

Inelastic Neutron Scattering of Phonons



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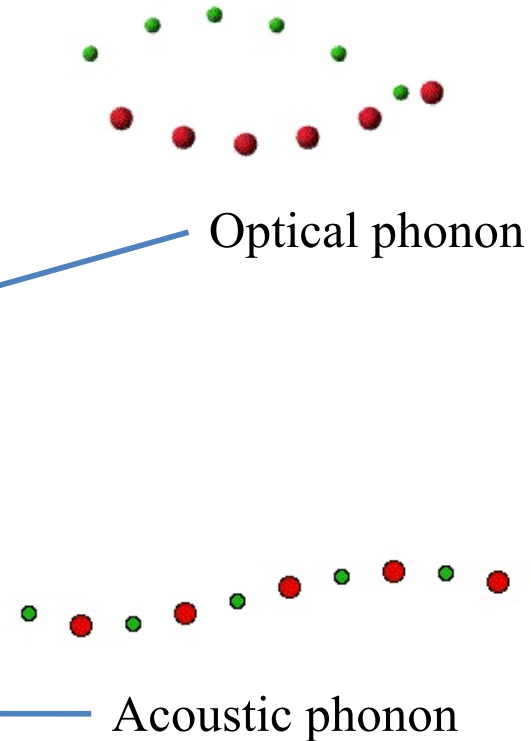
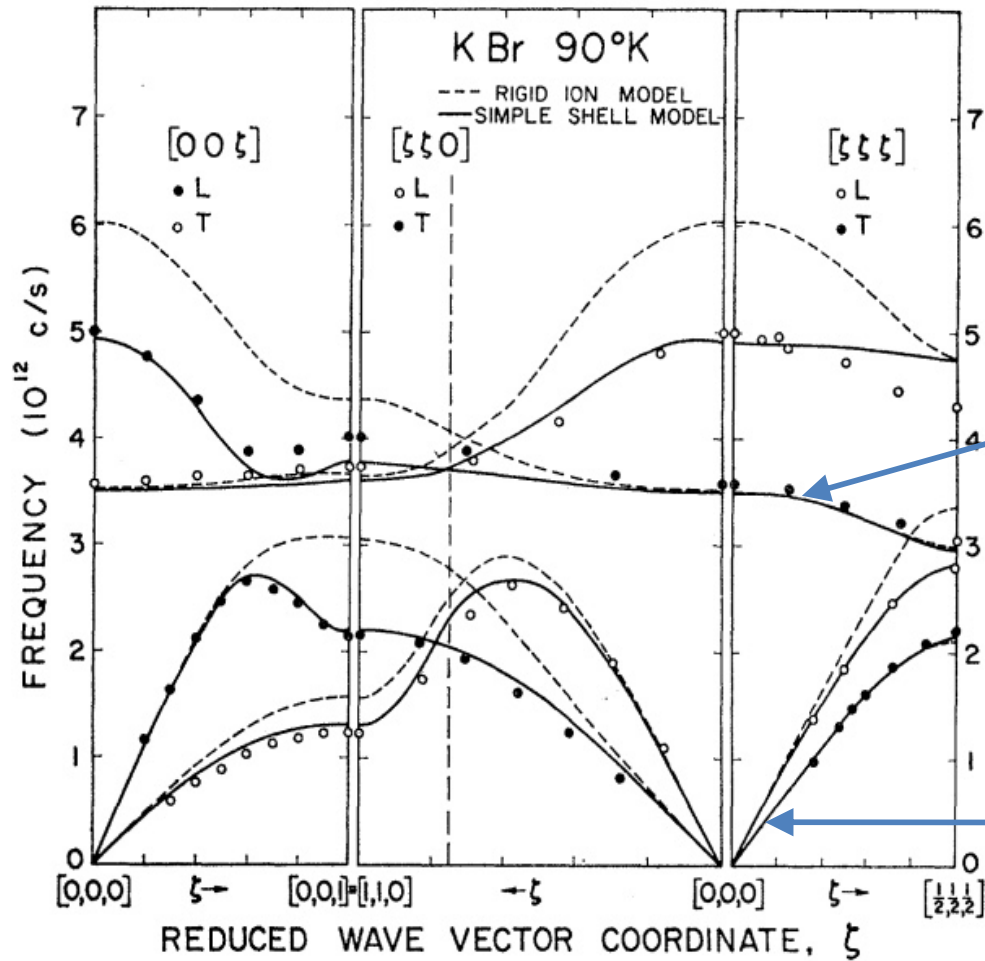


Outline

- Phonons (and thermodynamics)
- Instruments
- Measurements of phonons for thermodynamics
- Non-harmonic phonons; nonlinear effects
- Appendix 1: concept of Van Hove function
- Appendix 2: some relations between scattering functions

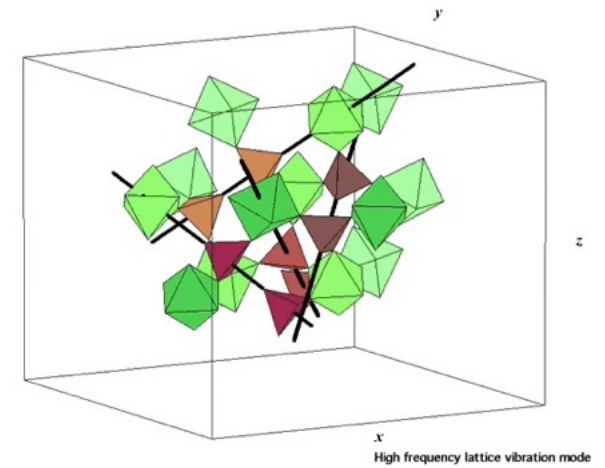
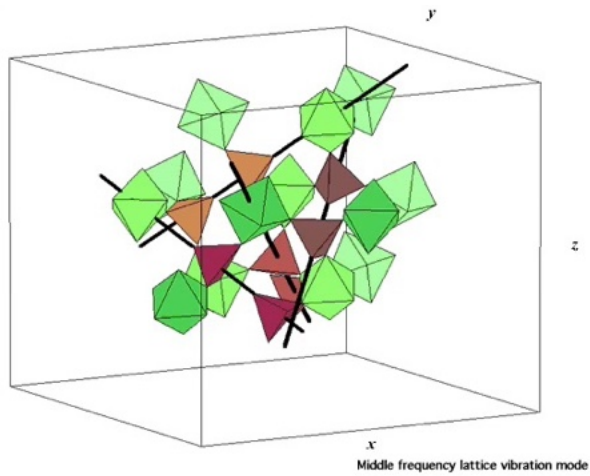
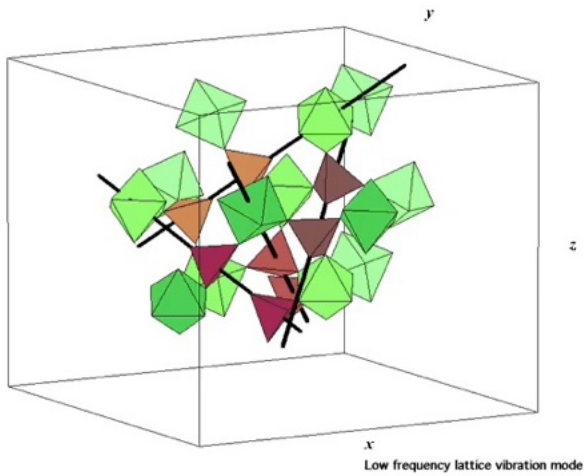
It is not realistic to understand this in 90 minutes! (some pieces will take you years)
This talk is a guided tour, but you must re-read some of these slides, and refer to the text or other references to cover these topics properly.

Crystal with 2 Atoms per Unit Cell



Woods, et al., Phys. Rev. 131, 1025 (1963).

More Complicated Vibrational Modes



<http://physics.ucsc.edu/research/images/>

Normal Modes are from Equations of Motion in Periodic Crystal

In the harmonic approximation, the equations of motion for all nuclei are

$$m_{\kappa} \ddot{\mathbf{u}}_{l\kappa}(t) = - \sum_{l', \kappa'} \Phi_{l\kappa l' \kappa'} \mathbf{u}_{l' \kappa'}(t) \quad \forall l, \kappa . \quad (4.55)$$

ma = F

In Eq. 4.55 there are $3 \times \mathcal{R} \times N^{\text{cell}}$ equations of motion to solve for a finite crystal containing N^{cell} unit cells. We seek solutions having the form of plane waves⁷ of wavevector $\mathbf{k}$, angular frequency $\omega_{\mathbf{k}j}$, and “polarization” $\mathbf{e}_{\kappa j}(\mathbf{k})$ (where j is a “branch index” for mode polarization)

$$\mathbf{u}_{l\kappa \mathbf{k}j}(t) = \sqrt{\frac{2\hbar}{N m_{\kappa} \omega_{\mathbf{k}j}}} \mathbf{e}_{\kappa j}(\mathbf{k}) e^{i(\mathbf{k} \cdot \mathbf{r}_l - \omega_{\mathbf{k}j} t)} . \quad (4.56)$$

↑ ↑ ↑ ↑
atom displacement = (quantized) (unit vector) (phase factor)

When you put phonon solution for $u(t)$ into Equation of Motion

Second derivative returns exponentials, with factors $\sim k^2$.

Sum over unit cells, setting one at origin.

Exponentials give Fourier Transform

$$\underline{D}(\vec{k}) = \begin{pmatrix} \underline{D}_{11}(\vec{k}) & \cdots & \underline{D}_{1\mathcal{R}}(\vec{k}) \\ \vdots & \ddots & \vdots \\ \underline{D}_{\mathcal{R}1}(\vec{k}) & \cdots & \underline{D}_{\mathcal{R}\mathcal{R}}(\vec{k}) \end{pmatrix}$$

Fine print:

R is number of atoms in basis

Elements of $\underline{D}$ are really 3x3 in 3D.

As usual, origin is anywhere,
so relative distances are important

$$\underline{D}_{\kappa\kappa'}(\vec{k}) = \frac{1}{\sqrt{m_{\kappa}m_{\kappa'}}} \sum_{l'} \Phi_{0\kappa l' \kappa'} e^{i\vec{k} \cdot (\vec{r}_{l'} - \vec{r}_0)}$$

Resulting eigenvalue equation for the polarization vector at $\vec{k}_j$, with eigenvalue ω_{kj}

$$\underline{D}(\vec{k}) \vec{e}_j(\vec{k}) = \omega_{\vec{k}j}^2 \vec{e}_j(\vec{k})$$

When you put phonon solution for $u(t)$ into Equation of Motion

Resulting eigenvalue equation for the polarization vector $\mathbf{e}$ at $\mathbf{k}_j$, with eigenvalue ω_{kj}

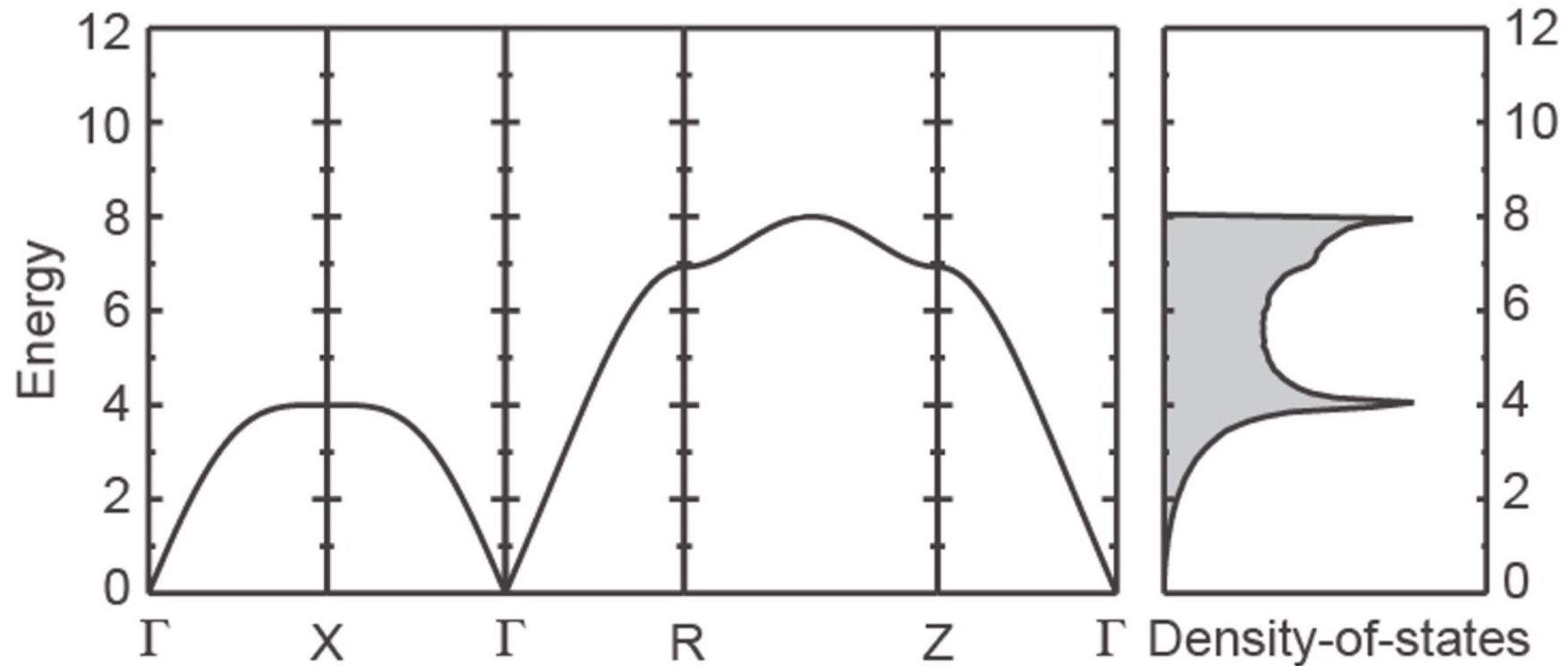
$$\underline{D}(\vec{k}) \vec{e}_j(\vec{k}) = \omega_{kj}^2 \vec{e}_j(\vec{k})$$
$$\vec{e}_j(\vec{k}) = \begin{pmatrix} e_{x1j}(\vec{k}) \\ e_{y1j}(\vec{k}) \\ e_{z1j}(\vec{k}) \\ e_{x2j}(\vec{k}) \\ \vdots \\ e_{z\mathcal{R}j}(\vec{k}) \end{pmatrix}$$

$$\underline{D}(\vec{k}) = \begin{pmatrix} \underline{D}_{11}(\vec{k}) & \cdots & \underline{D}_{1\mathcal{R}}(\vec{k}) \\ \vdots & \ddots & \vdots \\ \underline{D}_{\mathcal{R}1}(\vec{k}) & \cdots & \underline{D}_{\mathcal{R}\mathcal{R}}(\vec{k}) \end{pmatrix}$$

Fine print:

$\mathcal{R}$ is number of atoms in basis
Elements of $\underline{D}$ are really 3x3 in 3D.
There are $3\mathcal{R}$ polarization vectors
and $3\mathcal{R}$ eigenvalues (frequencies,
hopefully $\omega^2 > 0$).
 $3\mathcal{R}$ “branches” of dispersions vs. $\mathbf{k}$.

Dispersions and Density of States



Dispersions from single crystal
Oriented along different crystallographic directions

Density of states from powders
Accounts for all modes in a crystal

Entropy is the Core Concept of Thermodynamics

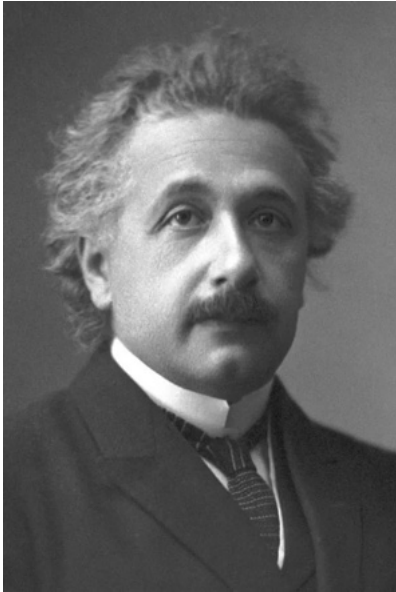
$$\text{Free Energy: } F = E - TS$$



In world without entropy S , simply minimize E and ignore T .
This reduces thermodynamics to one hand clapping.

Where does S come from?

Einstein 1907 Quantized the Harmonic Oscillator to explain why C_p goes to 0 at low T



— $3\varepsilon_i$

— $2\varepsilon_i$

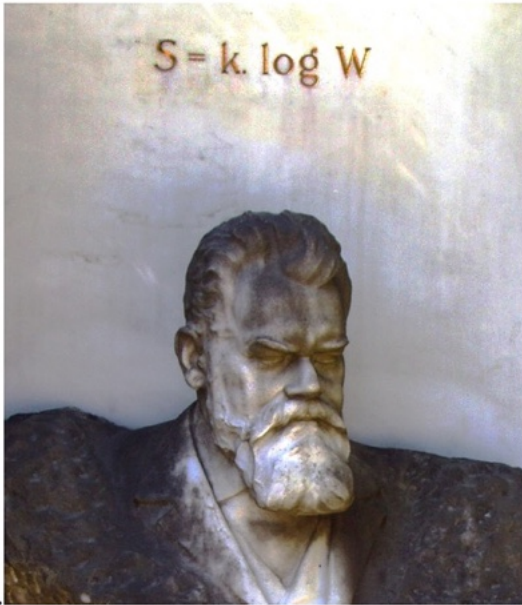
— $\varepsilon_i = \hbar\omega_i$

$\updownarrow k_B T$
— 0

Quantum levels of
a single oscillator
mode of frequency ω_i

When $k_B T < \varepsilon_i$,
then exponentially
unlikely input of heat
input of ε_i

Calculate the Entropy of a Harmonic Mode with Phonons



For N atoms,
 $3N$ oscillator modes of energy $\{\epsilon_i\}$

$$\mathcal{Z}_N = \prod_i \frac{e^{-\beta\epsilon_i/2}}{1 - e^{-\beta\epsilon_i}},$$

Helmholtz Free Energy

$$F = -k_B T \ln \mathcal{Z},$$

$$\partial F / \partial T = -S$$

After a bit of work:

$$S(T) = 3k_B \int_0^\infty g(\epsilon) [(n+1) \ln(n+1) - n \ln(n)] d\epsilon$$

Phonon DOS

Planck factor $n(\epsilon, T)$

$$n(\epsilon, T) = \frac{1}{e^{\epsilon/(k_B T)} - 1}$$

$$S = k_B \ln \Omega$$

Entropy Contributions at ~ 1000 K

Matter: configurational entropy

Nuclei (locate the nuclei, electrons then accommodate) $(\sim 0.5 + 1 - 0.5) k_B/\text{atom}$

Energy: Dynamics of nuclei (phonons) and electrons

Harmonic $(\sim 8 \pm 1) k_B/\text{atom}$

Quasiharmonic $(\sim 1 \pm 0.5) k_B/\text{atom}$

Excitations of electrons (electronic heat capacity)
 $(\sim 0.5 \pm 0.2) k_B/\text{atom}$

Interactions of Excitations

Phonon-phonon interaction: anharmonic $(\sim 1 \pm 1) k_B/\text{atom}$

Electron-phonon interaction $(\sim 0.5 \pm 0.5) k_B/\text{atom}$

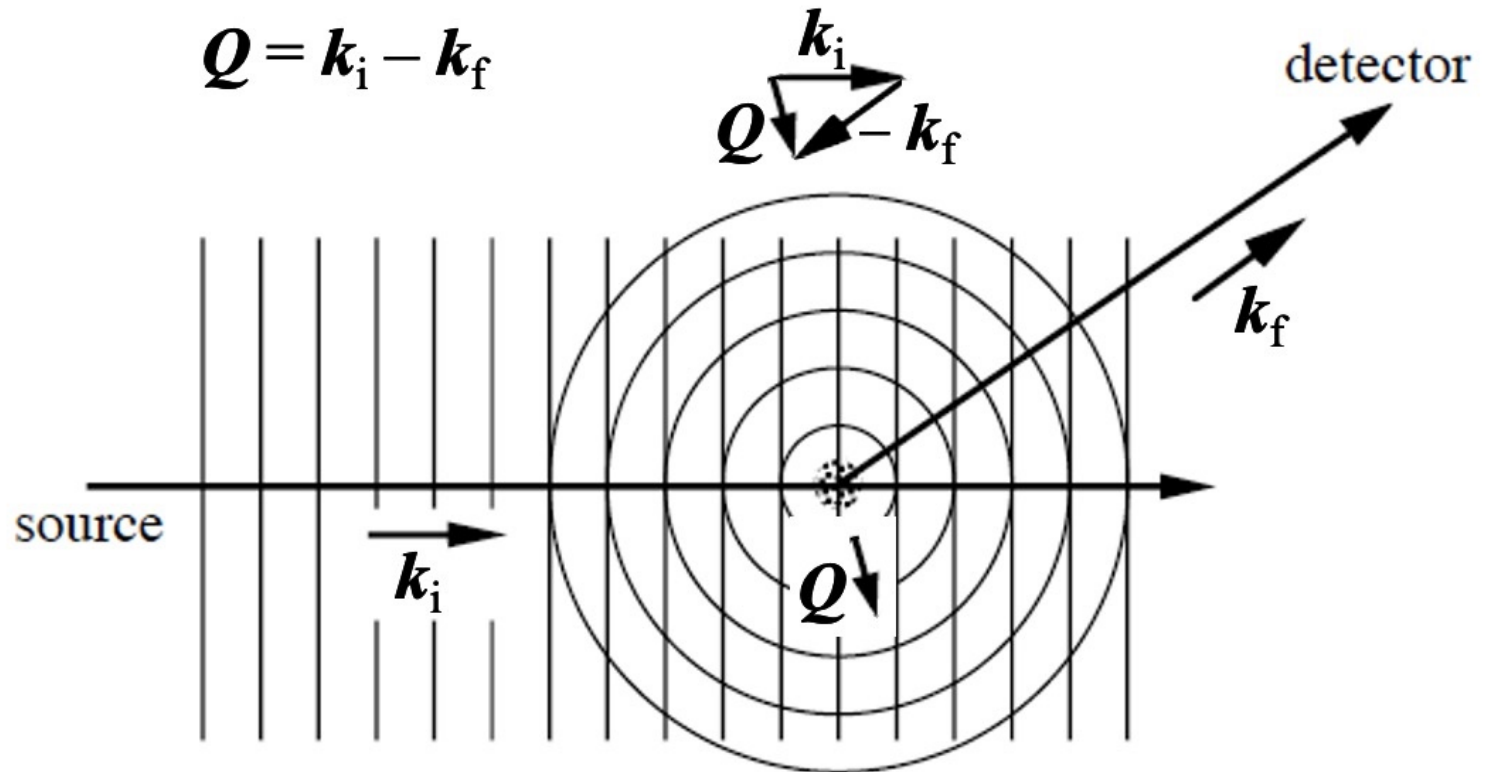


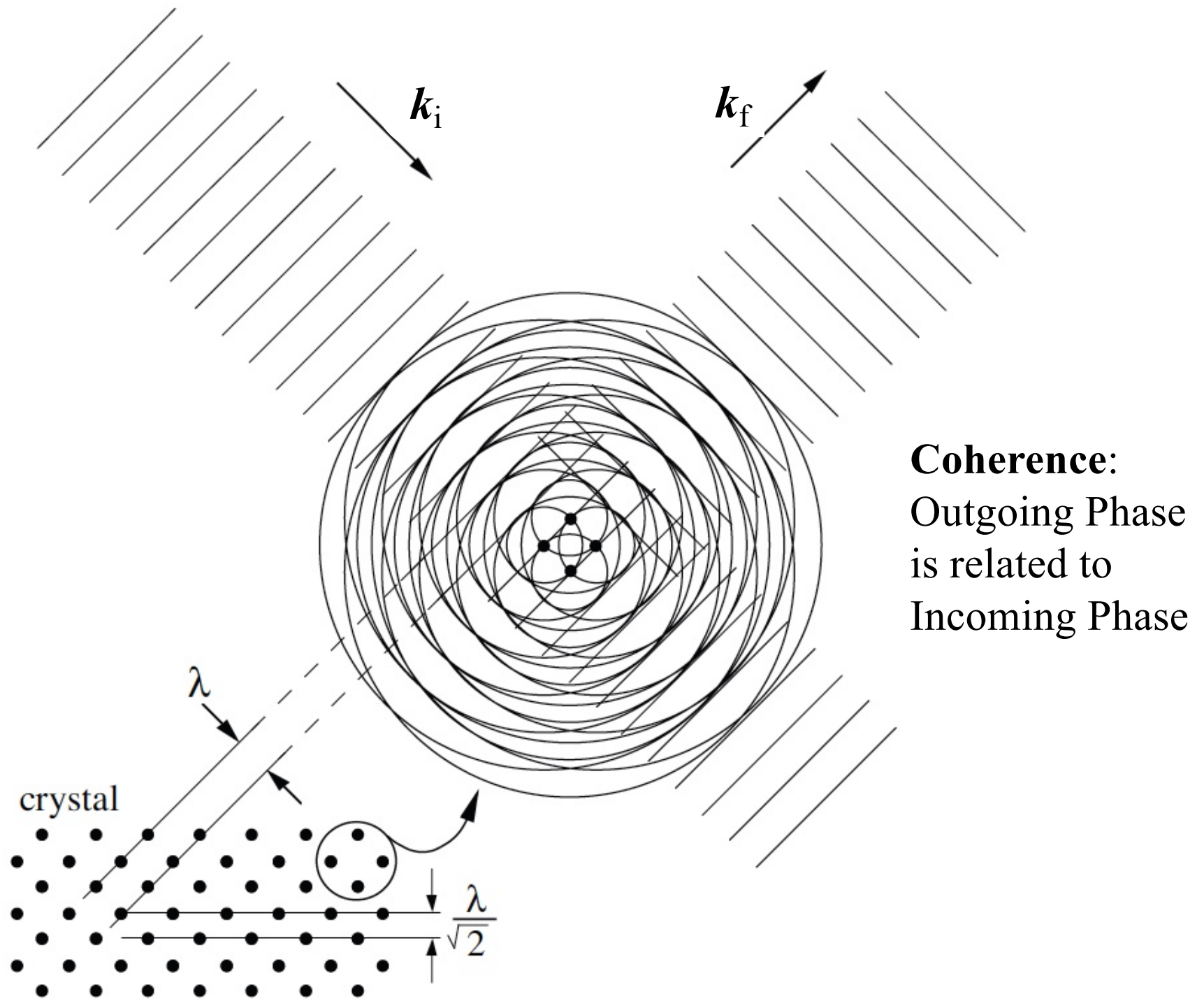
Scattering

Waves and wavefunctions, ψ

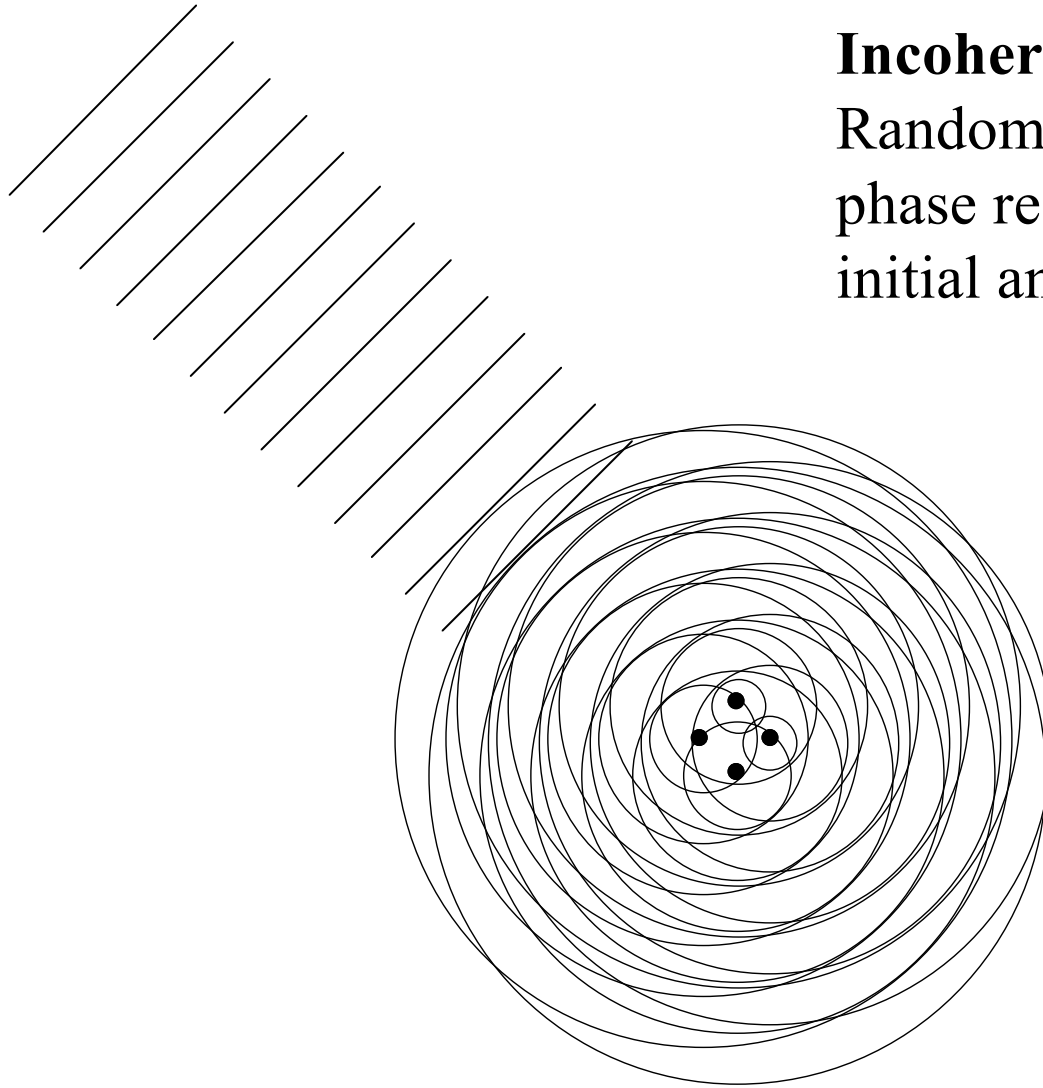
Relative phases, $\mathbf{Q} \cdot \mathbf{r} - \omega t$

Intensity (at detector), $\psi^* \psi$





Incoherence:
Randomness of
phase relation between
initial and final waves



no interference — individual scatterings (particle-like)

Key Words for Scattering

elastic or inelastic — energy change of the wave

coherent or incoherent — preservation of phase of wave

Four Pairs of Words

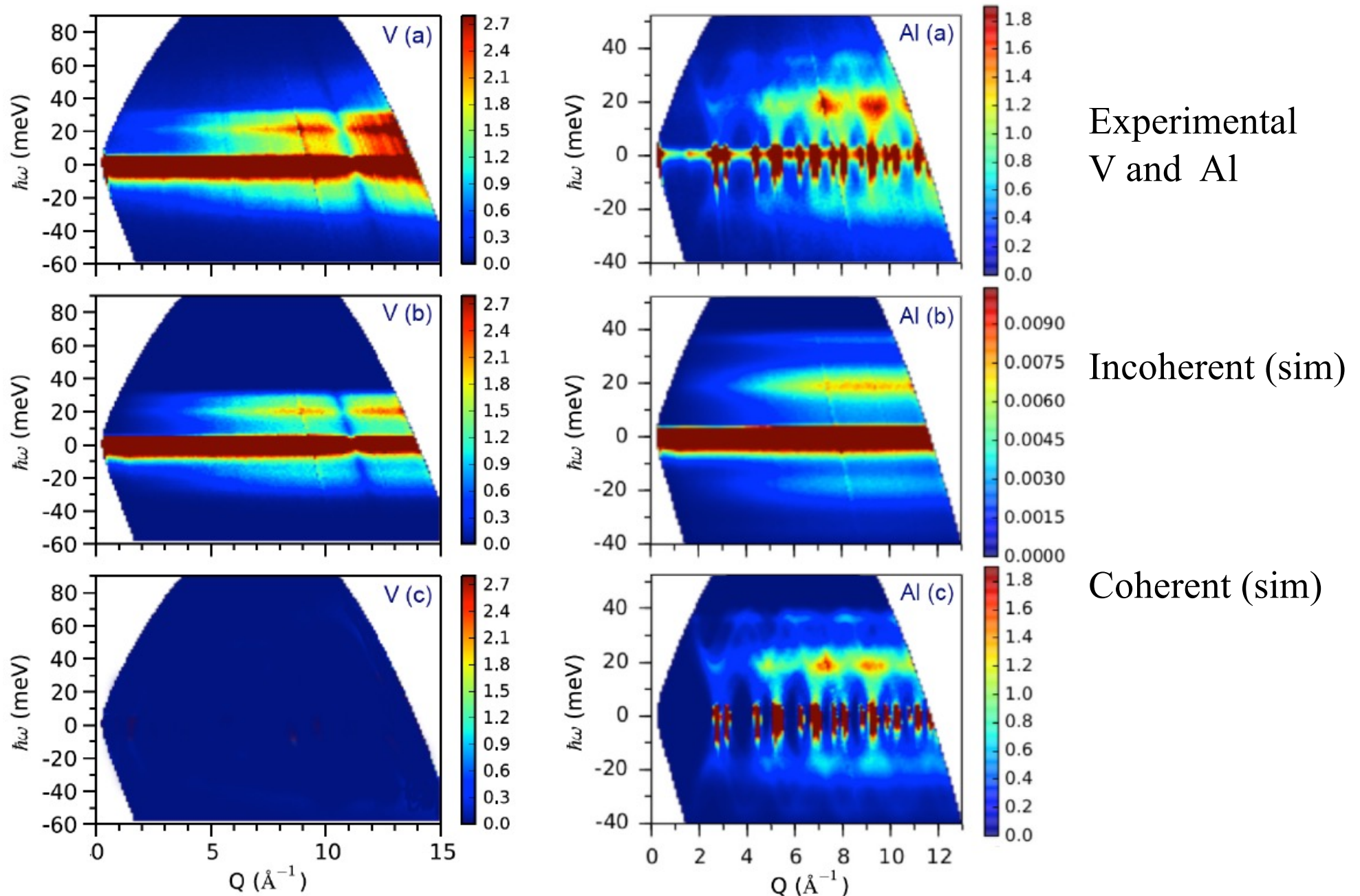
coherent, elastic diffraction, SANS

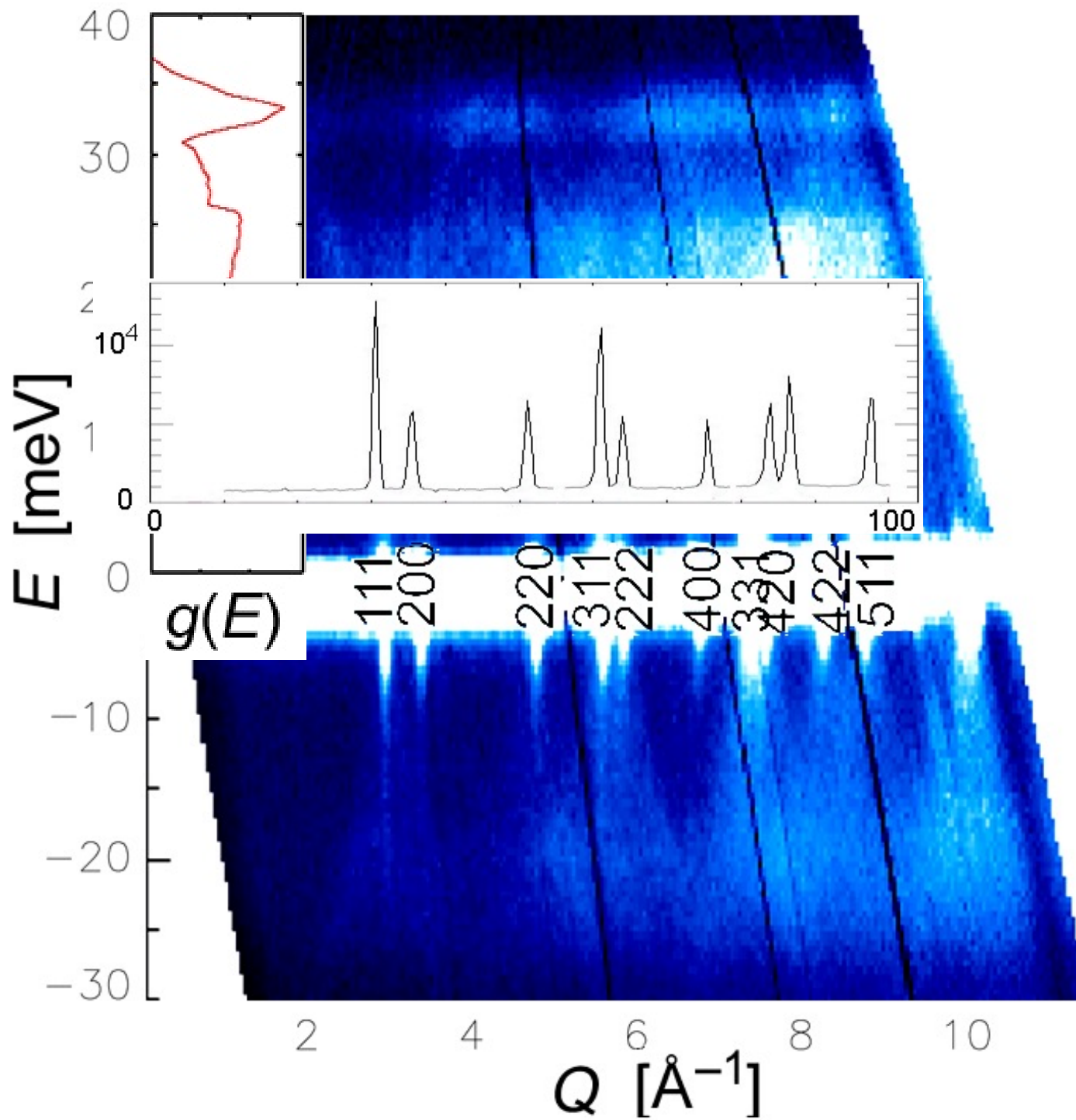
incoherent, elastic atom displacement disorder

incoherent, inelastic energy spectra (phonon DOS)

coherent, inelastic dispersions (phonons, magnons)

Appearance of Coherent and Incoherent Scattering





fcc
Fe-Ni
polycrystalline
sample

(fcc has cubic
indices all even
or all odd)

Fermi's Golden Rule (within the 1st Born Approximation)

Textbook starts with Fermi's Golden Rule

$$W(t') = \frac{2\pi}{\hbar} |\langle \Psi_f(\mathbf{r}, t') | V(\mathbf{r}, t') | \Psi_i(\mathbf{r}, t') \rangle|^2$$

and after some effort obtains the general result

$$I(\mathbf{Q}, \omega) \sim \sum_j \sum_k b_j^* b_k \int e^{i\omega t} \left\langle e^{i\mathbf{Q} \cdot \underline{\mathbf{R}}_j(t)} e^{-i\mathbf{Q} \cdot \underline{\mathbf{R}}_k(0)} \right\rangle dt .$$

Essentials of a Fermi Chopper Inelastic Spectrometer



fermion

Fermi-Dirac statistics

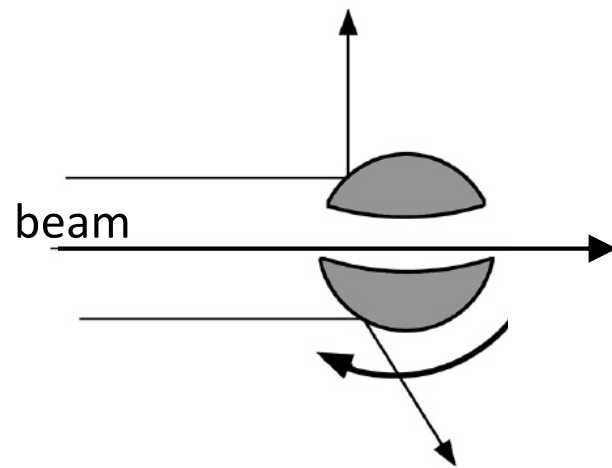
...

Fermi chopper

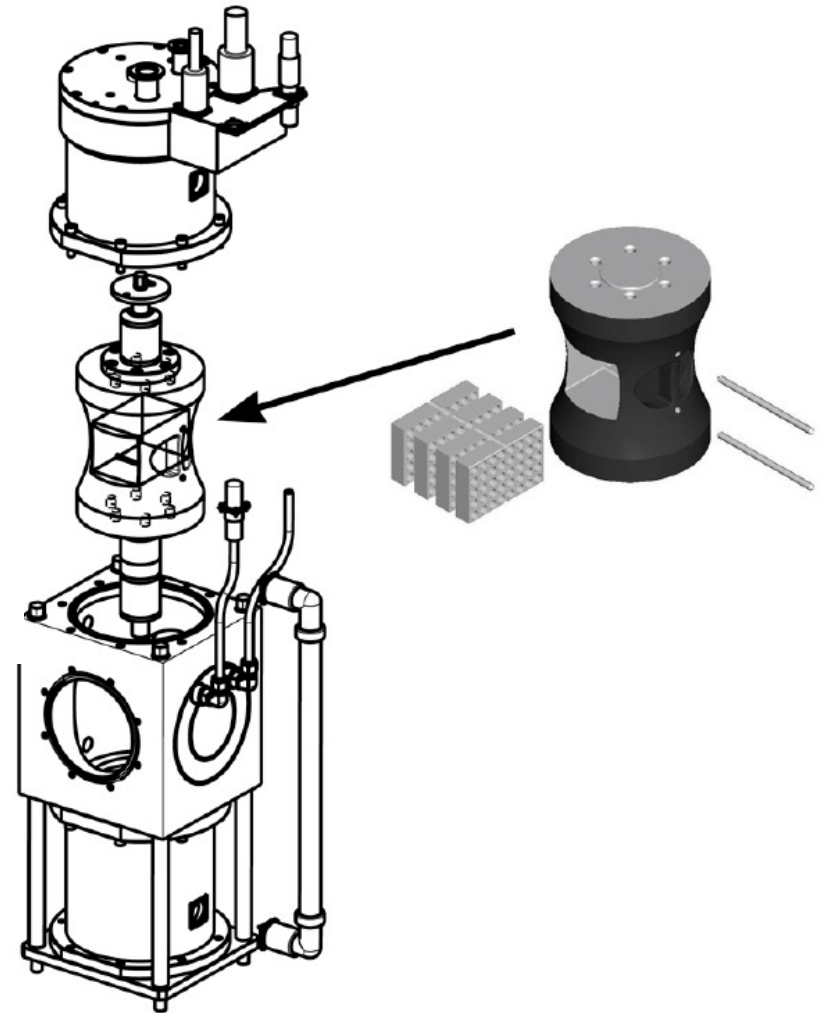
Fig. 5.1. Enrico Fermi works with an electronic control for a neutron chopper during his Argonne days.

Fermi Chopper

Concept (top view)



Real Chopper (exploded view)





ARCS Vacuum Tank in Assembly



ARCS Vacuum Tank in Assembly



COMMONWEALTH OF MASSACHUSETTS

Massachusetts Highway Department

10 Park Plaza, Boston, MA 02116

Permit For Movement of Non-Divisible Oversize & Overweight Loads

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APPLICANT INFO	COMPANY NAME OR AGENT	PERMIT NO.	EFFECTIVE DATE	EXPIRATION DATE
	J F LOMMA INC	8747209152445	9/19/2006	9/24/2006
	MAILING ADDRESS	MUNICIPALITY	STATE	ZIP CODE
	48 THIRD ST	S. KEARNY	NJ	07032

VEHICLE INFO	VEHICLE I.D. NO.	REGISTRATION OF HAULING VEHICLE	REGISTRATION OF TRAILER
	1FUYDKYEXKL987472	AR588E	T25P7H
	VEHICLE LENGTH	VEHICLE WIDTH	VEHICLE HEIGHT
	72 Ft 0 in.	14 Ft 0 in.	13 Ft 6 in.
	LOAD TYPE	GROSS WEIGHT	NO OF AXLES
	CHAMBER COVER	80000 Lbs.	5

PAYMENT DESTINATION	VENDOR CODE	TYPE OF PAYMENT	FEE PAID
		Credit Card	\$ 15.00
	ORIGIN	DESTINATION	NO. OF TRIPS
	WEST MINSTER	CT LINE	1

MA - 2A-140-190-290-395

05: ** FLAG CARS FRONT AND REAR WITH WIDE LOAD SIGNS AND FLASHING AMBER LIGHTS MUST BE
NEED.

ARCS Vacuum Tank



ARCS at the Spallation Neutron Source

Source x 15 (1.7 MW of protons at SNS, vs. 0.1 MW)

Neutron guide technology x 2

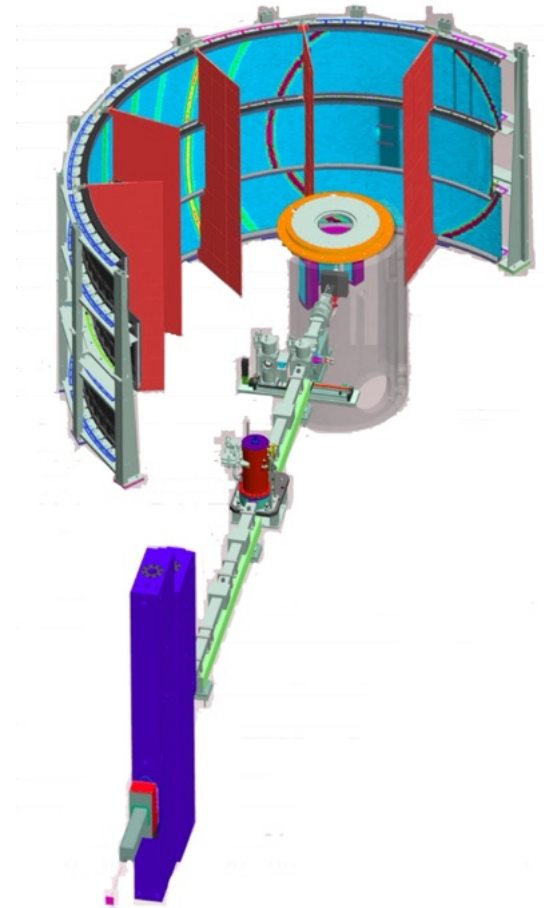
Detector solid angle x 30+ (covers π sr)

Factor of 1,000 improvement in efficiency for INS.

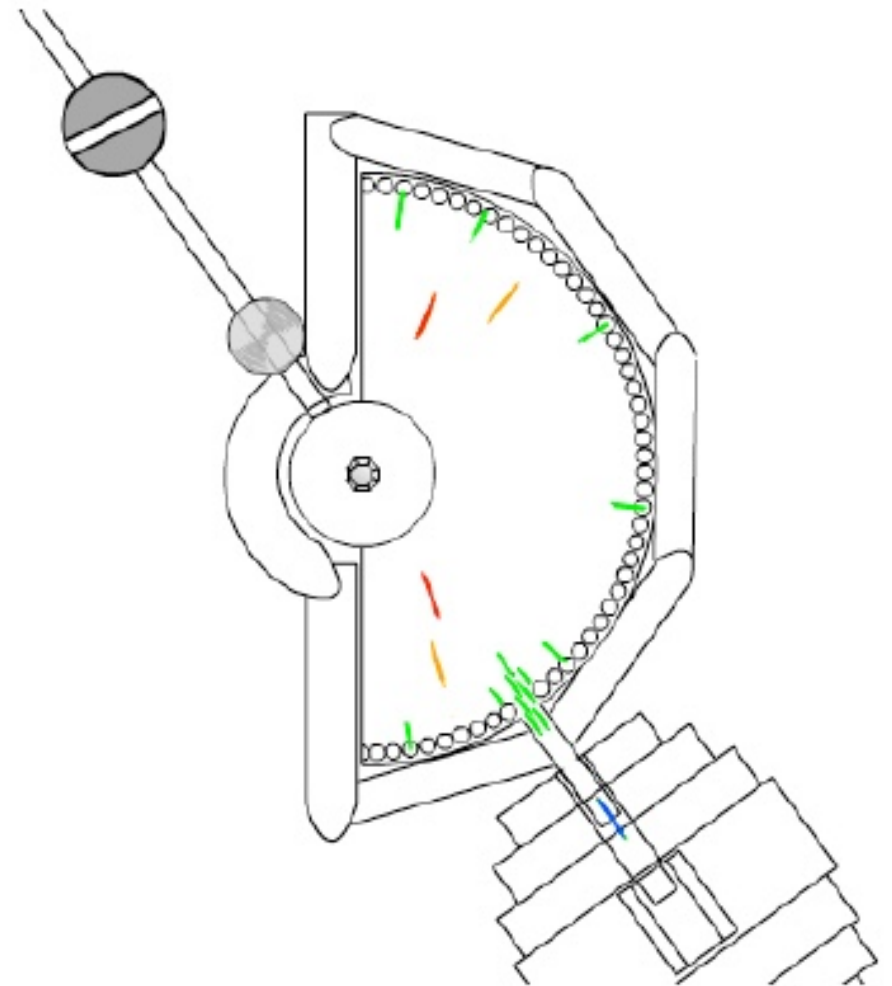
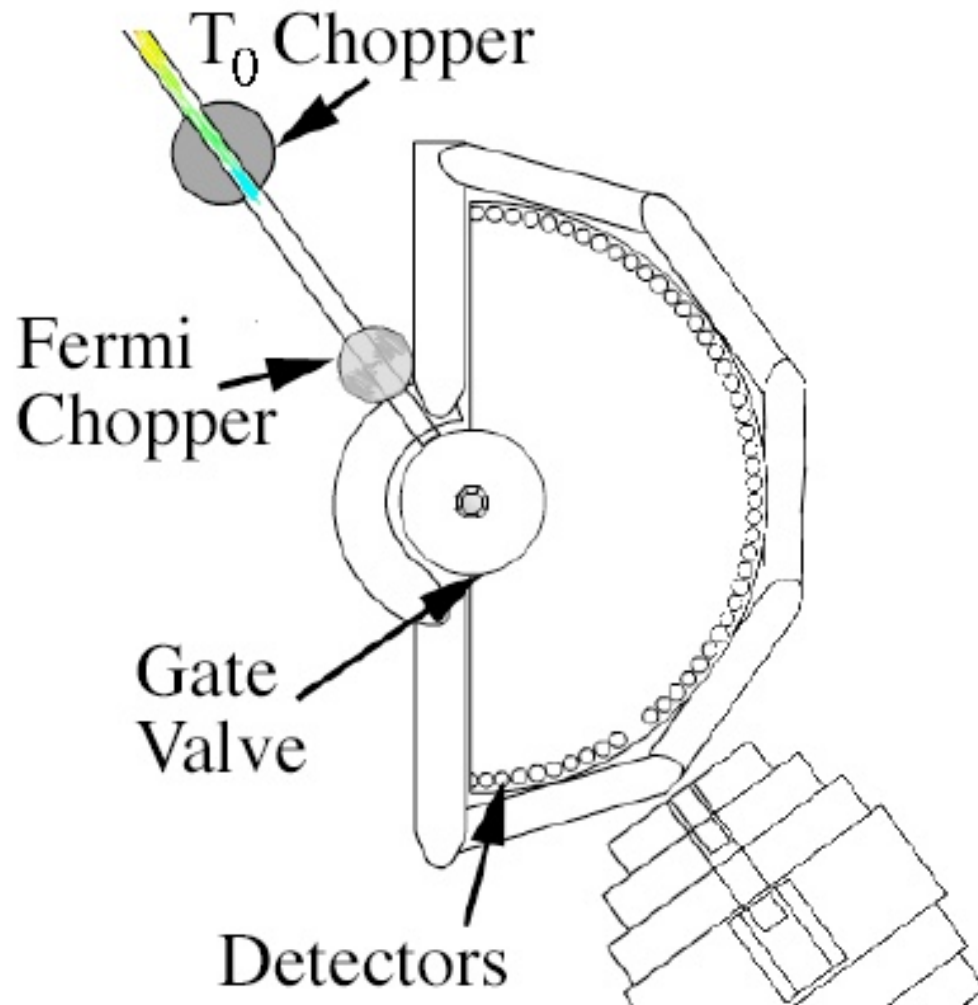
Also, investment in **low background**.

All neutron energy is kinetic, so energy transfer E from neutron to sample is measured by arrival time of detected neutron.

With both scattering angle and energy transfer, we obtain the momentum transfer Q .



Energy (velocity) selection. Snapshot at elastic peak arrival.



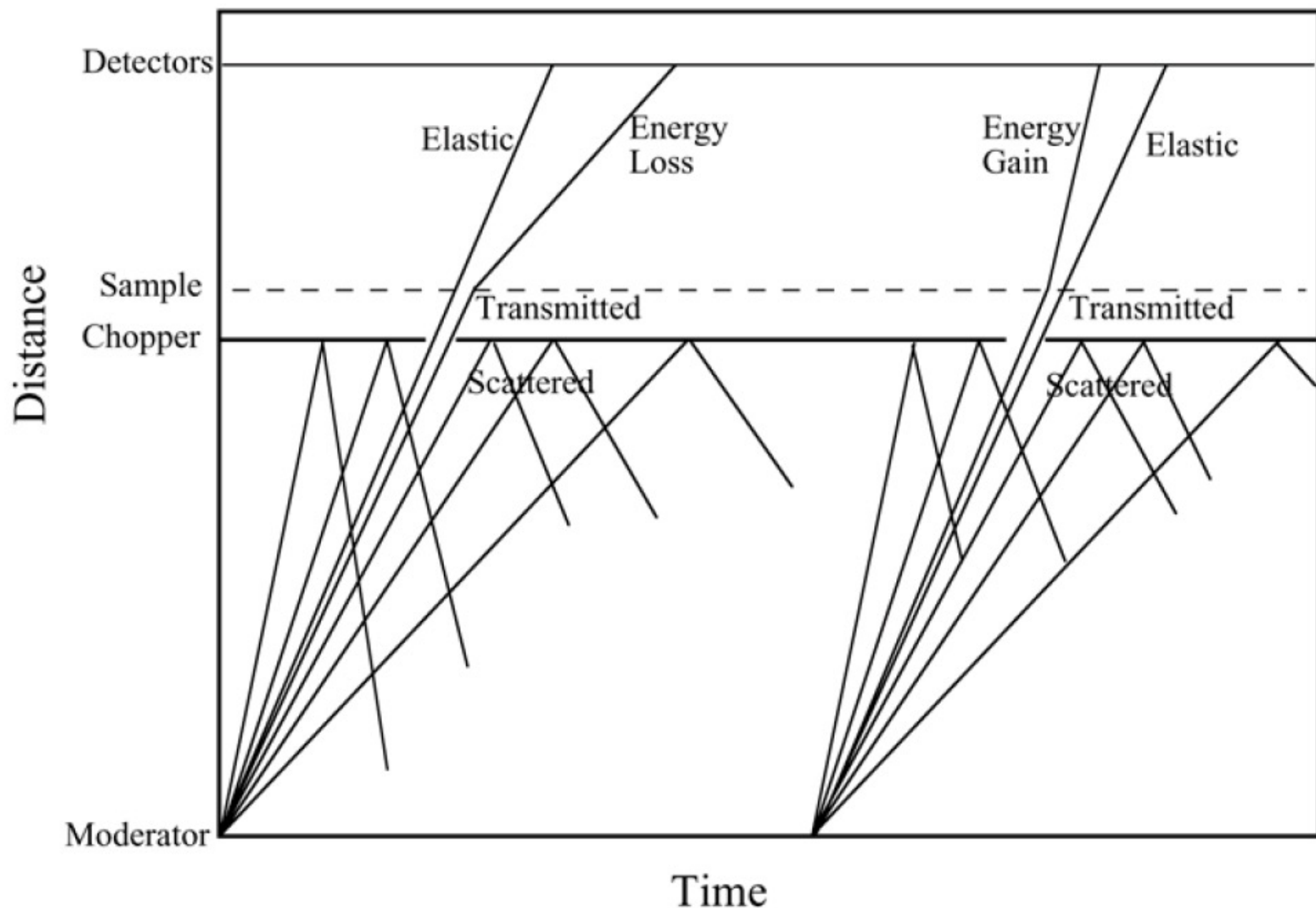
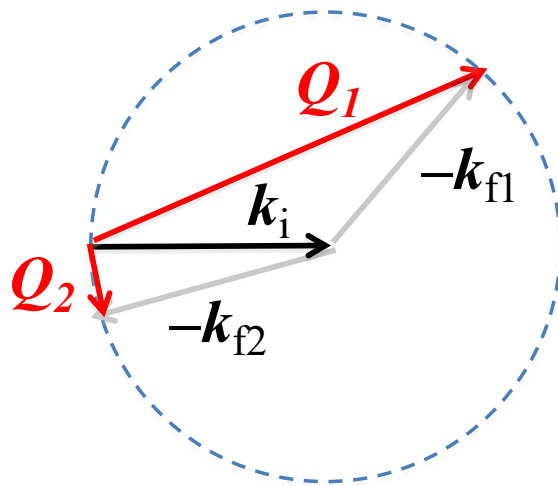


Fig. 5.3. Distance–time diagram for inelastic scattering by a direct geometry chopper spectrometer. Positions of the moderator, chopper, sample, and detectors are marked on the vertical axis. Two moderator pulses occur at points on the x -axis.

Kinematical limitations for INS (unlike elastic)

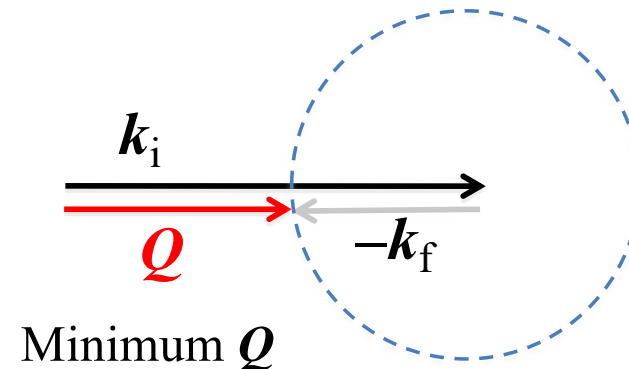
- $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ $|\mathbf{k}_f|$ is smaller than $|\mathbf{k}_i|$ if neutron loses energy to the sample
- $E = \hbar^2/2M (k_i^2 - k_f^2)$

Elastic: $E = 0$ so $k_i^2 = k_f^2$



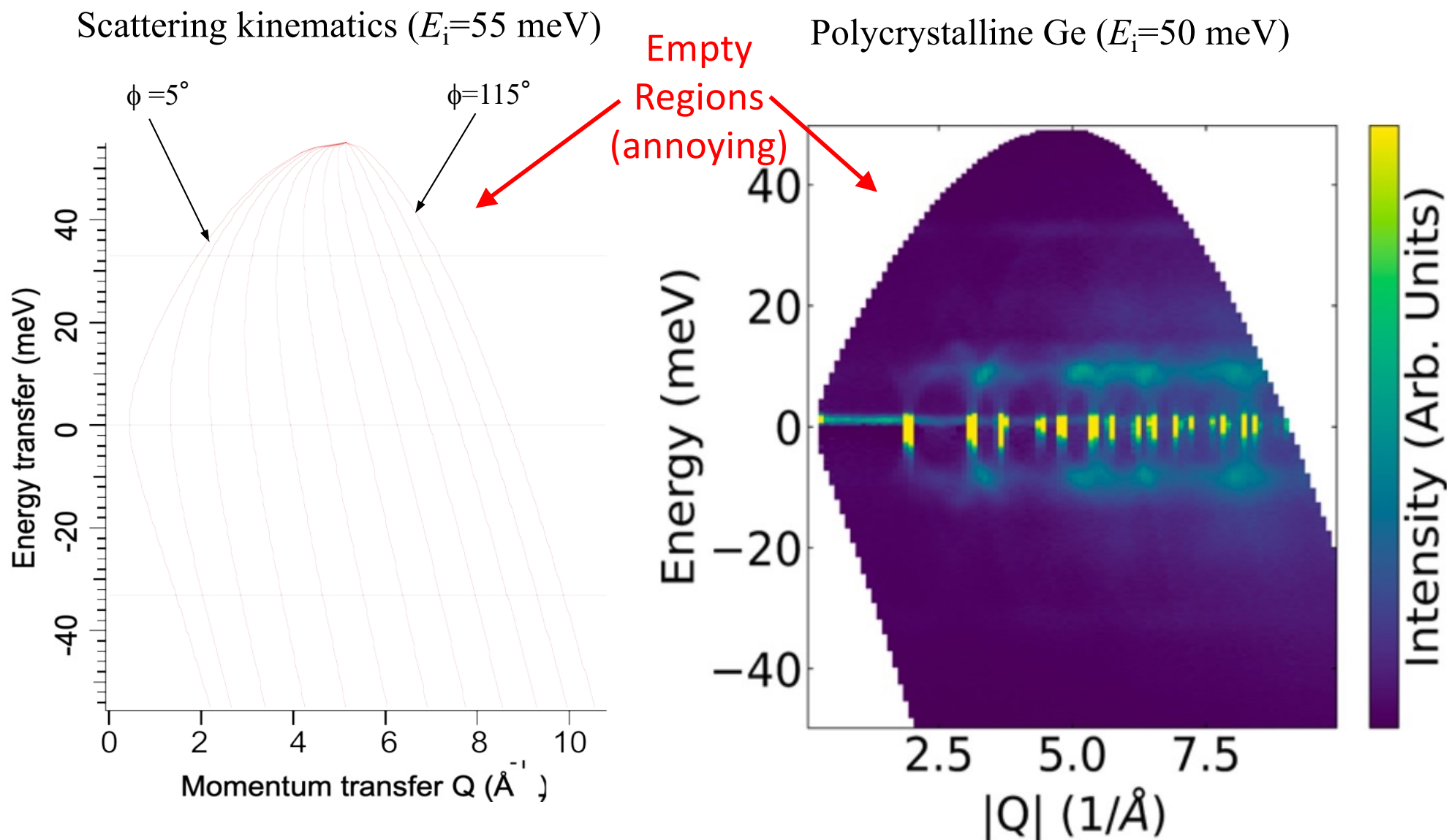
Allows any Q from 0 to $2k_i$
Diffraction measurements to $Q = 0$
(Ewald sphere in diffraction)

Inelastic: $E > 0$ and $k_i > k_f$



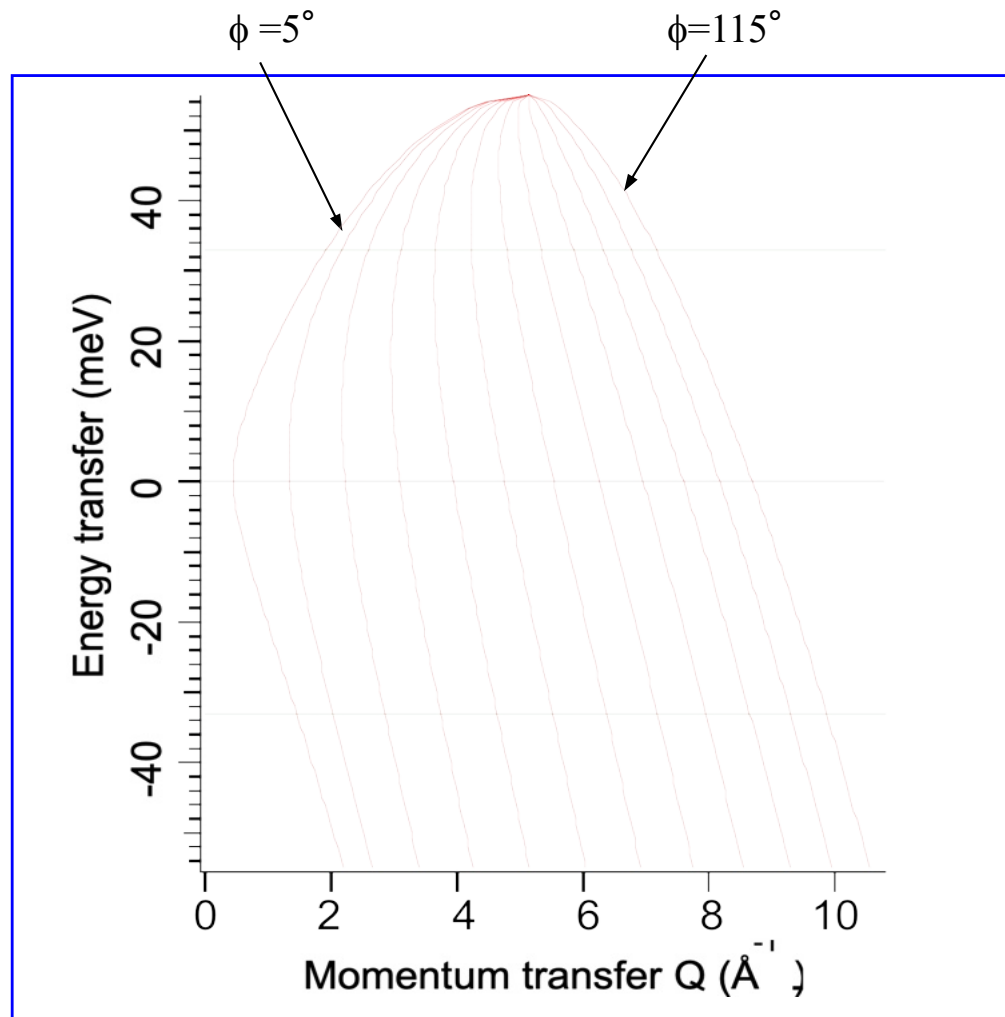
Measurements are “kinematically forbidden” at small Q
with small k_f or some $E > 0$

Kinematical limitations in real INS data

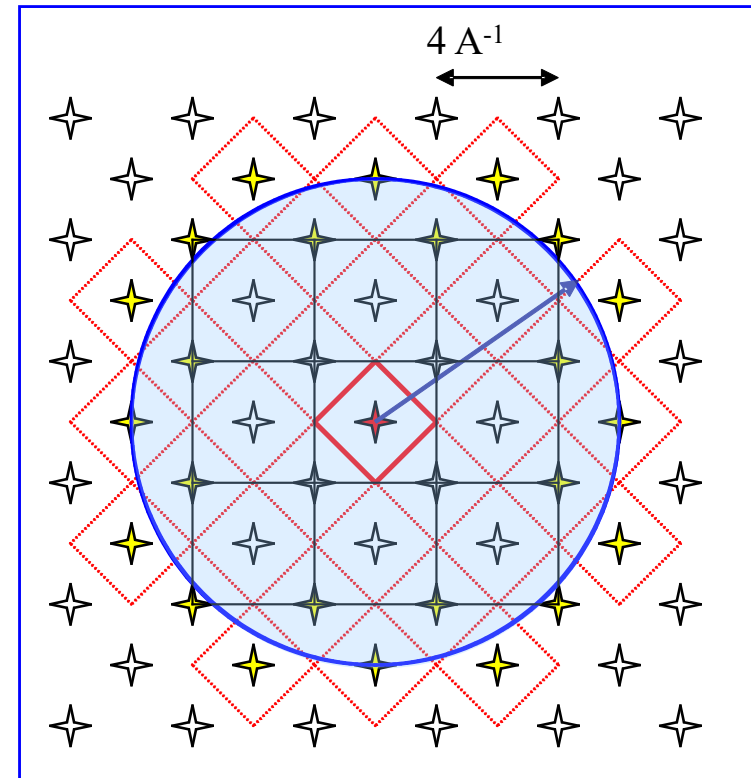


Many Brillouin zones typically sampled at 55 meV E_i

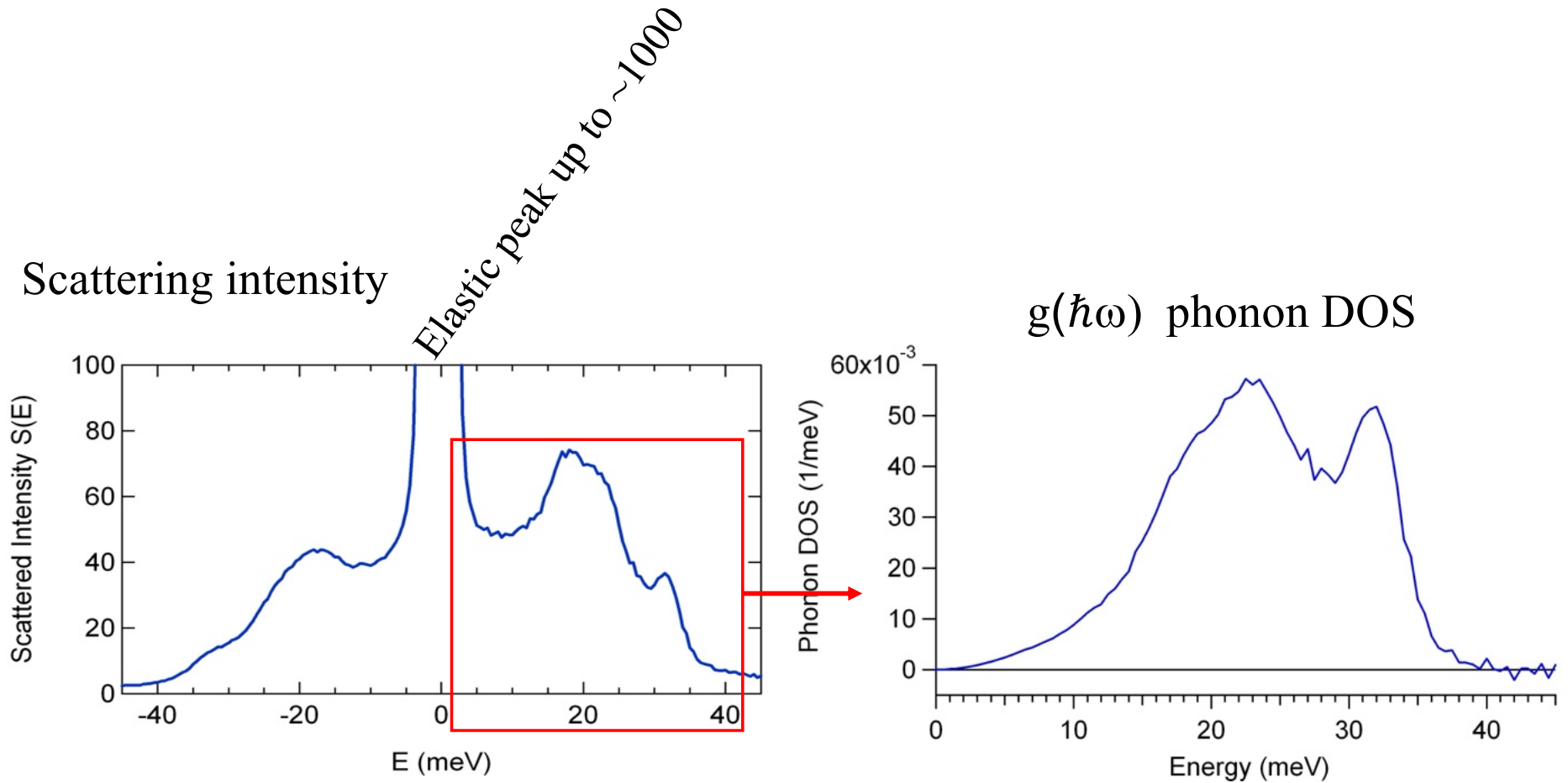
Scattering kinematics ($E_i=55$ meV)



Brillouin zones and typical reciprocal space sampling ($Q=8 \text{ \AA}^{-1}$)



Data Analysis



More phonons in modes at low energy,
so more phonon scattering

DOS requires corrections for
thermal factors...

Data Analysis

Incoherent inelastic neutron scattering gives a direct measurement of the phonon density of states (DOS), $g(\omega)$.

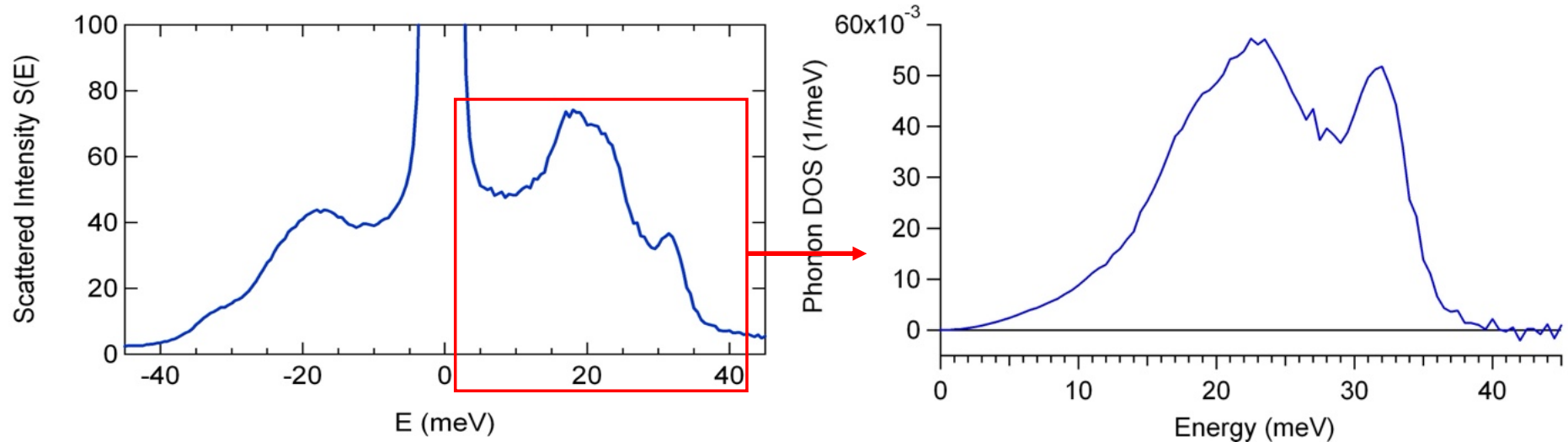
$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'} \right)_{+1 \text{ phonon}}^{inc} = \frac{\sigma_{inc}}{4\pi} \frac{k'}{k} \frac{e^{-2W}}{2M} \frac{Q^2}{3\omega} g(\omega) \langle n(\omega) + 1 \rangle$$

$\exp(-2W)$: Debye-Waller factor,
 $n(\omega)$: Planck distribution
 $n(T) = (\exp(E/(k_B T)) - 1)^{-1}$

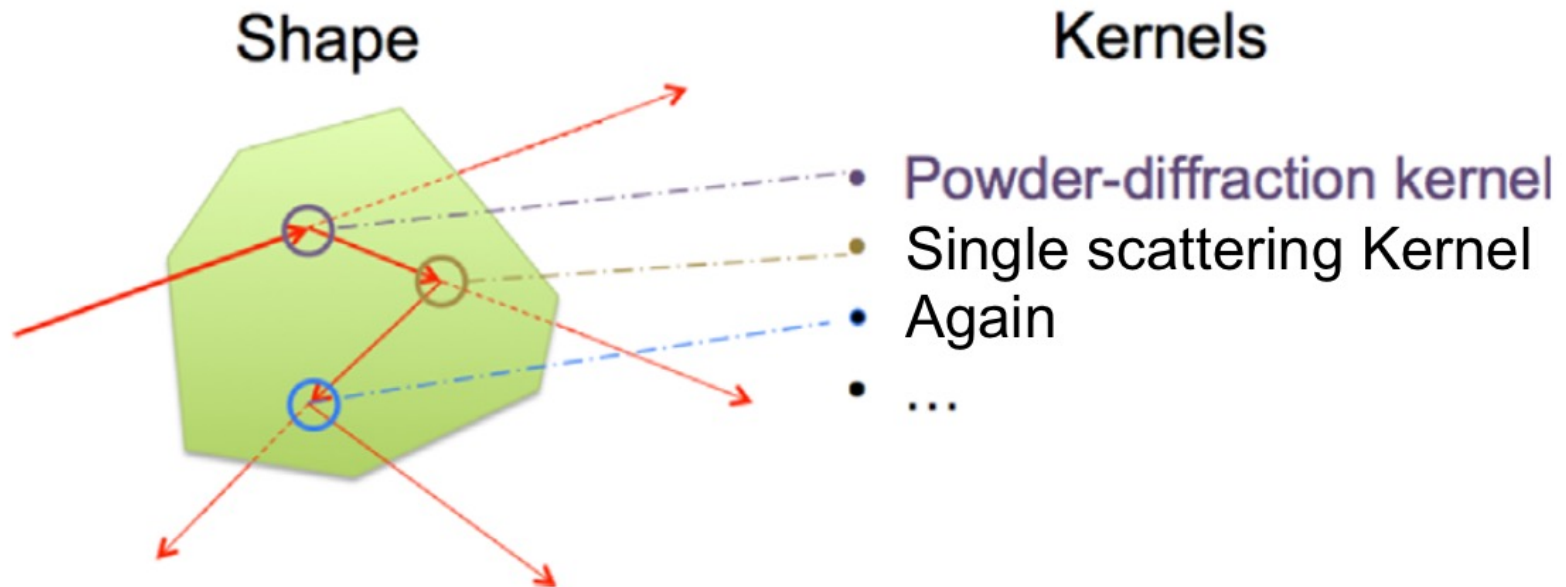
scattering
intensity

Neutron-weighting

$g(\omega)$: phonon DOS

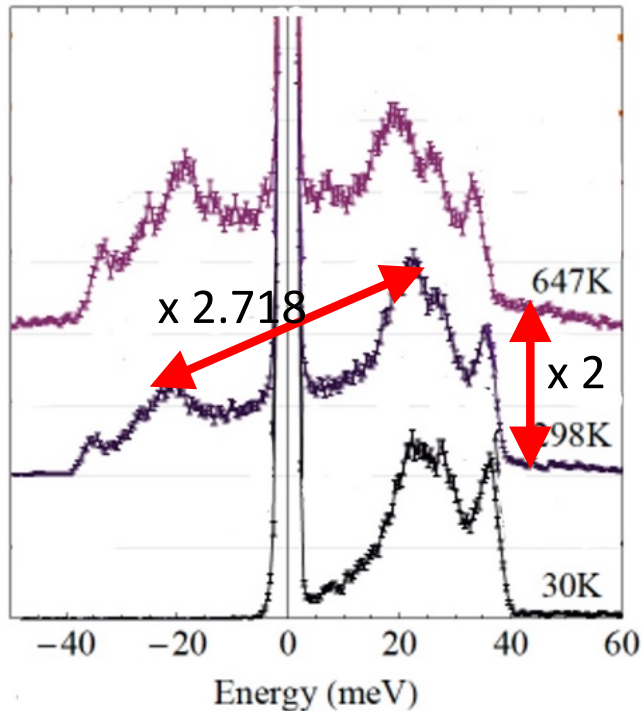


Multiple Scattering (ray tracing)



An example of multiple scattering within one scatterer.

Temperature and Incoherent Inelastic Scattering (on bcc ^{57}Fe)



Detailed Balance

Intensity ratio across elastic peak: $I(+\varepsilon) = \exp(\varepsilon/k_B T) I(-\varepsilon)$

For $25 \text{ meV} = k_B 300 \text{ K}$, so at 300 K:

$$I(+25) = 2.718 I(-25)$$

Multiphonon Scattering

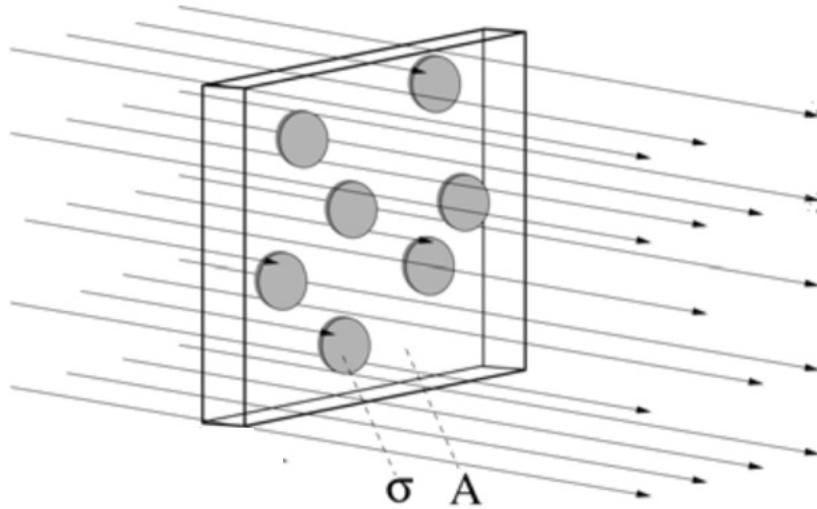
create/annihilate two phonons of energy $\varepsilon = \pm \varepsilon_1 \pm \varepsilon_2$

Convolution of single scattering thermal spectrum with itself

Maximum at $\varepsilon = 0$, broad and washed out

Grows $\sim T$ (fixed Q for NRIXS)

Cross-Section is Conserved, even if atoms are moving



Moving atoms

Still cover the same area to the beam.

Thermal motions cause a
Debye-Waller factor for the
intensity of elastic scattering

$$I_{\text{elastic}} \sim \text{D.W.}$$

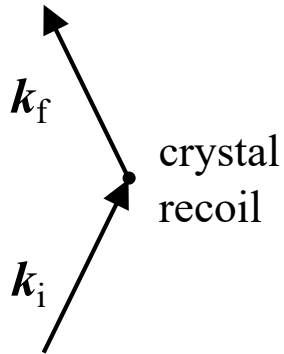
$$I_{\text{elastic}} \sim e^{-2W}$$

$$2W = Q^2 \langle u^2 \rangle$$

Conservation of cross section requires
intensity transfer from elastic to inelastic
when atoms have thermal motion

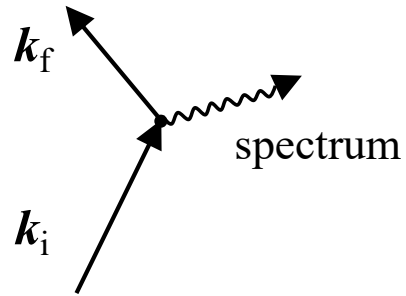
Correct for Multiphonon Scattering (concept)

Elastic
Scattering



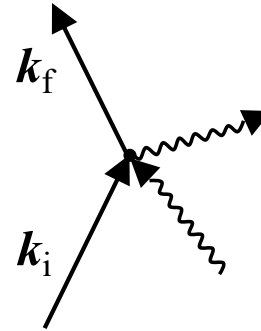
Diffraction
 $|k_i| = |k_f|$

1-Phonon
Scattering



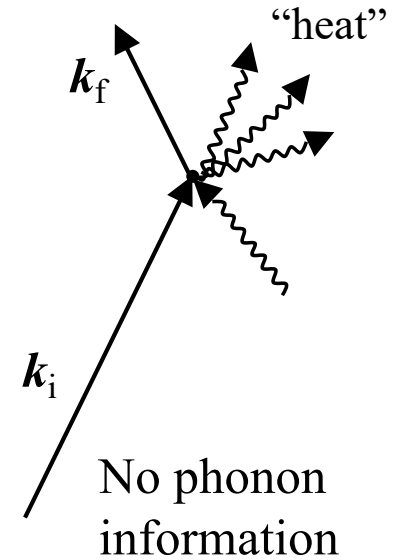
Phonon
Spectra

2-Phonon
Scattering



Calculate
And Delete

Classical
Scattering



Strong change with temperature $\sim T^2$
Weak change with thickness

Multiphonon scattering, temperature, momentum

Total cross-section conserved at high T when Debye-Waller factor attenuates elastic peaks as $\exp(-2W)$. Compensate with $\exp(+2W)$.

$$1 = e^{-2W} e^{+2W} = \sum_{n=0}^{\infty} e^{-2W} \frac{(2W)^n}{n!} \quad \text{if isotropic: } 2W = Q^2 \langle u^2 \rangle$$

$$I(\mathbf{Q}, \omega) \sim \sum_{\kappa} e^{-\langle (\mathbf{Q} \cdot \mathbf{u}_{\kappa})^2 \rangle} \left(1 + \langle (\mathbf{Q} \cdot \mathbf{u}_{\kappa})^2 \rangle + \frac{1}{2} (\langle (\mathbf{Q} \cdot \mathbf{u}_{\kappa})^2 \rangle)^2 + \dots \right)$$

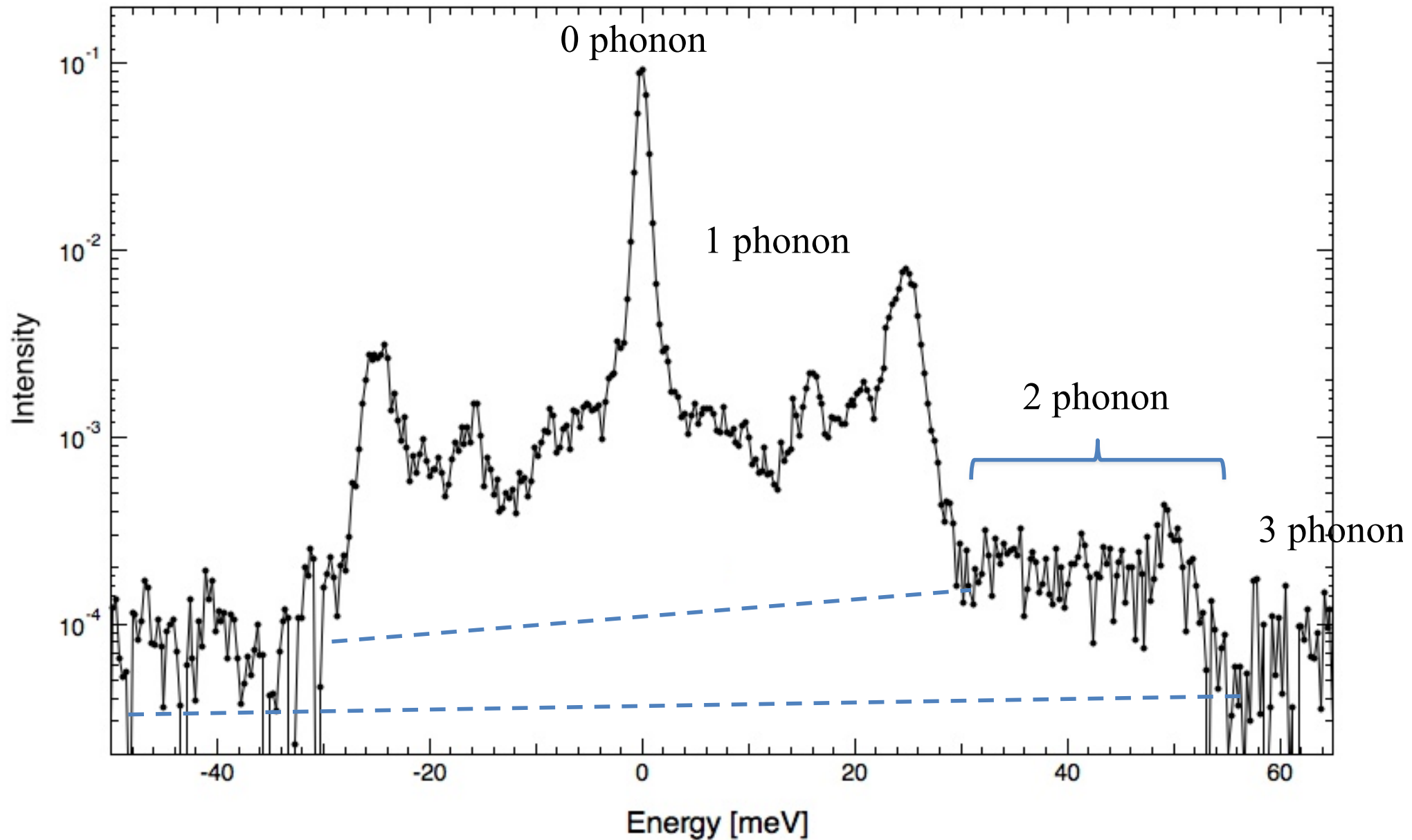
0 phonon, 1 phonon, 2 phonons

Recoil energy, thermal energy, Debye-Waller factor

$$E_R = \frac{\hbar^2 Q^2}{2m} \quad k_B T = 2m\omega^2 \langle u^2 \rangle \quad Q^2 \langle u^2 \rangle = \frac{E_R}{\hbar\omega} \frac{k_B T}{\hbar\omega}$$

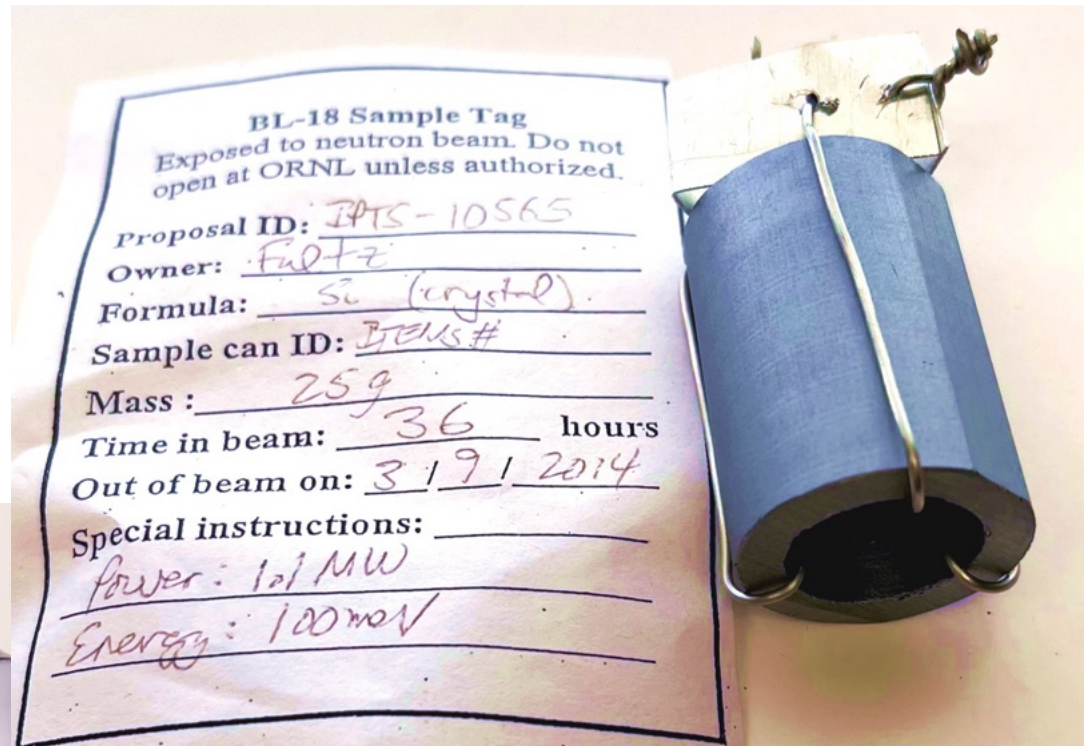
Multiphonon scattering increases with momentum transfer and temperature.

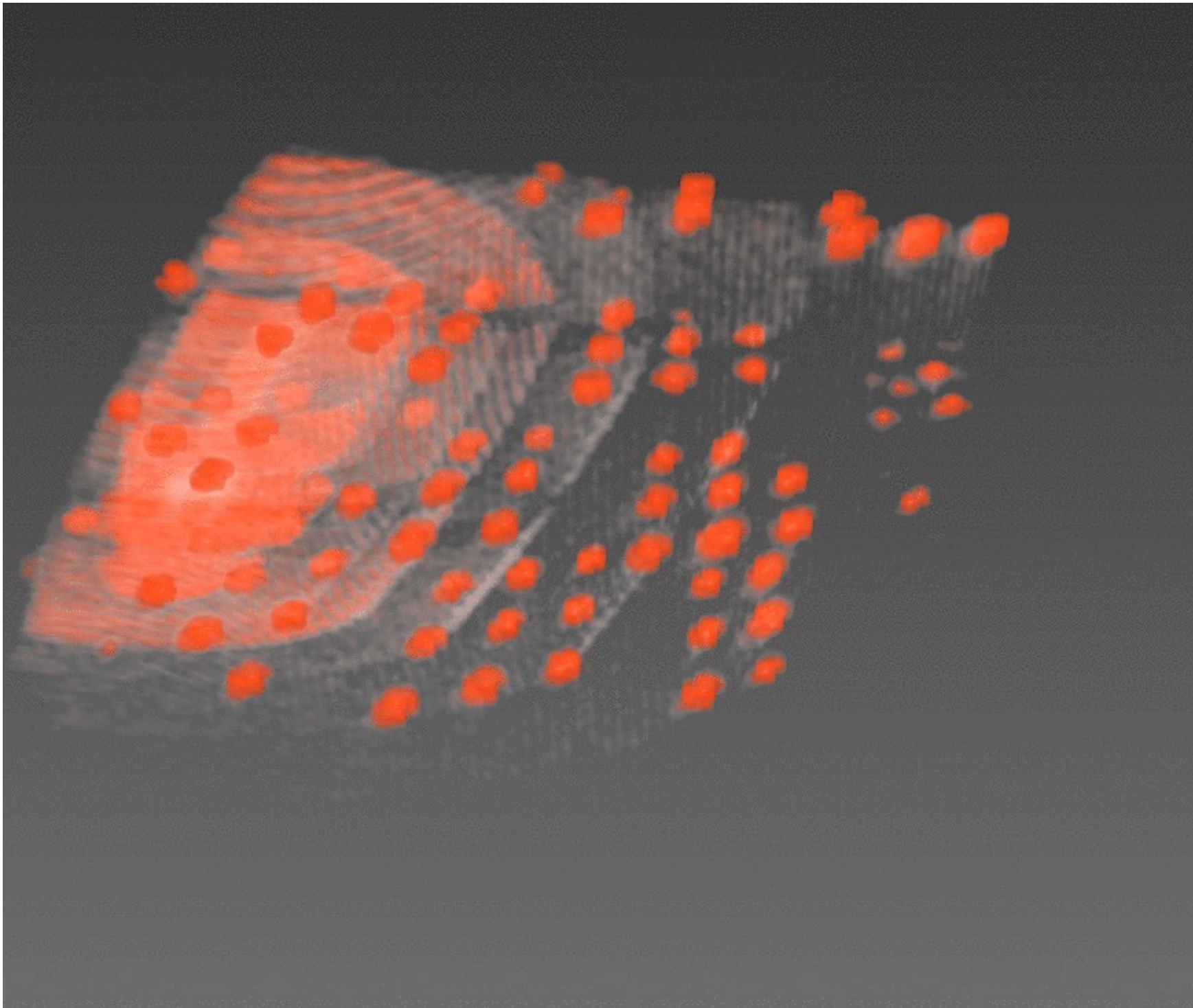
Multiphonon components of (incoherent) NRIXS of $\text{Pt}_3^{57}\text{Fe}$



Silicon Single Crystal

Zero thermal expansion
at 123 K

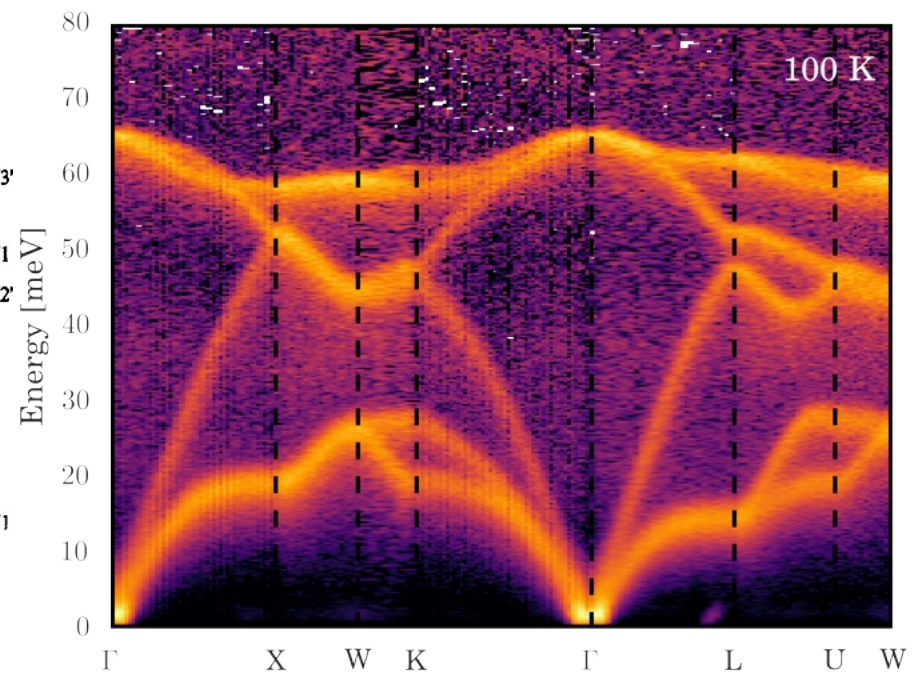
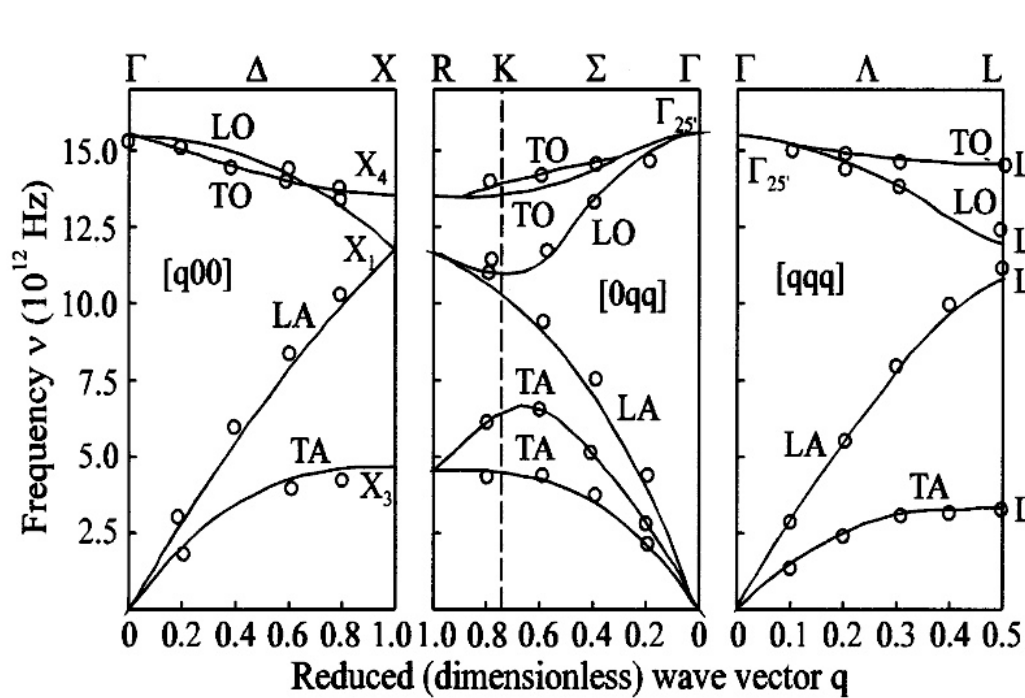




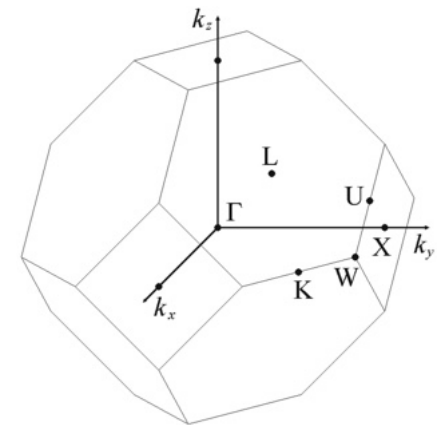
Silicon Phonon Dispersions 4D Data

Dennis Kim,
Ph.D. Thesis 2018

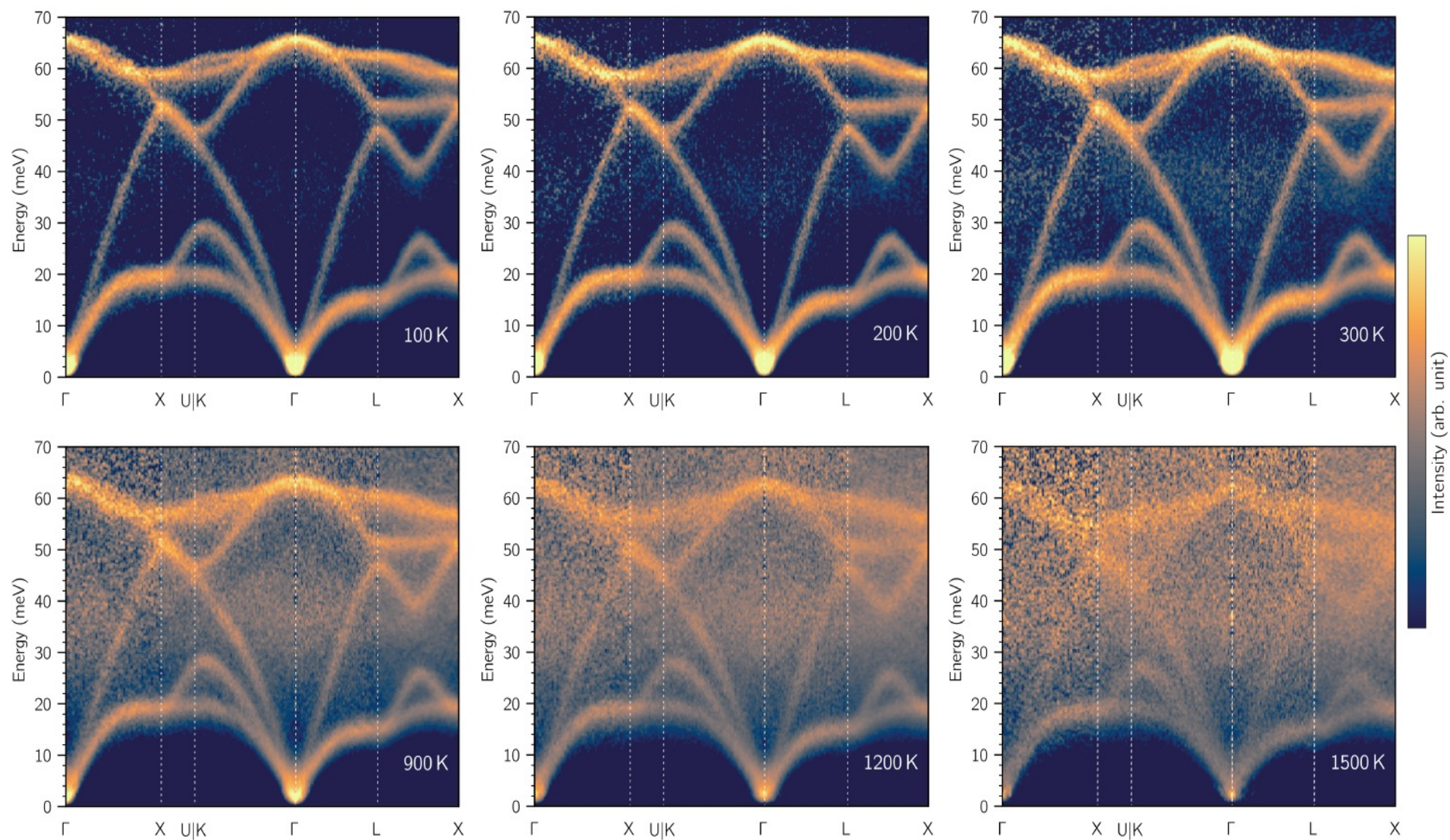
Phonon Dispersions, along usual k -directions



G. Dolling, *Proc. Symp. Inelastic Scattering Neutrons in Solids and Liquids*, Chalk River, IAEA, Vienna, vol. 2, 1963, p. 37.
 R. Tubino, et al., *J. Chem. Phys.* **56**, 3 (1972) 1022-1039.



Thermal background between dispersions



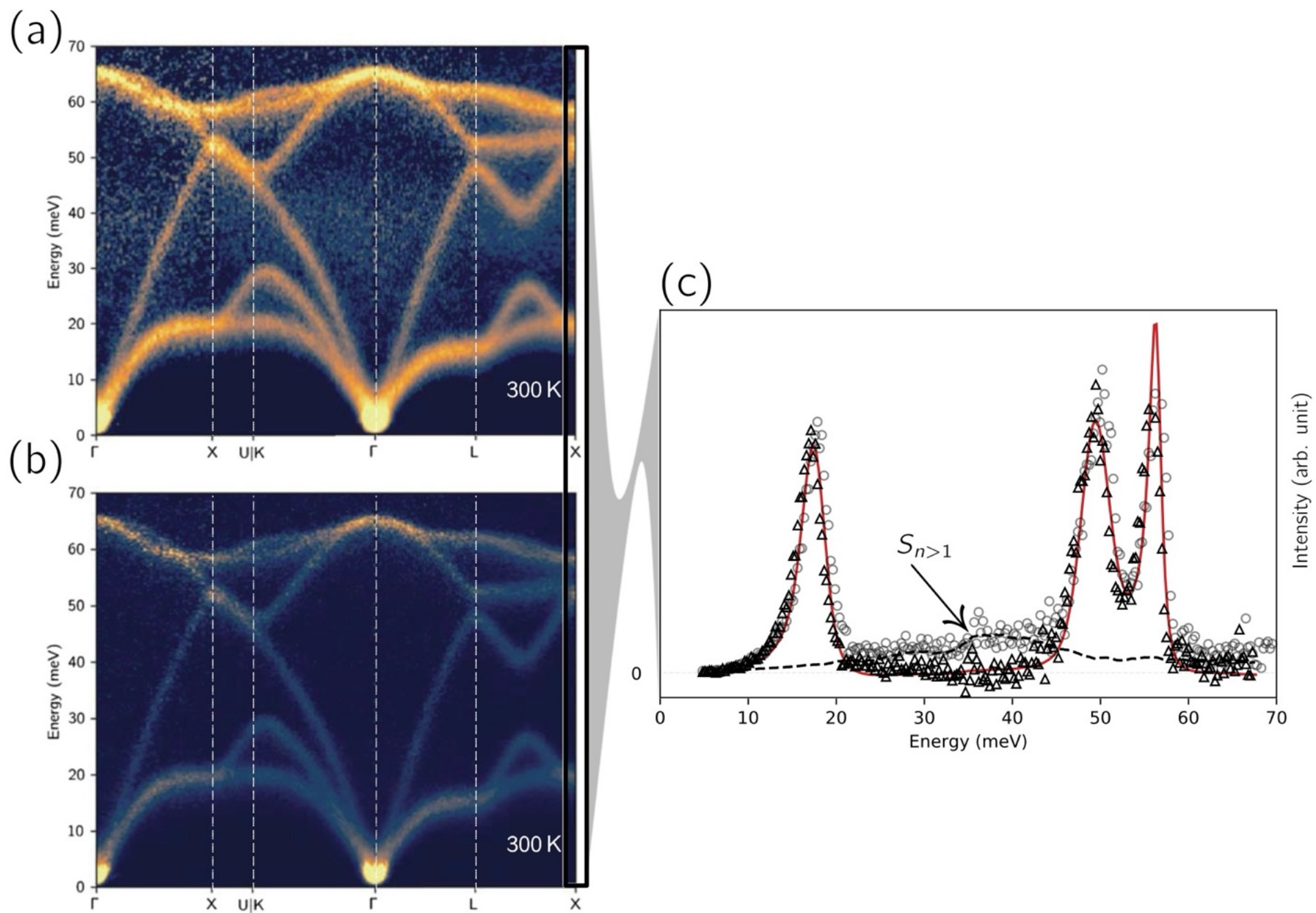
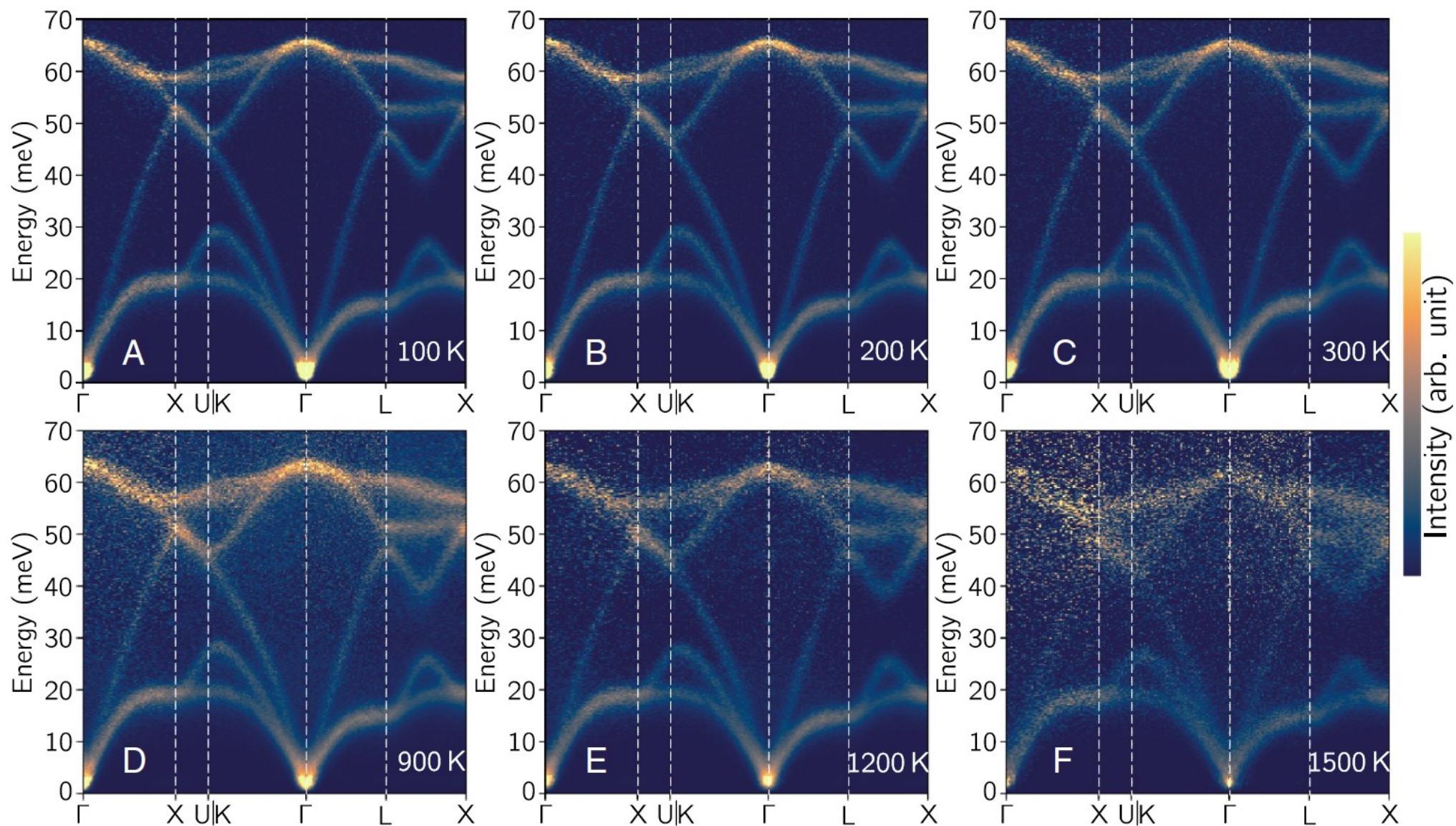
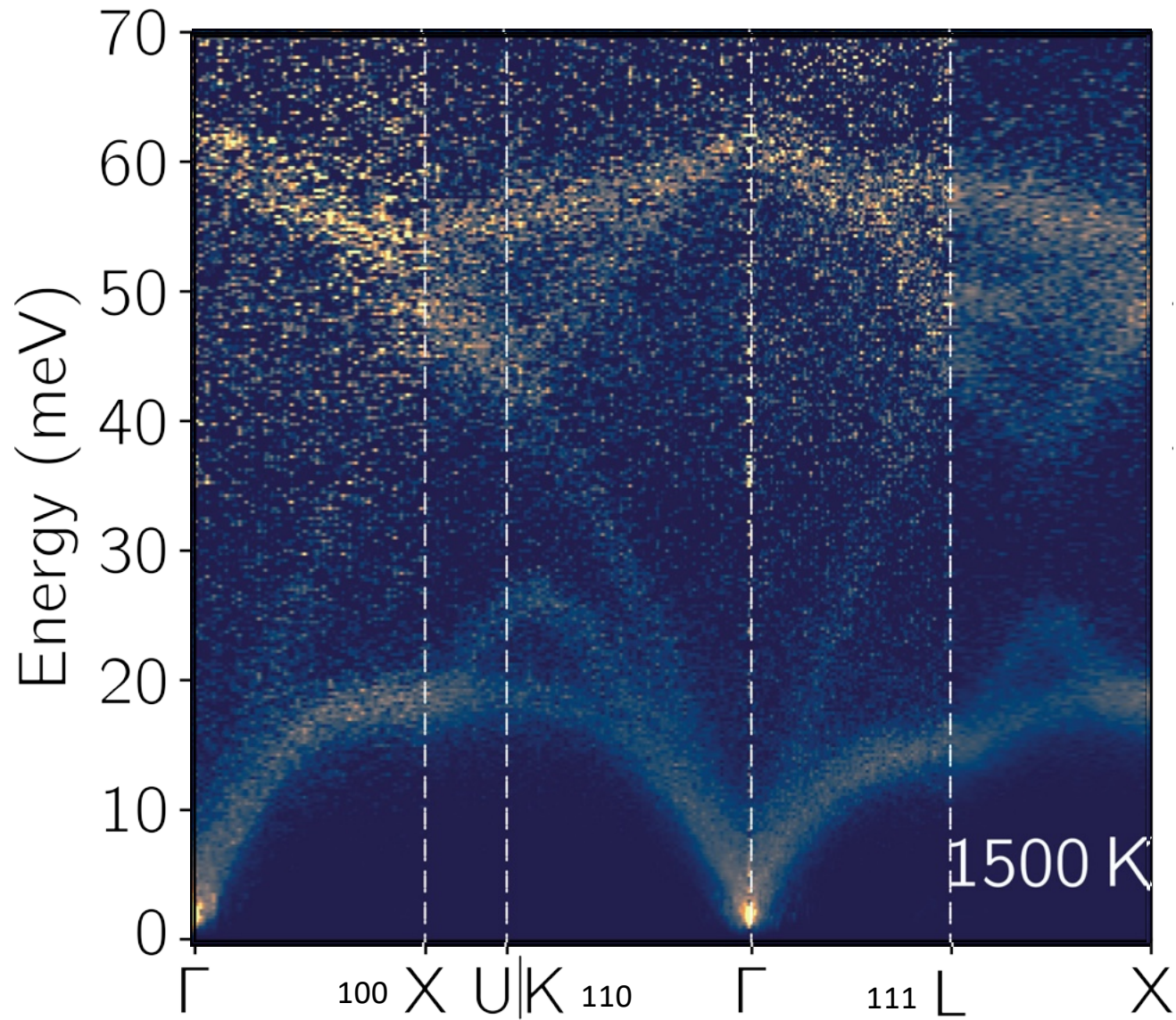


Fig. S1. Folded inelastic neutron scattering data (A) without and (B) with multiphonon subtracted $S(q, \epsilon)$ at 300 K. (C) Scattering intensity and fitted spectrum at the X point. Fitted peaks are shown as the red solid line. Gray circles are without (from A) and black triangles are with (from B) multiphonon scattering subtracted. Black dashed line shows subtracted multiphonon scattering intensity.

After correction for multiphonon scattering



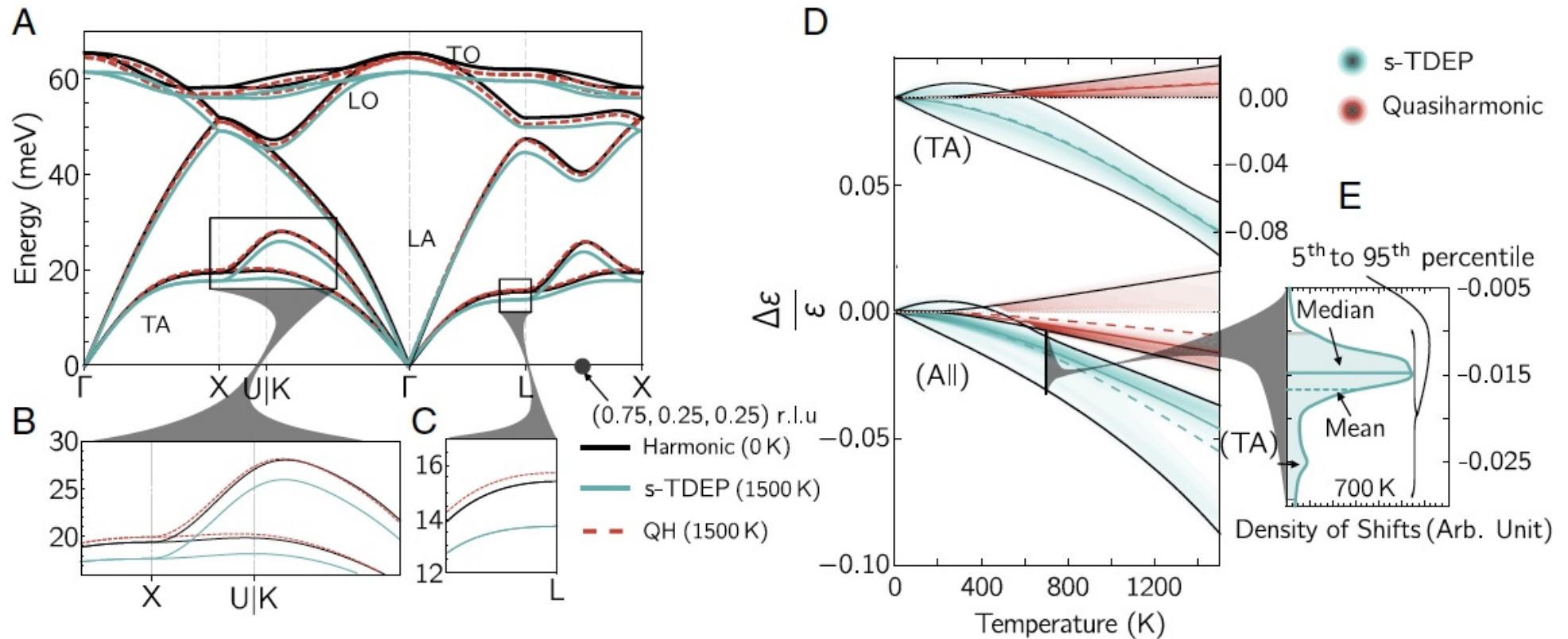
Phonon Dispersions In Silicon



Dennis Kim, Ph.D. thesis.

D.S. Kim, O. Hellman, et al., Proc. Nat'l Acad. Sciences 115, 1992 (2018).

Follow the thermal shifts of 1,000 mode energies



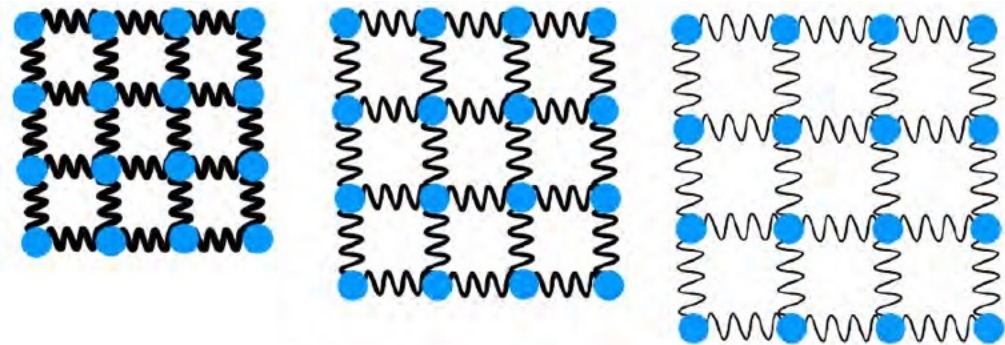
Thermal Expansion: $F(V, T) = E - TS$

E from changes in bond lengths

S from phonon entropy – depends on spectrum $g(\omega)$

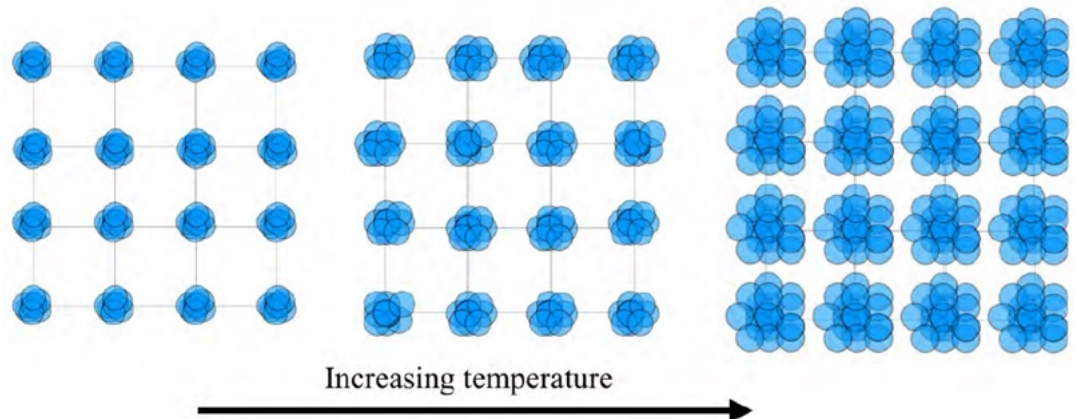
quasiharmonicity:
 $\omega(V)$

PHONOPY for quasiharmonic calculations, used $\omega(V)$



pure anharmonicity:
 $\omega(T)$

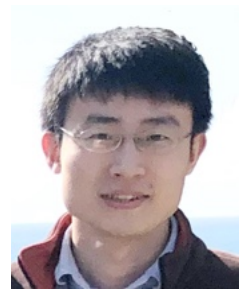
Atom displacements by sTDEP, used $\omega(V, T)$



Something New With Phonons Highly Nonlinear Crystals

1. Intermodulation phonon sidebands
2. Second harmonic generation
3. Diffuse inelastic intensity

Intermodulation Phonon Sidebands in an Anharmonic Crystal of NaBr



Yang Shen

N atoms have $3N$ degrees of freedom.

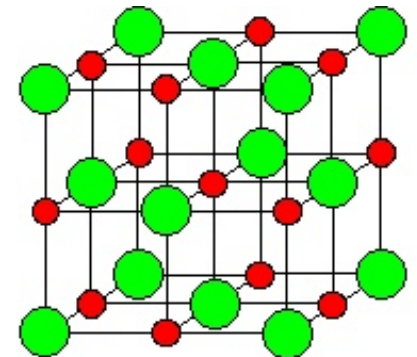
Still have $3N$ after linear Fourier transformation.

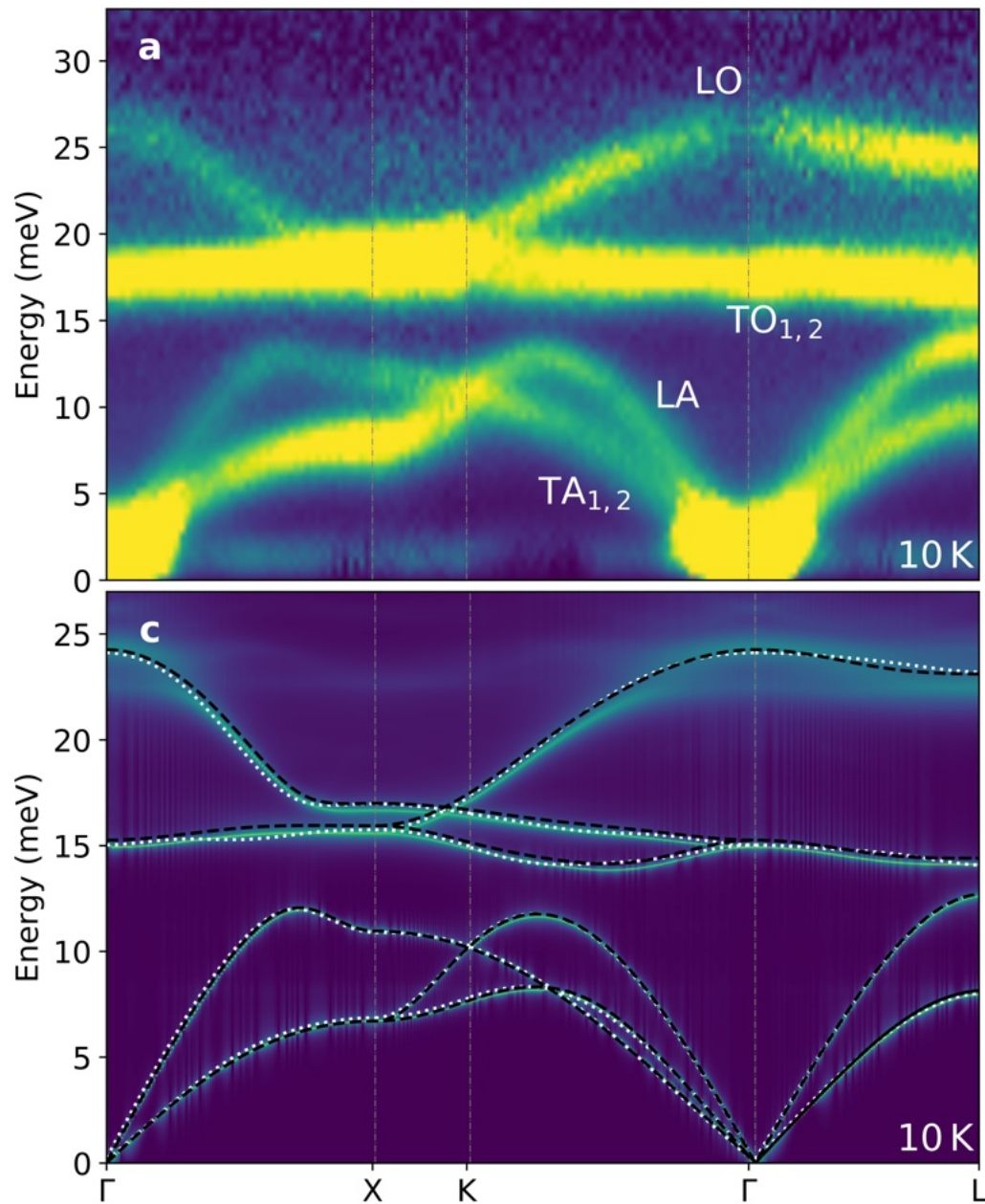
NaBr has 2 atom basis, therefore 6 phonon branches in k -space.

We observed 9 branches!

Where do new modes come from?

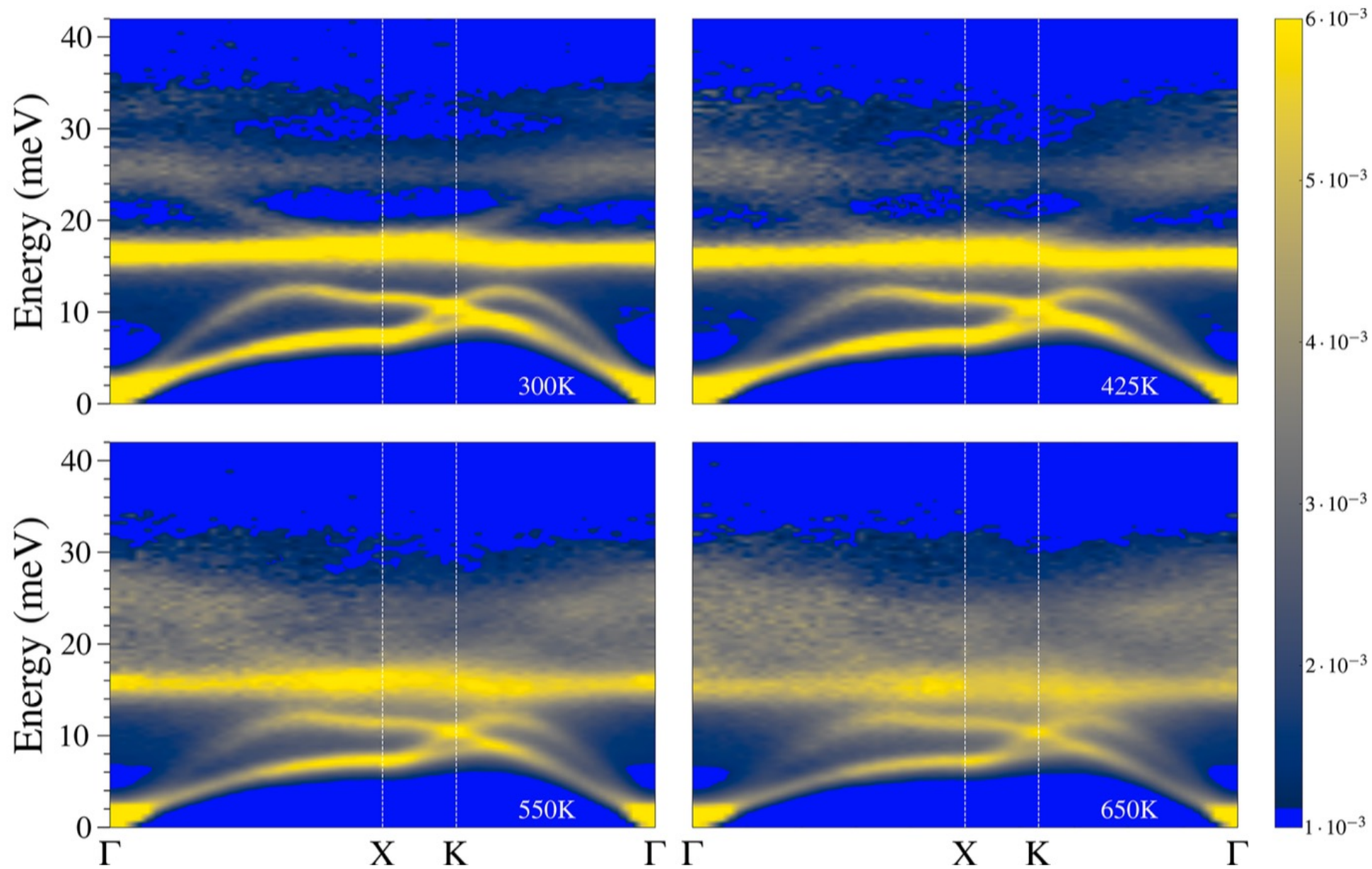
(hint: nonlinear transformation of $3N$ displacements)



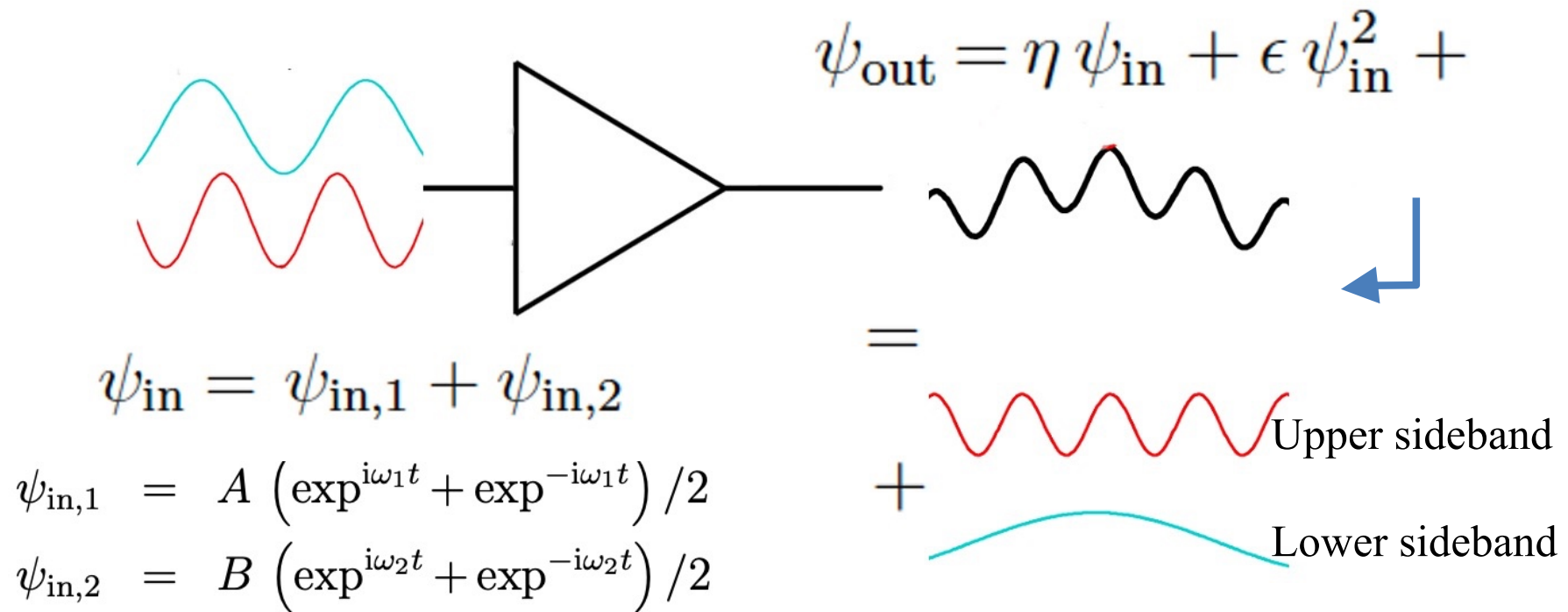


Y. Shen, C.N. Saunders, C.M. Bernal, et al.,
PRL 2020, Phys. Rev. B, 2021

V. Ladygin, C.N. Saunders, C.M. Bernal, et al.,
PRM 9, 015002 2025.



Intermodulation (nonlinear medium)



Intermodulation (nonlinear medium)

$$\psi_{\text{in},1} = A (\exp^{i\omega_1 t} + \exp^{-i\omega_1 t}) / 2$$

$$\psi_{\text{in},2} = B (\exp^{i\omega_2 t} + \exp^{-i\omega_2 t}) / 2$$

$$\psi_{\text{out}} = \eta \psi_{\text{in}} + \epsilon \psi_{\text{in}}^2$$

$$\psi_{\text{out}} = \eta (\psi_{\text{in},1} + \psi_{\text{in},2}) + \epsilon (\psi_{\text{in},1} + \psi_{\text{in},2})^2$$

$$\begin{aligned} \epsilon \psi_{\text{in}}^2 = \frac{\epsilon}{2} \{ & (A^2 + B^2) + A^2 \cos 2\omega_1 t + B^2 \cos 2\omega_2 t \\ & + AB [\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t] \} \end{aligned}$$

For a nonlinear system with $\epsilon > 0$ we have four additional frequencies: $\omega_1 + \omega_2, \omega_1 - \omega_2, 2\omega_1, 2\omega_2$. If $A \simeq B$, then all these four new frequencies are equally important, being proportional to ϵ .

Second Harmonic Generation

Intermodulation Phonon Sidebands

Intermodulation (nonlinear medium)

$$\epsilon \psi_{\text{in}}^2 = \frac{\epsilon}{2} \left\{ (A^2 + B^2) + A^2 \cos 2\omega_1 t + B^2 \cos 2\omega_2 t \right. \\ \left. + AB [\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t] \right\}$$

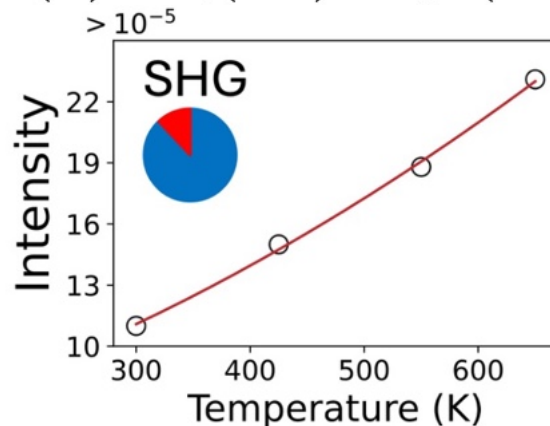
Second Harmonic Generation

Intermodulation Phonon Sidebands

Are they quasiparticles like phonons? Do they have their own thermal Planck factor?
If so, we can treat them like the rest of the phonon spectrum for thermodynamics.

Test fit:

$$I(T) = I_0(300) + I_1 n(2\omega_{\text{TO}}, T) + I_2 n^2(\omega_{\text{TO}}, T)$$



Yes, second harmonics behave like the rest of the vibrational spectrum for thermodynamic purposes!

Large Phonon Anharmonicity – What Next?

Improved intensity and low background of makes possible new measurements of weak and diffuse intensities. (x 1000 really helps!)

Need to confirm sidebands and frequency doubling in more systems (computational work will help)

Phonons in sidebands are entangled in EPR sense — can we carry this into infrared photons?

Calculate the Inelastic Intensity from Dynamics of Scatterer

$$I(\omega) = \mathcal{K} \int_{-\infty}^{\infty} e^{i\omega t} \langle \psi^*(t) \psi(0) \rangle_{\text{th}} dt$$

The Schrödinger

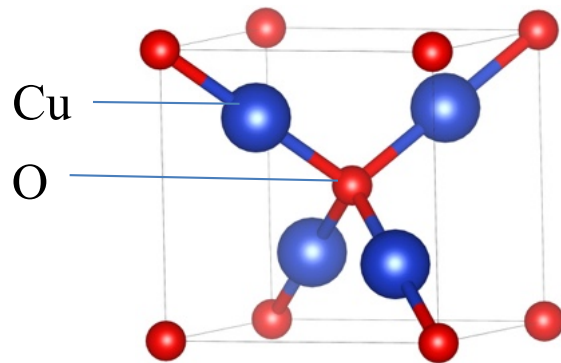
$$\frac{d\psi}{dt} = -i(\mathcal{H}/\hbar)\psi$$

$$\psi(0) = \psi_0 + l(0)V\psi,$$

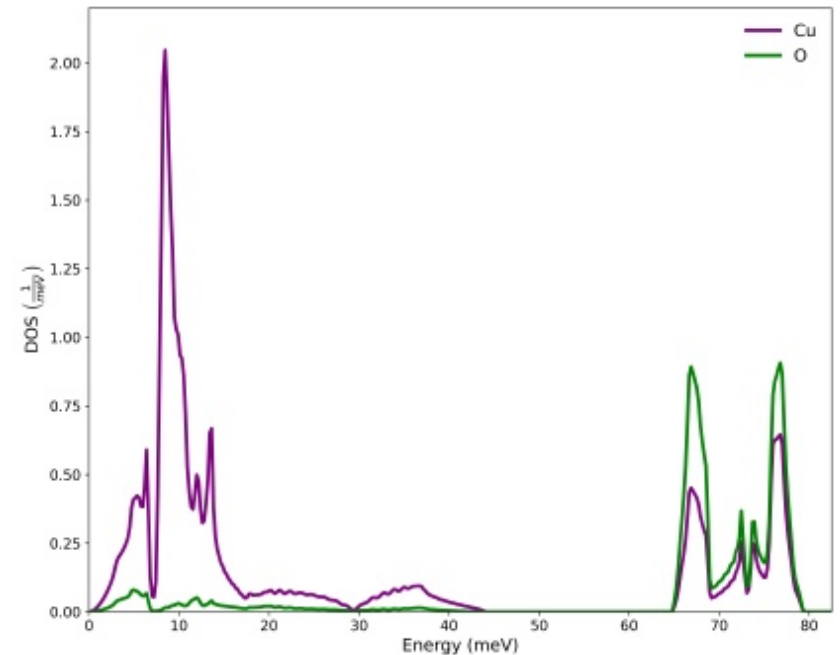
$$\psi^*(t) = \psi^*(0) \left[\exp\left(-i\omega_0 - \frac{1}{2}V^2\right)t + V \int_0^t l(t') dt' \right]$$

$$\langle \psi^*(t) \psi(0) \rangle_{\text{th}} = \langle \psi^*(0) \psi(0) \rangle_{\text{th}} \left[e^{-i\omega_0 t} e^{-\frac{1}{2}V^2 t} + V^2 P_l(t) \right]$$

New Anharmonic Effect in Cu₂O Cuprite

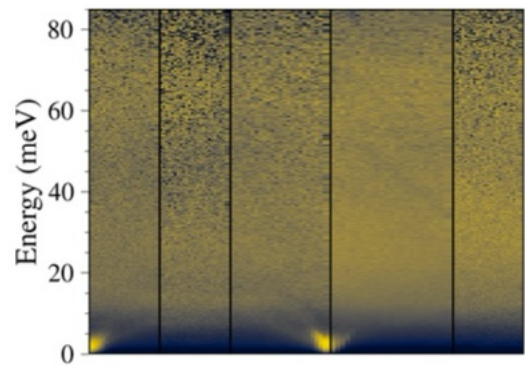


$$m_{\text{Cu}} / m_{\text{O}} = 4$$

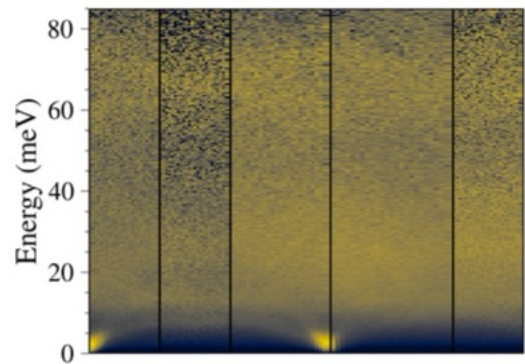


From partial DOS, $\omega_{\text{Cu}} \sim 6 \omega_{\text{O}}$

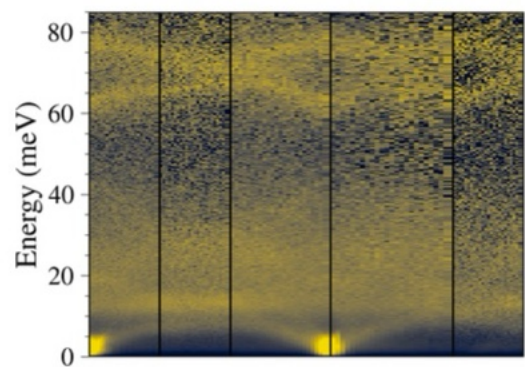
900 K



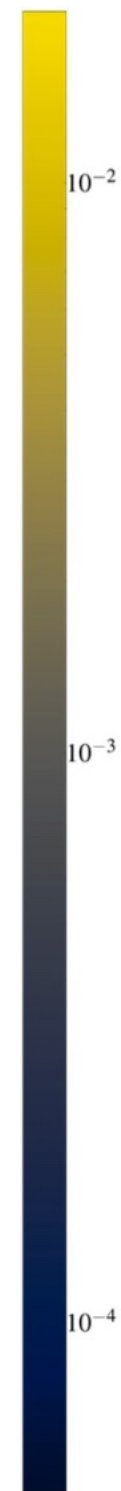
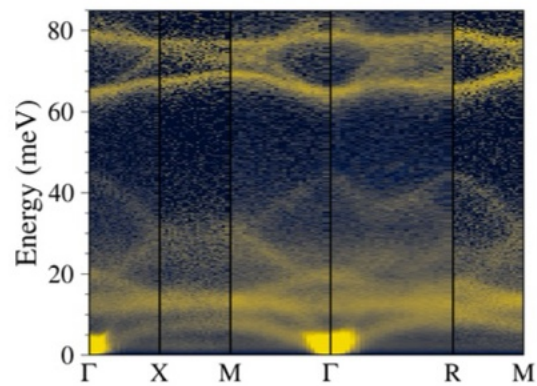
700 K



300 K



10 K



Diffuse Inelastic Intensity

Phase disorder in the time domain
causes wide energy spread in energy domain

Needs some randomness in the anharmonic interactions
between vibrating atoms.

Analog for elastic scattering is atom displacement disorder
that gives broad intensity in Q .

References

General neutron scattering

- * A. T. Boothroyd, “Principles of Neutron Scattering from Condensed Matter”, (Oxford, 2020).
- G. Squires, “Intro to theory of thermal neutron scattering”, (Dover, 1978).
- S. Lovesey, “Theory of neutron scattering from condensed matter”, (Oxford, 1984).

Time-of-flight techniques

B. Fultz, http://www.its.caltech.edu/~matsci/btfgrp/Inelastic_Neutron_Book.pdf. (free)

* New and Highly Recommended!

Appendix 1: Introduction to the Van Hove Function

Concepts of Inelastic Scattering

Coherence... the scattered wave has a phase that can be predicted from the phase of the incident wave.

phase of the wavelet

$$\vec{Q} \cdot \vec{r}_j - \omega t_k$$

phase factor for kinematical scattering

$$e^{-i(\vec{Q} \cdot \vec{r}_j - \omega t_k)}$$

Incoherence... no phase relationship between incident and scattered waves.

$$e^{-i(\vec{Q} \cdot \vec{r}_j - \omega t + \mathcal{R})}$$

$\mathcal{R}$ is a random variable

$f_j(\mathbf{r}, t)$ is the scattering factor of nucleus j .

$\mathbf{r}, t$ describe where it is and how it moves.

That's what we want ! (or a sum of scattered waves from all j).

Fourier transformation: $f(\vec{r}) = F_{\vec{Q}}\psi(\vec{Q})$

$$f(\vec{r}, t) = F_{\vec{Q}}F_E\psi(\vec{Q}, E)$$

This $\psi(\vec{Q}, E)$ may be what we want to measure, but it is not what we get.

We get the intensity, $\psi^* \psi$.

We can Fourier transform the intensity to get the Van Hove Function.

Whereas the inelastically scattered wave, $\psi(Q, E)$, is the double Fourier transform of the moving scattering factor distribution, the scattered intensity, $I(\vec{Q}, E)$, is the double Fourier transform of the Van Hove correlation function of the scattering factor distribution, $G(\vec{r}, t)$.

Van Hove function

$$I(\vec{Q}, E) = F_{\vec{r}} F_t G(\vec{r}, t) ,$$

so by the inverse transformation

$$G(\vec{r}, t) = F_{\vec{Q}} F_E I(\vec{Q}, E)$$

2.2. DEFINITION OF THE VAN HOVE FUNCTION

We define the “Van Hove function,” $G(\vec{r}, t)$

$$G(\vec{r}, t) \equiv \int\limits_{-\infty}^{+\infty} \int\limits_{-\infty}^{+\infty} f^*(\vec{r}', t') f(\vec{r} + \vec{r}', t + t') d^3\vec{r}' dt' . \quad (6)$$

Equation 6 is a double autocorrelation function – a space-time correlation function with limits of integration over all space and all time.

$$I(\vec{Q}, E) = \psi^* \times \psi$$

$$I(\vec{Q}, E) = \int_{-\infty}^{+\infty} \int f^*(\vec{r}') e^{i(\vec{Q} \cdot \vec{r}' - \omega t')} d^3 \vec{r}' dt' \times \int_{-\infty}^{+\infty} \int f(\vec{r}'', t'') e^{-i(\vec{Q} \cdot \vec{r}'' - \omega t'')} d^3 \vec{r}'' dt'' . (7)$$

Since $\vec{r}'$ and $\vec{r}''$ are independent variables, as are t' and t''

$$I(\vec{Q}, E) = \int_{-\infty}^{+\infty} \int \left(\int_{-\infty}^{+\infty} \int f^*(\vec{r}', t') f(\vec{r}'', t'') e^{-i[\vec{Q} \cdot (\vec{r}'' - \vec{r}') - \omega(t'' - t')]} d^3 \vec{r}'' dt'' \right) d^3 \vec{r}' dt' . (8)$$

Define $\vec{r} \equiv \vec{r}'' - \vec{r}'$ and $t \equiv t'' - t'$, and change variables $\vec{r}'' \rightarrow \vec{r} + \vec{r}'$ and $t'' \rightarrow t + t'$. In so doing, the limits of integration for $\vec{r}$ are shifted by $-\vec{r}'$ and $-t'$, but this is not of concern for integrations performed over all of space and all of time

$$I(\vec{Q}, E) = \int_{-\infty}^{+\infty} \int \left(\int_{-\infty}^{+\infty} \int f^*(\vec{r}', t') f(\vec{r} + \vec{r}', t + t') e^{-i(\vec{Q} \cdot \vec{r} - \omega t)} d^3 \vec{r} dt \right) d^3 \vec{r}' dt' , (9)$$

$$I(\vec{Q}, E) = \int_{-\infty}^{+\infty} \int \left(\int_{-\infty}^{+\infty} \int f^*(\vec{r}', t') f(\vec{r} + \vec{r}', t + t') d^3 \vec{r}' dt' \right) e^{-i(\vec{Q} \cdot \vec{r} - \omega t)} d^3 \vec{r} dt . (10)$$

Using the definition of Eq. 6, we rewrite Eq. 10

$$I(\vec{Q}, E) = \int_{-\infty}^{+\infty} \int G(\vec{r}, t) e^{-i(\vec{Q} \cdot \vec{r} - \omega t)} d^3 \vec{r} dt . (11)$$

$$I(\vec{Q}, E) = \int\limits_{-\infty}^{+\infty} \int G(\vec{r}, t) e^{-i(\vec{Q} \cdot \vec{r} - \omega t)} d^3\vec{r} dt . \quad (11)$$

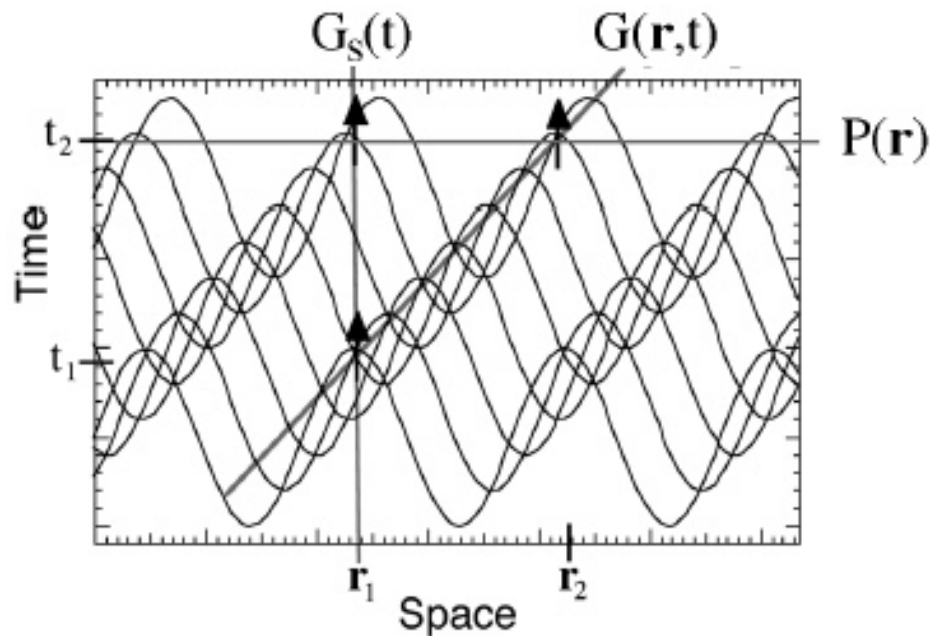
Van Hove function

$$I(\vec{Q}, E) = F_{\vec{r}} F_t G(\vec{r}, t) ,$$

so by the inverse transformation

$$G(\vec{r}, t) = F_{\vec{Q}} F_E I(\vec{Q}, E) .$$

Example: Van Hove Function for a Traveling Wave



This single wave has specific
 $\mathbf{q}$ wavevector
 ω_0 frequency

Figure 4. A simple sine wave, moving to the right with increasing time. Three methods of sampling the intensity of the wave in space and time are shown as straight lines, as explained in the text. The relevant correlation functions for each sampling are shown for each line.

2.3. EXAMPLES OF VAN HOVE FUNCTIONS

one spatial dimension

$$I(Q, E) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G(x, t) e^{-i(Qx - \omega t)} dx dt$$

4.2.1 Traveling Wave

First consider an elementary excitation in a solid that provides a periodic modulation of the scattering factor in space and time

$$f(x, t) = e^{i(qx - \omega_0 t)} . \quad (18)$$

obtain its Van Hove function:

$$G(x, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_0^* e^{-i(qx' - \omega_0 t')} f_0 e^{i[q(x+x') - \omega_0(t+t')]} dx' dt' , \quad (4.17)$$

$$G(x, t) = |f_0|^2 \int_{-\infty}^{\infty} e^{iqx} dx' \int_{-\infty}^{\infty} e^{-i\omega_0 t} dt' = e^{iqx} \int_{-\infty}^{\infty} dx' e^{-i\omega_0 t} \int_{-\infty}^{\infty} dt' , \quad (4.18)$$

$$G(x, t) = |f_0|^2 e^{i(qx - \omega_0 t)} . \quad (4.19)$$

If we ignore the prefactor $|f_0|^2$, we find $G(x, t) = f(x, t)$.

$G(x, t)$ has the form of a wave

$$I(Q, E) = |f_0|^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i(qx - \omega_0 t)} e^{-i(Qx - \omega t)} dx dt , \quad (4.20)$$

$$I(Q, E) = |f_0|^2 \int_{-\infty}^{\infty} e^{i(q-Q)x} dx \int_{-\infty}^{\infty} e^{i(\omega - \omega_0)t} dt , \quad (4.21)$$

$$I(Q, E) = |f_0|^2 \delta(q - Q - g) \delta(\omega - \omega_0) . \quad (4.22)$$

An elementary excitation in a solid with unique $\{q, \omega_0\}$ provides intensity at a single point in energy, and at a distance of Q away from each reciprocal lattice point.¹

(Long) waves of constant velocity $\omega = ck$

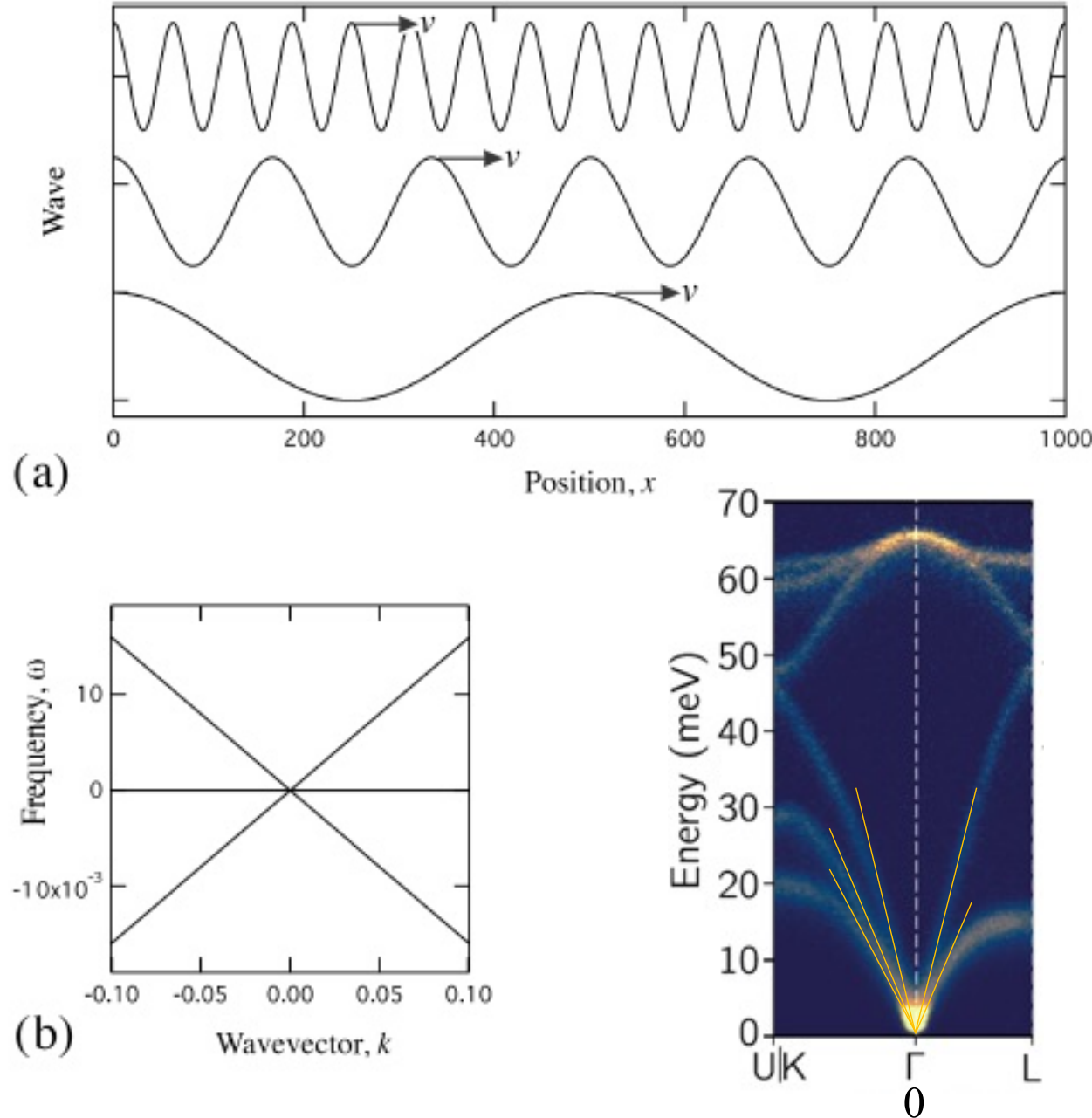


Fig. 4.1. (a) Variations of a scattering function in space and time. Simple cosine waves are assumed, moving with equal velocities v . Their Van Hove functions are also cosine waves of the same wavelengths and frequencies. (b) The scattered intensity. (c) Phonon dispersions of Si with straight lines from origin.

Appendix 2: Relations Between Functions Used In Scattering

3. Full Universe of Scattering Functions

- $S(Q, \omega)$ is the “scattering law.”
- $Y(Q, \tau)$ is the momentum-time correlation function. It is called the “intermediate scattering function.”
- $\Gamma(R, \omega)$ is the dynamical pair distribution function.
- $G(R, \tau)$ is the Van Hove space-time correlation function.
- $P(R)$ is the Patterson function.
- $\mathcal{M}(\tau)$ is the “memory function,” a time correlation function for dynamics at a site (sometimes called $G_s(\tau)$, a self-correlation function).
- $I(Q)$ is a diffraction pattern.
- $I(\omega)$ is an inelastic spectrum.
- $f(r, t)$ is a scattering length density.
- $\psi(Q, \omega)$ is a wavefunction.

Mathematical Operations that Connect Scattering Functions

F , Fourier transformation

$\otimes$, autocorrelation

$||^2$, multiplication

$\langle \rangle$, averaging

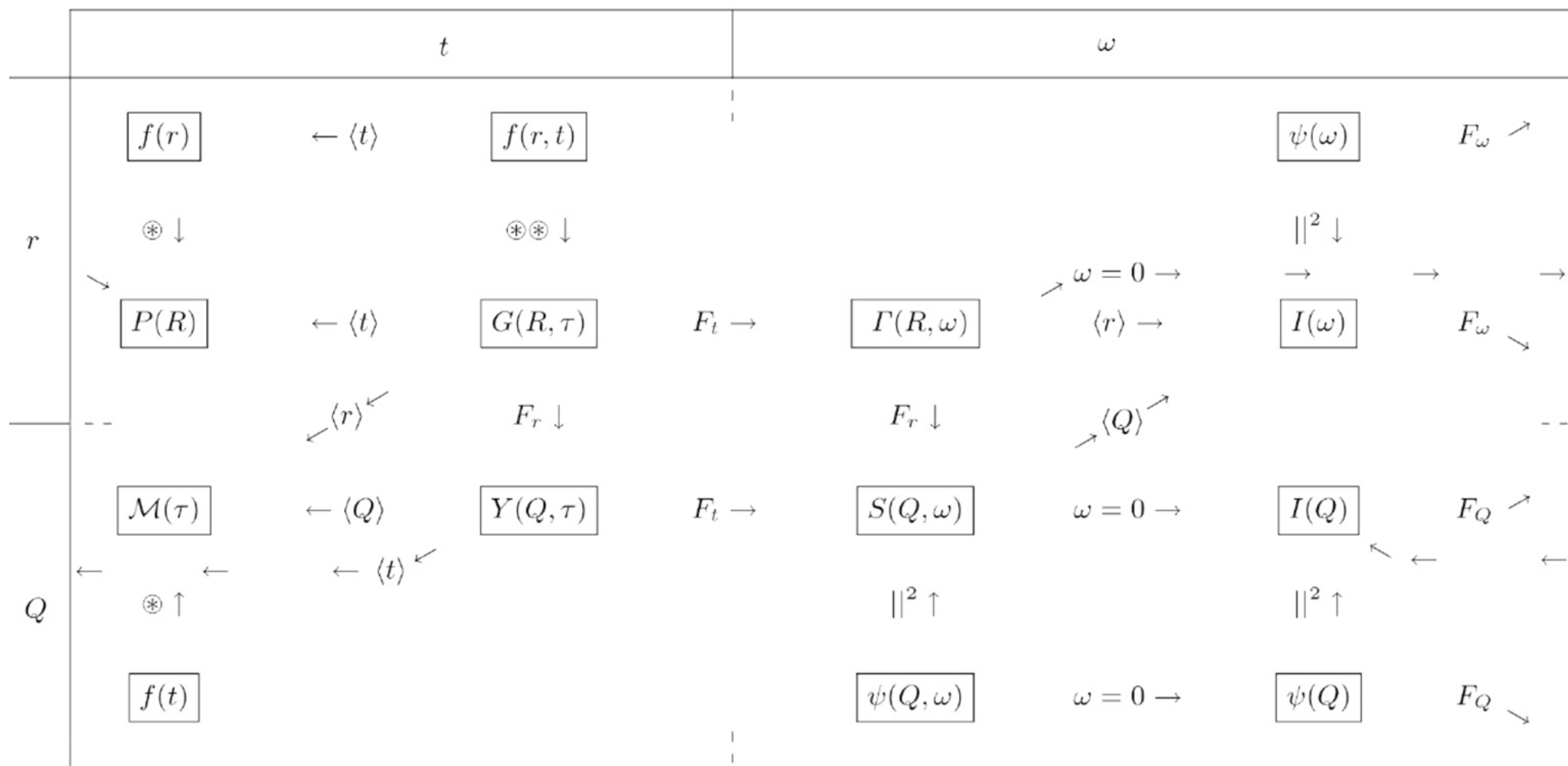


Figure 5. Map of the universe of interrelationships between correlation functions, scattering length densities, intensities, and wavefunctions.

