Introduction to phonons in crystalline solids

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TIMES Workshop
MPSD Hamburg

These slides:
cs2t.de/publications

Christian-Albrechts-Universität zu Kiel

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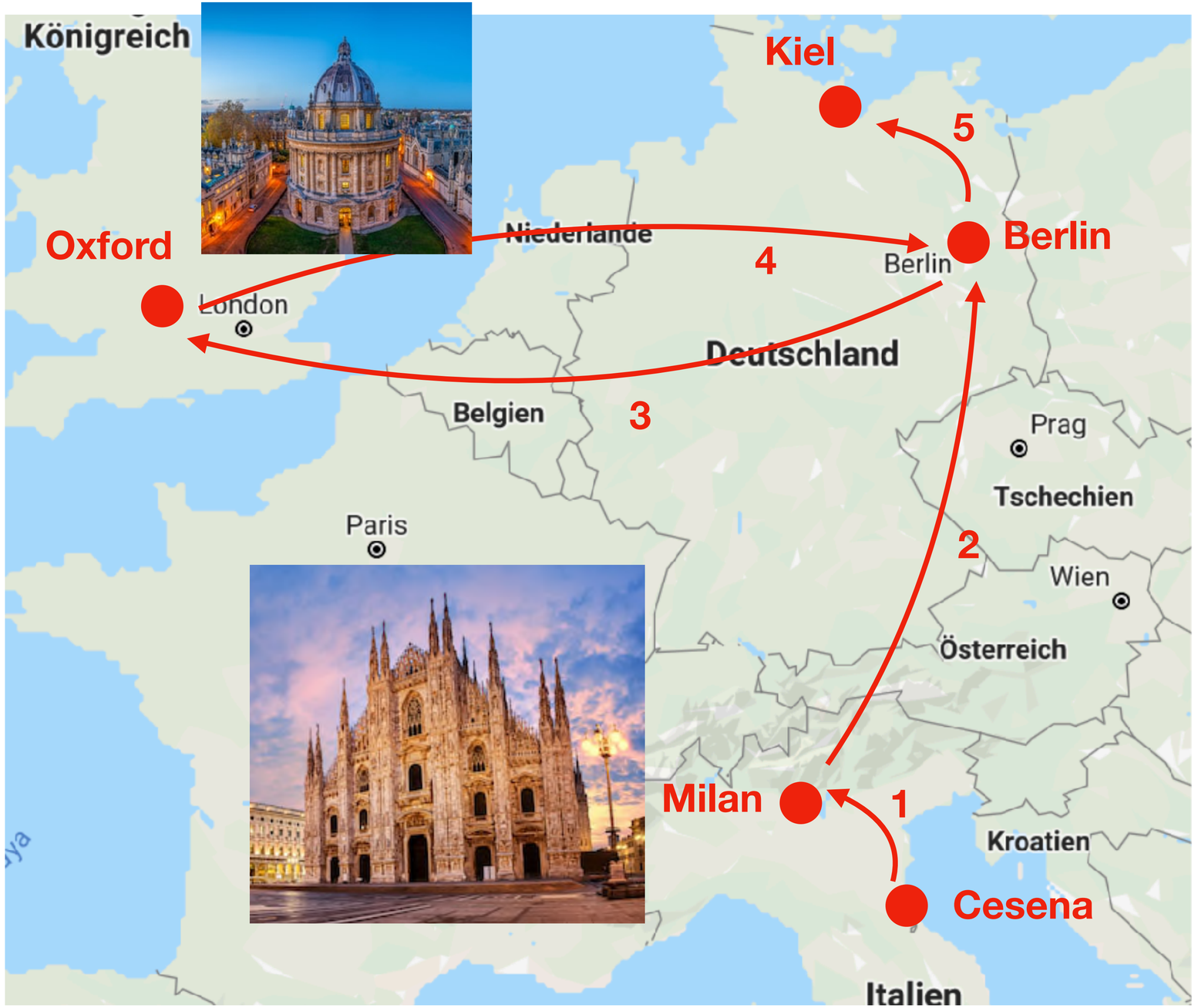
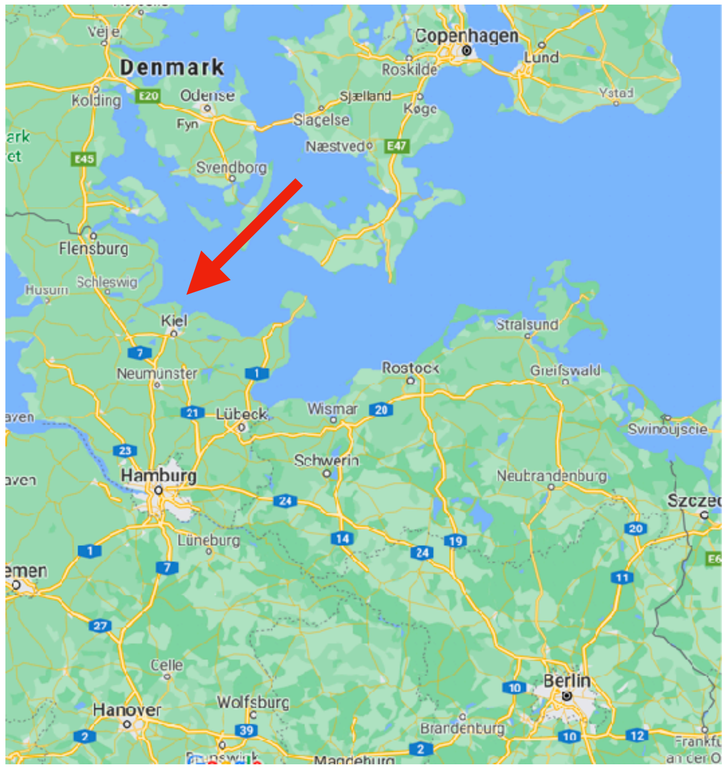
About me



from Cesena
1 Master in Milan
2 PhD in Berlin (FHI)
3 Postdoc in Oxford
4 Postdoc in Berlin
5 Since March 2020 Kiel

The University of Kiel (founded in 1665)

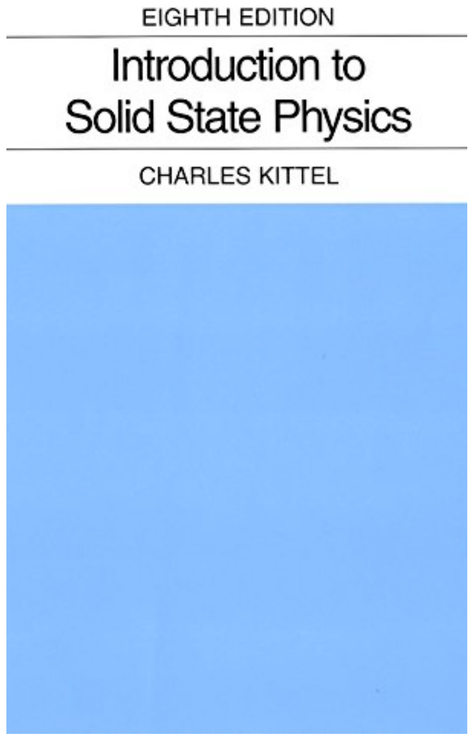


Max Planck

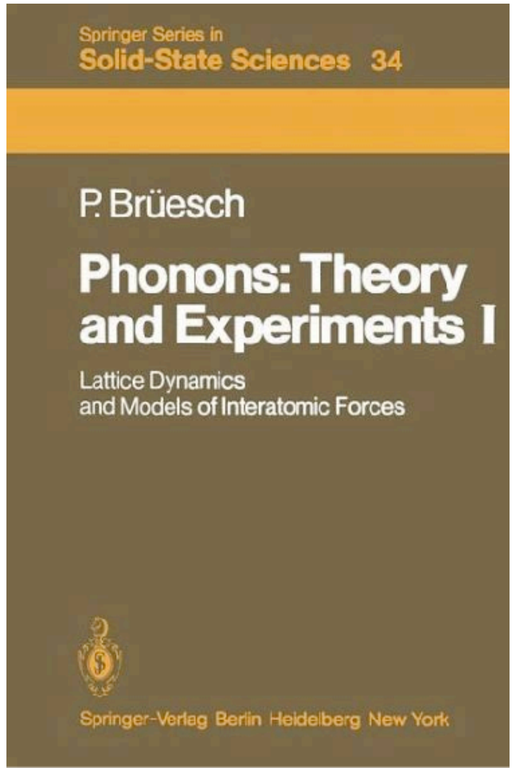
Hans Geiger

Heinrich Hertz

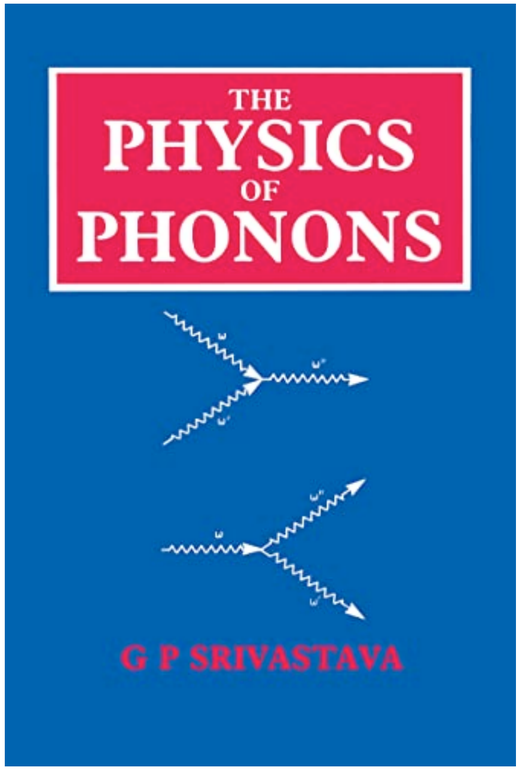
Phonons: recommended books



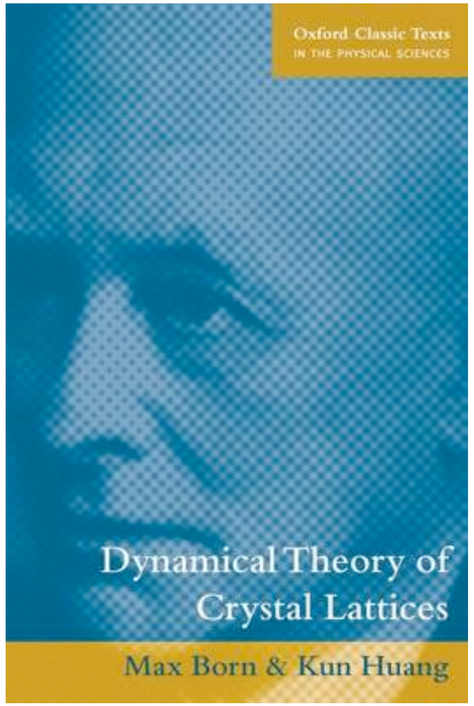
C. Kittel
Introduction to Solid-State Physics
Wiley (2004)



P. Brüesch
Phonons: Theory and experiments
Volumes 1, 2
Springer (1982)

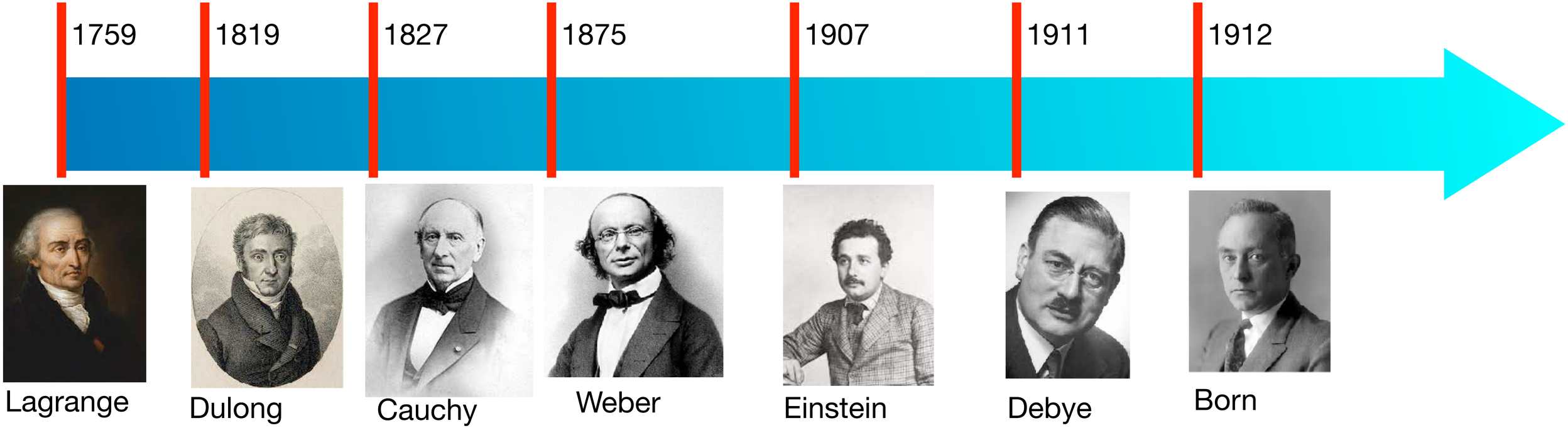


G. P. Srivastava
The Physics of Phonons
Taylor & Francis (1990)



M. Born, K. Huang
Dynamical Theory of Crystal Lattices
Oxford University Press (1954)

Early developments of the lattice dynamics



(1759) Lagrange: Equation of motions for a continuous string

(1819) Dulong and **Petit**: Measurement of the specific heat for 13 solids

Dulong-Petit law : The product of the atomic masses and the specific heat is (roughly) a constant.

(1827) Cauchy: Dynamics of mass points with forces between them

(1875) Weber: The specific heat of Si, B, C deviates from the Dulong-Petit law.

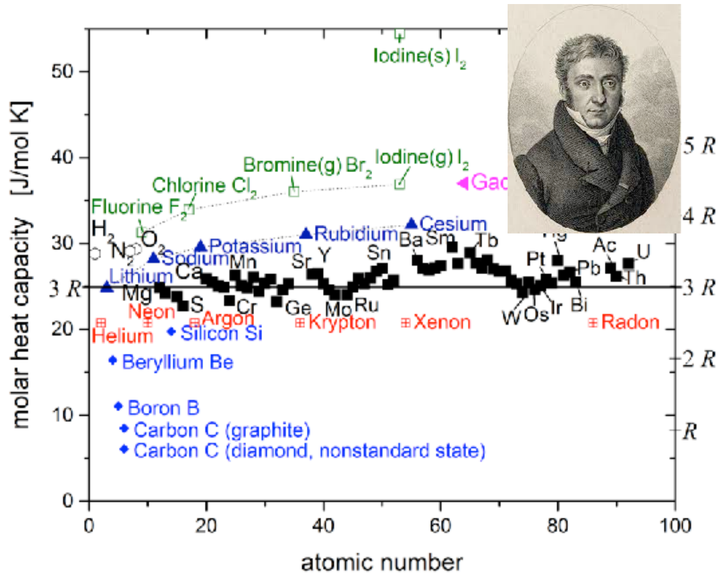
(1907) Einstein: Theory of specific heat: including atomic motion

(1911) Debye: Theory of specific heat: including **collective** atomic motion

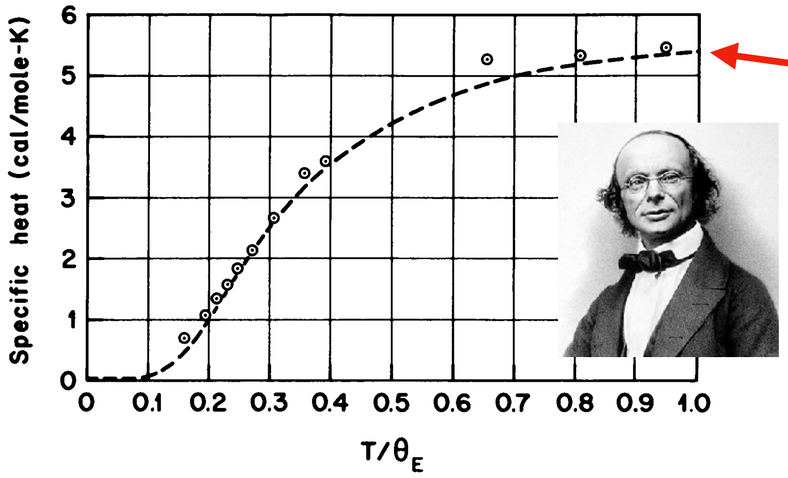
(1912) Born-van-Karman: Modern theory of phonons in a periodic 3D lattice

Early theory of specific heat

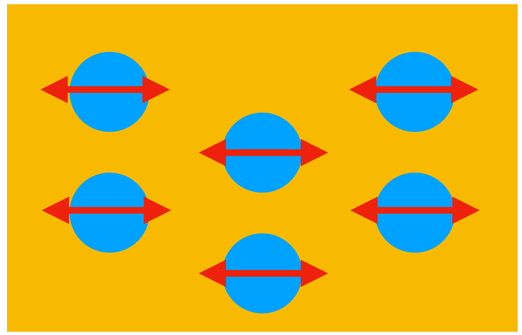
The Dulong-Petit Law: $c_v(T) \approx 3N_a k_B$



... and its break down:



The Einstein model of the specific heat



Each atom → harmonic oscillator

Frequency ω_E

Bose-Einstein statistics

$$n(T) = [e^{\hbar\omega_E/k_BT} - 1]^{-1}$$

Vibrational energy of the oscillators

$$U(T) = \sum \hbar\omega_E n(T)$$

Specific heat:

$$c(T) = \partial U(T)/\partial T = 3N_a k_B \left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{e^{\frac{\hbar\omega_E}{k_B T}}}{(e^{\frac{\hbar\omega_E}{k_B T}} - 1)^2}$$

The model reproduces the low and high-temperature limit

New paradigm: **Atom vibrations determine the temperature dependence of the specific heat**

Part 1

Phonons: from 1D to real materials

Rigorous formulation: the many-body Hamiltonian

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{e-e} + \hat{V}_{e-n} + \hat{V}_{n-n}$$

Kinetic energy

$$\hat{T}_e = \sum_{i=1}^{N_e} -\frac{\hat{\nabla}_i^2}{2} \quad , \quad \hat{T}_n = \sum_{I=1}^{N_n} -\frac{\hat{\nabla}_I^2}{2M_I}$$

Coulomb interaction

$$\hat{V}_{e-e} = \frac{1}{2}\sum_{ij}^{N_e} \frac{1}{|\hat{r}_i - \hat{r}_j|} \quad , \quad \hat{V}_{e-n} = \sum_{i}^{N_e}\sum_{I}^{N_n} \frac{-Z_I}{|\hat{r}_i - \hat{R}_I|} \quad , \quad \hat{V}_{n-n} = \frac{1}{2}\sum_{IJ}^{N_n} \frac{Z_I Z_J}{|\hat{R}_I - \hat{R}_J|}$$

$$\hat{H}\,|\Phi\rangle = E\,|\Phi\rangle$$

- $\hat{H}$: Many-body Hamiltonian
- E: Energy of electrons + nuclei
- $|\Phi\rangle$: wave-function for electrons and nuclei

$$\hat{H} = \hat{H}(\{\hat{r}_i, \hat{R}_I\})$$

$$\Phi_n = \Phi_n(\{\hat{r}_i, \hat{R}_I\})$$

The Born-Oppenheimer approximation

The Born-Oppenheimer approximation:

$$\Psi_s(r, R) \simeq \psi_\nu(r; R)\chi_{\nu s}(R)$$

electrons (fixed nuclei)

$$\hat{H}^{\mathrm{el}}\,\psi_\nu(r) = E_\nu^{\mathrm{el}}\psi_\nu(r)$$

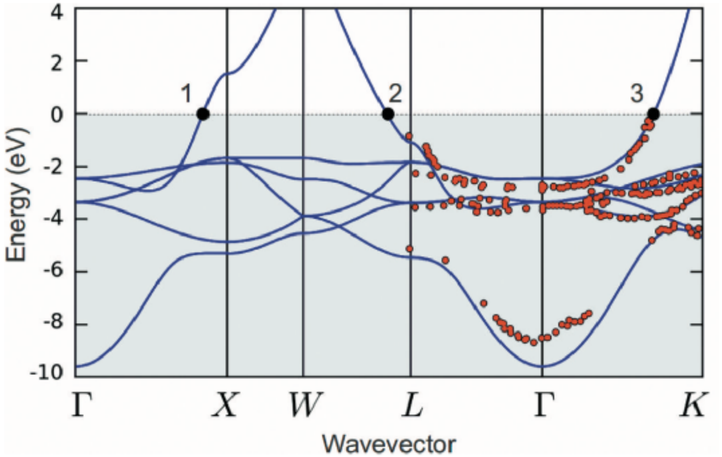
nuclei (fixed electrons)

$$\hat{H}^{\mathrm{nuc}}\,\chi_{\nu s}(R) = E_s\,\chi_{\nu s}(R)$$

Density functional theory (DFT): $n(r) \Leftrightarrow \Psi$

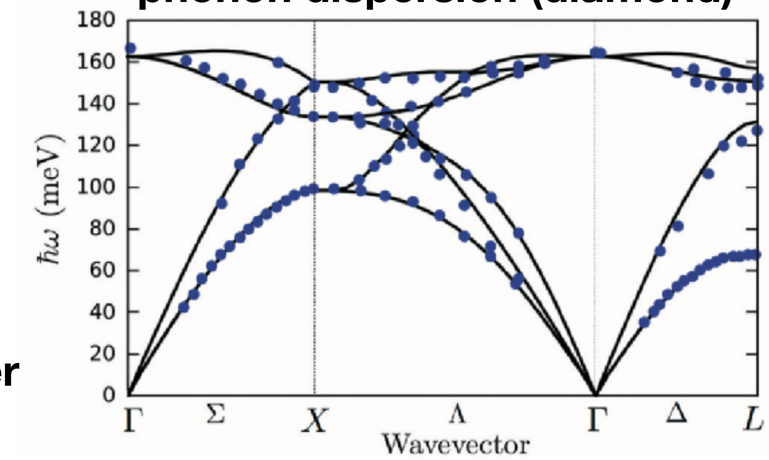
Hohenberg and Kohn, Phys. Rev. (1964)
Kohn and Sham, Phys. Rev. (1965)

Electron band structure (Copper)



electron-phonon interactions (beyond the Born-Oppenheimer approximation)

phonon dispersion (diamond)



Figs.: Giustino, Materials Modelling using Density Functional Theory (2014)

Exp.: [1] Courths, and Hüfner, Phys. Rep. 112, 53 (1984)
[2] Warren et al., Phys. Rev. 158, 805 (1967)

The lattice Schrödinger equation (or equation of motion)

Quantum

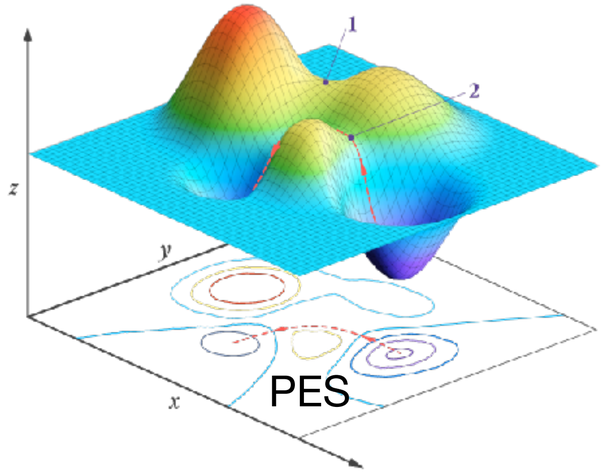
Nuclear Schrödinger equation

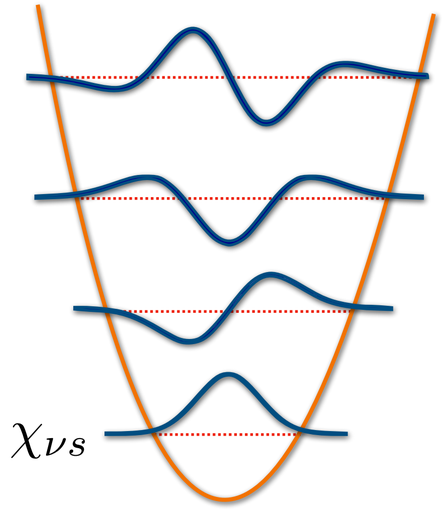
$$\hat{H}^{\text{nuc}}\,\chi_{\nu s}(R) = E_s\,\chi_{\nu s}(R)$$

$$\hat{H}^{\text{nuc}} = \hat{T}_n + \hat{U}$$

nuclear kinetic energy

potential energy surface (PES)





Classical

Classical problem:

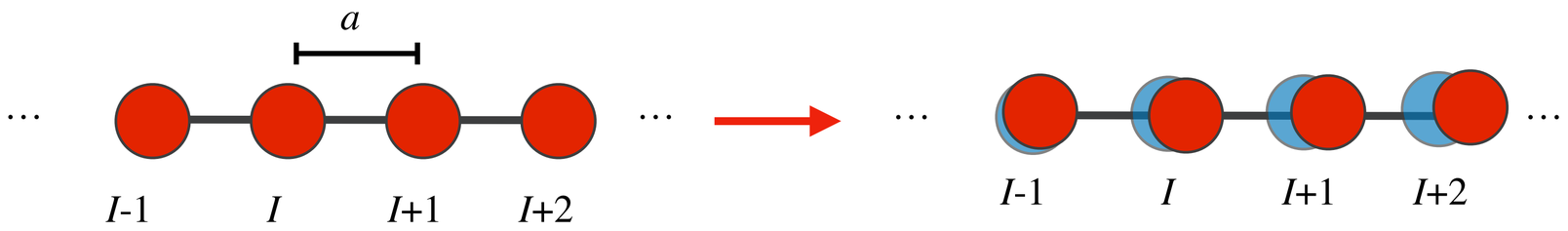
$$M_I \ddot{R}_I = -\frac{\partial U(\{R\})}{\partial R_I}$$

Quantum picture ⟷ **Classical picture**

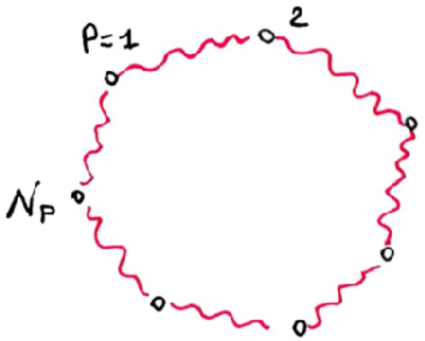
Equivalent in the Harmonic approximation

Atomic displacements in a (1D) crystal lattice

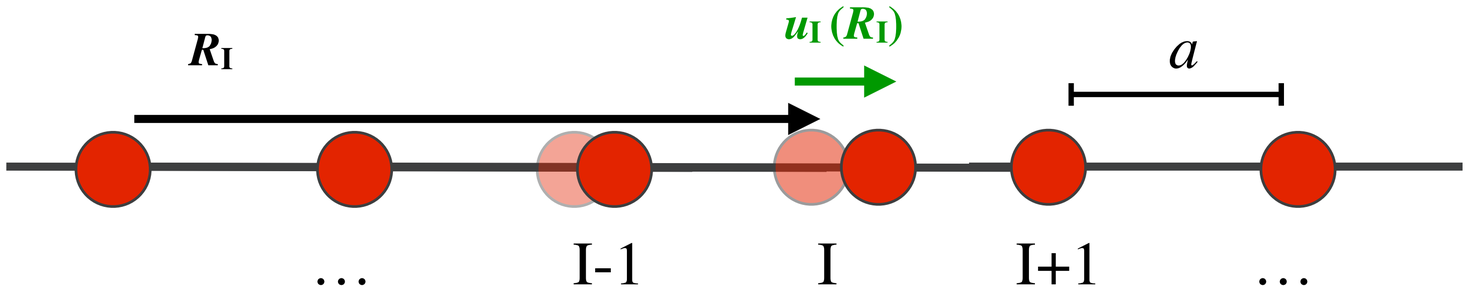
One-dimensional case
(Born-von-Karman boundary conditions)



- 1 atom per unit cell
- N unit cells (periodically repeated)



3D case has more complex notation, but otherwise equivalent



R_I atomic position at equilibrium

u_I displacement from equilibrium

Nuclei at equilibrium → Displaced nuclei

$$\{R_I\} \rightarrow \{R_I + u_I\}$$
$$U(\{R_I\}) \rightarrow U(\{R_I + u_I\})$$

Classical equation of motion (Newton's law)

$$M_I \ddot{R}_I = -\frac{\partial U(\{R\})}{\partial R_I} \rightarrow M_I \ddot{u}_I = -\frac{\partial U(\{u\})}{\partial u_I}$$

Our goal: solve the lattice equation of motion

The harmonic approximation

Central ingredient: The potential energy surface $U(\{R\}) = U(R_1, R_2, \ldots, R_N)$
Highly-dimensional and very complex to handle **(approximation needed)**

$$M_I \ddot{u}_I = -\frac{\partial U(\{R\})}{\partial u_I}$$

If the displacements $\{u_I\}$ are small … we can Taylor expand the electronic ground-state energy

$$U(\{R_I + u_I\}) = U_0(\{R_I\})$$

1st order $+\sum_I \left.\frac{\partial U}{\partial u_I}\right|_{u_I=0} u_I$ — exactly zero at equilibrium

2nd order $+\frac{1}{2}\sum_{IJ} \left.\frac{\partial^2 U}{\partial u_I \partial u_J}\right|_{u_I=0} u_I u_J$

3rd order $+\frac{1}{3!}\sum_{IJL} \left.\frac{\partial^3 U}{\partial u_I \partial u_J \partial u_L}\right|_{u_I=0} u_I u_J u_L + \cdots$ — neglected

Harmonic approximation (not valid for liquids/gases)

$$U \simeq U^{(\mathrm{h})} = U_0 + \frac{1}{2}\sum_{IJ} \left.\frac{\partial^2 U}{\partial u_I \partial u_J}\right|_{u_I=0} u_I u_J$$

second-order force constant matrix (2FC)

$$\Phi_{IJ} \equiv \left.\frac{\partial^2 U}{\partial u_I \partial u_J}\right|_{u_I=0}$$

$$U^{(\mathrm{h})} = U_0 + \frac{1}{2}\sum_{IJ} \Phi_{IJ}\, u_I u_J = U_0 + \mathbf{u}^\dagger \cdot \mathbf{\Phi} \cdot \mathbf{u}$$

Lattice equation of motion in the harmonic approximation

$$F_I = M_I \ddot{u}_I = -\frac{\partial U^{(\mathrm{h})}(\{u\})}{\partial u_I} \rightarrow M_I \ddot{u}_I = -\frac{\partial}{\partial u_I}\left[U_0 + \frac{1}{2}\sum_{IJ} \Phi_{IJ}\, u_I u_J\right] = \sum_J \Phi_{IJ}\, u_J$$

Dynamics of a 1D lattice in the harmonic approximation

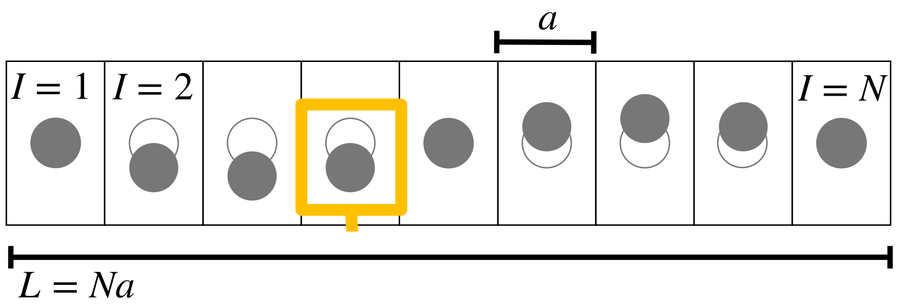
$$M\ddot{u}_I = \sum_J \Phi_{IJ} u_J$$ ***A second-order differential equation for the displacements***

Ansatz for the displacement.
Most general function that:
(i) satisfies the EOM
(ii) obey the boundary conditions
***(iii)* not an approximation**

$$u_I = u_q e^{iqR_I} e^{-i\omega_q t}$$

Bloch form — time periodicity

Key quantities:
- Phonon frequency ω_q
- Phonon eigenvector u_q



wave vector $q = 2\pi/\lambda$
wave length $\lambda = L/n$ with $n = \{1,2,\ldots,N\}$

$$M\omega_q^2 u_q = \sum_J \Phi_{IJ} e^{iq(R_J - R_I)} u_q$$

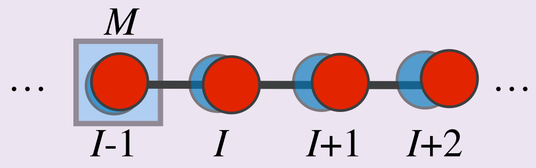
Dynamical matrix: $$D(q) = \sum_J M^{-1}\Phi_{IJ} e^{iq(R_J - R_I)} = g\sin(qa)$$

Secular equation (can be solved to obtain ω_q and u_q)

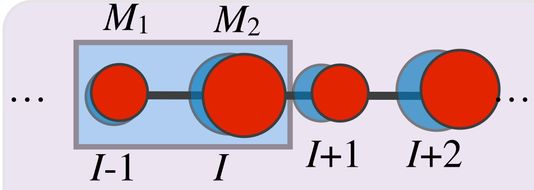
$$[D(q) - \omega_q^2]u_q = 0 \rightarrow \omega_q^2 = D(q)$$

The problem is most easily solved by considering the collective motion of the ions (i.e., a phonon)

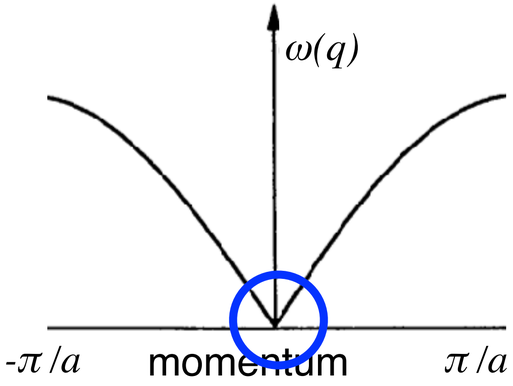
Phonon dispersion for the 1D chain

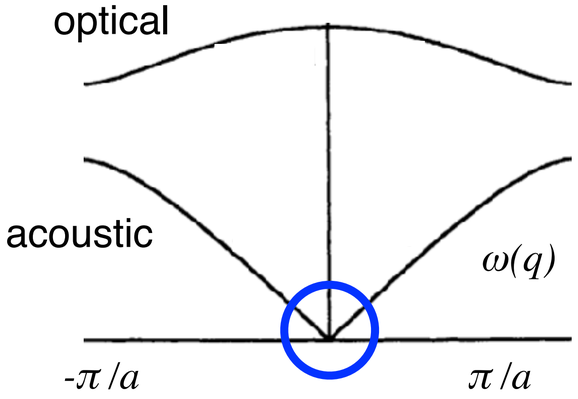


1D chain with identical atoms



1D chain with different atoms





Acoustic modes vanish at q=0 (equivalent to crystal translation)

In general: $N_{\text{ph}}^{\text{1D}} = N_{\text{atoms}}$ $N_{\text{ph}}^{\text{3D}} = 3N_{\text{atoms}}$

Summary of phonon calculations (1D chain)

0 $M_I \ddot{u}_I = -\dfrac{\partial U(\{R\})}{\partial u_I}$ Lattice EOM

$M\ddot{u}_I = \sum_J \Phi_{IJ} u_J$

1 Second-order force constant $\Phi_{IJ} \equiv \left.\dfrac{\partial^2 U}{\partial u_I \partial u_J}\right|_{u_I=0}$

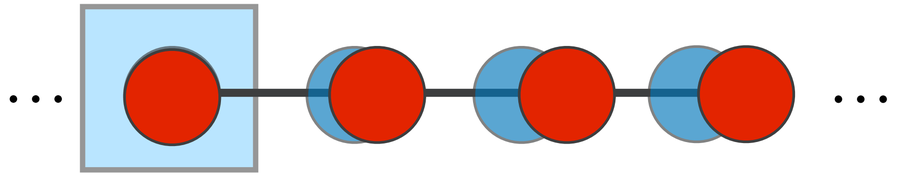
2 Ansatz $u_I = u_q e^{iqR_I} e^{-i\omega_q t}$

3 Dynamical matrix $D(q) = \sum_J M^{-1}\Phi_{IJ} e^{iq(R_J - R_I)}$

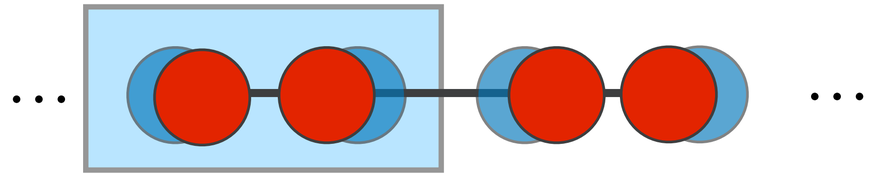
4 $M\omega(q)^2 = D(q)$ Secular equation

Classification of lattice vibrations

- **Acoustic phonons:** *in-phase* vibrations of the atoms in the unit cell



- **Optical phonons:** *out-of-phase* vibrations of the atoms in the unit cell

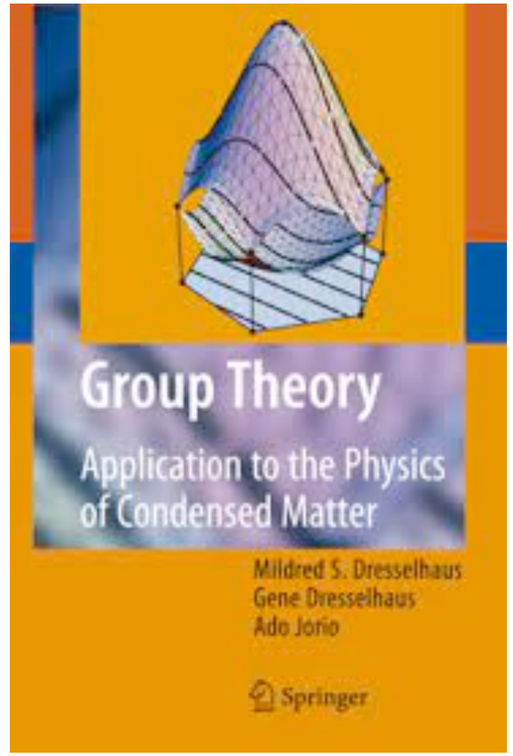


(at least 2 atoms per unit cell are needed)

- **Transverse phonons:** displacement perpendicular to propagation
- **Longitudinal phonons:** displacement parallel to propagation

- **Transverse Optical (TO)**
- **Longitudinal Optical (LO)**
- **Transverse Acoustic (TA)**
- **Longitudinal Acoustic (LA)**

Symmetry classification based on group theory



Dresselhaus,
Group Theory: Applications to the Physics of Condensed Matter
Springer

Phonons: from 1D to 3D

- N unit cells
- N_b atoms in a unit cell
- 3 spatial dimensions

$$\{\mathbf{R}_I\} \rightarrow \{\mathbf{R}_I + \mathbf{u}_I\}$$

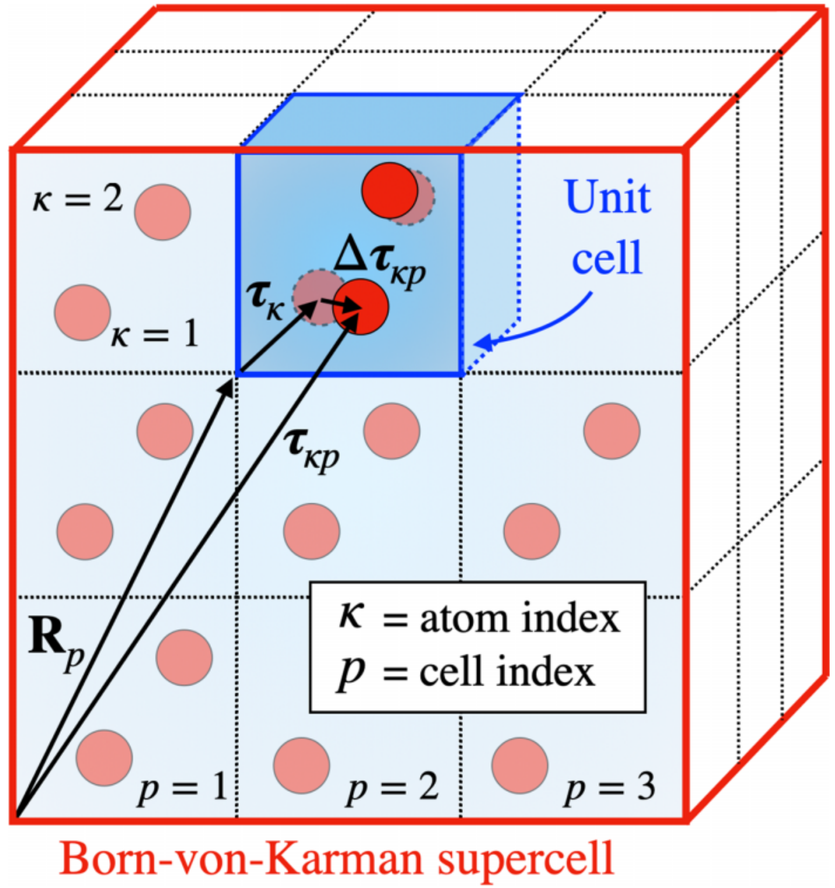
The potential energy surface

In 1D:
$$U^{(h)}(R_1, \cdots, R_N) \simeq U_0 + \frac{1}{2} \sum_{IJ} \left. \frac{\partial^2 U}{\partial u_I \partial u_J} \right|_{u_I=0} u_I u_J$$

In 3D:
$$U^{(h)}(\mathbf{R}_1, \mathbf{R}_2, \cdots) \simeq U_0 + \frac{1}{2} \sum_{\kappa\kappa'}^{N_{atoms}} \sum_{pp'}^{N_p} \sum_{\alpha\alpha'}^{x,y,z} \left. \frac{\partial^2 U}{\partial u_{\kappa\alpha p} \partial u_{\kappa'\alpha' p'}} \right|_{u=0} u_{\kappa\alpha p} u_{\kappa'\alpha' p'}$$

second-order force constant matrix
$\Phi_{\kappa\alpha p, \kappa'\alpha' p'}$

atoms — cells — coordinates



Born-von-Karman supercell

Straightforward generalization from 1D to 3D

Summary of phonon calculations (1D chain)

0 $M_I \ddot{u}_I = -\dfrac{\partial U(\{R\})}{\partial u_I}$ Lattice EOM

$$M\ddot{u}_I = \sum_J \Phi_{IJ} u_J$$

1 Second-order force constant $\Phi_{IJ} \equiv \left.\dfrac{\partial^2 U}{\partial u_I \partial u_J}\right|_{u_I=0}$

2 Dynamical matrix $D(q) = \sum_J M^{-1}\Phi_{IJ} e^{iq(R_J - R_I)}$

3 Ansatz $u_I = u_q\, e^{iqR_I}\, e^{-i\omega_q t}$

4 $M\omega(q)^2 = D(q)$ Secular equation

Phonon calculations in 3D crystals

0 $M_\kappa \ddot{u}_{\kappa\alpha p} = -\dfrac{\partial U(\{R\})}{\partial u_{\kappa\alpha p}}$ Lattice EOM

$$M\ddot{u}_{\kappa\alpha p} = \sum_{\kappa\alpha p} \Phi_{\kappa\alpha p,\kappa'\alpha' p'} u_{\kappa'\alpha' p'}$$

1 Second-order force constant $\Phi_{\kappa\alpha p,\kappa'\alpha' p'} = \dfrac{\partial^2 U}{\partial u_{\kappa\alpha p}\partial u_{\kappa'\alpha' p'}}$

2 Dynamical matrix $D(q) = \sum_{\kappa\alpha p} \dfrac{\Phi_{\kappa\alpha p,\kappa'\alpha' p'}}{\sqrt{M_\kappa M_{\kappa'}}} e^{i\mathbf{q}(\mathbf{R}_p - \mathbf{R}_{p'})}$

3 Ansatz $u_{\kappa\alpha p} = u_{\mathbf{q}}^{\kappa\alpha}\, e^{i\mathbf{q}\mathbf{R}_{\kappa\alpha p}}\, e^{-i\omega_q t}$

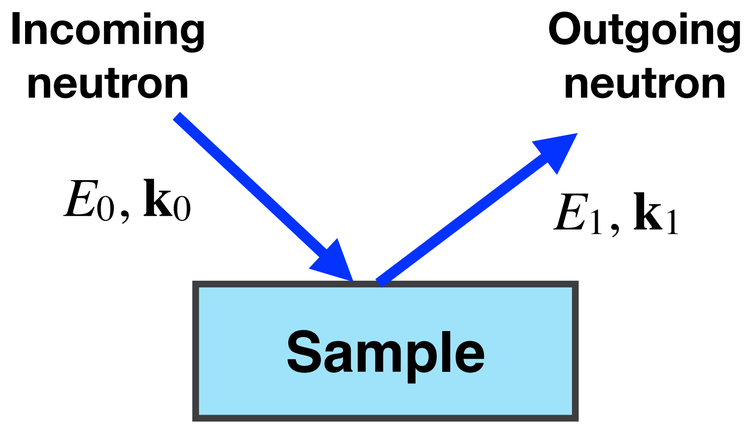
4 $\left[\mathbf{D}(\mathbf{q}) - \omega_{\mathbf{q}}^2\right] \mathbf{u}_{\mathbf{q}}^{\kappa} = 0$ **Secular equation** (eigenvalue problem, easy solution)

κ : atom index
p : cell index
α : cartesian coordinate

Part 2

Experimental measurements of the phonon dispersion

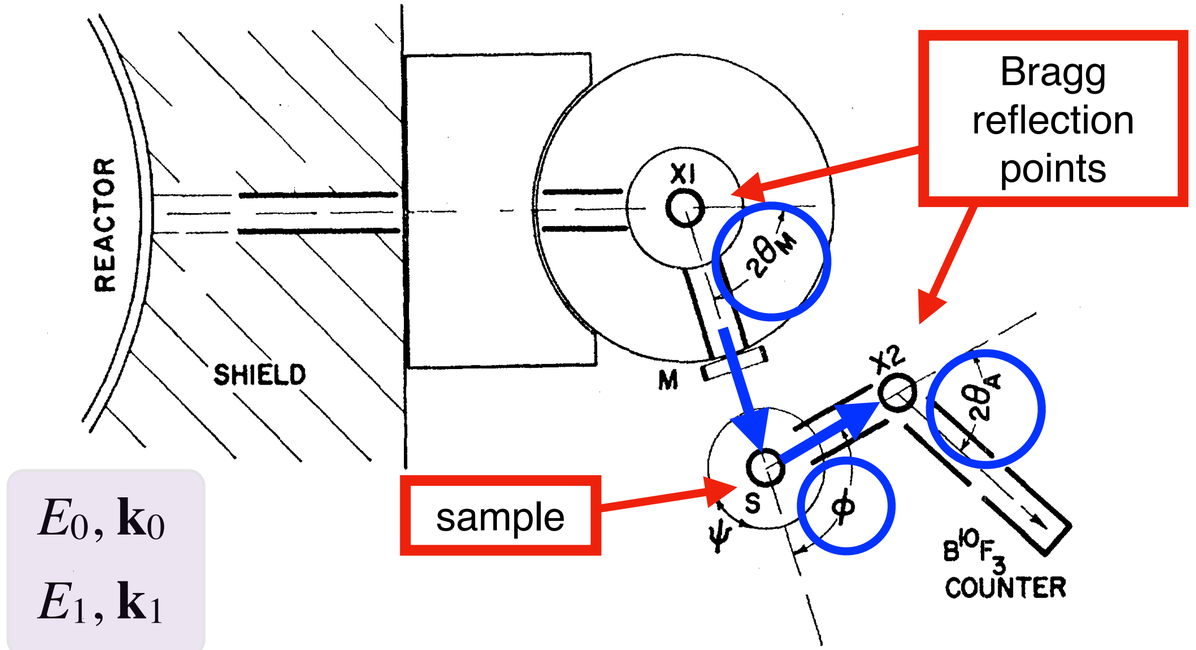
Phonon dispersions from Inelastic neutron scattering



momentum and energy conservation

$$\mathbf{k}_0 = \mathbf{k}_1 + \mathbf{q}$$ → phonon momentum

$$E_0 = E_1 + \hbar\omega_{\mathbf{q}\nu}$$ → phonon energy

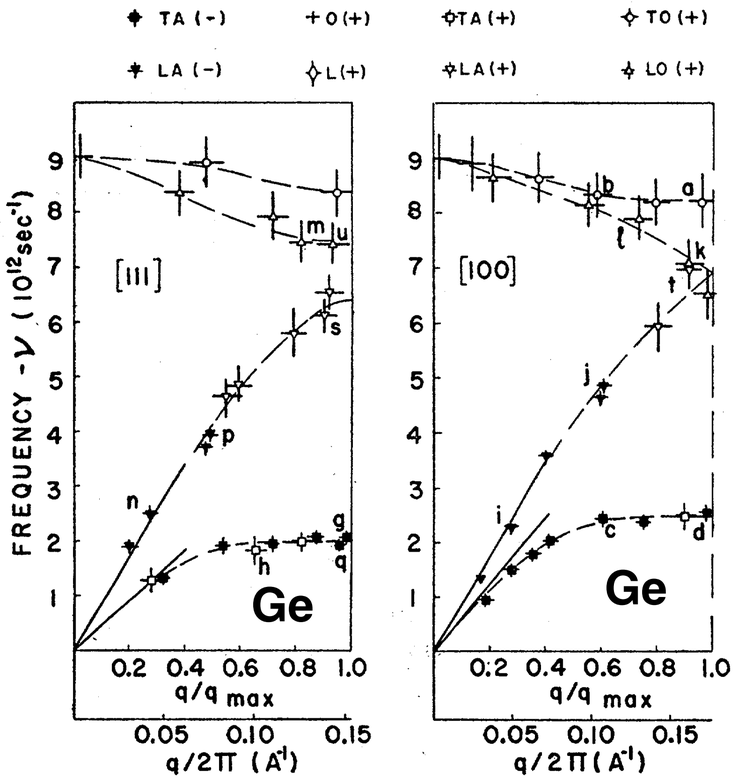


Bertram Brockhouse,
Nobel prize in Physics 1994

"for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter"

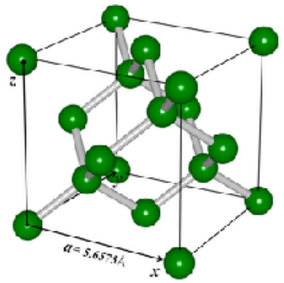
Brockhouse et al., Phys. Rev. **111**, 747 (1958)

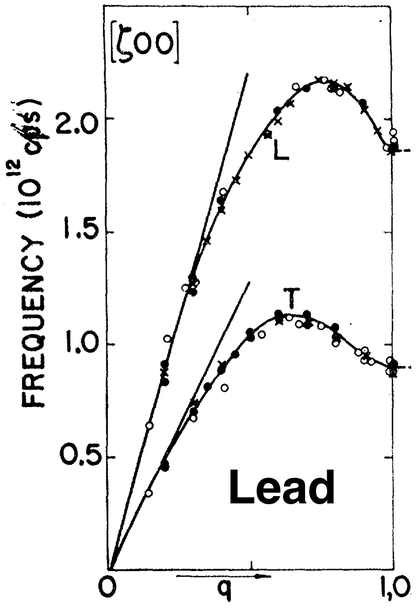
Phonons in solids: elemental semiconductors and metals



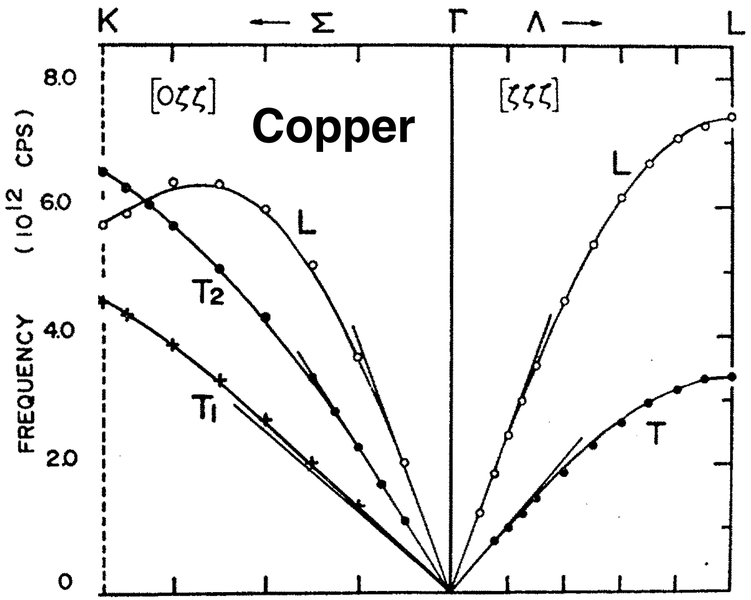
Brockhouse et al., Phys. Rev. **111**, 747 (1958)

diamond-like
crystal structure





Brockhouse et al.
Phys. Rev. **128**, 1099 (1962)



Svensson et al.
Phys. Rev. **155**, 619 (1967)

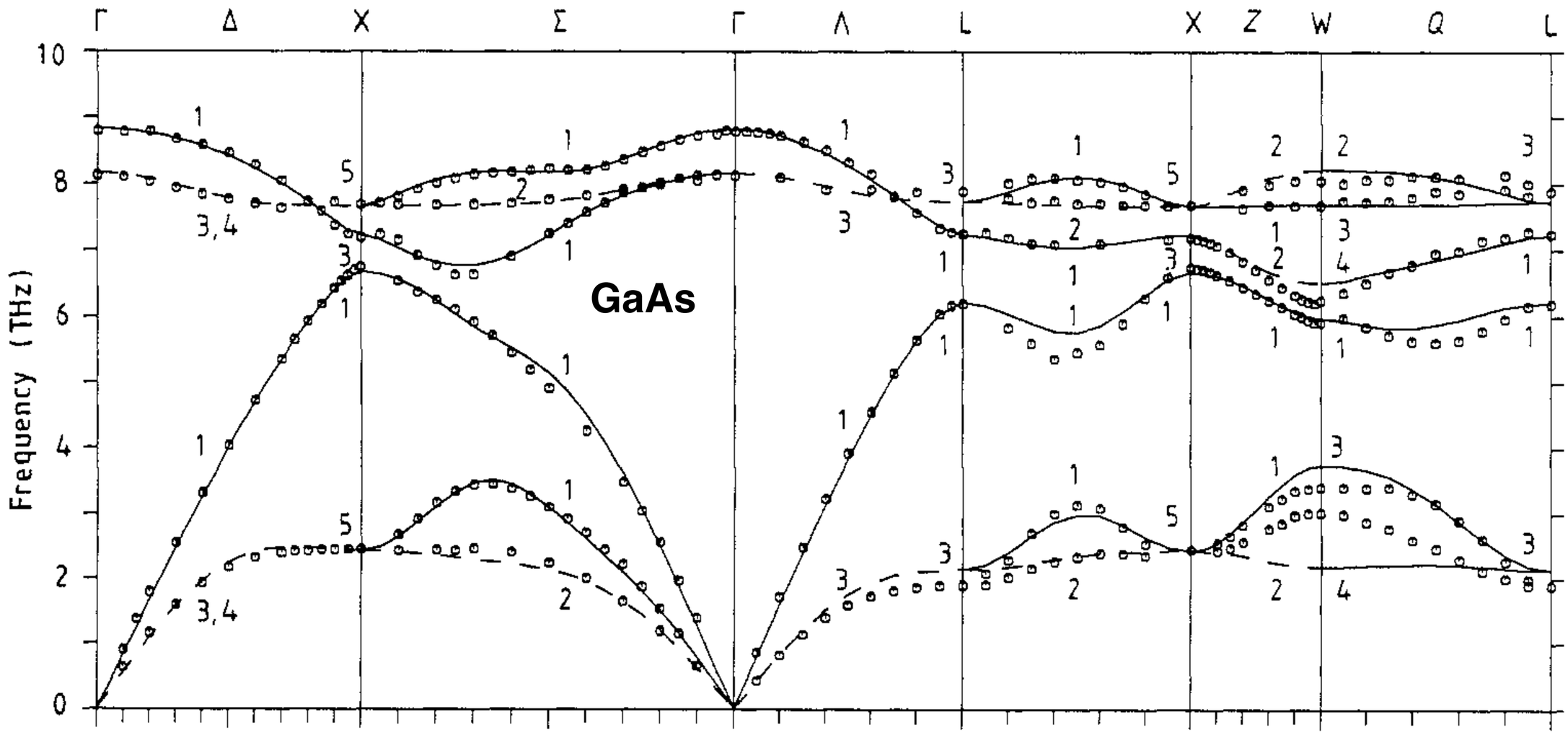
2 atoms per unit cell → 6 phonon modes
symmetry → degeneracies (only 4 modes visible)

- Longitudinal Acoustic = LA
- Transverse Acoustic = TA
- Longitudinal Optical = LO
- Transverse Optical = TO

1 atoms per unit cell → 3 phonon modes

- Longitudinal Acoustic = LA
- Transverse Acoustic = TA

Phonon dispersions of GaAs



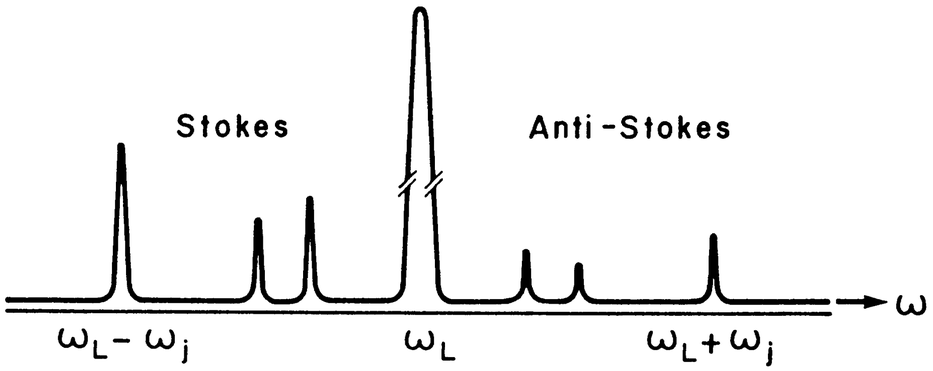
Points: **experiment**
Lines: **parametrized model** (12-14 parameters)

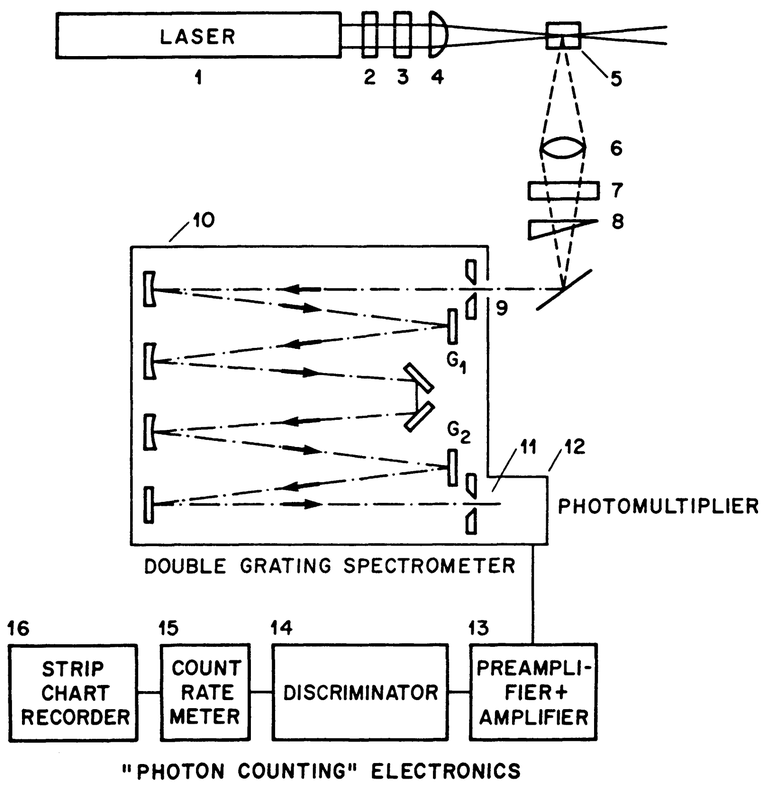
Strauch et al., J. Phys. Cond. Mat. **2**, 1457 (1990)

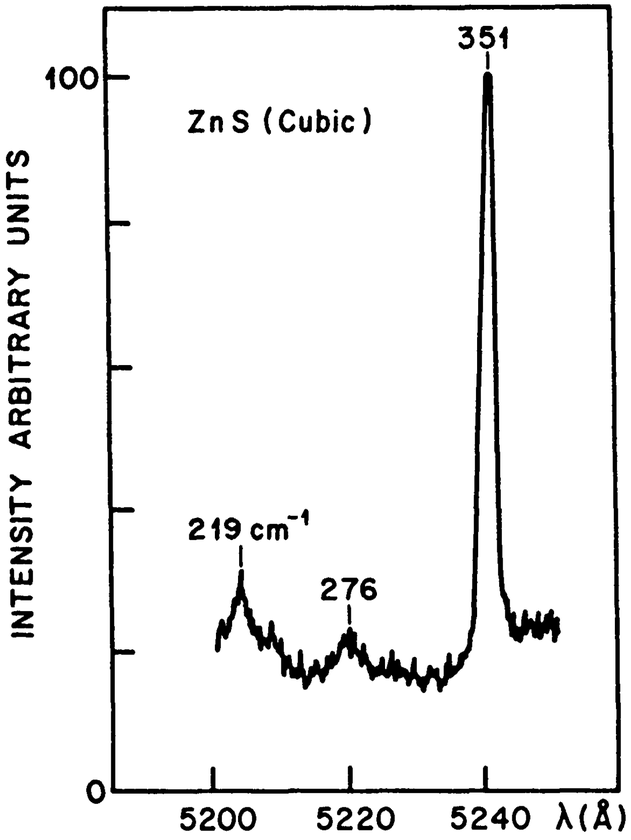
Phonons in experiments: Raman and Brillouin scattering

Raman

Nobel prize in Physics 1930

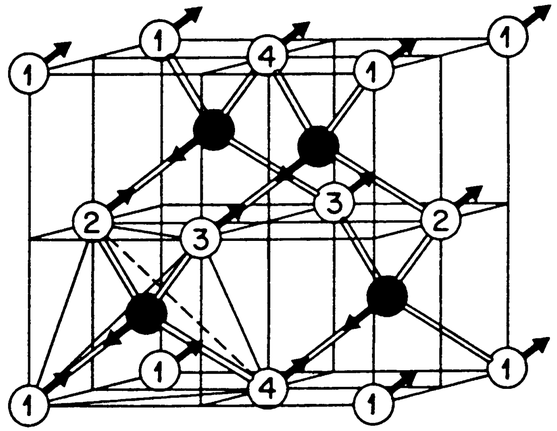




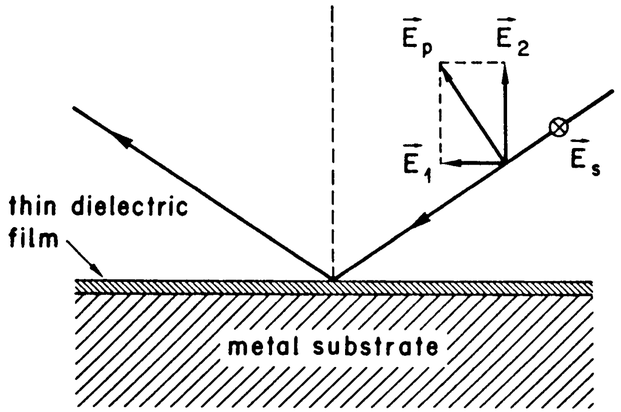


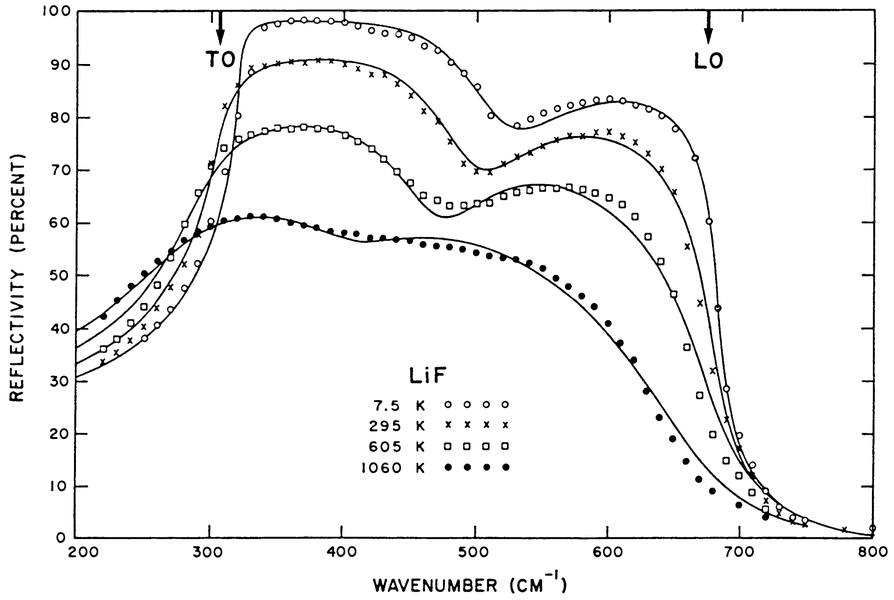
Brafman, Phys. Rev. **171**, 931 (1968)

Zinc-blend structure



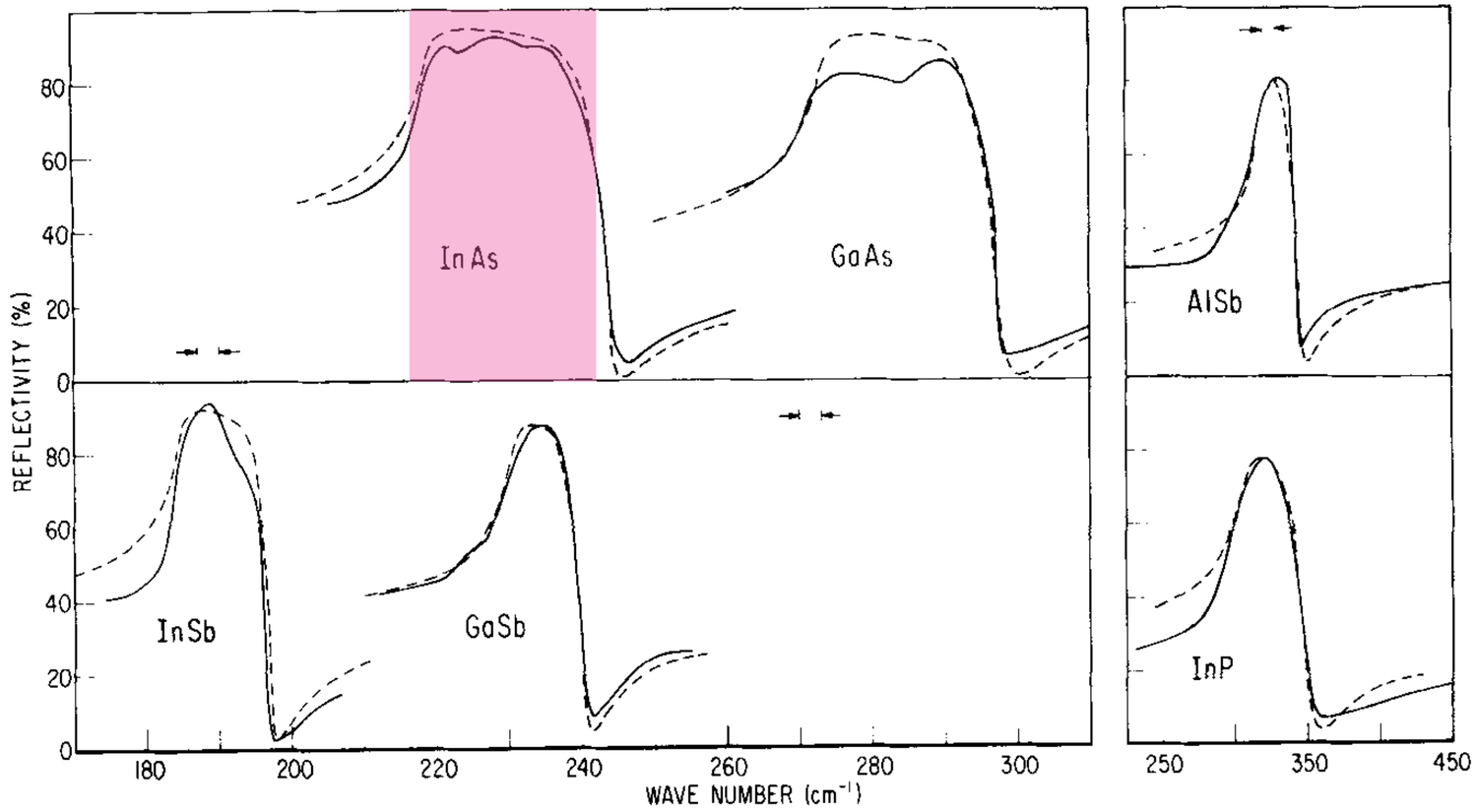
Phonons in experiments: Reflectivity measurements of polar semiconductors





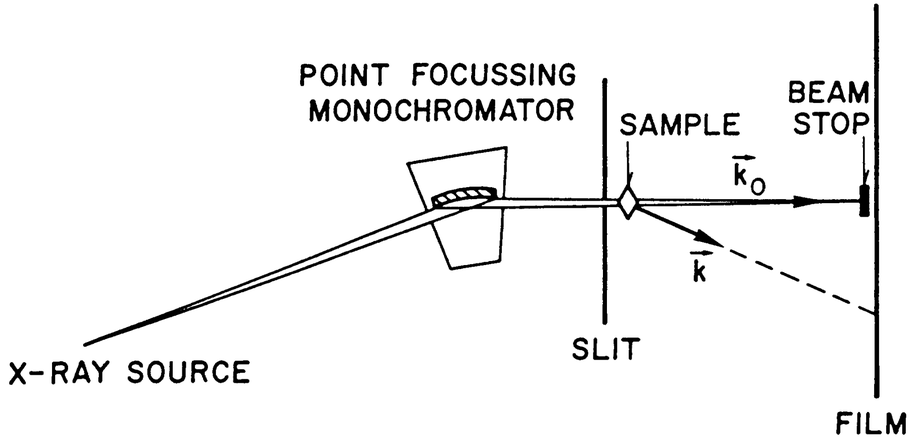
Jasperse et al, Phys. Rev. **146**, 526 (1966)

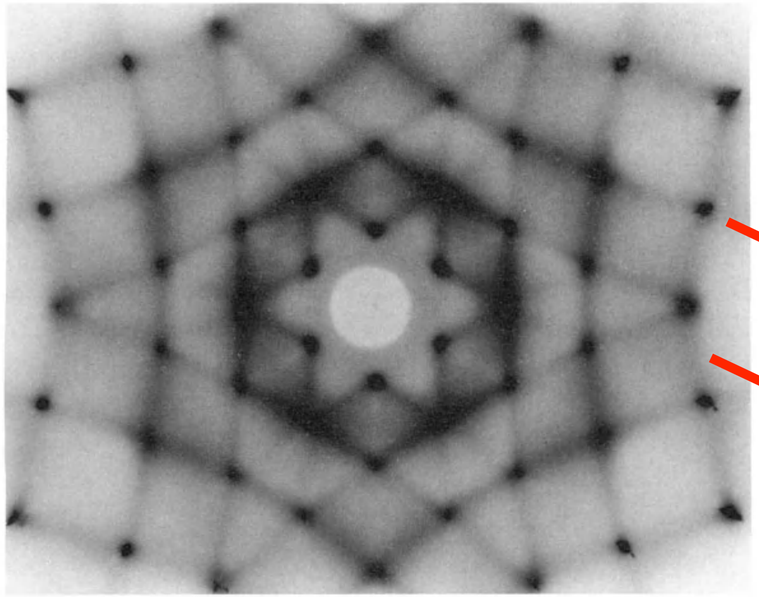
Rehstrahlen band



M. Hass, Semiconductors and Semimetals **3**, 3 (1967)

Phonons in experiments: Diffuse and elastic X-ray and electron scattering



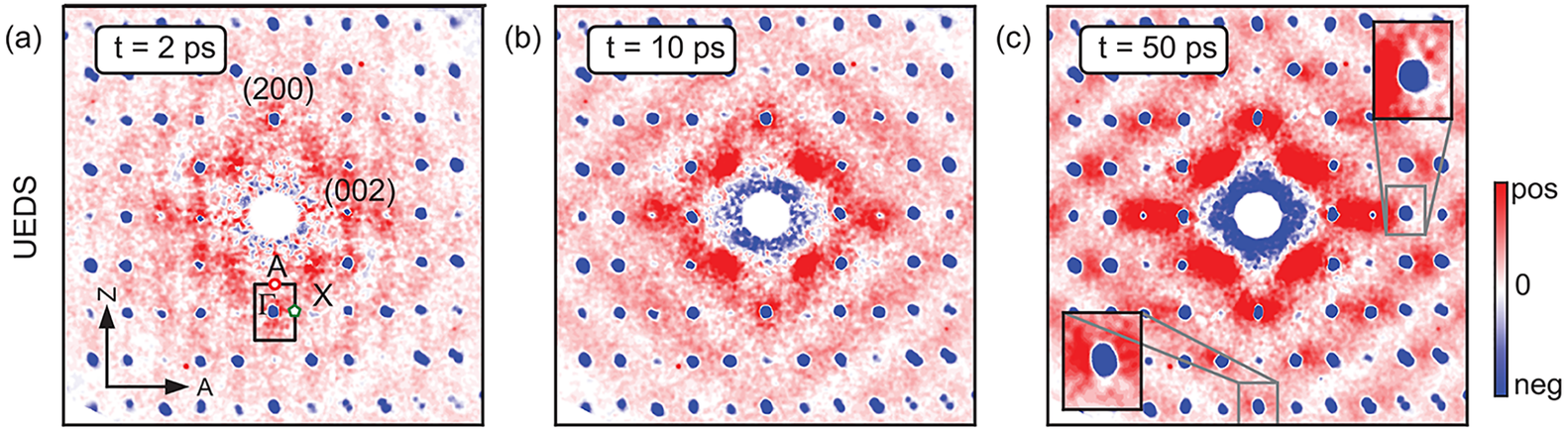


β-AgI

elastic scattering
(Bragg peak)

diffuse scattering
(phonon-assisted)

Beyeler et al. Phys. Rev. B **18**, 4570 (1978)



Ultrafast electron-diffuse scattering

Seiler, Caruso et al. Nano Lett. **21**, 6171 (2021)

Part 3

Towards ab-initio calculations of phonons

Back to theory: Phonon calculations in practice

Quantities of interest for the lattice dynamics

- phonon frequency $\omega_{\mathbf{q}\nu}$
- phonon eigenvector $u^{\kappa}_{\mathbf{q}\nu}$

- thermal conductivity
- electron-phonon interactions
- phonon lifetimes $\tau_{\mathbf{q}\nu}$
- influence of phonon in spectroscopy

Directly available from the **secular equation**

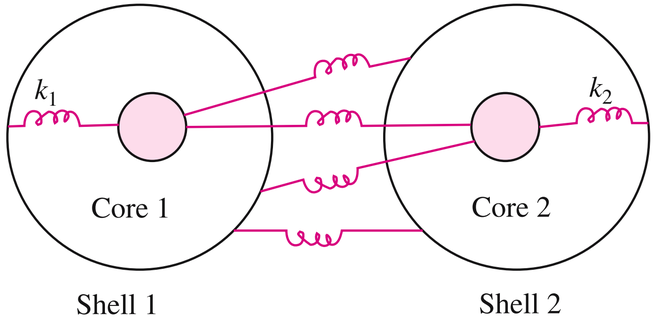
$$\left[\mathbf{D}(\mathbf{q}) - \omega^2_{\mathbf{q}}\right] \mathbf{u}^{\kappa}_{\mathbf{q}} = 0$$

We need the second-derivatives of the potential energy surface

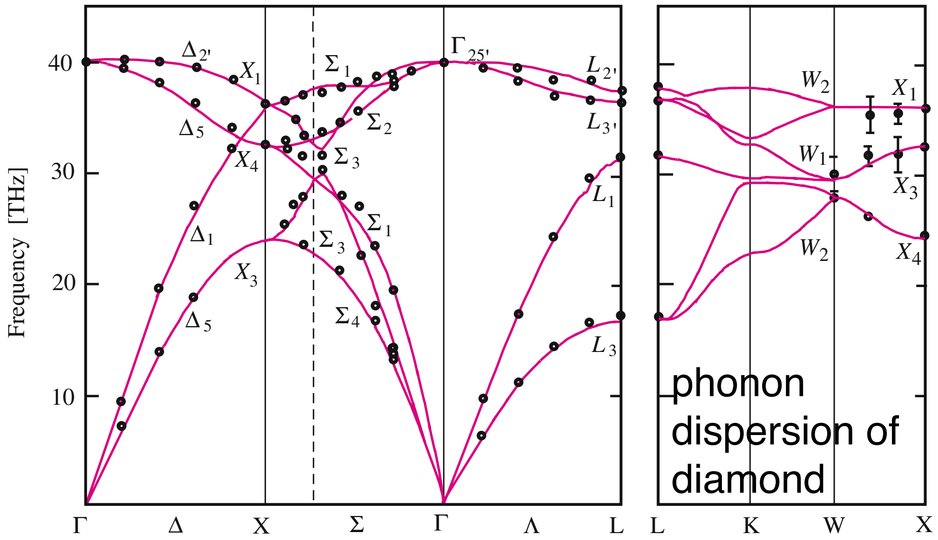
$$\Phi_{\kappa\alpha p,\kappa'\alpha' p'} = \frac{\partial^2 U}{\partial u_{\kappa\alpha p} \partial u_{\kappa'\alpha' p'}}$$

$$D(q) = \sum_{\kappa\alpha p} \frac{\Phi_{\kappa\alpha p,\kappa'\alpha' p'}}{\sqrt{M_\kappa M_{\kappa'}}} e^{i\mathbf{q}(\mathbf{R}_p - \mathbf{R}_{p'})}$$

Before ab-initio methods: Phenomenological models



Problems:
- highly-parametrized
- not predictive (need experiments)



Yu, Cardona, Fundamentals of Semiconductors, Springer

Phonon calculations from first principles

Potential energy surface from **Density functional theory** (formally exact theory)

$$U(R) = E^{\mathrm{el}}[n] + \frac{1}{2}\sum_{IJ}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

electronic energy

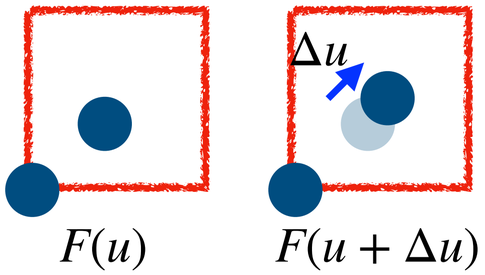
nuclear Coulomb energy

How to calculate the second derivatives?

$$\Phi_{\kappa\alpha p,\kappa'\alpha' p'} = \frac{\partial^2 U}{\partial u_{\kappa\alpha p}\partial u_{\kappa'\alpha' p'}}$$

Option 1: Finite differences

$$\Phi_{\kappa\alpha p,\kappa'\alpha' p'} = -\frac{\partial F_{\kappa\alpha p}}{\partial u_{\kappa'\alpha' p'}}$$



$$\frac{\partial F}{\partial u} = \frac{F(u+\Delta u) - F(u)}{\Delta u}$$

- [x] Very stable algorithm
- [ ] High computational cost
- [ ] Requires many DFT calculations for large supercell

Option 2: Density functional perturbation theory

REVIEWS OF MODERN PHYSICS, VOLUME 73, APRIL 2001

Phonons and related crystal properties from density-functional perturbation theory

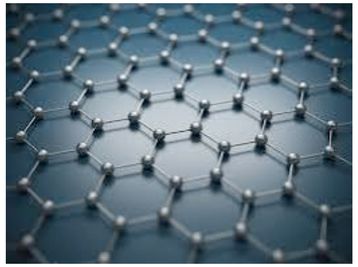
Stefano Baroni, Stefano de Gironcoli, and Andrea Dal Corso

SISSA–Scuola Internazionale Superiore di Studi Avanzati and INFM–Istituto Nazionale di Fisica della Materia, I-34014 Trieste, Italy

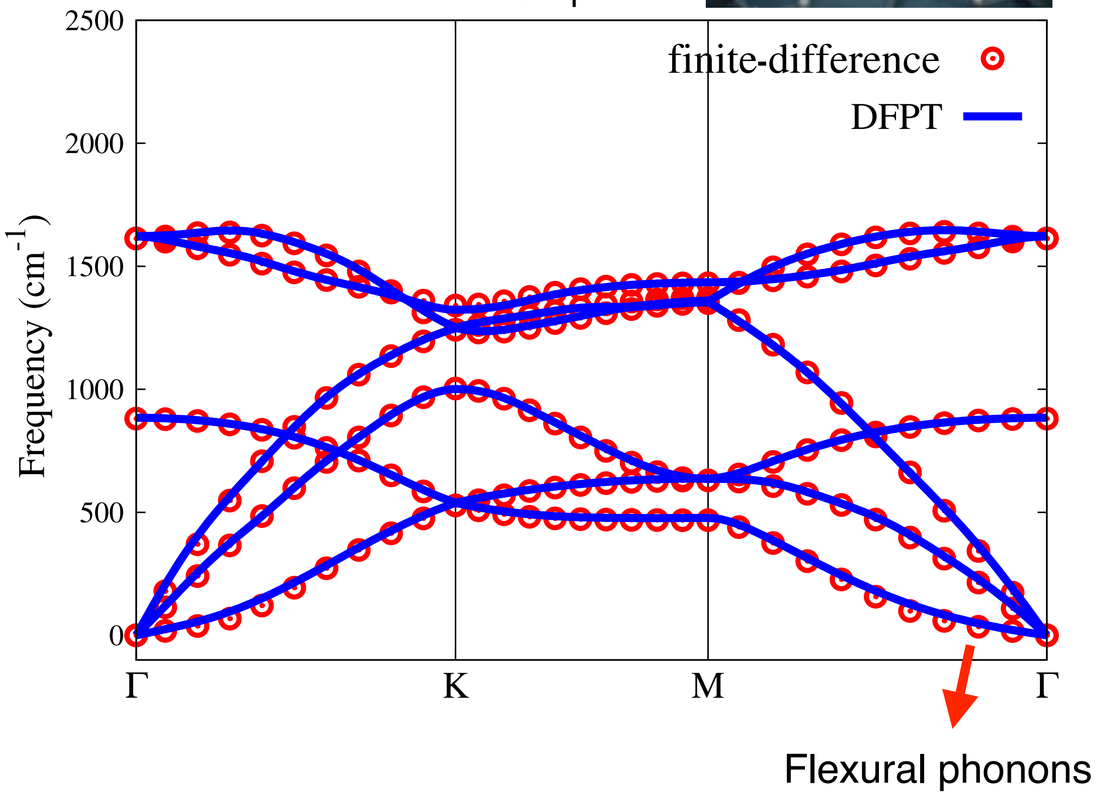
Paolo Giannozzi*

- [x] Does not requires supercell.
- [ ] More difficult to converge

Phonon calculations from first principles: DFPT vs finite differences

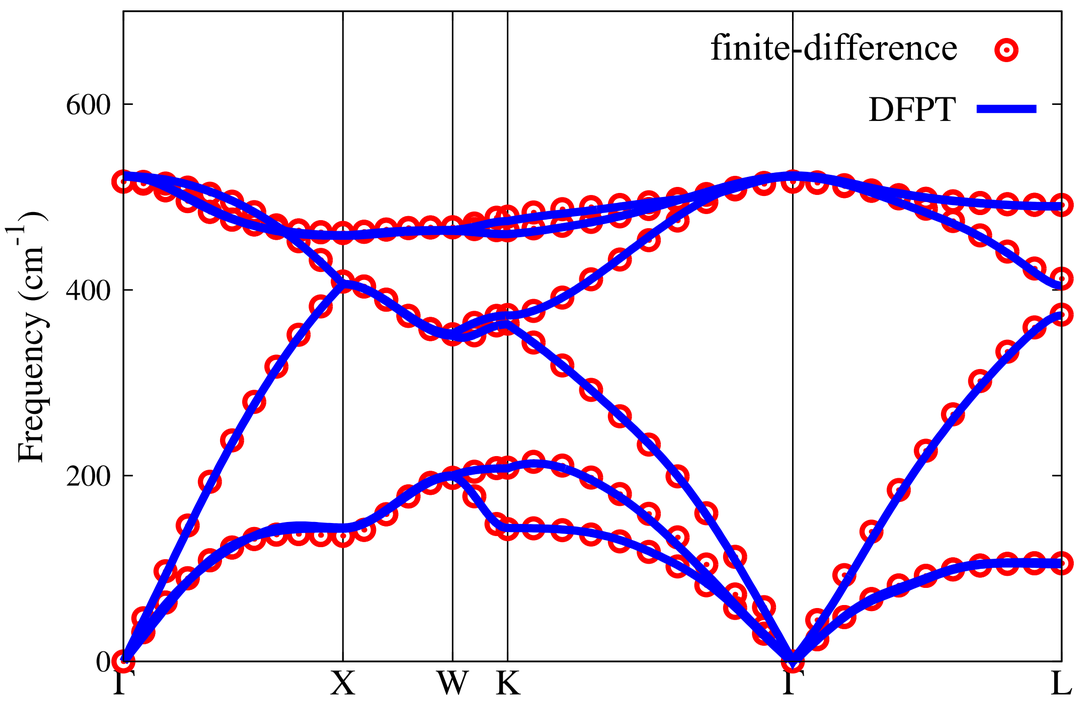


Graphene



Flexural phonons

Silicon

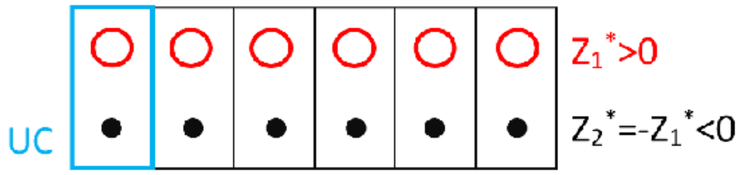


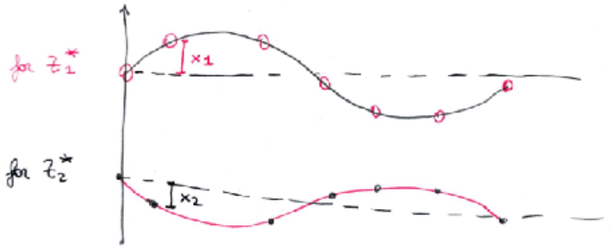
H. Shang, Comp. Phys. Commun. **215**, 26 (2017)

Phonons in polar semiconductors and long-range electric fields

Lattice vibrations are coupled to macroscopic electric fields in polar semiconductors

Polar materials: materials with finite Born effective charges $\mathbf{Z}^{\star}_{\kappa} = -\frac{\partial \mathbf{P}}{\partial \mathbf{R}_{\kappa}}$





Electric fields must be included in the lattice equation of motion

$$\mathbf{F}_I = M\ddot{\mathbf{u}}_I = -\sum_J \Phi_{IJ}\,\mathbf{u}_J - e\sum_I \mathbf{Z}^{\star}_I \mathbf{E}$$

Maxwell equation in solids:

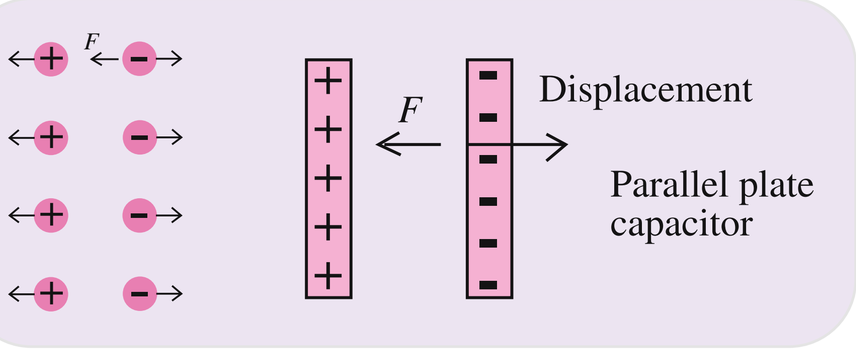
① $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}_{el} + 4\pi\mathbf{P}_{ion} = \epsilon_\infty \mathbf{E} + \frac{4\pi e}{\Omega}\sum_I \mathbf{Z}^{\star}{}_I \mathbf{u}_I$ Lattice contribution to the polarization

② $\mathbf{q}\cdot \mathrm{D} = 0$ **and** $\mathbf{q}\times \mathrm{E} = 0 \implies \mathrm{E} = \hat{\mathbf{q}}(\hat{\mathbf{q}}\cdot \mathrm{E})$

$$\mathbf{E} = -\frac{4\pi e}{\Omega}\sum_I \frac{\mathbf{q}\left(\mathbf{q}\cdot \mathbf{Z}^{\star}_I \mathbf{u}_I\right)}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}}$$

Replace $\mathbf{E}$ into $\mathbf{F}_I$

$$\mathbf{F}_I = M\ddot{\mathbf{u}}_I = -\sum_J \left[\Phi_{IJ} - \frac{4\pi e^2}{\Omega}\sum_I \frac{(\mathbf{Z}^{\star}_I\cdot\mathbf{q})\left(\mathbf{q}\cdot\mathbf{Z}^{\star}_J\right)}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}}\right]\mathbf{u}_J$$

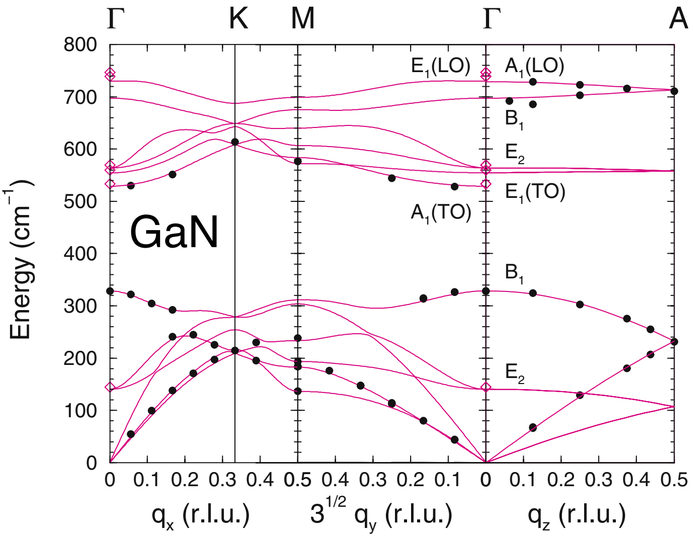


The non-analytic part fo the dynamical matrix

$$\mathbf{F}_I = M\ddot{\mathbf{u}}_I = -\sum_J \left[\Phi_{IJ} - \frac{4\pi e^2}{\Omega}\sum_I \frac{(\mathbf{Z}_I^\star\cdot\mathbf{q})(\mathbf{q}\cdot\mathbf{Z}_J^\star)}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}}\right]\mathbf{u}_J$$

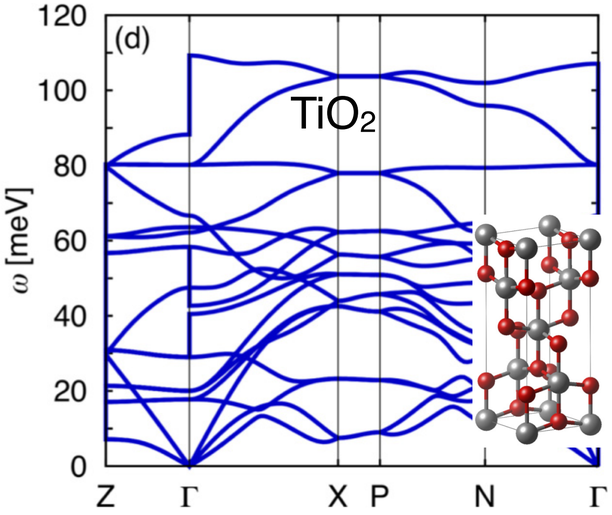
$$\Phi_{IJ}^{(na)} = \frac{4\pi e^2}{\Omega}\sum_I \frac{(\mathbf{Z}_I^\star\cdot\mathbf{q})(\mathbf{q}\cdot\mathbf{Z}_J^\star)}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}}$$

$$\tilde{\Phi}_{IJ} = \Phi_{IJ} + \Phi_{IJ}^{(\mathrm{na})}$$



Phenomena associated to polar semiconductors (and to $\Phi_{IJ}^{(\mathrm{na})}$)

- LO-TO splitting
- Lyddane-Sachs-Teller relations $\dfrac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = \dfrac{\varepsilon^0}{\varepsilon^\infty}$
- Absorption of infrared light (Rehstrahlen bands)
- Modern theory of polarization in ferroelectrics
- Fröhlich electron-phonon coupling
- Polarons



X. Gonze, C. Lee Phys. Rev. B **55**, 10355 (1997)
S. Baroni et al, Rev. Mod. Phys. **73**, 515 (2001)

Limits of the approximations involved

① Adiabatic (Born-Oppernheimer) approx.

Assumption: timescales of ionic motions much slower than electronic timescales

timescales of ionic dynamics $\tau_{\mathrm{ph}} = \dfrac{2\pi}{\omega_{\mathrm{ph}}} \simeq 50 - 200 \text{ fs}$

timescales of electron dynamics $\tau_{\mathrm{e}} = \dfrac{2\pi}{\omega_{\mathrm{pl}}}$

	insulators	metals	doped insulators
ω_{pl}	10-20 eV	5-10 eV	10-100 meV
τ_{e}	< 1 fs	< 1 fs	50 -200 fs
	$\tau_{\mathrm{e}} \ll \tau_{\mathrm{ph}}$		$\tau_{\mathrm{e}} \sim \tau_{\mathrm{ph}}$

Phenomena beyond the adiabatic approximation:

- Phonon "*damping*" due to electron-phonon scattering
- Non-adiabatic renormalization of the phonon energies

② Harmonic approximation

$$E_0(\{R_I + u_I\}) = E_0(\{R_I\}) + \frac{1}{2}\sum_{II'} \left.\frac{\partial^2 E_0}{\partial u_I \partial u_{I'}}\right|_{R_I} u_I u_{I'}$$

Assumption:

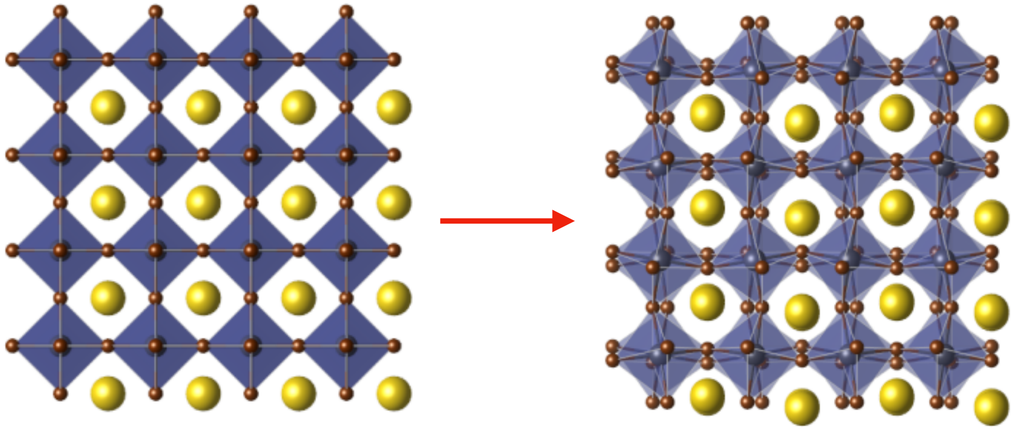
$$+ \frac{1}{3!}\sum_{II'I''} \left.\frac{\partial^3 E_0}{\partial u_I \partial u_{I'} \partial u_{I''}}\right|_{R_I} u_I u_{I'} u_{I''} + \cdots$$

Phenomena beyond the harmonic approximation:

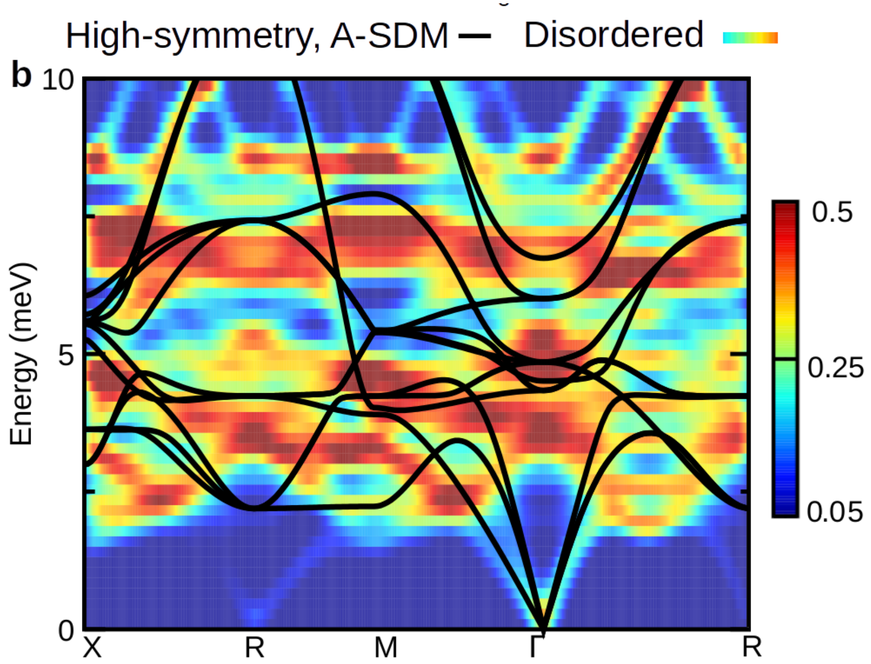
- Phonon-phonon scattering
- Thermal expansion
- Thermal conductivity
- Non-equilibrium dynamics of the lattice
- Ferroelectricity, piezoelectricity

Beyond phonons: Breakdown of the harmonic approximation

Perovskite structure ABO_3



high-symmetry locally disorder



anharmonic effects become dominant

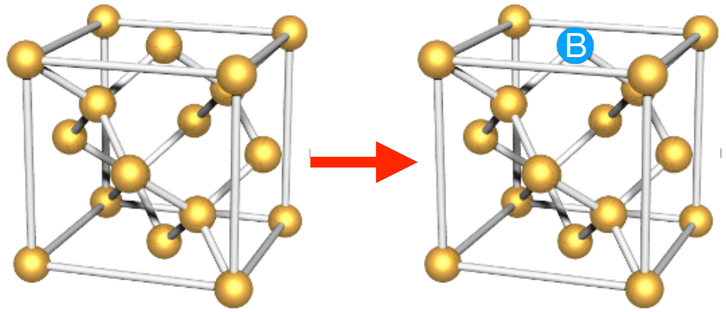
- Anharmonic effects can become important in "soft" crystals
- Structural disorder can alter the vibrational spectrum
- Does it make sense to talk about phonons?

M. Zacharias et al., arXiv:2302.09625 (2023)

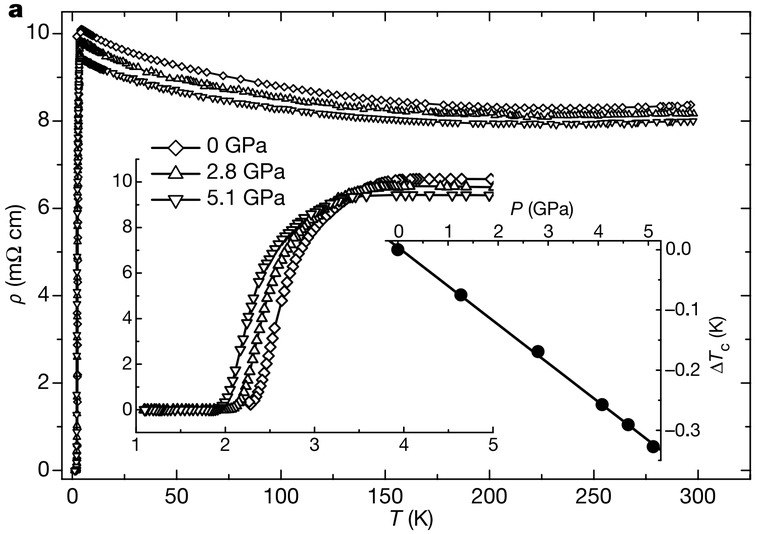
Beyond phonons: Breakdown of the adiabatic approximation

Phonon softening in B-doped diamond

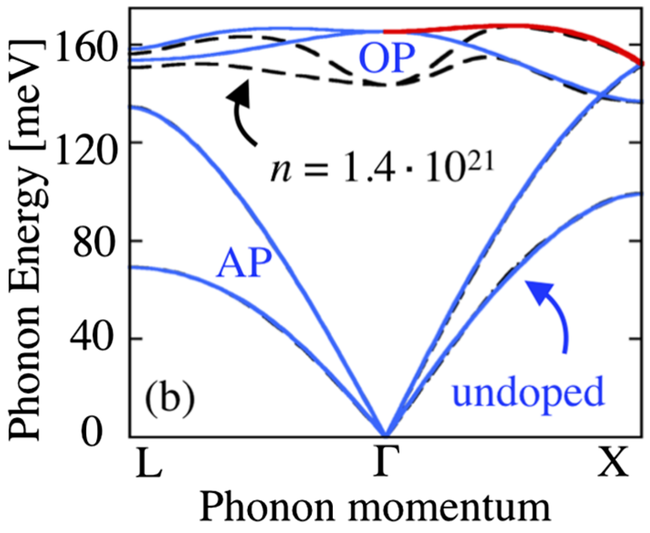
diamond (undoped) **B-doped** diamond



superconductivity for $T < T_c = 4$ K



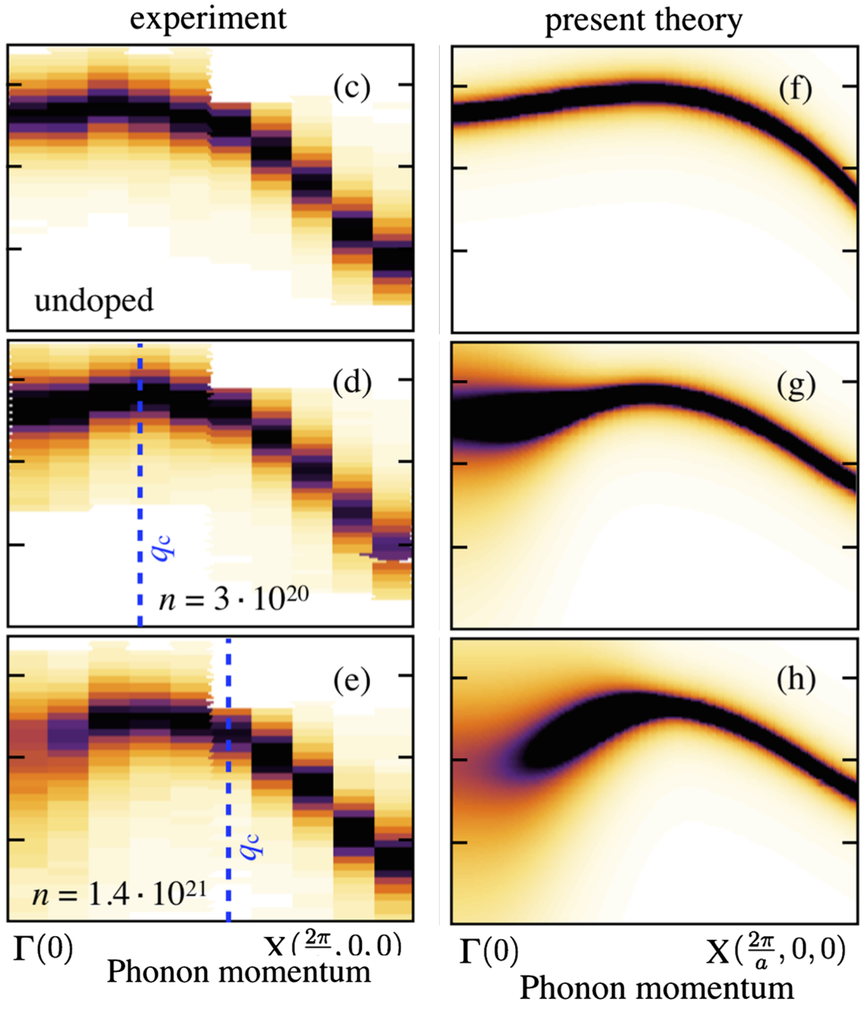
Ekimov et al., Nature **428.** 542 (2004)



Non-adiabatic phonon damping

Exp.: Ineastic X-ray scattering

Theory: many-body electron-phonon coupling



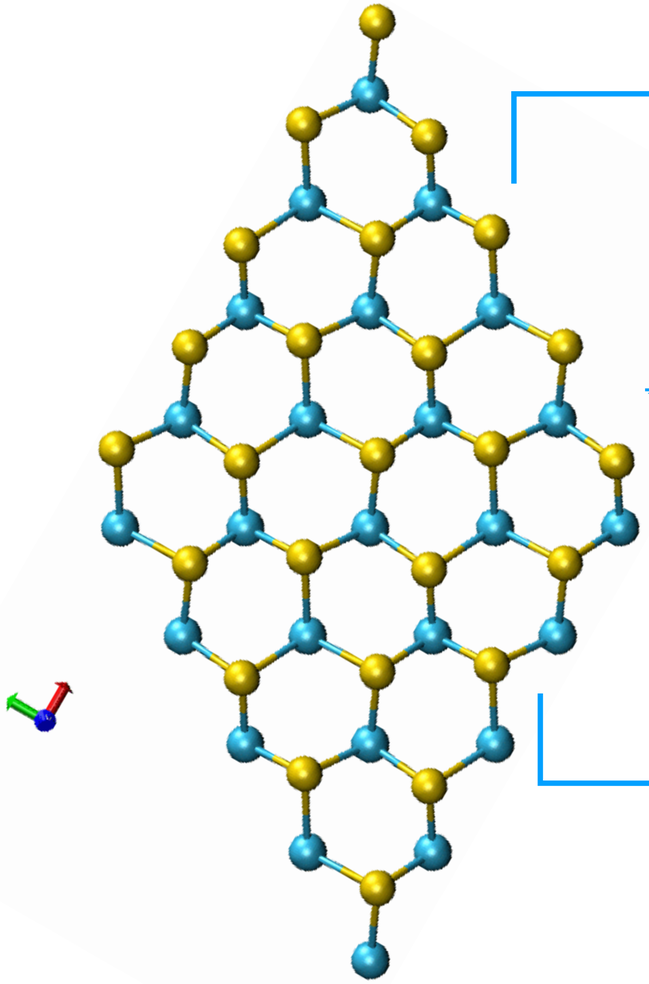
F. Caruso, M. Hoesch, P. Achatz, et al., Phys. Rev. Lett. **119**, 017001 (2017)

Phonon visualization

1. https://henriquemiranda.github.io/phononwebsite/phonon.html

2. https://interactivephonon.materialscloud.io/

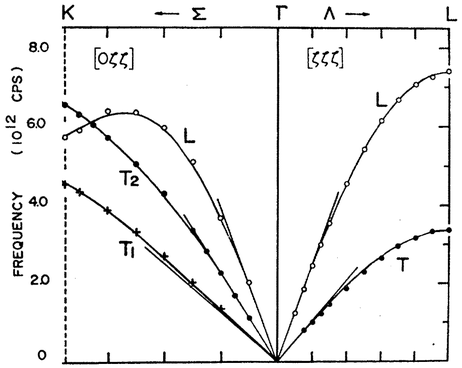
Summary: introduction to phonons



Theory of phonons in crystalline solids

$$\hat{H}^{\mathrm{nuc}}\,\chi_{\nu s}(R) = E_s\,\chi_{\nu s}(R)$$

Phonons in experiments



Ab-initio calculations of phonons in solids