



Aalto University  
School of Chemical  
Engineering

# Functional Inorganic Materials

## Lecture 6: Thermal Conductivity

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**Lecture Exercise 6 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 7)

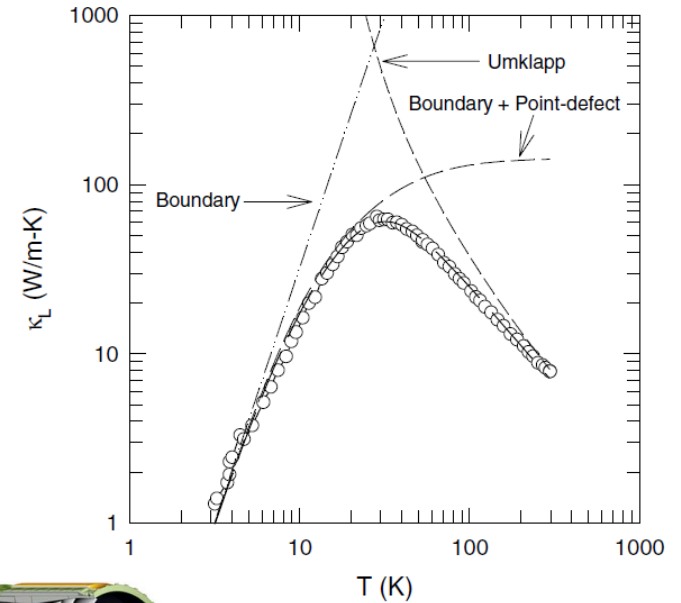


Figure: Terry M. Tritt

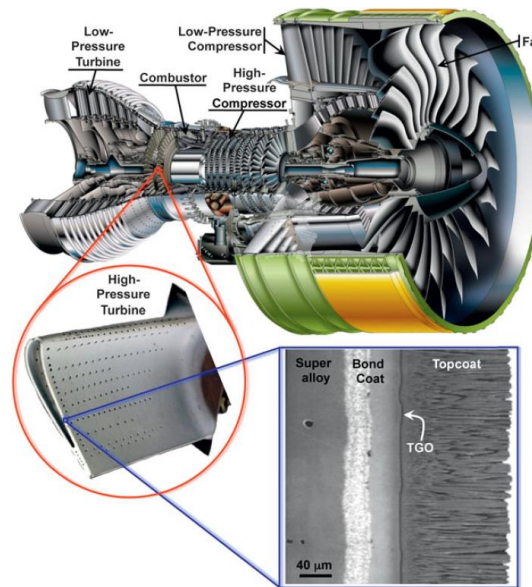
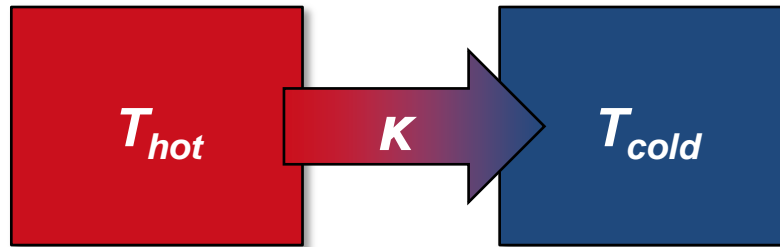


Figure: *MRS Bulletin* 2012, 37, 891.

# Thermal conductivity $\kappa$



- **Ability of a substance to conduct heat** (units:  $\text{W m}^{-1} \text{K}^{-1}$ )
- 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)

# Warm-up

Do the following materials possess high or low thermal conductivity? Why?



Diamond



Graphite



Polyethylene

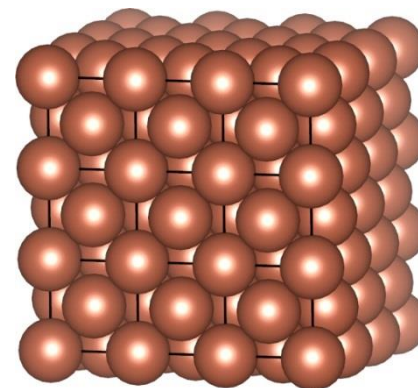
Figures: Wikipedia



Silicon



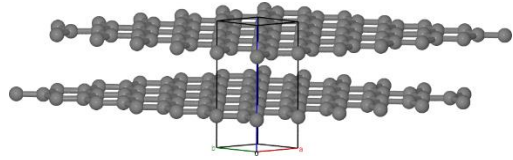
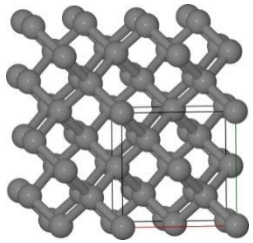
Silica aerogel



Copper

Figure: AJK

# $\kappa$ at 300 K ( $\text{W m}^{-1} \text{K}^{-1}$ )



Figures: Wikipedia



~2200 (natural diamond)

Diamond



Anisotropic!

~2000 (in-plane);  
~6 (out-of-plane)

Graphite



~0.5

Polyethylene



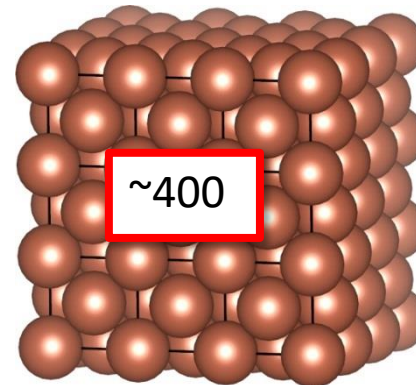
~155

Silicon



~0.005 (air = 0.026!)

Silica aerogel



~400

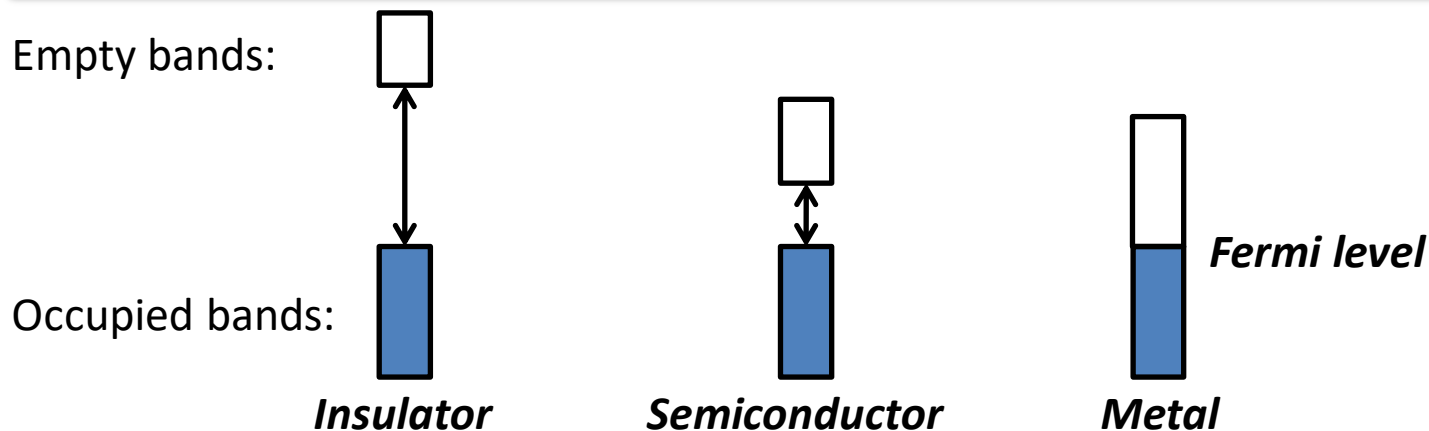
Copper

Figure: AJK

# 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:



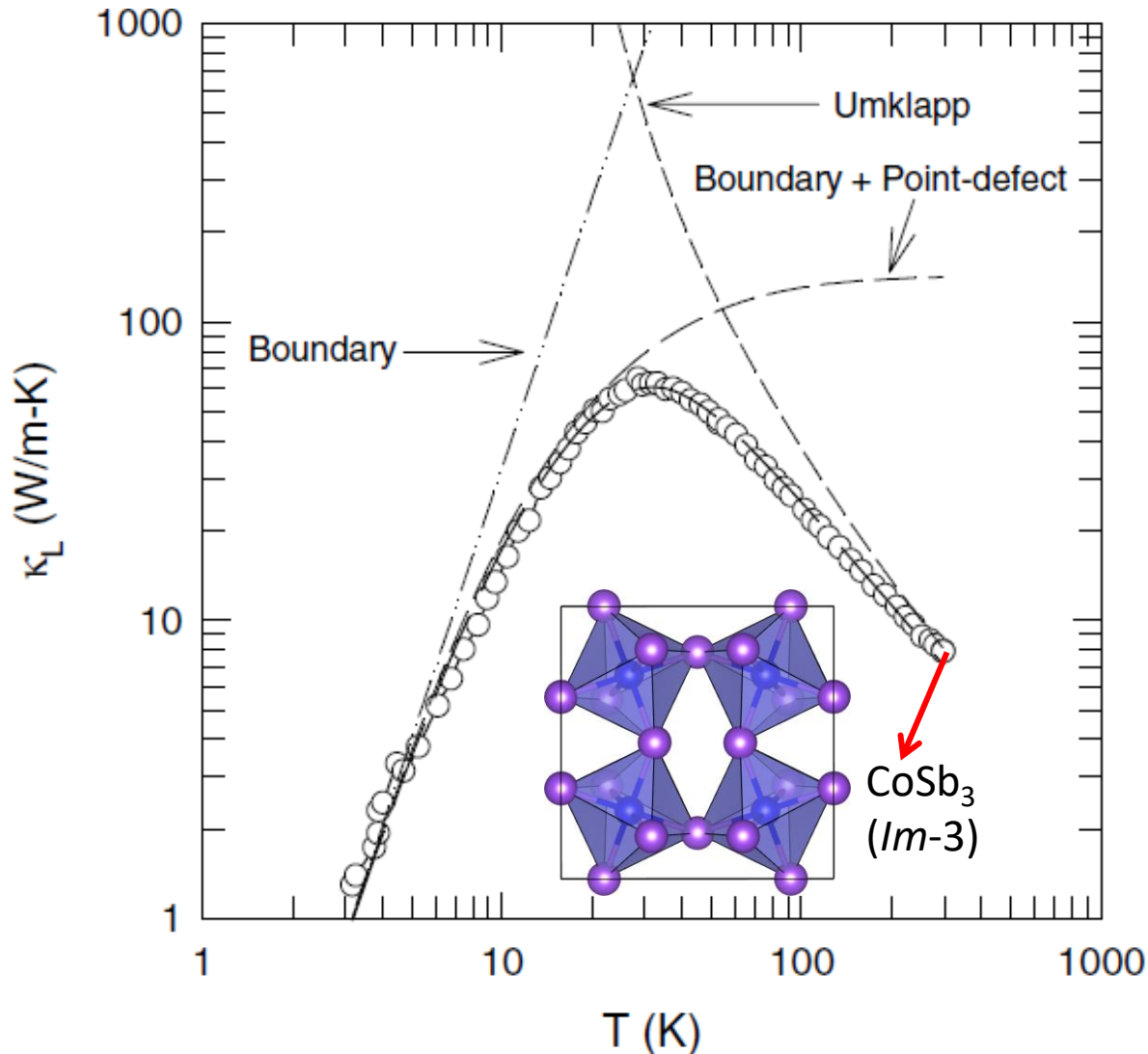
# Electronic thermal conductivity

- Heat is carried by conduction electrons
- Electronic thermal conductivity  $\kappa_e$  is directly proportional to the electrical conductivity  $\sigma$  (Wiedemann-Franz law):  
 $\kappa_e = LT\sigma$ , where  
 $L = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$
- $L$  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 $\sigma$ (S/m) at 300 K	Thermal conductivity $\kappa$ ( $\text{W m}^{-1} \text{K}^{-1}$ )
Ag	$6.3 \times 10^7$	430
Cu	$6.0 \times 10^7$	400
Al	$3.5 \times 10^7$	235
Zn	$1.7 \times 10^7$	120
Pb	$4.6 \times 10^6$	35

# Thermal conductivity of an insulator

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



Dots = experiment ( $\text{CoSb}_3$ )

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

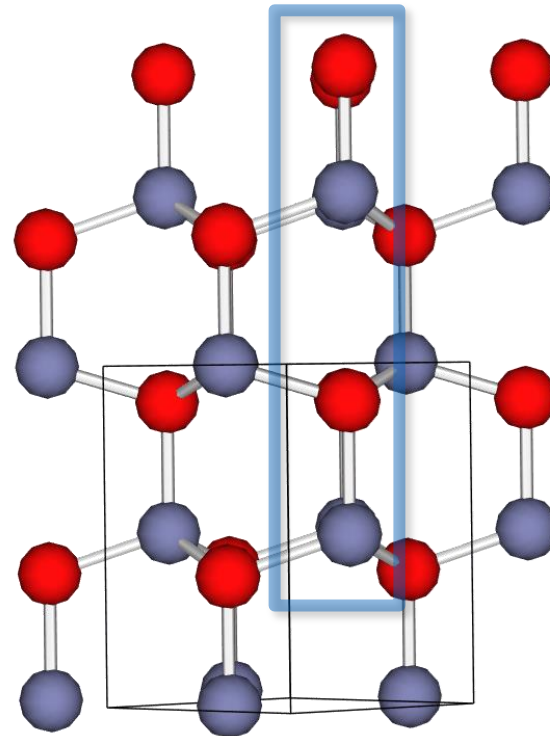
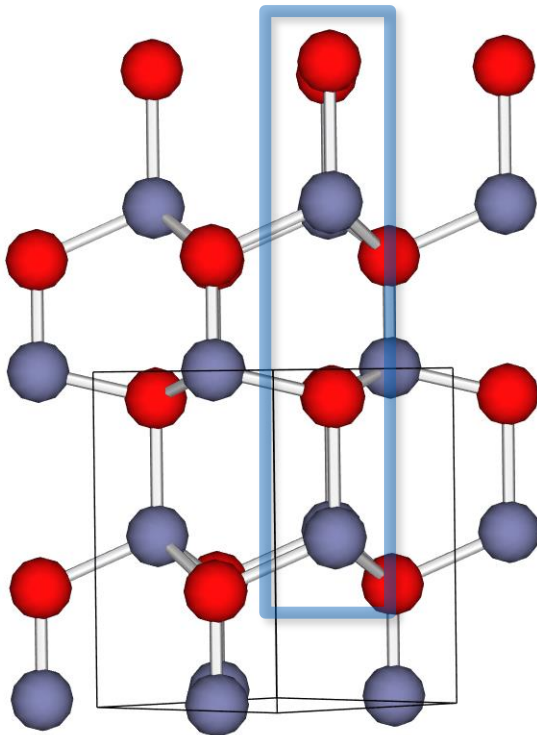


# Lattice thermal conductivity

- In insulating solid-state materials, heat is carried by vibrational excitations called *phonons* (from greek φωνή = *phone* = **sound** – we will soon hear why)
- Phonons give rise to ***lattice thermal conductivity***,  $\kappa_L$
- 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)

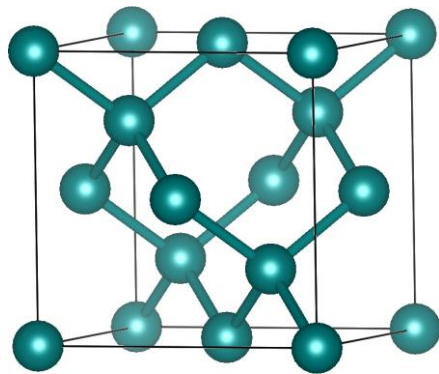
# Vibrations in molecules and solids

- A molecule with  $N$  atoms shows  $3N - 6$  vibrational modes  $\omega_i$
- 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:

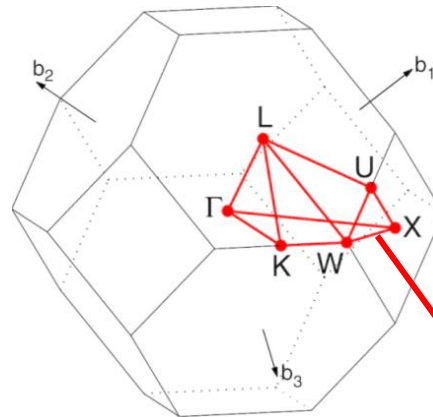


# Phonon dispersion relations

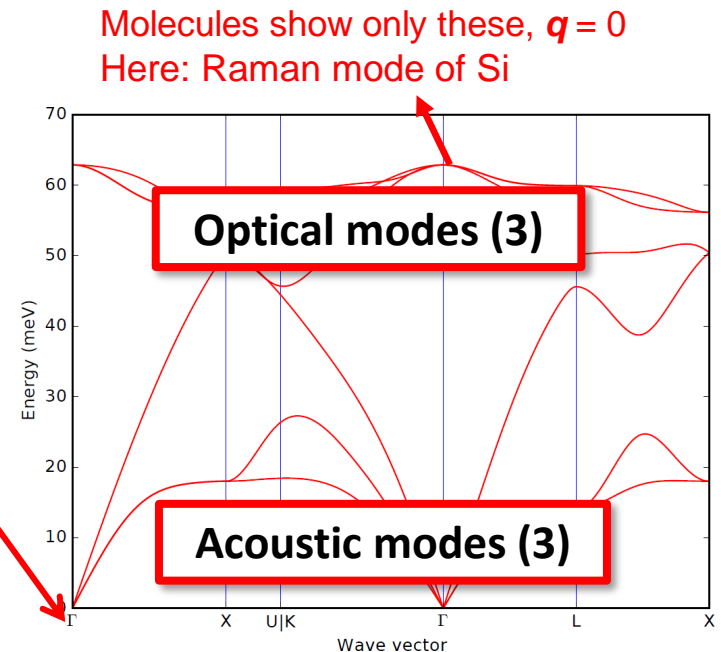
- The vibrational modes of a solid are described as a function of wavevector  $q$  in the reciprocal space:  $\omega_i(q) = \textit{phonon dispersion relations}$ 
  - Phonon dispersion relations account for the periodic nature of the crystal
  - Atoms in neighboring cells can vibrate in a different phase



$\alpha$ -silicon ( $Fd\bar{3}m$ )  
Two atoms in the primitive cell  
-> six phonon modes

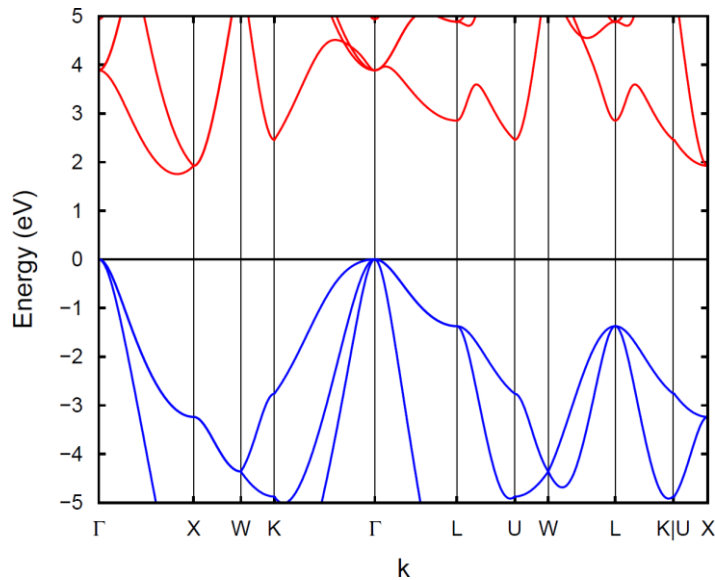


Brillouin zone of FCC lattice (reciprocal space path in red)

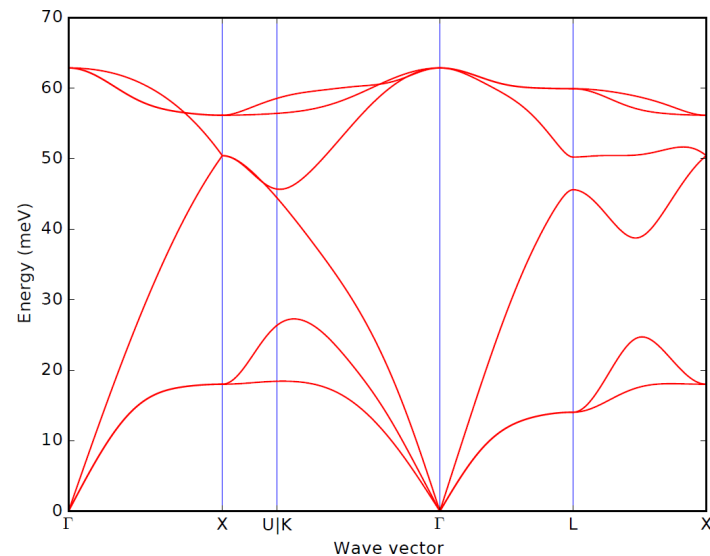


# Phonons vs. electrons

- 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



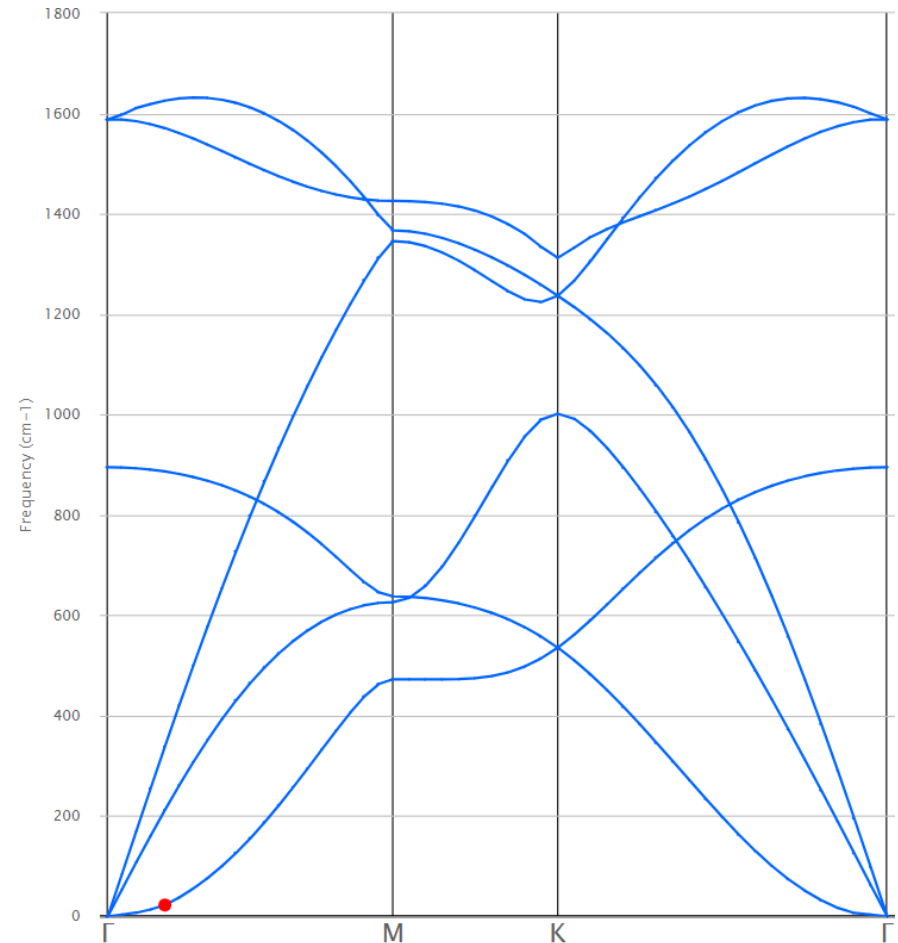
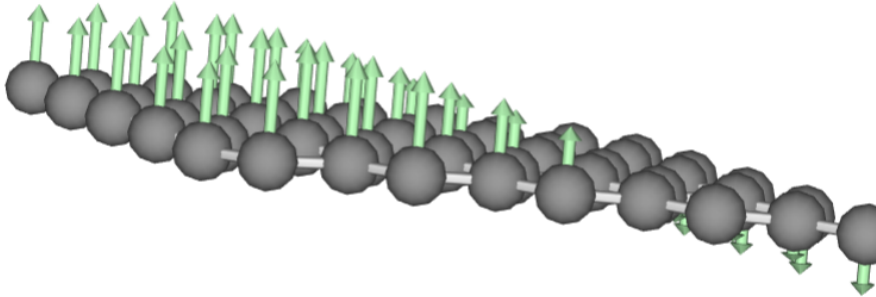
Electronic band structure  
of  $\alpha$ -silicon



Phonon dispersion  
relations of  $\alpha$ -silicon

# Visualization of phonons

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

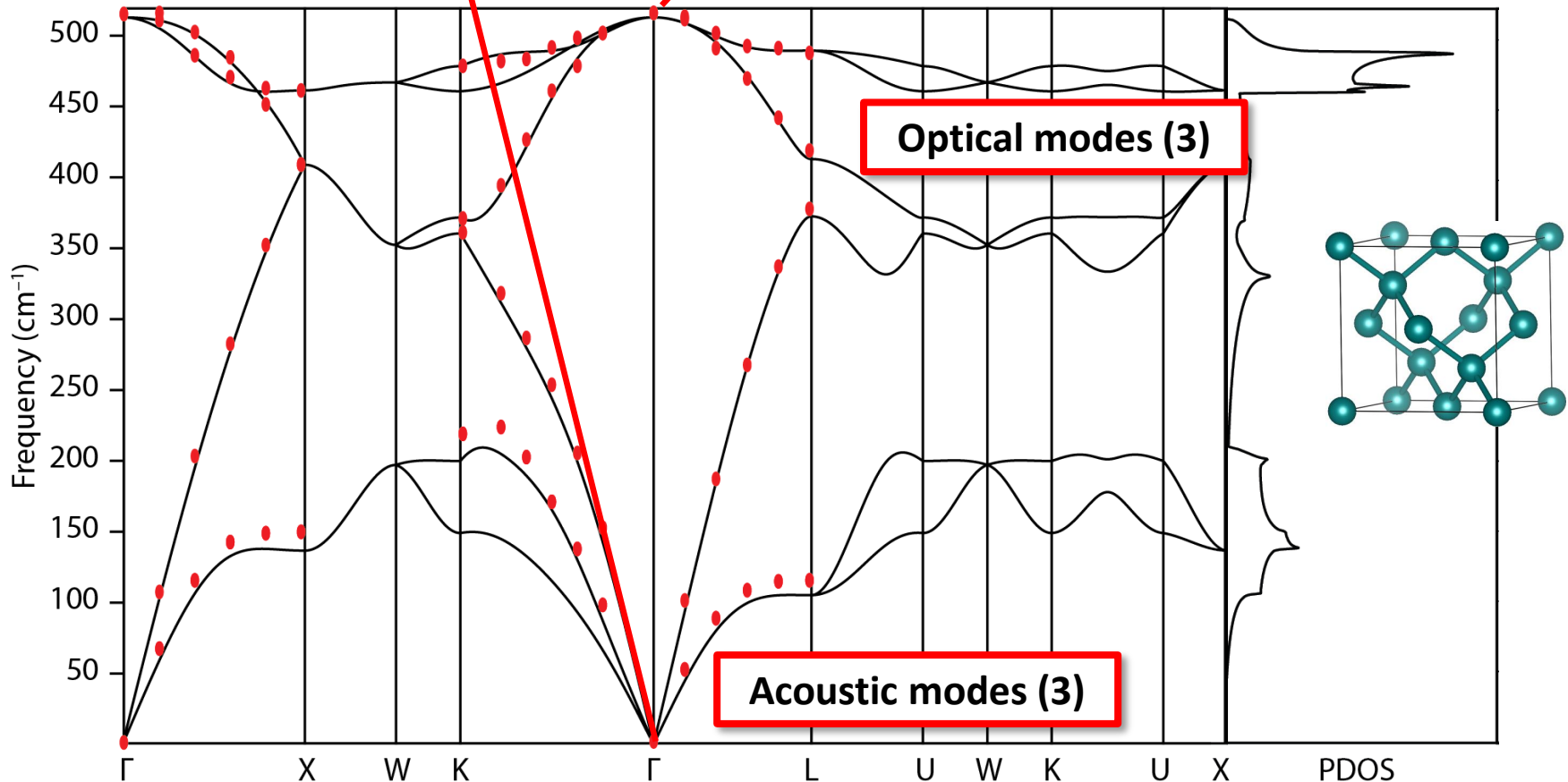


# Phonon dispersions for silicon (1)

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

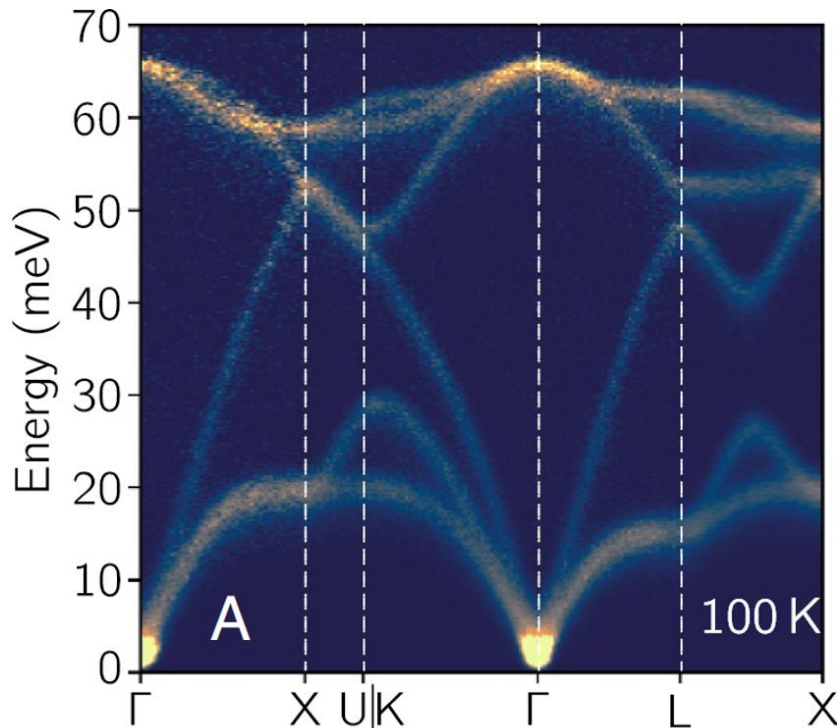
Tangent = phonon group velocity  $\approx$  speed of sound

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

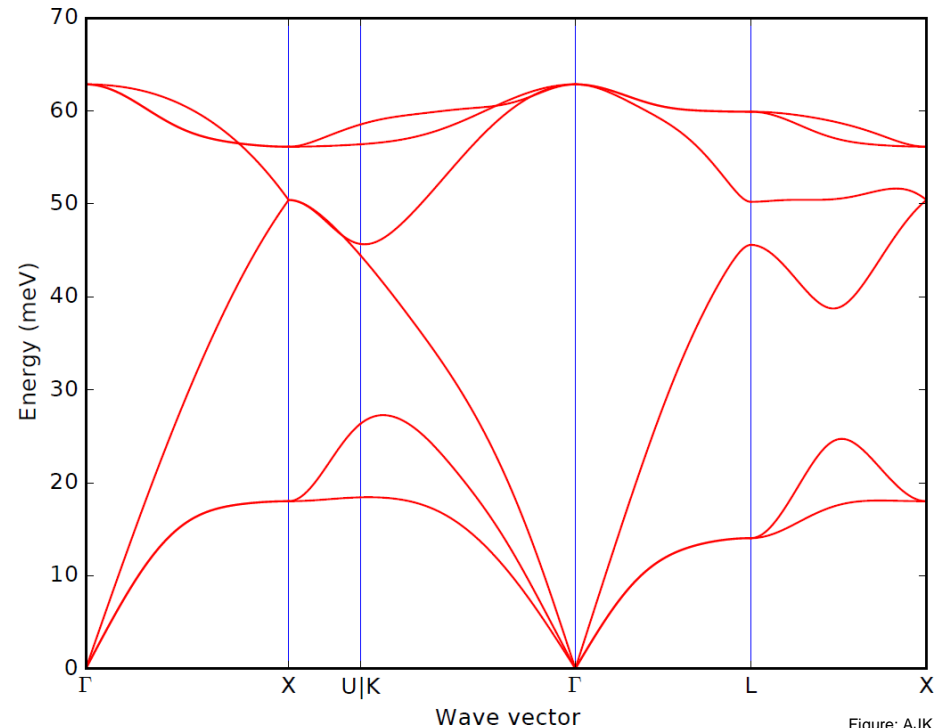


# Phonon dispersions for silicon (2)

- 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)



**Density Functional Theory**  
(DFT-PBE0/SVP)

Figure: AJK

# Lattice thermal conductivity $\kappa_L$ 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%)
- $\kappa_L$  can be solved with the help of the semiclassical Boltzmann Transport Equation
- In Single-Mode Relaxation Time approximation:

$$\kappa = \frac{1}{NV_0} \sum_{\lambda} C_{\lambda} \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} \tau_{\lambda}^{\text{SMRT}}$$

Heat capacity, calculated from phonon dispersions

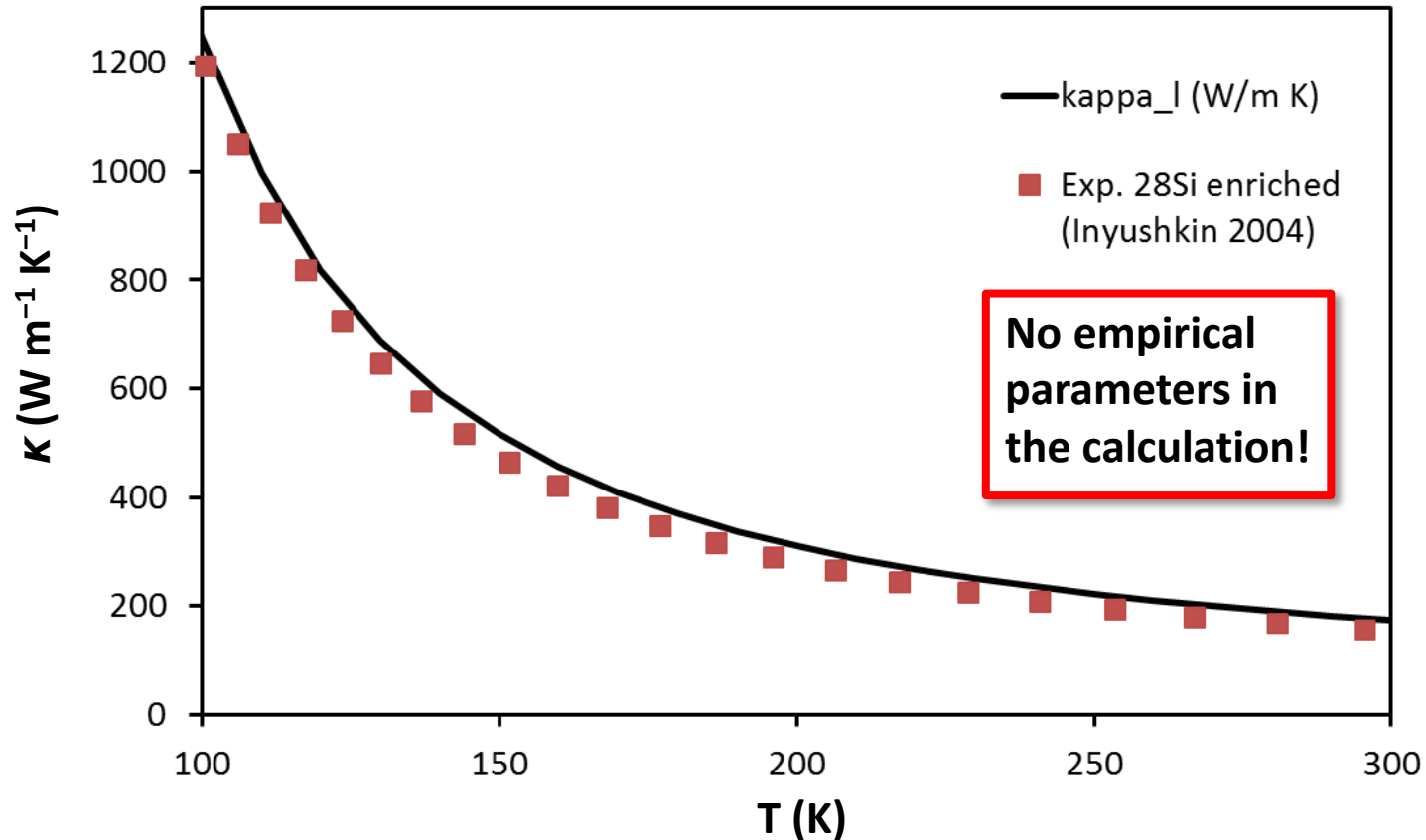
Phonon group velocity, calculated from phonon dispersions

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



# Lattice thermal conductivity of silicon

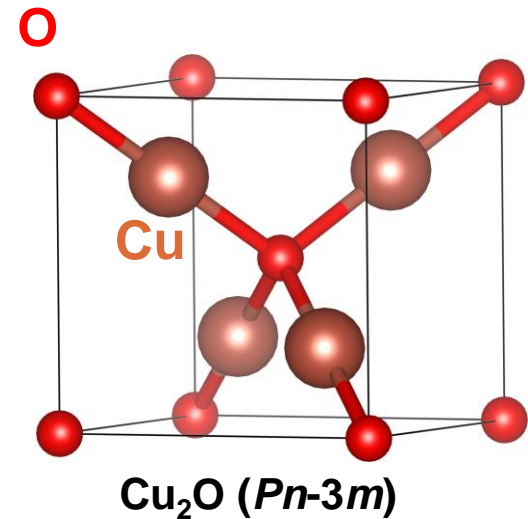
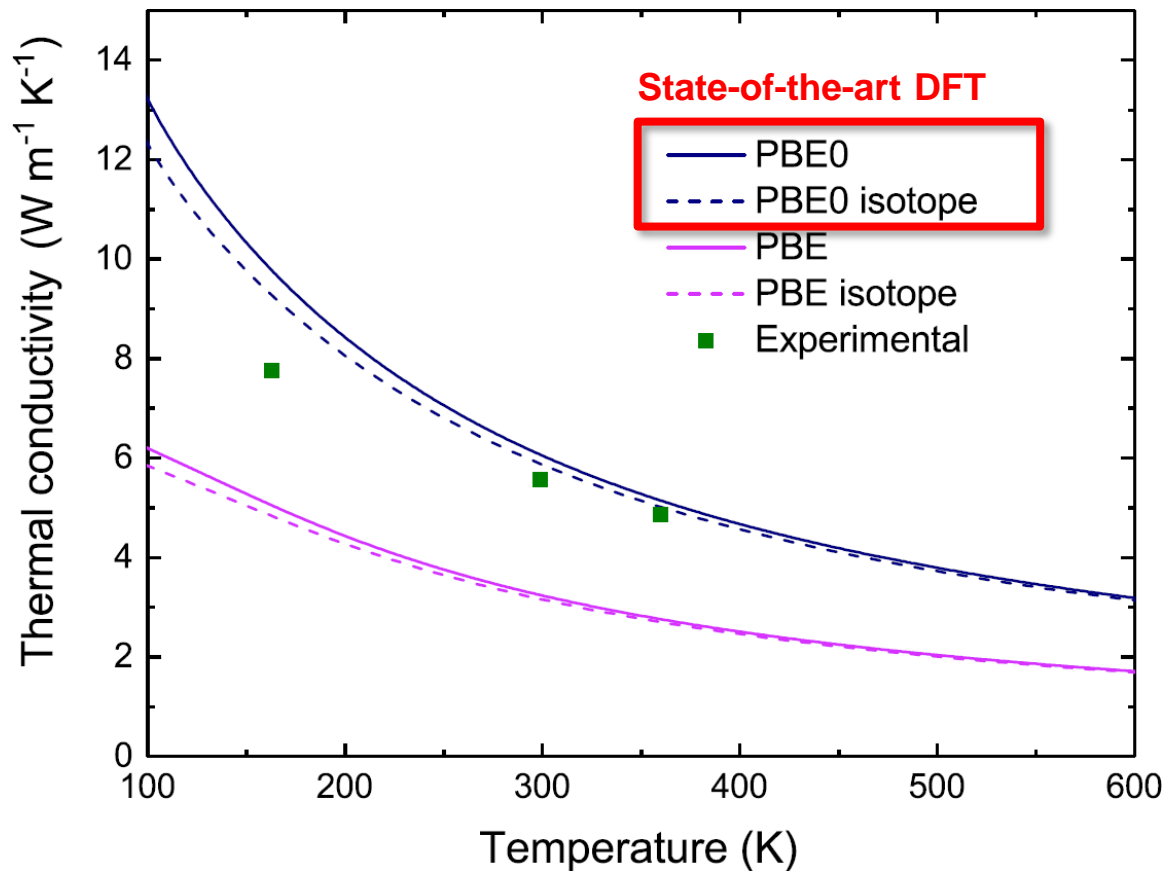
For a simple semiconductor like silicon,  $\kappa_l$  can be predicted with good accuracy using Density Functional Theory (DFT) and semiclassical Boltzmann Transport Equation



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

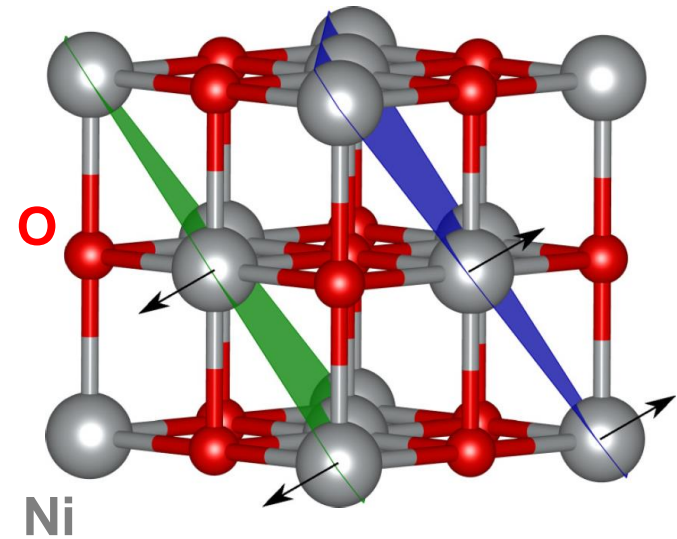
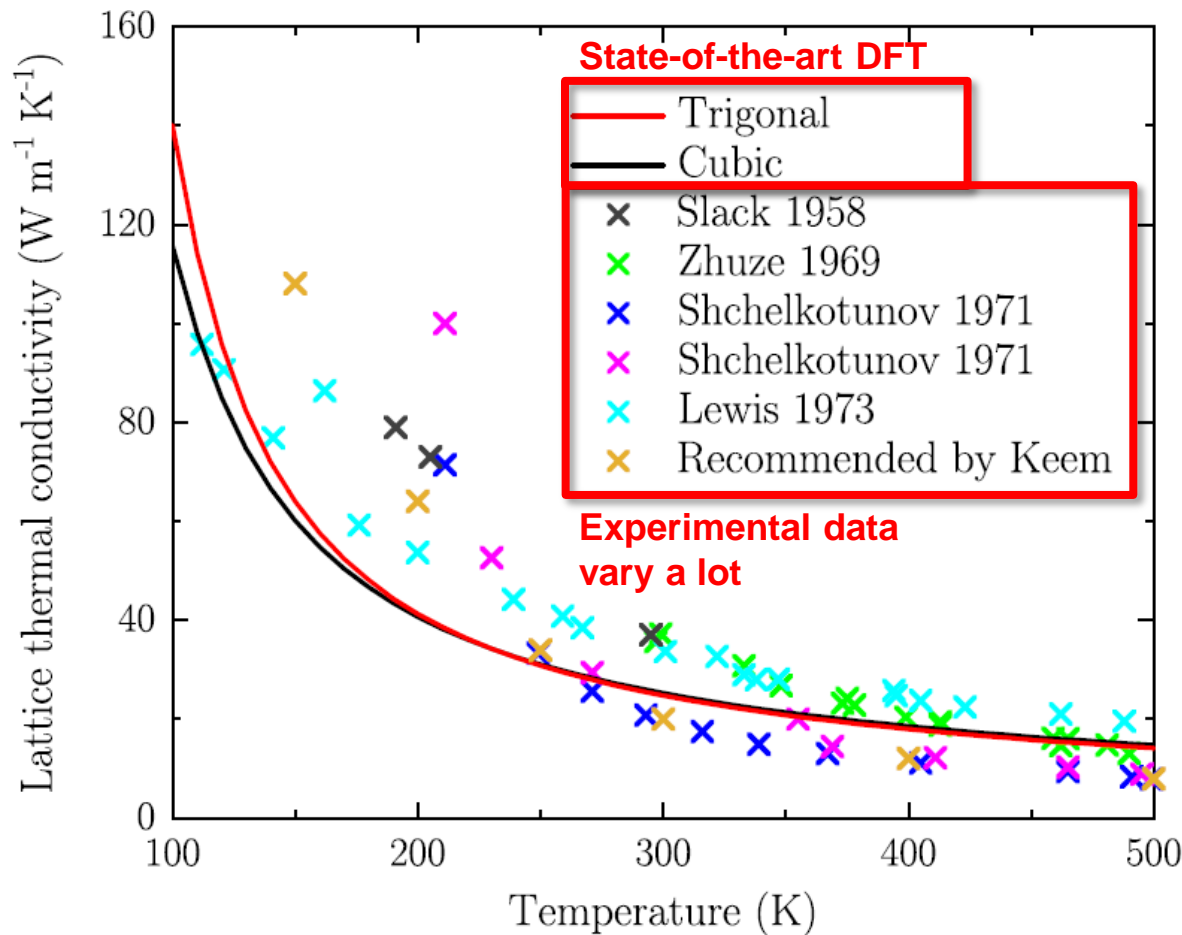
DFT results: A. J. Karttunen, unpublished results.

# Lattice thermal conductivity of $\text{Cu}_2\text{O}$



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

# Lattice thermal conductivity of NiO



**NiO ( $Fm\text{-}3m$ )**  
**Antiferromagnetic up to 525 K**  
**Magnetic ordering:  $R\text{-}3m$**

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].

# Periodic trends

- Lattice thermal conductivity depends strongly on the interatomic forces
- The stronger the interatomic forces, the more strongly the atoms are coupled to each other
  - Strong 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 ionic materials, the interatomic force constants and phonon velocities are smaller
  - For NaCl,  $\kappa = 6.5 \text{ W m}^{-1} \text{ K}^{-1}$

	<b>Thermal conductivity <math>\kappa</math> (<math>\text{W m}^{-1} \text{ K}^{-1}</math>)</b>
C	~2200 (diamond)
Si	~150
Ge	~60
Sn	~60 (metal)
Pb	~35 (metal)

# 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  $0.2 \text{ W m}^{-1} \text{ K}^{-1}$ )

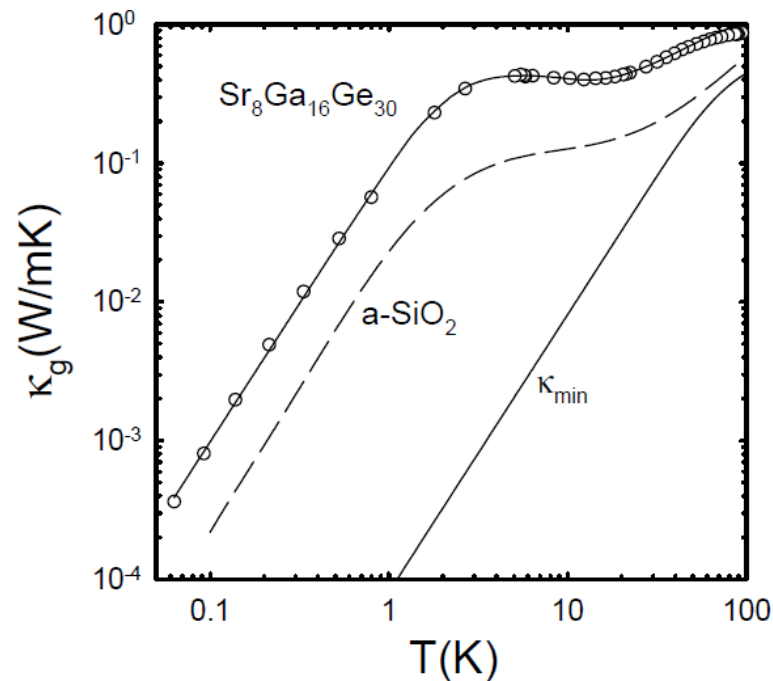


FIG. 2. Lattice thermal conductivity measured from 60 mK to 100 K for  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$  with a fit (solid curve) to the model discussed in the text (see also Fig. 3). The dashed line is for  $a\text{-SiO}_2$ , and the solid curve labeled  $\kappa_{\text{min}}$  is the calculated minimum thermal conductivity of Ge.

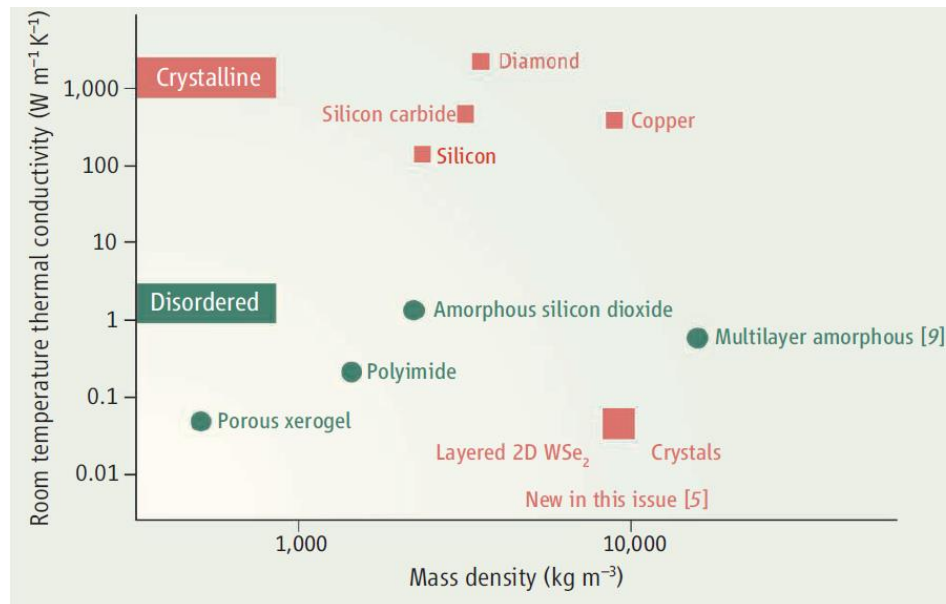
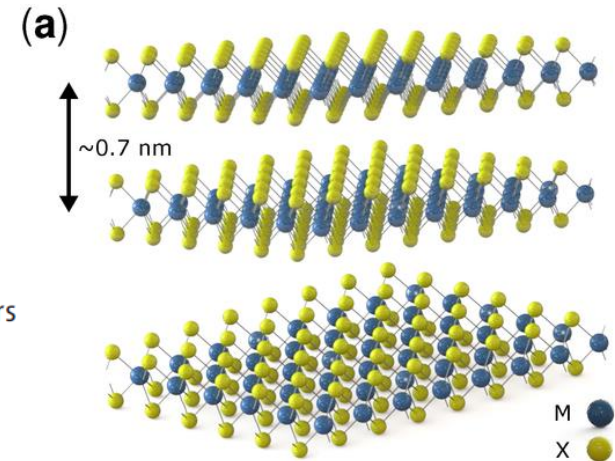
# Low- $\kappa_L$ crystalline materials

19 JANUARY 2007 VOL 315 SCIENCE www.sciencemag.org

## Ultralow Thermal Conductivity in Disordered, Layered $WSe_2$ Crystals

Catalin Chiritescu,<sup>1</sup> David G. Cahill,<sup>1\*</sup> Ngoc Nguyen,<sup>2</sup> David Johnson,<sup>2</sup> Arun Bodapati,<sup>3</sup> Pawel Keblinski,<sup>3</sup> Paul Zschack<sup>4</sup>

The cross-plane thermal conductivity of thin films of  $WSe_2$  grown from alternating W and Se layers is as small as 0.05 watts per meter per degree kelvin at room temperature, 30 times smaller than the *c*-axis thermal conductivity of single-crystal  $WSe_2$  and a factor of 6 smaller than the predicted minimum thermal conductivity for this material. We attribute the ultralow thermal conductivity of these disordered, layered crystals to the localization of lattice vibrations induced by the random stacking of two-dimensional crystalline  $WSe_2$  sheets. Disordering of the layered structure by ion bombardment increases the thermal conductivity.



### *Search for the worst.*

Room-temperature thermal conductivities of a few representative materials compared with new data for ordered  $WSe_2$  films. The material sets a record for the lowest thermal conductivity of a fully dense material at 300 K. Remarkably, the ultralow conductivity is achieved through the introduction of crystalline order.

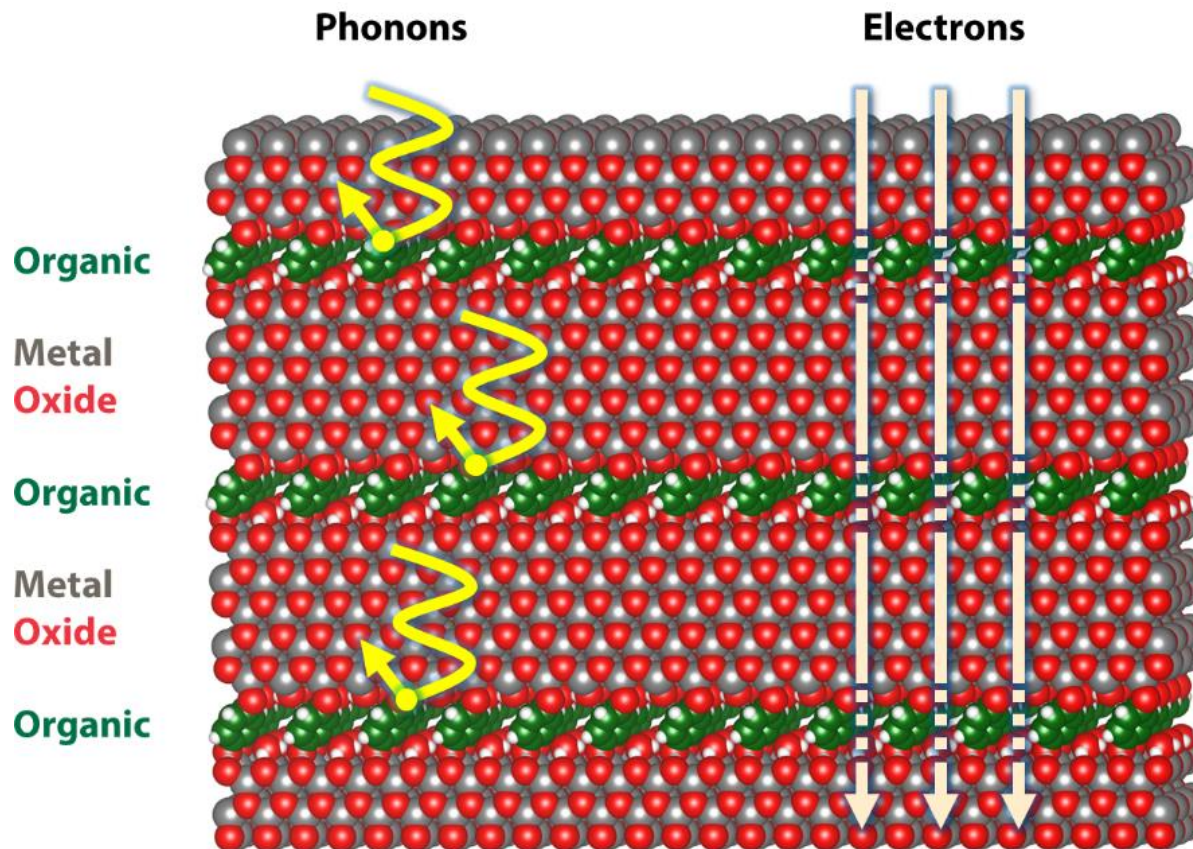
# Thermal engineering

- How to decrease the thermal conductivity of materials?
  - In general: add ***disorder***
  - Alloying
    - Si: **150** W m<sup>-1</sup> K<sup>-1</sup>
    - Ge: **60** W m<sup>-1</sup> K<sup>-1</sup>
    - 50:50 Si-Ge alloy: **10** W m<sup>-1</sup> K<sup>-1</sup>
  - Doping: electronic doping also introduces kind of point defects, decreasing lattice thermal conductivity.
    - For example, ZnO: **43** W m<sup>-1</sup> K<sup>-1</sup>; 2% Al doping decreases the thermal conductivity to **~7** W m<sup>-1</sup> K<sup>-1</sup>
  - Create interfaces that scatter phonons
    - **Superlattices**
- How to increase thermal conductivity?
  - Prepare samples with high isotopic purity (the effect will be large < 100 K, but only ~10% at room temperature)
  - Create better materials!



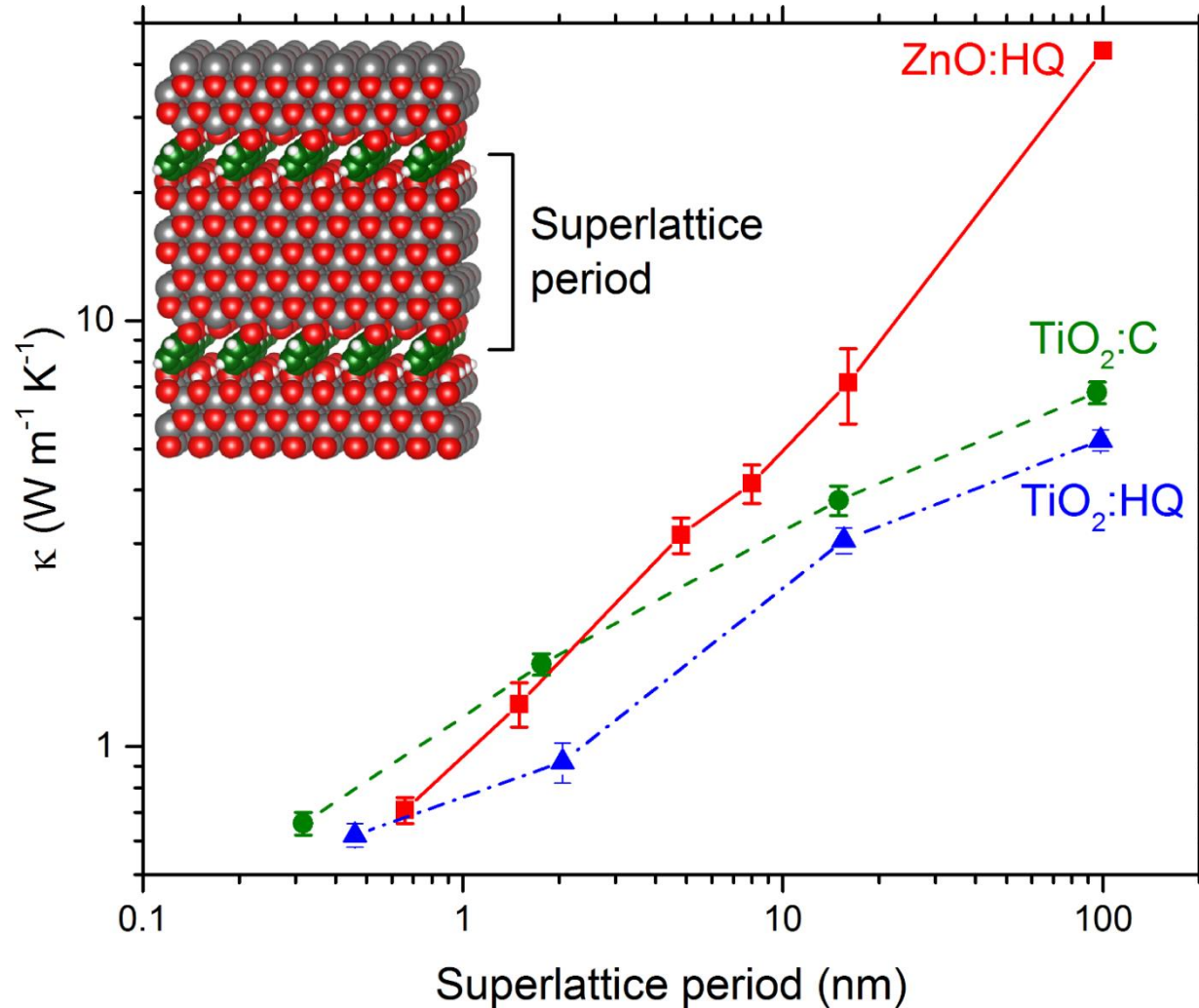
# Oxide-organic superlattices

- ZnO:organic superlattices fabricated by ALD/MLD
- Try to 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.





# Oxide-organic superlattices



# Thermal barrier coatings for gas-turbine engines

MRS BULLETIN • VOLUME 37 • OCTOBER 2012 • [www.mrs.org/bulletin](http://www.mrs.org/bulletin) ■ 891

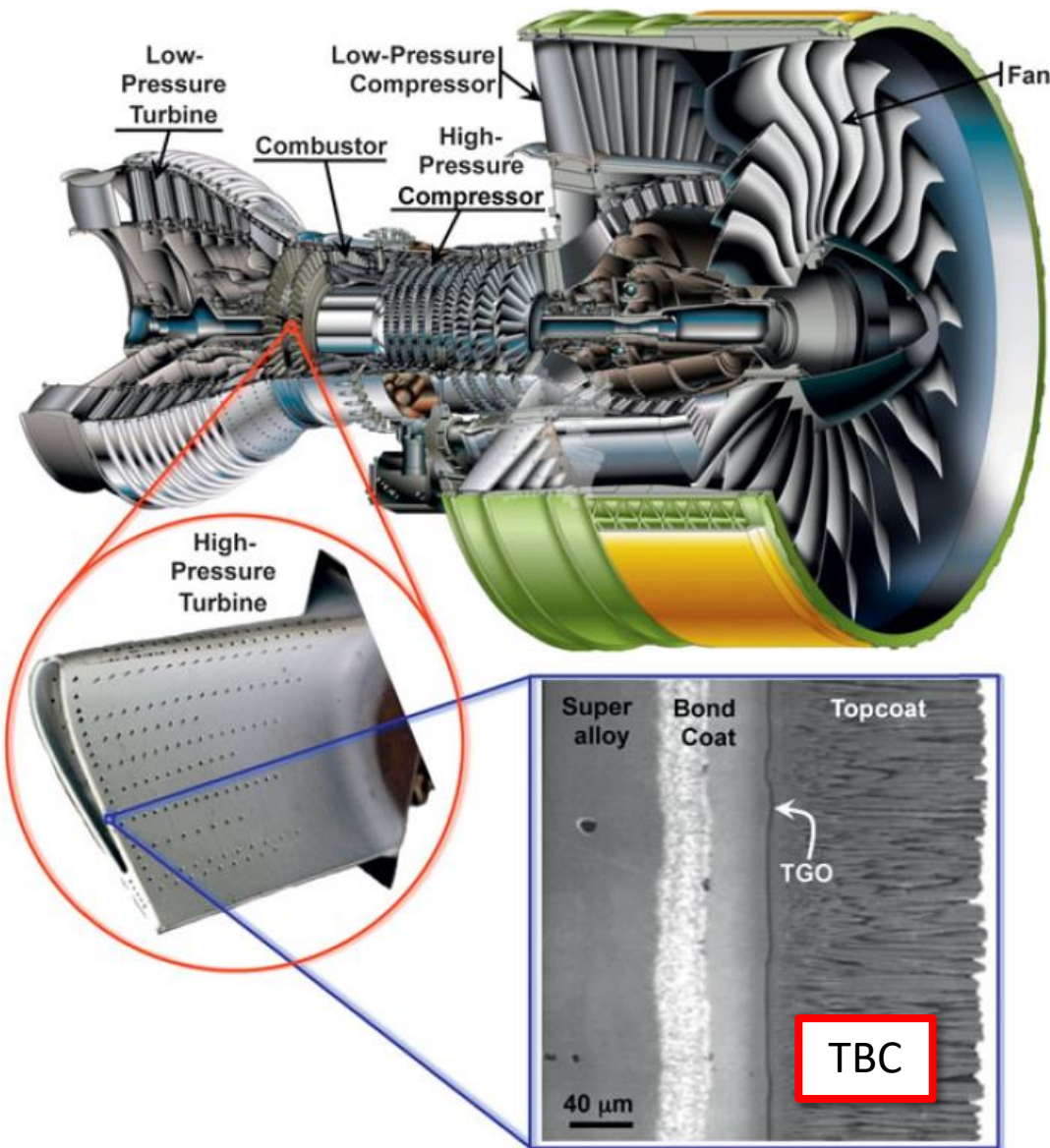
## Introduction

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<sup>1-6</sup>). 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.<sup>7,8</sup> 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.

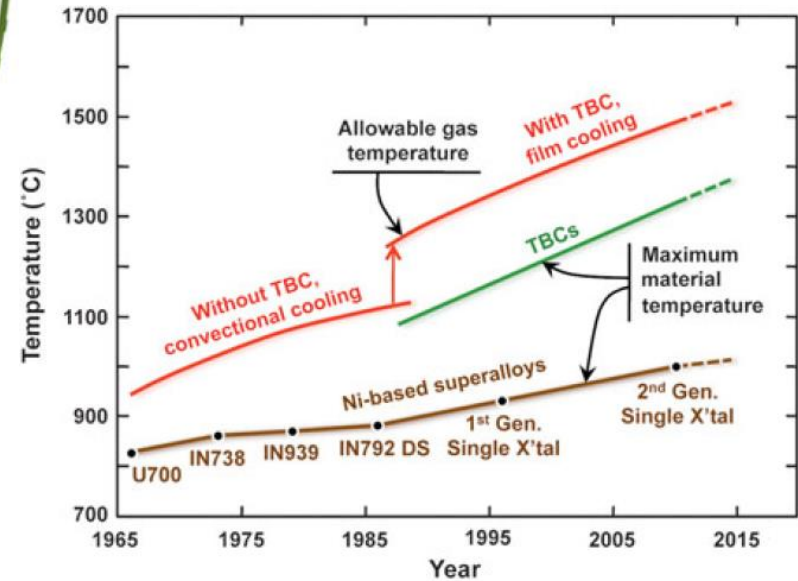
To place this in context, gas-turbine engines are a \$42 billion industry worldwide (2010), with ~65% of the sales accounting for jet engines and the remainder land-based engines for electricity generation.<sup>9</sup> The latter, fueled by natural gas or liquid

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.



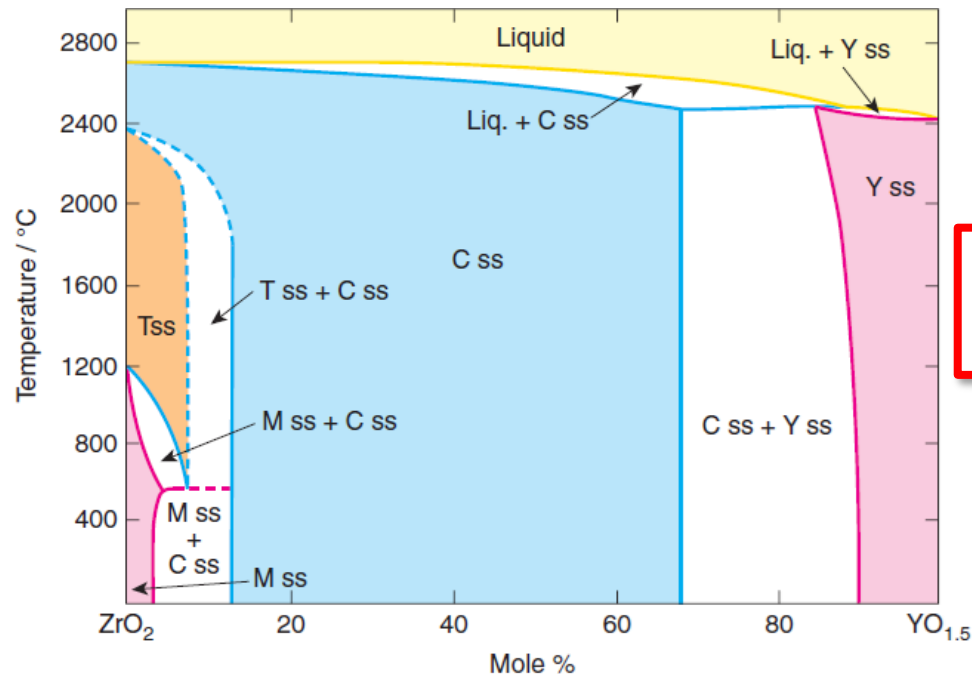
**Figure 3.** Progression of temperature capabilities of Ni-based superalloys and thermal-barrier coating (TBC) materials over the past 50 years. The red lines indicate progression of maximum allowable gas temperatures in engines, with the large increase gained from employing TBCs. Based on a diagram 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  $\sim 2700^\circ C$  but on cooling it undergoes a series of phase transitions:

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

- The tetragonal to monoclinic transition is associated with an increase in unit cell volume by  $\sim 9\%$   $\rightarrow$  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:  
 $3 \text{ W m}^{-1} \text{ K}^{-1}$  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,  $Y_2O_3$ .