PSI Master School 2017

Introducing photons, neutrons and muons for materials characterization

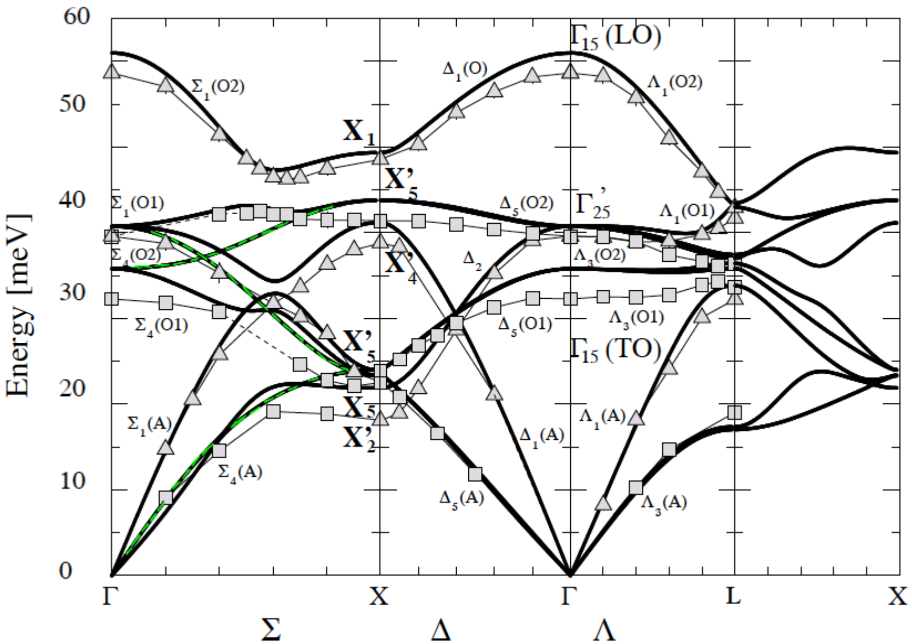
Lecture 13: Neutron Spectroscopy, Local Excitations and Phonons

Inelastic neutron scattering

- So far mostly looked at structures
  - static arrangement of atoms
  - magnetic structures
- Neutrons can also tell us what atoms and magnetic moments do: dynamics
  - phonons
  - spin-waves
- Microscopic degree of freedom
  - crystal-fields

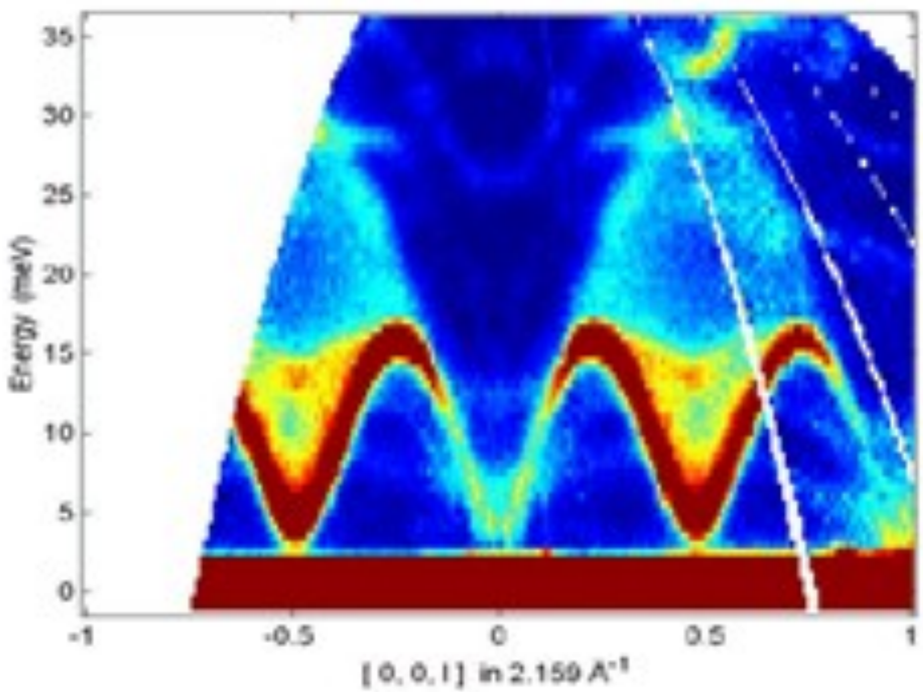
Why measure dynamics in solids?

Microscopic understanding of lattice dynamics



K. Schmalzl, D. Strauch, H. Schober, Phys. Rev. B **68**, 144301 (2003)

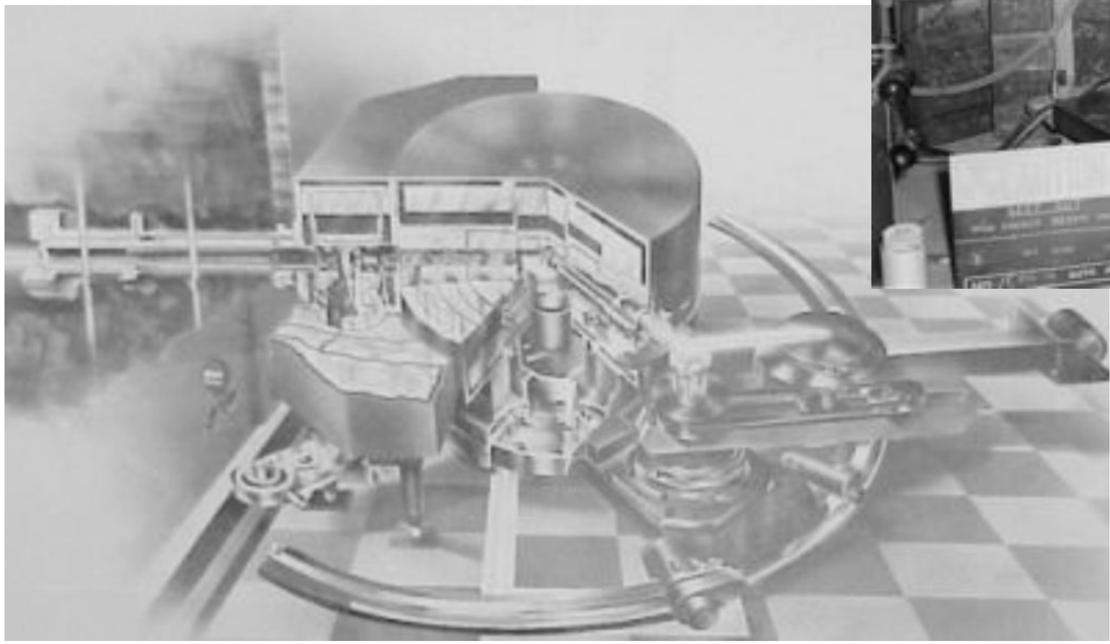
Novel magnetic excitations

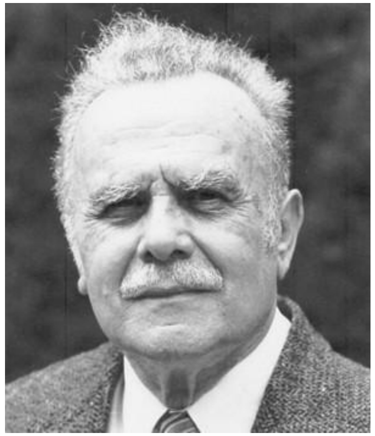


M. Arai et al, unpublished

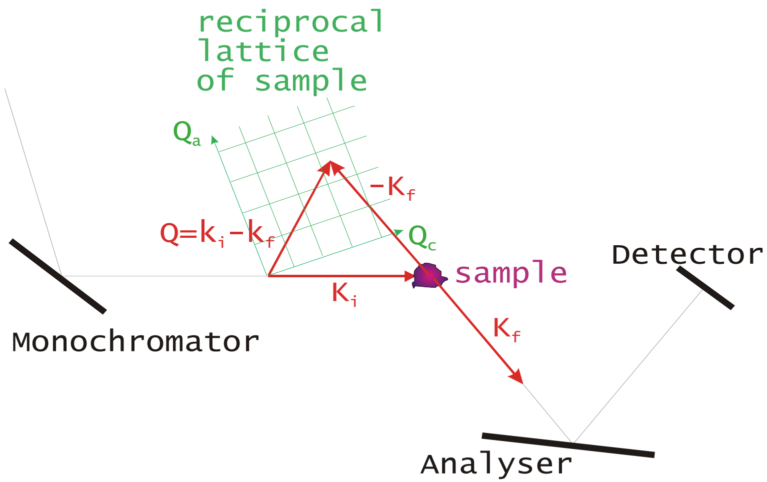
Invention of triple-axis spectrometer

- Invented in 1957 by Brockhouse
- Nobel Prize 1994

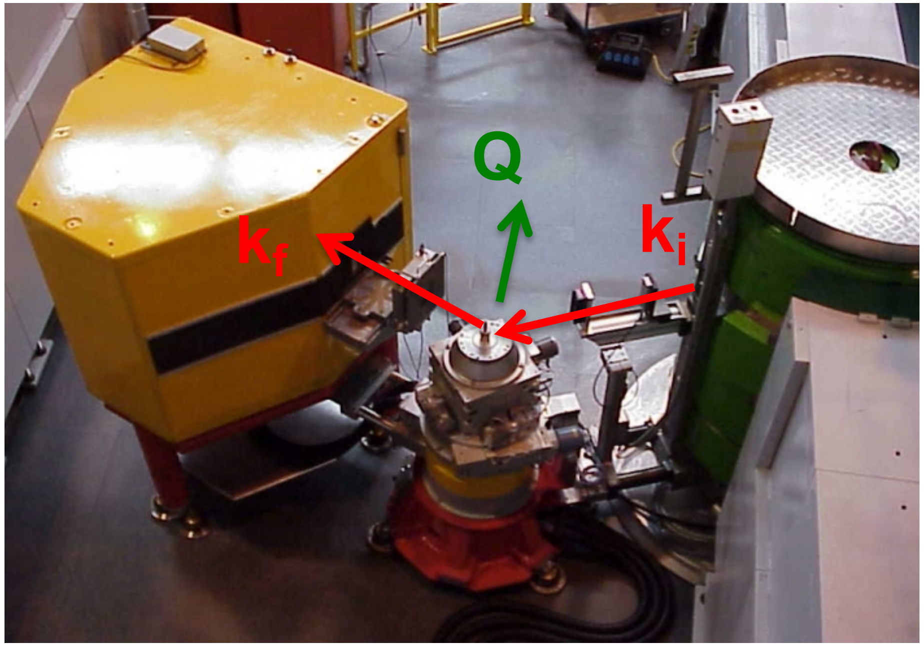




Triple-axis neutron spectrometer



Complete control of wave-vector and energy transfer

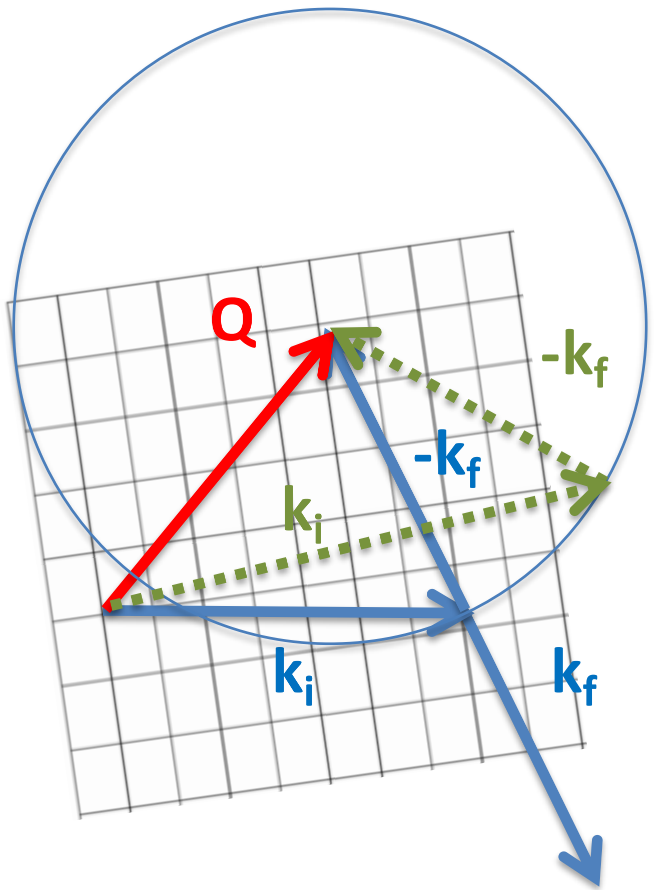


RITA spectrometer at PSI

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_{\lambda} p_{\lambda} \sum_{\lambda'} \left|\langle \mathbf{k}'\lambda' | \hat{U} | \mathbf{k}\lambda \rangle\right|^2 \delta\{\hbar\omega + E_{\lambda} - E_{\lambda'}\}$$

Measuring with a triple-axis spectrometer?

- Momentum conservation $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$
- Energy conservation $\hbar\omega = E_f - E_i = \frac{\hbar^2}{2m}(k_f^2 - k_i^2)$

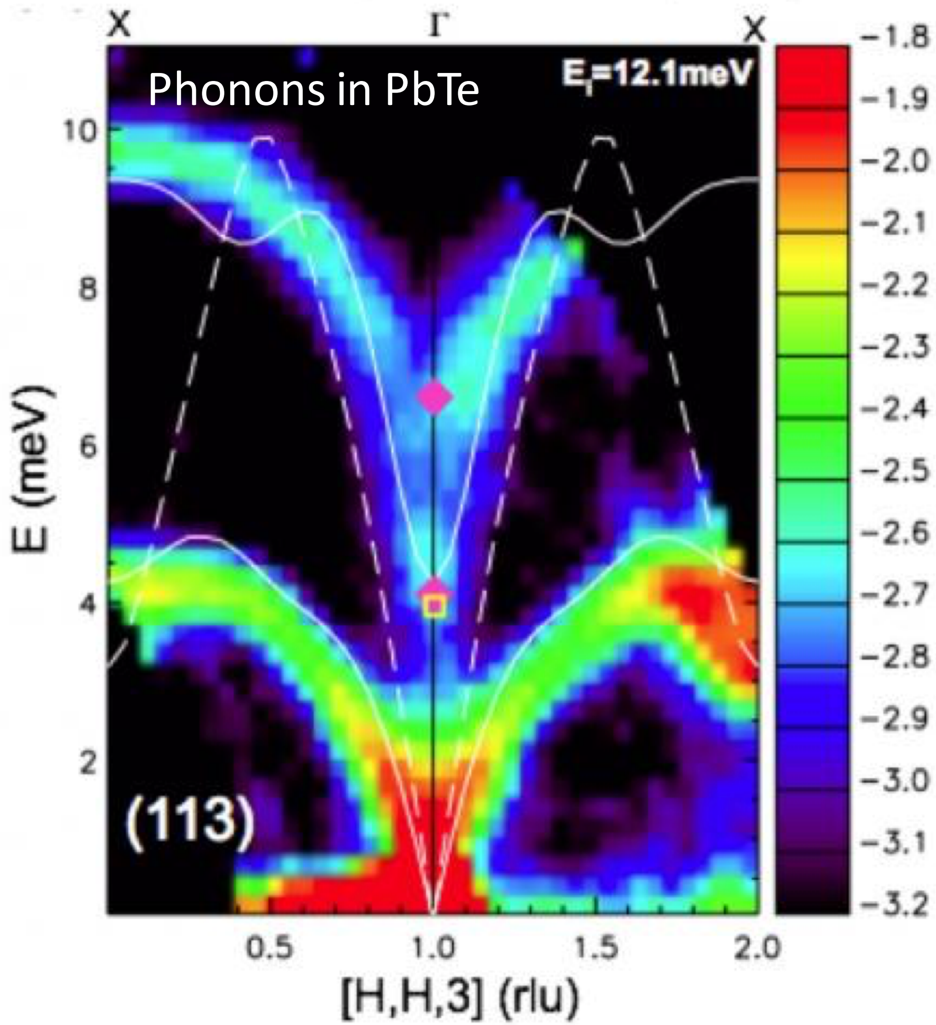


Constant-**Q** scan with |**k**| fixed

With increasing energy transfer:

- 2Θ changes
- **k**$_i$ changes (both direction and length)

Typical excitation spectrum: sharp excitations

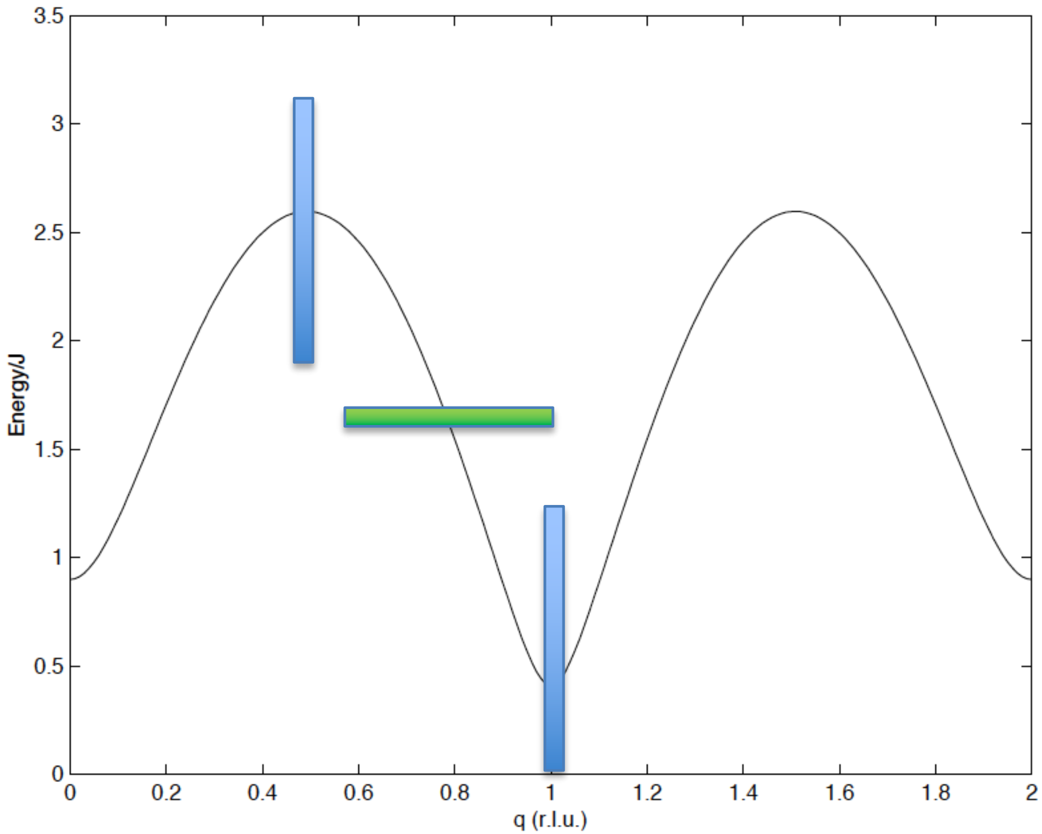


O. Delaire et al, Nat. Mat. **10** 614 (2011).

Quasi-particle excitations

- Phonons
- Spin-waves
- Crystal-fields
- Molecular motions
- Triplons
- Spinons
- Spin-resonance in superconductors
- Excitations of atomic motions in liquids and glasses

Constant **Q** or constant energy scans

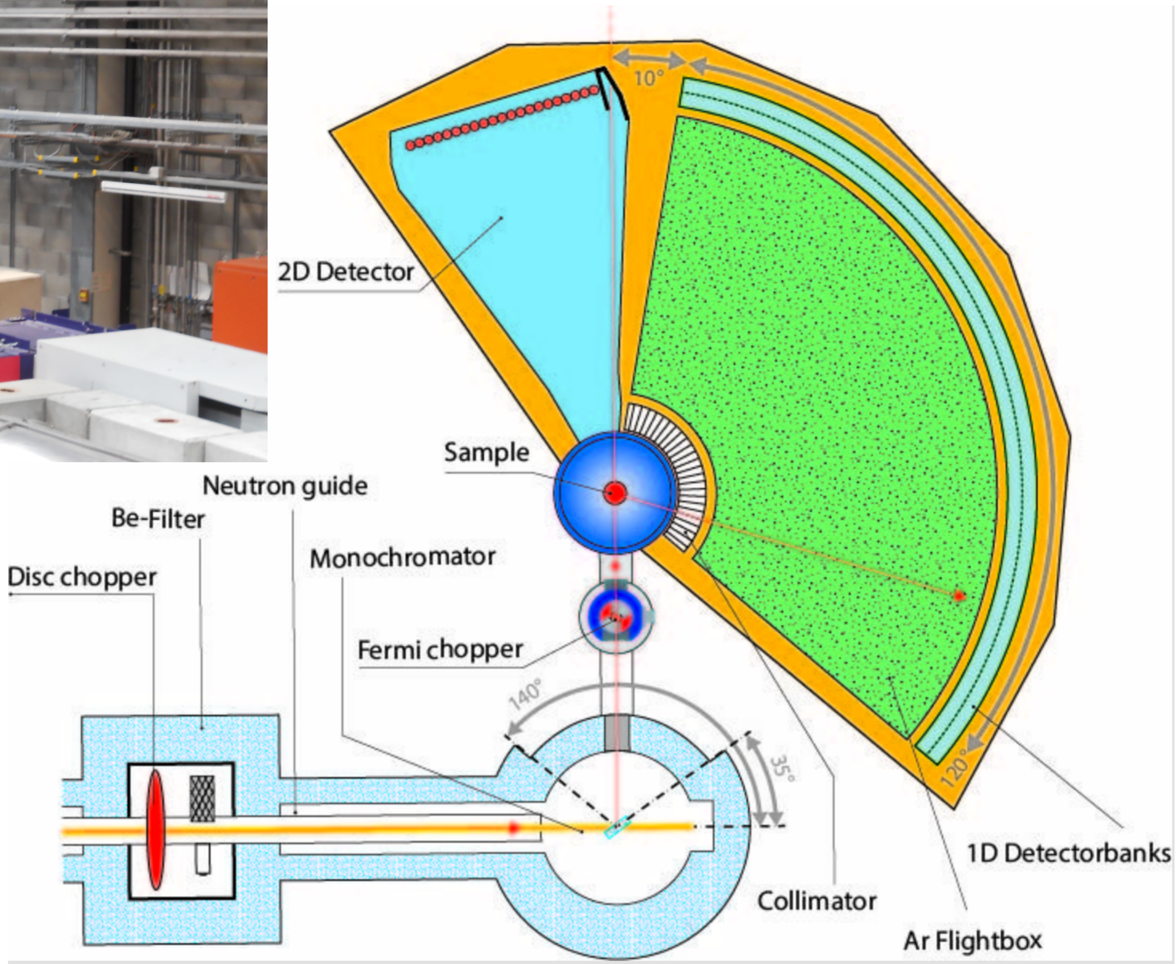


Depending on the dispersion, it's better to perform constant-Q or constant-energy scans

- Constant-**Q** scan: energy scan with constant wave-vector transfer
- Constant-energy scan: wave-vector scans with constant energy

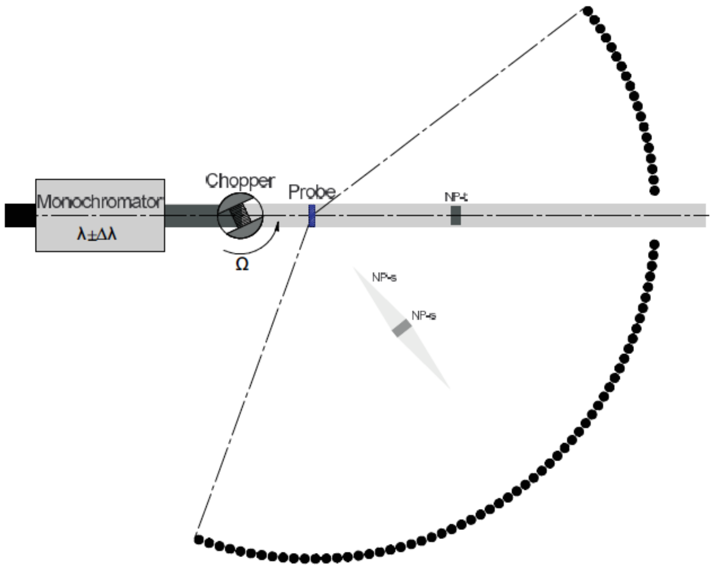
Time-of-Flight neutron spectroscopy

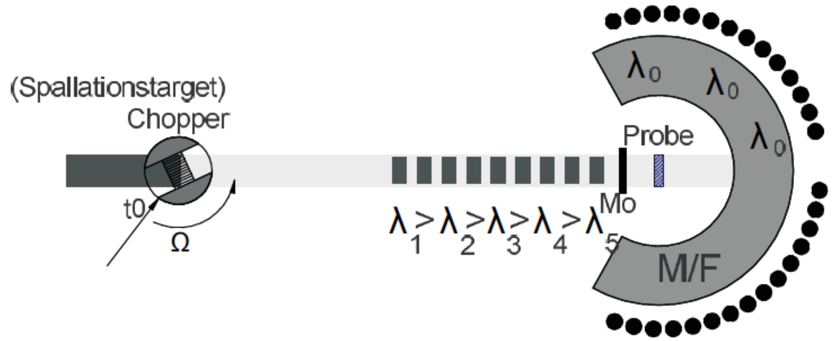
FOCUS instrument at SINQ



- Energy transfer determined from time-of-flight
- A broad range of 2Θ measured

Direct/indirect time-of-flight spectrometers





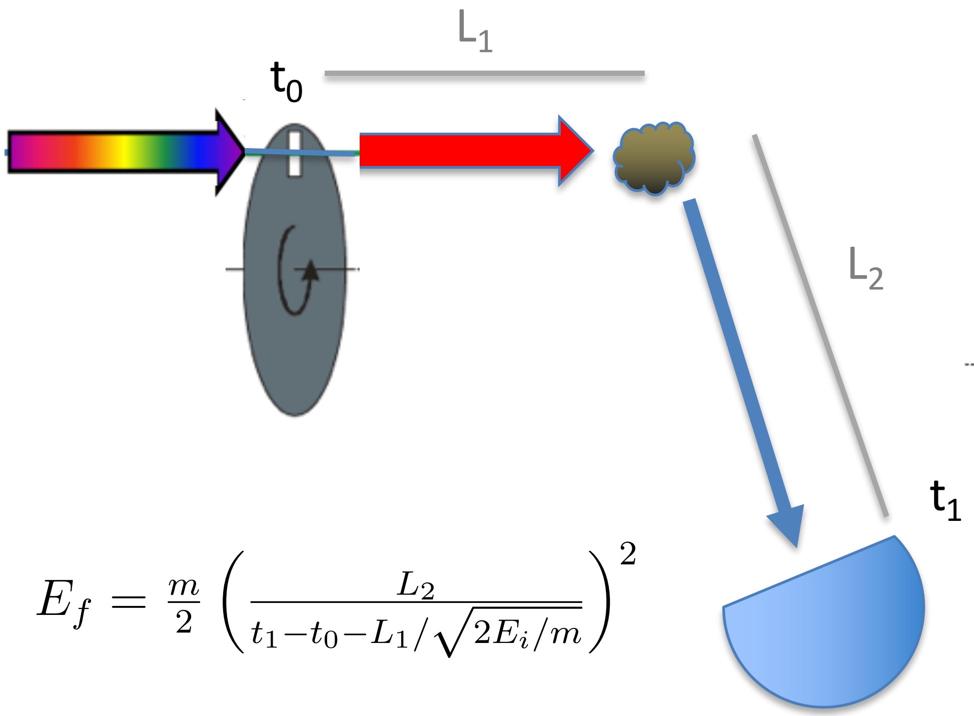
Direct spectrometer

E_i is selected

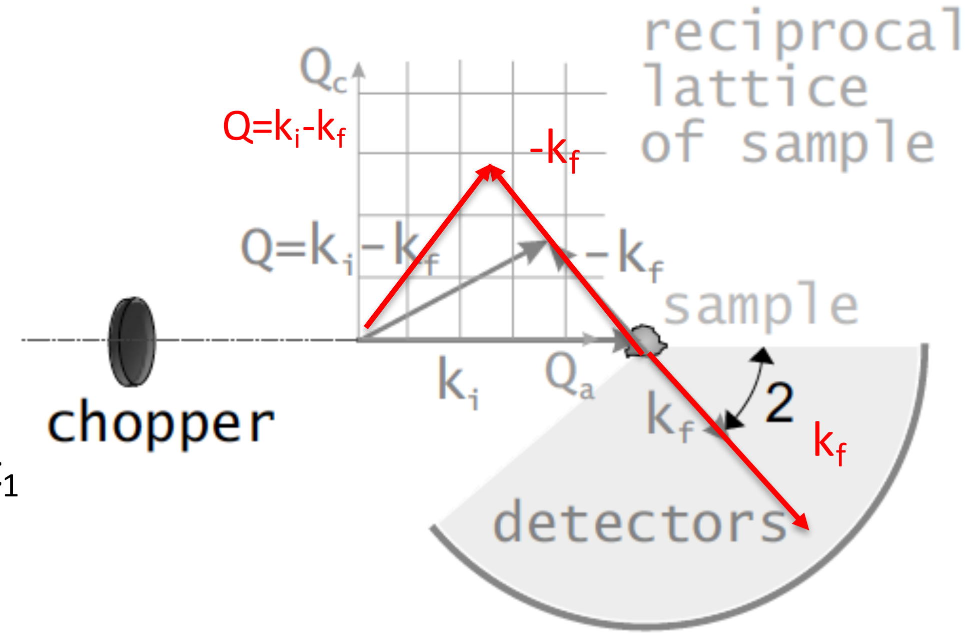
Indirect spectrometer

E_f is selected

Example: direct time-of-flight measurement

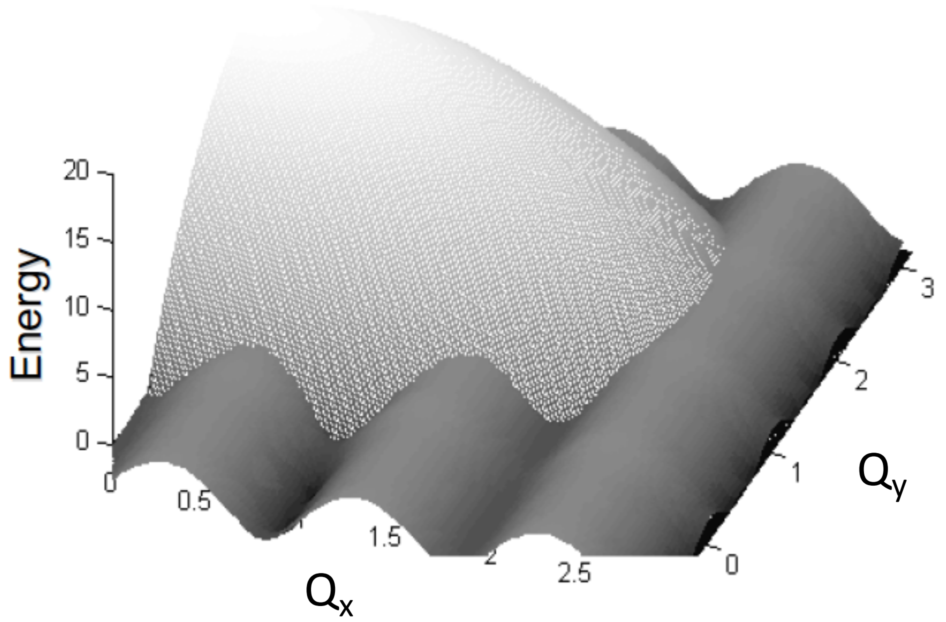


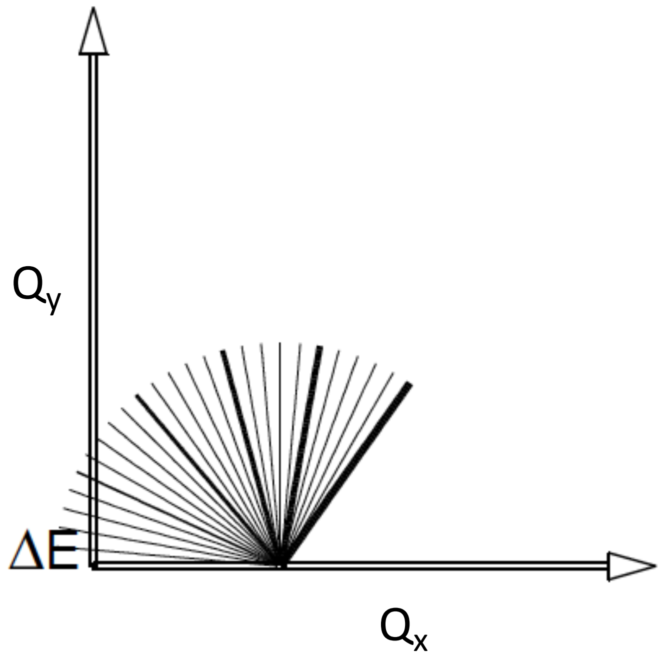
$$E_f = \frac{m}{2}\left(\frac{L_2}{t_1 - t_0 - L_1/\sqrt{2E_i/m}}\right)^2$$



- E_f is calculated from the time of flight of scattered neutron
- Scattered neutrons for a range of E_f as measured simultaneously

Direct TOF scattering surface





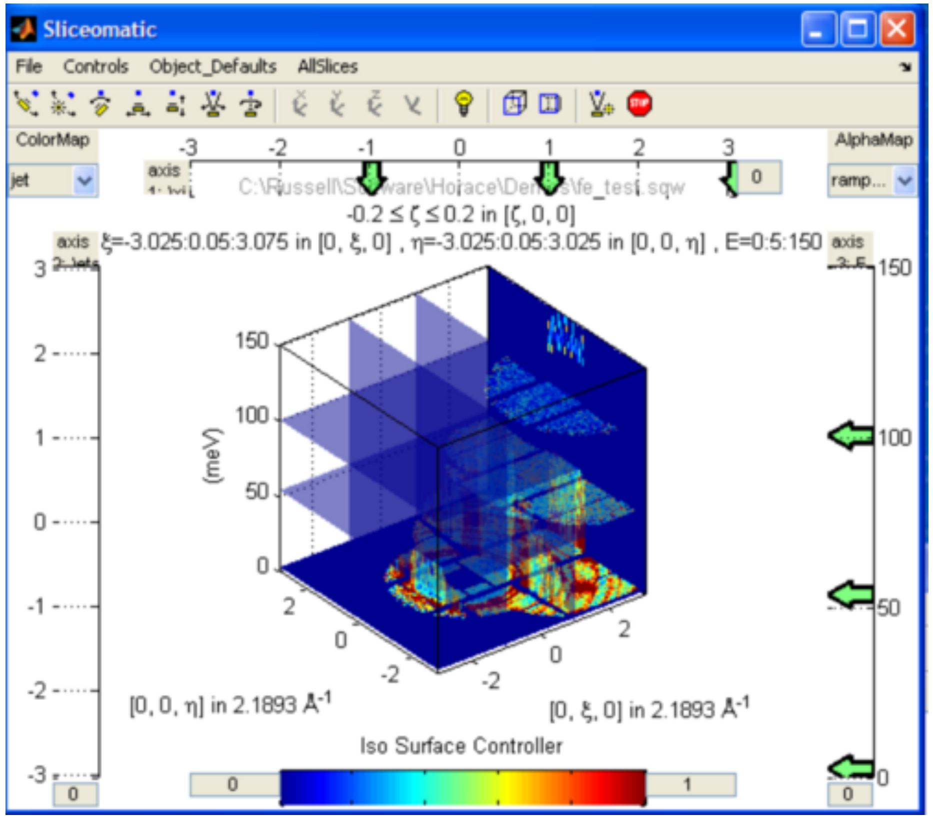
For a set E_i and sample orientation, scattering is simultaneously measured on a surface in the four-dimensional (**Q**,ω) phase space

Measure 4D scattering

- Rotate sample to measure entire 4D (**Q**,ω) phase space

- Horace analysis tool

  - Allows to analyze S(**Q**,ω)
  - Projection along high-symmetry directions
  - Visualization of dispersion along specific directions



http://horace.isis.rl.ac.uk/

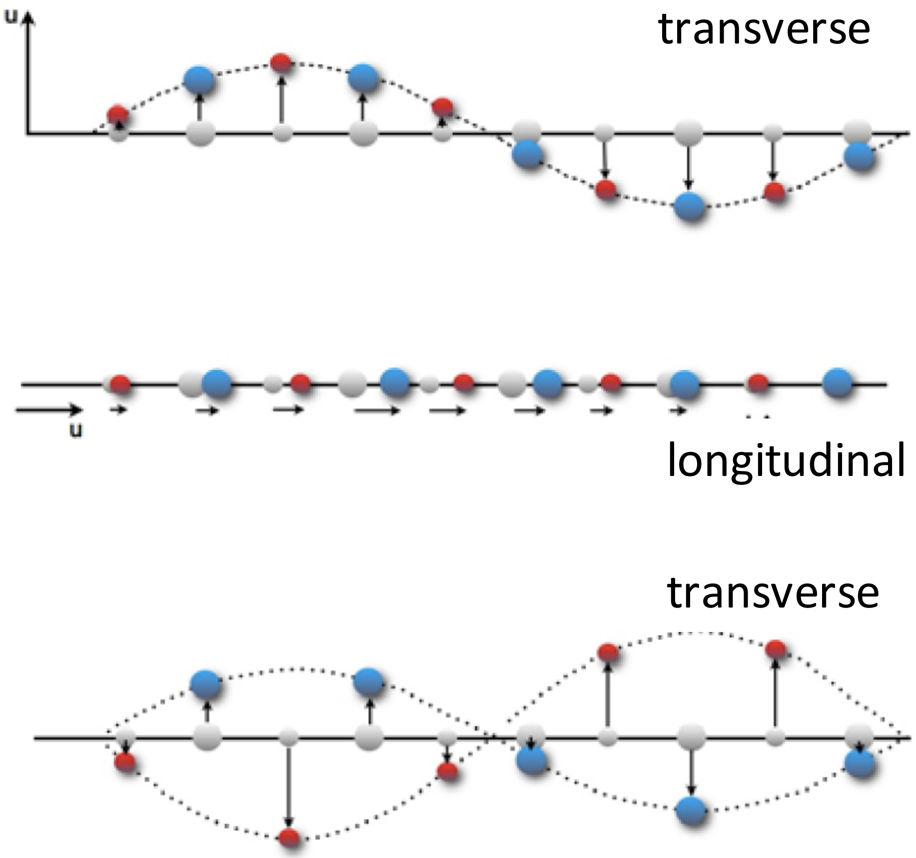
Phonons

Normal modes of atomic structure characterized by wave vector **q**, frequency ω and polarization **e**

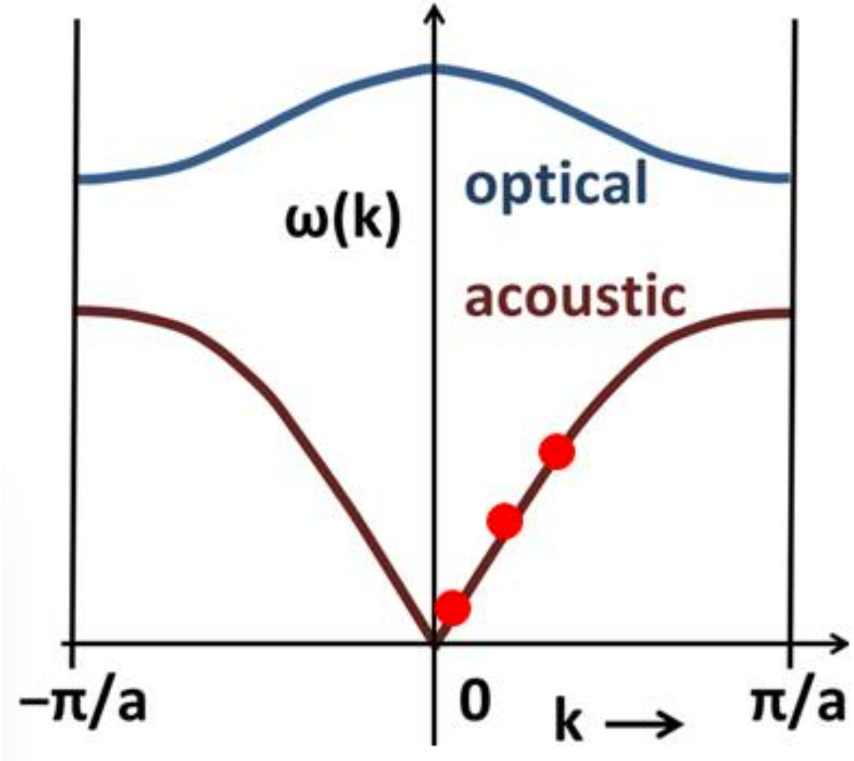
$\mathbf{e} \parallel \mathbf{q}$ —> longitudinal

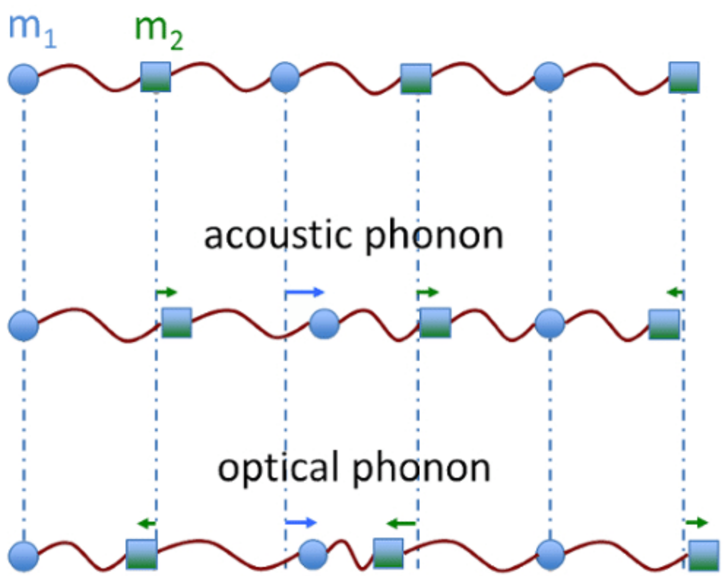
$\mathbf{e} \perp \mathbf{q}$ —> transverse

Frequency related to **q** by dispersion relation $\omega(\mathbf{q})$



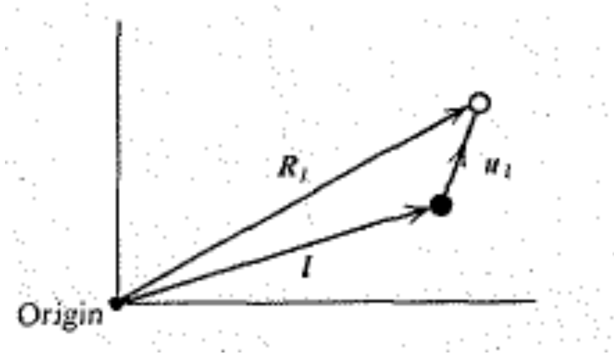
Phonons

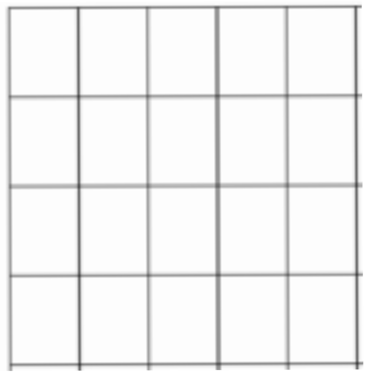




For N atoms in the unit cell: three acoustic modes, 3N-3 optics phonons with non-zero energy at Q=0

Phonon modes





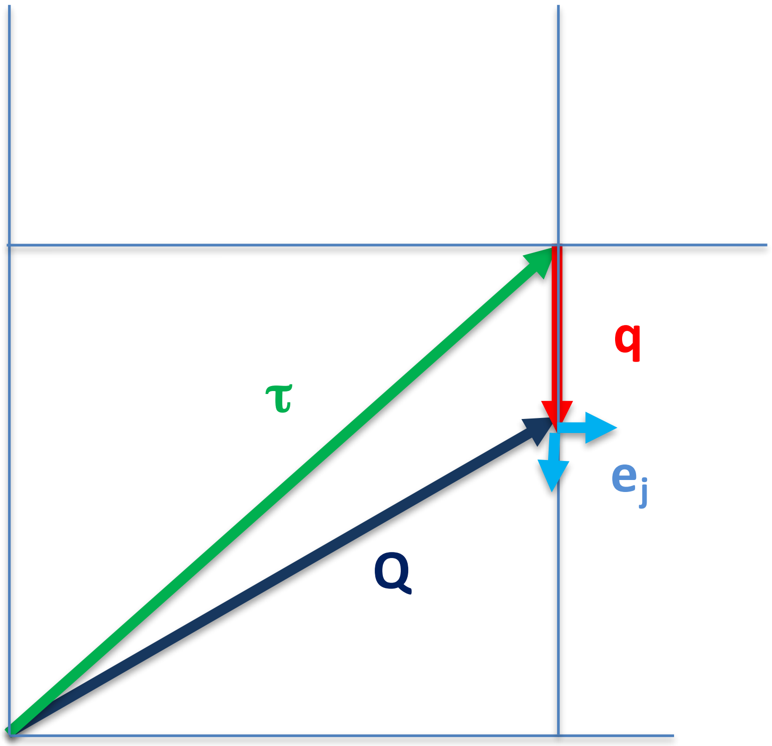
$$\mathbf{u}_l = (\frac{\hbar}{2MN})^{(1/2)} \sum_{j,\mathbf{q}} \frac{\mathbf{e}_{j,\mathbf{q}}}{\sqrt{\omega_{j,\mathbf{q}}}} [a_{j,\mathbf{q}} \exp(i\mathbf{q}\cdot\mathbf{l}) + a^{+}_{j,\mathbf{q}} \exp(-i\mathbf{q}\cdot\mathbf{l})]$$

q is the wave-vector of mode

j is the polarization

e $_{\mathbf{q},j}$ is the polarisation vector

Phonons in reciprocal space



$$\mathbf{u}_l = \left(\frac{\hbar}{2MN}\right)^{(1/2)} \sum_{j,\mathbf{q}} \frac{\mathbf{e}_{j,\mathbf{q}}}{\sqrt{\omega_{j,\mathbf{q}}}} [a_{j,\mathbf{q}} \exp(i\mathbf{q}\cdot\mathbf{l}) + a^{+}_{j,\mathbf{q}} \exp(-i\mathbf{q}\cdot\mathbf{l})]$$

Phonons in a Bravais lattice

- Creation of phonon

$$(\frac{d^2\sigma}{d\Omega dE_f})_{\mathrm{coh}+1} = \frac{\sigma_{\mathrm{coh}}}{4\pi}\frac{k_f}{k_i}\frac{(2\pi)^3}{2V_0}\frac{1}{M}\exp(-2W)$$

$$\sum_{j,\mathbf{q}}\sum_{\boldsymbol{\tau}}\frac{(\mathbf{Q}\cdot\mathbf{e}_{j,\mathbf{q}})^2}{\omega_{j,\mathbf{q}}}\langle n_{j,\mathbf{q}}+1\rangle\cdot\delta(\omega-\omega_{j,\mathbf{q}})\delta(\mathbf{Q}-\mathbf{q}-\boldsymbol{\tau})$$

- Annihilation of phonon

$$(\frac{d^2\sigma}{d\Omega dE_f})_{\mathrm{coh}-1} = \frac{\sigma_{\mathrm{coh}}}{4\pi}\frac{k_f}{k_i}\frac{(2\pi)^3}{2V_0}\frac{1}{M}\exp(-2W)$$

$$\sum_{j,\mathbf{q}}\sum_{\boldsymbol{\tau}}\frac{(\mathbf{Q}\cdot\mathbf{e}_{j,\mathbf{q}})^2}{\omega_{j,\mathbf{q}}}\langle n_{j,\mathbf{q}}\rangle\cdot\delta(\omega+\omega_{j,\mathbf{q}})\delta(\mathbf{Q}-\mathbf{q}-\boldsymbol{\tau})$$

Phonon cross section for non-Bravais lattice

- Phonon creation

$$(\frac{d^2\sigma}{d\Omega dE_f})_{\mathrm{coh}+1} = \frac{k_f}{k_i}\frac{(2\pi)^3}{2V_0}\sum_s \sum_{\boldsymbol{\tau}} \frac{1}{\omega_{j,\mathbf{q}}}|F_{j,\mathbf{q}}(\mathbf{Q})|^2\langle n(\omega)+1\rangle$$
$$\delta(\omega-\omega_{j,\mathbf{q}})\delta(\mathbf{Q}-\mathbf{q}-\boldsymbol{\tau})$$

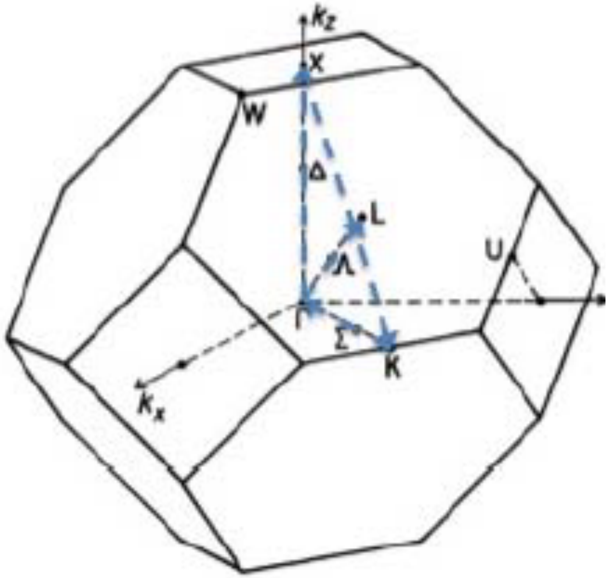
- Phonon annihilation

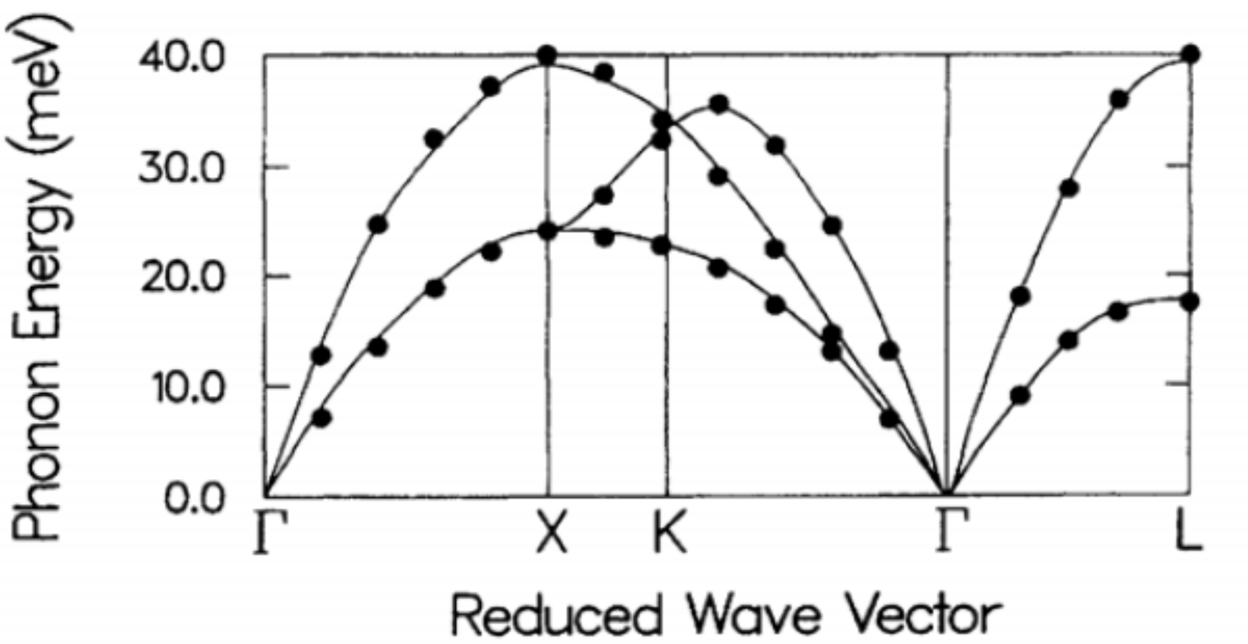
$$(\frac{d^2\sigma}{d\Omega dE_f})_{\mathrm{coh}-1} = \frac{k_f}{k_i}\frac{(2\pi)^3}{2V_0}\sum_s \sum_{\boldsymbol{\tau}} \frac{1}{\omega_{j,\mathbf{q}}}|F_{j,\mathbf{q}}(\mathbf{Q})|^2\langle n(\omega)\rangle$$
$$\delta(\omega+\omega_{j,\mathbf{q}})\delta(\mathbf{Q}-\mathbf{q}-\boldsymbol{\tau})$$

- Phonon structure factor

$$F_{j,\mathbf{q}}(\mathbf{Q}) = \sum_d \frac{\bar{b}_d}{\sqrt{M}_d}(\mathbf{Q}\cdot\mathbf{e}_{d,j,\mathbf{q}})\exp(-W_d)\exp(i\mathbf{Q}\cdot\mathbf{d})$$

Example: phonons in Al





Dispersive modes
Strong dependence in wave-vector → Propagation?

A. A. Quang and B.M. Klein, Phys. Rev. B 46, 10734 (1992).

Detailed balance

$$S(\mathbf{Q}, -\omega) = \exp(-\hbar\omega/k_B T) S(\mathbf{Q}, \omega)$$

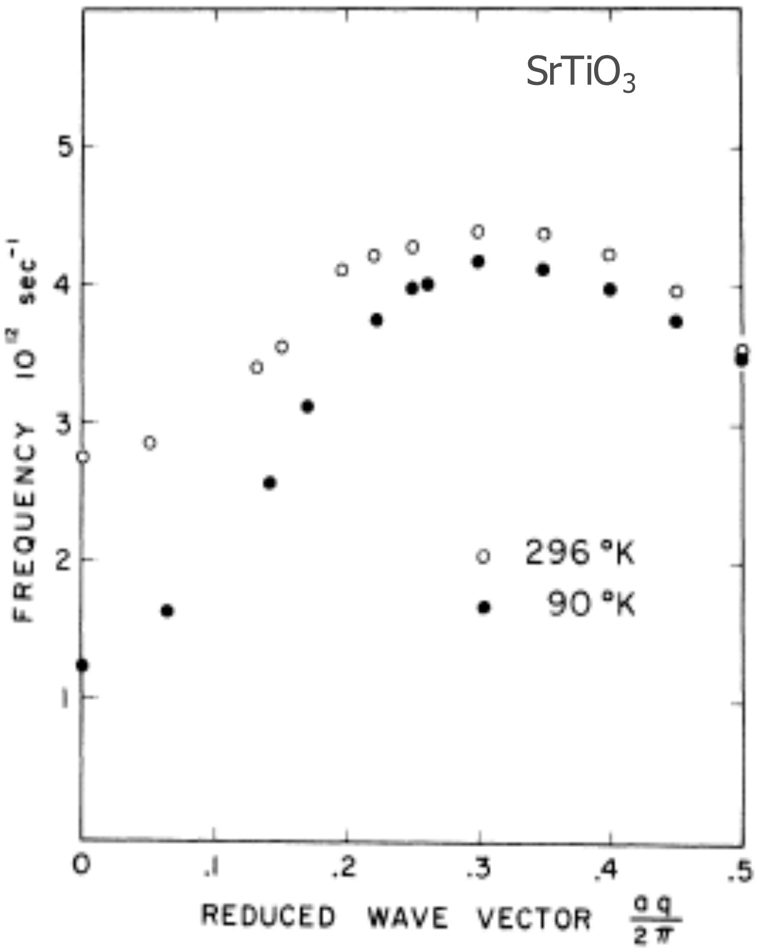
- At positive energy, neutron scattering creates quasi-particles such as phonons
- With increasing temperature, quasi-particles are populated
- Neutron can annihilate quasi-particles, and thereby gain energy
- This leads to a peak at negative energy (energy gain)

Phonons near phase transitions

• for a crystal to be stable, all normal modes should have real frequencies

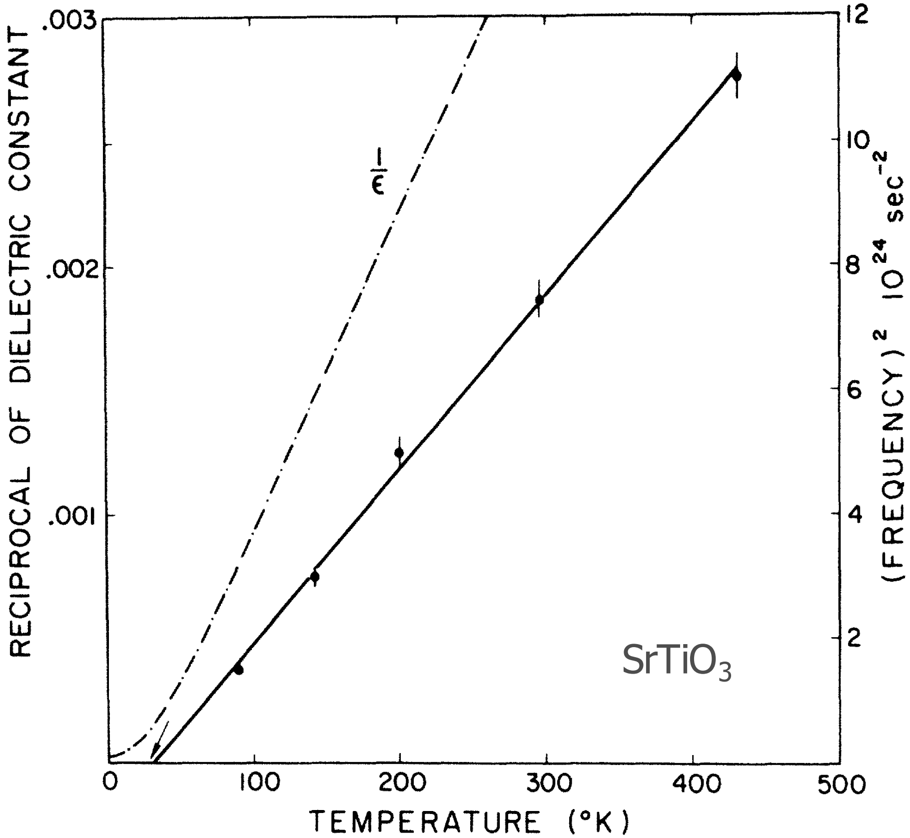
• if a particular lattice vibrational mode becomes zero, then the crystal transforms

• the displacements in the low-T structures reflect the symmetry of the vibrational modes



R. A. Cowley, Phys. Rev. Lett. 9, 159 (1962)

Phonons near phase transitions



divergent dielectric constant

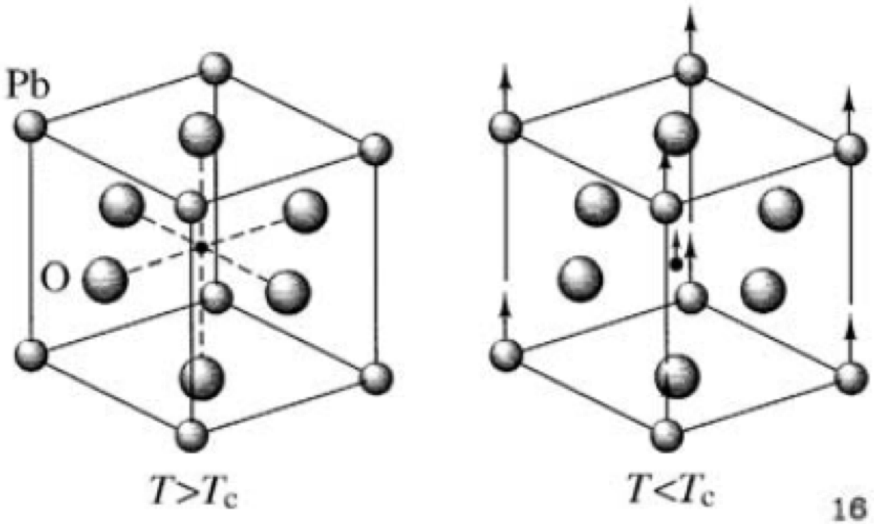
$$\frac{\varepsilon_0}{\varepsilon_\infty} = \frac{\omega_L^2}{\omega_T^2} \qquad \varepsilon_0 \sim (T - T_c)^{-1}$$

$$\Rightarrow \quad \omega_T^2 \sim (T - T_c) \qquad \text{soft mode}$$

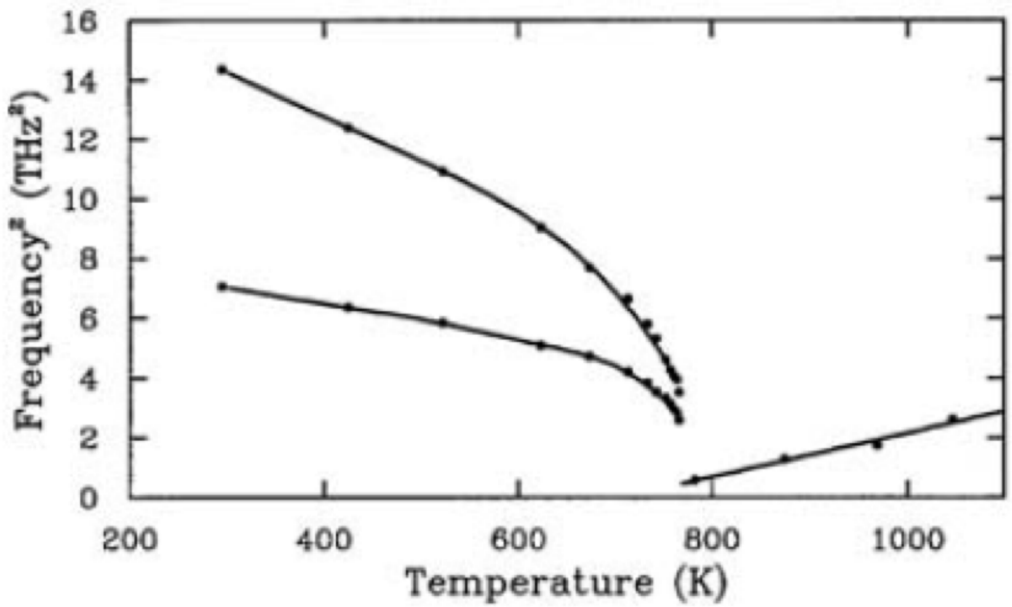
When the phonon reaches zero (becomes soft), the transition occurs

R. A. Cowley, Phys. Rev. Lett. 9, 159 (1962)

Example $PbTiO_3$



- Phase transition at around 750K
- Excitations are affected



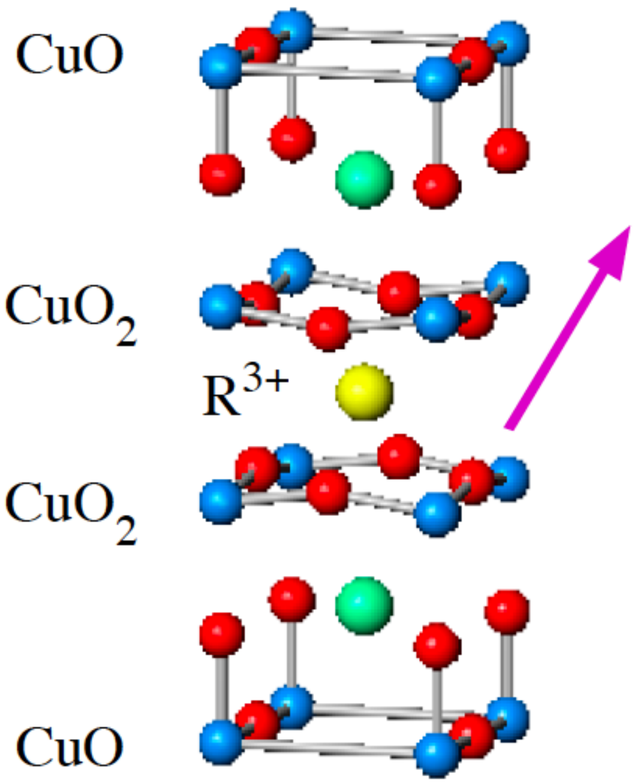
- Soft phonon at transition
- New phonon below transition

Neutron spectroscopy from local magnetism

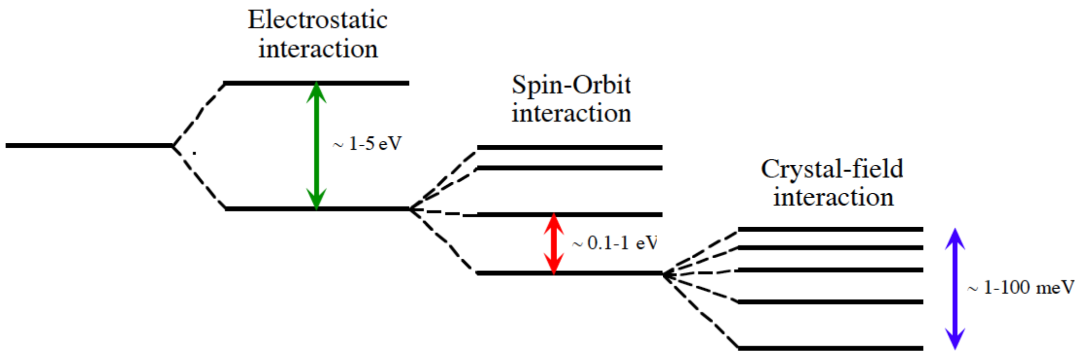
R^{3+} : $[Xe]4f^n$ + Hund's rules

1) S maximum   2) L maximum

3) $J = |L - S|$ if $n < 7$ $J = L + S$ if $n > 7$



$$V_{CF} = \sum_i \frac{\rho(\mathbf{r}_i)}{|\mathbf{r}_i - \mathbf{R}_i|} \quad \text{with} \quad \rho(\mathbf{r}_i) = Z_i e^2$$



Neutron scattering at crystal fields

Electronic wave-function

$$|\Gamma_n\rangle = \sum_{M=-J}^{J} a_n(M)\;|M\rangle$$

Correlation function

$$S^{\alpha\beta}(\omega) = Np_{\Gamma_n}\langle\Gamma_n|\hat{J}^\alpha|\Gamma_m\rangle\langle\Gamma_m|\hat{J}^\beta|\Gamma_n\rangle\delta(\hbar\omega + E_{\Gamma_n} - E_{\Gamma_m})$$

Cross-section

$$\frac{d^2\sigma}{d\Omega d\omega} = N\left(\tfrac{1}{2}g\gamma r_o\right)^2\frac{k'}{k}F^2(\mathbf{Q})\exp\{-2W(\mathbf{Q})\}p_{\Gamma_n} \times \sum_\alpha\left[1-\left(\tfrac{Q_\alpha}{Q}\right)^2\right]^2\left|\langle\Gamma_m|\hat{J}^\alpha|\Gamma_n\rangle\right|^2\delta(\hbar\omega + E_{\Gamma_n} - E_{\Gamma_m}).$$

Powder-average

Peaks at transitions between electronic states if allowed by selection rules

$$\frac{d^2\omega}{d\Omega d\omega} = N(\tfrac{1}{2}g\gamma r_o)^2\frac{k'}{k}F^2(Q)\exp\{-2W(Q)\}p_{\Gamma_n} \times \left|\langle\Gamma_m|\hat{\mathbf{J}}_\perp|\Gamma_n\rangle\right|^2\delta(\hbar\omega + E_{\Gamma_n} - E_{\Gamma_m}) \;,$$

Intensity is proportional to matrix element → information about wave-function

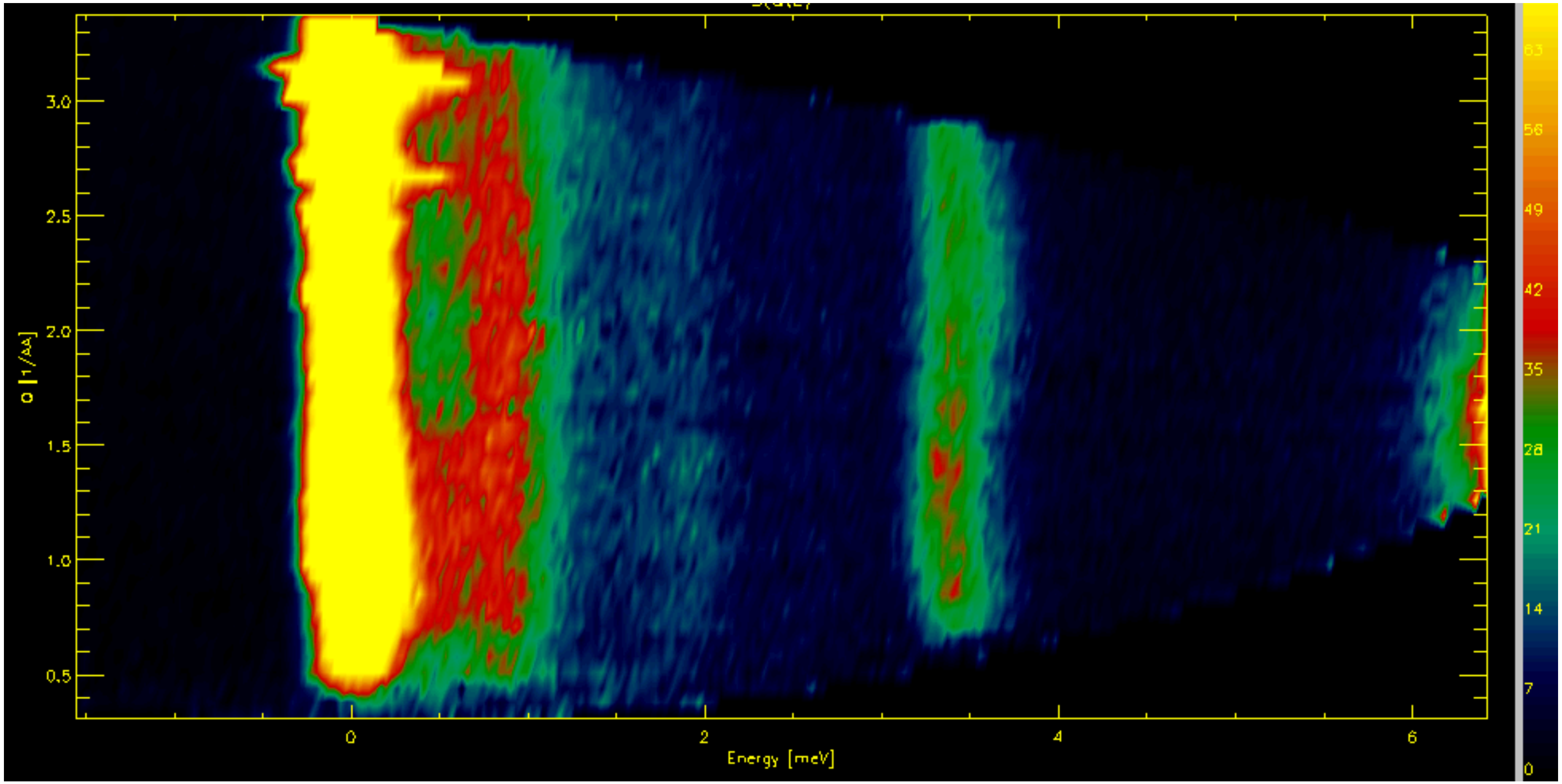
$$\hat{\mathbf{J}}_\perp = \hat{\mathbf{J}} - (\hat{\mathbf{J}}\cdot\mathbf{Q})\mathbf{Q}/Q^2$$

$$\left|\langle\Gamma_m|\hat{\mathbf{J}}_\perp|\Gamma_n\rangle\right|^2 = \tfrac{2}{3}\sum_\alpha\left|\langle\Gamma_m|\hat{\mathrm{J}}^\alpha|\Gamma_n\rangle\right|^2 \;.$$

ΔJ=0

ΔJz=0, ±1

Example of a measurement



What does the Q-dependence of the excitations mean?