harmonic lattice vibrations and anharmonicity signatures

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OUTLINE

- Harmonic approximation for nuclear motion of a molecular system
- Quantum and classical description in term of normal mode
- Periodic crystal Bloch representation, quasi-momentum and phonon dispersion
- Measuring phonon with inelastic scattering (X-ray, neutron, electrons)
- Weak failures of the harmonic approximation
- Strong failures of the harmonic approximation

BORN-OPPENHEIMER (BO) APPROXIMATION

HAMILTONIAN FOR NUCLEAR MOTION

$$H = \sum_{I=1}^{N_N} \frac{1}{2}\frac{\vec{P}_I^{\,2}}{M_I} + V(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N_N})$$

(N_N: # OF NUCLEI; M_I: NUCLEAR MASSES; $\{\vec{R}_I\}_{I=1,\dots N_N}$: NUCLEAR POSITIONS)

$V(\{\vec{R}_I\})$ = BO POTENTIAL OF THE GROUND STATE ELECTRONIC HAMILTONIAN

$\vec{P}_I = -\hbar \vec{\nabla}_{\vec{R}_I}$ = MOMENTUM OF NUCLEUM I

QUANTUM EIGENSTATES OF THE SYSTEM $\{\varepsilon_i\}$ FROM $H|\chi_i\rangle = \varepsilon_i|\chi_i\rangle$ $\quad |\chi_i\rangle \in$ N_N NUCLEI HILBERT SPACE

IF $K_b T \lesssim$ OR $\sim (\varepsilon_{i+1} - \varepsilon_i) \Rightarrow$ QUANTUM MECHANICS IS NEEDED

IF $K_b T \gg (\varepsilon_{i+2} - \varepsilon_i) \sim 10/100$ meV $\Rightarrow$ WE CAN USE CLASSICAL MECHANICS

NEWTON EQUATION

$$M_{I'} \ddot{\vec{R}}_{I'} = -\vec{F}_{I'} = -\frac{\partial V(\{\vec{R}_I\})}{\partial \vec{R}_{I'}}$$

HARMONIC APPROXIMATION FOR THE BO POTENTIAL

- IF THE FLUCTUATIONS (QUANTUM OR THERMAL) OF THE NUCLEI AROUND THE CLASSICAL EQUILIBRIUM POSTIONS $\{\vec{R}_I^{eq}\}$ [NAMELY AROUND THE MIMIMUM OF THE $V(\{\vec{R}_I\})$] ARE SMALL COMPARED TO THE INTERNUCLEAR DISTANCE AT EQUILIBRIUM

WE CAN TAYLOR-EXPAND $V(\{\vec{R}_I\})$ AROUND $\{\vec{R}_I^{eq}\}$ $\quad \vec{u}_I \overset{def}{=} \vec{R}_I - \vec{R}_I^{eq}$

$$V(\{\vec{R}_I\}) = \underbrace{V(\{\vec{R}_I^{eq}\})}_{E^{eq}} + \sum_I \underbrace{\frac{dV(\{\vec{R}_I^{eq}\})}{d\vec{R}_I}}_{=0 \text{ FOR THE EQUILIBRIUM CONDITION}} \cdot \vec{u}_I + \sum_{II'} \vec{u}_I \cdot \underbrace{\frac{\partial^2 V(\{\vec{R}_I^{eq}\})}{\partial \vec{R}_I \partial \vec{R}_{I'}}}_{\overset{def}{\Leftrightarrow} \overleftrightarrow{K}_{II'}} \cdot \vec{u}_{I'} + \underbrace{O(u^3)}_{\text{SMALL (NEGLIGIBLE)}}$$

SCALAR PRODUCT

HARMONIC APPROXIMATION

$$\boxed{V(\{\vec{R}_I\}) \simeq E^{eq} + \frac{1}{2} \sum_{II'} \vec{u}_I \cdot \overleftrightarrow{K}_{II'} \cdot \vec{u}_{I'}}$$

FAILURE (OF THE TAYLOR EXPANSION) AND OF THE HARMONIC APPROXIMATION

WHEN THE NUCLEAR FLUCTUATIONS ARE LARGE (WITH RESPECT TO THE INTER NUCLEAR DISTANCE)

- IN A DIFFUSIVE STATE: E.G. IN THE LIQUID CASE OR WITH ATOMS THAT DIFFUSE (NAMELY FOR $T > T_{MELTING}$)

- IN PRESENCE OF STRONG ZERO-POINT QUANTUM FLUCTUATIONS: E.G. IN PRESENCE OF H (SMALL $M_I \rightarrow$ LARGE QUANTUM FLUCTUATIONS)

- WHEN THE EXPERIMENTAL AVERAGE POSITIONS $\{\vec{R}_I^{exp}\}$ ARE DIFFERENT FROM THE CLASSICAL MINIMUM $\{\vec{R}_I^{eq}\}$: E.G. IN THE HIGH TEMPERATURE FASE (HIGH SYMMETRY PHASE) OF A MATERIAL EXHIBITING A SYMMETRY BROKEN LOW-T PHASE:
  - FERROELECTRIC MATERIALS
  - CHARGE-DENSITY-WAVE MATERIALS
  - ...

IN THESE CASES $\{\vec{R}_I^{exp}\}$ COULD BE NOT A MINIMUM BUT A SADDLE POINT OF $V(\{\vec{R}_I\})$

SOLUTION OF THE HARMONIC HAMILTONIAN

IN THE CLASSICAL APPROXIMATION

$$M_I \ddot{\vec{u}}_I = -\sum_{I'} \overleftrightarrow{K}_{II'} \cdot \vec{u}_{I'}$$

AUXILIARY VARIABLE

$$\vec{V}_I \overset{def}{=} \sqrt{M_I}\,\vec{u}_I$$

AUXILIARY MATRIX

$$\overleftrightarrow{C}_{II'} \overset{def}{=} \frac{1}{\sqrt{M_I}} \overleftrightarrow{K}_{II'} \frac{1}{\sqrt{M_{I'}}}$$

$$\ddot{\vec{V}}_I = -\sum_{I'} \overleftrightarrow{C}_{II'} \cdot \vec{V}_I$$

NORMAL MODES OBTAINED FROM DIAGONALISATION OF $\overleftrightarrow{C}_{II'}$

$$\sum_{I'} \overleftrightarrow{C}_{II'} \cdot \vec{e}^{\,\nu}_{I'} = (\omega^\nu)^2 \vec{e}^{\,\nu}_I$$

ω^ν VIBRATIONAL PULSATION

$\{\vec{e}^{\,\nu}_I\}$ VIBRATIONAL POLARISATION

$$\sum_I^{N_N} \vec{e}^{\,\nu}_I \cdot \vec{e}^{\,\nu'}_I = \delta_{\nu,\nu'}$$

ORTHONORMAL VECTORS IN THE $3N_N$ SPACE

$$\sum_\nu^{3N_N} e^{\nu}_{I\alpha} e^{\nu}_{I'\alpha'} = \delta_{II'}\delta_{\alpha\alpha'}$$

$\alpha, \alpha' = x, y, z$

NORMAL MODE COORDINATE

$$q_\nu \overset{def}{=} \sum_I \vec{e}^{\,\nu}_I \cdot \vec{V}_I$$

DECOUPLED EQUATION OF MOTION

$$\ddot{q}_\nu = -(\omega^\nu)^2 q_\nu$$

SOLUTION

$$q_\nu(t) = q_\nu(t_0) \cos\left[\omega^\nu (t - t_0) + \varphi_0^\nu\right]$$

SOLUTION OF THE QUANTUM HAMILTONIAN

VIBRATION ANNIHILATION OPERATOR

(I) $$a_r \overset{def}{=} \sum_I \vec{e}_I^{\,r} \cdot \left[\frac{i}{\sqrt{2\hbar\omega^r}} \frac{\vec{P}_I}{\sqrt{M_I}} + \sqrt{\frac{\omega^r}{2\hbar}}\, \vec{u}_I \sqrt{M_I} \right]$$

VIBRATION CREATION OPERATOR

$$a_r^+ = (a_r)^+ \qquad [a_r, a_{r'}^+] = \delta_{r,r'} \qquad [a_r, a_{r'}] = 0 \qquad [a_r^+, a_{r'}^+] = 0$$

$$\sum_r \frac{e^r_{I'\alpha'}}{\sqrt{\omega^r}} (a_r + a_r^+) = \frac{2}{\sqrt{2\hbar}}\, u_{I'\alpha'} \sqrt{M_{I'}}$$

$\sum_r e^r_{I\alpha'} e^r_{I\alpha} = \delta_{II'}\delta_{\alpha\alpha'}$

(II) $$\vec{u}_I = \sum_r \sqrt{\frac{\hbar}{2\omega^r M_I}}\, \vec{e}_I^{\,r} (a_r + a_r^+)$$

ONE OSCILLATOR

$a|0\rangle = 0$

$a^+|0\rangle = |1\rangle$

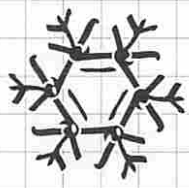
$n = 0, 1, \ldots$ $\quad a^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$

$a|n\rangle = \sqrt{n}\,|n-1\rangle$

$a^+ a|n\rangle = n|n\rangle$

(III) $$H = \sum_r \hbar\omega_r \left(a_r^+ a_r + \frac{1}{2} \right) + E_0$$

$$H|\{n_r\}\rangle = \left\{ \left[\sum_r \hbar\omega_r \left(n_r + \frac{1}{2} \right) \right] + E_0 \right\} |\{n_r\}\rangle$$



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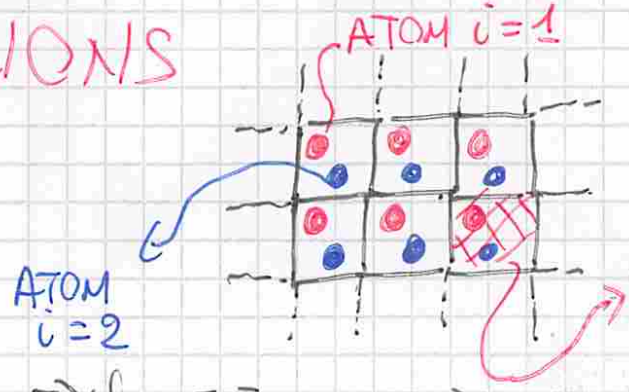
HARMONIC VIBRATIONS IN PERIODIC SOLIDS
PHONONS



I = ATOM IN AN INFINITE SOLID $= i, \vec{R}$

$$\vec{R}_I = \vec{R}_{i\vec{R}} = \vec{R} + \vec{r}_i$$

$\vec{R}$ → WHICH UNIT CELL

$\vec{r}_i$ → POSITION OF ATOM i IN THE UNIT CELL

$i = 1, 2, \dots, N_{AT}$

$\vec{R} \overset{def}{=}$ DIRECT LATTICE VECTORS $= n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

n_1, n_2, n_3 = SIGNED INTEGERS

$\{\vec{R}\} \overset{def}{=}$ SET OF LATTICE VECTOR

MATRIX WHOSE EIGENVALUES ARE $(\omega r)^2$

INVARIANCE UPON TRANSLATION BY $\{\vec{R}\}$

$$C_{I\alpha, I'\alpha'} = C_{i\alpha\vec{R}, i'\alpha'\vec{R}'} = C_{i\alpha(\vec{R}-\vec{R}'), i'\alpha'\vec{0}} \overset{def}{=} C_{i\alpha, i'\alpha'}(\vec{R}-\vec{R}'), \quad (\vec{R}-\vec{R}') \in \{\vec{R}\}$$

$I\alpha, I'\alpha'$ → x, y, z

$\Downarrow$

ALL INFORMATION CONTAINED IN $C_{i\alpha, i'\alpha'}(\vec{R})$

PHONONS

$$\tilde{C}_{i\alpha,i\alpha'}(\vec{q}) \overset{\text{def}}{=} \sum_{\vec{R}}^{\{\vec{R}\}} e^{-i\vec{q}\cdot\vec{R}} C_{i\alpha,i\alpha'}(\vec{R}) \left[\underbrace{e^{-i\vec{q}\cdot(\vec{r}_{i'} - \vec{r}_i)}}_{\text{TWO POSSIBLE CONVENTIONS}} \right]$$

a) WITHOUT THIS TERM

b) WITH THIS TERM

$\Downarrow$

EIGEN-VALUES ARE THE SAME (PHONON DISPERSION) BUT NOT EIGENSTATES

$\vec{q}$ = QUASIMOMENTUM (BELONGING TO THE FIRST BRILLOUIN ZONE)

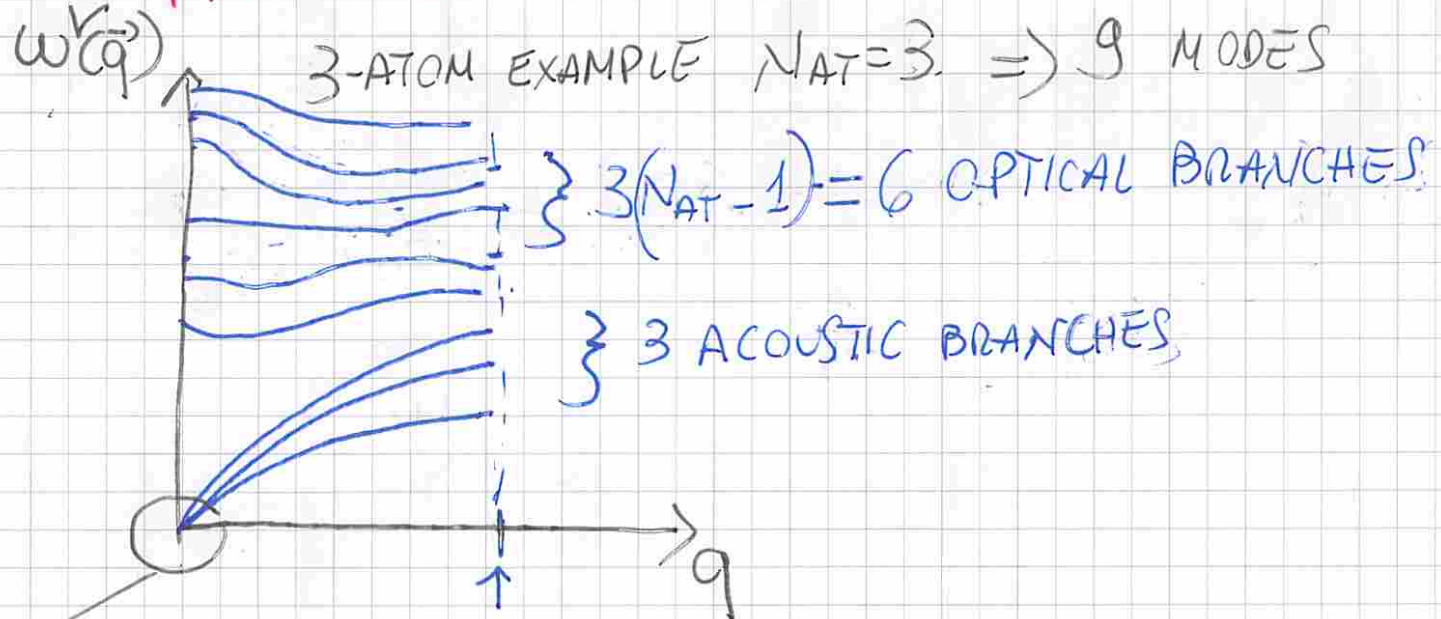
$C_{II'}$ IS BLOCK DIAGONAL IN THE $C_{i\alpha,i'\alpha'}(\vec{q})$ "BLOCH REPRESENTATION"

VIBRATIONAL EIGENVALUES CAN BE OBTAINED BY DIAGONALISING $\tilde{C}_{i\alpha,i'\alpha'}(\vec{q})$ INDEPENDENTLY FOR EACH $\vec{q}$

↳ A QUADRATIC MATRIX OF DIMENTION $3N_{AT} \times 3N_{AT}$

$\forall \vec{q}$ $3N_{AT}$ EIGENSTATES $[\omega^\nu(q)]^2$

PHONONS



↳ FOR THE 3 ACOUSTIC BRACHES

$$\lim_{|\vec{q}|\to 0} \omega^r(\vec{q}) = 0 \iff \text{THANKS TO ACOUSTIC SUM RULE}$$

$$\Updownarrow$$

$$\boxed{\sum_{\vec{R}} C_{i\alpha,i'\alpha'}(\vec{R}) = 0}$$

ENERGY INVARIANT UPON A RIGID TRANSLATION OF THE ALL CRYSTAL

MEASURING PHONONS

$\vec{q}=\vec{0}$ PHONONS

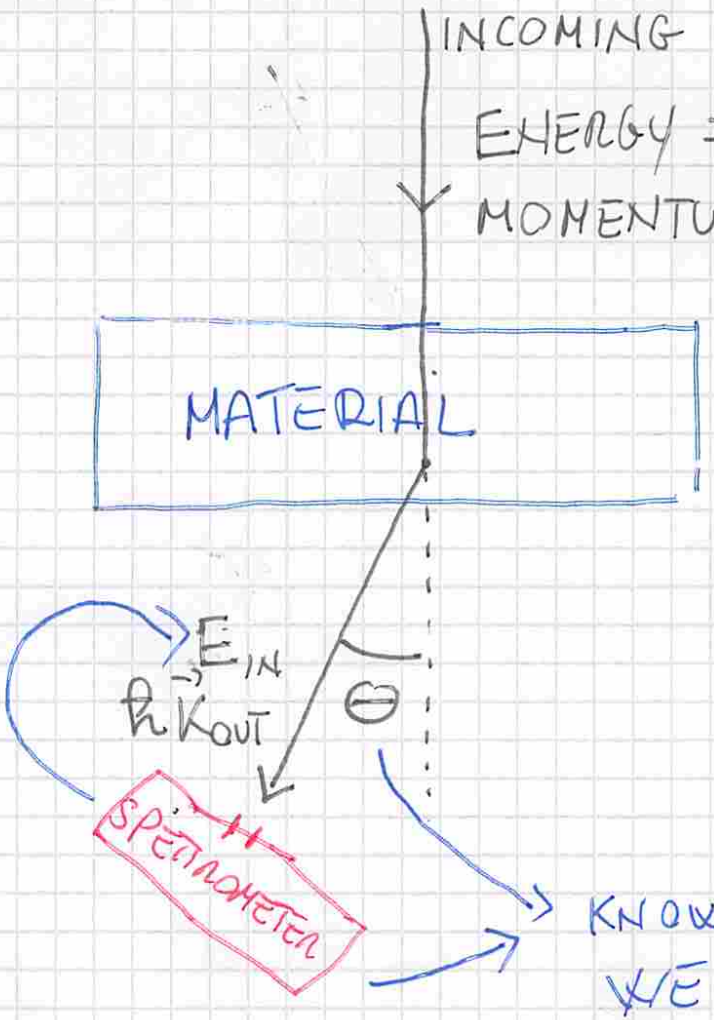
- BY IR SPECTROSCOPY (RELFECTIVITY - TRANSMISSION - ..)
  WE MEASURE $\overleftrightarrow{\varepsilon}_r(\omega)$ → MACROSCOPIC DIELECTRIC TENSOR
  $Im(\overleftrightarrow{\varepsilon}_r(\omega))$ PEAKS AT $\omega^v(\vec{q}\to\vec{0})$ [TRANVERSE - BRANCHES]

- BY SCATTERING WITH VISIBLE LIGHT TO MEASURE $\omega^v(\vec{q}\to 0)$ [BOTH TRANVERSE / LONGITUDINAL] Raman spectroscopy

$\vec{q}\neq 0$ PHONONS

- SCATTERING WITH PARTICLE WITH SIZABLE MOMENTUM WITH RESPECT TO $\frac{2\pi}{a}$ $a \simeq$ LATTICE PARAMETER NAMELY
  NEUTRONS - X-RAY - ELECTRONS

SCATTERING GEOMETRY



STOKES PROCESS $E_{OUT} < E_{IN}$

WE CREATED IN THE MATERIAL AN EXCITATION WITH MOMENTUM AND ENERGY

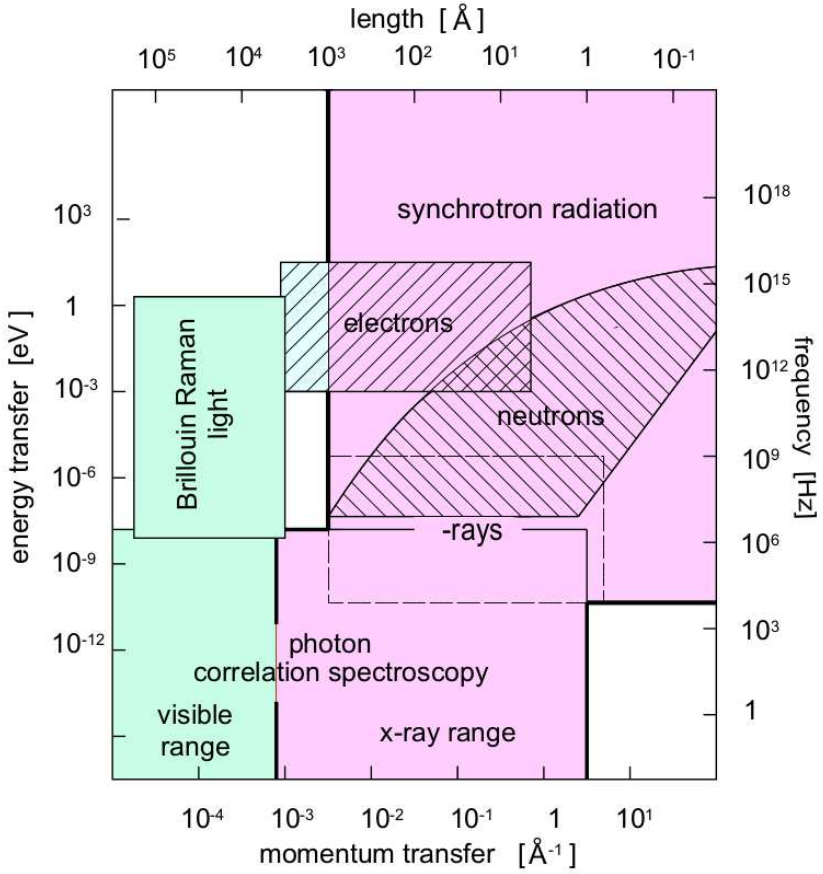
$$\vec{q} = \vec{K}_{IN} - \vec{K}_{OUT}$$

$$\hbar\omega(\vec{q}) = E_{IN} - E_{OUT}$$

WE OBTAIN THE DISPERSION RELATION $\omega(\vec{q})$ OF THE MATERIAL

ELEMENTARY EXCITATION : PHONONS, PLASMONS, MAGNONS, EXCITONS, ...

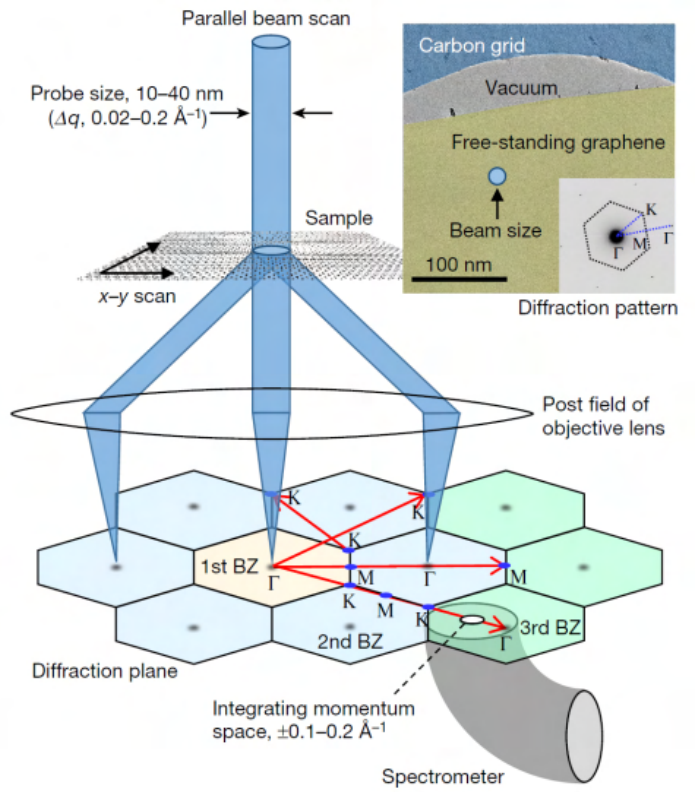
Measuring charge-excitations (e.g. phonons, plasmons, excitons) in energy and momentum space



E. Burkel, Rep. Prog. Phys. **63**, 171 (2000)

Electron Energy Loss Spectroscopy in a **Transmission** Electron Microscope (EELS - TEM)

monocromatic e-beam ~ 30 KeV



from suspended monolayer to ~ 20 layers (to avoid multiple scattering)

Heisenberg uncertainty principle

$$\Delta q \Delta x \geq \frac{1}{2}$$

spot on sample size ~ 10-40 nm
momentum resolution $\Delta q \sim 0.02 - 0.2$ Å^{-1}

possibility of atomic (real space) resolution: excitations with momentum integrated over the full Brillouin Zone

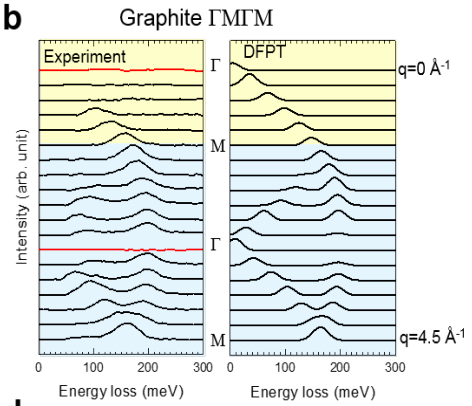
Present energy resolution (microscope at AIST) ~ 25 meV

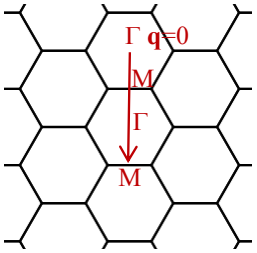
MORE-TEM project aiming to an energy resolution of ~ 1 meV (for phonons and low-energy excitations of correlated systems)

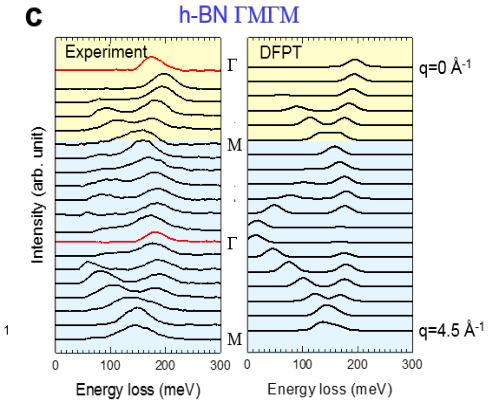
Phonon in graphene and h-BN nanostructures in the TEM

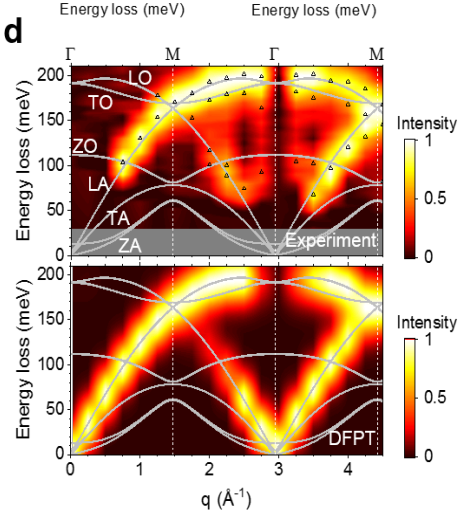
[Senga, Suenaga, Barone, Morishita, Mauri, Pichler, Nature 573, 247 (2019)]

- momentum resolution 0.1 Å^{-1} with 25 meV energy resolution
- bulk-like samples 10-20 layers



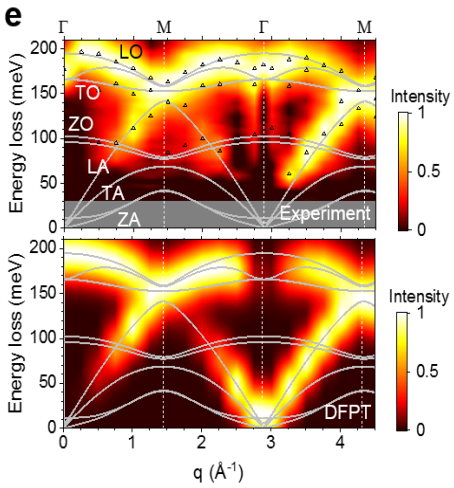






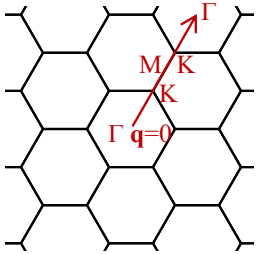
h-BN: near q ~ 0 the intensity of polar LO phonon diverges as $1/q^2$, but also LA phonon visible at large q

Graphite: screened (weak) polar phonons, no EELS near q ~ 0, but at large q intensities similar to those of h-BN

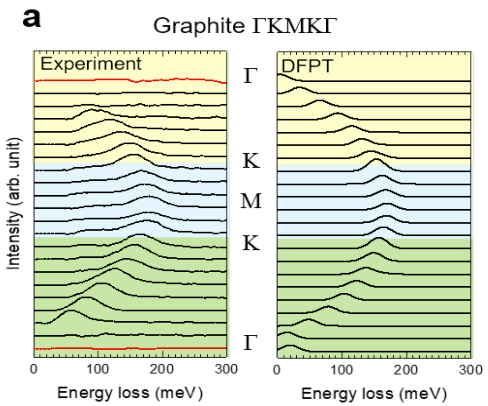


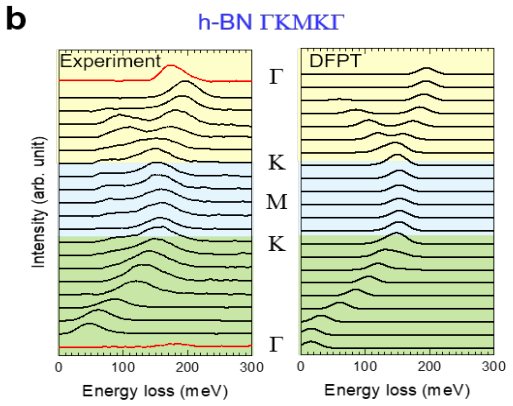
graphite and h-BN multi-layers

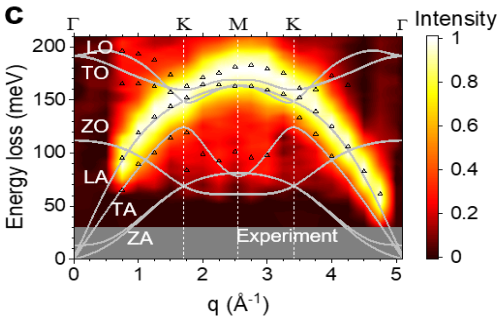
[Senga, Suenaga, Barone, Morishita, Mauri, Pichler, Nature 573, 247 (2019)]

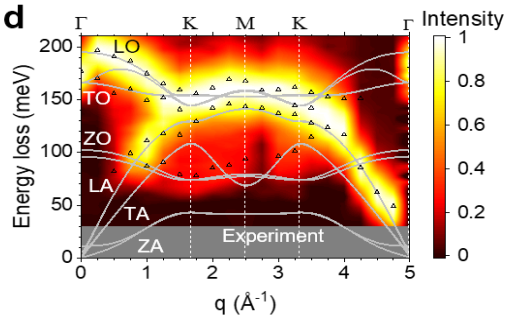


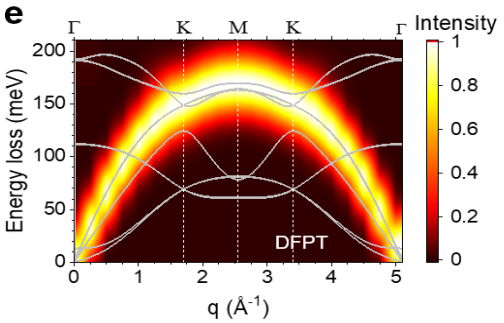
similar results in the ΓKMKΓ direction

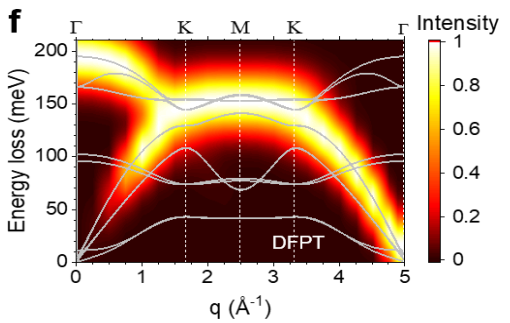




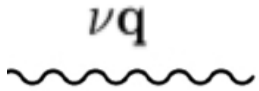








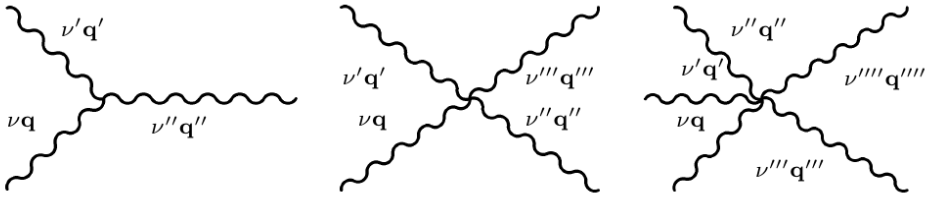
(Weak) failures of the harmonic approximation



- No lattice expansion (or contraction) with temperature or isotope mass
- High T specific heat per atom is equal to $3k_b$, namely it is T-independent
- Phonon frequencies are T independent, scaling with isotope mass as $M^{-1/2}$
- Phonon life-time is infinite, phonon ballistically propagate and thermal conductivity diverges

weak anharmonic corrections

Higher order terms of the potential are considered, phonons interact *in a perturbative manner*:



strong anharmonicity beyond the perturbative approach

for large fluctuations from equilibrium at **high temperature** or with **zero-point quantum motion** (with H or other light atoms)

close to a dynamical instability, e.g. near a second-order phase transition like a **ferroelectric** of a **charge density wave** (CDW) transition

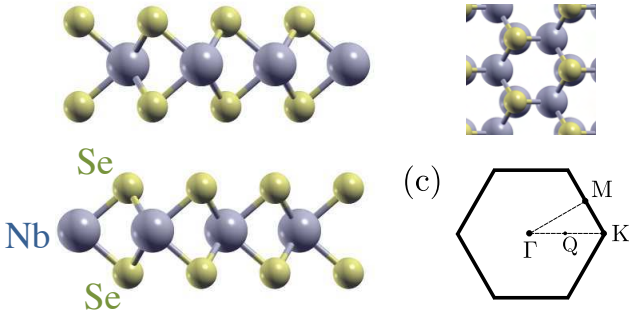
thermoelectric with strong anharmonicity (to lower lattice thermal conductivity)

Anharmonic fluctuations determines the CDW phase diagram

softening of a phonon modes at the CDW transition:

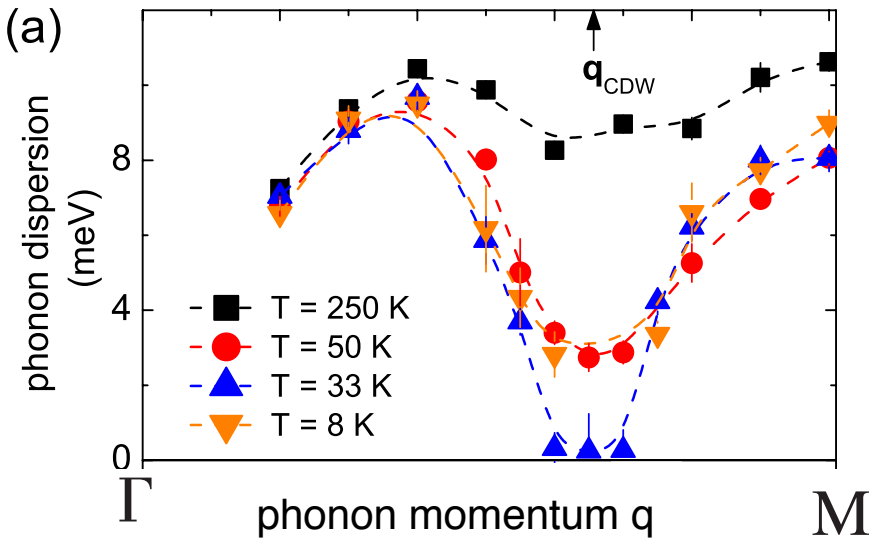
2H-$NbSe_2$ Inelastic X-Ray scattering (IXS)

[Weber *et al.* PRL 107, 107403 (2011)]

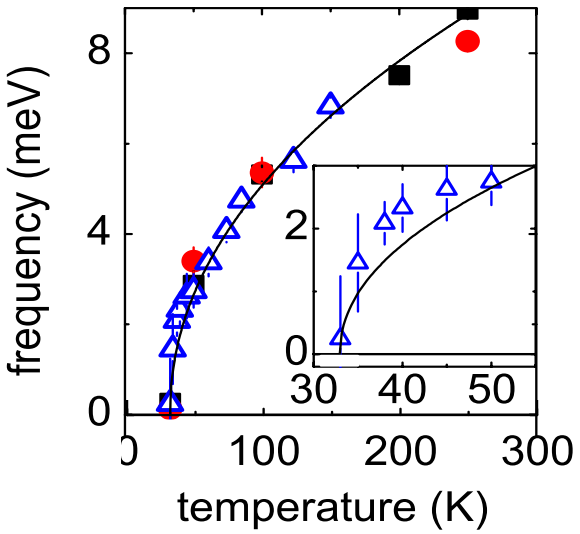


CDW transition temperature, $T_c \sim 33$ K

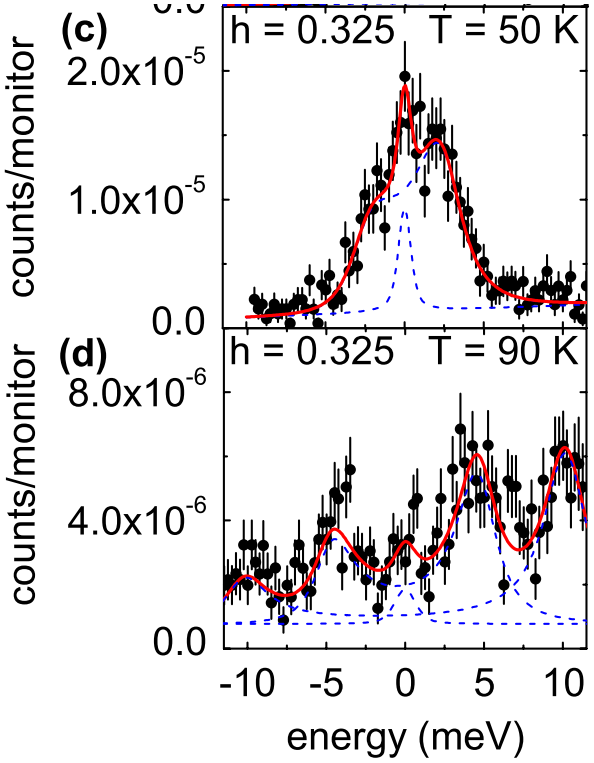
for $T<T_c$ a superstructure appears with periodicity close to a (3x3x1) reconstruction



frequency at $\mathbf{q}_{CDW}$



Phonon-like peaks

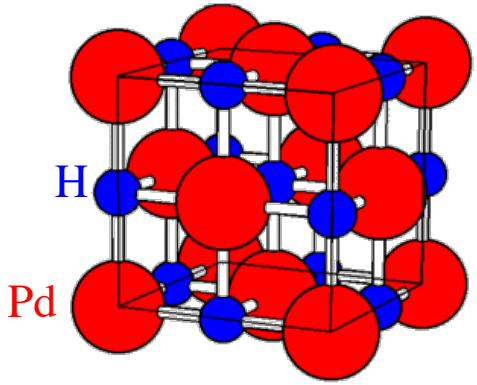


Strong-anharmonic zero-point fluctuations hardens phonon by 500%

rock-salt anharmonic system PdH

[Errea, Calandra, Mauri, PRL 111, 177002 (2013),
Paulatto, Errea, Calandra, Mauri, PRB 91, 054304 (2015)]

Full first principle PBE calculations (not a toy model here!)

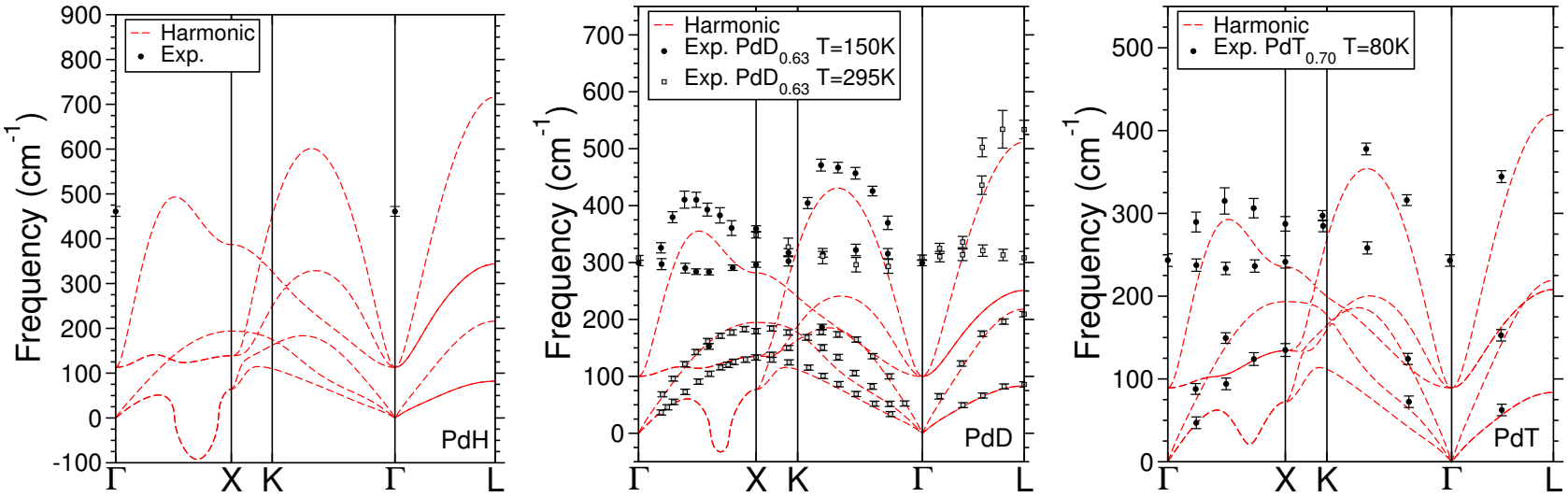


- The small H atoms occupy the octahedral cages of the FFC lattice formed by the large Pd atoms
- H atoms perform a rattling (anharmonic) quantum motion inside the cage
- Superconductor with inverse isotope effect (T_c increases with D and T)

harmonic, SCHA auxiliary and measured phonons

[Errea, Calandra, Mauri, PRL 111, 177002 (2013)]

DFT-PBE first-principles phonons (quantum espresso)



- Harmonic frequency imaginary in PdH/ and PdD and up to ~ 5 times smaller than in experiment

Strong-anharmonic zero-point fluctuations stabilize
“statically” unstable high symmetry phases

Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride

Nature | Vol 578 | 6 February 2020

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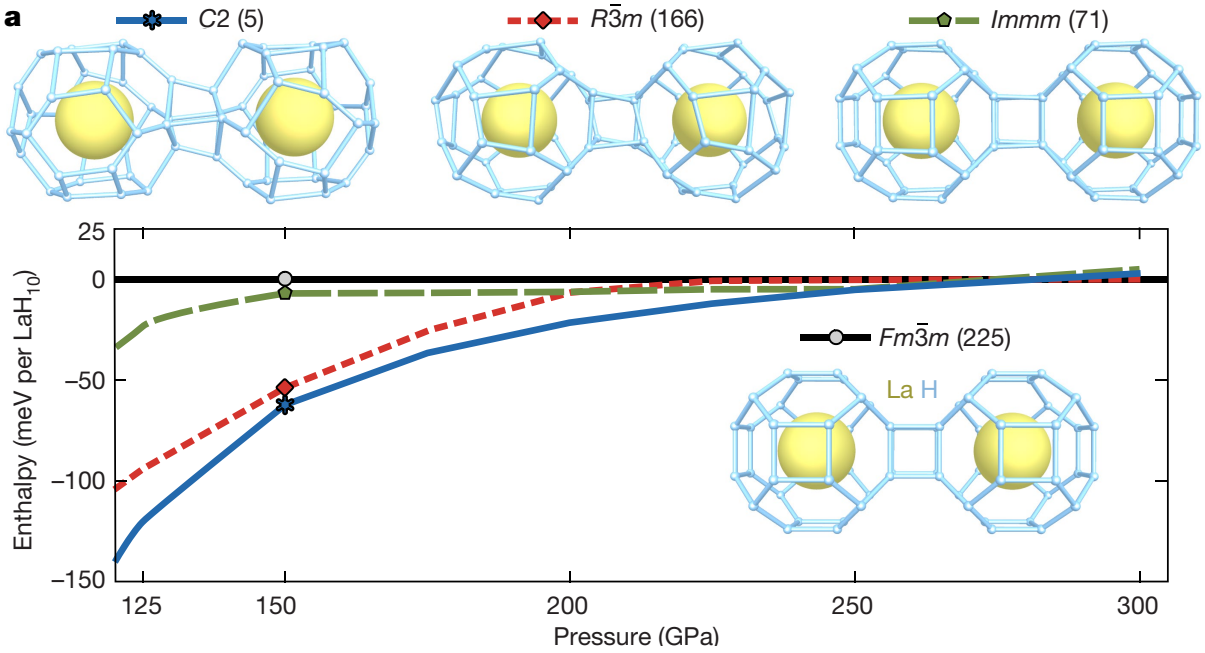
Experimentally the high-Tc Fm-3m cubic-phase is stable down to 130 Gpa, but without zero-point motion is unstable below 270 Gpa



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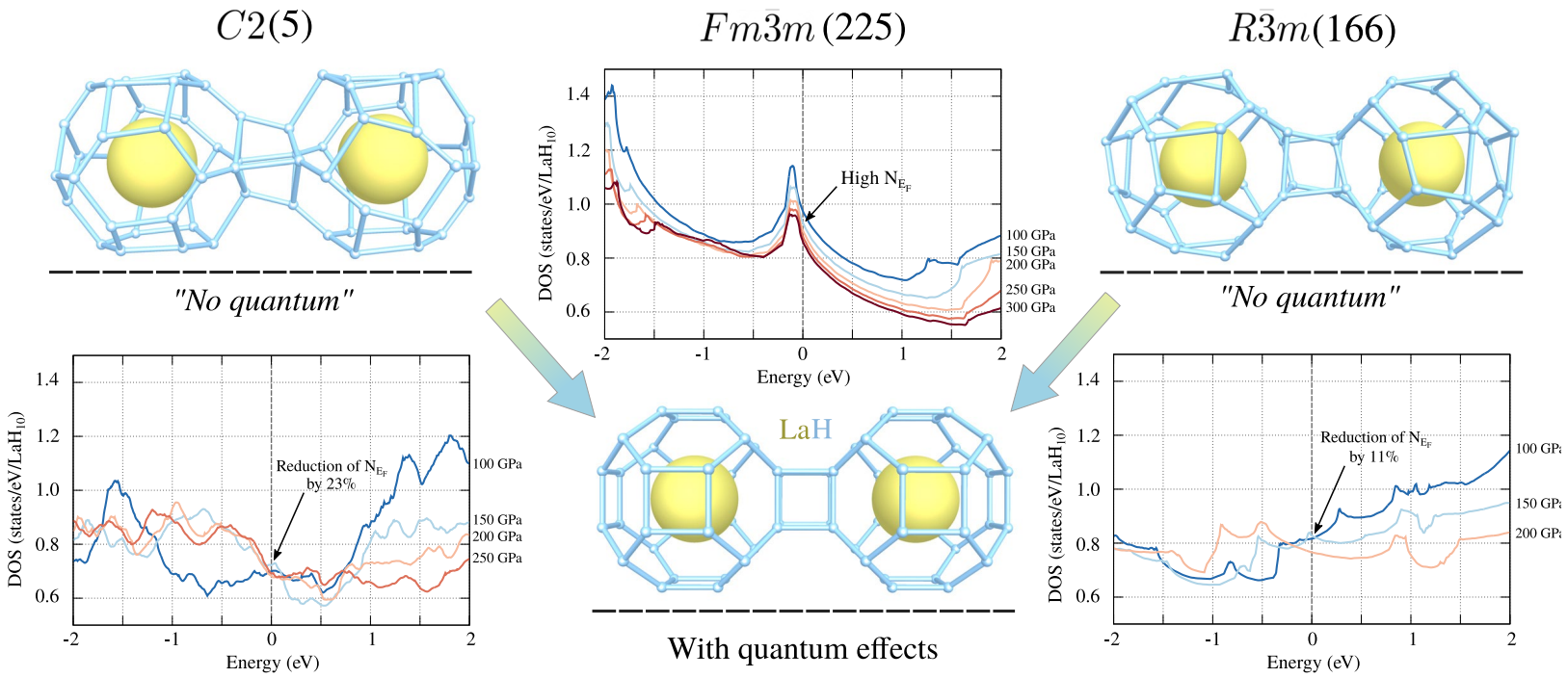
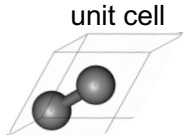


Violation of Boltzmann theory to describe phonon thermal conductivity in strong anharmonic regime

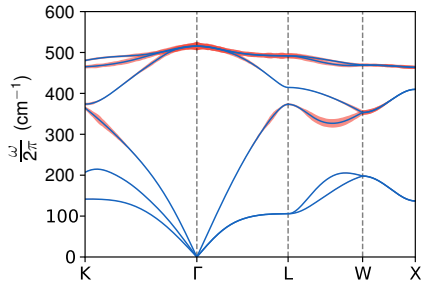
Boltzmann equation Phonon heat propagation in crystals: Boltzmann equation

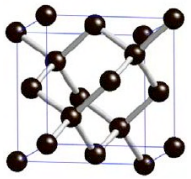
[Peierls, Ann. der Phys. 395, 1055 (1929)]

unit cell



Silicon phonon dispersions





free (particle-like) propagation scattering (**anharmonicity**, isotopic disorder, …)

$$\frac{\partial n_{\mathbf{k}s}(\mathbf{r},t)}{\partial t} + \mathbf{v}_{\mathbf{k}s} \cdot \nabla_{\mathbf{r}}\, n_{\mathbf{k}s}(\mathbf{r},t) = \left.\frac{\partial n_{\mathbf{k}s}}{\partial t}\right|_{\text{col}}$$

$n_{\mathbf{k}s}(\mathbf{r},t)$ = phonon occupation of mode $\mathbf{k}s$ at position and time $(\mathbf{r},t)$

$\mathbf{v}_{\mathbf{k}s} = \frac{d\omega_{\mathbf{k}s}}{d\mathbf{k}}$ = phonon group velocity

semi-classical approximation:
the free (particle-like) propagation doesn't change the phonon branch but only the spatial position!

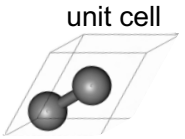
Phonon heat propagation in crystals: Boltzmann equation

[Peierls, Ann. der Phys. 395, 1055 (1929)]

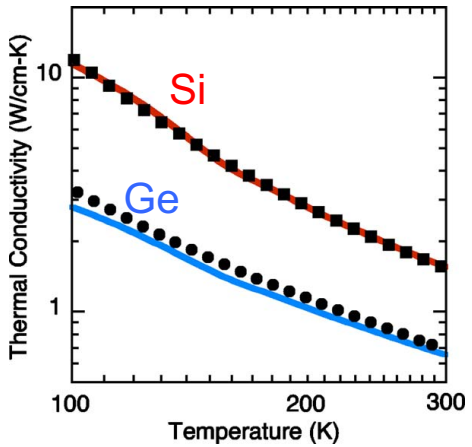
$$\frac{\partial n_{\mathbf{k}s}(\mathbf{r},t)}{\partial t} + \mathbf{v}_{\mathbf{k}s} \cdot \nabla_{\mathbf{r}}\, n_{\mathbf{k}s}(\mathbf{r},t) = \left.\frac{\partial n_{\mathbf{k}s}}{\partial t}\right|_{\mathrm{col}}$$

in “simple” crystals (few atoms per unit cell) with DFT phonons and scattering rates well reproduces the experimental conductivity

Omini & Sparavigna, Physica B 212, (1995).
Broido et al., Appl. Phys. Lett. 91 (2007).
Garg et al., Phys. Rev. Lett. 106 (2011).
Fugallo et al., Phy. Rev. B 88 (2013).
Chaput, Phys. Rev. Lett. 110 (2013).
Cepellotti & Marzari, Phys. Rev. X 6 (2016).
Lindsay, Thermophys. Eng. (2016).
Carrete et al., Comput. Phys. Commun. 220 (2017).
Ding et al., Phis. Rev. B. 98 (2018).
McGaughey et al., J. Appl. Phys. 125 (2019).
…



Broido et al., Appl. Phys. Lett. 91 (2007).



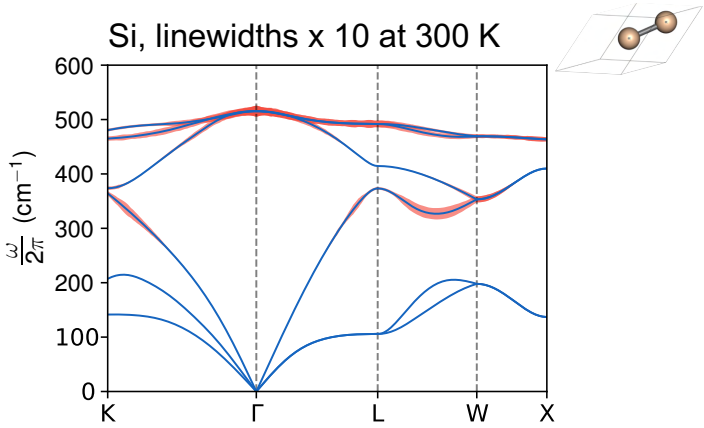
If cubic anharmonicity dominates, for $T>T_{Debye}$ the conductivity k decreases as 1/T (as experimentally observed in many low-defect “*simple*” crystals)

Complex crystals as intermediate state between *simple* crystal and glasses

[M. Simoncelli, N. Marzari & F. Mauri, Nat. Phys. (2019)]

Simple crystals (clean limit)

Interbranch energy difference much larger than the linewidths



small unit cell and/or weak anharmonicity

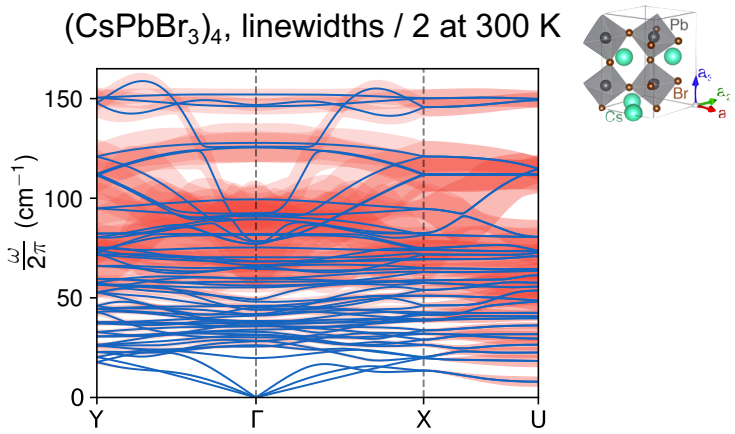
high thermal conductivity

well described by Boltzmann theory

Complex crystals (dirty limit)

Interbranch energy difference comparable or smaller than the linewidths

Perovskite close to a ferroelastic transition (~ 400K)



large unit cell and/or strong anharmonicity

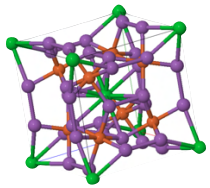
low thermal conductivity (good for thermoelectrics)

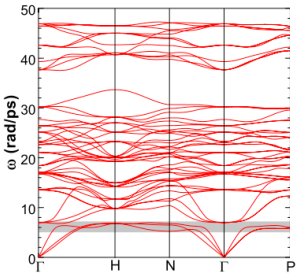
badly described by Boltzmann theory (if the branches are badly resolved how do we define and use the group velocity?

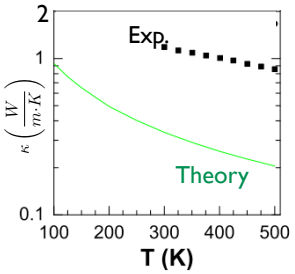
$$\mathbf{v}_{\mathbf{k}s} = \frac{d\omega_{\mathbf{k}s}}{d\mathbf{k}}$$

Failure of Boltzmann theory in *Complex* crystals

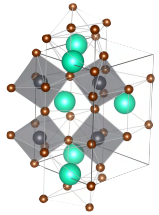
Skutterudite $YbFe_4Sb_{12}$ *Li & Mingo, Phys. Rev. B 91(2015).*

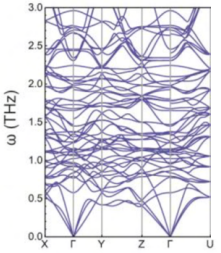


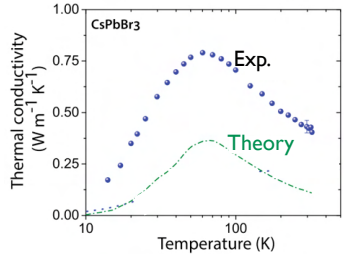




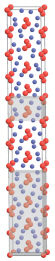
Perovskite $CsPbBr_3$ *Lee et al., PNAS 114 (2017).*

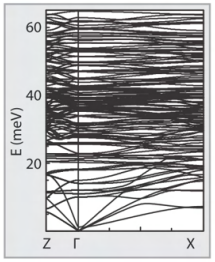


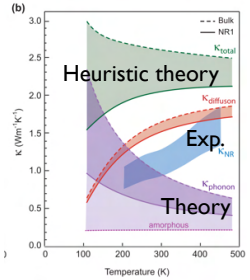




Higher Manganese Silicide *Weathers et al. Phys. Rev. B 96 (2017).*





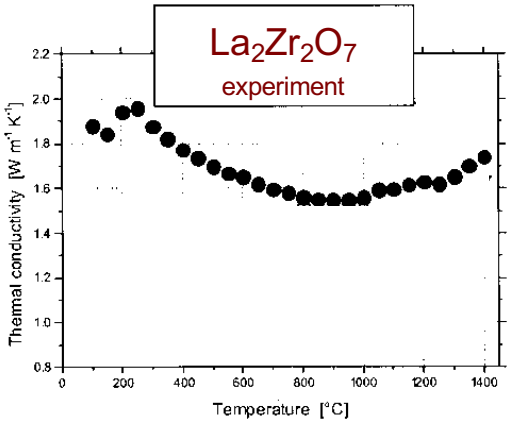


Phenomenological hybrid phonon-diffuson model

Donadio and Galli, PRL, 102 (2009), Chen et al. Nat. Commun. 6 (2014)

$$\kappa_{\mathrm{TOT}} = \kappa_{\mathrm{Peierls}} + \kappa_{\mathrm{Allen}}$$

Allen & Feldman, Phys. Rev. Lett. 62 (1989).



Lehmann et al., J. Am. Ceram. Soc. 86, 1338 (2003)

Boltzmann theory systematically underestimates the conductivity

experimental conductivity decreases slower than 1/T and could also increase with T (glass-like behavior)

problem addressed with phenomenological models

Take-home message

If we measure excitations even if the strong anharmonic regime by, e.g. Xray inelastic scattering we observe quasiparticles that looks like phonon with finite (large) line-width.

It should be possible to find an interacting mean-field approach to describe phonon-phonon interaction with an effective phonon-like description

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MOmentum and position REsolved mapping Transmission Electron energy loss Microscope

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