Aalto University
School of Chemical
Engineering

Functional Inorganic Materials
Lecture 7: Thermal Conductivity

Fall 2023

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Lecture Exercise 7 is a MyCourses Quiz

Contents

- Introduction to thermal conductivity
  - Atomic-level mechanisms
  - Electronic thermal conductivity
  - Lattice thermal conductivity
- Materials perspective
  - High thermal conductivity materials
  - Thermal insulators
- Applications
  - Microelectronics
  - Thermal barrier coatings
  - Thermoelectrics (Lecture 8)

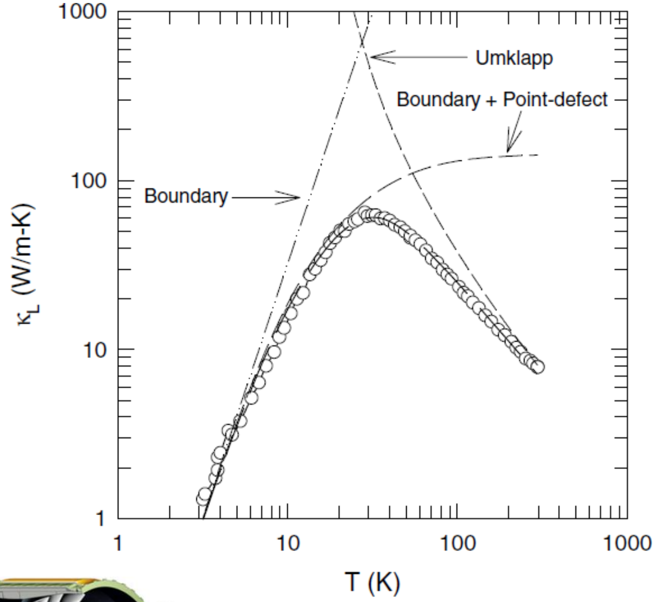


Figure: Terry M. Tritt

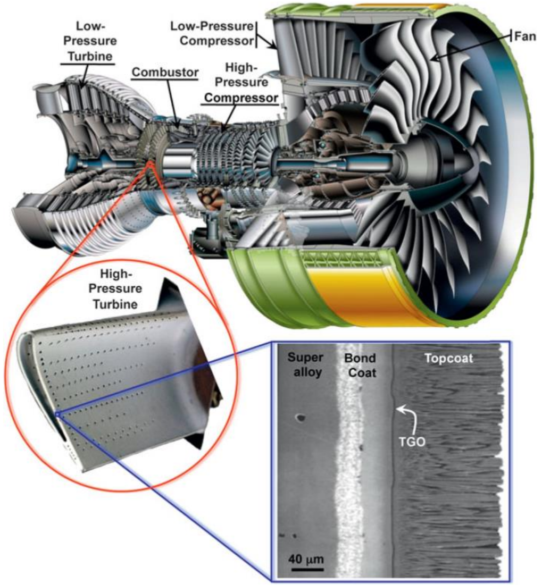
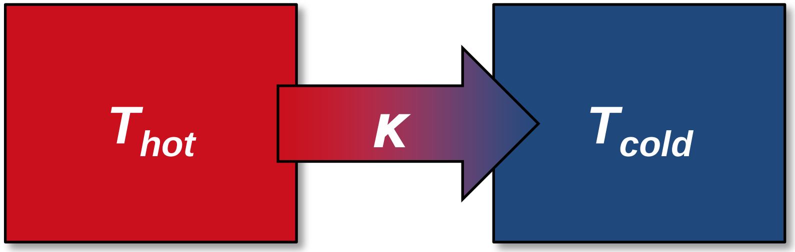


Figure: *MRS Bulletin* **2012,** *37*, 891.

Thermal conductivity κ



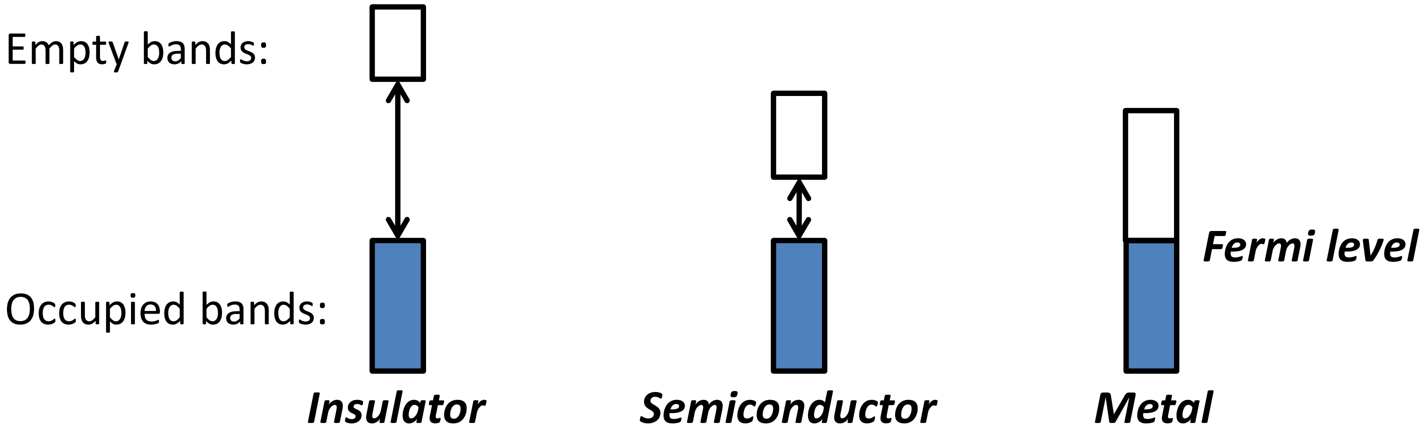
- **Ability of a substance to conduct heat** (units: W m^{-1} K^{-1})
- Very concrete property in our everyday life
  - Perhaps you've burnt your hand by touching the surface of a ***hot metal*** (a very good conductor of heat)
  - Perhaps after that, you've worn a ***thermally insulating*** glove in your hand
  - During the Finnish winter, it's good to live in a thermally insulated place
- Thermal conductivity is also very important material property for various technological applications:
  - Microelectronics (for example, CPU heat management)
  - Thermal barrier coatings in gas turbines (for example, airplane engines)
  - Thermoelectrics (direct heat-to-electricity conversion)

Atomic-level mechanisms behind thermal conductivity

Atomic-level mechanisms behind thermal conductivity

- Metals
  - Heat is primarily carried by ***conduction electrons***
- Insulators
  - Heat is primarily carried by ***phonons*** (lattice vibrations)
- Semiconductors
  - Low doping levels -> insulator-like behavior
  - High doping levels -> both phononic and electronic thermal conductivity

Insulator – semiconductor – metal classification based on band structure:



Empty bands:

Occupied bands:

Fermi level

Insulator ***Semiconductor*** ***Metal***

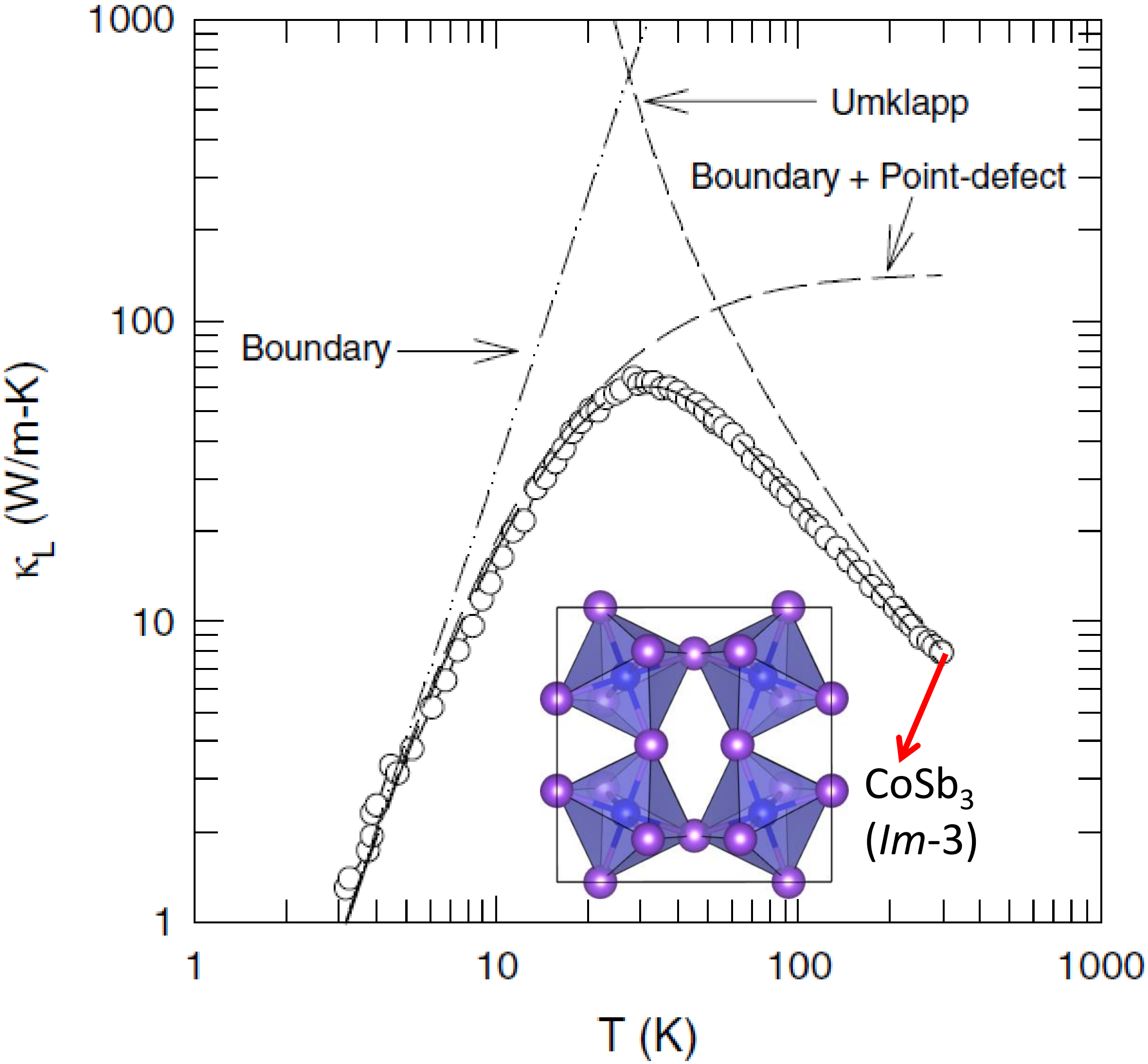
Electronic thermal conductivity

- Heat is carried by conduction electrons
- Electronic thermal conductivity κ_e is directly proportional to the electrical conductivity σ (Wiedemann-Franz law):
  $\kappa_e = LT\sigma$, where
  $L = 2.44 \times 10^{-8}$ WΩK^{-2}
- L is roughly constant, but not exactly same for all metals!
- Electrical conductivity
  - increases when T decreases
  - Decreases when T increases (electron-phonon scattering increases)

Metal	**Electrical conductivity σ (S/m) at 300 K**	**Thermal conductivity κ (W m^{-1} K^{-1})**
Ag	6.3×10^7	430
Cu	6.0×10^7	400
Al	3.5×10^7	235
Zn	1.7×10^7	120
Pb	4.6×10^6	35

Thermal conductivity of an insulator

Thermal conductivity of crystalline materials is usually highly **temperature-dependent**



Dots = experiment ($CoSb_3$)

Dashed curves = Theoretical limits imposed by various **phonon scattering** mechanisms:

- Boundary
- Point-defect / mass-defect (isotope)
- Umklapp = **phonon-phonon** scattering
- At T > 100, phonon-phonon scattering dominates (1/*T* dependence)

Here we focus on room temperature thermal conductivity

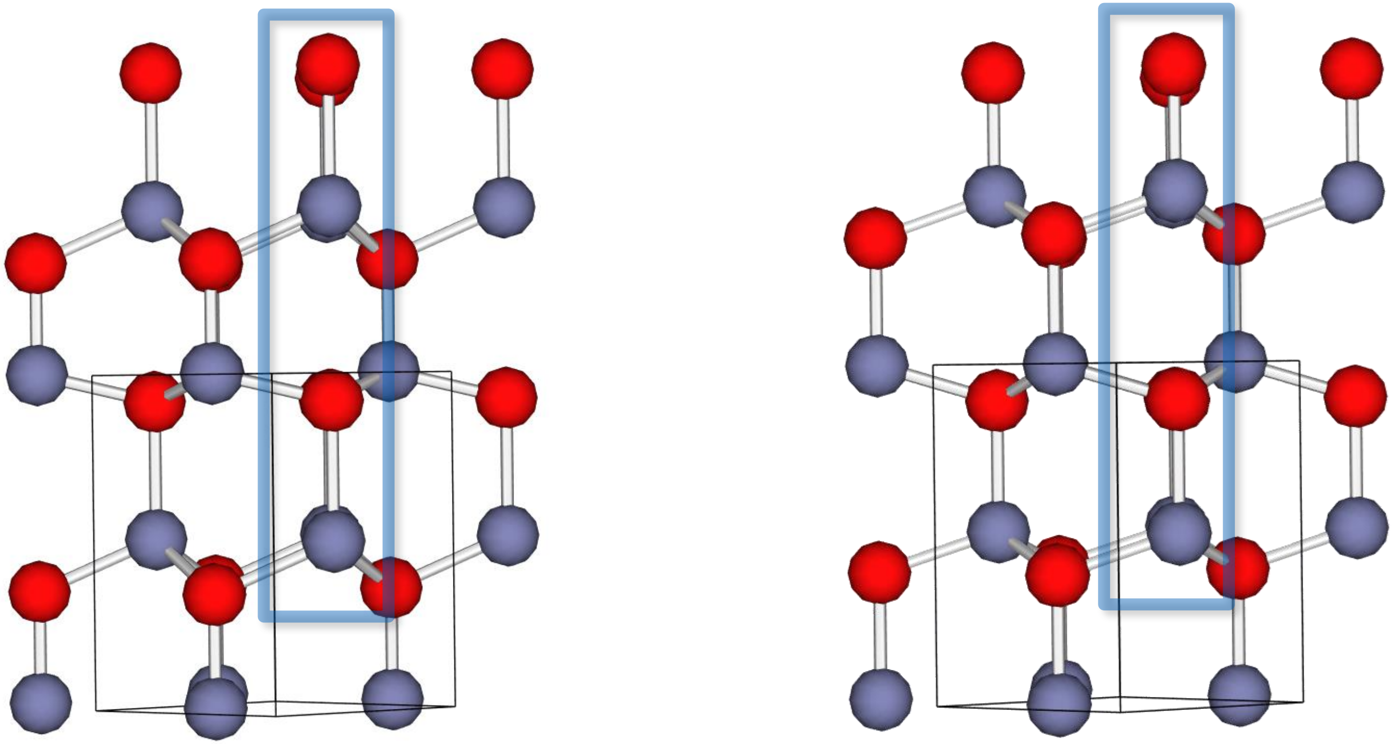
Lattice thermal conductivity

- In insulating solid-state materials, heat and sound is carried by vibrational excitations called *phonons* (from greek φωνή = *phone* = ***sound***)
- Phonons give rise to ***lattice thermal conductivity***, κ_L

- Materials have finite thermal conductivity because of various phonon ***scattering mechanisms*** (boundary, point-defect, isotope, phonon-phonon, electron-phonon)
- Phonon-phonon scattering is the most important scattering mechanism for crystalline, electrically insulating materials at room temperature
  - Note that crystal with only harmonic phonons (vibrations) would have no phonon–phonon scattering
  - Phonon-phonon scattering arises due to ***anharmonicity*** (deviation from harmonic oscillator behavior)
  - Phonon anharmonicity is also the reason for ***negative thermal expansion*** (for example, silicon contracts when temperature increases from 18 K to 120 K)

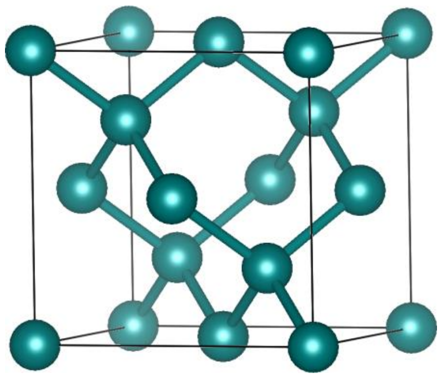
Vibrations in molecules and solids

- A molecule with N atoms shows $3N - 6$ vibrational modes ω_i
- A crystal with N atoms in the primitive cell shows $3N$ vibrational modes
  - Atoms in neighboring cells can vibrate **in-phase** or **out-of-phase**!
- In-phase and anti-phase Zn–O stretching in ZnO:

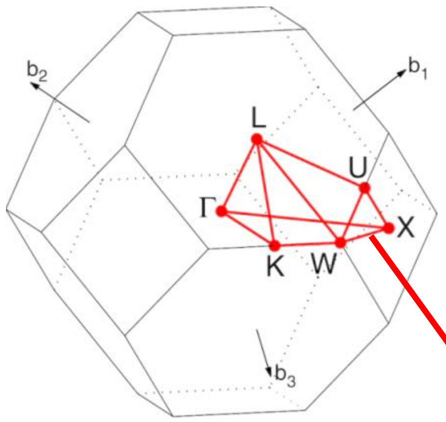


Phonon dispersion relations

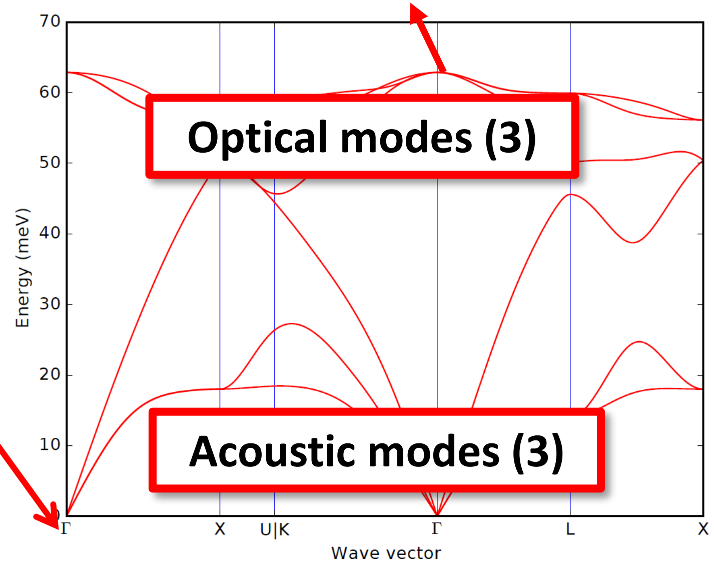
- The vibrational modes of a solid are described as a function of wavevector *q* in the reciprocal space: $\omega_i(q)$ = ***phonon dispersion relations***
  - Phonon dispersion relations account for the periodic nature of the crystal
  - Atoms in neighboring cells can vibrate in a different phase



α-silicon (*Fd*-3*m*)
Two atoms in the primitive cell
-> six phonon modes



Brillouin zone of FCC lattice (reciprocal space path in red)



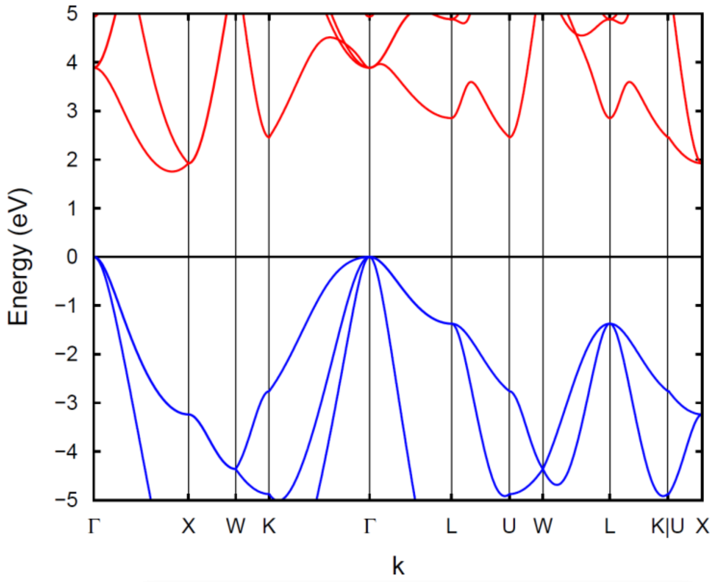
Molecules show only these, ***q*** = 0
Here: Raman mode of Si

Optical modes (3)

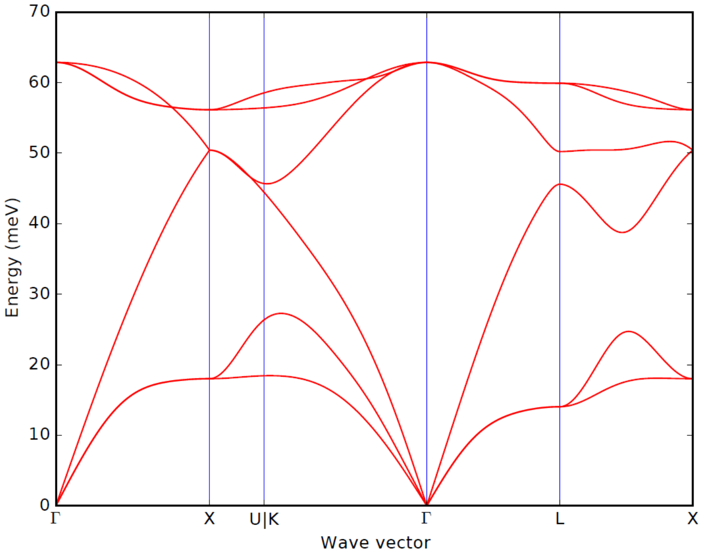
Acoustic modes (3)

Phonons vs. electrons

- Electronic band structures are plotted as a function of wavevector ***k***
  - The crystal orbitals can be in a different phase in neighboring cells
- Phonon dispersion relations are plotted as a function of wavevector ***q***
  - Atoms in neighboring cells can vibrate in a different phase



Electronic band structure of α-silicon

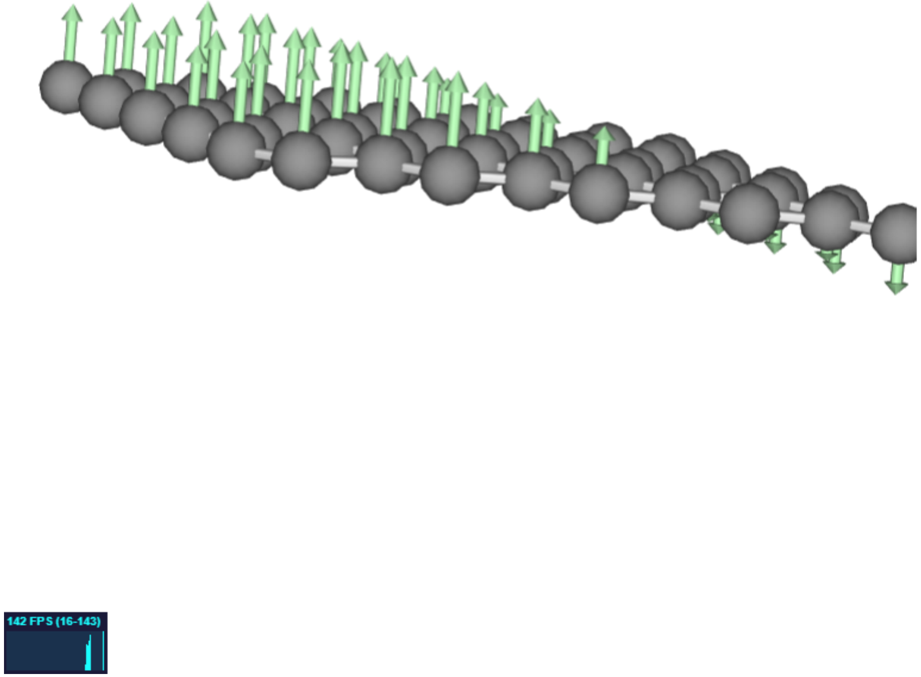


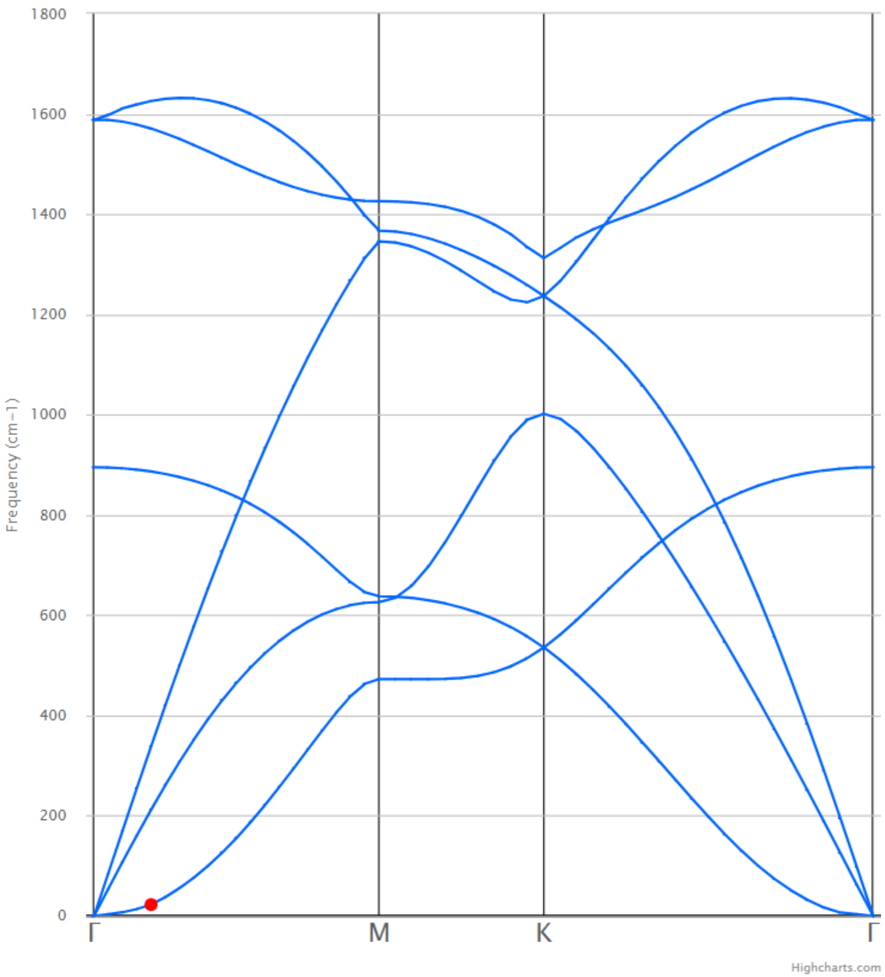
Phonon dispersion relations of α-silicon

Figures: AJK

Visualization of phonons

- http://henriquemiranda.github.io/phononwebsite/phonon.html
- Let’s have a look for example on the acoustic modes of graphene



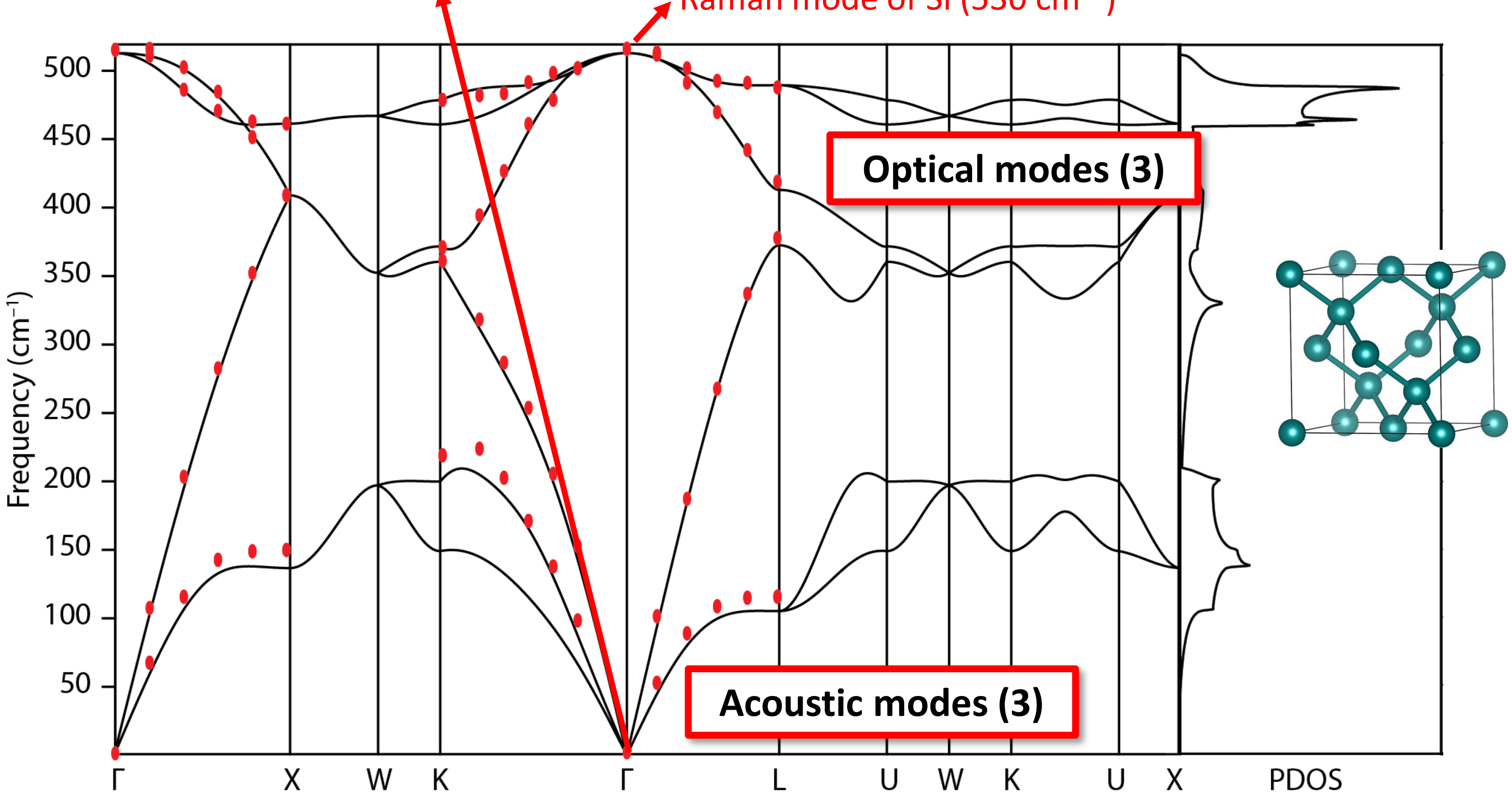


Phonon dispersions for silicon (1)

Red = ***Inelastic Neutron Scattering***. Calculated lines: Density Functional Theory.

Tangent = phonon group velocity ≈ speed of sound

Raman mode of Si (530 cm^{-1})



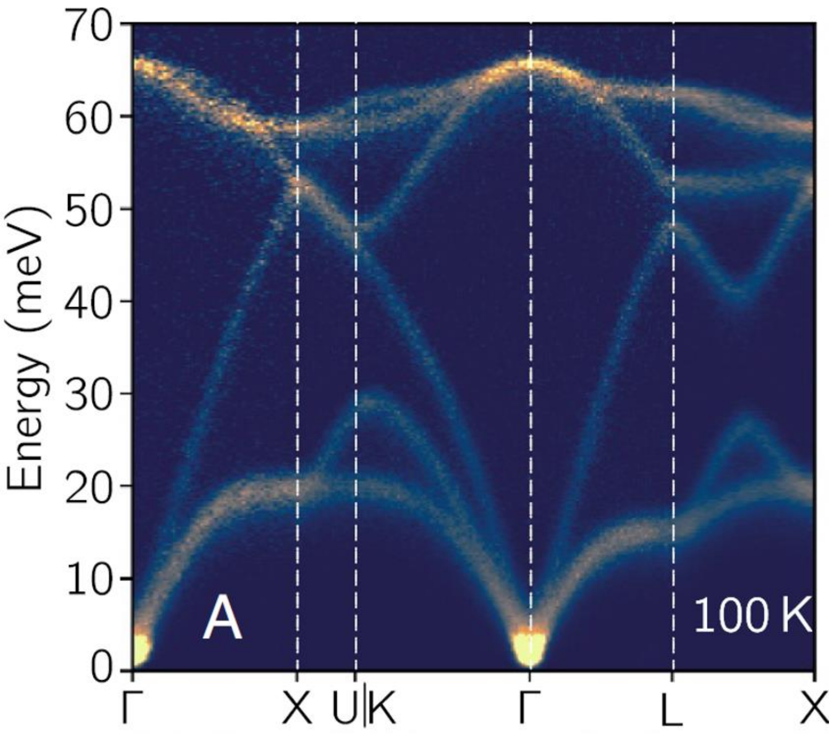
Optical modes (3)

Acoustic modes (3)

Experiment: G. Dolling, Inelastic Scattering of Neutrons in Solids and Liquids, Vol. II, p. 37

Phonon dispersions for silicon (2)

- Experimental data on previous slide were from the 1960s
- Excellent agreement also between theory and recent state-of-the-art inelastic neutron scattering data



Inelastic neutron scattering data at 100 K (*Proc. Natl. Acad. Sci.* 2018, *115*, 1192)

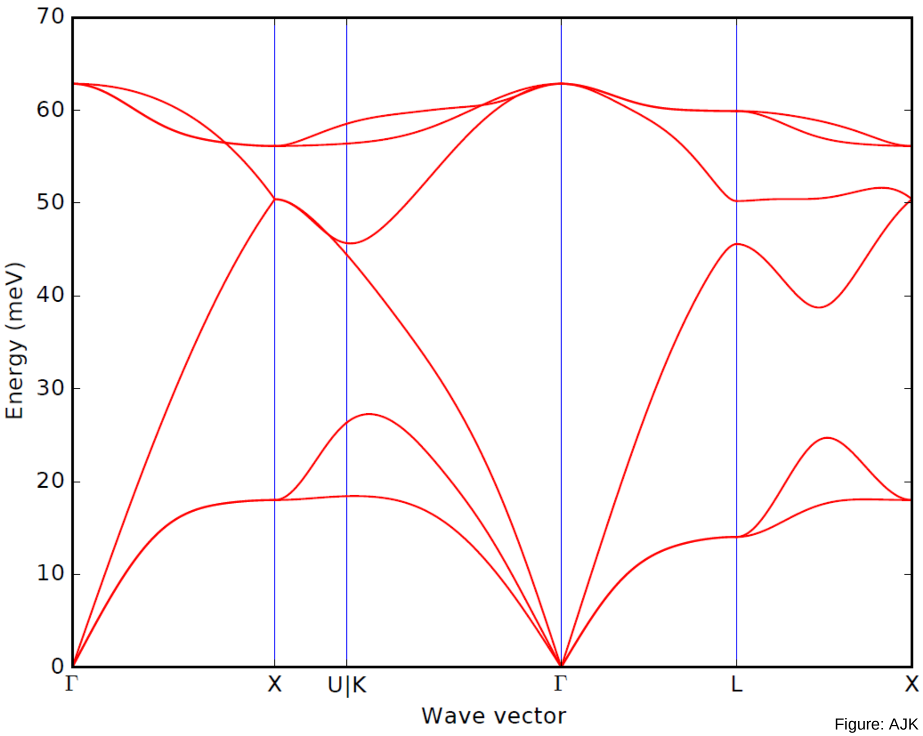


Figure: AJK

Density Functional Theory (DFT-PBE0/SVP)

Lattice thermal conductivities can be explained and predicted computationally with DFT methods

Lattice thermal conductivity κ_L from Boltzmann Transport Equation

- In the past few years, the theoretical methods have evolved to a level, where it is possible to predict the lattice thermal conductivity of non-metallic materials with a good precision (5-10%)
- κ_l can be solved with the help of the semiclassical Boltzmann Transport Equation
- In Single-Mode Relaxation Time approximation:

$$\kappa = \frac{1}{N V_0} \sum_{\lambda} C_{\lambda} \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} \tau_{\lambda}^{\mathrm{SMRT}}$$

Phonon relaxation time, calculated from phonon scattering rates (using phonon dispersions and anharmonic force constants)

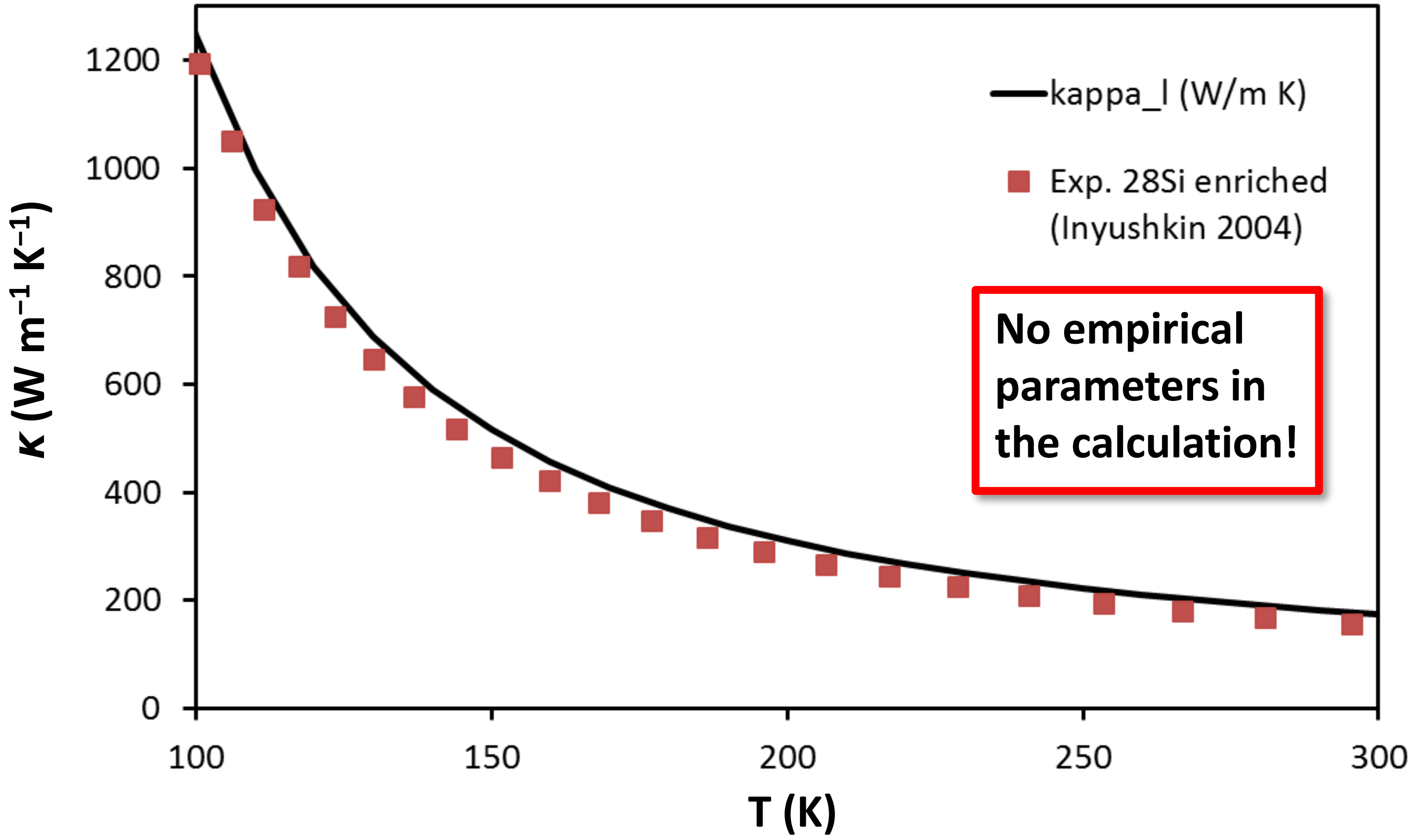
Heat capacity, calculated from phonon dispersions

Phonon group velocity, calculated from phonon dispersions

See for example: J. Linnera, A. J. Karttunen, *Phys. Rev. B* **2017**, *96*, 014304.

Lattice thermal conductivity of silicon

For a simple semiconductor like silicon, κ_l can be predicted with good accuracy using Density Functional Theory (DFT) and semiclassical Boltzmann Transport Equation

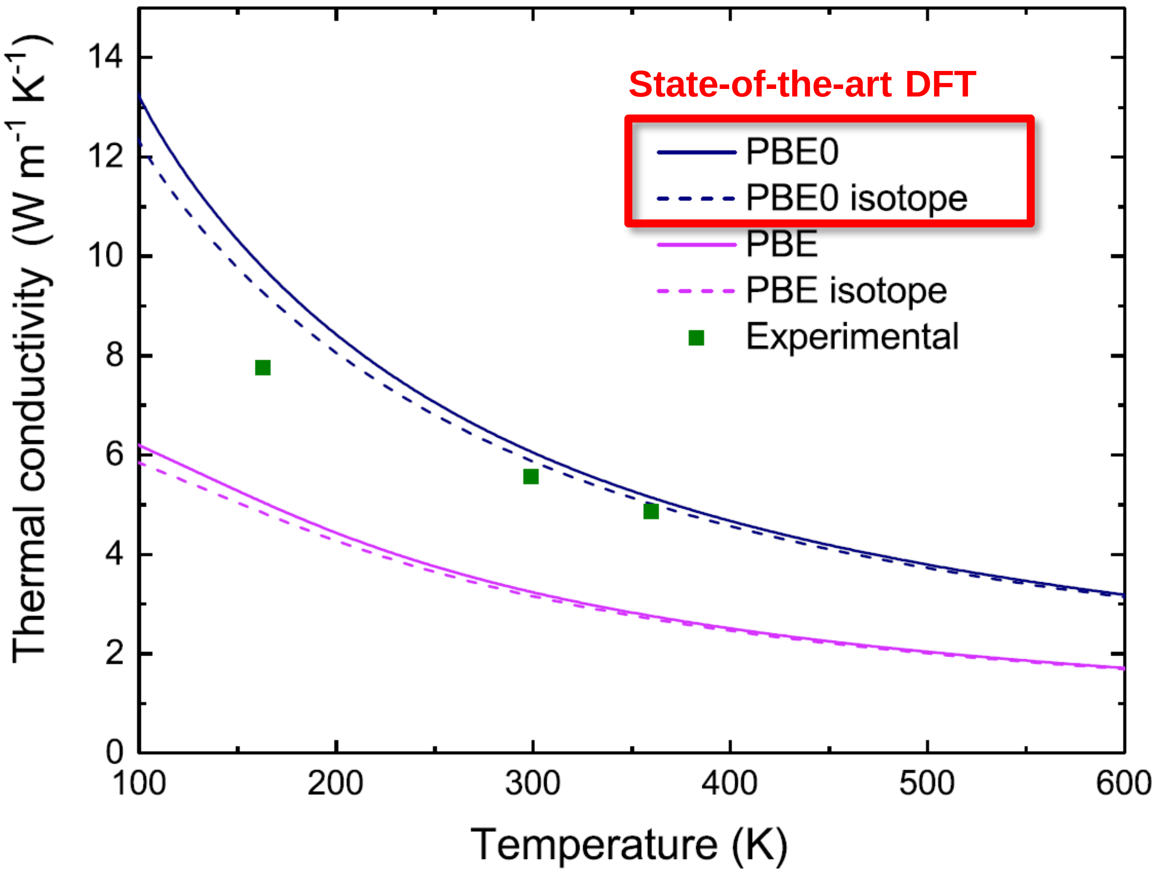


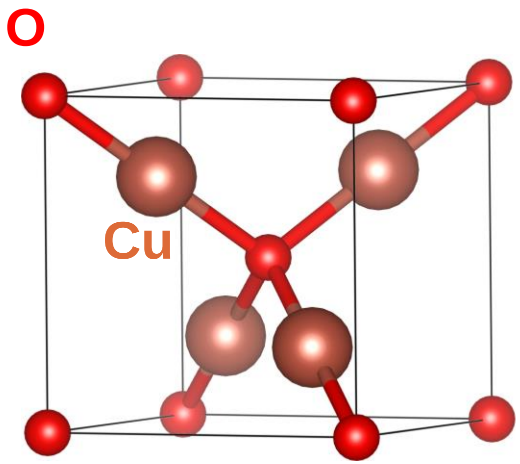
No empirical parameters in the calculation!

Experiment: A. V. Inyushkin *et al. Phys. Status Solidi C* **2004**, *1*, 2995–2998.

DFT results: A. J. Karttunen, unpublished results.

Lattice thermal conductivity of Cu_2O



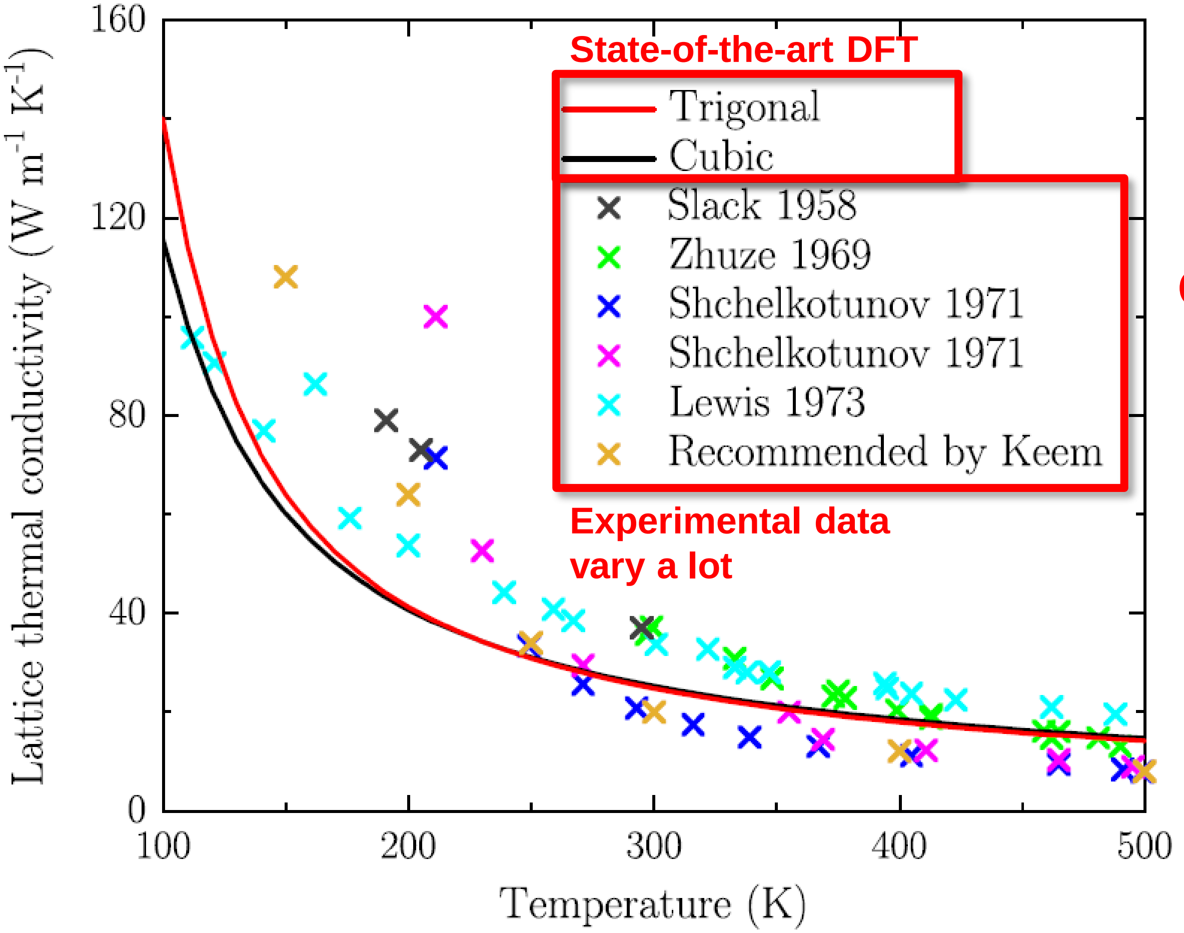


Cu_2O (*Pn*-3*m*)

κ_l at 300 K (W m^{-1} K^{-1})
Exp.: 5.6
PBE0: 5.9 (+5%)
PBE: 3.2 (-44%)

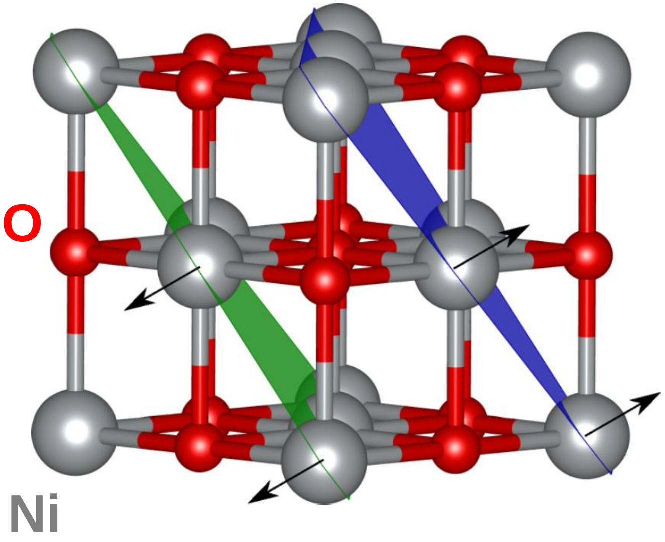
J. Linnera, A. J. Karttunen, *Phys. Rev. B* **2017**, *96*, 014304.

Lattice thermal conductivity of NiO



State-of-the-art DFT

Experimental data vary a lot



NiO (*Fm*-3*m*)
Antiferromagnetic up to 525 K
Magnetic ordering: *R*-3*m*

FIG. 4. Lattice thermal conductivity of NiO calculated using both the trigonal (red line) and cubic (black line) primitive cells. Crosses denote the different experimental data points [48–52].

J. Linnera, A. J. Karttunen, *Phys. Rev. B* **2019**, *100*, 144307.

Thermal engineering of crystalline materials

Thermal engineering

- How to **decrease** the thermal conductivity of **crystalline** solid-state materials?
  - In general: add ***disorder***
  - Alloying
    - Pure Si: **150** W m^{-1} K^{-1}; Pure Ge: **60** W m^{-1} K^{-1}
    - 50:50 Si-Ge alloy: **10** W m^{-1} K^{-1}
  - Doping: electronic doping also introduces kind of point defects, decreasing lattice thermal conductivity.
    - For example, ZnO: **43** W m^{-1} K^{-1}; 2% Al doping decreases the thermal conductivity to ~**7** W m^{-1} K^{-1}
  - Create interfaces that scatter phonons
    - **Superlattices**

- How to **increase** thermal conductivity?
  - Prepare samples with high isotopic purity. The effect is large < 100 K, but typically only ~10% at 300 K. There are exceptions like cubic BN (below).
  - Create better materials!
    - Recent prediction from DFT: Ultrahigh Thermal Conductivity of θ-Phase Tantalum Nitride (DOI)

Review on extreme thermal conductivity materials

Nature Materials **2021**, *20*, 1188–1202, https://doi.org/10.1038/s41563-021-00918-3.

Discusses both experimental and computational (DFT) state-of-the-art.

REVIEW ARTICLE
https://doi.org/10.1038/s41563-021-00918-3

nature materials

Phonon-engineered extreme thermal conductivity materials

Xin Qian[1,2], Jiawei Zhou[1,2] and Gang Chen[1] ✉

Materials with ultrahigh or low thermal conductivity are desirable for many technological applications, such as thermal management of electronic and photonic devices, heat exchangers, energy converters and thermal insulation. Recent advances in simulation tools (first principles, the atomistic Green's function and molecular dynamics) and experimental techniques (pump-probe techniques and microfabricated platforms) have led to new insights on phonon transport and scattering in materials and the discovery of new thermal materials, and are enabling the engineering of phonons towards desired thermal properties. We review recent discoveries of both inorganic and organic materials with ultrahigh and low thermal conductivity, highlighting heat-conduction physics, strategies used to change thermal conductivity, and future directions to achieve extreme thermal conductivities in solid-state materials.

Periodic trends for lattice thermal conductivity

- Lattice thermal conductivity depends strongly on the **interatomic forces**.
- The stronger the interactomic forces, the more strongly the atoms are coupled to each other
  - Strong covalent bonds -> larger phonon velocities
  - Speed of sound in diamond: 12 000 m/s
  - Si: 8500 m/s
  - Pb: 1300 m/s
- Strong covalent bonds show the largest interatomic force constants, resulting in the highest lattice thermal conductivity.
- In simple ionic materials, the interatomic force constants and phonon velocities are typically smaller
  - For NaCl, $\kappa = 6.5$ W m^{-1} K^{-1}

	Thermal conductivity κ (W m^{-1} K^{-1})
C	~2200 (diamond)
Si	~150
Ge	~60
Sn	~60 (metal)
Pb	~35 (metal)

Increasing thermal conductivity with isotope enrichment

Science **2020**, *367*, 555–559, https://doi.org/10.1126/science.aaz6149

Thermal conductivity of cubic BN at 300 K was increased from about 850 m^{-1} K^{-1} to over 1600 W m^{-1} K^{-1} by isotopic enrichment: ^{10}BN or ^{11}BN instead of ^{nat}BN.

Proven experimentally, atomic-level mechanism explained with DFT calculations.

REPORT

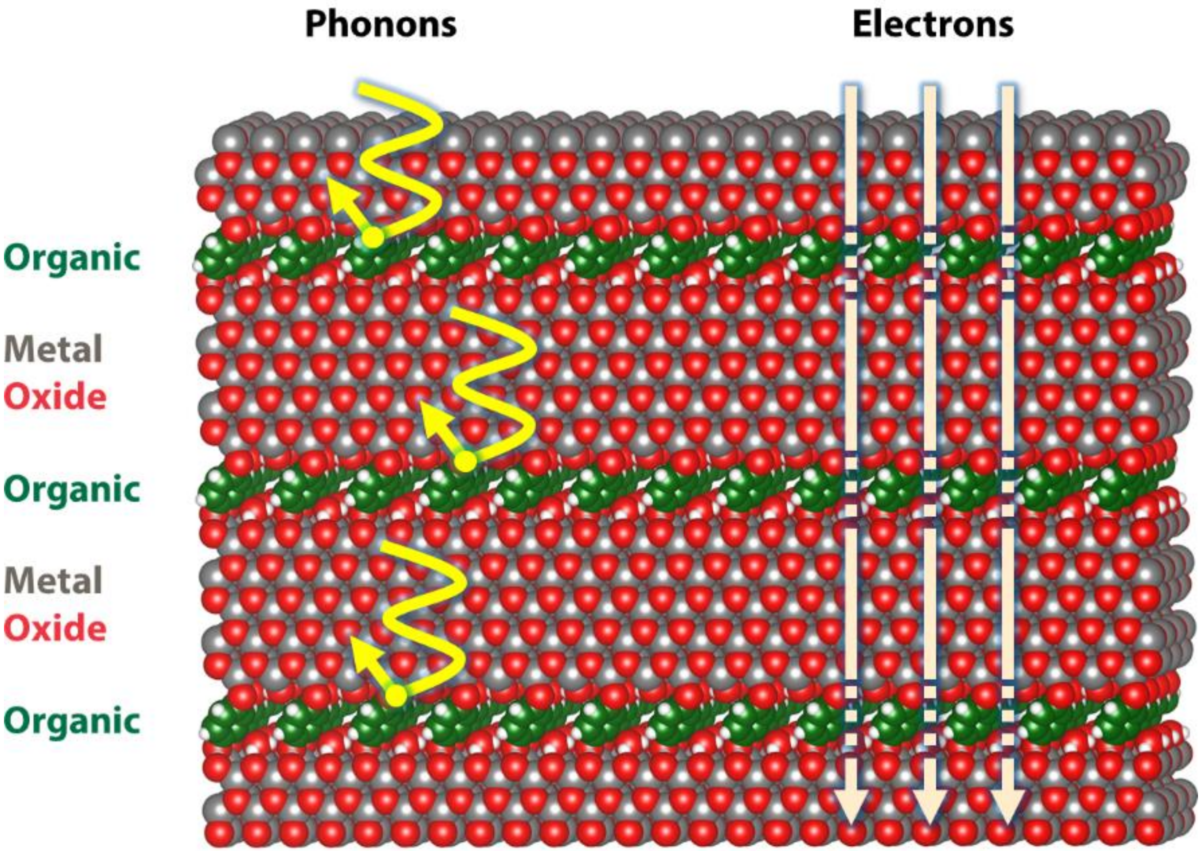
THERMAL CONDUCTIVITY

Ultrahigh thermal conductivity in isotope-enriched cubic boron nitride

Ke Chen[1]*, Bai Song[1]*†‡, Navaneetha K. Ravichandran[2]*, Qiye Zheng[3]§, Xi Chen[4]¶, Hwijong Lee[4], Haoran Sun[5], Sheng Li[6], Geethal Amila Gamage Udalamatta Gamage[5], Fei Tian[5], Zhiwei Ding[1], Qichen Song[1], Akash Rai[3], Hanlin Wu[6], Pawan Koirala[6], Aaron J. Schmidt[1], Kenji Watanabe[7], Bing Lv[6], Zhifeng Ren[5], Li Shi[4,8], David G. Cahill[3], Takashi Taniguchi[7], David Broido[2]†, Gang Chen[1]†

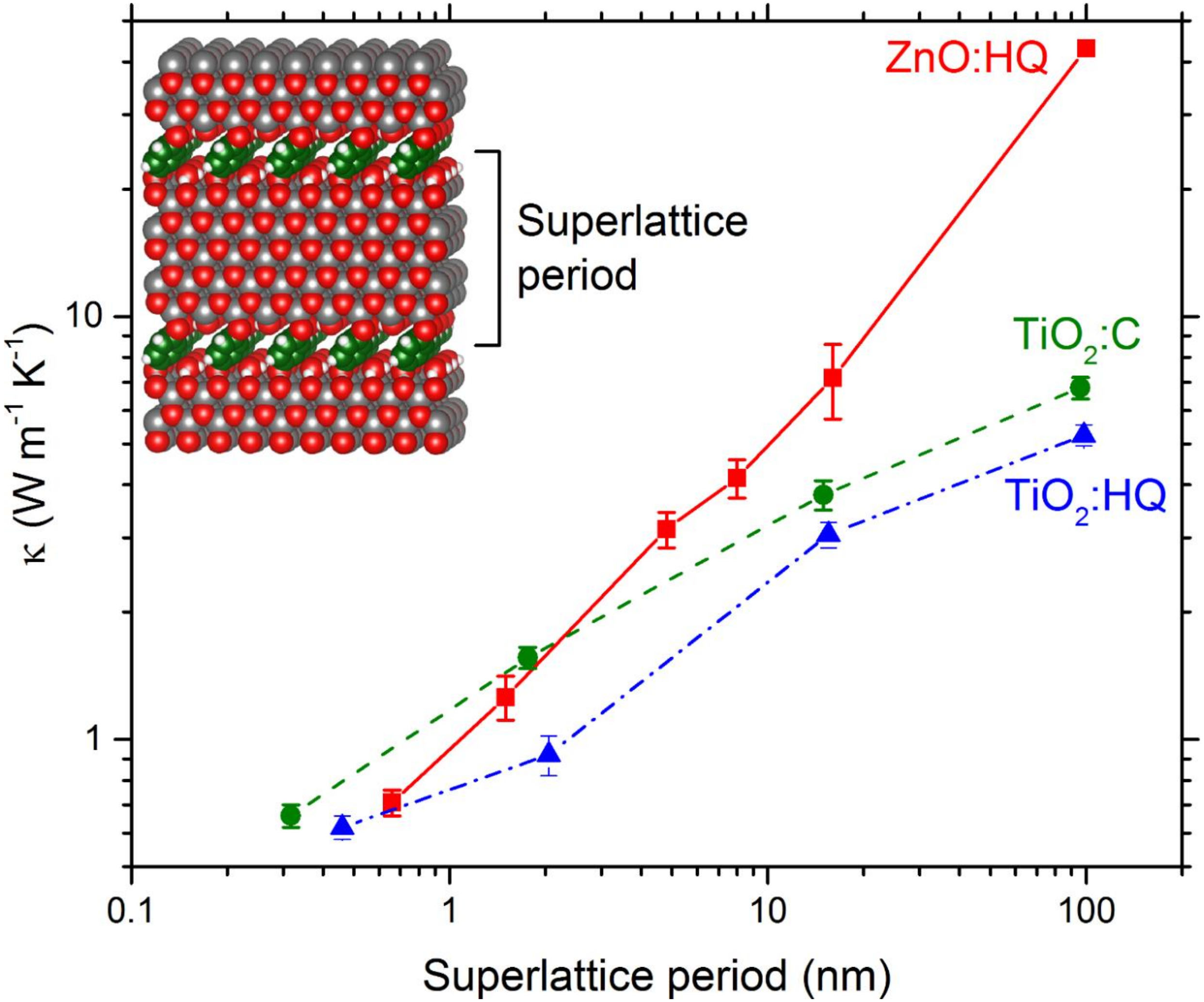
Decreasing thermal conductivity with oxide-organic superlattices (1)

- ZnO:organic superlattices fabricated by ALD/MLD
- Create phonon-blocking interfaces (that would not scatter electrons too much)



J.-P. Niemelä, A. J. Karttunen, M. Karppinen, *J. Mater. Chem C* **2015**, *3*, 10349 (DOI).

Decreasing thermal conductivity with oxide-organic superlattices (2)



J.-P. Niemelä, A. J. Karttunen, M. Karppinen, *J. Mater. Chem C* **2015**, *3*, 10349.

Crystalline vs. amorphous

- So far, we have mainly discussed crystalline materials
- For amorphous, non-crystalline materials, phonons are not well-defined
- Generally, they possess low thermal conductivity (e.g. acrylic glass 0.2 W m^{-1} K^{-1})

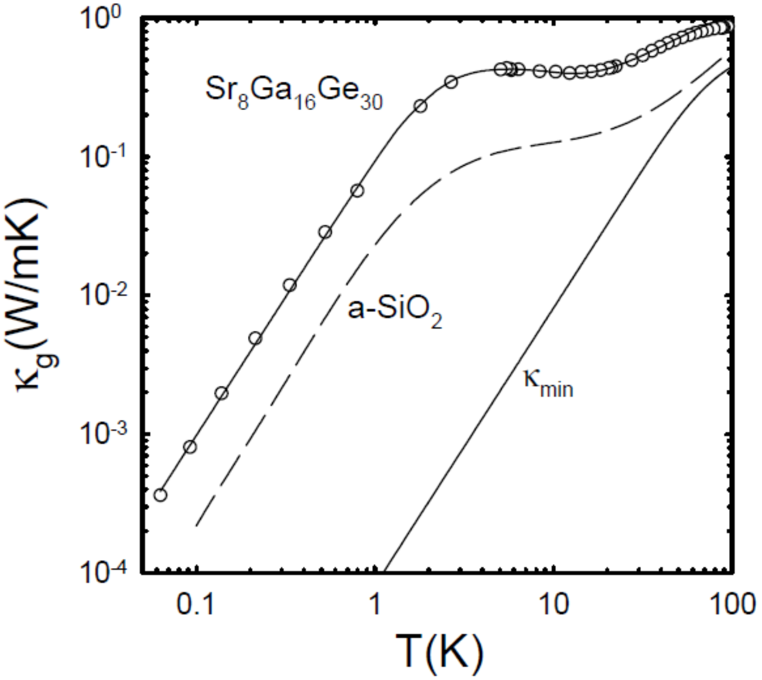
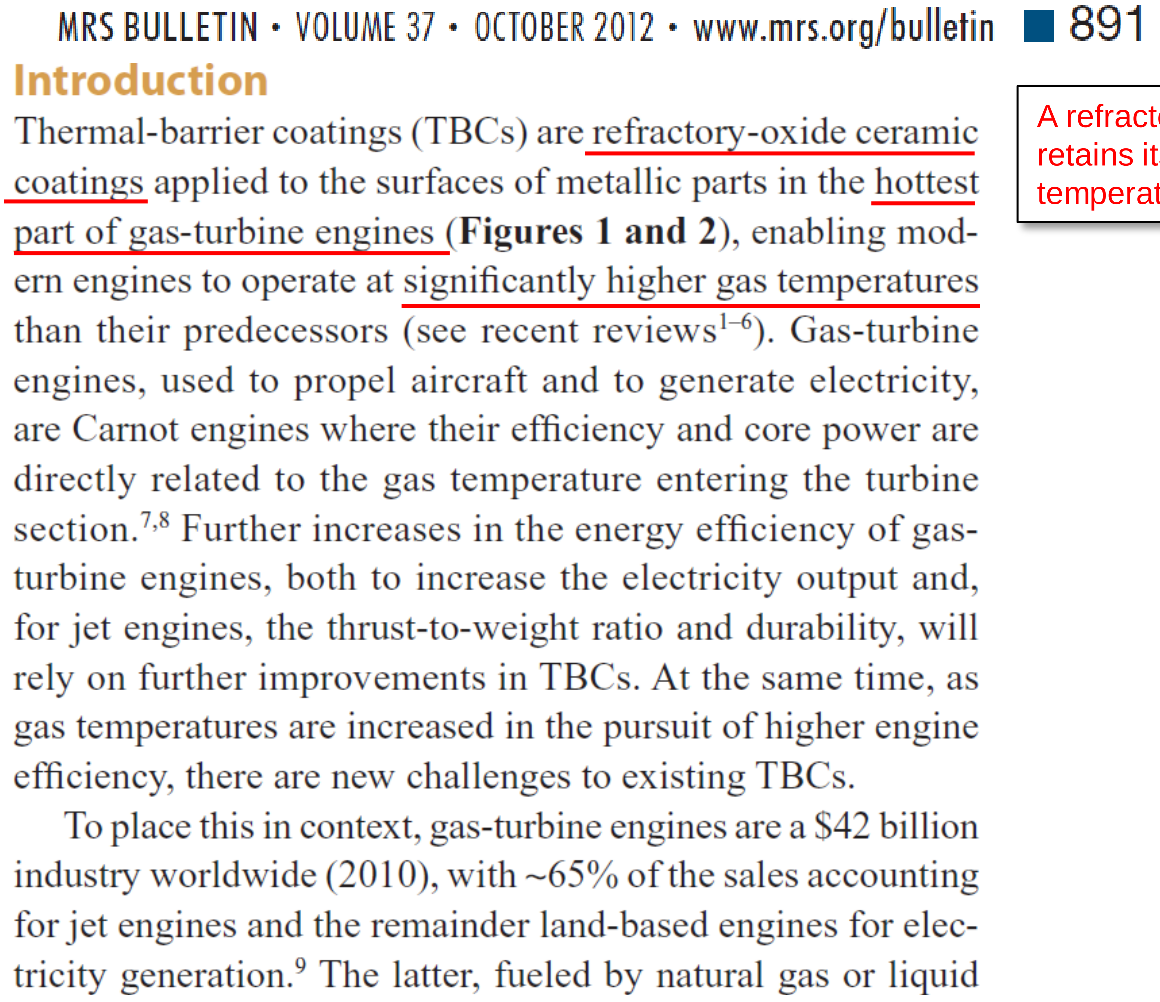


FIG. 2. Lattice thermal conductivity measured from 60 mK to 100 K for $Sr_8Ga_{16}Ge_{30}$ with a fit (solid curve) to the model discussed in the text (see also Fig. 3). The dashed line is for a-SiO_2, and the solid curve labeled κ_{min} is the calculated minimum thermal conductivity of Ge.

VOLUME 82, NUMBER 4 PHYSICAL REVIEW LETTERS 25 JANUARY 1999

Thermal insulator application: Thermal barrier coatings for gas-turbine engines

Thermal barrier coatings for gas-turbine engines



MRS BULLETIN • VOLUME 37 • OCTOBER 2012 • www.mrs.org/bulletin 891

Introduction

Thermal-barrier coatings (TBCs) are refractory-oxide ceramic coatings applied to the surfaces of metallic parts in the hottest part of gas-turbine engines (**Figures 1 and 2**), enabling modern engines to operate at significantly higher gas temperatures than their predecessors (see recent reviews[1–6]). Gas-turbine engines, used to propel aircraft and to generate electricity, are Carnot engines where their efficiency and core power are directly related to the gas temperature entering the turbine section.[7,8] Further increases in the energy efficiency of gas-turbine engines, both to increase the electricity output and, for jet engines, the thrust-to-weight ratio and durability, will rely on further improvements in TBCs. At the same time, as gas temperatures are increased in the pursuit of higher engine efficiency, there are new challenges to existing TBCs.

To place this in context, gas-turbine engines are a $42 billion industry worldwide (2010), with ~65% of the sales accounting for jet engines and the remainder land-based engines for electricity generation.[9] The latter, fueled by natural gas or liquid

A refractory material retains its strength at high temperatures

Thermal barrier coatings

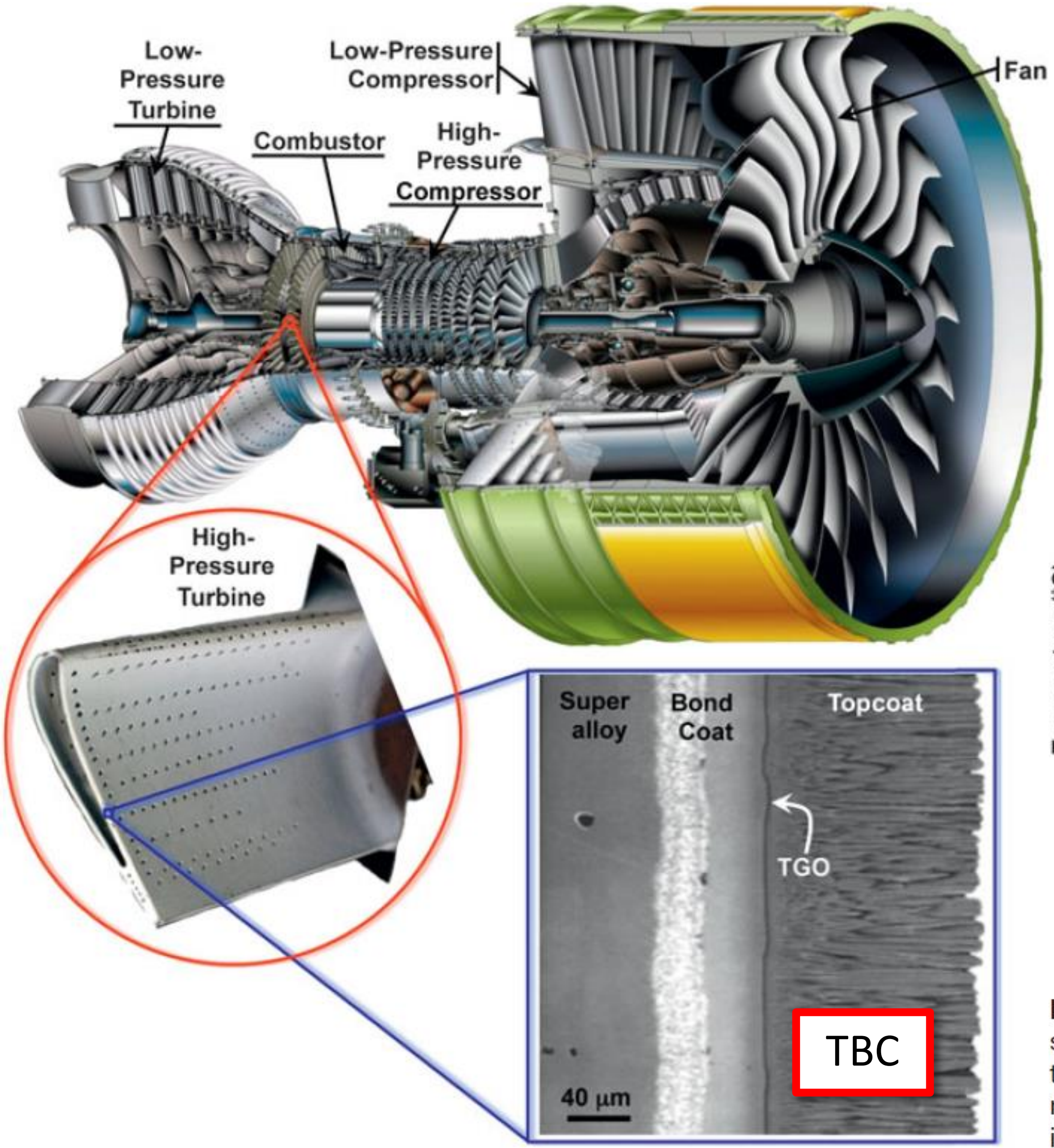


Figure 1. Cutaway view of Engine Alliance GP7200 aircraft engine, photograph of a turbine blade (~10 cm long) with thermal-barrier coating (TBC) from the high-pressure hot section of an engine, and a scanning electron microscope (SEM) image of a cross-section of an electron beam physical vapor deposited 7 wt% yttria-stabilized zirconia TBC. (Engine image courtesy of Engine Alliance, turbine blade photograph courtesy of YXLON, and the SEM micrograph is from Reference 44.) TGO, thermally grown oxide.

YSZ

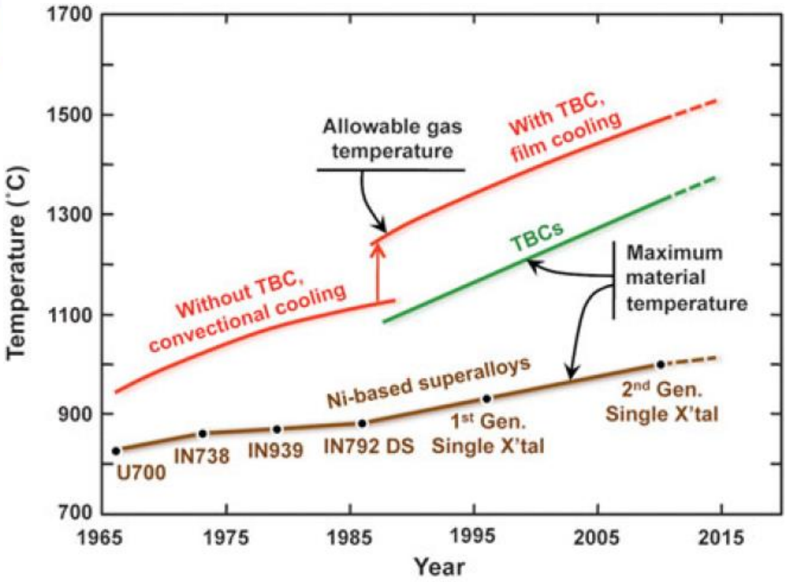


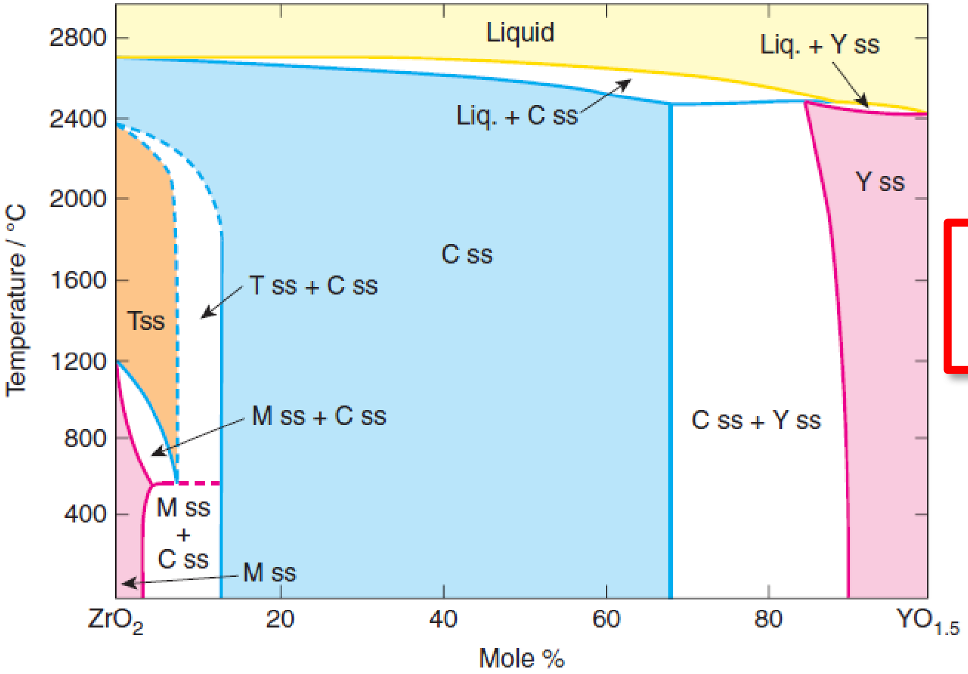
Figure 3. Progression of temperature capabilities of Ni-based superalloys and thermal-barrier coating (TBC) materials over the past 50 years. The red lines indicate progression of maximum allowable gas temperatures in engines, with the large increase gained from employing TBCs. Based on a diagram from the late Professor Tony Evans.

Yttria-stabilized Zirconia (YSZ)

- Zirconia, ZrO_2, is potentially a very useful ceramic material with a high melting point of ~2700 ◦C but on cooling it undergoes a series of phase transitions:

$$\text{cubic (fluorite)} \xrightarrow{2400\,^{\circ}\mathrm{C}} \text{tetragonal} \xrightarrow{1050\,^{\circ}\mathrm{C}} \text{monoclinic (baddeleyite)}$$

- The tetragonal to monoclinic transition is associated with an increase in unit cell volume by ~9% -> ceramic bodies fabricated at high *T* shatter on cooling
- The transitions can be avoided by creating a solid solution ZrO_2–Y_2O_3



Thermal conductivity: 3 W m^{-1} K^{-1} or lower

Ref: West p. 355

Figure 7.28 ZrO_2–Y_2O_3 phase diagram. M, T and C refer to the monoclinic, tetragonal and cubic polymorphs of zirconia, and their solid solutions, ss. Y = yttria, Y_2O_3.