Inelastic x-ray scattering from polycrystals: mutual fertilization of experiment and theory

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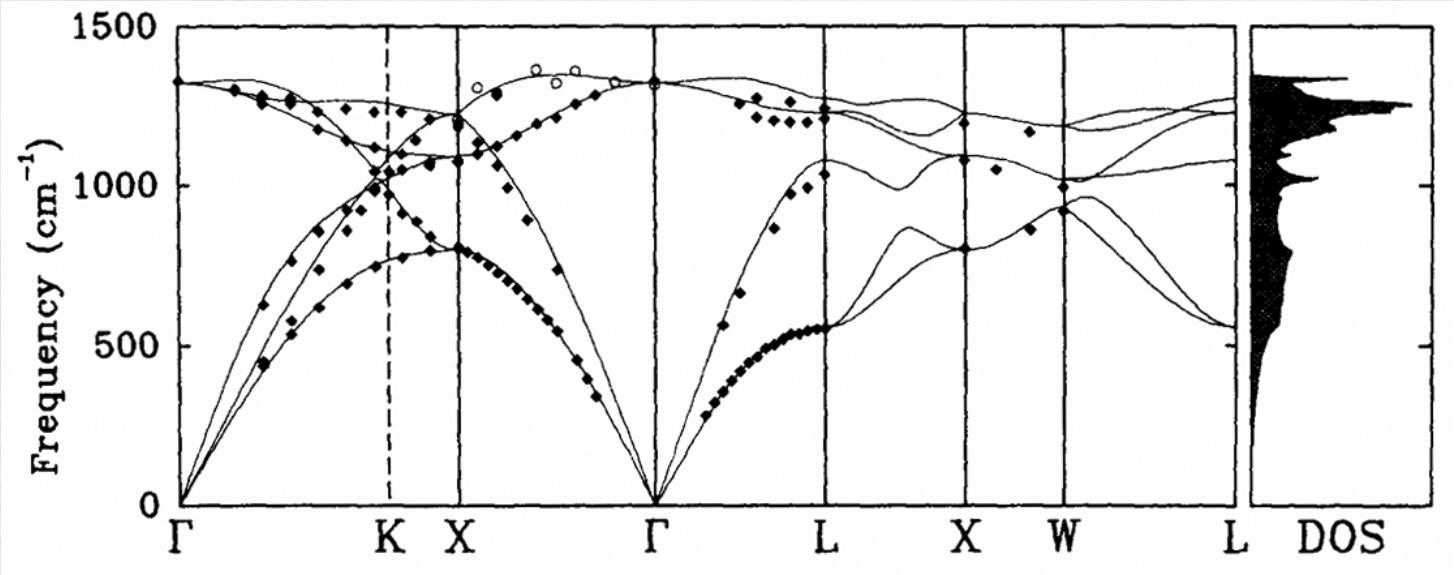
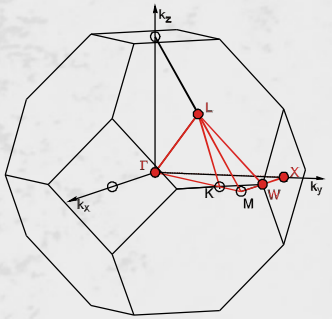
OUTLINE

- ☑ *basic introduction to IXS*
- ☑ *IXS from polycrystals*
  - something without theory
  - something with theory

Lattice dynamics studies



diamond



- Sound velocities
- Elasticity
- Interatomic force constants

- Thermodynamics (C_V, S_V, θ_D, …)

- Dynamical instabilities (phonon softening)
- Anharmonicity
- Phonon-electron coupling

P. Pavone, K. Karch, O.Schütt, W. Windl, D. Strauch, P. Giannozzi, S. Baroni, Phys. Rev. B ***48****, 3156 (1993)*

Vibrational spectroscopy: historical insight

Infrared absorption - 1881

W. Abney and E. Festing, R. Phil. Trans. Roy. Soc. 172, 887 (1881)

Brillouin light scattering - 1922

L. Brillouin, Ann. Phys. (Paris) 17, 88 (1922)

Raman scattering – 1928

C. V. Raman and K. S. Krishnan, Nature 121, 501 (1928)

TDS: Phonon dispersion in Al – 1948

P. Olmer, Acta Cryst. 1 (1948) 57

INS: Phonon dispersion in Al – 1955

B.N. Brockhouse and A.T. Stewart, Phys. Rev. 100, 756 (1955)

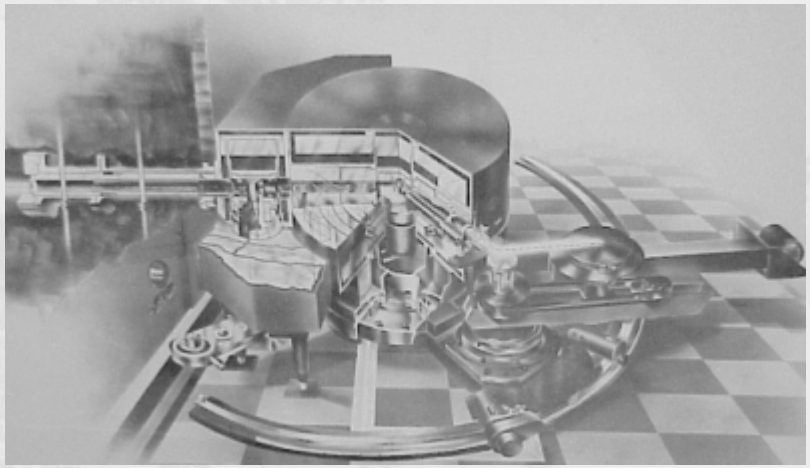
IXS: Phonon dispersion in Be – 1987

B. Dorner, E. Burkel, Th. Illini and J. Peisl, Z. Phys. B – Cond. Matt. 69, 179 (1987)

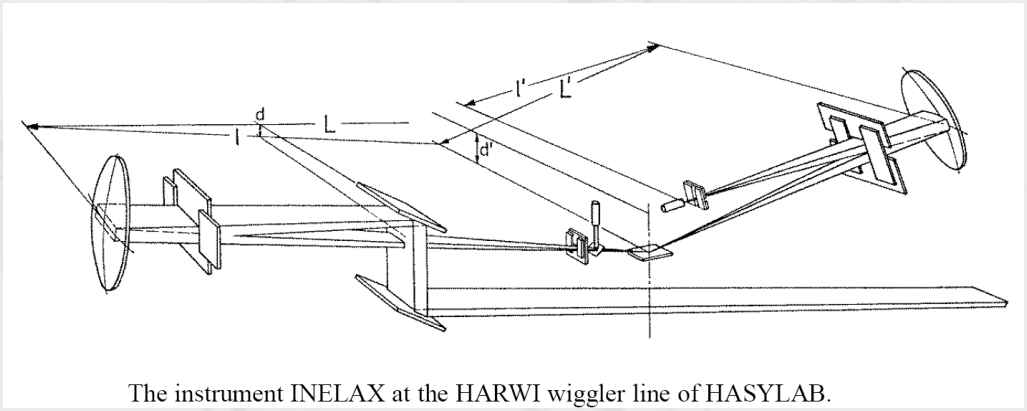
NIS: Phonon DOS in Fe – 1995

M. Seto, Y. Yoda, S. Kikuta, X.W. Zhang and M. Ando, Phys. Rev. Lett. 74, 3828 (1995)

INS and IXS



Brockhouse (1955)



The instrument INELAX at the HARWI wiggler line of HASYLAB.

Burkel, Dorner and Peisl (1987)

Thermal neutrons:

E_i = 25 meV

k_i = 38.5 nm^{-1}

$\Delta E/E$ = 0.01 – 0.1

large beams: few mm or larger

Hard X-rays:

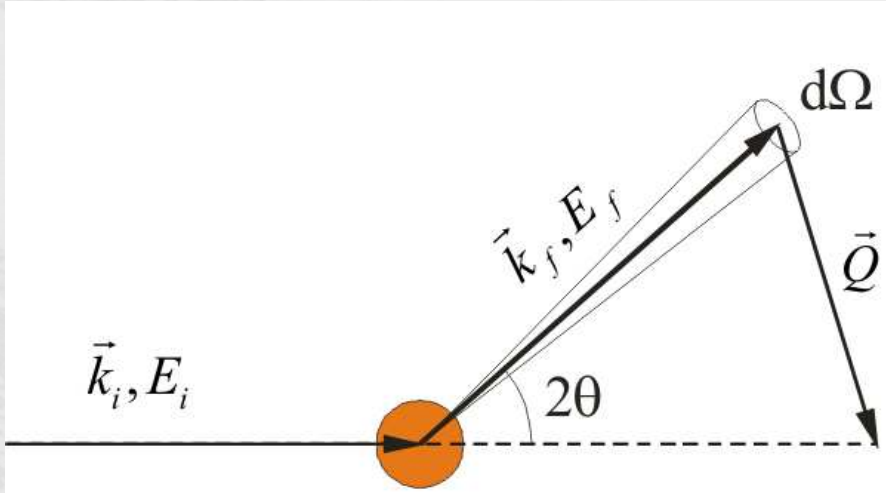
E_i = 18 keV

k_i = 91.2 nm^{-1}

$\Delta E/E \leq 1 \times 10^{-7}$

small beams: 100 μm or smaller

IXS kinematics



$$E = E_i - E_f$$

energy conservation

$$\vec{Q} = \vec{k}_f - \vec{k}_i$$

momentum conservation

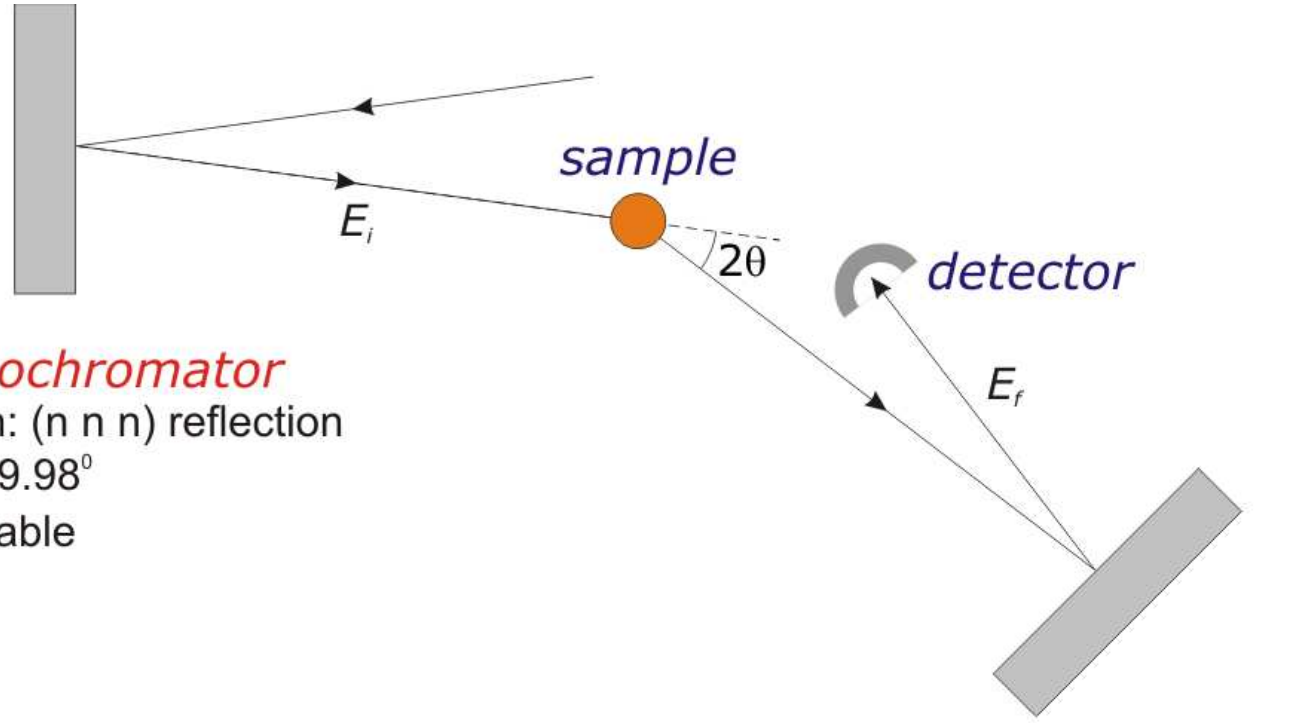
$$\Delta k/k \sim 10^{-7}$$

$$\left|\vec{Q}\right| = 2\left|\vec{k}_i\right| \sin(\theta)$$

energy and momentum transfers are uncoupled

NB: for neutrons $E = E_i - \frac{\hbar^2}{2m_n}(k_i - Q)^2$

Experimental IXS setup



monochromator
silicon: (n n n) reflection
$\theta_B = 89.98^0$
λ_1 tunable

$\Delta d/d = \Delta E/E = -\alpha(T)\Delta T$

$\alpha = 2.58 \times 10^{-6}$ at RT

analyzer
silicon: (n n n) reflection
$\theta_B = 89.98^0$
λ_2 fixed

ESRF: ID16 and ID28

The dynamical structure factor

Scattering function:

$$S(Q,E) = \sum_j G(Q,j) F(E,T,Q,j)$$

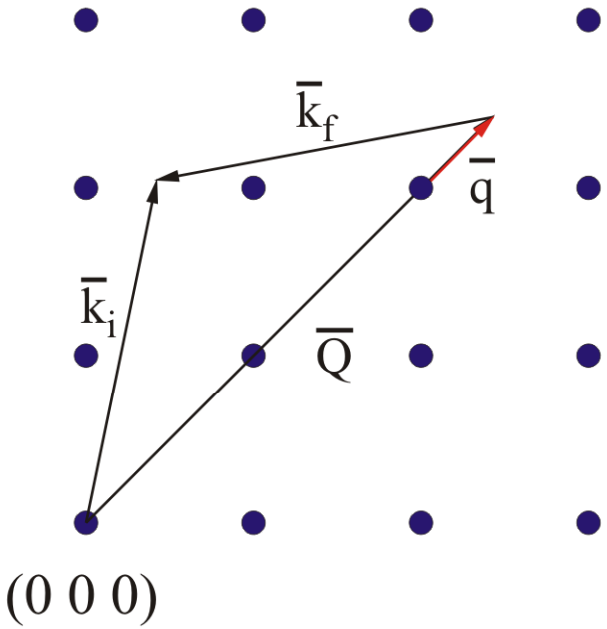
Thermal factor:

$$F(E,T,Q,j) = \frac{1}{1-\exp\left(-\frac{E}{kT}\right)} \frac{1}{E_j(q)} \cdot \left[\delta(E-E_j(q)) - \delta(E+E_j(q))\right]$$

Dynamical structure factor:

$$G(Q,j) = \left| \sum_d f_d(\vec{Q}) e^{-W_d(\vec{Q}) + i\vec{Q}\cdot\vec{r}_d} (\vec{Q}\cdot\vec{\sigma}_d^{\,j}(\vec{q})) M_d^{-1/2} \right|^2$$

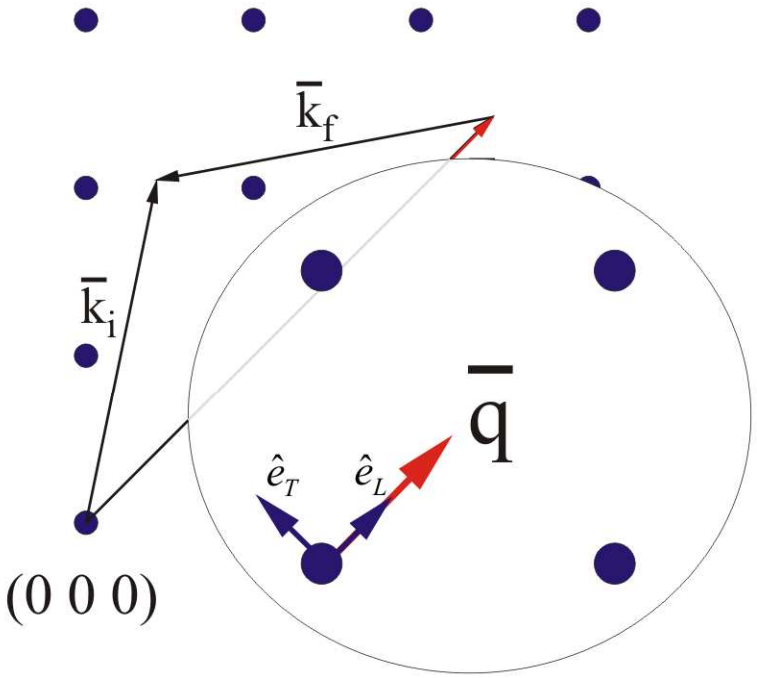
Single crystal: selection rules



$$\left|(\vec{Q}\cdot\hat{e}_L)\right|^2 > 0 \qquad \left|(\vec{Q}\cdot\hat{e}_T)\right|^2 \approx 0$$

well-defined momentum transfer for given scattering geometry

Single crystal: selection rules



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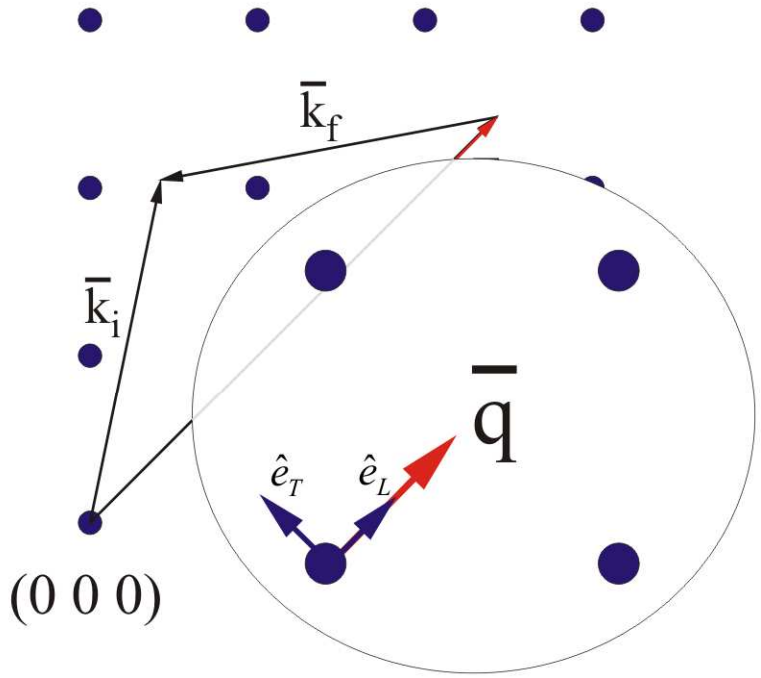

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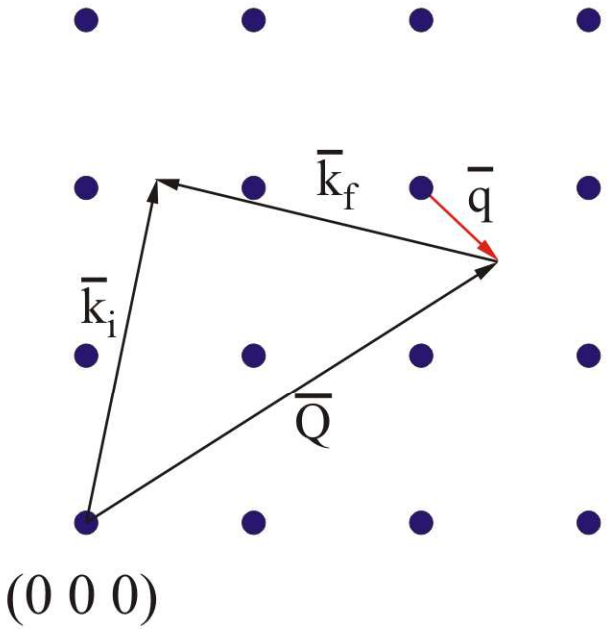

$$\left|(\vec{Q}\cdot\hat{e}_L)\right|^2 \approx 0 \qquad \left|(\vec{Q}\cdot\hat{e}_T)\right|^2 > 0$$

well-defined momentum transfer for given scattering geometry

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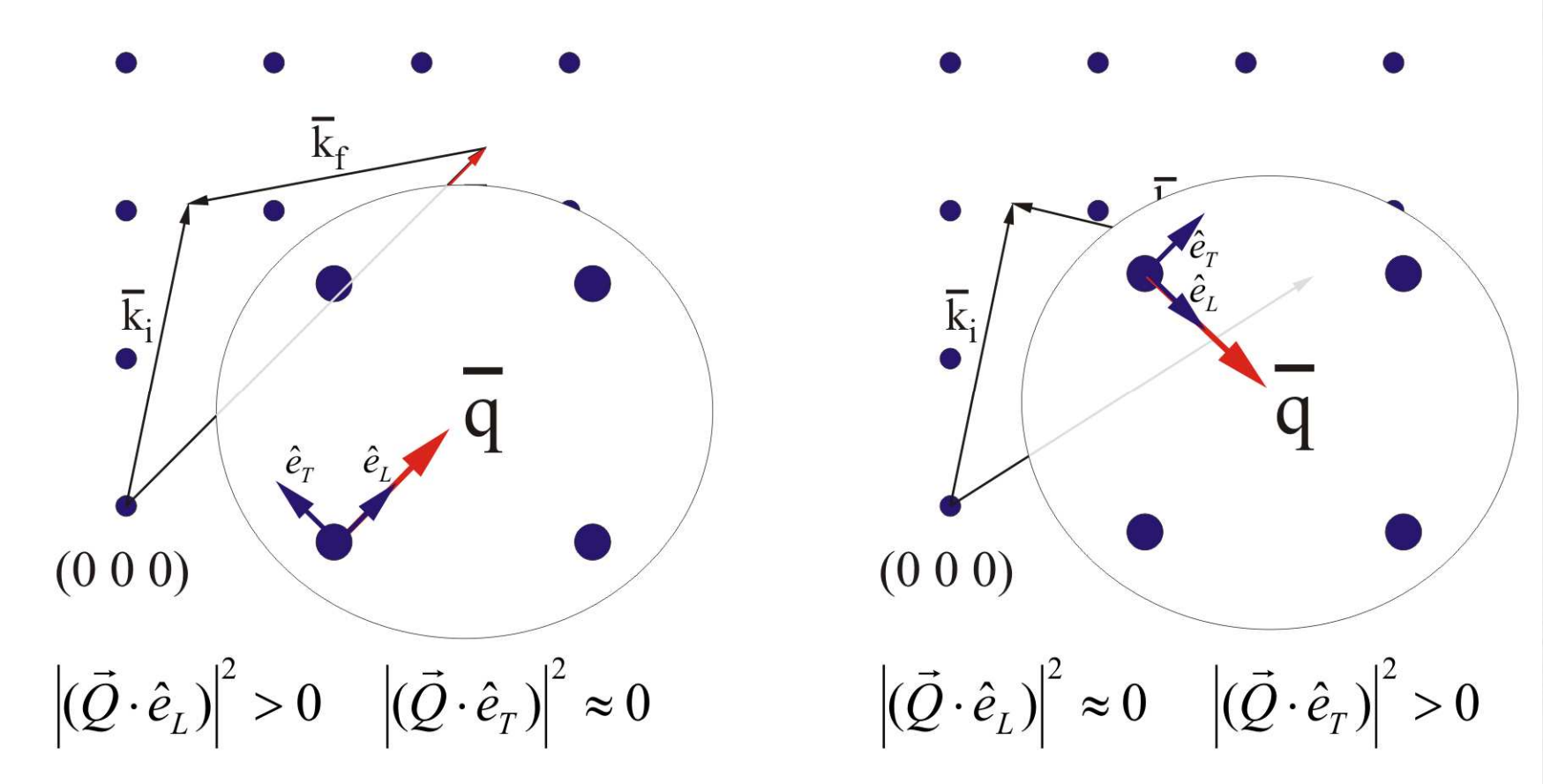
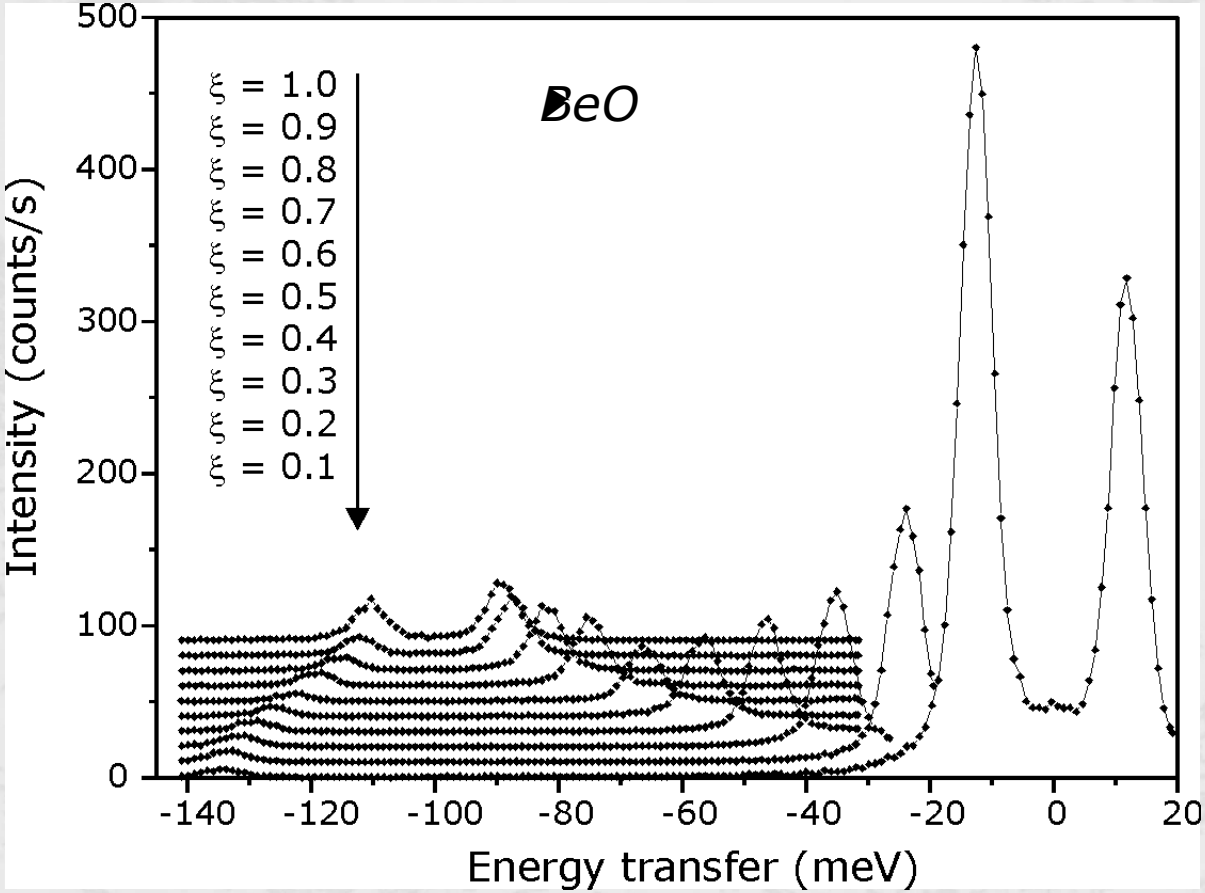


well-defined momentum transfer for given scattering geometry

Single crystal: example



6 meV resolution

λ = *0.7839Å*

LA and LO phonons propagating along Γ-A at (0 0 2+ξ)

*A. Bosak, M. Krisch, K. Schmalzl, W. van Beek, V. Kolobanov, Phys. Rev. B **77**, 224303 (2008)*

I. Scattering from polycrystals

Scattering from powders

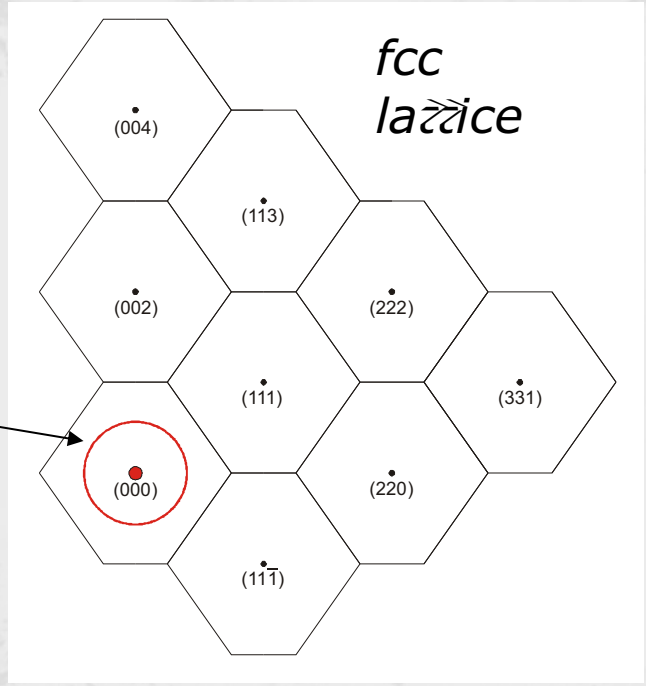
direction of momentum transfer is not defined:

integration over shell with radius |Q|

low Q – long-wave limit

orientational average of LA phonon energy /linked to the elasticity/

very large Q – DOS limit



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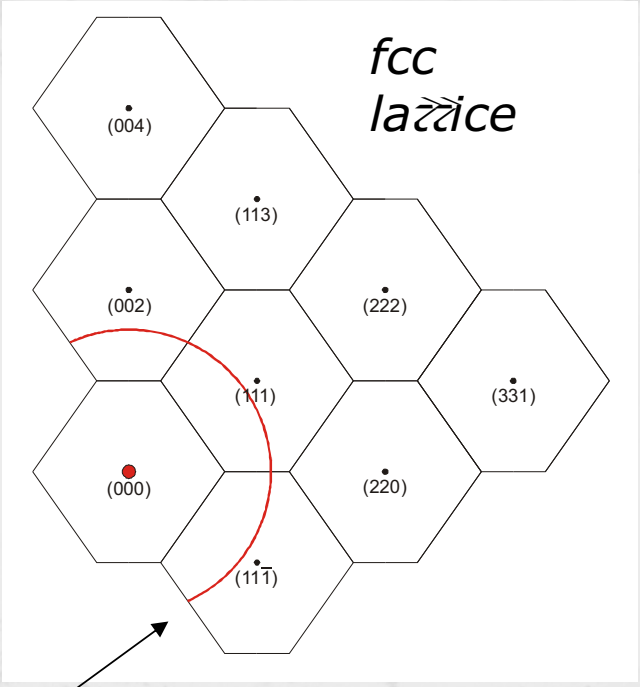

intermediate Q – reminiscence of selection rules

Scattering from powders

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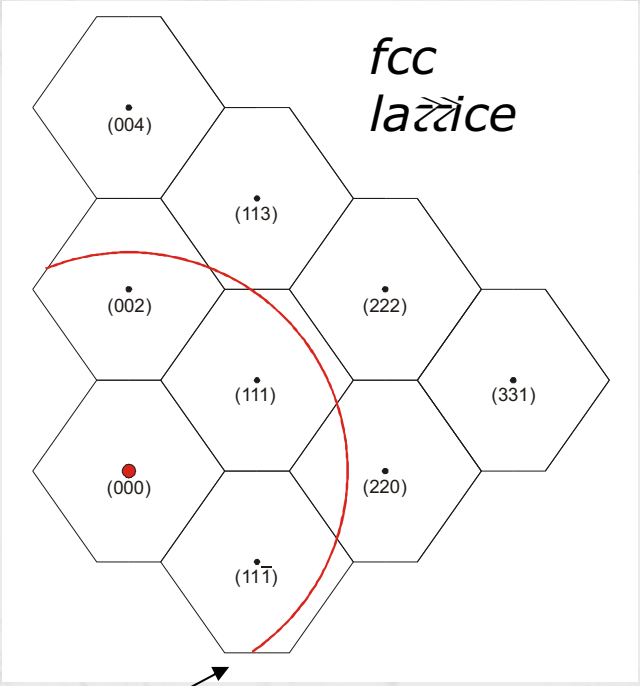

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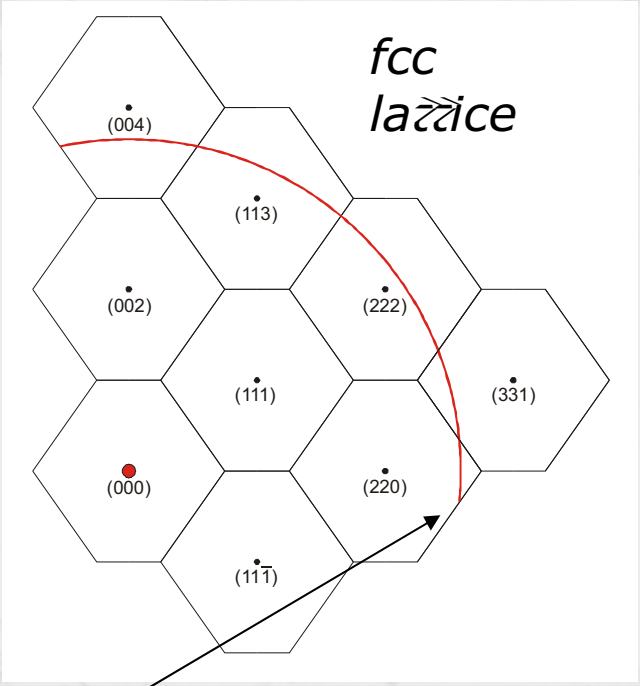


intermediate Q – reminiscence of selection rules

Something without modelling?

Easy cases:

- very low momentum transfer
- very high momentum transfer

Long wave limit

Q→0: spectral shape determined by elastic tensor ***only***

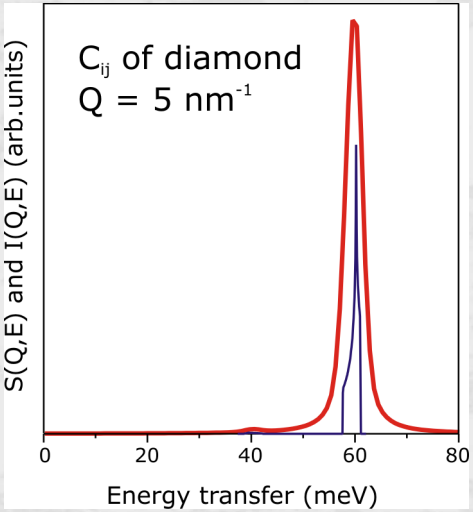
$$\left|\Lambda - V^2\right| = 0 \qquad \Lambda_{jk} = \frac{1}{\rho} C_{ijkl} n_i n_l$$

Christoffel's equation

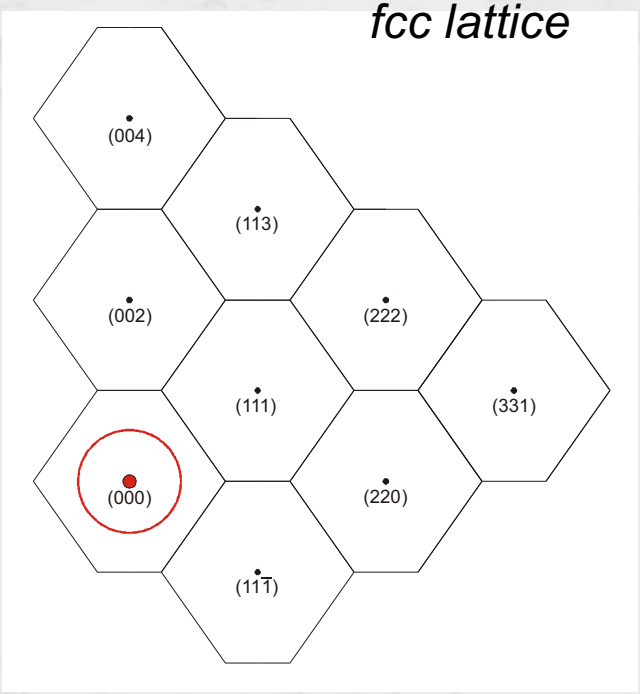
$$g(Q,E) \to A\left\langle \left|\vec{Q}\cdot\vec{u}(\vec{n},j)\right|^2 \delta\left(E - V_{\vec{n},j}\left|\vec{Q}\right|\right)\right\rangle$$

$$S(Q,E,T) = g(Q,E')F(E,E',T)$$

thermal factor

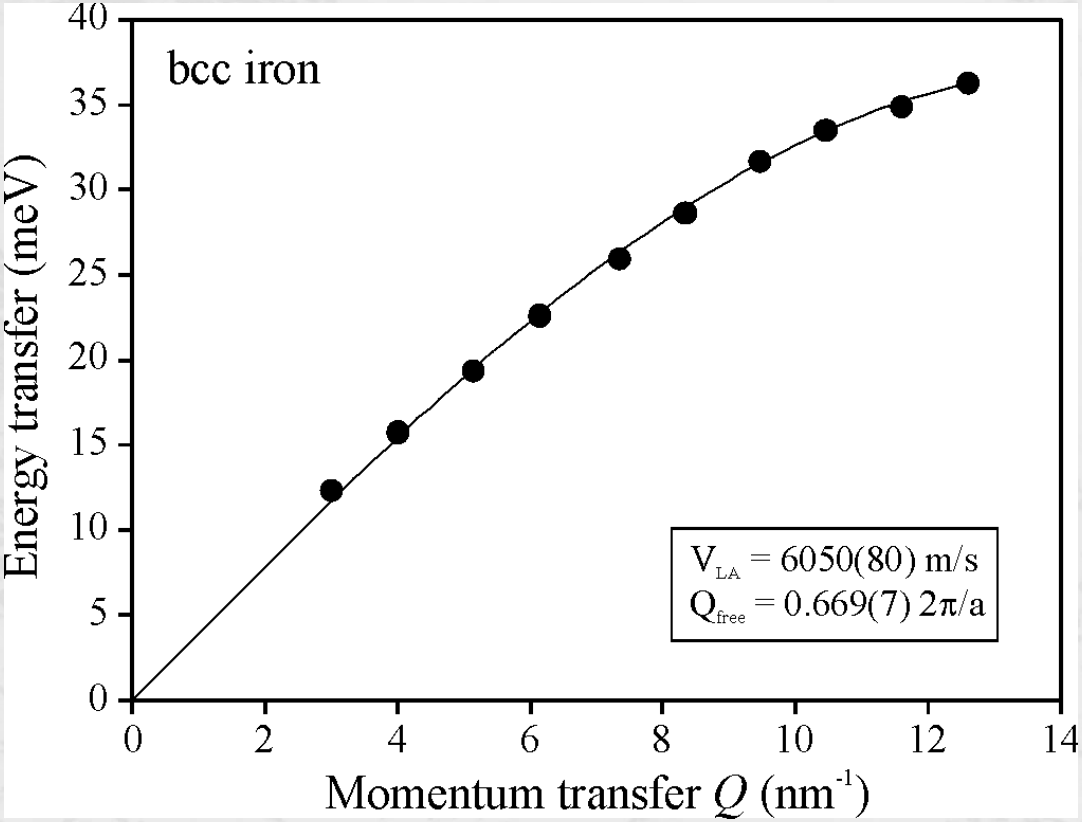


fcc lattice



average LA phonon dispersion

Average sound velocity

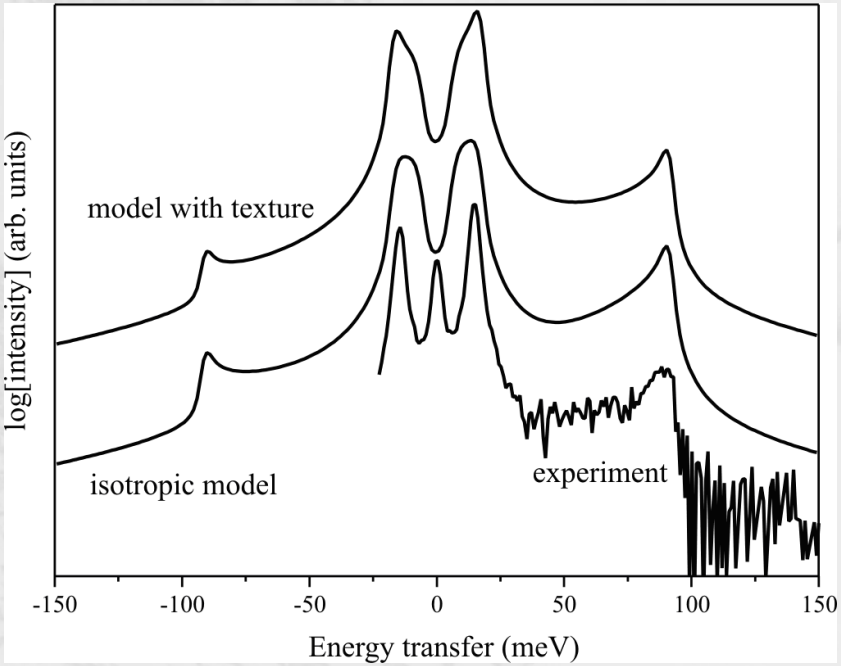


good example:
polycrystalline bcc iron

first-neighbor approximation: $E = \frac{2\hbar}{\pi} V_{LA} Q_{free} \sin\left(\frac{\pi}{2}\frac{Q}{Q_{free}}\right)$

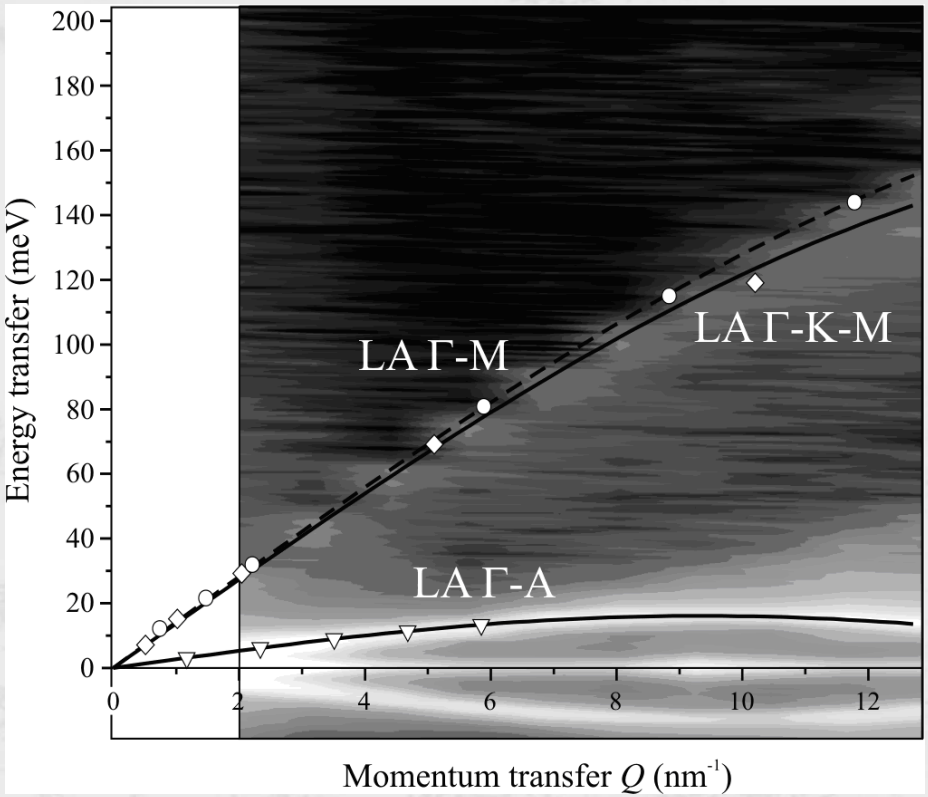
A. Bosak, M. Krisch, I. Fischer, S. Huotari, G. Monaco, Phys. Rev. B **75**, 064116 (2007)

Average sound velocity?



bad example: texture!
graphite

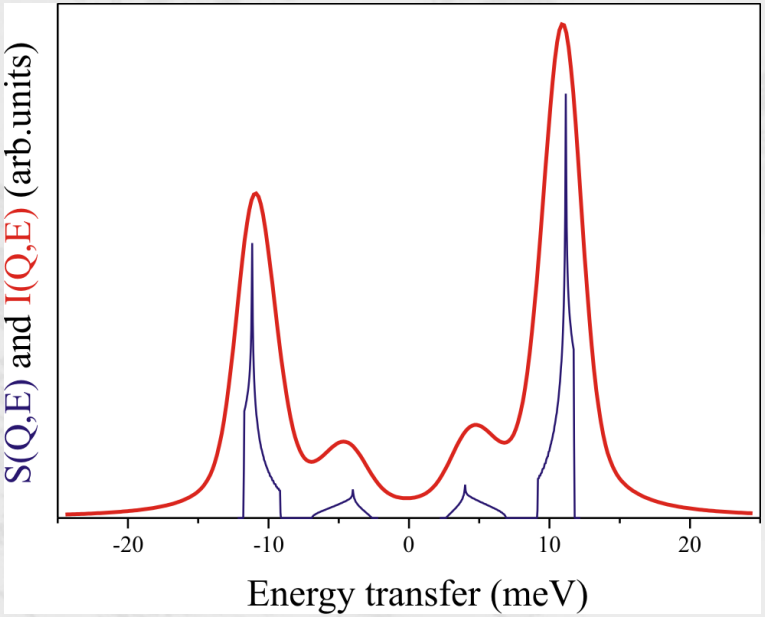
O.D.F. $f(g) = 4\delta(\psi)/\sin(\theta)$



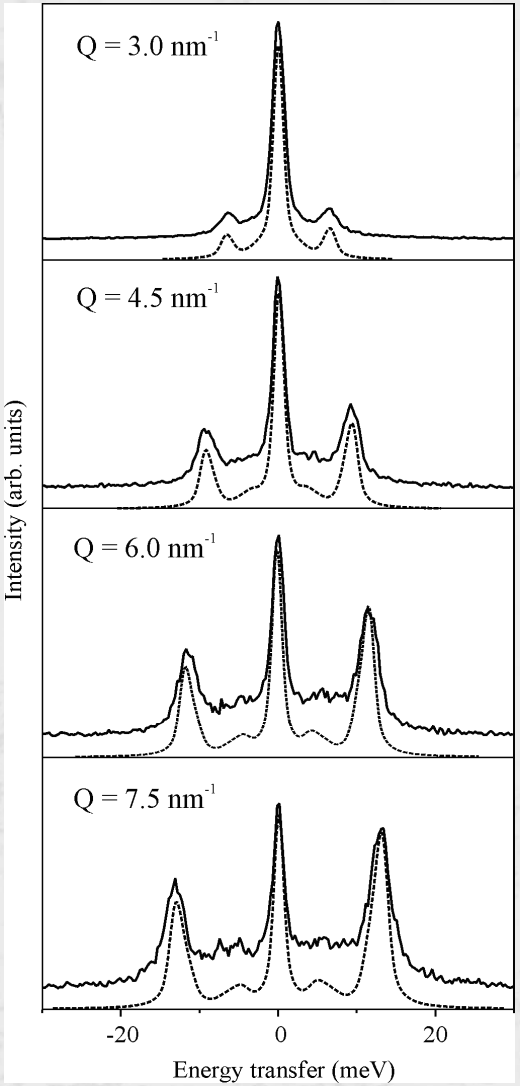
averaging is sometimes senseless…

Average sound velocity?

bad example: sodium



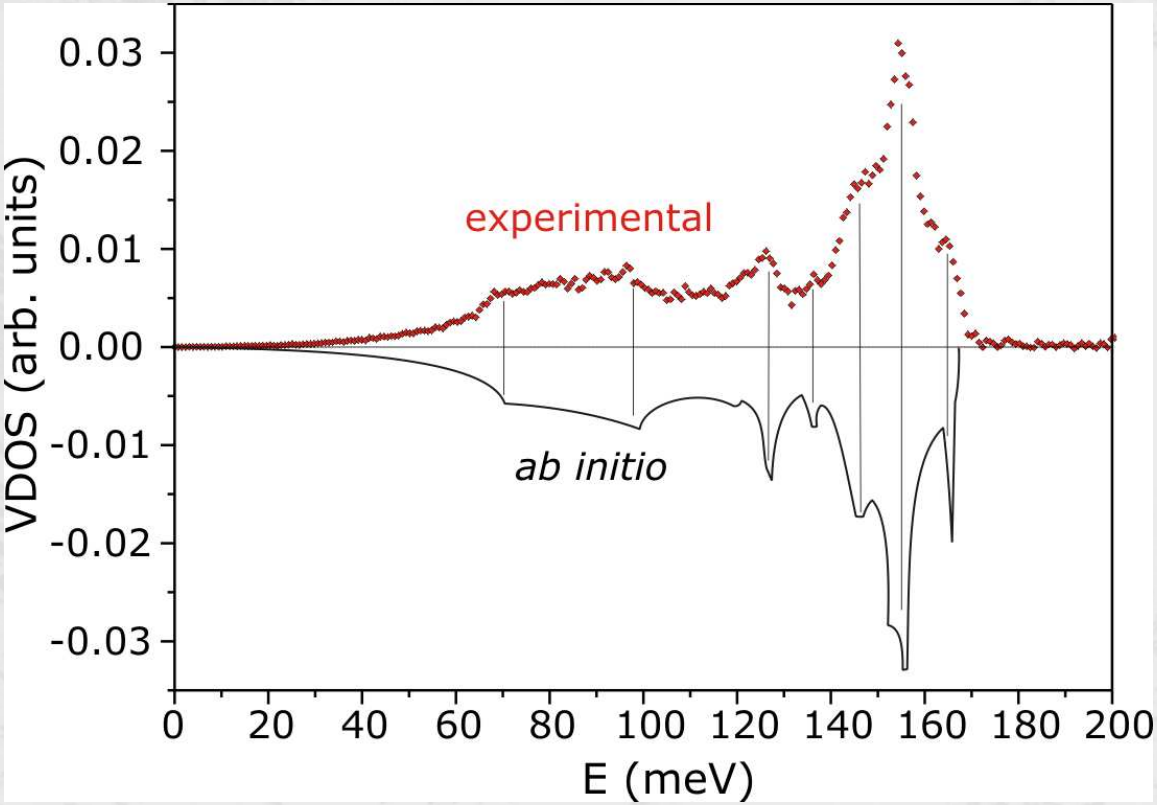
non-negligible TA contribution even for a cubic crystal



Warnings

- *even if well-defined, IXS-average sound velocity does not necessarily coincide with the macroscopic sound velocity in the polycrystalline sample*
- *texture MUST be taken into account*

Large-Q limit: vibrational DOS



incoherent approximation benchmark study: diamond

ab initio:

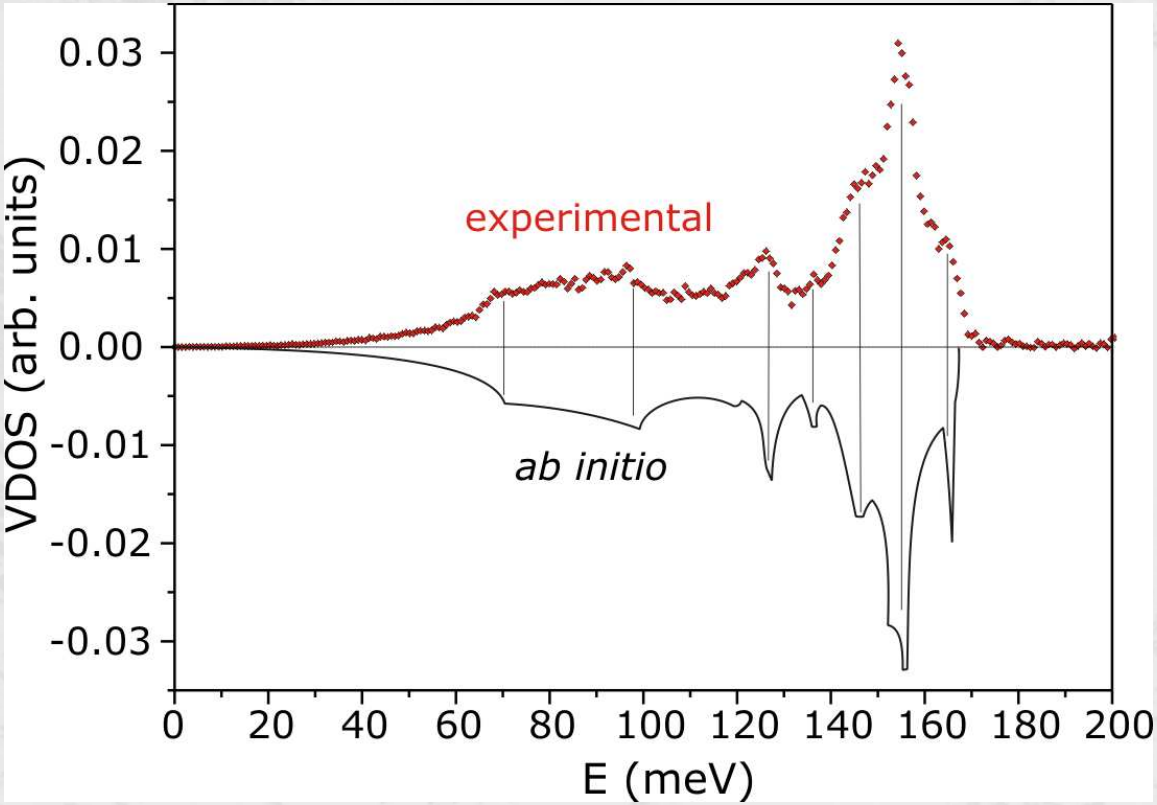
*P. Pavone, K. Karch, O Schütt, W. Windl, D. Strauch, P. Giannozzi, S. Baroni, Phys. Rev. **B 48**, 3156 (1993)*

data treatment:

*V.G. Kohn and A.I. Chumakov, Hyperfine Interactions **125**, 205 (2000)*

*A. Bosak, M. Krisch, Phys. Rev. **B 72**, 224305 (2005)*

Large-Q limit: vibrational DOS



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monoatomic systems:

direct calculation of

- *thermodynamic functions*
- *mean kinetic energy*
- *mean force constant*
- *mean-square atomic displacements*

Large-Q limit: vibrational DOS

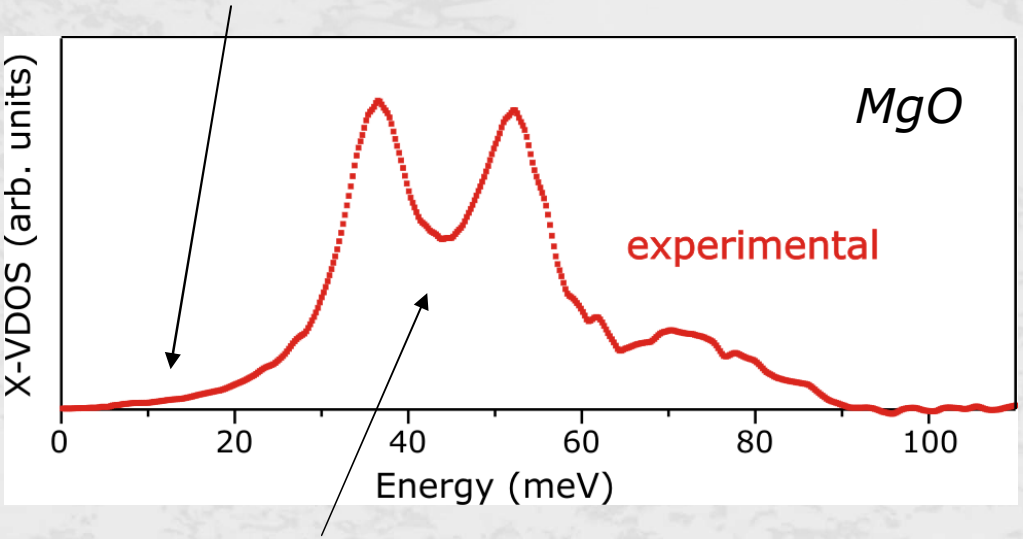
non-monoatomic systems:

only the generalized VDOS is accessible

$$\tilde{g}(E) = \sum_n \frac{G_n(E)}{\sum_n \sigma_n} \cdot \frac{\sigma_n}{M_n} Q^2 \exp(-2W_n)$$

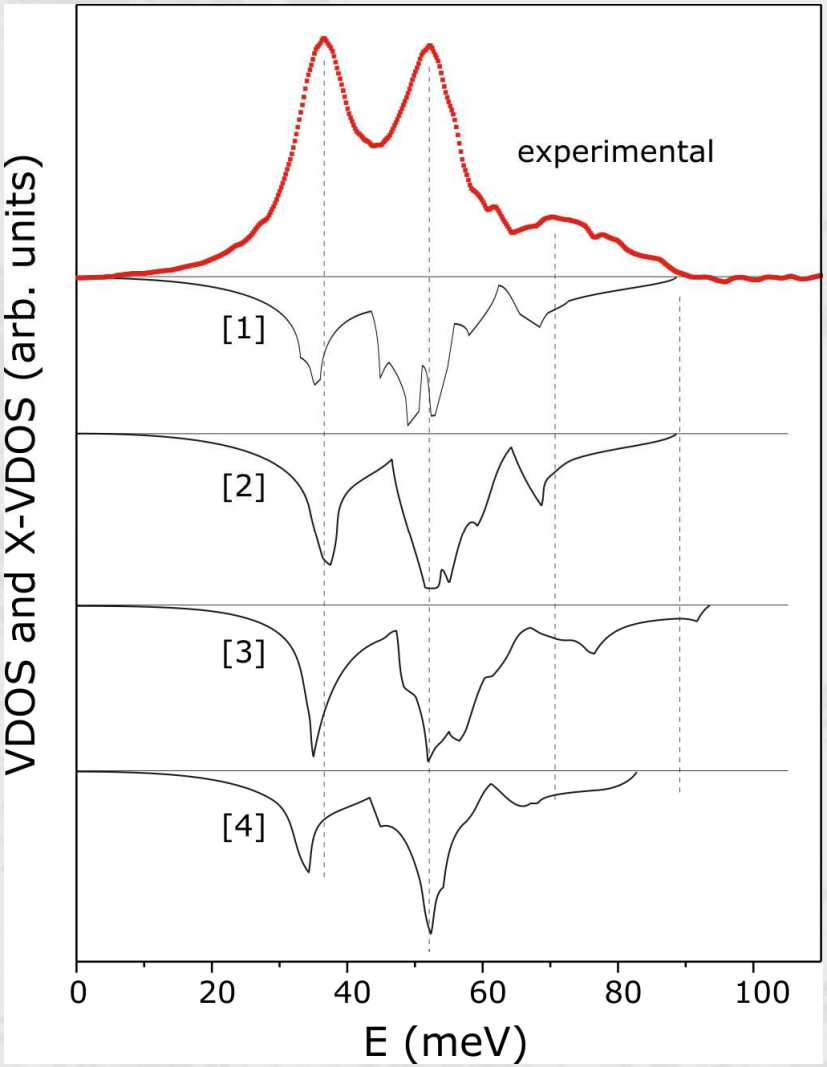
$$G_n(E) = \sum_{\vec{Q},j} \left|\vec{e}_n(\vec{Q},j)\right|^2 \delta(E - E_{\vec{Q},j})$$

low-energy part of generalized VDOS can be rescaled to the real VDOS



out of the parabolic part: modeling must be employed for the quantitative treatment

Comparative approach



full set of theoretical data is needed for quantitative comparison

*[1] O. Schütz, P. Pavone, W. Windl, K. Karch, D. Strauch, Phys. Rev B **50**, 3746 (1994)*

*[2] S. Ghose, M. Krisch, A.R. Oganov, A. Beraud, A. Bossak, R. Gulve, R. Seelaboyina, H. Yang, S.K. Saxena, Phys. Rev. Lett. **96**, 035507 (2006)*

*[3] N.D. Drummond and G.J. Ackland, Phys. Rev. B **65**, 184104 (2002)*

*[4] K. Parlinski, J. Łażewski and Y. Kawazoe, J. Phys. Chem. Solids **61**, 87 (2000)*

Intermediate Q:

(high-level) modeling is unavoidable

Information content for poly-IXS spectra?

single crystal spectrum

- *phonon frequencies (up to 3N)*
- *relative intensities for given **Q** (without precautions)*

polycrystalline spectrum

- *distribution of phonon frequencies (continuum)*
- *relative intensities for given |**Q**|*

warning:
energy resolution and statistics become crucial for polycrystalline IXS spectra

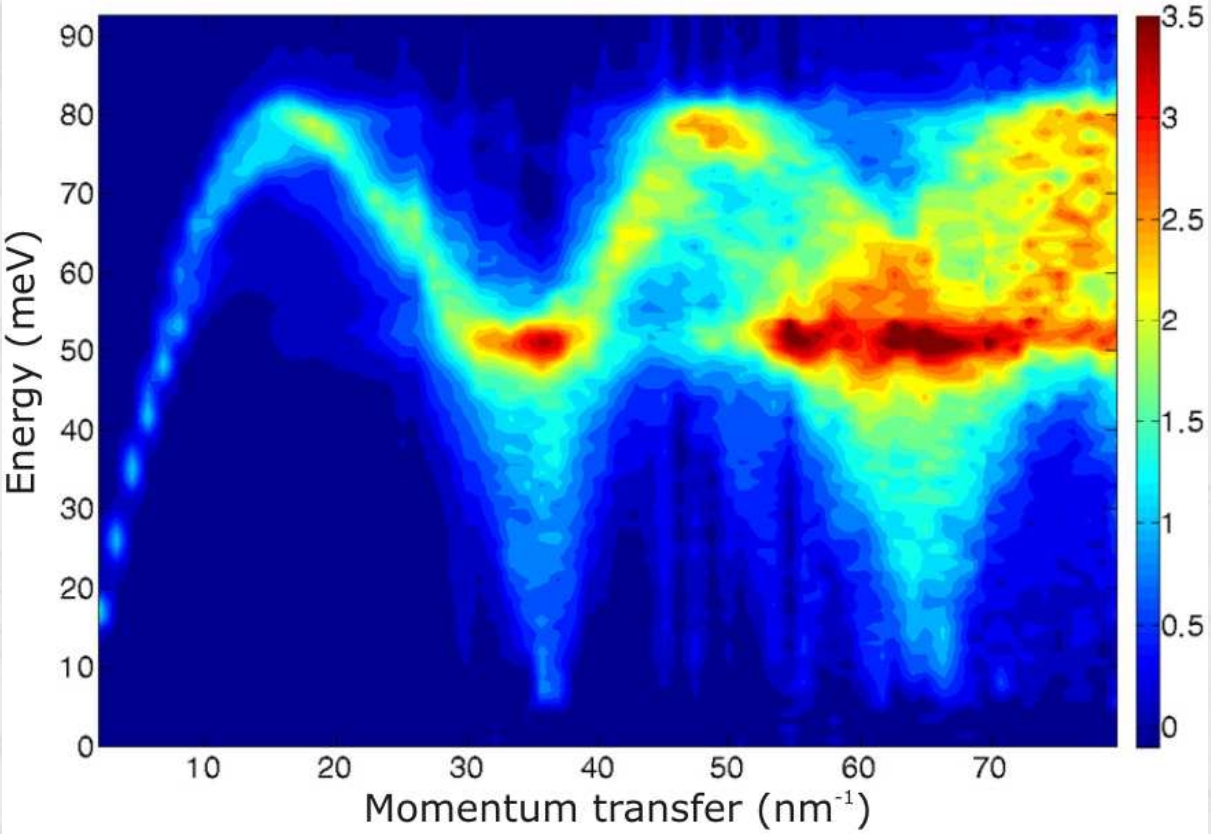
Beryllium / isotropic polycrystal

- *simple hcp structure*
- *good scatterer*
- *known phonon dispersion*

PhD thesis:
Irmengard FISCHER, ESRF

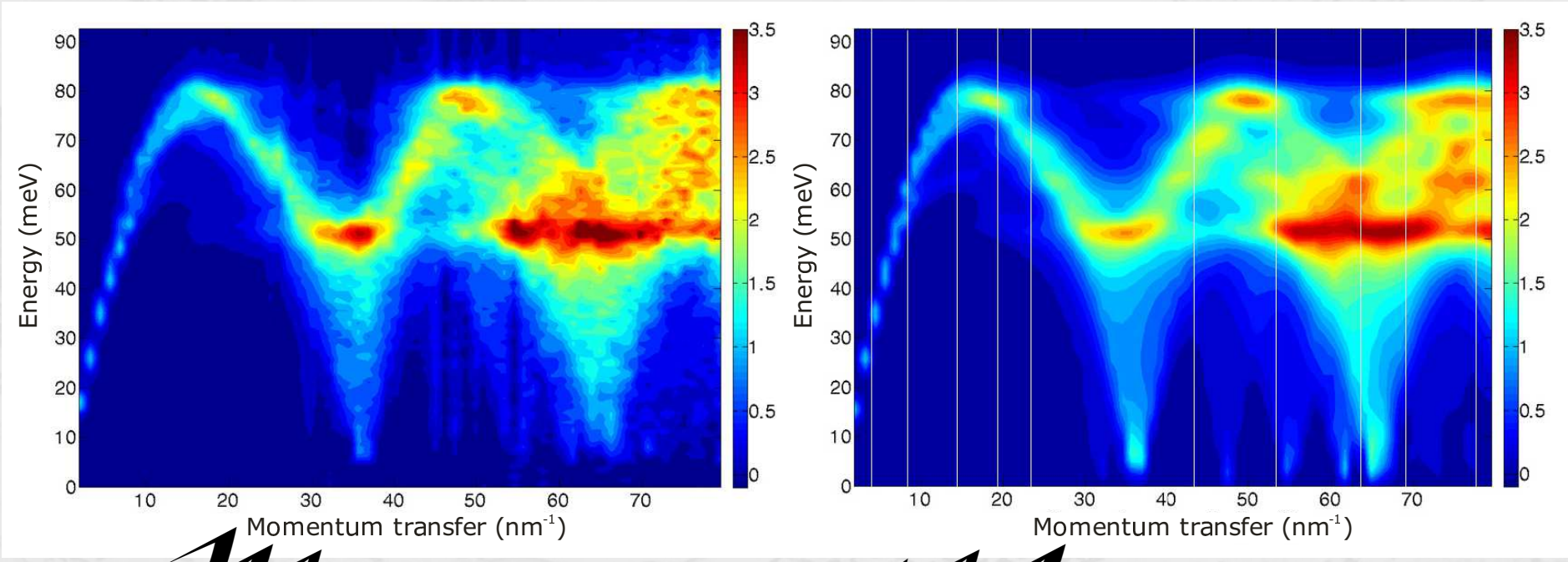
plan of action:

take a model with a simple parameterization and refine it to the powder spectra



Beryllium: model refinement

model: Born-von Karman, 7 interaction shells and 29 refinable parameters



experiment *refined model*

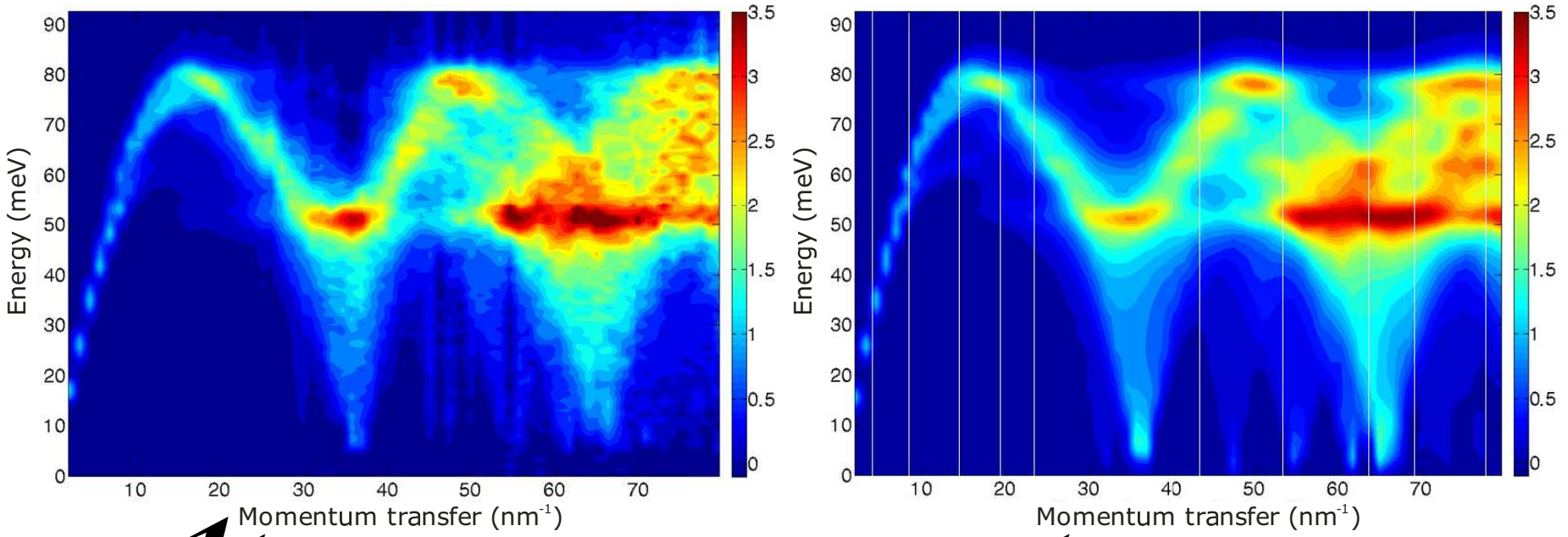
refinement of 10 spectra → good fit over whole Q range

kernel: OpenPhonon

collaboration with Alessandro MIRONE

Beryllium: model refinement

model: Born-von Karman, 7 interaction shells and 29 refinable parameters



experiment *refined model*

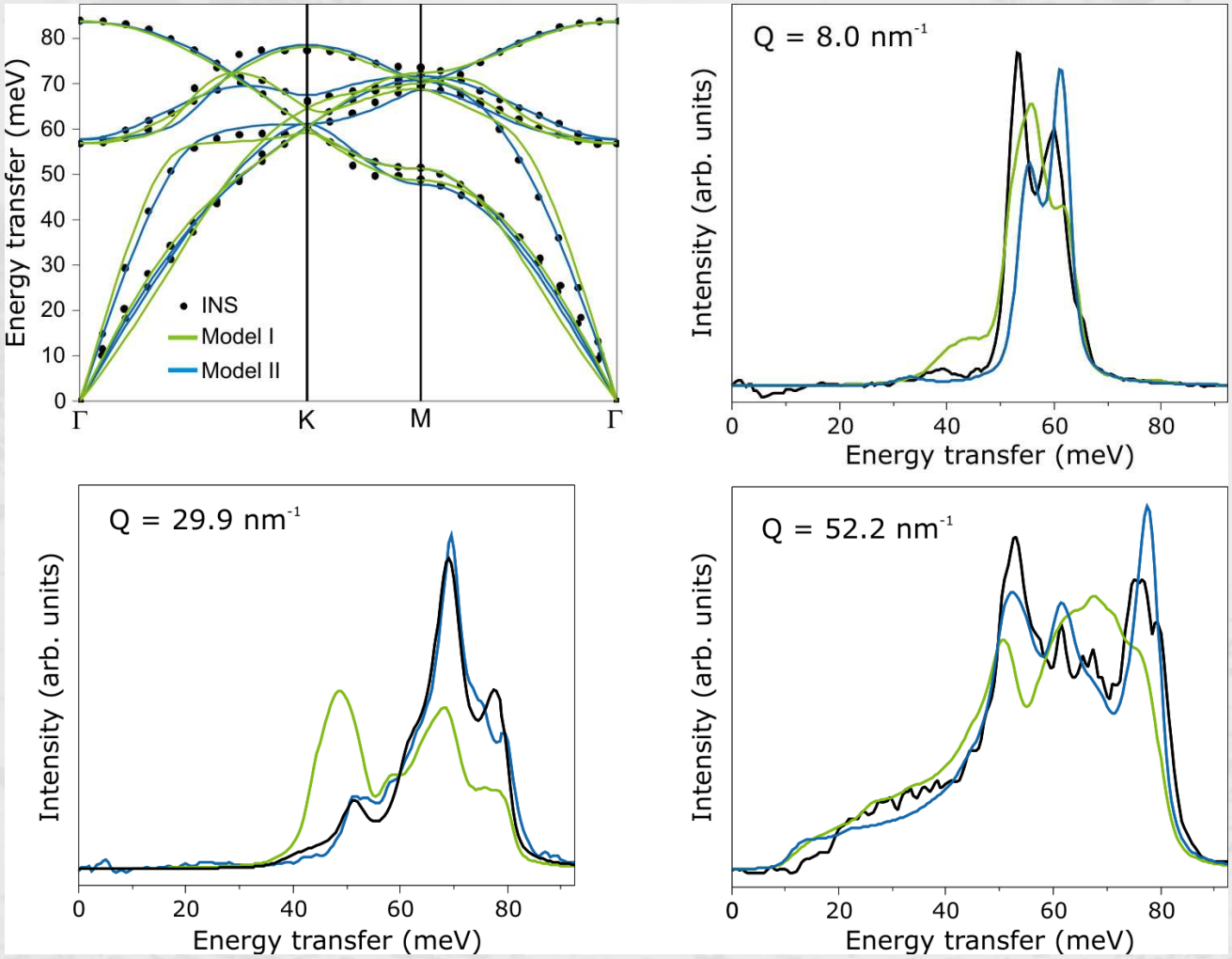
refinement of 10 spectra → good fit over whole Q range

***warning**: (too) many free parameters*

kernel: OpenPhonon

collaboration with Alessandro MIRONE

Comparative approach



good agreement along high symmetry directions does not guarantee the correctness of the model

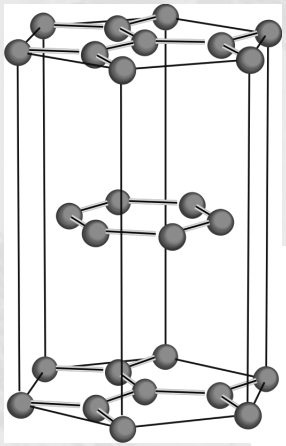
INS:
R. Scherm, Z. Amilius, R. Pauli, F. Suzuki, Metal Physics ***6****, 157 (1976)*

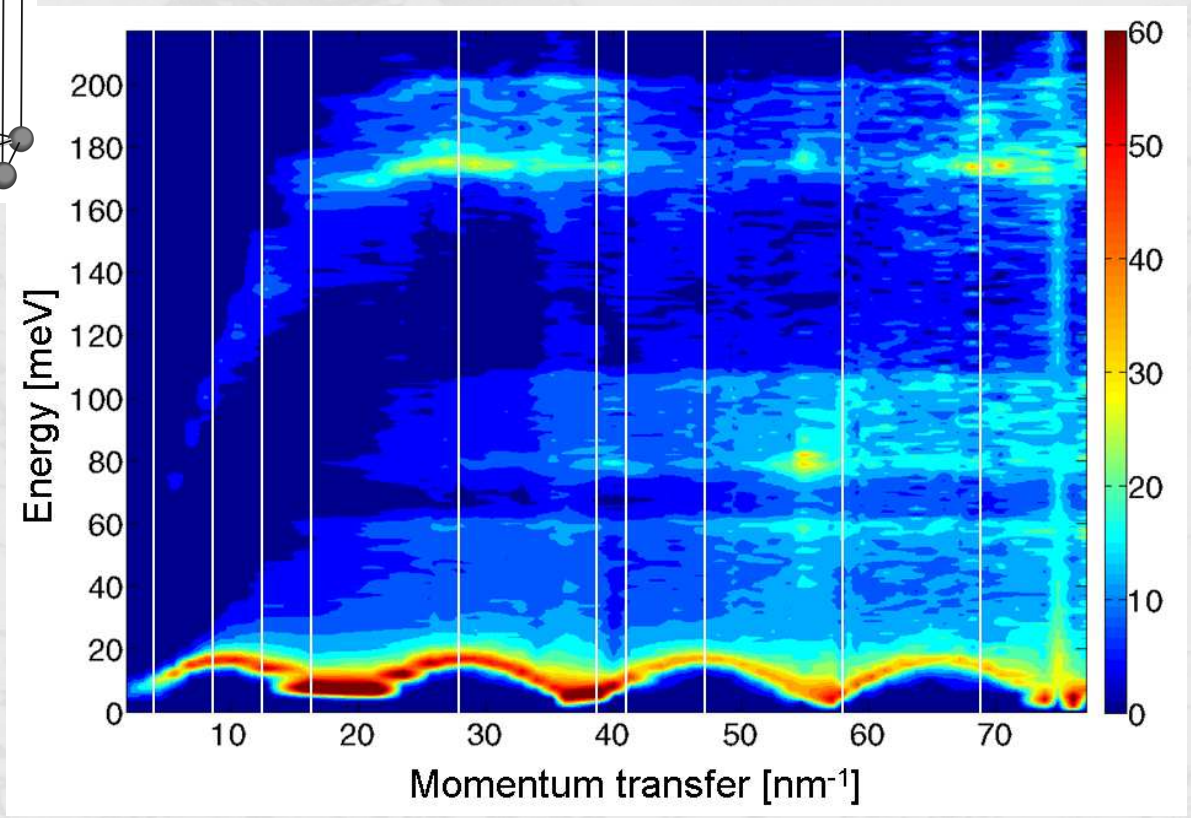
Model I:
F. Kwasniok, Surface Science ***329****, 90 (1995)*

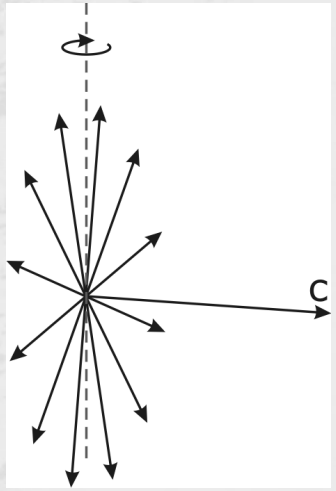
Model II:
J.B. Taylor, E.J. Mele, E.W. Plummer, Phys. Rev. B ***53****, 2090 (1996)*

Graphite / strongly textured

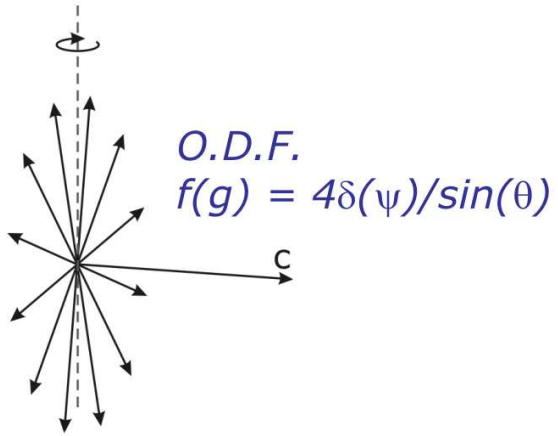
O.D.F. $f(g) = 4\delta(\psi)/\sin(\theta)$

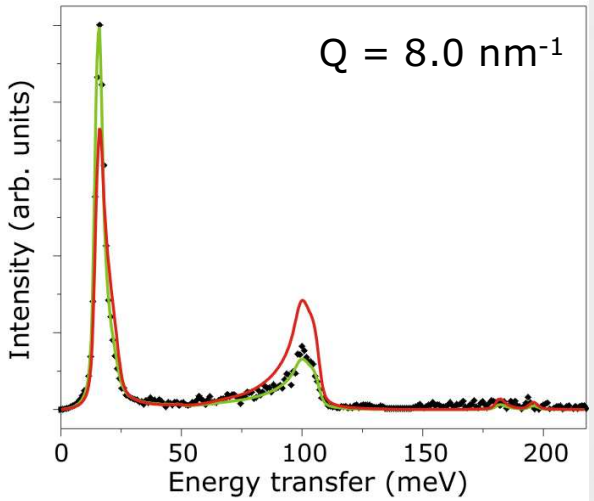


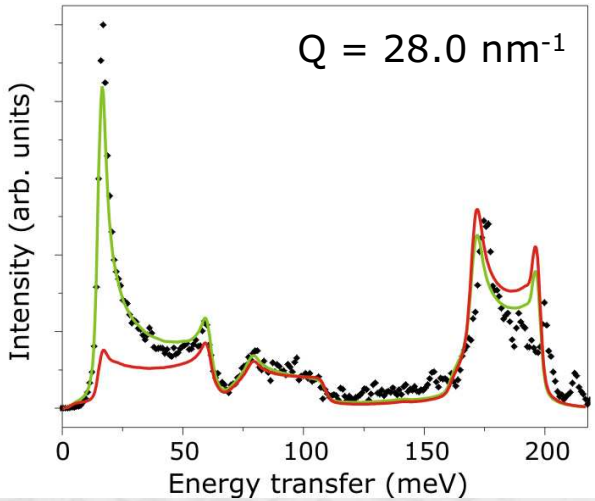


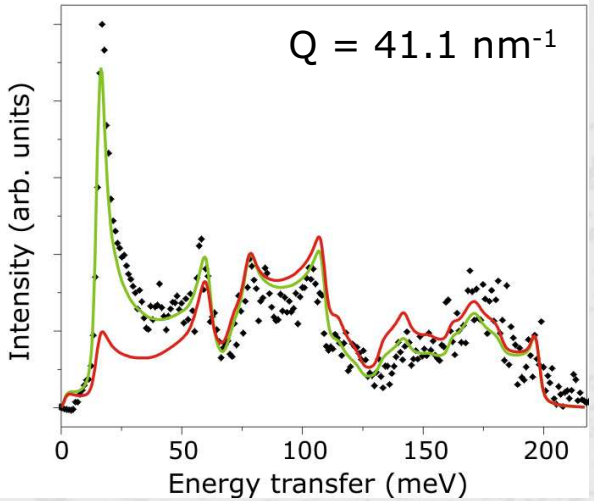


Graphite: texture effect







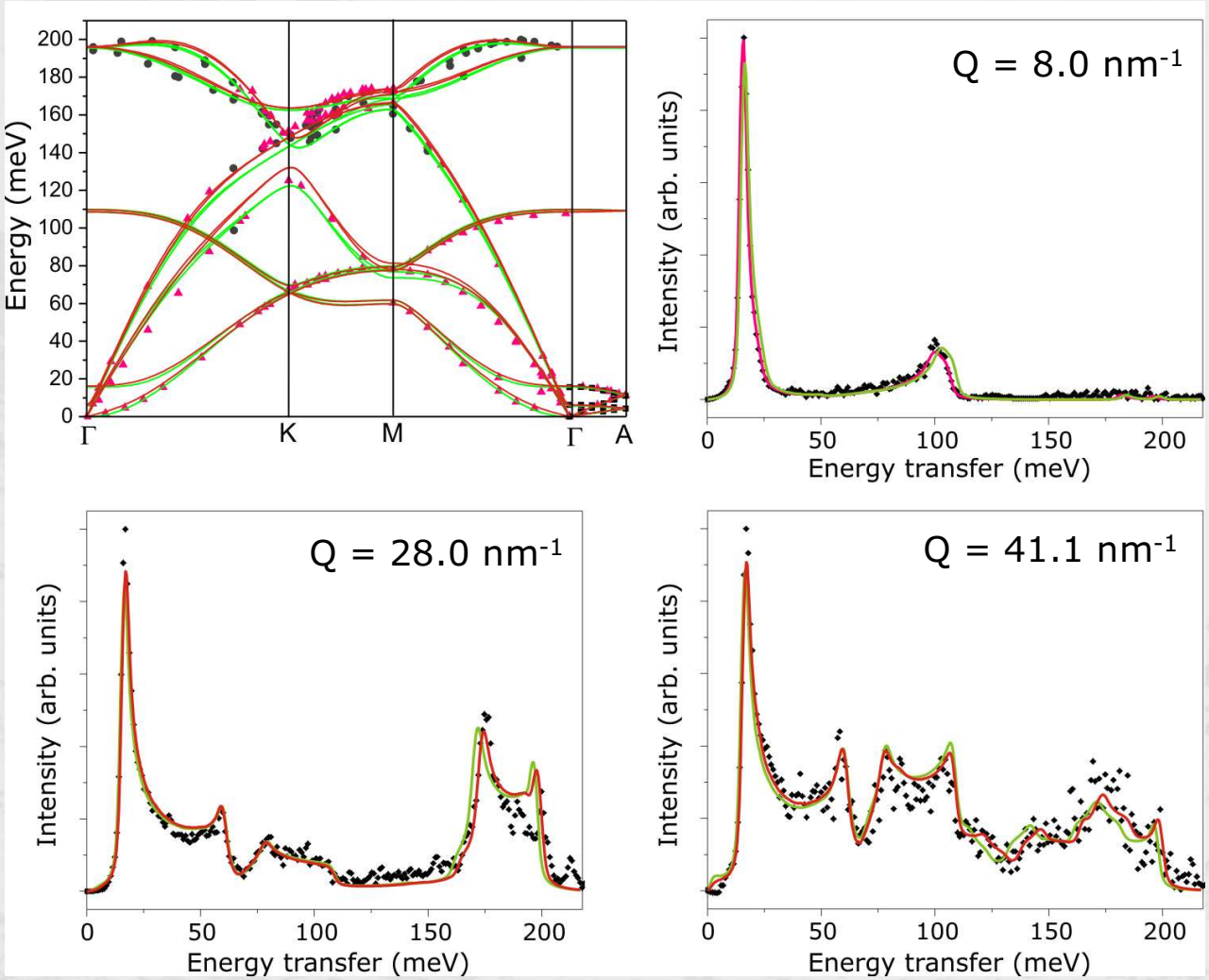


textured
non-textured

kernel: OpenPhonon

collaboration with Alessandro MIRONE

Graphite: model refinement



Born-von Kármán
6 interaction shells
17 refinable parameters

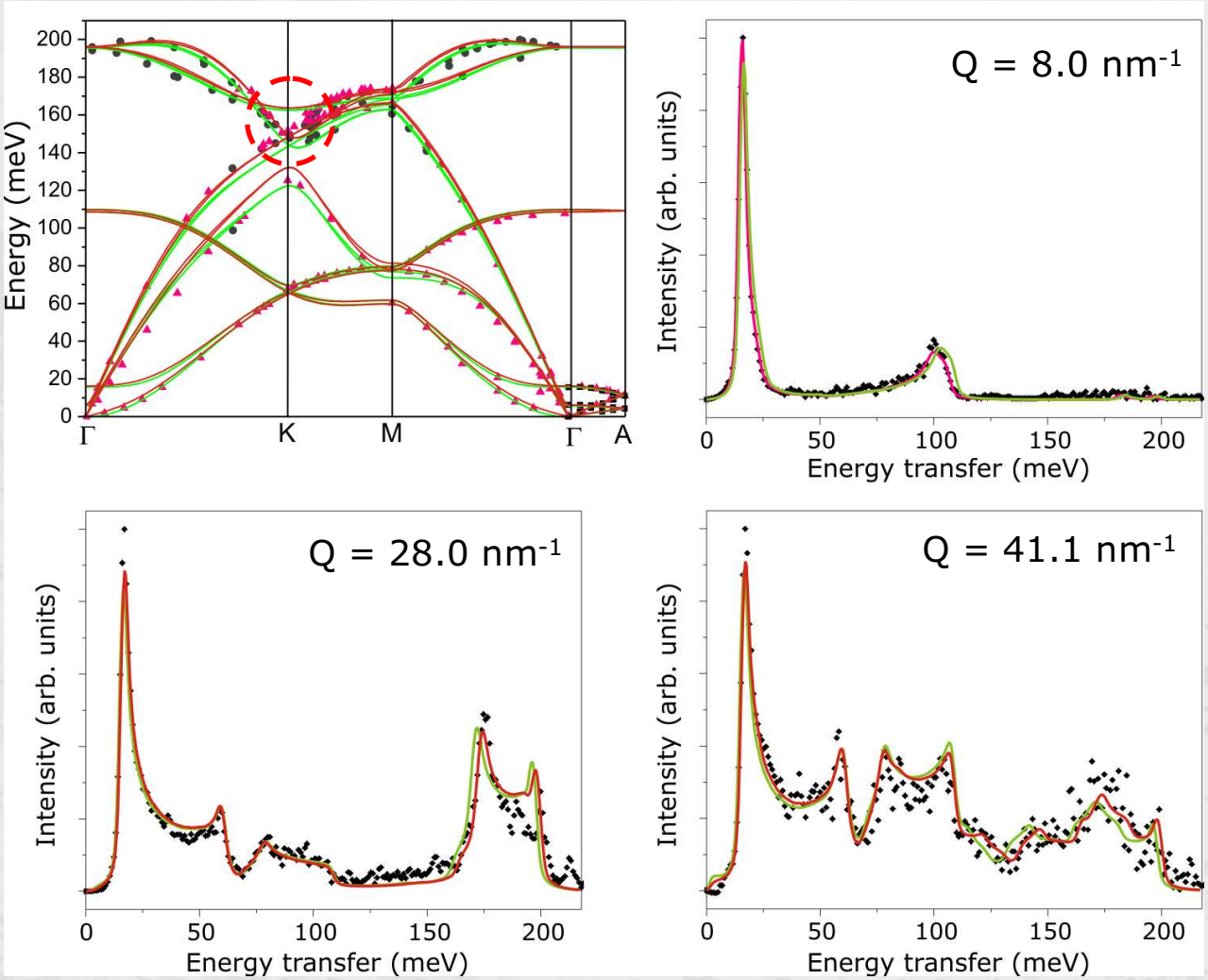
initial
refined

phonon dispersion (IXS):

*M. Mohr, J. Maultzsch, E. Dobardžić, S. Reich, I. Milošević, M. Damnjanović, A. Bosak, M. Krisch, C. Thomsen, Phys. Rev. B **76**, 035439 (2007)*

*J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, P. Ordejón, Phys. Rev. Lett. **92**, 075501 (2004)*

Graphite: model refinement



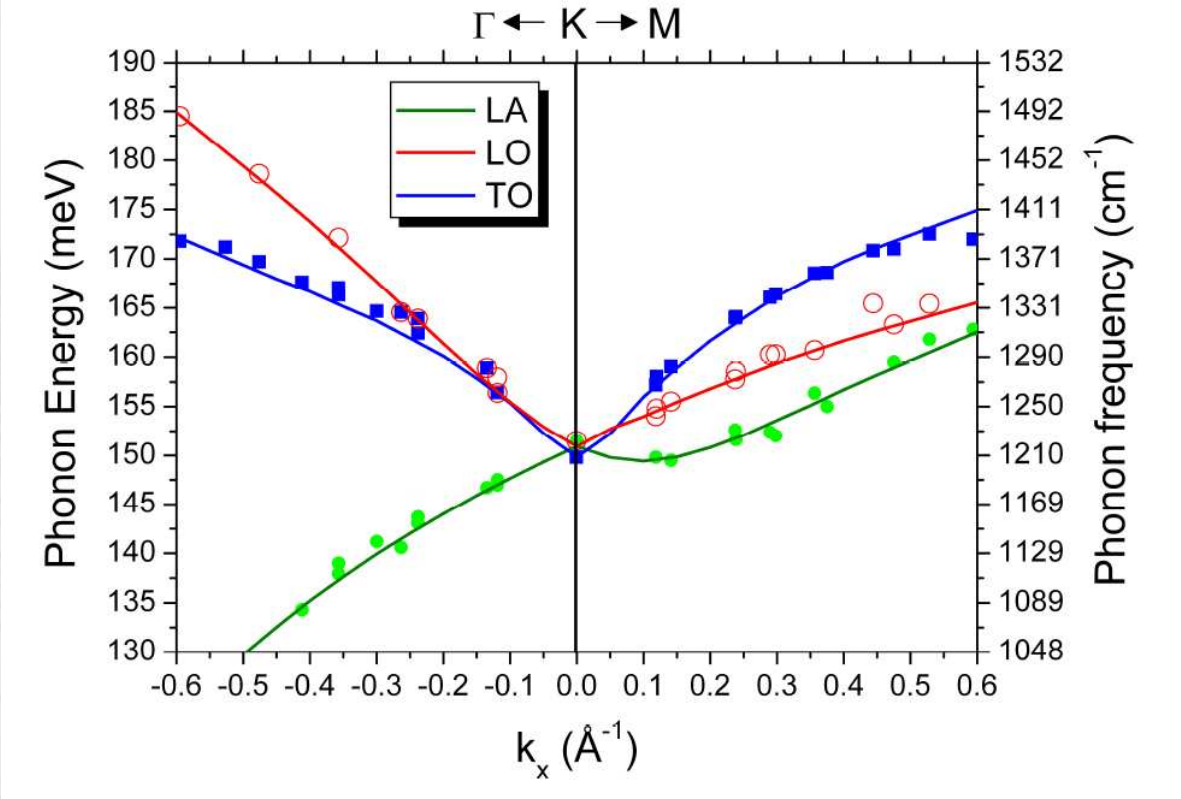
Born-von Kármán
6 interaction shells
17 refinable parameters

initial
refined

warning:
*some features cannot be repoduced by **any** BvK model*

(Kohn anomaly at K point!)

Graphite: reality



Direct observation of a Kohn anomaly in the phonon spectrum of graphene layers

A. Grueneis, J. Serrano, A. Bosak, M. Lazzeri, F. Mauri, A. Rubio, S.L. Molodtsov, L. Wirtz, M. Krisch, T. Pichler

submitted

warning:

*some features cannot be repoduced by **any** BvK model*

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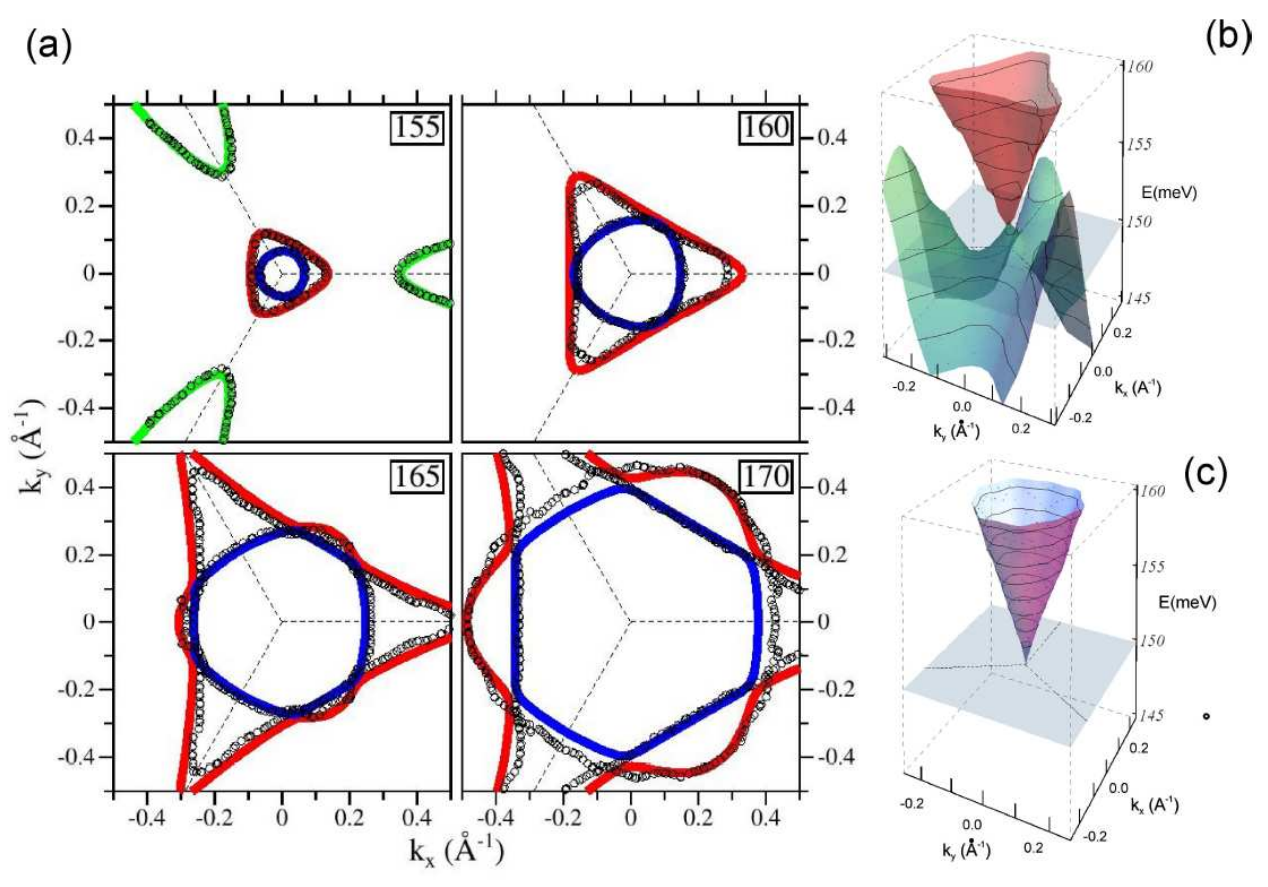
Graphite: reality



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warning:

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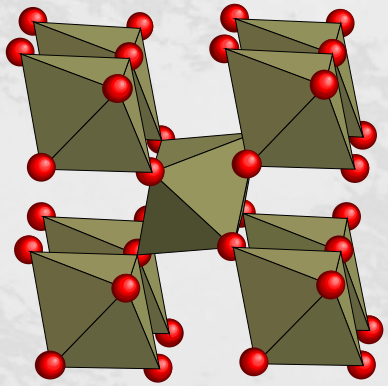
Stishovite

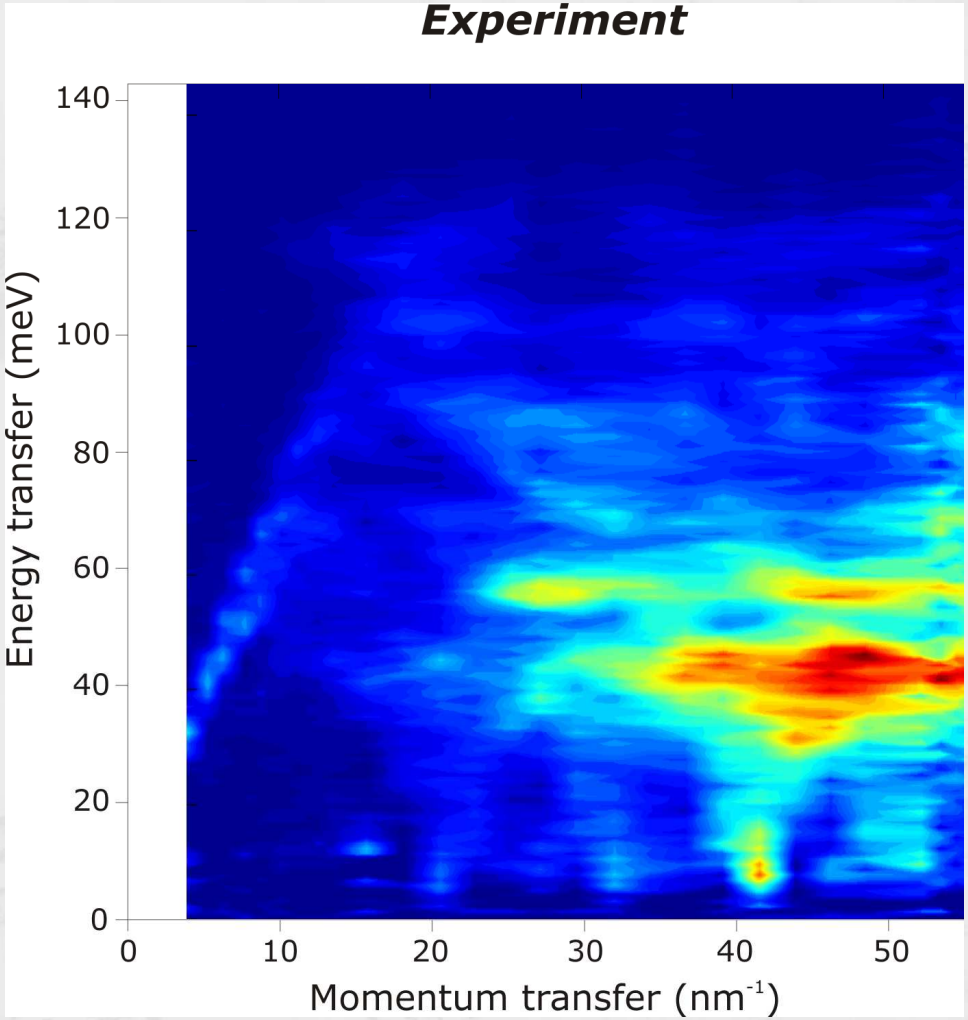


rutile structure
N = 6
18 phonon branches

Γ-point frequencies:

Raman + IR + BLS

Institute for High Pressure Physics
Troitsk, Russia
V. Braznikin, T. Dyuzheva



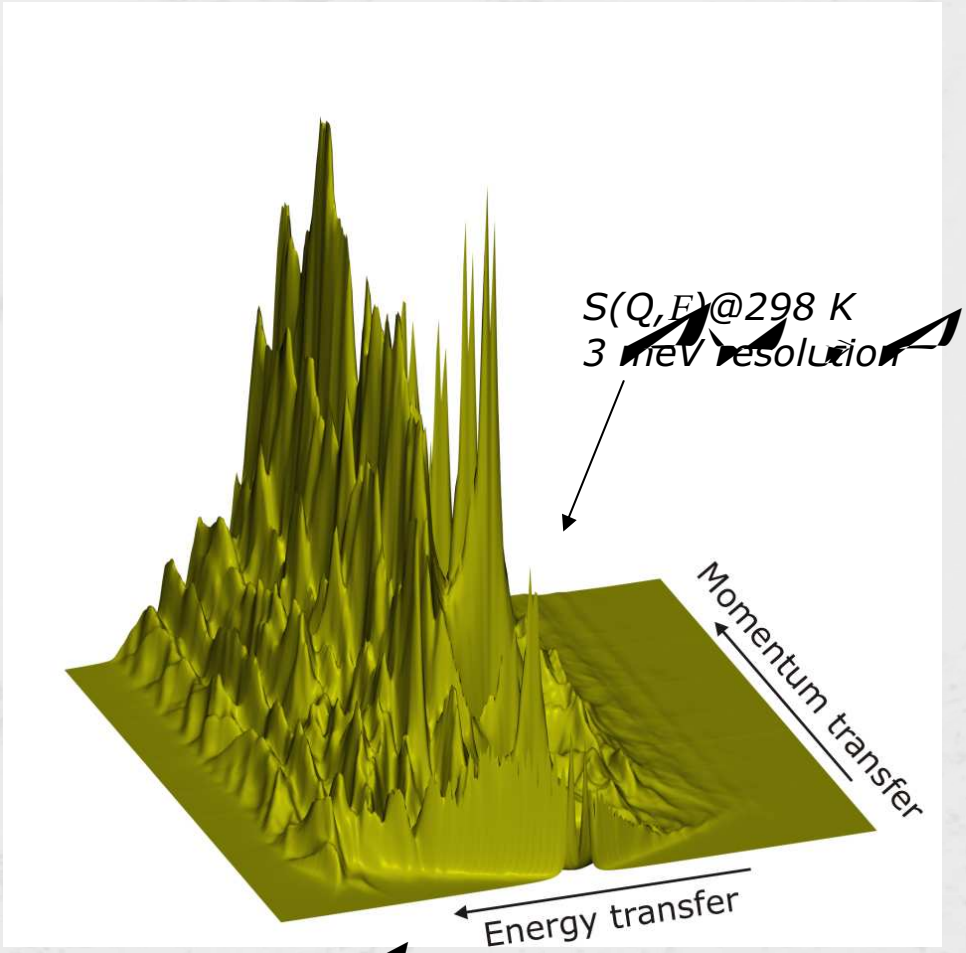
Stishovite: theoretical calculations

CASTEP[1] code

collaboration with
Bjoern WINKLER and Dan WILSON,
Institut für Geowissenschaften
Universität Frankfurt
DFT theory for phonons

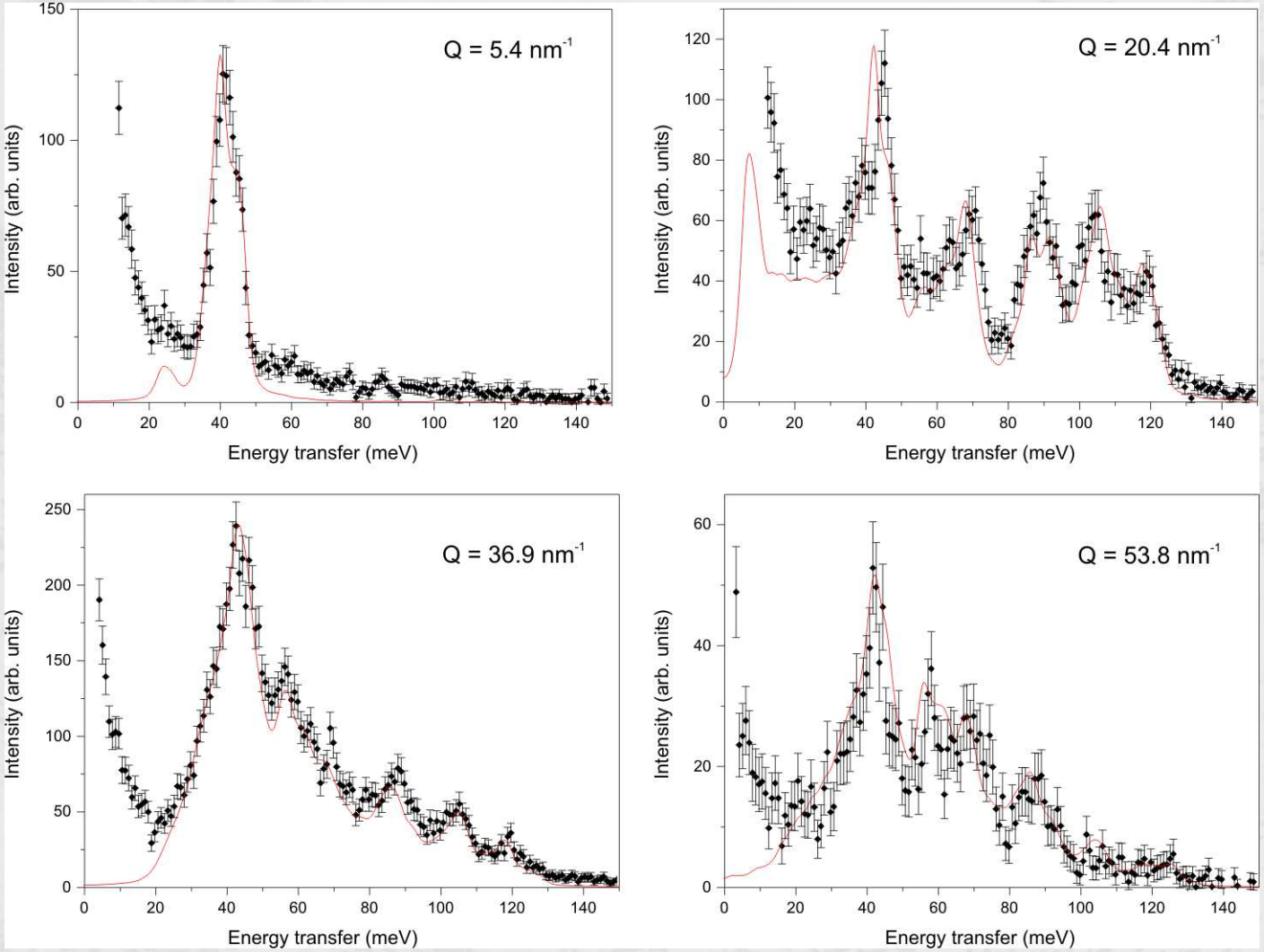
+

powder sampling code (C++)
compatible with CASTEP
and PHONON packages



[1]*S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne*
Zeitschrift für Kristallographie **220**, *567 (2005)*

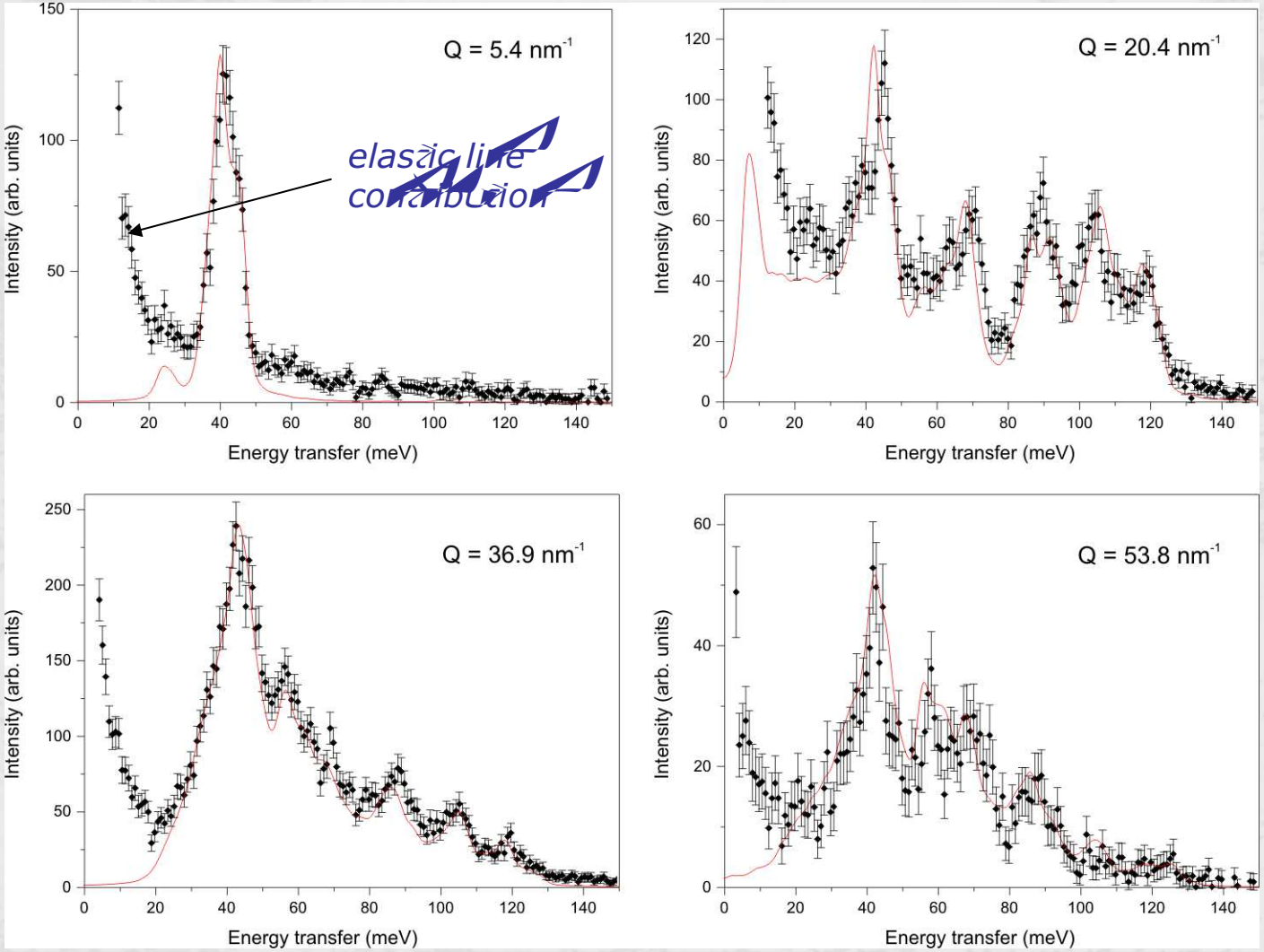
Stishovite powder: experiment *vs.* theory



*single scaling factor of **1.05** is introduced*

2 days of beamtime

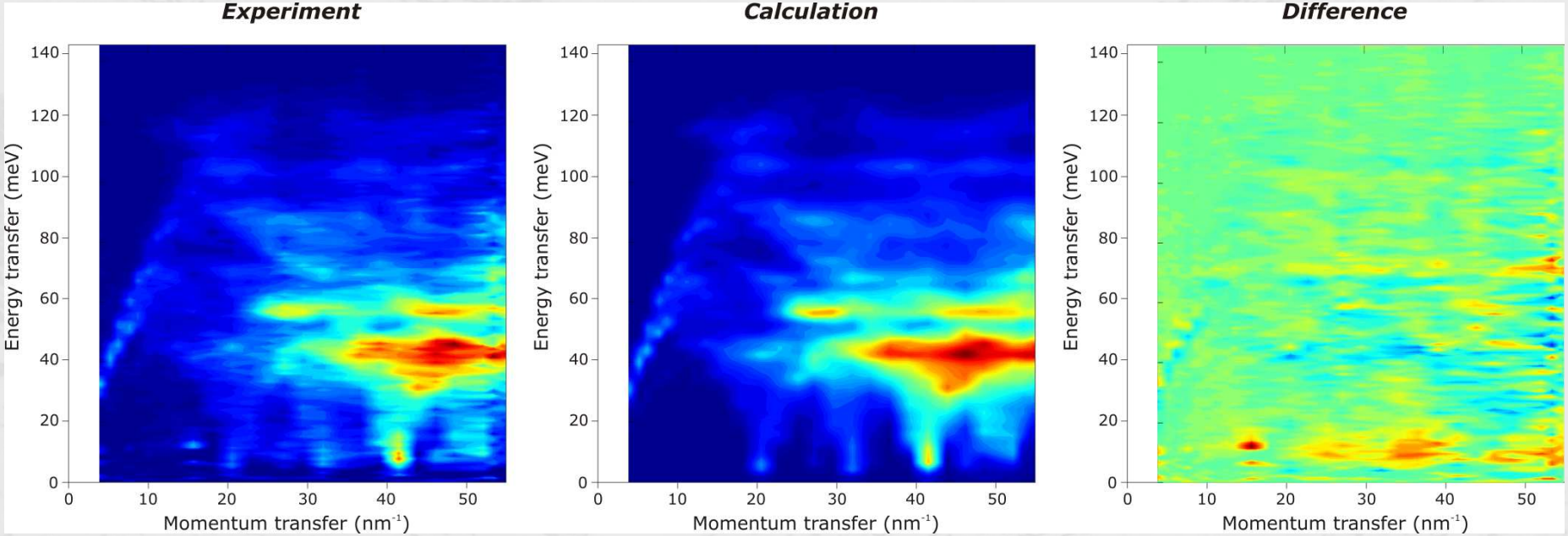
Stishovite powder: experiment *vs.* theory



*single scaling factor of **1.05** is introduced*

2 days of beamtime

Stishovite powder: experiment *vs.* theory



Cross-check?

Single crystal: pre-optimization

MODELLING

POINT OF MODEL DISPERSION

$N := 27$

RECIPRICAL LATTICE NODE

$\begin{pmatrix} h \\ k \\ l \end{pmatrix} := \begin{pmatrix} 0 \\ 2 \\ 0 \end{pmatrix}$

CUTOFF ENERGY

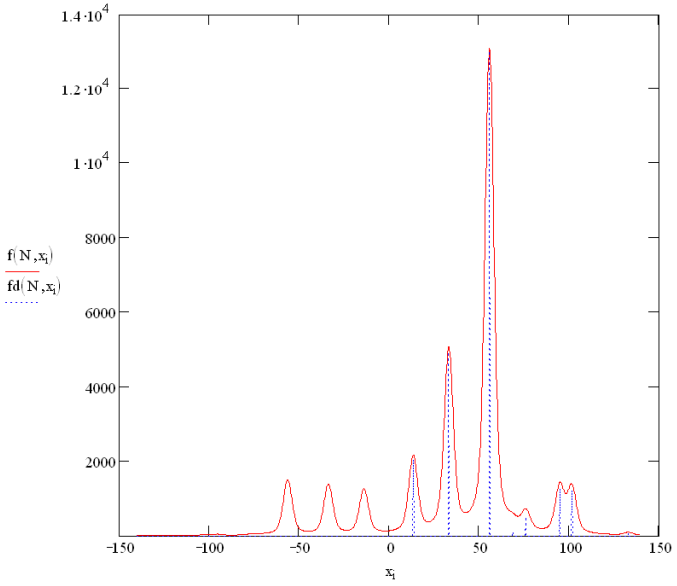
$Emax := 140$

MODE INTENSITY OPTIMIZATION $M := 15$

Reference:C:\Documents and Settings\Propriétaire\Mes documents\Stishovite_2008_07\casted_hidden.xmcd(R)

MODEL SPECTRUM FOR FOLLOWING POINT

$q = \begin{pmatrix} 0 \\ 0 \\ 0.114 \end{pmatrix}$ $Q = \begin{pmatrix} 0 \\ 2 \\ 0.114 \end{pmatrix}$



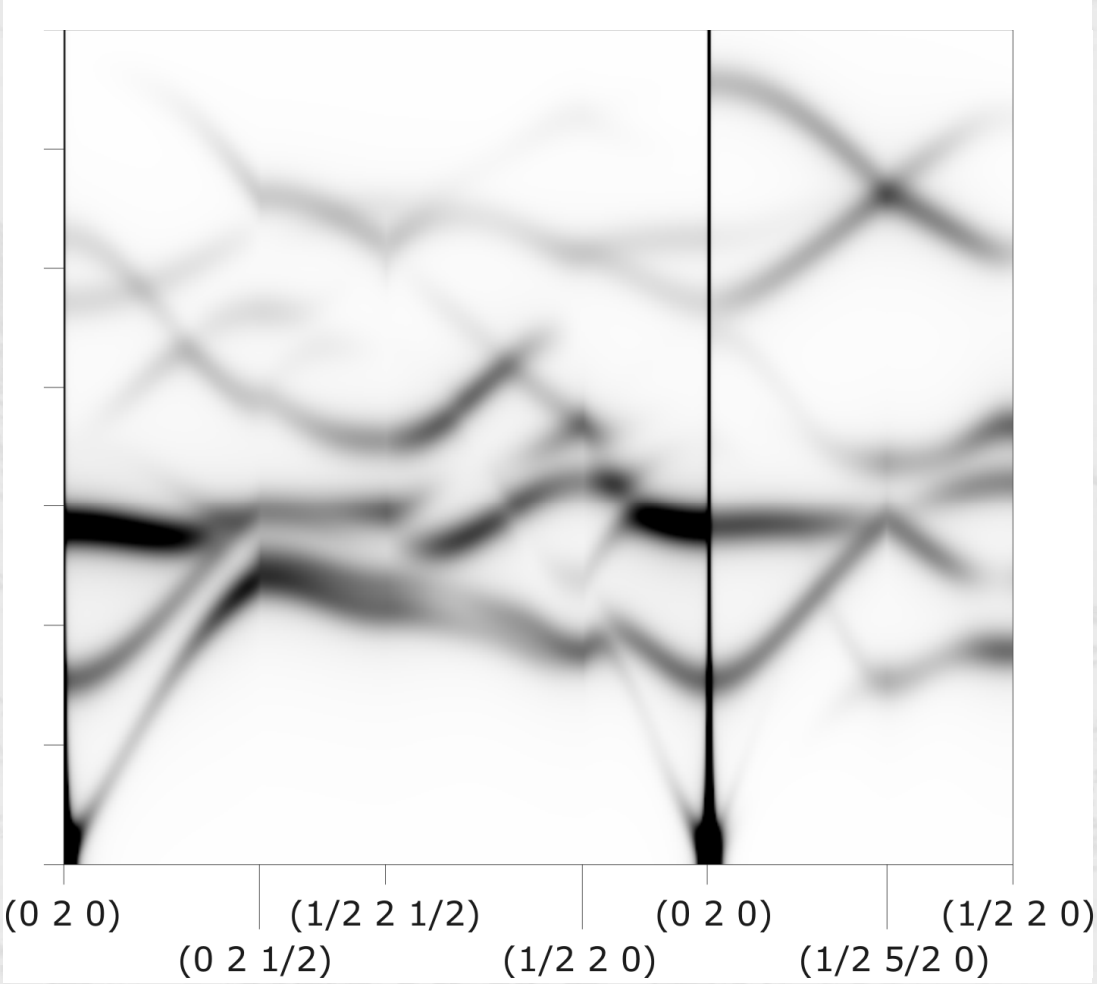
OUTPUT OF SPECTRUM filespec = "scanst_0_2_0p114407"

CASTEP input for the experiment planning

parameters to choose
- closest Bragg's reflection
- temperature
- experimental resolution

output: ASCII

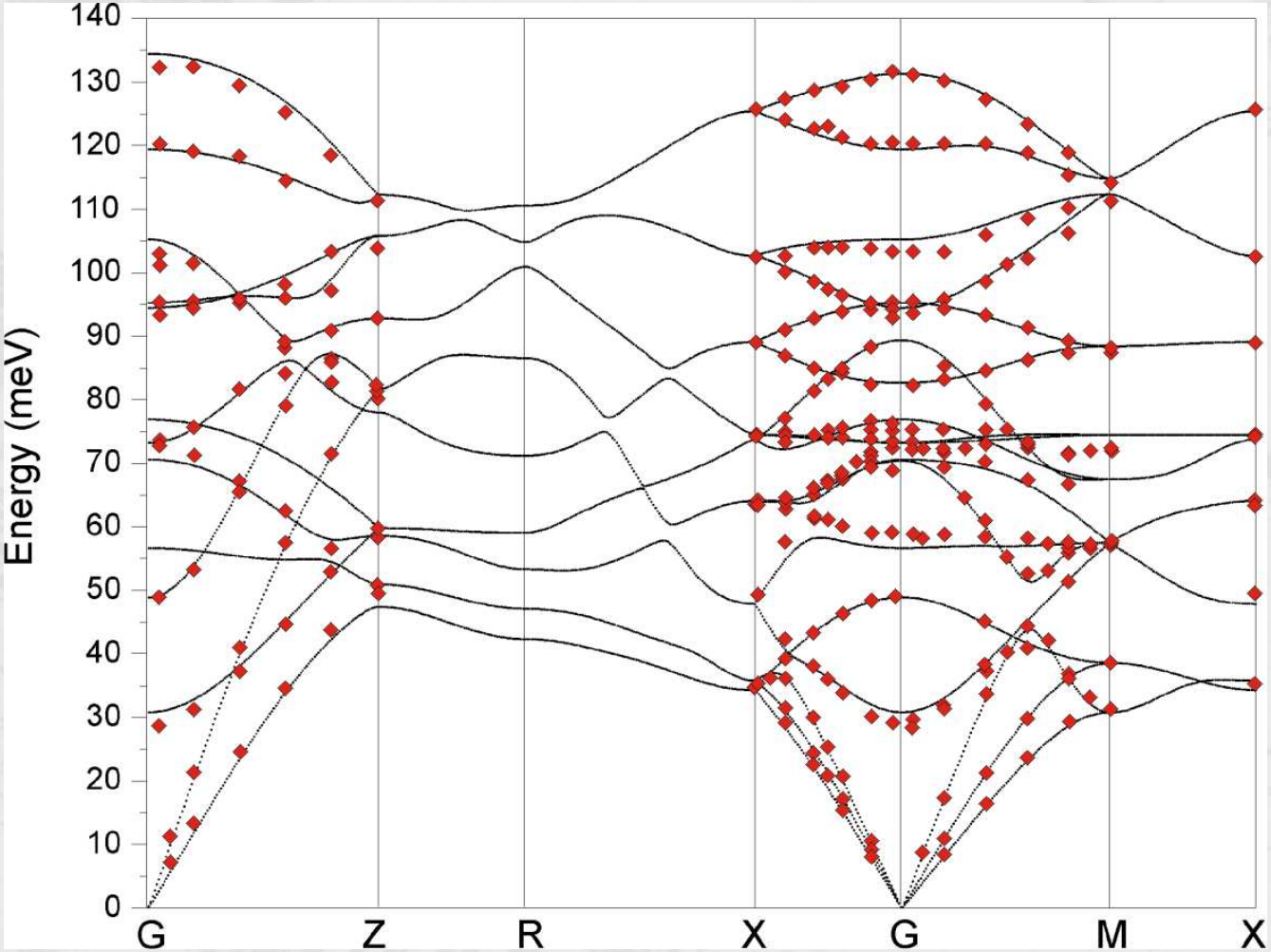
Single crystal: pre-optimization



- *intensity map calculation for given Brillouin zone*

output: BMP

Phonon dispersion: high-symmetry directions

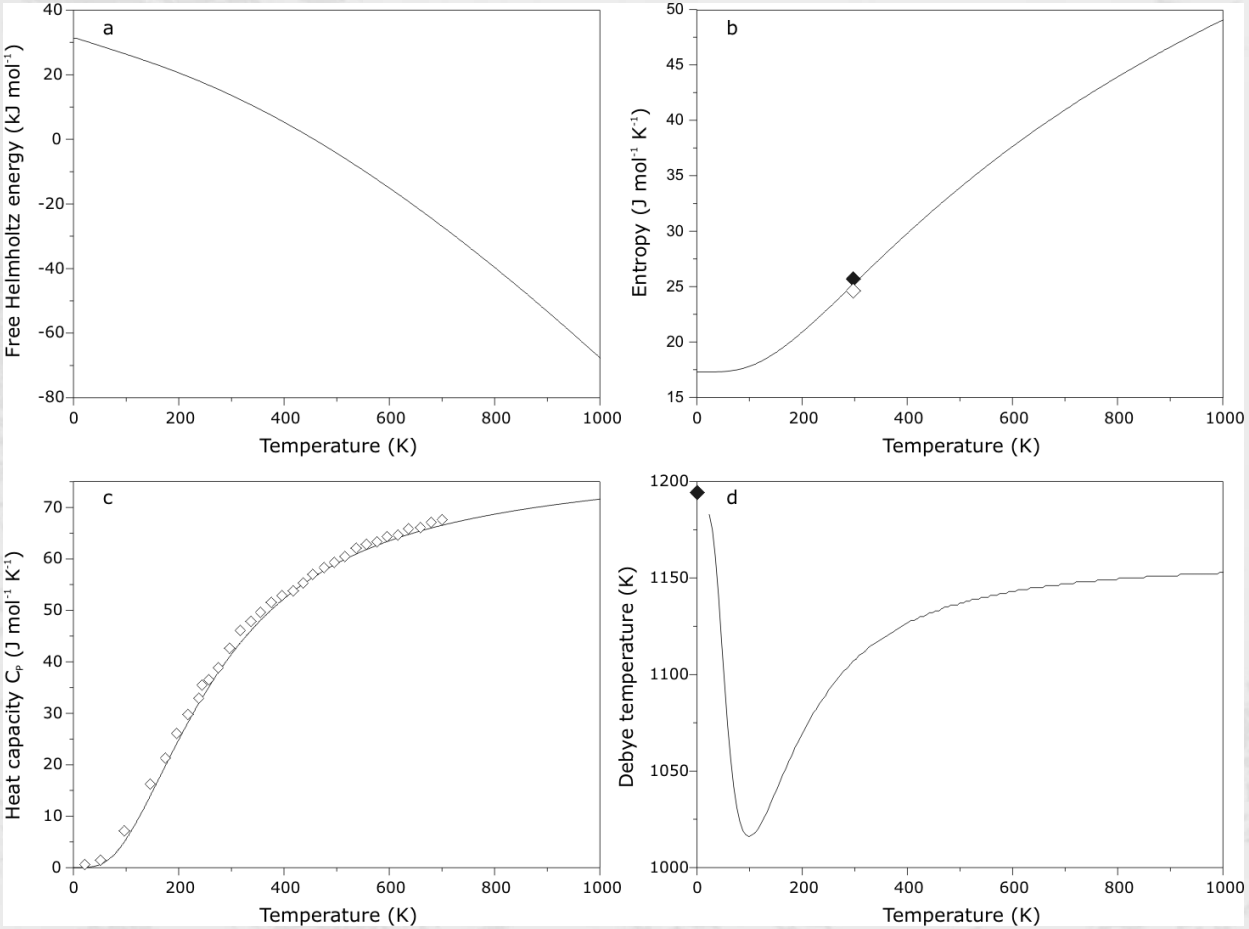


CASTEP input for the experiment planning

the same scaling factor of **1.05** is applied

6 days of beamtime

All we can derive…



Clark, S.P. Jr. (1966), Ed., Handbook of Physical Constants, Geol. Soc. Am. Mem 97, New York, USA.

Akaogi, M., E. Yusa, K. Shiraishi, and T. Suzuki (1995), J. Geophys. Res., 100, 22337-22347.

Holm, J.L., O.L. Kleppa, and E.F. Westrum (1967) Geochim. Cosmochim. Acta, 31, 2289-2307.

Saxena, S.K. (1996) Geochim. Cosmochim. Acta, 60, 2379-2395.

Jiang, F., G.D. Gwanmesia, T.I. Dyuzheva, and T.S. Duffy (2009), Physics of the Earth and Planetary Interiors, 172, 235-240.

All we can derive…

Ref.	C_{11}	C_{33}	C_{12}	C_{13}	C_{44}	C_{66}	B	V_D
Weidner et al., 1982	453(4)	776(5)	211(5)	203(4)	252(2)	302(3)	318	7.84
Brazhkin et al., 2005	466(4)	775(4)	207(8)	204(4)	258(2)	310(6)	321	7.97
Jiang et al., 2009	455(1)	762(2)	199(2)	192(2)	258(1)	321(1)	310	7.97
this work	449	776	165	207	255	341	306	8.03

Jiang, F., G.D. Gwanmesia, T.I. Dyuzheva, and T.S. Duffy (2009), Physics of the Earth and Planetary Interiors, 172, 235-240.

Weidner, D.J., J.D. Bass, A.E. Ringwood, and W. Sinclair (1982), J. Geophys. Res., 87, 4740-4746.

Brazhkin, V., L. McNeil, M. Grimsditch, N. Bendeliani, T. Dyuzheva, and L. Livagina (2005), J. Phys.: Condens. Matter, 17, 1869-1875.

Poly-IXS + *ab initio*: applicability of approach

- moderately complex structure
- distinct inelastic features in the polycrystalline spectra
- similar scattering factors of constituents
- well characterized texture

Fine tuning of model?

- *ab initio* calculation
  - simple parameterization mimicking the *ab initio* model
    - tuning of adjustable parameters

Projects of immediate interest

- geophysically relevant minerals

  $(Mg,Fe)_2SiO_4$: olivine, ringwoodite and wadsleyite

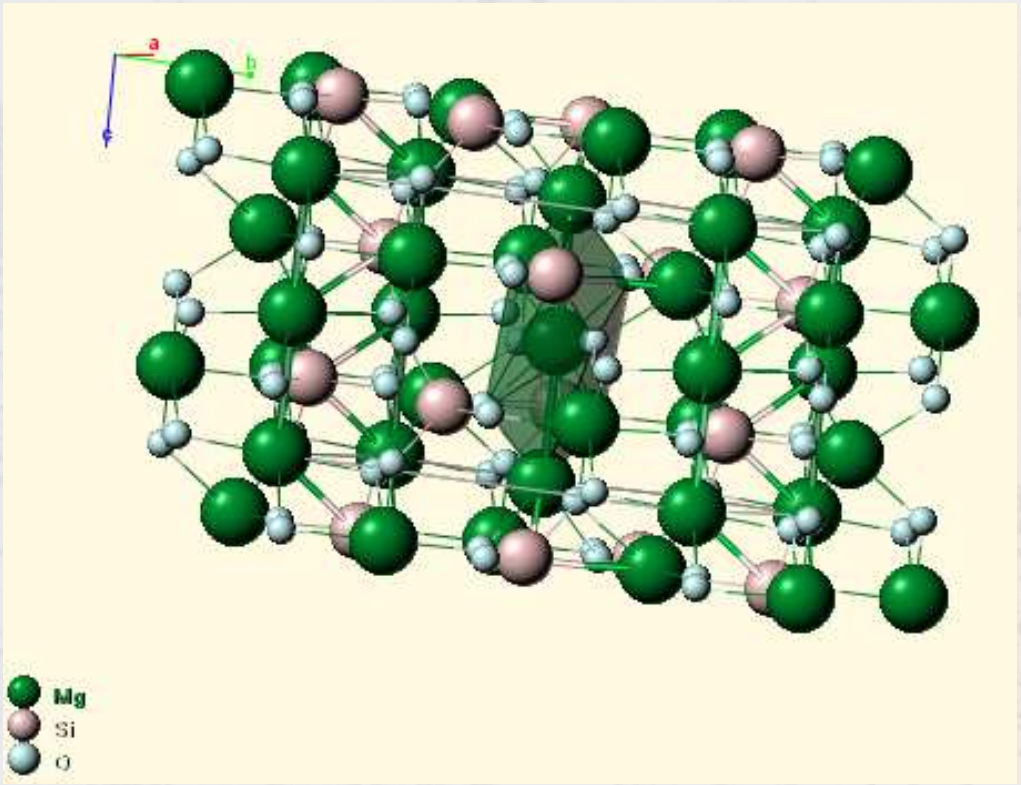
  $(Mg,Fe)SiO_3$: perovskite and postperovskite

- materials under extreme conditions

  hcp iron

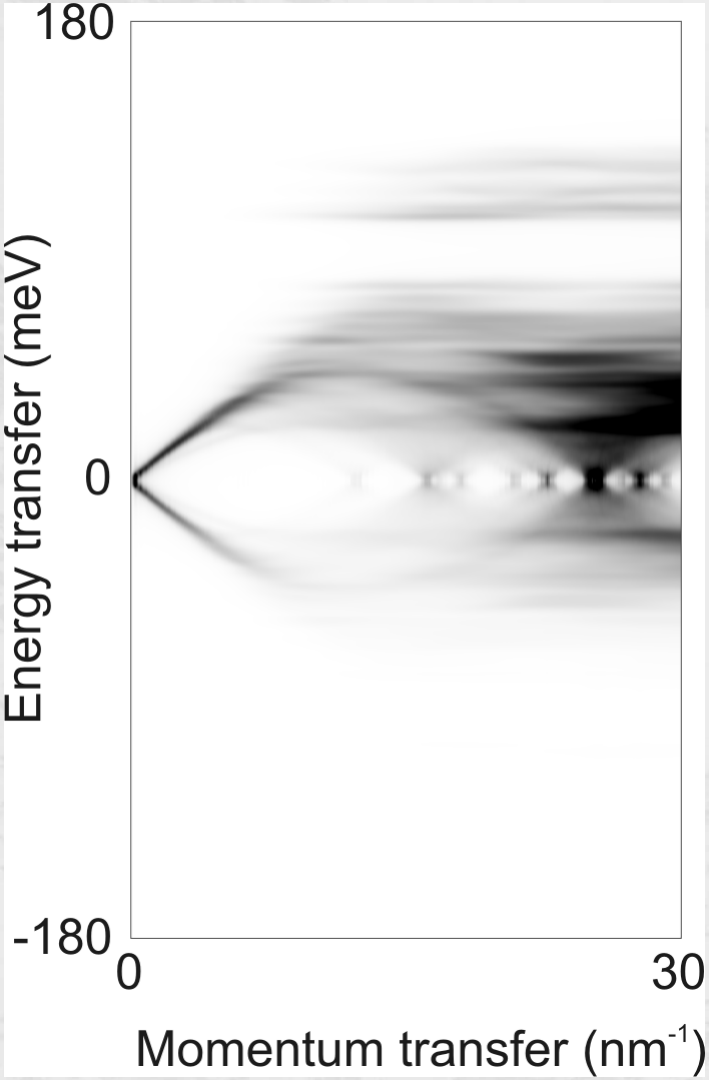
Forsterite Mg_2SiO_4

28 atoms => 84 phonon branches



Earth model are discontinuities in seismic waves velocities at 410, 520, and 660 km that are thought to be caused by the ***olivine–wadsleyite–ringwoodite–perovskite*** *phase transitions*

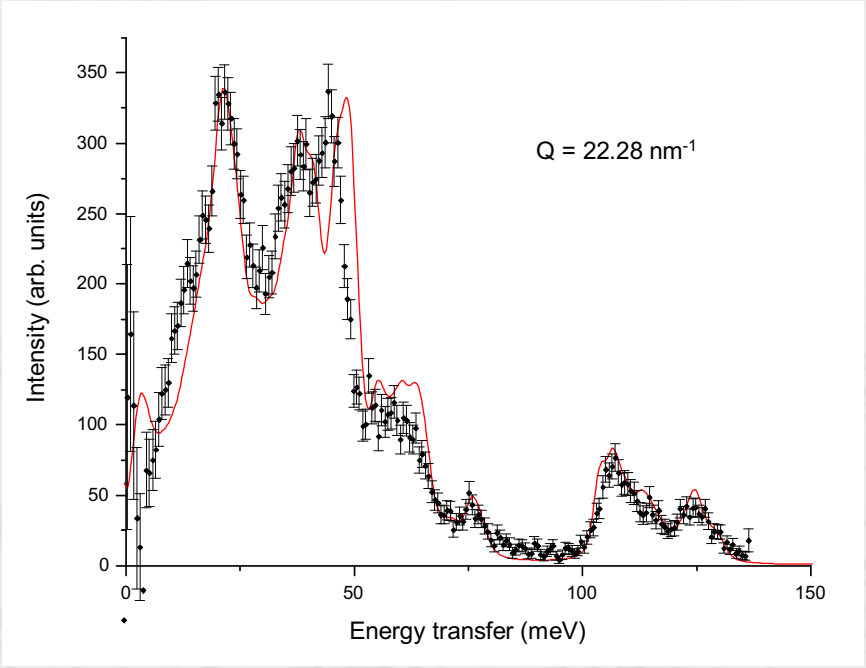
Forsterite Mg_2SiO_4



Map derived from CASTEP results

Institut für Geowissenschaften, Universität Frankfurt, Germany, B. Winkler, D. Wilson

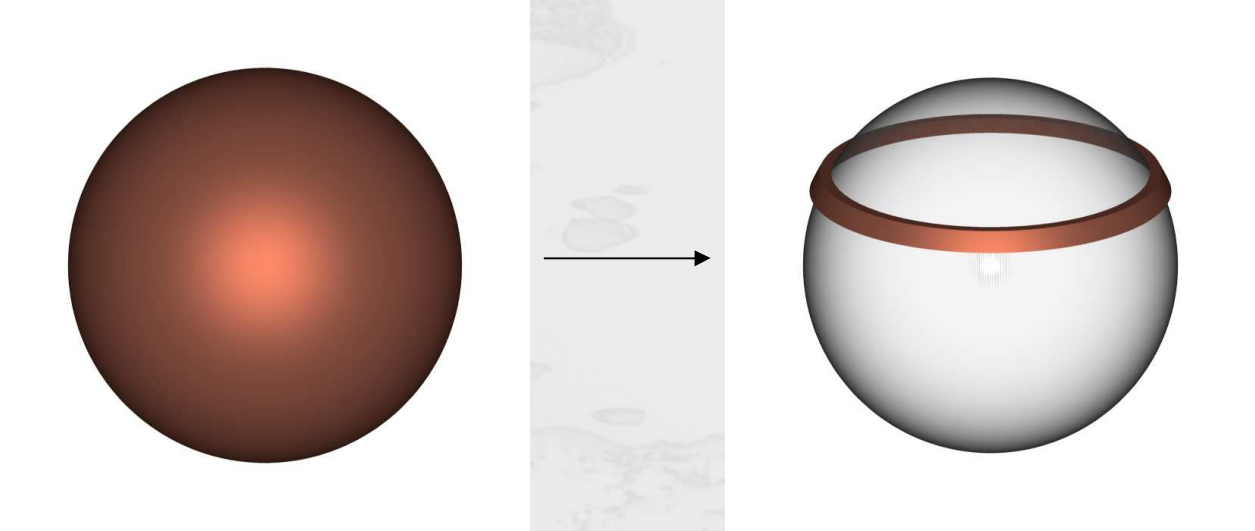
Data acquisition in progress...



Half-way back to the single crystals?

- sharp axial texture
- spinning single crystal

integration over sphere collapses to the integration over "belts"

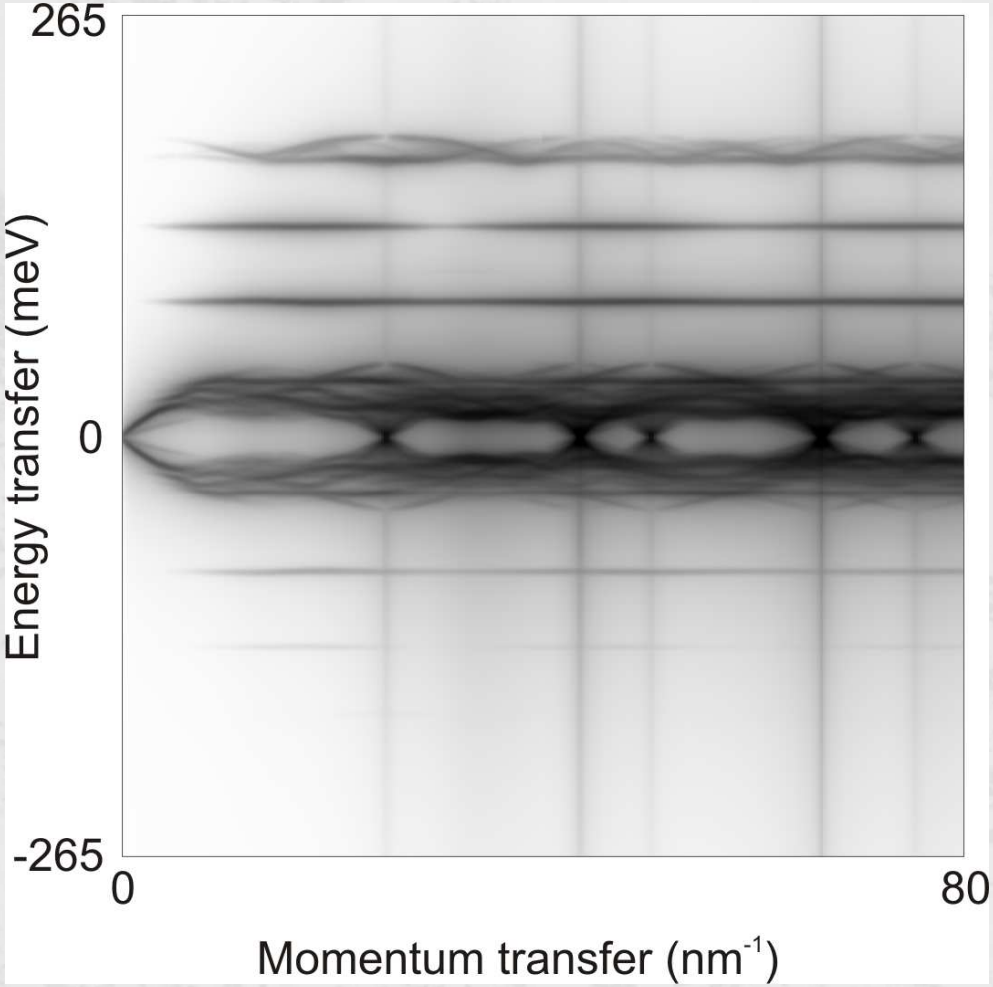


- smaller integration region
- less features in the individual spectrum

} more complex structures can be treated?

Case study: calcite

spinning about three-fold axis



map derived from CASTEP results:

Institut für Geowissenschaften,
Universität Frankfurt, Germany
B. Winkler, D. Wilson

data treatment in progress

To be continued…