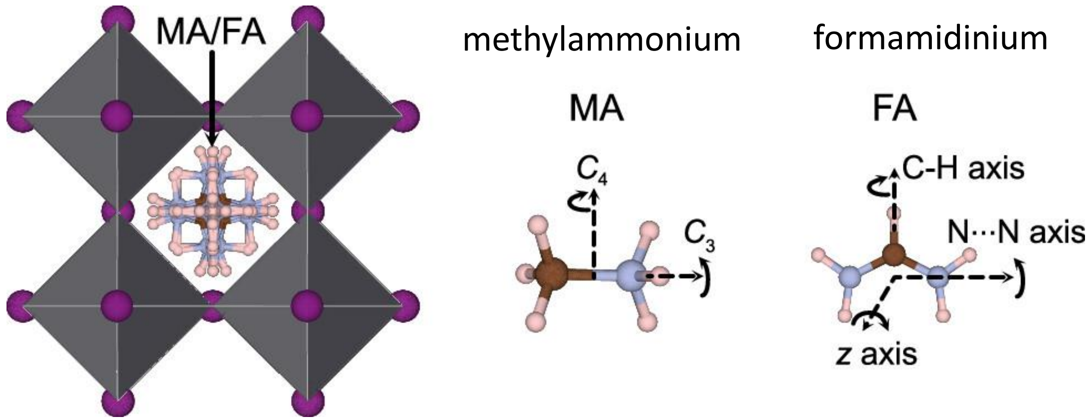


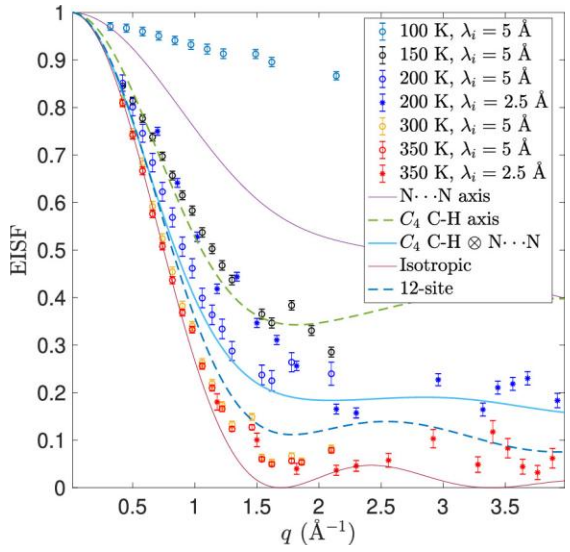
1-N-butylpyridinium bis-[(trifluoromethyl)sulfonyl]imide ([BuPy][Tf2N])

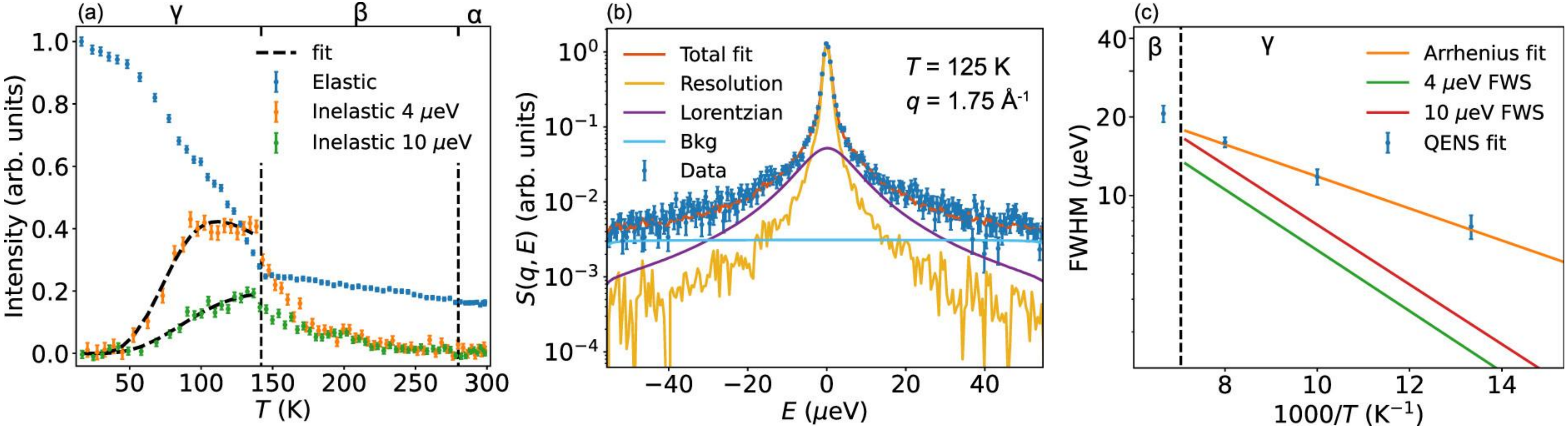
	Localized dynamics E_a^{local} (kJ/mol)	Diffusive motion E_a^{global} (kJ/mol)
bulk IL	9.7	12.3–14.8
MoC-15+IL	7.1	15.1
BC-6-no+IL	6.9	14.9
SiC-2+IL	6.0	12.0

Rotational Dynamics of Organic Cations in Perovskites

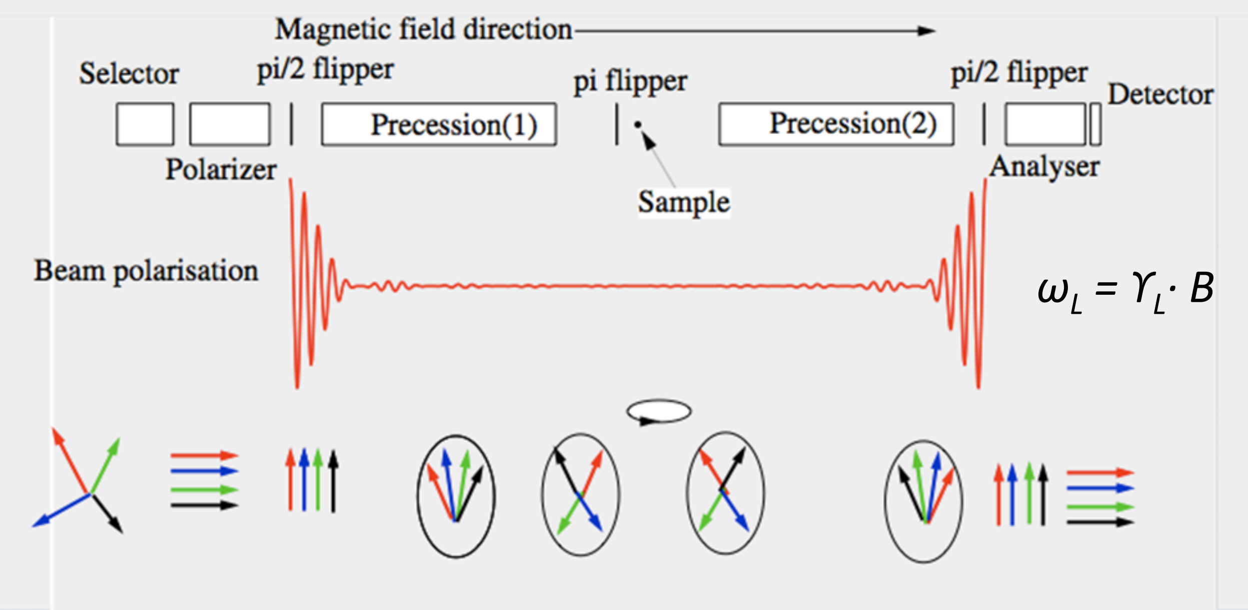
R. Lavén et al., J. Phys. Chem. Lett. 14 (2023)







Neutron Spin Echo

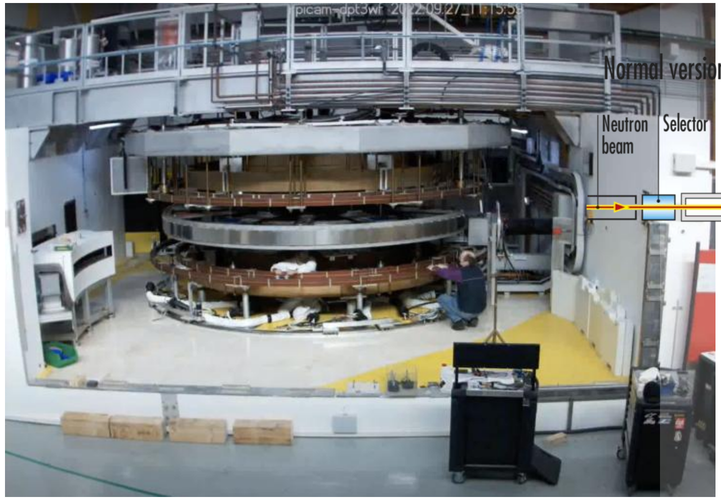


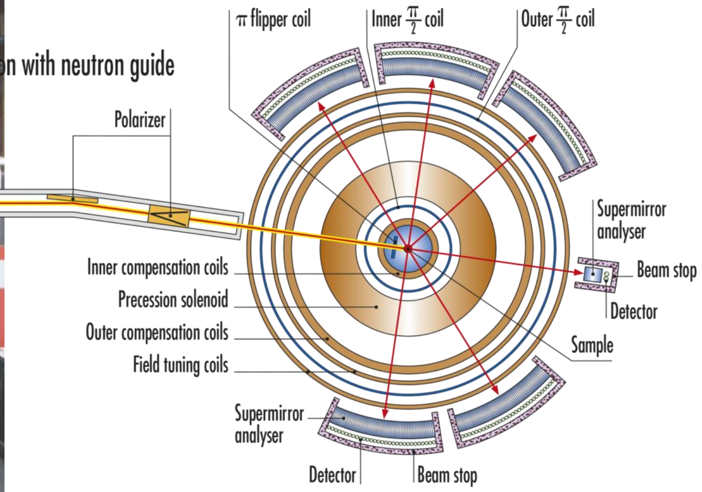
$\omega_L = \Upsilon_L \cdot B$

Ferenc Mezei first NSE prototype

Fourier time : $t = \pi/\omega$

Resolution : $\Delta t \sim B \cdot \lambda^3$





Wide Angle SPin echo - WASP

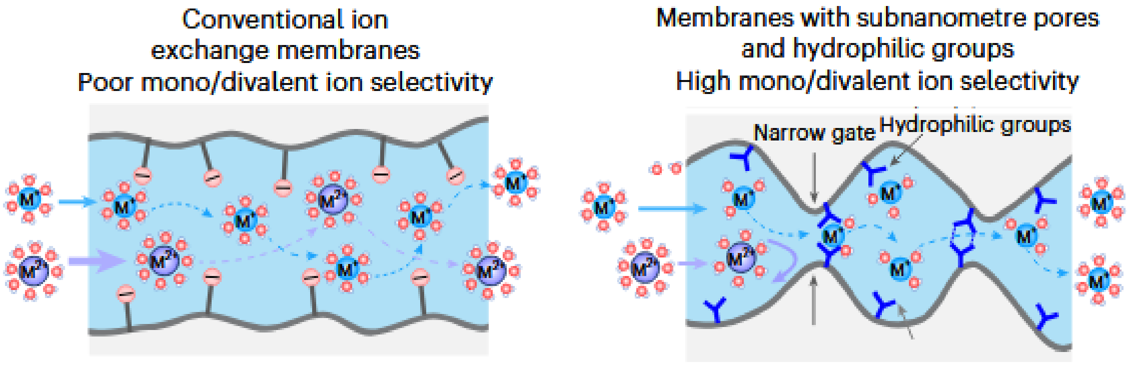
λ_i/Å (E_i)	Fourier t	Q / $Å^{-1}$
10 (2.9)	15 ps - 18 ns	.05 – 1.1
7 (3.4)	6 ps - 6 ns	.07 – 1.6
3.2 (5)	.6 ps - .6 ns	.15 – 3.6

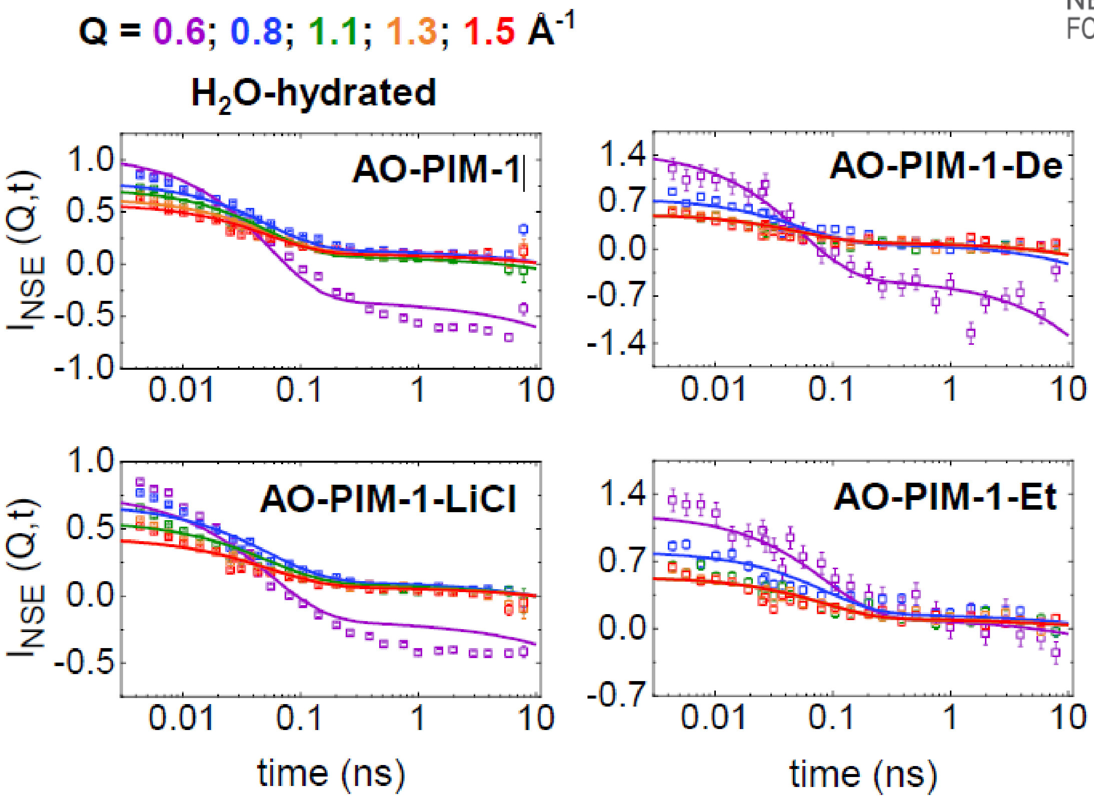
IN15

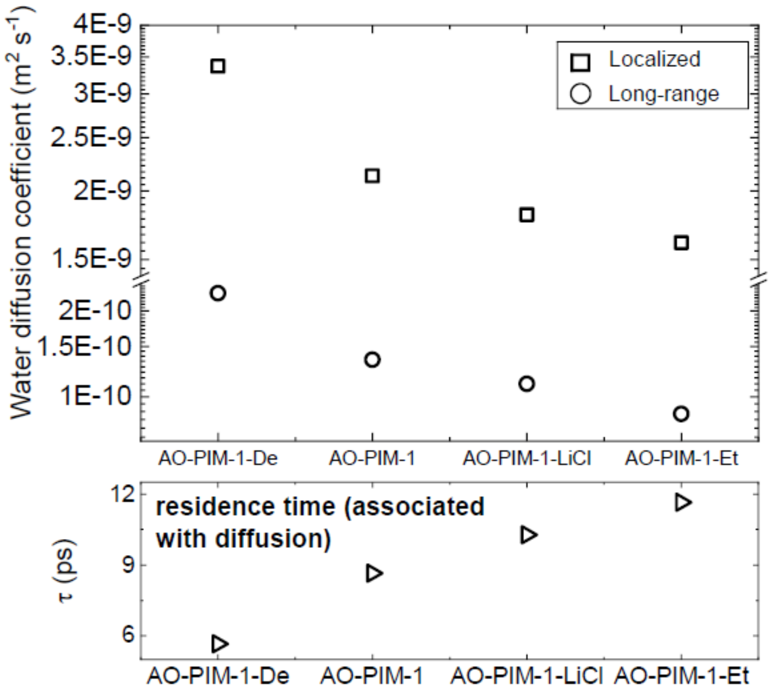
λ_i/Å (E_i)	Fourier t	Q / $Å^{-1}$
17.3 (2)	< 1000 ns	.01 – .42

Lithium Ion Extraction from Salt Lake Brines

D. Yang et al., *Nature Water* 3 (2025)







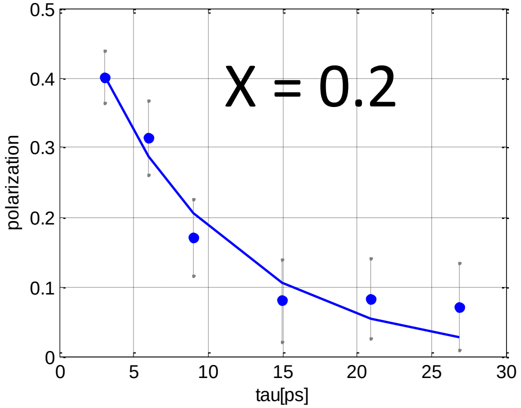
Scientific Interest :

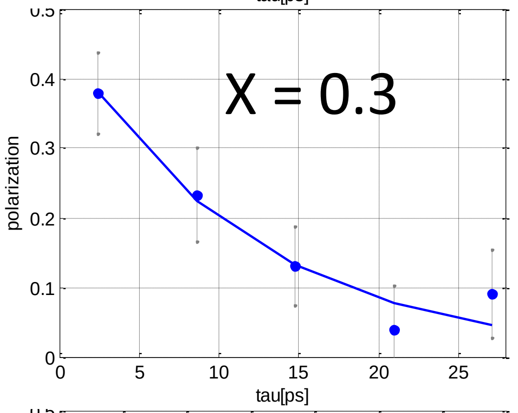
- Optimize Li extraction through selective membrane
- Study microscopic mechanism of Li^{+}/Mg^{2+} separation
- Select best polymer-surface functionalization

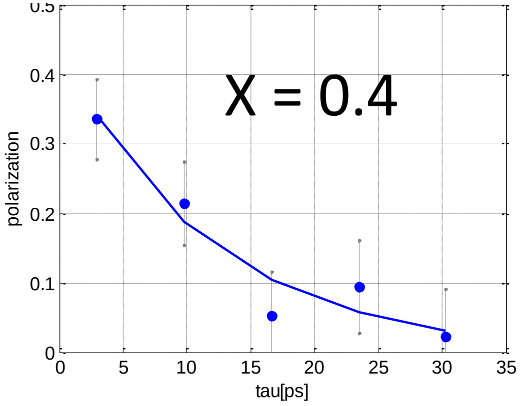
Lifetime of Phonons in Thermoelectric Skutterudites

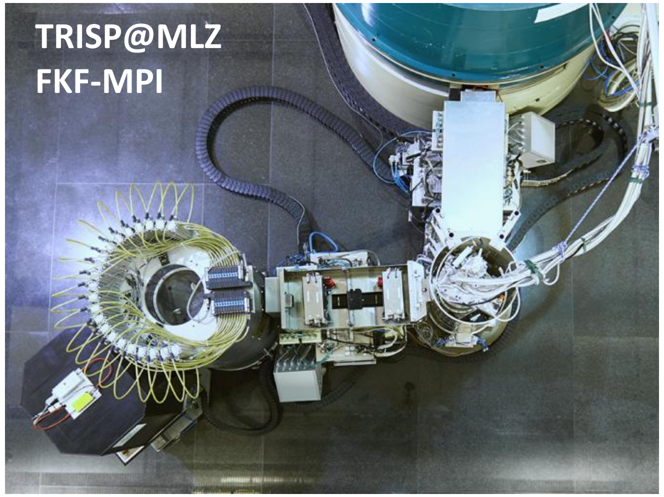
TRISP@MLZ
FKF-MPI

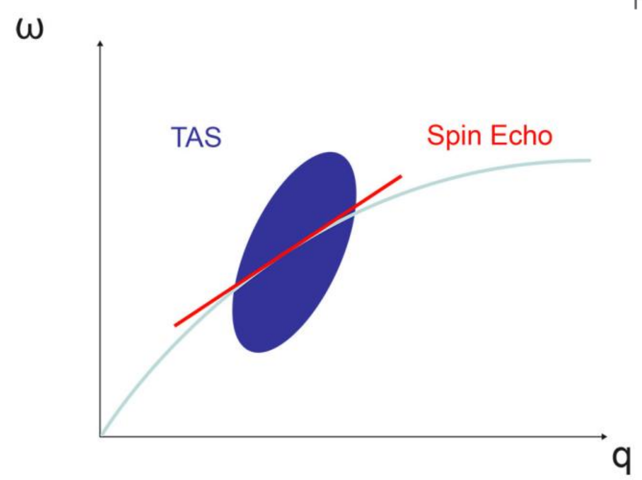
Zeta@IN22



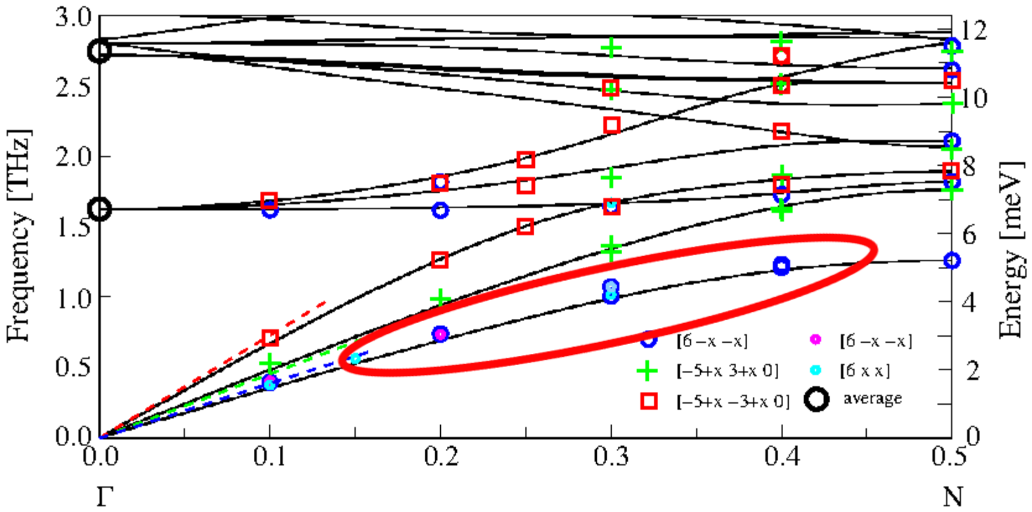






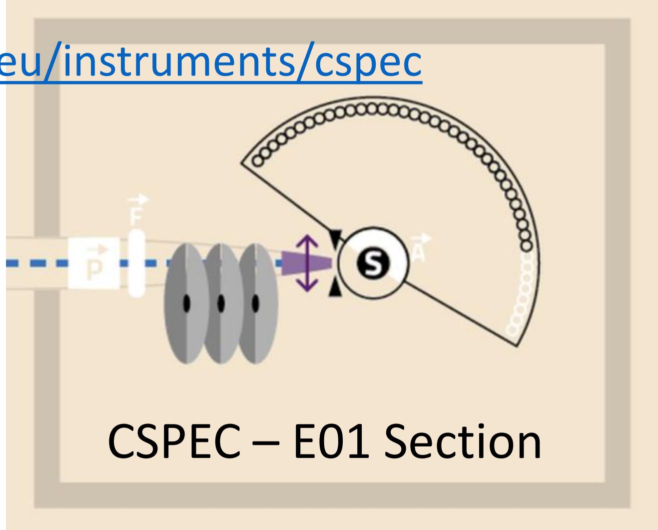


Mean Free Path >20 Unit Cells in $LaFe_4Sb_{12}$

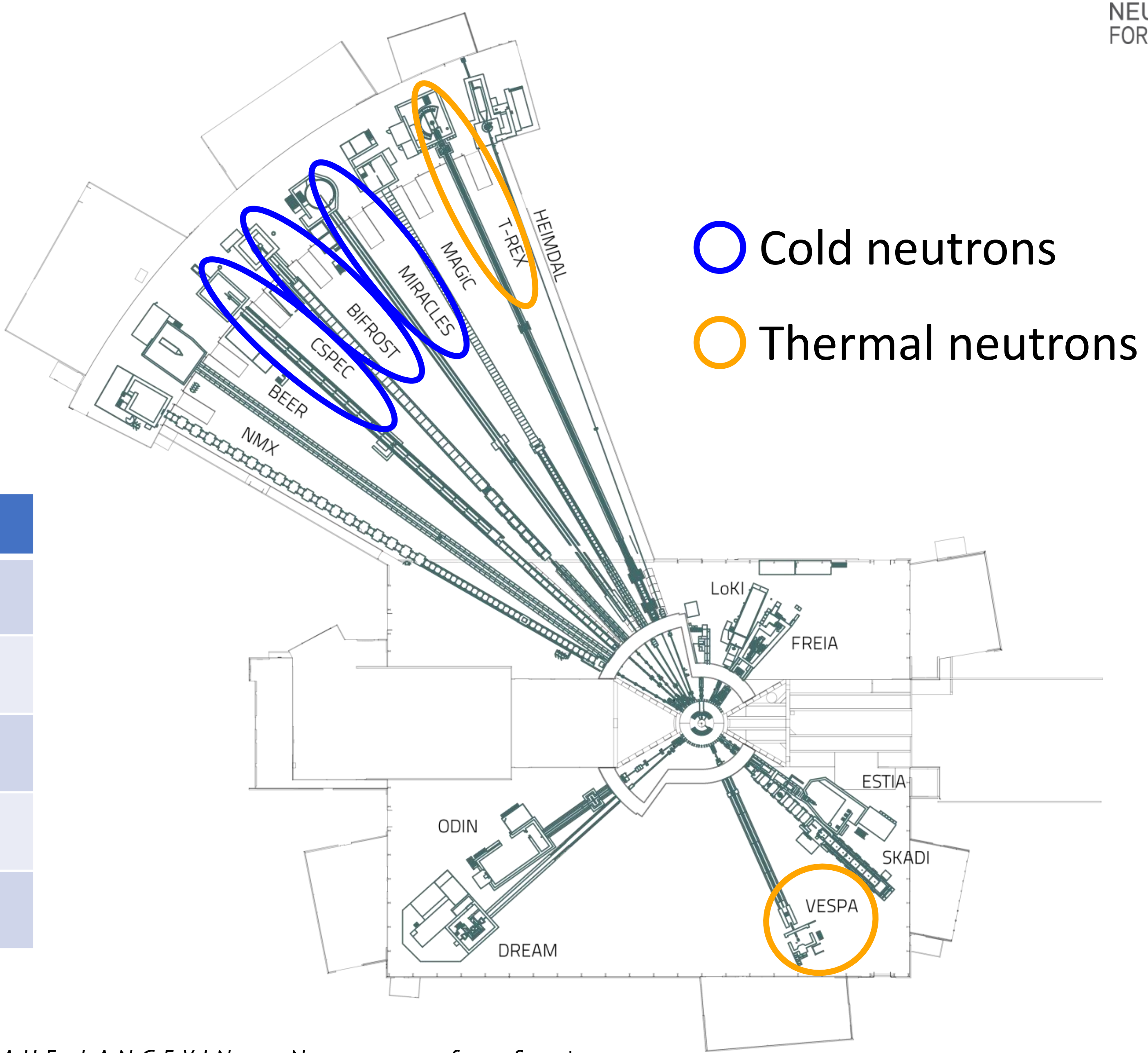


Spectrometers at the ESS

https://ess.eu/instruments/cspec



Primary	Secondary	Instruments
v	v	CSPEC
v	v	T-REX
v	λ	MIRACLES
v	λ	BIFROST
v	λ	VESPA



Wrap-up

- What is the time and spatial scale of the process to study ?
  - ➢ Energy range, energy resolution, wavevector range
  - ➢ Cold, thermal or hot neutrons
  - ➢ BS/NSE or ToF/TAS or Vibrational Spectrometer

- What is the physical process to study ?
  Spectral distribution, collective dynamics, diffusive processes

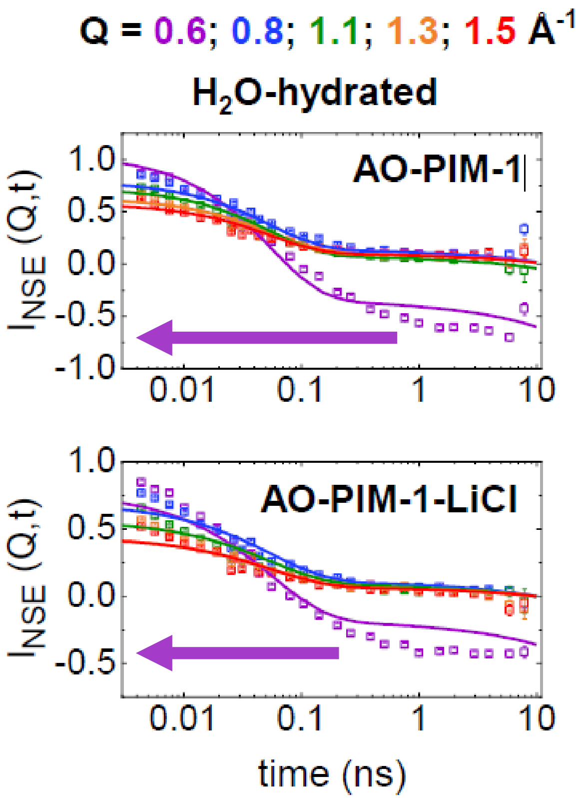
- What is the state of the sample to measure ?
  Single crystal, polycrystalline, powder, liquid, gas

- What are the scattering cross sections of the elements ?
  - ➢ Coherent, incoherent (spin and/or isotope)

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i}\left[\frac{\sigma_{inc}}{4\pi}S_{inc}(\vec{Q},\omega) + \frac{\sigma_{coh}}{4\pi}S_{coh}(\vec{Q},\omega)\right]$$

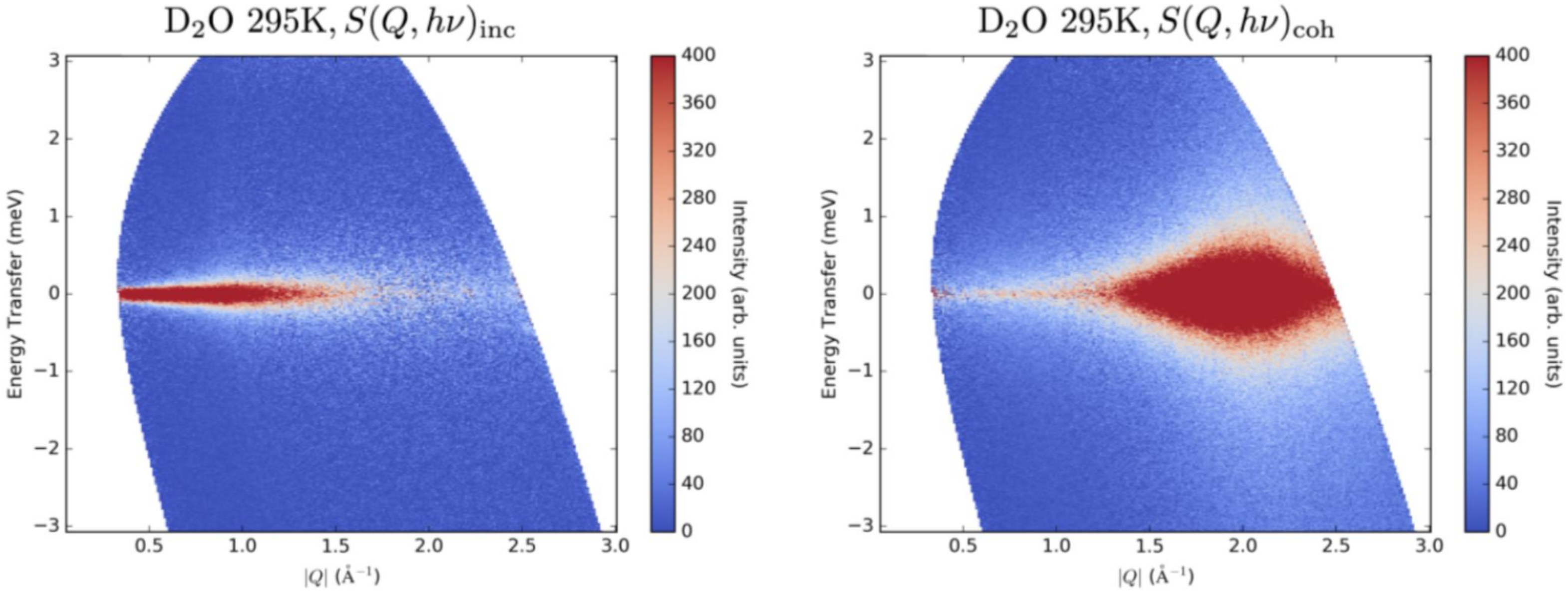
There is much more to it !

Non-Magnetic Polarization Analysis



NSE measures polarization!

A. Arbe et al. *Phys. Rev. Res.* 2 (2020)



Polarized LET - PLET@ISIS : Cold Neutron Chopper Spectrometer

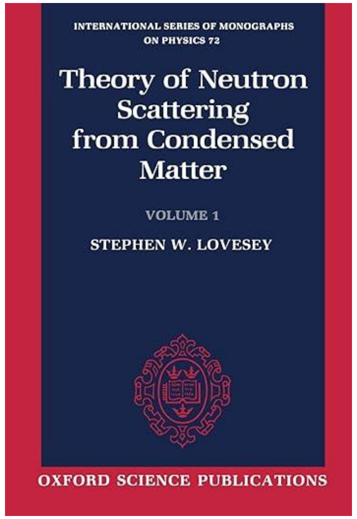
$$\left(\frac{d\sigma}{d\Omega}\right)_{NSF} = \left(\frac{d\sigma}{d\Omega}\right)_{C} + \left(\frac{d\sigma}{d\Omega}\right)_{II} + \frac{1}{3}\left(\frac{d\sigma}{d\Omega}\right)_{SI}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{SF} = \frac{2}{3}\left(\frac{d\sigma}{d\Omega}\right)_{SI}$$

C = Coherent
II = Isotope Incoherent
SI = Spin Incoherent
SF = Spin Flip
NSF = Non-Spin Flip

See for detailed cross sections: https://www.ncnr.nist.gov/resources/n-lengths/

Literature



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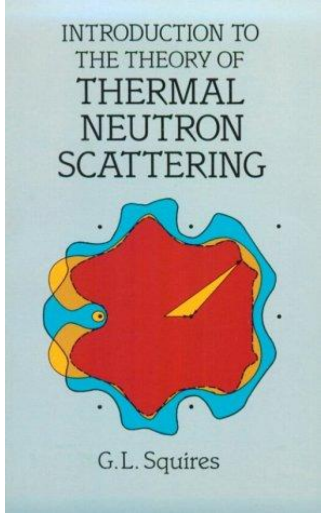

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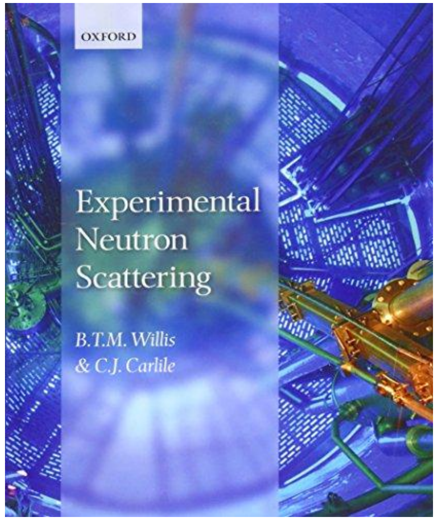

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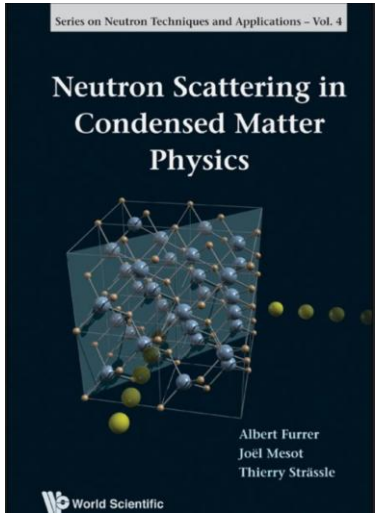
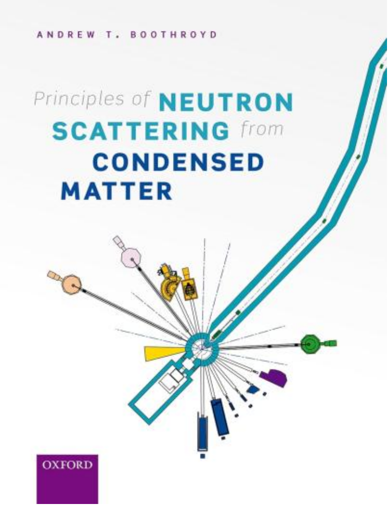


https://doi.org/10.1142/4870



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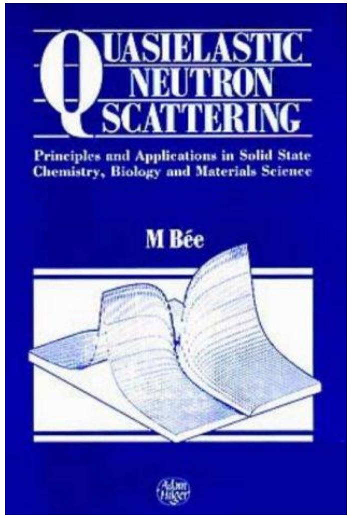

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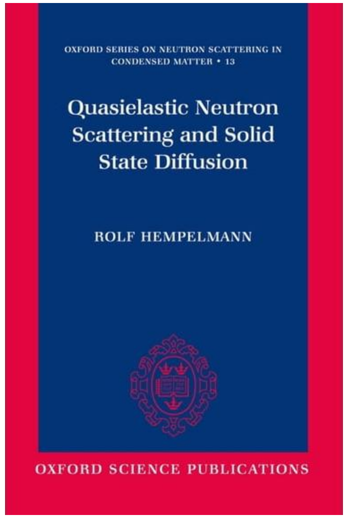

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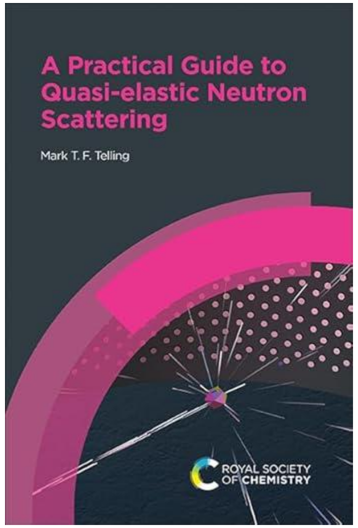

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