Beyond the Harmonic Approximation

Expectations within the harmonic approximation:

- modes independent
- no damping, infinite lifetime, sharp lines
- no thermal expansion
- elastic constants independent of T

Some findings from real crystals:

- 3-phonon processes
- non-zero line widths
- thermal expansion
- elastic constants depend on T

U(x) ~ *x*² ergibt keine thermische Ausdehnung, also *U(x)* ~ *ax*² - *bx*³

(b muss klein sein, sonst wäre Modell der Phononen schlechter)

mittlere Auslenkung <*x*> im thermischen Gleichgewicht:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx\, x \exp(-\beta U(x))}{\int_{-\infty}^{\infty} dx \exp(-\beta U(x))} \qquad \beta = \frac{1}{k_B T}$$

$$\exp(-\beta(a x^2 - bx^3)) = \exp(-\beta a x^2)\exp(\beta b x^3) \approx \exp(-\beta a x^2)(1+\beta b x^3)$$

$$Z\ddot{a}hler = \int dx \exp(-\beta a x^2)(x + \beta b x^4) \qquad \textit{ungerader Term} = 0$$

mit Substitution: $\beta a x^2 = y^2 \qquad x = y / \sqrt{a\beta} \qquad dx = dy / \sqrt{a\beta}$

$$Z\ddot{a}hler = \frac{b}{a^{5/2}\beta^{3/2}} \int dy \exp(-y^2) y^4 = \frac{b}{a^{5/2}} (k_B T)^{3/2} \frac{3}{4} \sqrt{(\pi)}$$

$$Nenner = \int dx \exp\left(-\beta a x^2\right)\left(1+\beta b x^3\right)$$ *ungerader Term =0*

$$= \frac{1}{\sqrt{a\beta}} \int dy \exp\left(-y^2\right) = \sqrt{\frac{\pi k_B T}{a}}$$

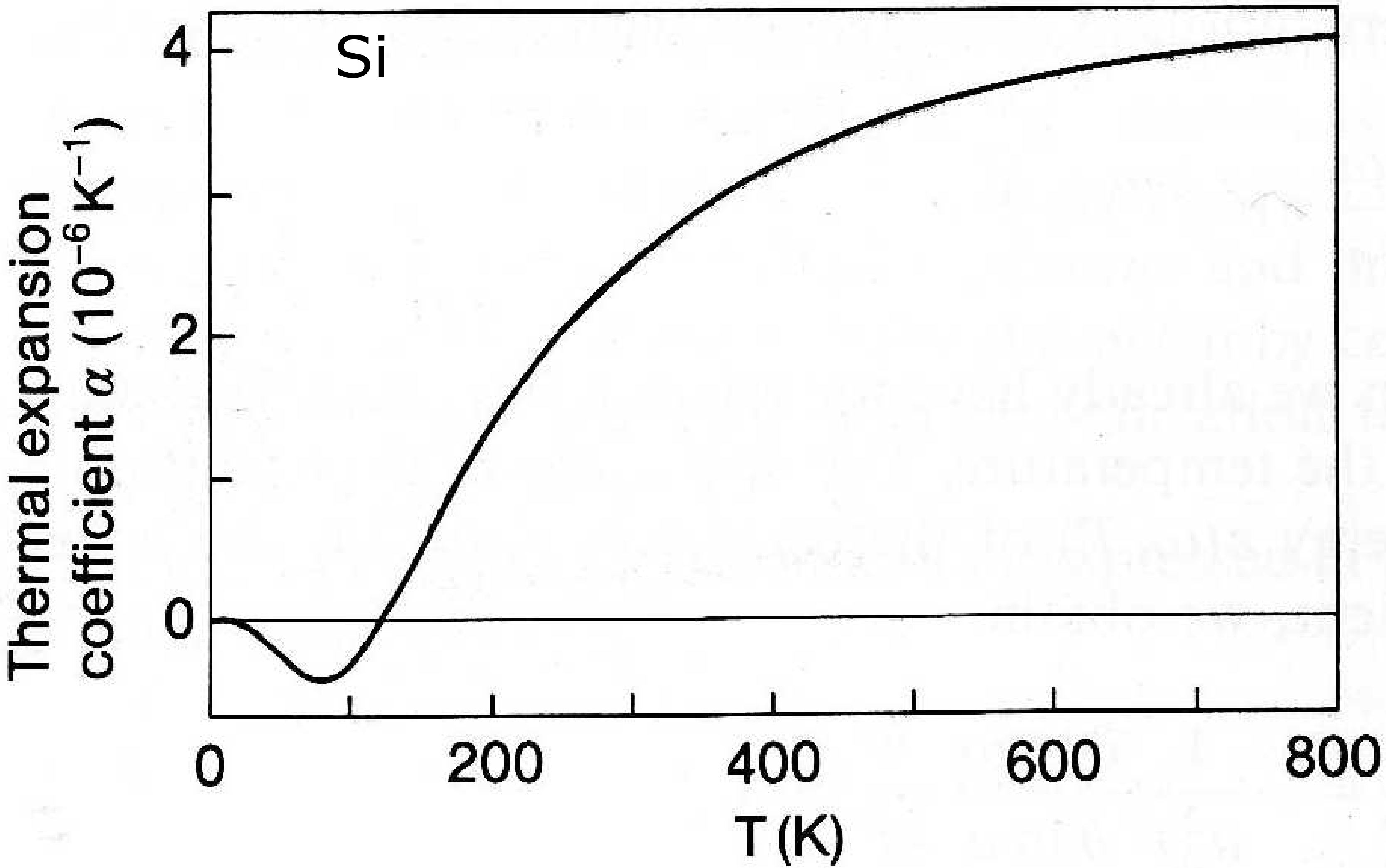
$$\langle x \rangle = \frac{3}{4}\frac{b}{a^2} k_B T \qquad \left(\langle x \rangle \to 0 \quad bei \quad b \to 0\right)$$

linearer Ausdehnungkoeffizient $$\alpha = \frac{d}{dT}\frac{\langle x \rangle}{x_0} = \frac{3}{4}\frac{b}{a^2}\frac{k_B}{x_0}$$

a,b Potentialparameter

x_0 Atomabstand

Thermal expansion need not be ~ T



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Thermal conductivity vs. Temperature

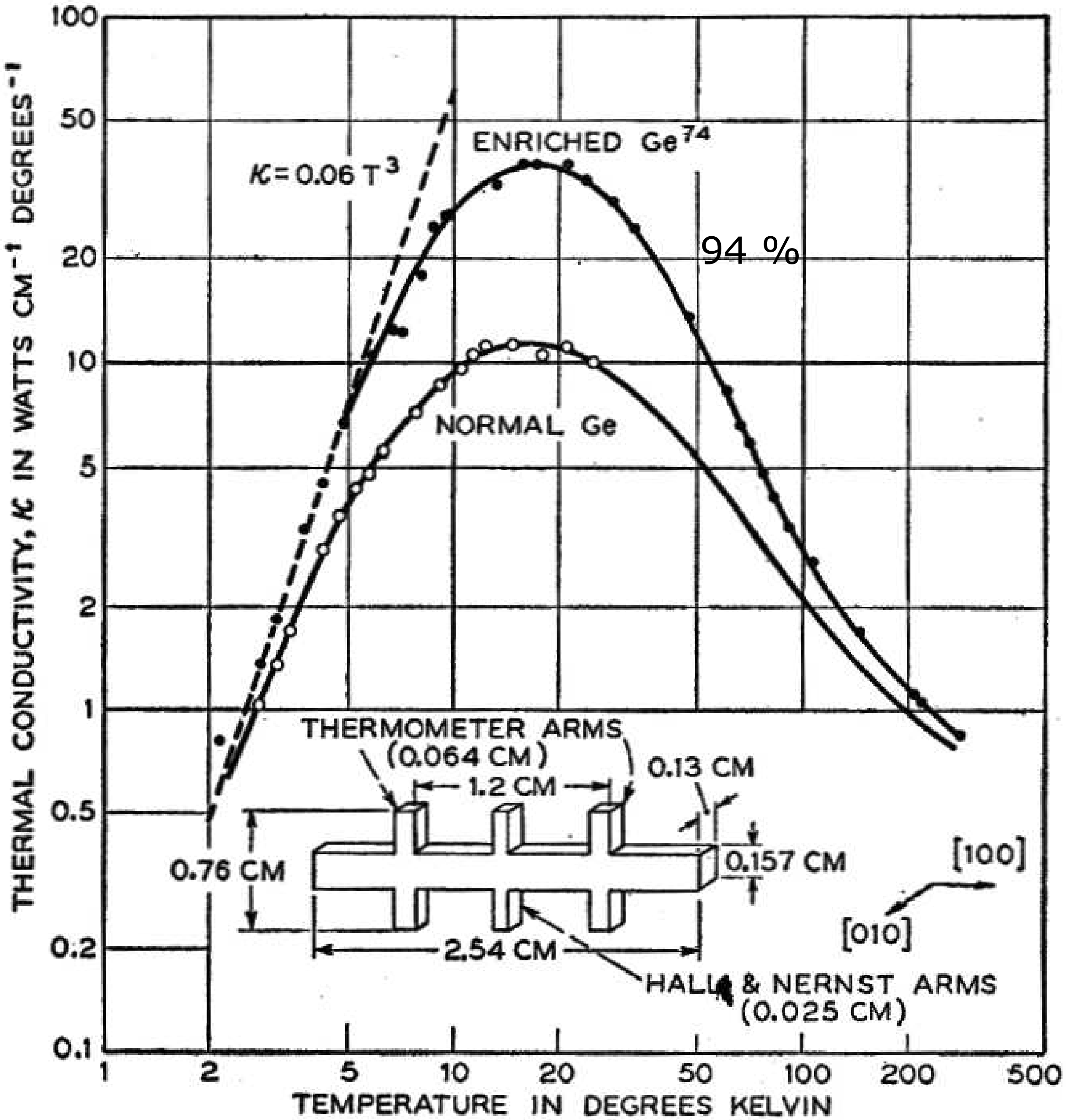


FIG. 1. Isotope effect on thermal conduction in Ge.

T. H. Geballe & G. W. Hull,
Phys. Rev. 110, 773 (1958)

Wärmemeleitung κ

harm. Kristall → Phononenlebensdauer unbegrenzt

→ Wellenpakete laufen unbegrenzt weit

→ κ unendlich groß

realer Kristall → hat Defekte, Berandungen und ist anharmonisch

→ Phononen streuen daran und untereinander

dabei gilt: $\vec{k} + \vec{k}\,' = \vec{k}\,'' + \vec{G}$

Miniexkurs: Frequenzmischung

Eingangssignale: $x = \sin(\omega t)$, $y = \sin(\omega' t)$

lineares System, z. B. $x + y$

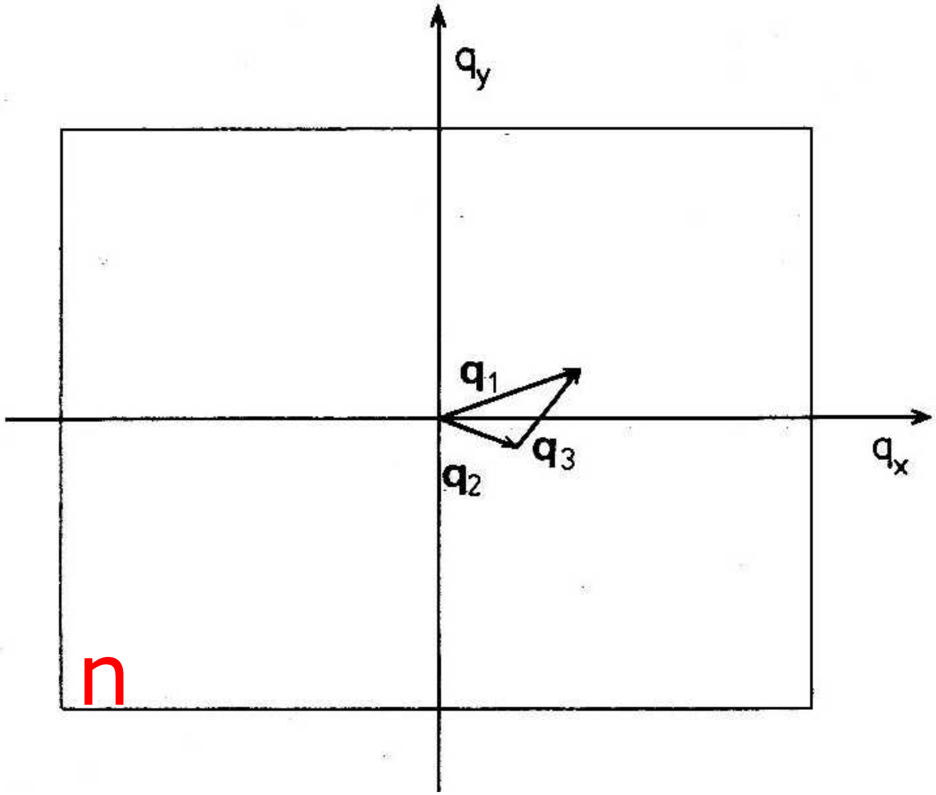
Spektrum des Ausgangssignals enthält nur ω und ω'

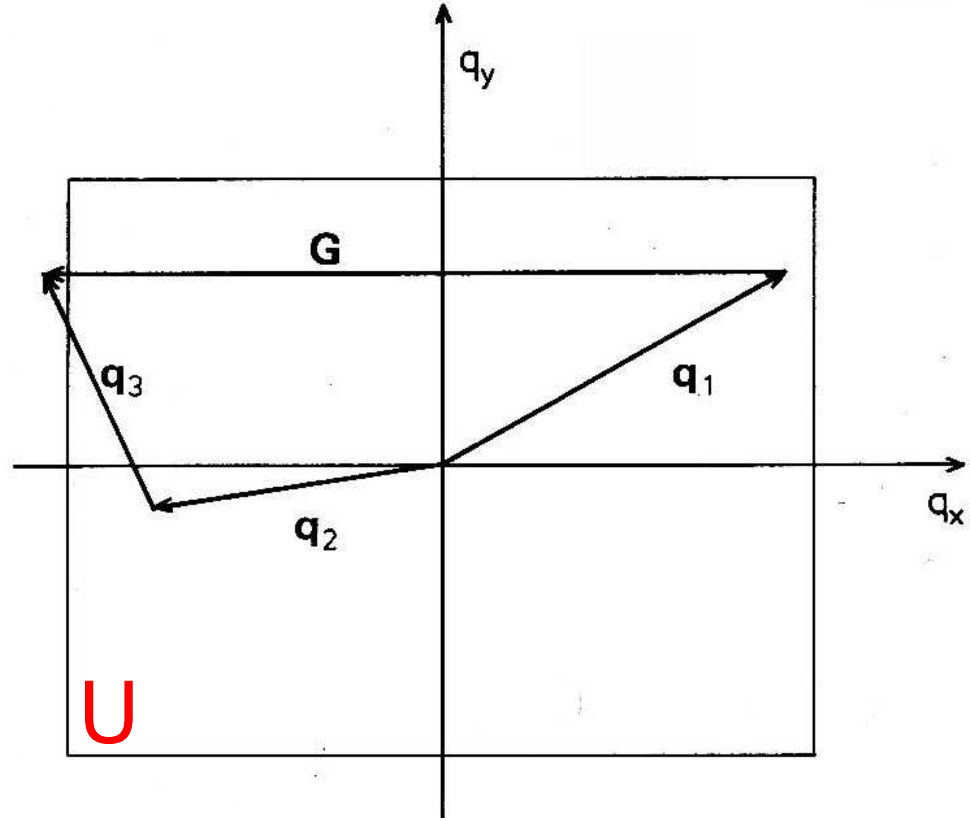
nichtlineares System, z. B. $x \cdot y$

Spektrum des Ausgangssignals enthält auch $\omega + \omega'$, $\omega - \omega'$

(falls $\omega = \omega'$ also 2ω)

denn $\sin(a) \sin(b) = \frac{1}{2} (\cos(a-b) - \cos(a+b))$





n-process: q_1 is split into two vectors q_2 and q_3.

The sign of *t*he x-component of the group velocity v_x remains unchanged.

The direction of energy flow is not affected.

U-process: q_1 is split with the help of *G.*

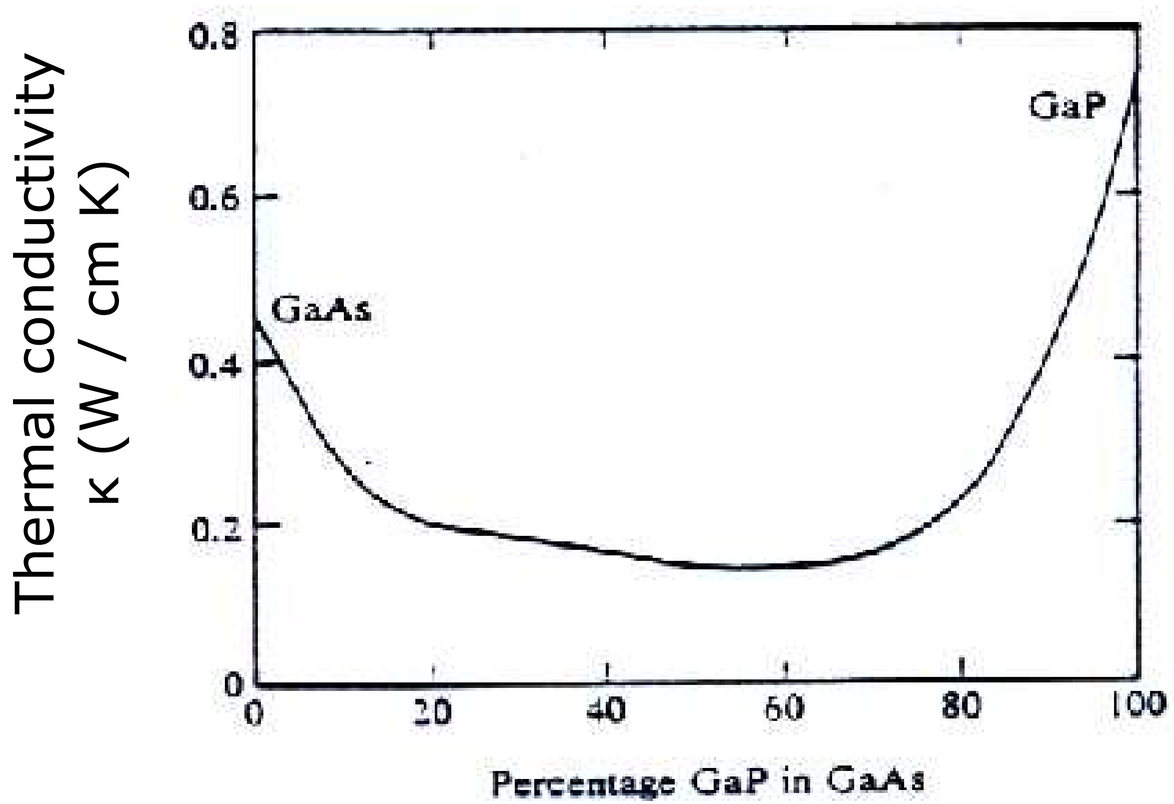
For q_2 and q_3, sign of v_x is inverted.

This reverses the direction of energy flow.

Low T → low ω → low q → No U

Ibach-Lüth

Chemical composition: Alloy scattering



Percentage GaP in GaAs

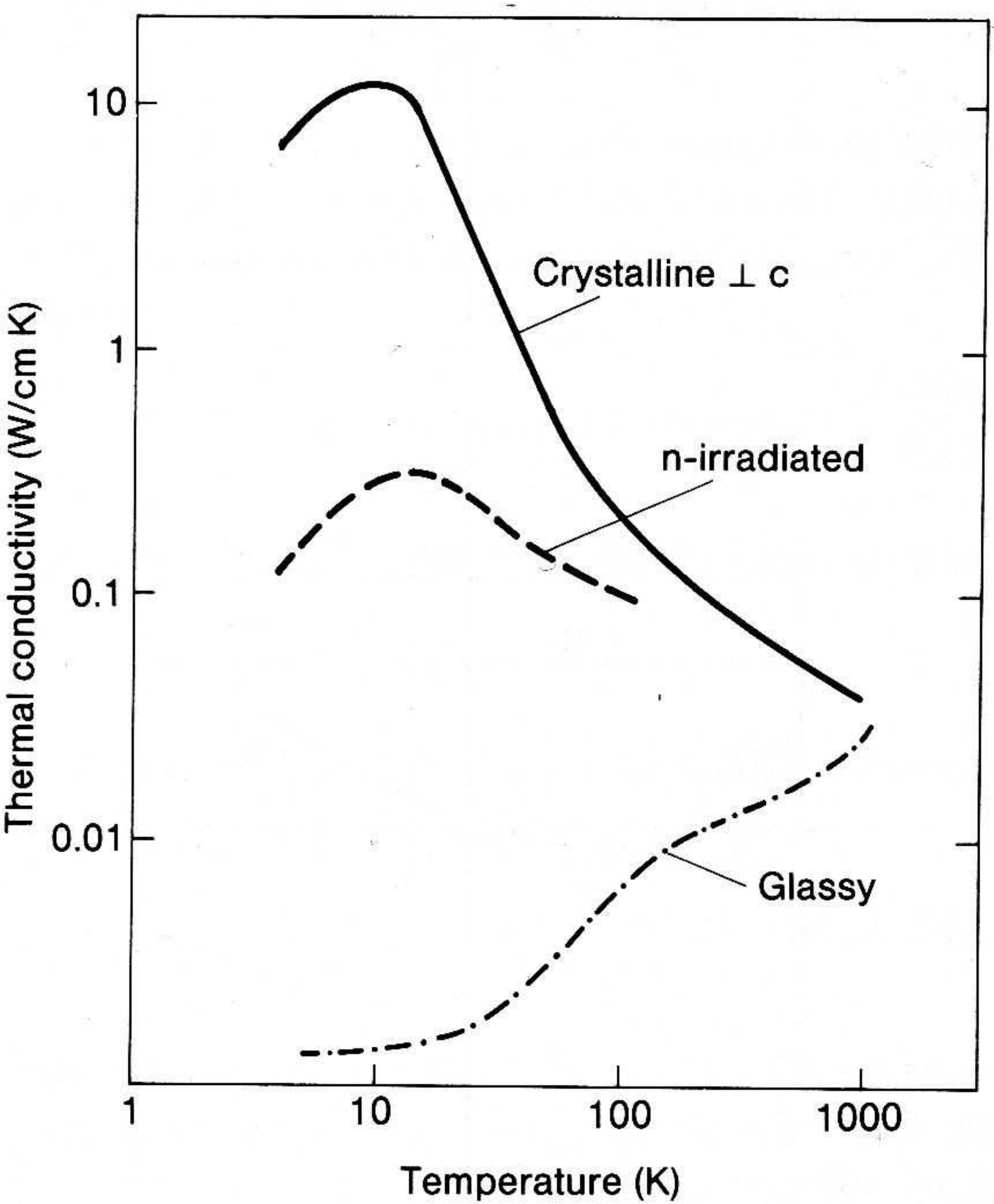
Thermal conductivity at 300 K for $GaAs_xP_{1-x}$

After P. D. Maycock. Solid State Electronics **10**, 161 (1967)

Disorder

Thermal conductivity of SiO_2 (quartz) perpendicular to the c-axis

- single-crystal
- same crystal with defects induced by n-bombardment
- quartz glass



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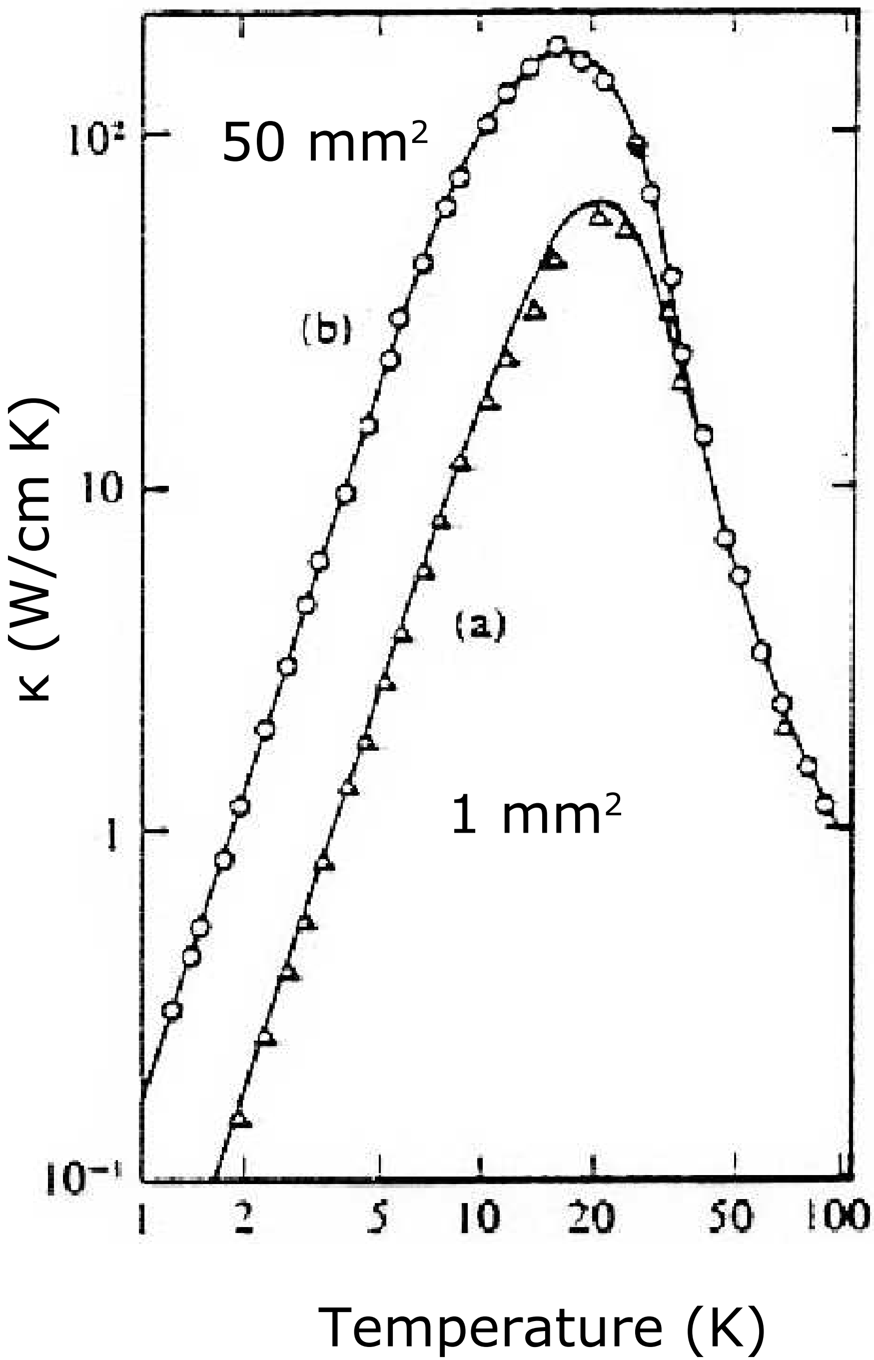
Sample size



Lattice thermal conductivity vs. T

LiF single crystal bars

(Li enriched to 99.9 % ^{7}Li to minimize isotope scattering)

cross-sections:

(a) 1.23 x 0.91 mm^2

(b) 7.55 x 6.97 mm^2

High T: U-processes

Low T: boundary scattering

Data from R. Bermann, Cryogenics **5**, 297 (1965)