

harmonic lattice vibrations and anharmonicity signatures

Francesco Mauri (University of Rome)

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

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

OF NUCLEI NUCLEAR POSITIONS
NUCLEAR MASSES $\{\vec{R}_I\}_{I=1,..N}$

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

$$\vec{p}_I = -\hbar \vec{\nabla}_{\vec{R}_I} \quad \vec{R}_I = \text{MOMENTUM OF NUCLEUS } I$$

QUANTUM EIGENSTATES $\{\psi_i\}$ FROM

$$H|\chi_i\rangle = \epsilon_i |\chi_i\rangle$$

$|\chi_i\rangle \in \text{HILBERT SPACE}^{N_N \text{ NUCLEI}}$

IF $k_b T \leq \text{or} \sim (\epsilon_{i+1} - \epsilon_i)$ \Rightarrow QUANTUM MECHANICS IS NEEDED

IF $k_b T \gg (\epsilon_{i+1} - \epsilon_i) \sim 10/100 \text{ meV}$ \Rightarrow WE CAN USE CLASSICAL MECHANICS

NEWTON EQUATION

$$m_I \ddot{\vec{R}}_I = -\vec{F}_I = -\frac{\partial V(\{\vec{R}\})}{\partial \vec{R}_I}$$

HARMONIC APPROXIMATION FOR THE BO POTENTIAL

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

WE CAN TAYLOR-EXPAND $V(\{\vec{R}_I\})$ AROUND $\{\vec{R}_I^{\text{eq}}\}$

$$V(\{\vec{R}_I\}) = \underbrace{V(\{\vec{R}_I^{\text{eq}}\})}_{E^{\text{eq}}} + \sum_I \frac{dV(\{\vec{R}_I\})}{d\vec{R}_I} \cdot \vec{u}_I + \sum_{II} \vec{u}_I \cdot \frac{\partial V(\{\vec{R}_I\})}{\partial \vec{R}_I \partial \vec{R}_{I'}} \cdot \vec{u}_{I'} + O(u^3)$$

$\vec{u}_I \stackrel{\text{def}}{=} \vec{R}_I - \vec{R}_I^{\text{eq}}$

≈ 0 FOR THE EQUILIBRIUM CONDITION

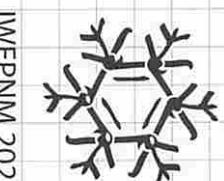
SCALAR PRODUCT

$\vec{u}_I \cdot \vec{u}_{I'} \stackrel{\text{def}}{=} K_{II'}$

SUMMATION OVER ALL PAIRS OF NUCLEI

$V(\{\vec{R}_I\}) \approx E^{\text{eq}} + \frac{1}{2} \sum_{II'} \vec{u}_I \cdot K_{II'} \cdot \vec{u}_{I'}$

HARMONIC APPROXIMATION



FAILURE OF THE TAYLOR EXPANSION AND OF THE HARMONIC APPROXIMATION

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

- IN A DIFFUSIVE STATE: E.G. IN THE LIQUID CASE OR WITH ATOMS THAT DIFFUSE (NAMELY FOR $T > T_{\text{MELTING}}$)
- 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 $\{\vec{R}_I^{\text{exp}}\}$ ARE DIFFERENT FROM THE CLASSICAL MINIMUM $\{\vec{R}_I^{\text{eq}}\}$: E.G. IN THE HIGH TEMPERATURE PHASE (HIGH SYMMETRY PHASE) OF A MATERIAL EXHIBITING A SYMMETRY BROKEN LOW-T PHASE:
 - FERROELECTRIC MATERIALS
 - CHARGE-DENSITY-WAVE MATERIALS
 - ...

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

SOLUTION OF THE HARMONIC HAMILTONIAN

IN THE CLASSICAL APPROXIMATION

$$\ddot{\vec{M}_I} \ddot{\vec{u}_I} = - \sum_{I'} \overset{\leftrightarrow}{K}_{II'} \cdot \ddot{\vec{u}}_{I'}$$

AUXILIARY VARIABLE

$$\vec{v}_I \stackrel{\text{def}}{=} \sqrt{M_I} \vec{u}_I$$

$$\ddot{\vec{v}_I} = - \overset{\leftrightarrow}{M}_{II'} \cdot \vec{v}_{I'}$$

AUXILIARY MATRIX

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

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

$$\sum_{I'} \overset{\leftrightarrow}{C}_{II'} \cdot \vec{e}_I^v = (\omega^v)^2 \vec{e}_I^v$$

ω^v VIBRATIONAL PULSATION

$\{\vec{e}_I^v\}$ VIBRATIONAL POLARISATION

$$\sum_{I'} \vec{e}_I^v \cdot \vec{e}_{I'}^{v'} = \delta_{v,v'}$$

ORTHONORMAL VECTORS
IN THE $3N_H$ SPACE

$$\sum_v \vec{e}_{Id}^v \cdot \vec{e}_{Id'}^{v'} = \delta_{Id} \delta_{Id'}$$

$d, d' = x, y, z$

NORMAL MODE COORDINATE

DECOUPLED EQUATION OF MOTION

$$q_v = \sum_I \vec{e}_I^v \cdot \vec{v}_I$$

$$\ddot{q}_v = -(\omega^v)^2 q_v$$



SOLUTION

$$q_v(t) = q_v(t_0) \cos[\omega^v(t-t_0) + \phi_0^v]$$

SOLUTION OF THE QUANTUM HAMILTONIAN

VIBRATION ANNIHILATION OPERATOR

$$(I) \quad a_r = \sum_I \vec{e}_I^r \cdot \left[-\frac{i}{\sqrt{2\hbar\omega}} \frac{\vec{p}_I}{\sqrt{\mu_I}} + \sqrt{\frac{\omega}{2\hbar}} \vec{u}_I \vec{u}_I^\top \right]$$

VIBRATION CREATION OPERATOR

ONE OSCILLATOR

$$a|0\rangle = 0$$

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

$$m=0,1, \dots \quad a^+|m\rangle = \sqrt{m+1}|m+1\rangle$$

$$a|m\rangle = \sqrt{m}|m-1\rangle$$

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

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

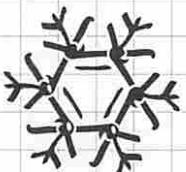
$$\sum_v \frac{e_{I'd}^v}{\sqrt{\omega^v}} (a_r + a_r^+) = \frac{2}{\sqrt{2\hbar}} u_{Id} \sqrt{\mu_I}$$

$$\sum_v e_{Id}^v e_{Id}^v = \delta_{Id} \delta_{dd}$$

$$(II) \quad \vec{u}_I = \sum_v \sqrt{\frac{\hbar}{2\omega^v \mu_I}} \vec{e}_I^v (a_r + a_r^+)$$

$$(III) \quad H = \sum_v \hbar\omega_v (a_r^+ a_r + \frac{1}{2}) + E_0$$

$$H|\{m_r\}\rangle = \left\{ \left[\sum_v \hbar\omega_v (m_r + \frac{1}{2}) \right] + E_0 \right\} |\{m_r\}\rangle$$



HARMONIC VIBRATIONS IN PERIODIC SOLIDS

PHONONS

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

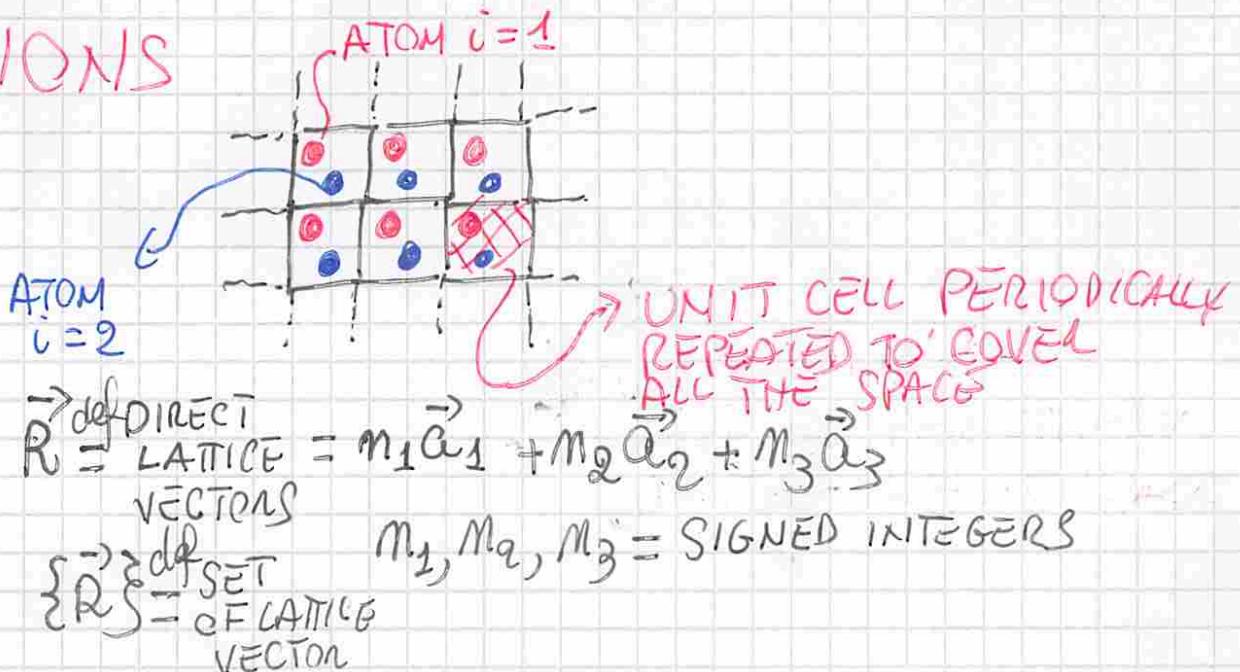
$$\vec{R}_I = \vec{R}_i + \vec{r} = \vec{R}_i + \vec{r}_i$$

↑ ↑
WITHIN WHICH POSITION OF ATOM i IN THE UNIT CELL

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

$$C_{I\alpha, I'\alpha'} = C_{i\alpha(\vec{R}), i'\alpha'(\vec{R}')} \quad \downarrow$$

x, y, z



$$l = 1, 2, \dots, N_{\text{AT}}$$

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

$$C_{i\alpha, i'\alpha'} = C_{i\alpha(\vec{R}), i'\alpha'(\vec{R}')} \stackrel{\text{def}}{=} C_{i\alpha(\vec{R} - \vec{R}'), i'\alpha'(\vec{R})} = C_{i\alpha, i'\alpha'}(\vec{R} - \vec{R}')$$

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

PHONONS

$$\tilde{C}_{i\alpha, i\alpha'}(\vec{q}) \stackrel{\text{def}}{=} \sum_{\vec{R}} e^{-i\vec{q} \cdot \vec{R}} C_{i\alpha, i\alpha'}(\vec{R}) [e^{-i\vec{q} \cdot (\vec{R}_i - \vec{R}_{i'})}]$$

TWO POSSIBLE CONVENTIONS

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

C_{II} IS BLOCK DIAGONAL

IN THE $C_{i\alpha\alpha'}(\vec{q})$ "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 $3N_{\text{AX}} \times 3N_{\text{AT}}$

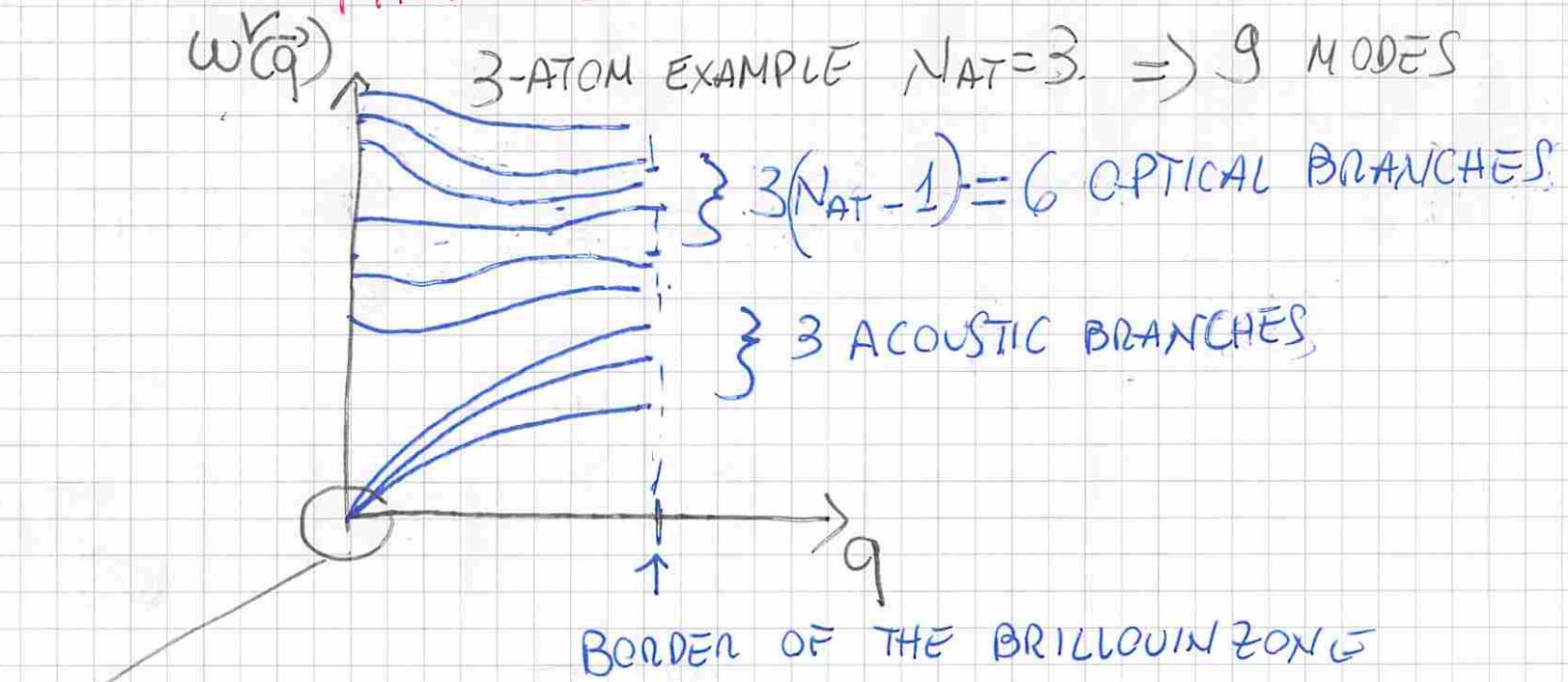
$\forall \vec{q} \quad 3N_{\text{AT}} \text{ EIGENSTATES } [\omega^r(q)]^2$

- a) WITHOUT THIS TERM
- b) WITH THIS TERM



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

PHONONS



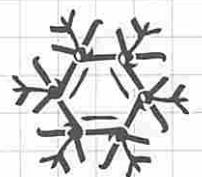
FOR THE 3 ACOUSTIC BRANCHES

$$\lim_{|\vec{q}| \rightarrow 0} \omega(\vec{q}) = 0 \Leftrightarrow \text{THANKS TO ACOUSTIC SUM RULE}$$



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

ENERGY INVARIANT
UPON A RIGID TRANSLATION
OF THE ALL-CRYSTAL



MEASURING PHONONS

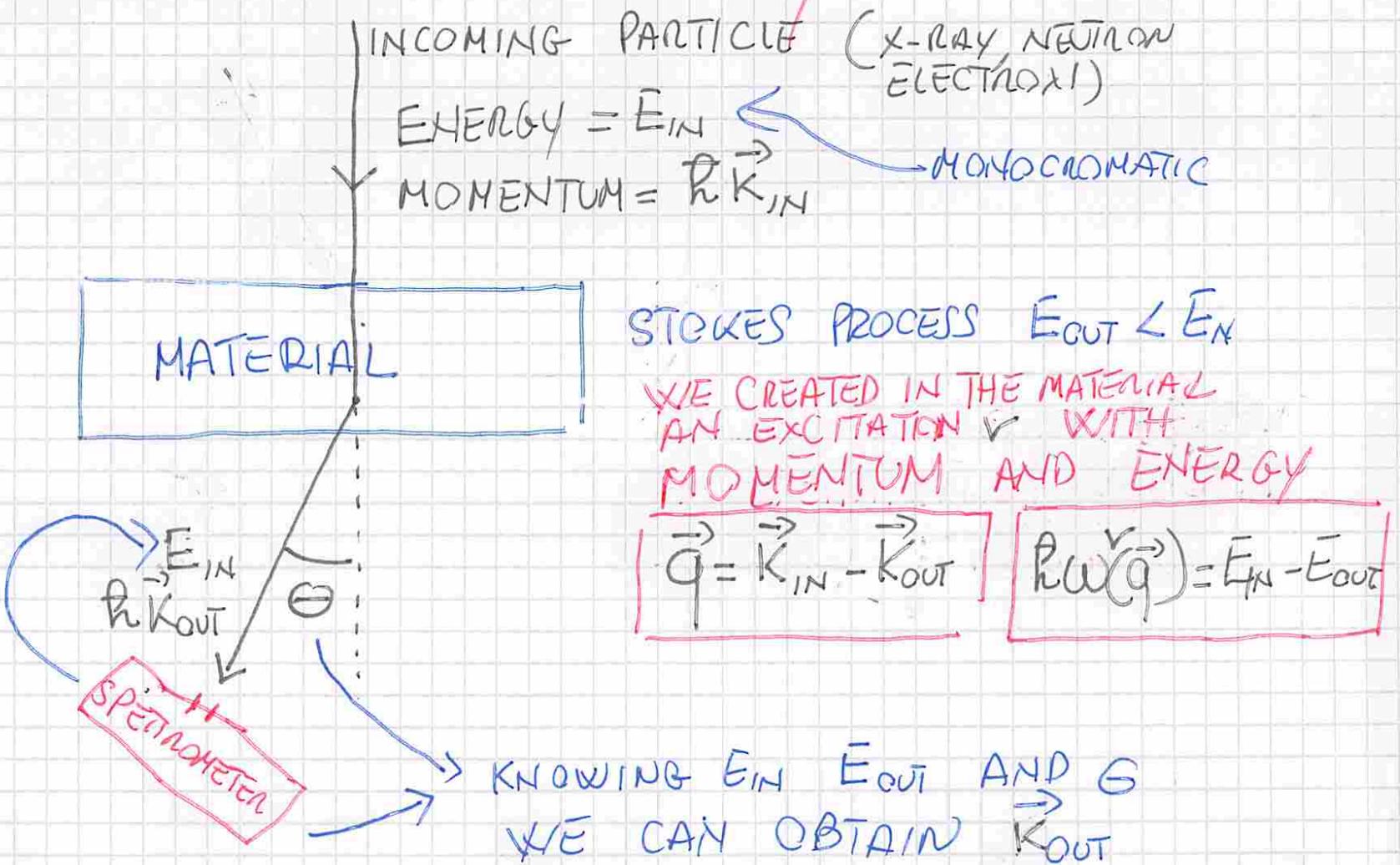
PHONONS

TO

PHONONS

- BY IR SPECTROSCOPY (REFLECTIVITY - TRANSMISSION - ...)
WE MEASURE $\overset{\leftrightarrow}{\epsilon}_r(\omega) \rightarrow$ MACROSCOPIC DIELECTRIC TENSOR
 $\text{Im}(\overset{\leftrightarrow}{\epsilon}(\omega))$ PEAKS AT $\omega^v(\vec{q} \rightarrow \vec{0})$ [TRANVERSE-BRANCHES]
- BY SCATTERING WITH VISIBLE LIGHT TO MEASURE
 $\omega^v(\vec{q} \rightarrow \vec{0})$ [BOTH TRANVERSE / LONGITUDINAL] Raman spectroscopy
- SCATTERING WITH PARTICLE WITH SIZABLE MOMENTUM
WITH RESPECT TO $\frac{2\pi}{a}$ QUANTUM LATTICE PARAMETER NAMELY
NEUTRONS - X-RAY - ELECTRONS

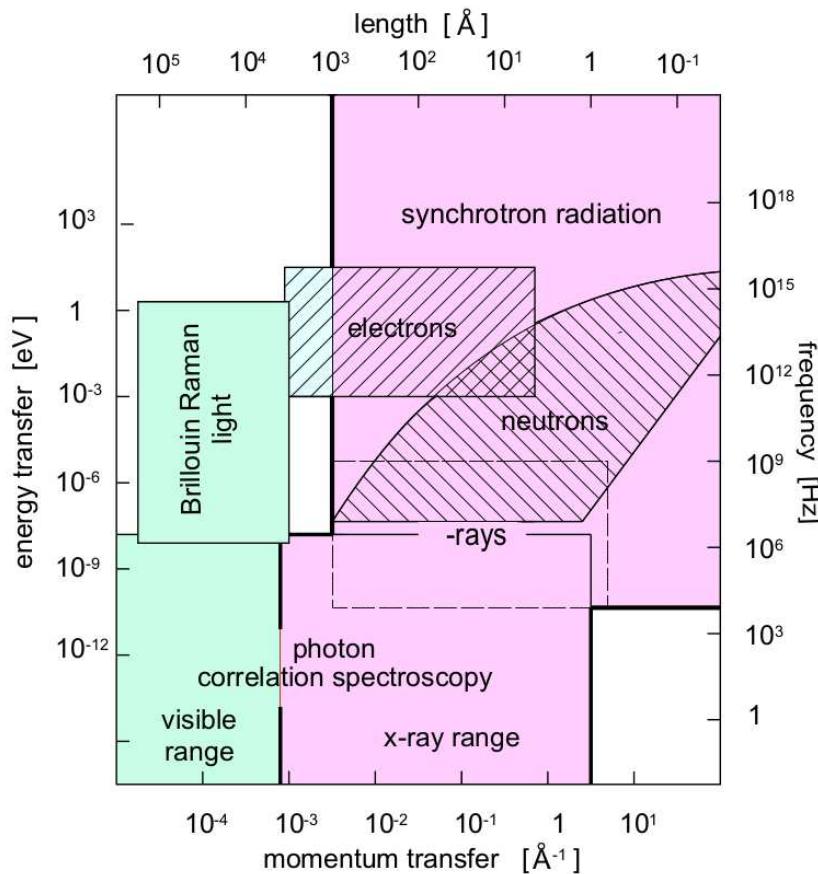
SCATTERING GEOMETRY



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

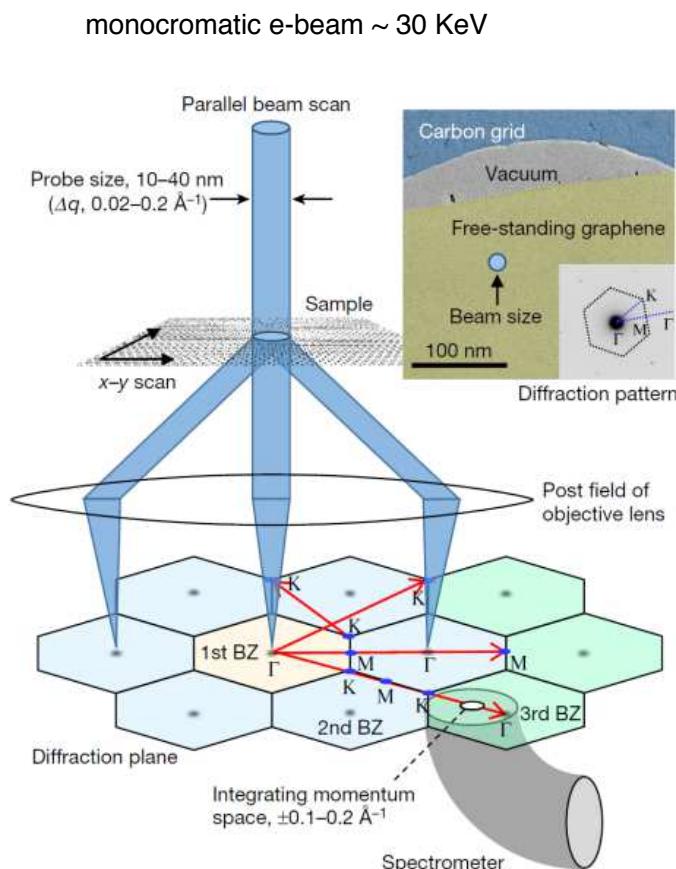
ELEMENTARY EXCITATION : PHONONS, PLASMONS, MAGNONS, EXCITONS, ...

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)



from suspended **monolayer** to \sim 20 layers (to avoid multiple scattering)

Heisenberg uncertainty principle

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

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

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

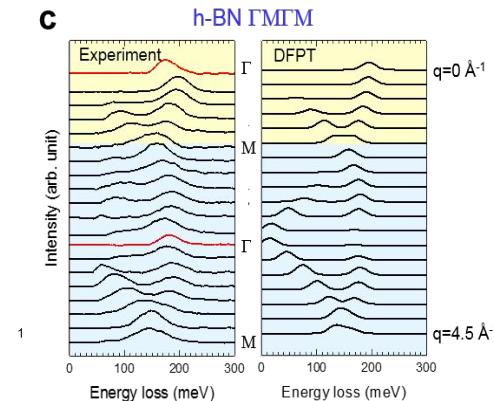
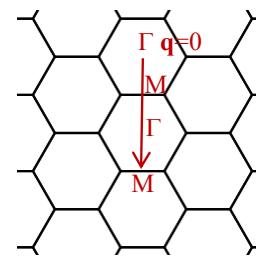
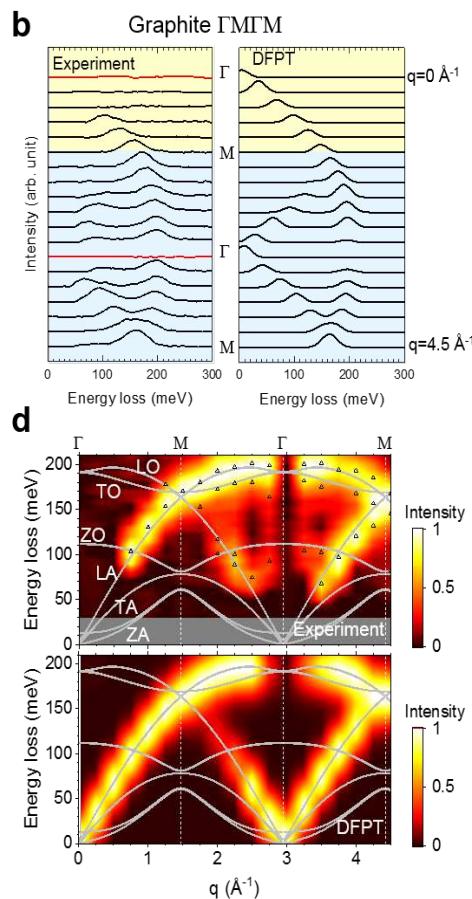
Present energy resolution (microscope at
AIST) \sim 25 meV

MORE-TEM project aiming to an energy
resolution of $\sim 1 \text{ meV}$ (for phonons and low-
energy excitations of correlated systems)

Phonon in graphene and h-BN nanostructures in the TEM

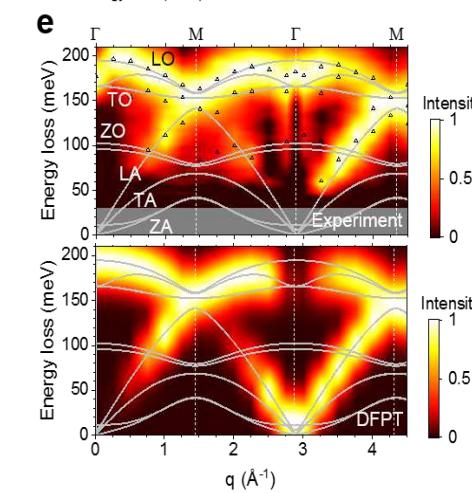
[Senga, Suenaga, Barone, Morishita, Mauri, Pichler, Nature 573, 247 (2019)]

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



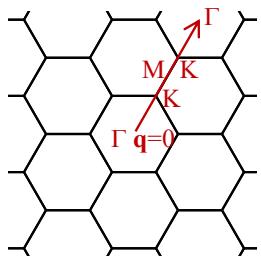
h-BN: near $q \sim 0$ the intensity of polar LO phonon diverges as $1/q^2$, but also LA phonon visible at large q

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

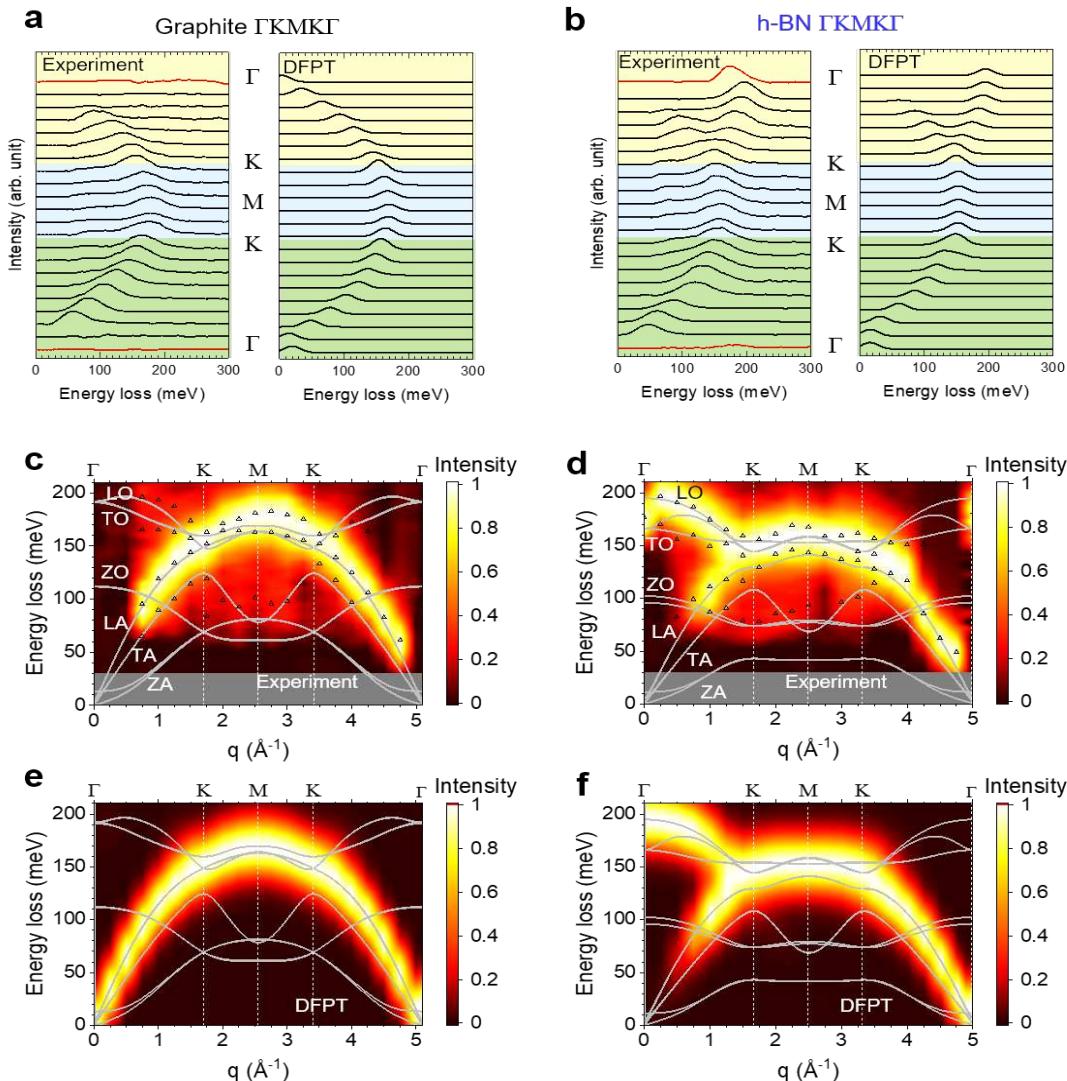


graphite and h-BN multi-layers

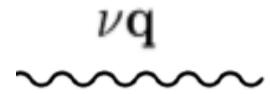
[Senga, Suenaga, Barone, Morishita, Mauri, Pichler, Nature 573, 247 (2019)]



similar results in the
 ΓKMKG direction



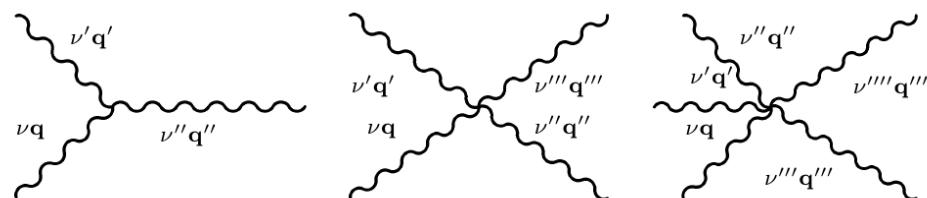
(Weak) failures of the harmonic approximation



- 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

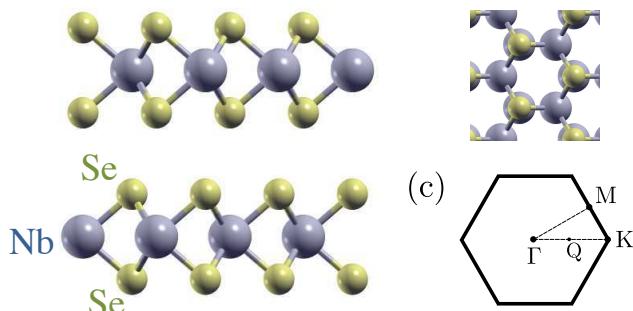
for large fluctuations from equilibrium at **high temperature** or with **zero-point quantum motion** (with H or other light atoms)

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

thermoelectric with strong anharmonicity (to lower lattice thermal conductivity)

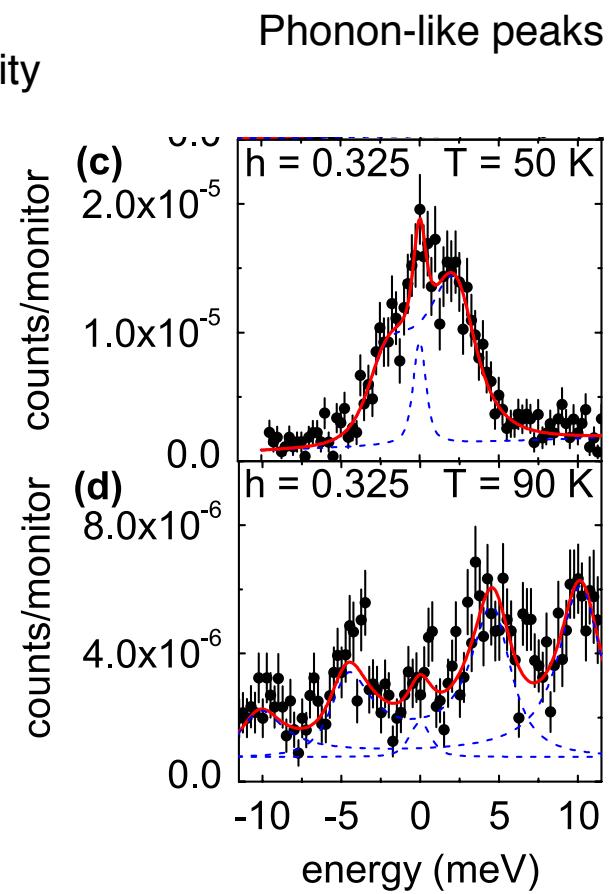
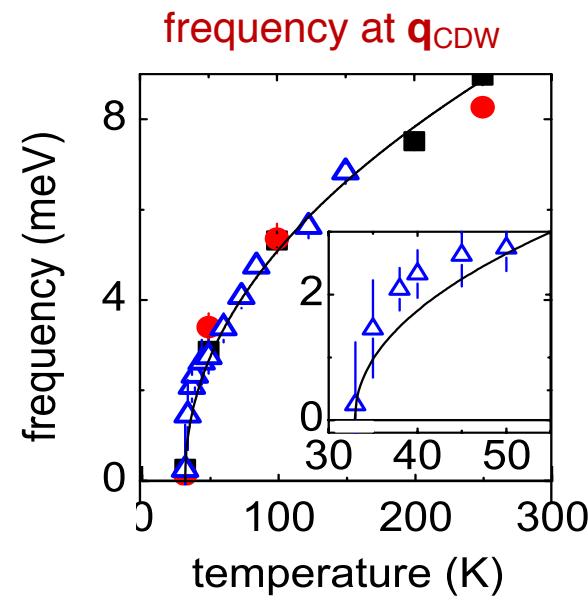
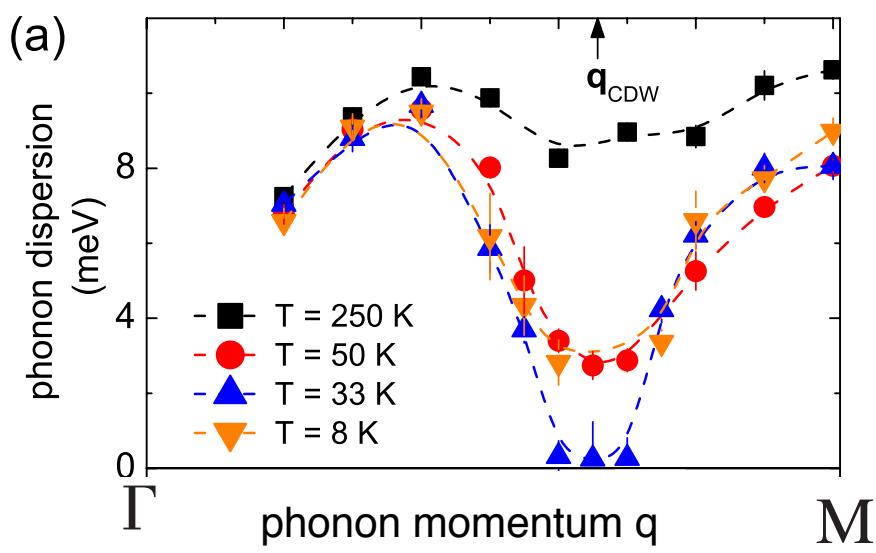
Anharmonic fluctuations determines the CDW phase diagram

softening of a phonon modes at the CDW transition: 2H-NbSe₂ 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

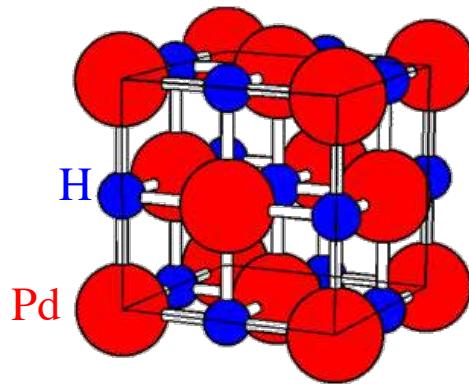


Strong-anharmonic zero-point fluctuations
hardens phonon by 500%

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!)

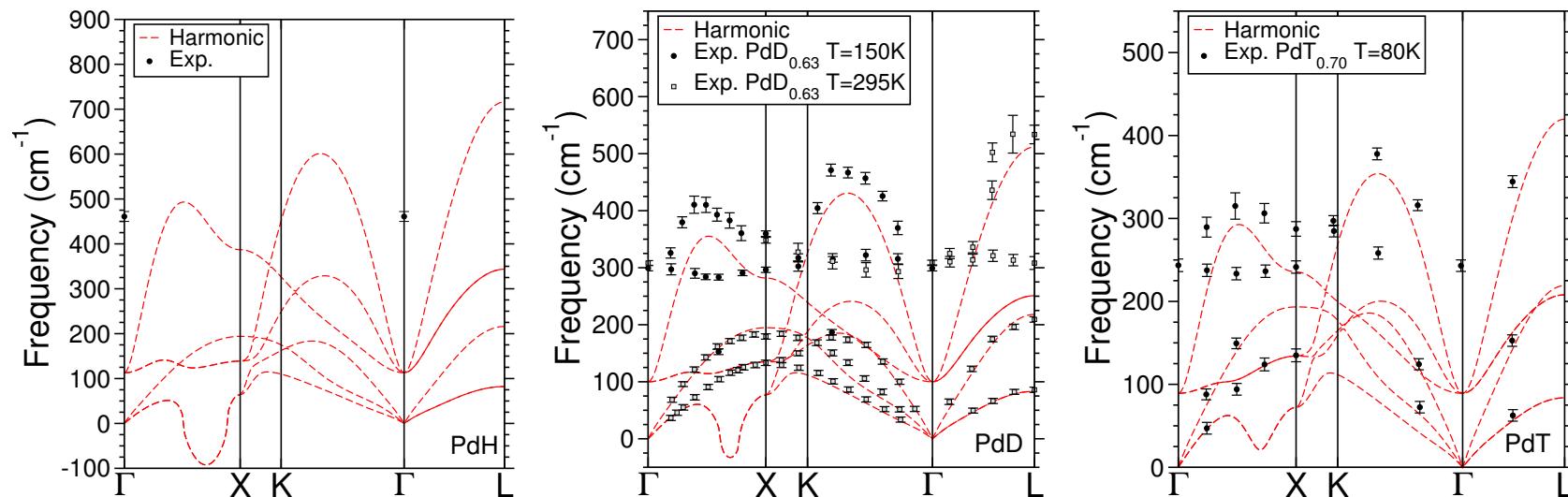


- The small H atoms occupy the octahedral cages of the FFC lattice formed by the large Pd atoms
- H atoms perform a rattling (anharmonic) quantum motion inside the cage
- Superconductor with inverse isotope effect (T_c increases with D and T)

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

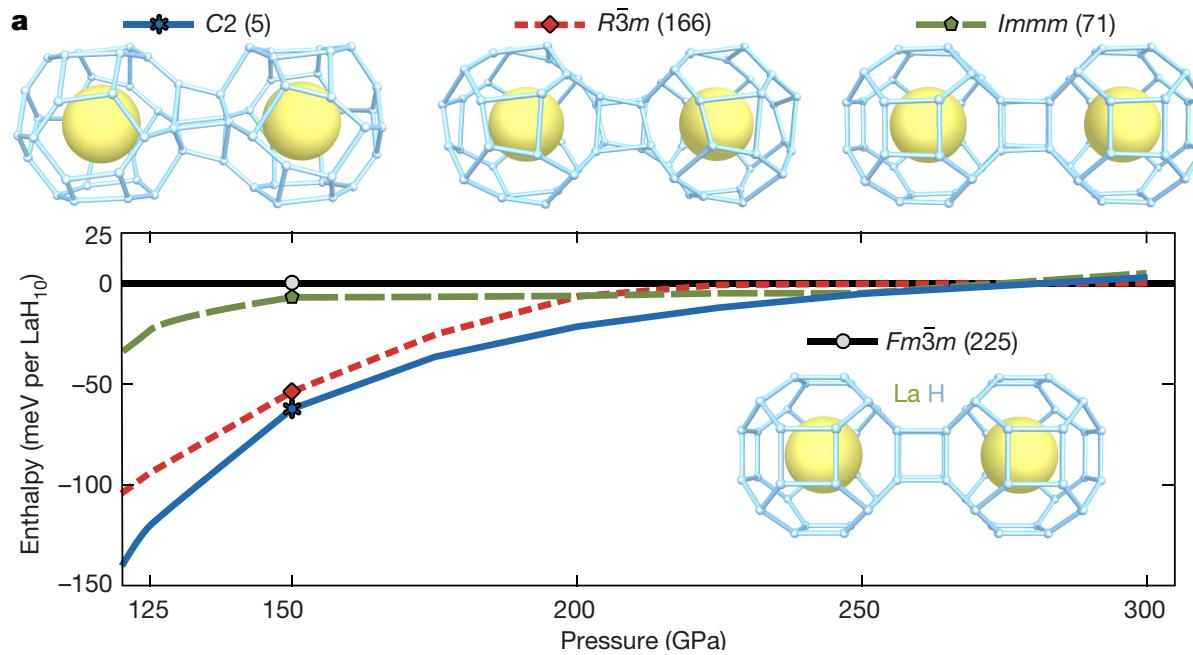
Strong-anharmonic zero-point fluctuations stabilize
“statically” unstable high symmetry phases

Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride

Nature | Vol 578 | 6 February 2020

Ion Errea^{1,2,3}, Francesco Belli^{1,2}, Lorenzo Monacelli⁴, Antonio Sanna⁵, Takashi Koretsune⁶, Terumasa Tadano⁷, Raffaello Bianco², Matteo Calandra⁸, Ryotaro Arita^{9,10}, Francesco Mauri^{4,11} & José A. Flores-Livas^{4*}

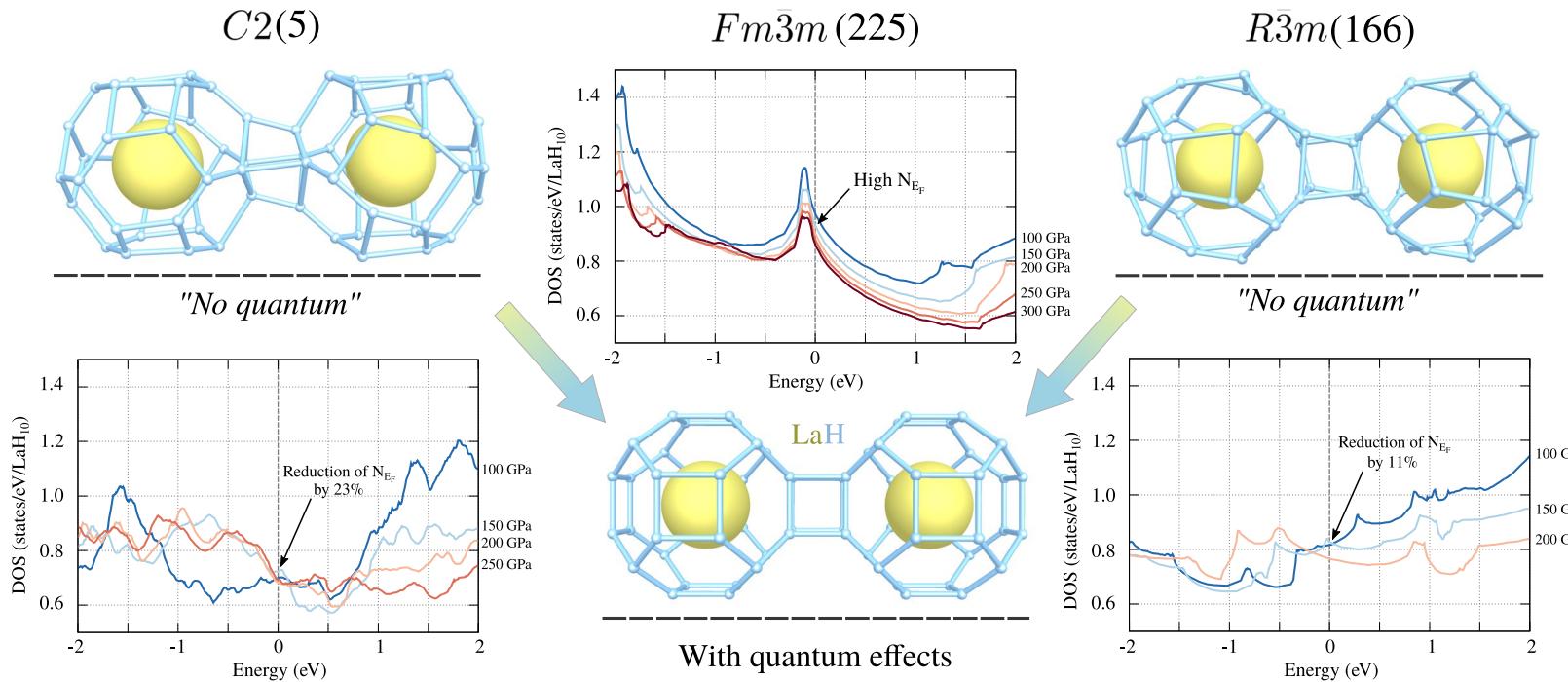
Experimentally the high-Tc Fm-3m cubic-phase is stable down to 130 Gpa, but without zero-point motion is unstable below 270 Gpa



Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride

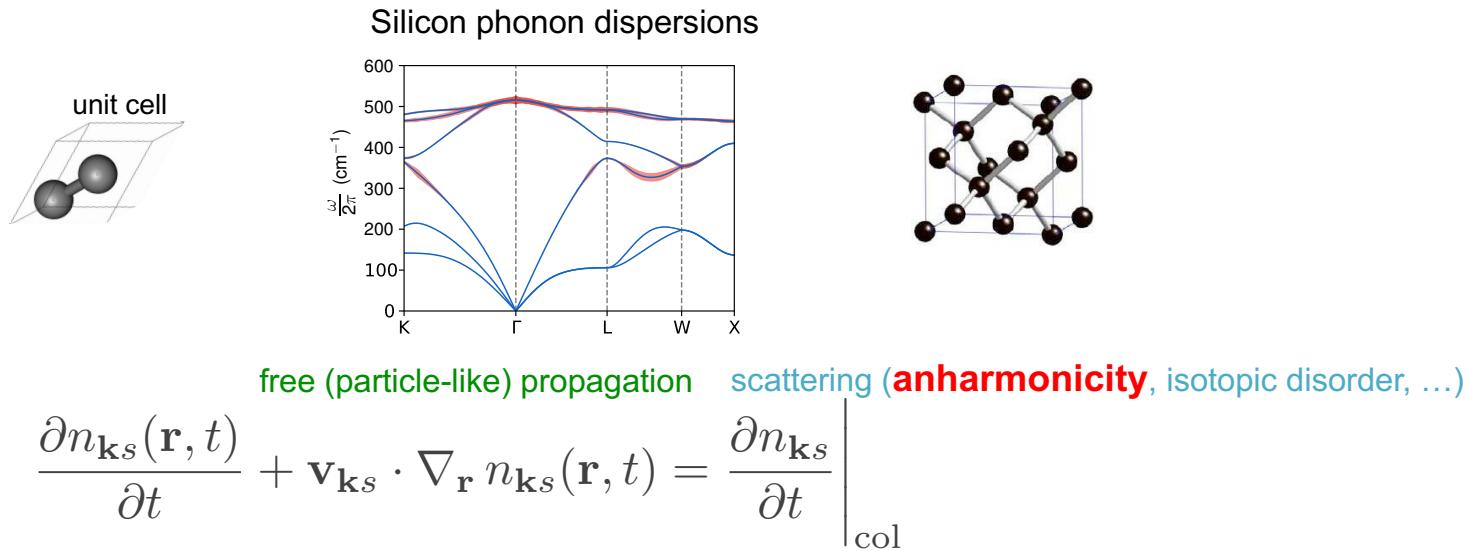
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Violation of Boltzmann theory to describe phonon thermal conductivity in strong anharmonic regime

Boltzmann equation Phonon heat propagation in crystals: Boltzmann equation [Peierls, Ann. der Phys. 395, 1055 (1929)]



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

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

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

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).

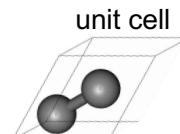
Lindsay, Thermophys. Eng. (2016).

Carrete et al., Comput. Phys. Commun. 220 (2017).

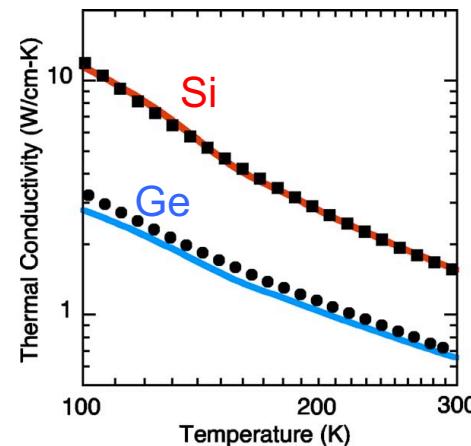
Ding et al., Phis. Rev. B. 98 (2018).

McGaughey et al., J. Appl. Phys. 125 (2019).

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

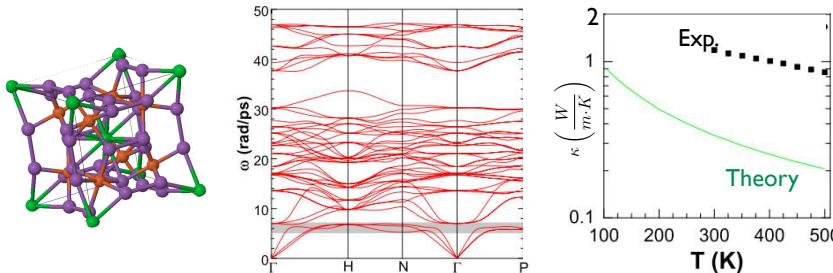


If cubic anharmonicity dominates, for $T > T_{\text{Debye}}$ the conductivity κ decreases as $1/T$ (as experimentally observed in many low-defect “simple” crystals)

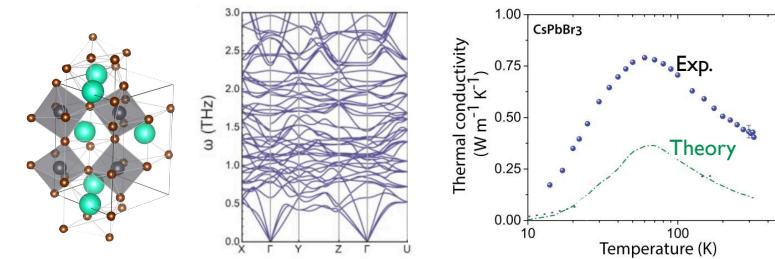
Complex crystals as intermediate state between *simple* crystal and glasses
[M. Simoncelli, N. Marzari & F. Mauri, Nat. Phys. (2019)]

Failure of Boltzmann theory in Complex crystals

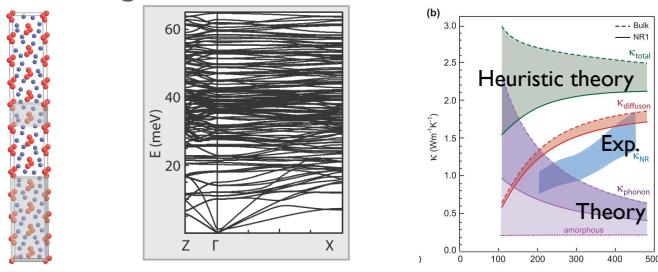
Skutterudite $\text{YbFe}_4\text{Sb}_{12}$ Li & Mingo, Phys. Rev. B 91 (2015).



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



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

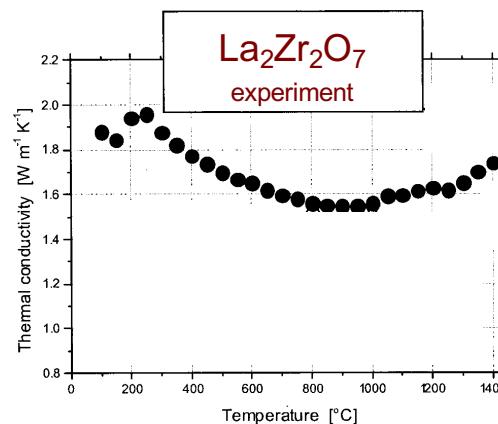


Phenomenological hybrid phonon-diffuson model

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

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

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