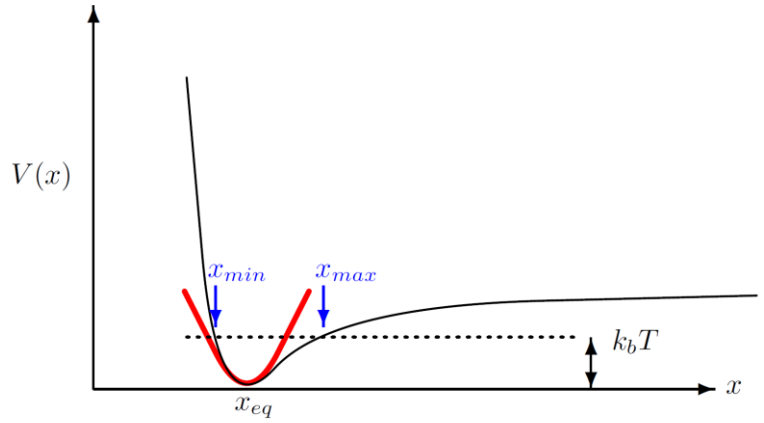
# Phonons: Thermal properties

Lecture 2

# Thermal properties – Goals recap

- Introduction: Why do we care?
- Debye's Model for heat capacity
- Einstein's Model for heat capacity
- **Thermal conductivity**

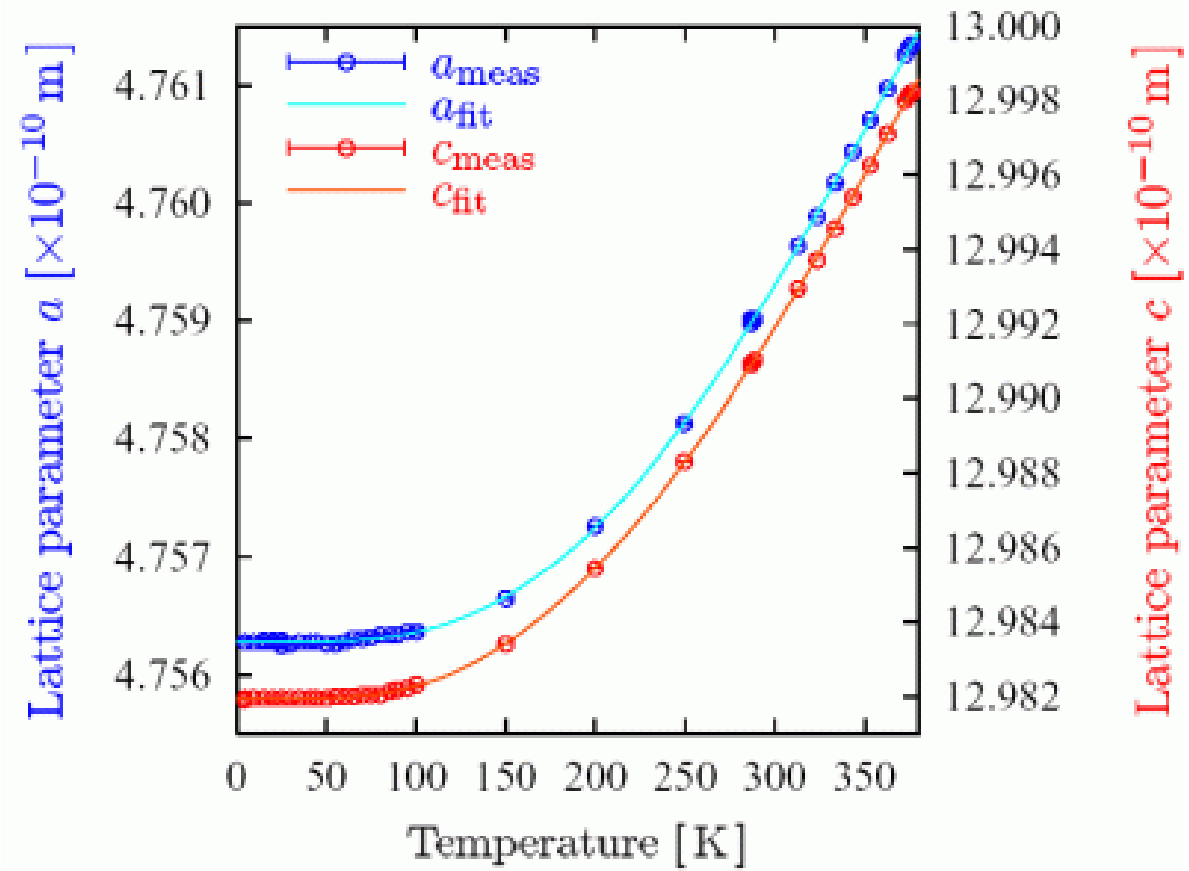
# Anharmonic crystal interactions




Limitations Harmonic approximation:

- There is no thermal expansion
- Two lattice waves do not interact
- The heat capacity becomes constant at high temperatures
- Adiabatic and isothermal elastic constants are equal
- The elastic constants are independent of pressure and temperature

## Lattice parameters of sapphire

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Sapphire: aluminum oxide (α-$Al_2O_3$) with trace amounts of elements such as iron, titanium, chromium, copper, or magnesium.

# Thermal expansion in anharmonic potential

Consider a classical 1D oscillator,

c, g : positive constants

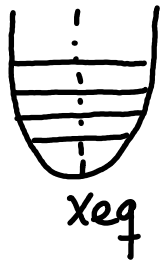
Potential energy $U(x) = \underbrace{cx^2}_{\text{term considered in the harmonic appr.}} - \underbrace{gx^3}_{\text{It takes into account asymmetry of the potential}} - \cdots$

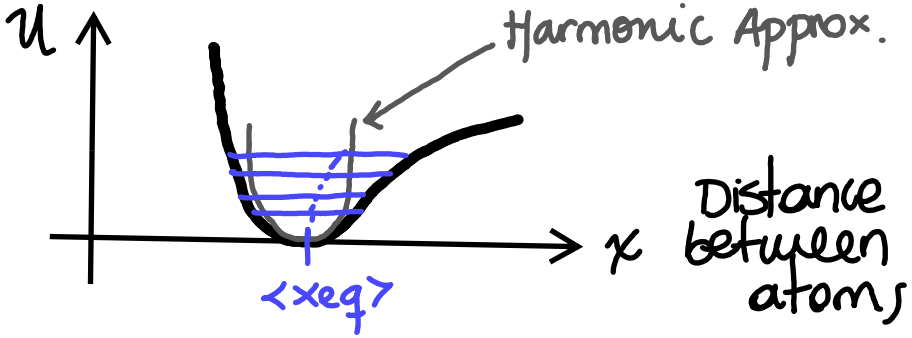
$F = Cx$

$\langle x \rangle = 0$

$\langle F \rangle = 0$

$\Rightarrow$ no thermal expansion




Average displacement :

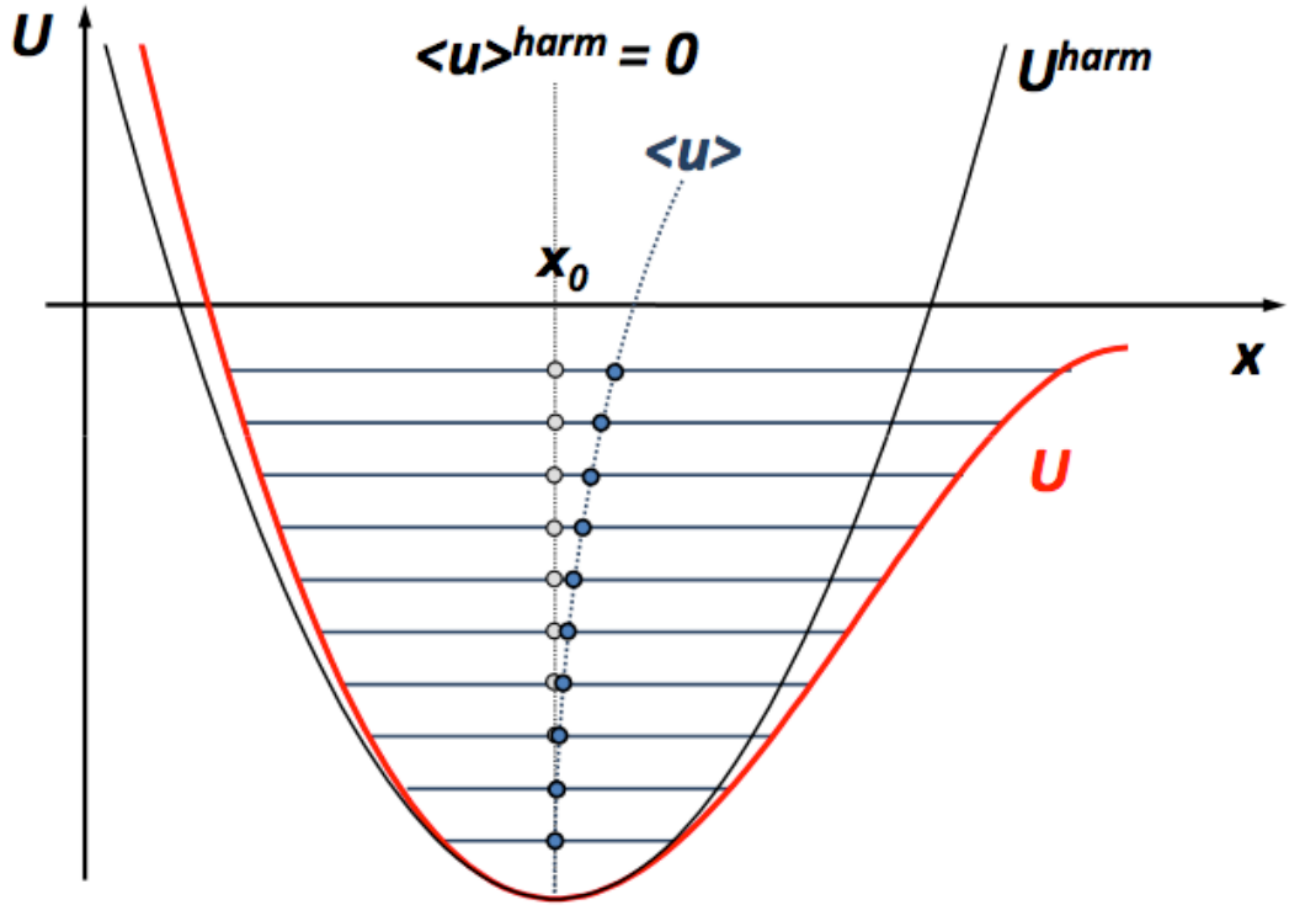
calculated using Boltzmann distribution function

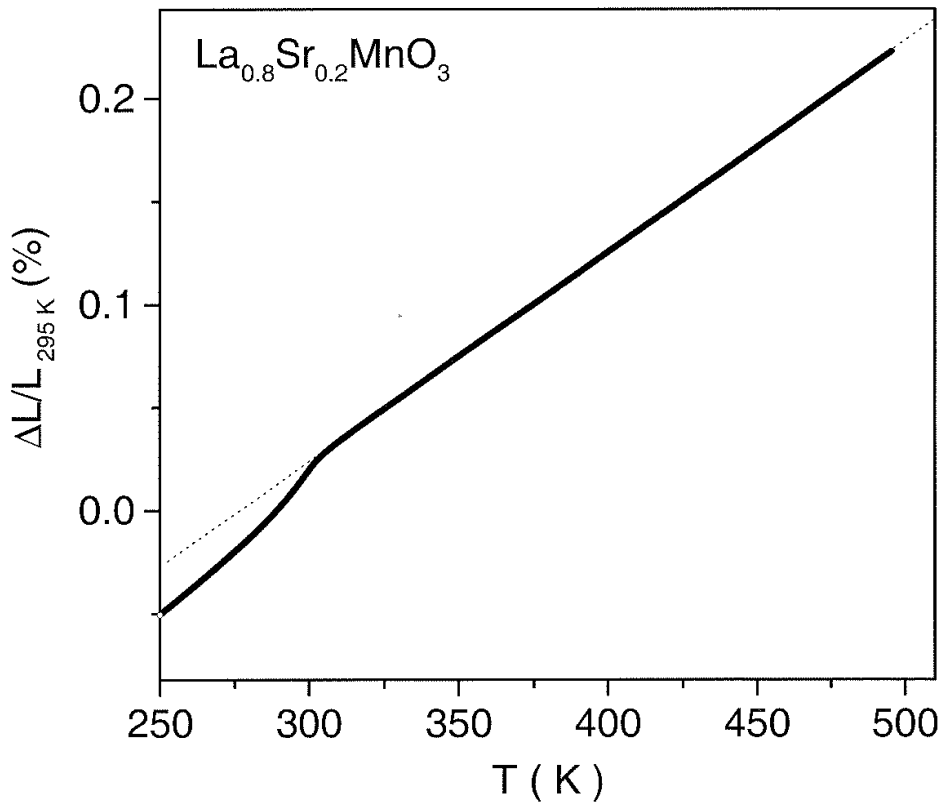
$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x \exp\left(\frac{-U(x)}{K_B T}\right) dx}{\int_{-\infty}^{\infty} \exp\left(\frac{-U(x)}{K_B T}\right) dx} \longrightarrow \langle x \rangle = \frac{3}{4}\frac{g}{c^2} K_B T$$

For displacements such the anharmonic terms in energy are small compared to $K_B T$

Expansion linear with T (ie classical domain)

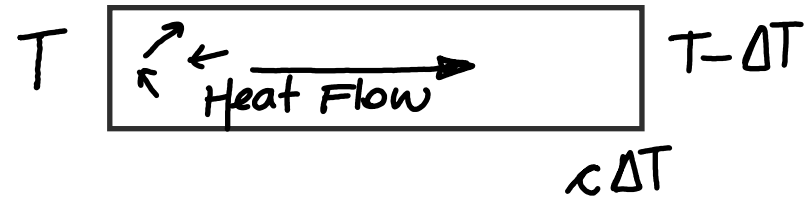
# Thermal expansion in anharmonic potential




La0.8Sr0.2MnO3
0.2
0.1
0.0
ΔL/L295 K (%)
250
300
350
400
450
500
T ( K )

# Thermal conductivity

"Phonon gas"




Flux of thermal energy $\quad \boxed{j_u = -\kappa \frac{dT}{dx}}$ temperature gradient

$\kappa$: THERMAL CONDUCTIVITY COEFFICIENT (it measures the ease of heat transmission)

$$\Delta T = \frac{dT}{dx} \cdot l_x = \frac{dT}{dx} v_x \cdot \tau$$

$\tau$: average time between two collisions

$l_x$: distance travelled by the particle between two collisions

$$j_u = -\underbrace{n \cdot v_x}_{\text{flux}} \cdot \underbrace{c \frac{dT}{dx} \cdot v_x \cdot \tau}_{\text{energy}} = -n \langle v_x \rangle^2 c \tau \frac{dT}{dx} = -\frac{1}{3} n \langle v^2 \rangle \cdot c \cdot \tau \frac{dT}{dx}$$

$u = \frac{\text{phonons}}{\text{density}} = \frac{N}{V}$

isotropic solid

$\langle v_x \rangle^2 = \langle v_y^2 \rangle = \langle v_z^2 \rangle$

$\Rightarrow \langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$

$$\boxed{j_u = -\frac{1}{3} C v l \frac{dT}{dx}}$$

$$\boxed{K \equiv \frac{1}{3} C v l}$$

$l = v \cdot \tau$ = mean free path

$C = n \cdot c$ = Heat Capacity

## Temperature-dependence

$$\kappa = \frac{1}{3} C v \ell$$

already studied in detailed in previous lecture

essentially insensitive to T

$\ell$ = mean free path = average distance a phonon travels between 2 successive collisions

$\ell$ strongly depends on T

$\Rightarrow$ Important mechanisms:

i) Collision of a phonon with imperfections in the crystal (i.e. impurities, defects)

ii) Collision of a phonon with other phonons

iii) Collision of a phonon with external boundaries of the crystal.

## Scattering by other phonons

- at high T, $\ell \propto 1/T$
- due to anharmonic interactions between phonons

Let's assume 2 phonons $\bar{K}_1$ and $\bar{K}_2$ that collide and produce a phonon of vector $\bar{K}_3$

Momentum must be conserved $\Rightarrow$ $\bar{K}_1 + \bar{K}_2 = \bar{K}_3$

it can be within 1st B.Z. or not

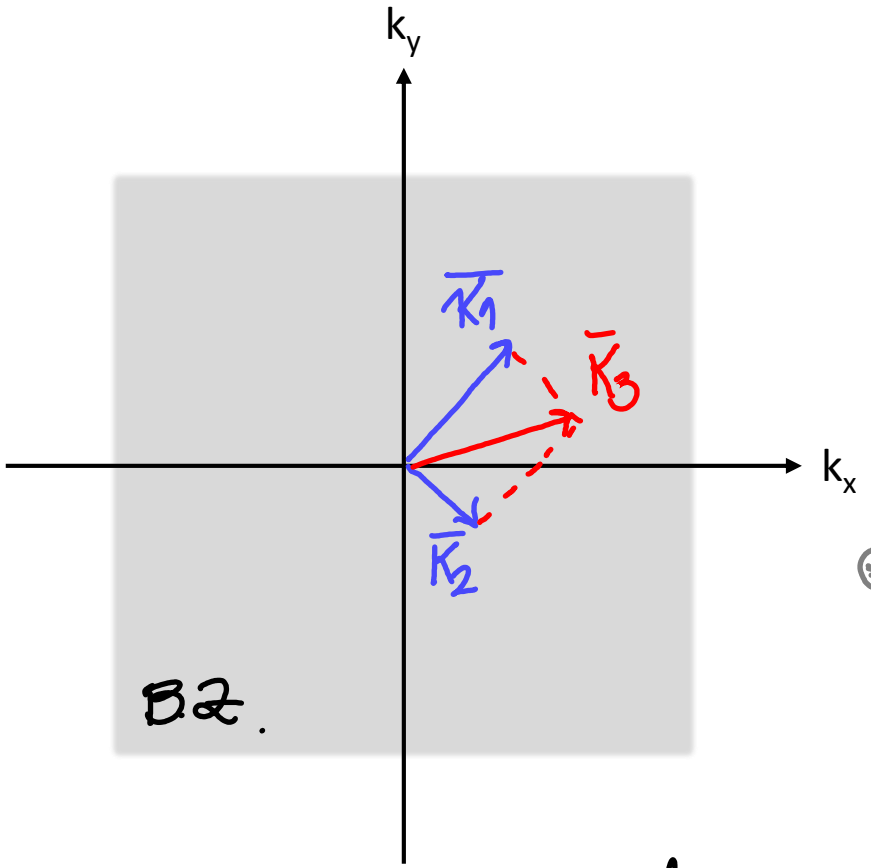
if yes: NORMAL PROCESS

if not: UMKLAPP PROCESS

see next →

# NORMAL PROCESS

$$\bar{K}_1 + \bar{K}_2 = \bar{K}_3$$



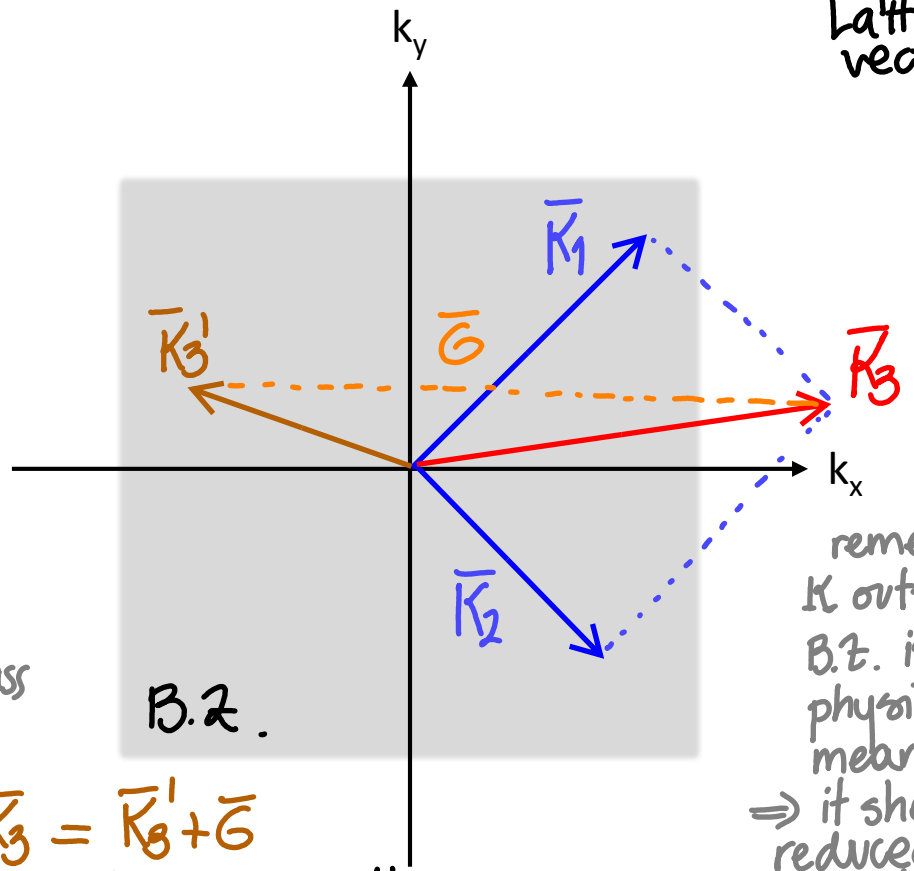

no effect on the flow of the phonons

(*) difference in momentum is transfered to the center of mass of the lattice

# UMKLAPP PROCESS

$$\bar{K}_1 + \bar{K}_2 = \bar{K}_3 + \bar{G}$$

reciprocal lattice vector




$$\bar{K}_3 = \bar{K}_3' + \bar{G}$$

$K_3'$ produced by the collision travels almost opposite to initial $K_1$ & $K_2$ → efficient changing ph. momentum (*)
→ responsible ph. scattering at T↑

remember:
K outside 1rst B.Z. is not physically meaninful
⇒ it should be reduced to its equivalent K' within 1rst B.Z

at very low T,

- ph-imperfection collisions not effective (excited phonons at low T are very long-$\lambda$, and thus not efficiently scattered by (much smaller) imperfections)
- ph-ph collisions also ineffective (only few phonons at low T)
- collisions with sample boundaries: main scattering ph mechanism at low T (if $\lambda$ excited phonon is comparable to sample dimensions)

→ <u>size or geometric effects</u>

$l \sim L$ ← being roughly the "diameter" of the sample

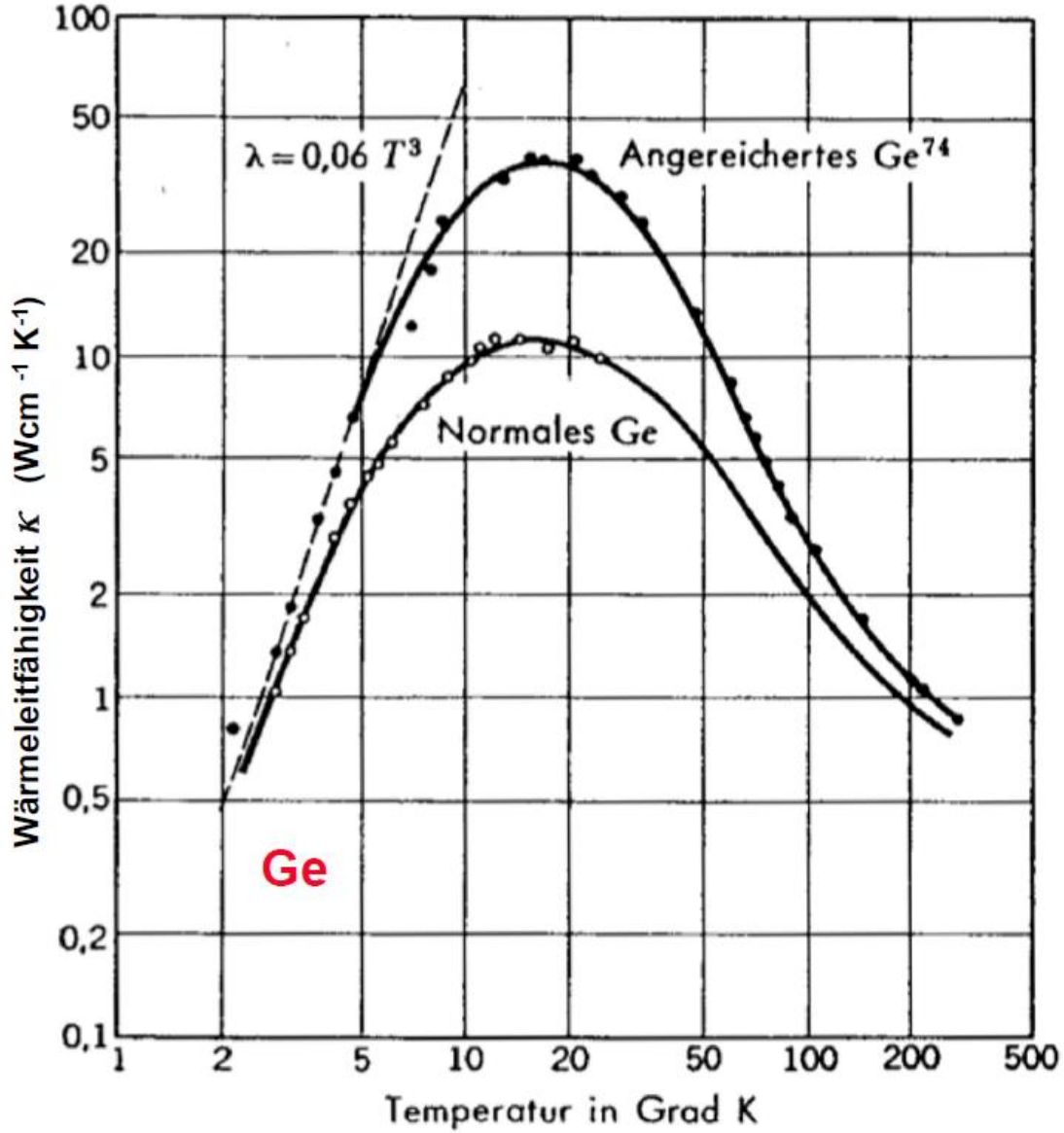
Recap

thermal conductivity $\kappa$ vs $T$

at low $T$ : $\kappa = \frac{1}{3} C v \ell \longrightarrow \kappa \propto T^3$

$C \propto T^3$ ; $v$ = velocity ; $\ell \sim$ size crystal $= ct$

at high $T$ : $\kappa \propto 1/T$ (dependence due to $\ell$)


100
50
20
10
5
2
1
0,5
0,2
0,1
Wärmeleitfähigkeit κ (Wcm⁻¹ K⁻¹)
λ = 0,06 T³
Angereichertes Ge⁷⁴
Normales Ge
Ge
1
2
5
10
20
50
100
200
500
Temperatur in Grad K

# Thermal properties – key points

- Much of the heat capacity of materials is due to atomic vibrations
- Debye's Model:
  - oscillations are treated as sound waves, $\omega = v|k|$
  - maximum cuttoff frequency (needed so there are a total of only 3*N* degrees of freedom)
  - Obtains Dulong-Petit at high T and the (expected) $C \sim T^3$ at low T.
- Einstein's Model:
  - N independent oscillators with frequency $\omega_o$
  - Einstein frequency is a fitting parameter
  - Obtains Dulong-Petit at high T, and heat capacity drops exponentially at low T
- Thermal conductivity *K*
  - *Analogy: "Phonon Gas"*
  - At high T, phonon-phonon scattering: Umklapp process *vs* Normal Process
  - At low T, size effects