Transient response of thermoelectric elements and dynamic measurement methods for thermoelectric materials

K. Zabrocki[1], W. Seifert[2], C. Goupil[3,4], H. Kolb[1], J. de Boor[1], T. Dasgupta[1,5], and E. Müller[1,6]

[1]Institute of Materials Research, German Aerospace Center (DLR), Köln, Germany

[2]Institute of Physics, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany

[3]LIED, CNRS, UMR 8236, Universite Paris Diderot, France

[4]Laboratoire CRISMAT ENSICAEN, Caen, France

[5] IITB, Mumbai, India

[6]Justus Liebig University Giessen, Giessen, Germany

Content

1. Fundamental equations for transient response
   Continuum theory – thermoelectricity

2. Direct and inverse problems

3. Transient performance calculations

4. Dynamic measurements (thermal conductivity)

   - Combined thermoelectric measurement (CTEM)

DLR

Thermoelectricity – Continuum approach

- Continuum theory: Description of the properties and measurements of thermoelectrics on a macroscopic level

- Characteristic time and length scales $\tau \geq 10^{-3}$ s and $l \geq 10^{-3}$ m

- Transport of energy and charges – description via differential equations, thermal energy balance equation

$$\vec{E}[\vec{r}(t), t] \qquad T[\vec{r}(t), t]$$

Electric field — Temperature field

Continuum theory: Two main categories of equations

Equations independent of the material: kinematic relations of the continuum, loading parameters, balance equations
Conservation laws

Equations dependent on the material: Coverage and description of material properties
Constitutive equations

Thermoelectricity – Generalized heat equation

Conservation equations

Differential form

- Charge conservation

$$\nabla \cdot \vec{j} = 0$$

- (thermal) energy conservation

$$\varrho_{\mathrm{d}}\, \mathrm{c} \frac{\partial T}{\partial t} + \nabla \cdot \vec{j}_Q = \vec{j} \cdot \vec{E}$$

Constitutive equations

Onsager's linear response theory

- Generalized Fourier's law – Heat flux

$$\vec{j}_Q = -\kappa \nabla T + \alpha T \vec{j} = \vec{j}_{Q,\kappa} + \vec{j}_{Q,\pi}$$

- Generalized Ohm's law – Electrical current density

$$\vec{j} = \sigma \vec{E} - \sigma \alpha \nabla T$$

$$\varrho_{\mathrm{d}}\, \mathrm{c} \frac{\partial T}{\partial t} - \nabla \cdot (\kappa \nabla T) + \tau \vec{j} \cdot \nabla T = \frac{j^2}{\sigma}$$

$\tau = T \frac{\partial \alpha}{\partial T}$ ... Thomson coefficient, ϱ_{d} … mass density, c ... specific heat capacity, κ ... thermal conductivity,

α ... Seebeck coefficient, σ… electrical conductivity

T. C. Harman, J. M. Honig: Thermoelectric and thermomagnetic effects and applications, McGraw – Hill (1967)
Charles A. Domenicali, Irreversible Thermodynamics of Thermoelectricity, Rev. Mod. Phys. 26, 237 – 275 (1954)

Solution of heat equation in thermoelectricity

- Initial conditions (IC)
Temperature distribution
at $t = 0$: $T_0[\vec{r}(t)]$

- Boundary conditions (BC)
- Dirichlet/Neumann/mixed BC
[Boundary value problem (BVP)]

$$\varrho_{\mathrm{d}}\, c \frac{\partial T}{\partial t} - \nabla \cdot (\kappa \nabla T) + \tau \vec{j} \cdot \nabla T = \frac{j^2}{\sigma}$$

Direct problem

Initial values, boundary conditions, material properties
well-posed problem

Performance calculation of thermoelectric devices and systems

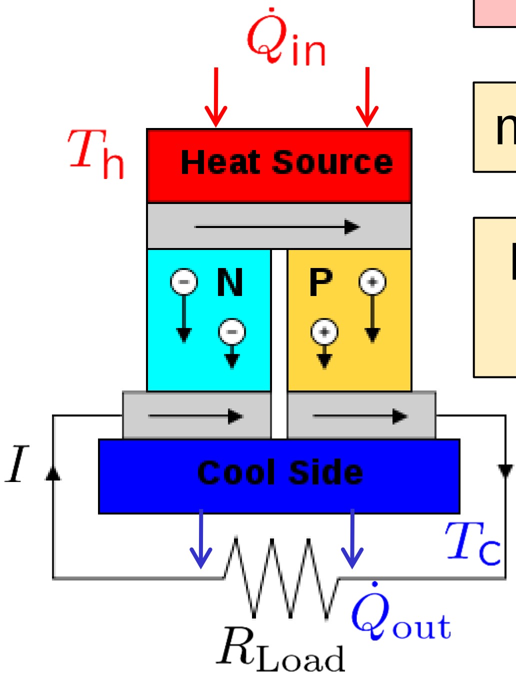
Inverse problem

Not all values are given, Experimental data for estimation of boundary values
ill-posed problem

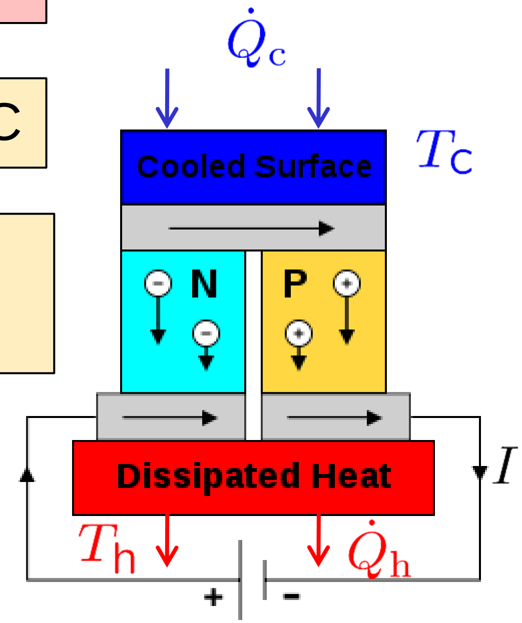
Determination of parameters in measurements systems, e.g. material properties

Performance calculation of thermoelectric devices

Thermoelectric Generator (TEG)



Thermoelectric Cooler (TEC)



Direct solution of the heat equation

material properties | IC | BC

Fixed boundary temperatures | Fixed heat input

Variation of R_L or I

$$T(\vec{r}, t)$$

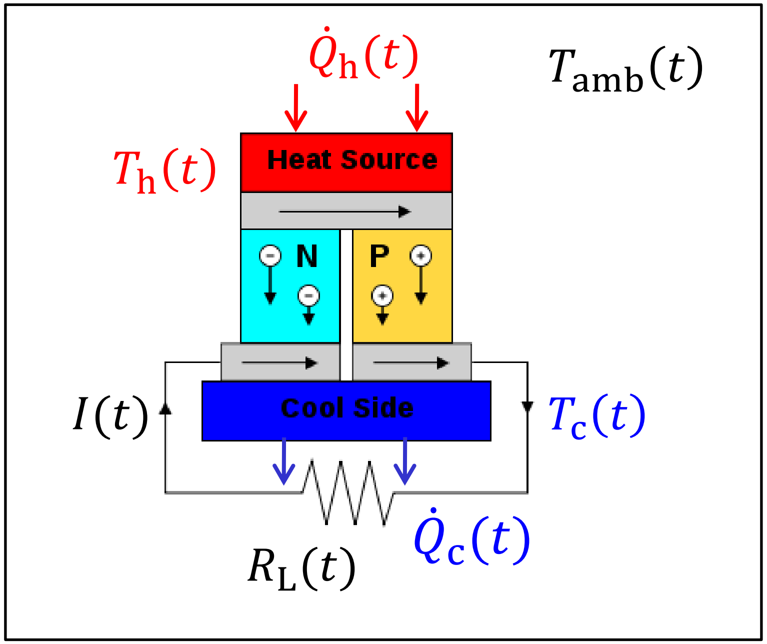
- Electrical power output P_{el}
- Efficiency η
- Heat flow $\dot{Q}$
- Coefficient of performance φ

Transient response in thermoelectricity

- Time dependent fields $T = T(\vec{r}, t)$ and $\vec{E} = \vec{E}\,(\vec{r}, t)$

- Dynamic working conditions:

BC	$T_\mathrm{h} = T_\mathrm{h}(t)$ $\quad T_\mathrm{c} = T_\mathrm{c}(t)$ $\quad \dot{Q}_\mathrm{h} = \dot{Q}_\mathrm{h}(t)$
Ambient	$T_\mathrm{amb} = T_\mathrm{amb}(t)$
Material	e.g. $\kappa = \kappa[T(\vec{r}, t), \vec{r}, t]$
Load/Current	$R_\mathrm{L} = R_\mathrm{L}(t)$ or $I = I(t)$



- Solution of the generalized heat equation:
  - Steady state $\Longrightarrow$ Ordinary differential equations
  - Transient response $\Longrightarrow$ Partial differential equations

- Analytical solutions only in particular cases with help of integral transformation (e.g. Laplace) or in a (Fourier) series expansion

- Approximative or numerical solution methods (CPM, FEM, FDM, Circuits...)

H.S. Carslaw/J.C. Jaeger “Conduction of heat in solids”, Oxford Science Publications,1986

J. Crank, “The mathematics of diffusion”, Oxford University Press, 1979

DLR

Transient performance calculations

- Quasi-stationary processes ⇒ Timescale of changes in the working/boundary conditions much greater than response time of the thermoelectric system ⇒ use of steady state equations for different times

- TEC pulsed supercooling

  Stil'bans/Fedorovich, Sov. Phys. Tech. Phys. **3**, 460 (1958)
  Snyder et al., J. Appl. Phys. **92**, 1564 (2002)
  Mao et al., J. Appl. Phys. **112**, 014514 (2012)

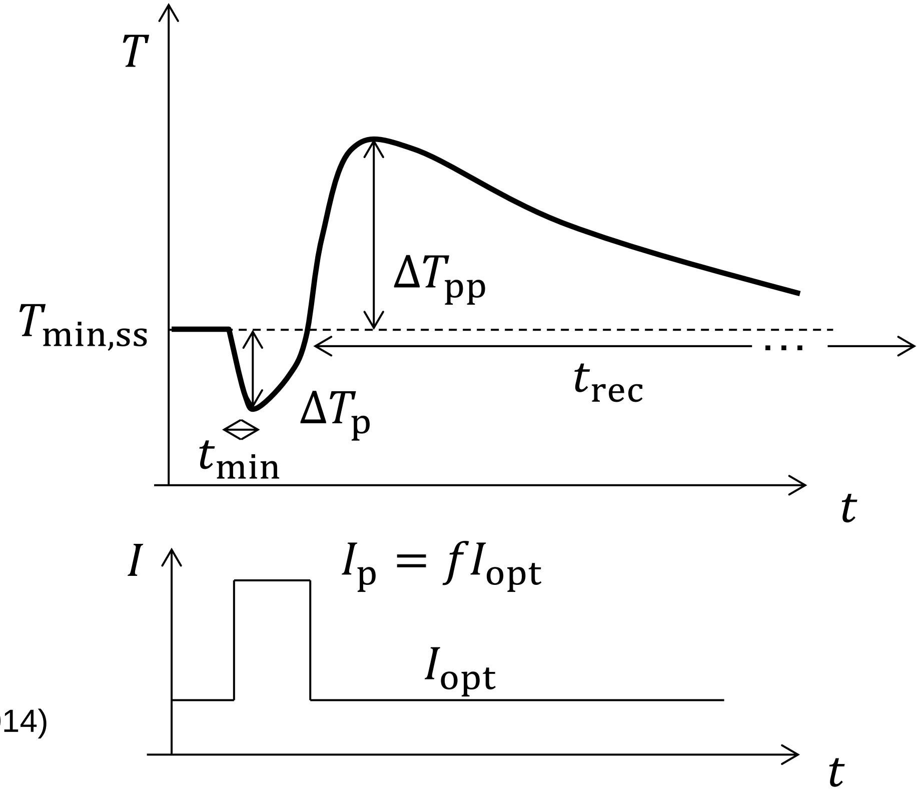
- Transient TEG

  P.E. Gray, The Dynamic Behavior of Thermoelectric Devices, John Wiley & Sons, Inc., New York, 1960

  Montecucco et al., Appl. Therm. Eng. **35** (2012) 177-184
  Nguyen/Pochiraju, Appl. Therm. Eng. **51** (2013) 1-9
  Meng, J. Power Sources, **245** (2014) 262-269

- AC impedance spectroscopy

  García-Cañadas/Min (previous talk), J. Electr. Mat. **43**, 2411 (2014)
  C. Goupil (talk yesterday), J. Stockholm (poster yesterday)



- Review: Separate chapter in the book "*Continuum theory and modelling of thermoelectric elements*" edited by C. Goupil, release date March 2015

DLR

Measurement of thermal conductivity

- Thermal conductivity for semiconductors often small ⇒ ≈1 W/(m K)
- Small samples, mechanically not easy to be processed
- Brittleness ⇒ not possible to put in thermocouples in the sample
- Hard to realize a good thermal contact via soldering
- Specific heat often not known

Measurement techniques κ

Steady-state/stationary methods

Absolute technique

Comparative technique

Dynamic/transient methods

- Laser Flash Thermal Diffusivity Method
- Generalized Ioffe method ⇒ CTEM
- 3ω method
- time-domain thermoreflectance

S. Reif-Acherman "Early and current experimental methods for determining thermal conductivities of metals" Int. J. Heat Mass Transfer 77 (2014), 542-563
T. M. Tritt "Electrical and Thermal Transport Measurement Techniques for Evaluation of the Figure-of-Merit of Bulk Thermoelectric Materials" Ch. 23, CRC Thermoelectric Handbook. Macro to Nano (2006)

Inverse heat conduction problems

- Inverse heat conduction problems (IHCP)

Temperature T measured (at some points, times)

- Classification IHCP:
  - **Material properties determination inverse problems**,
  - Boundary value determination inverse problems,
  - Initial value determination inverse problems,
  - Source determination inverse problems,
  - Shape determination inverse problems

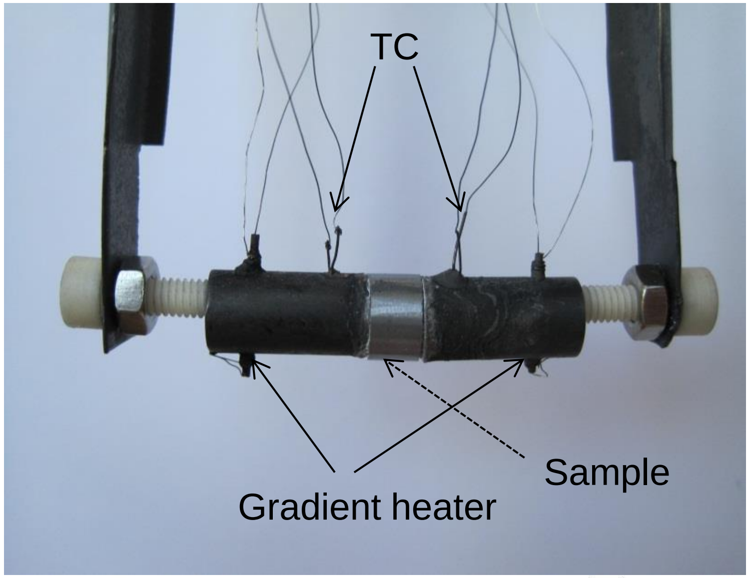
- Unknown thermal conductivity (material property) ⇒ inverse calculation

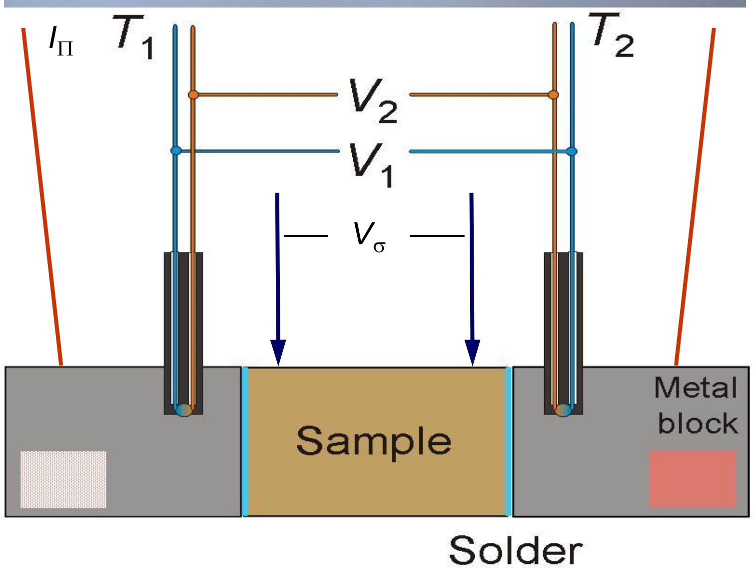
- Solution of the direct problem to get insights how to solve the IHCP

Krzysztof Grysa “Inverse Heat Conduction Problems” Chapter 1 in “Heat Conduction - Basic Research” ed. by V. S. Vikhrenko, InTech (2011)

CTEM – Measurement of thermal conductivity

- **C**ombined **t**hermo**e**lectric **m**easurement (CTEM):





- Simultaneous measurement method ⇒ all TE properties including Harman-*ZT*
- Here: focus on thermal conductivity measurement

- **Generalized Ioffe method**

Decrease of ΔT

↓

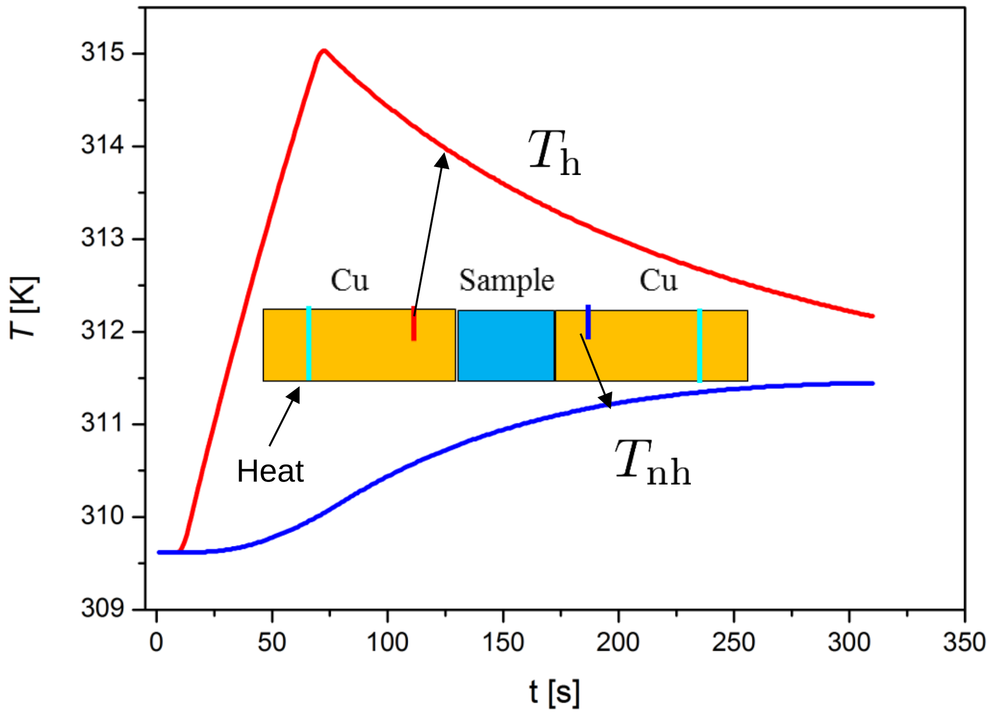
Thermal conductivity κ

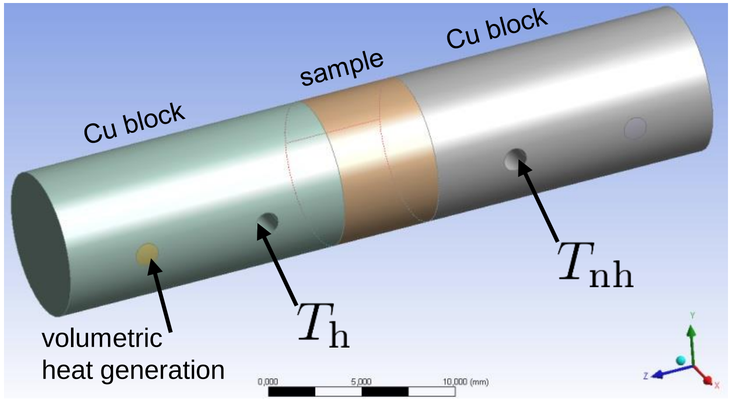
More experimental details on Poster P3.30

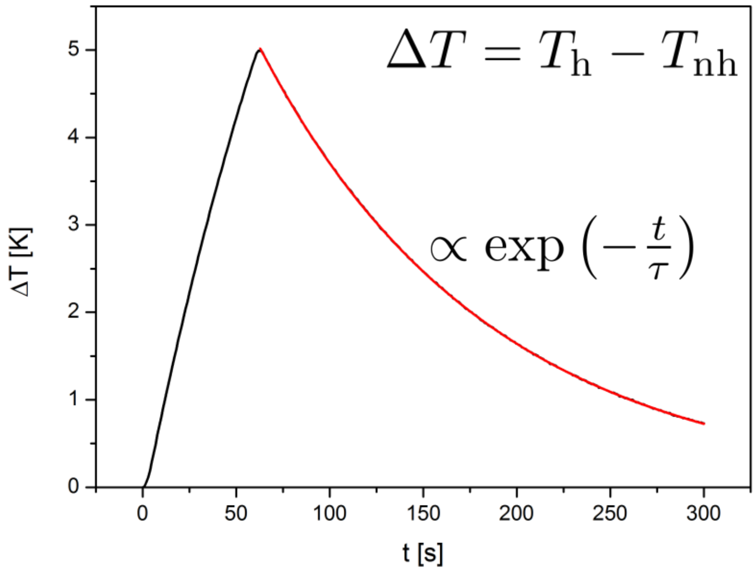
H.Kolb today

Transient temperature difference

- Heating of one Cu block
- Switching off after reaching $\Delta T \approx 5\mathrm{K}$
- Observing relaxation of temperatures







Relaxation time τ → Thermal conductivity κ_S

$$\kappa_\mathrm{s} = \frac{L_\mathrm{s}}{2\,A_\mathrm{c,s}}\,\frac{m_\mathrm{b}\,c_\mathrm{b}}{\tau}\left(1 + \frac{m_\mathrm{s}\,c_\mathrm{s}}{6\,m_\mathrm{b}\,c_\mathrm{b}}\right)$$

Solution of the direct problem – Simple Ioffe method

- Simple Ioffe method (sample and one block):

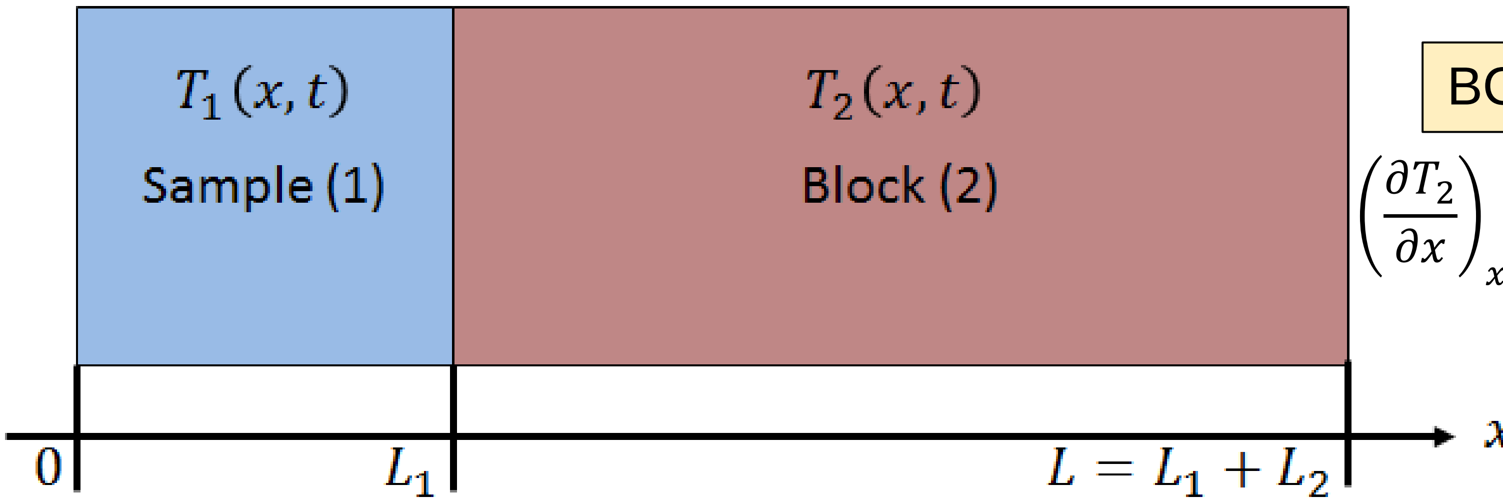
1. Analytical solution as Fourier series
2. Numerical solution with ANSYS (FEM)

System of PDE

$$\frac{\partial T_1}{\partial t} = \alpha_{\mathrm{d},1} \frac{\partial^2 T_1}{\partial x^2} \qquad \frac{\partial T_2}{\partial t} = \alpha_{\mathrm{d},2} \frac{\partial^2 T_2}{\partial x^2}$$

BC

$$T_1(x=0,t) = T_{\mathrm{amb}}$$



BC

$$\left(\frac{\partial T_2}{\partial x}\right)_{x=L} = 0$$

IC

$$T_1(x,t=0) = T_{\mathrm{amb}} \qquad T_2(x,t=0) = T_{20} > T_{\mathrm{amb}}$$

Interface

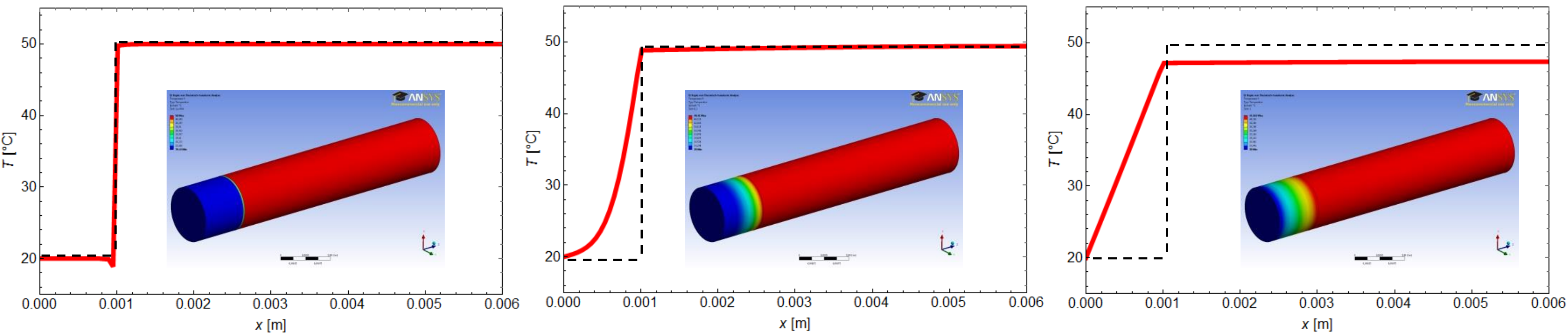
$$T_1(x=L_1-,t) = T_2(x=L_1+,t) \qquad -\kappa_1\left(\frac{\partial T_1}{\partial x}\right)_{x=L_1-} = -\kappa_2\left(\frac{\partial T_2}{\partial x}\right)_{x=L_1+}$$

Sequences of transient simulations

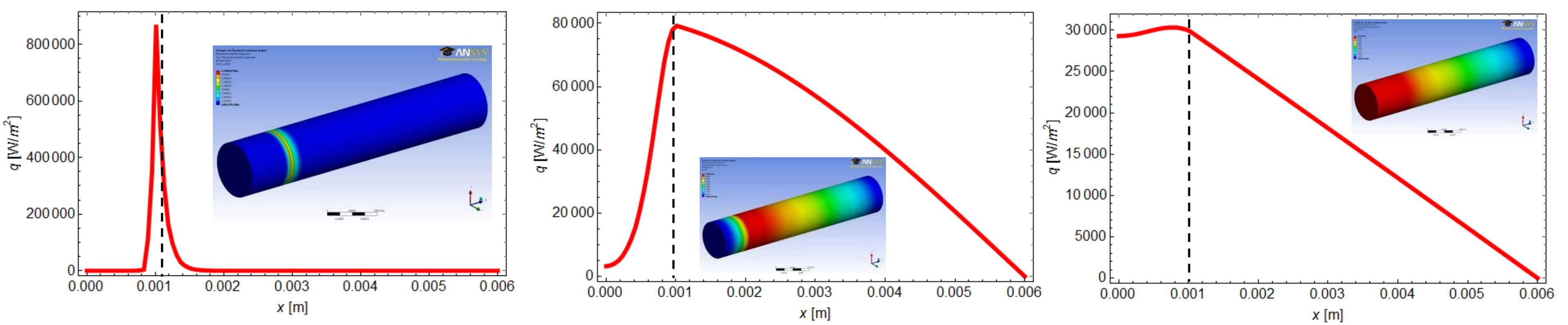
- Short time behavior – heat wave through the sample – non-exponential

$t = 10^{-4}\,s$ $\qquad$ $t = 10^{-1}\,s$ $\qquad$ $t = 1s$

Temperature

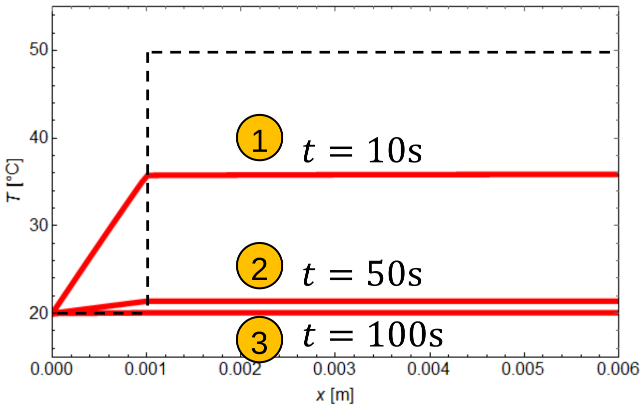


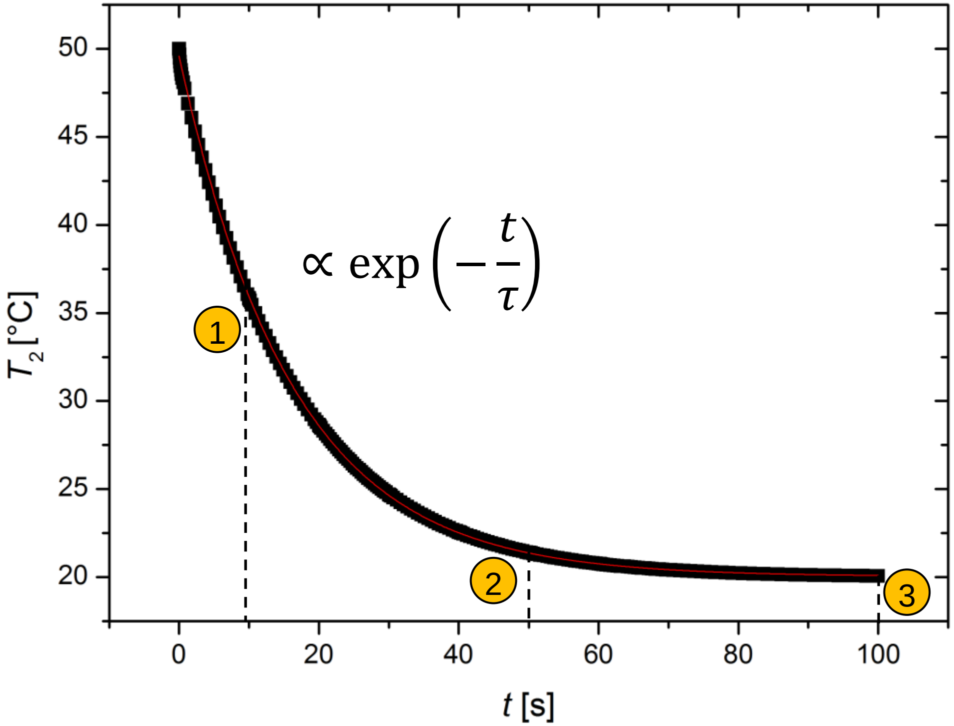
Heat flux



Relaxation of temperature difference

- Relaxation to equilibrium exponential





$\tau = (M_1)^{-1}$ ... relaxation time (from the experiment)

$C_1 = m_1 c_1 = \varrho_{d,1} V_1\, c_1$ ... thermal mass of the sample

$C_2 = m_2 c_2 = \varrho_{d,2} V_2\, c_2$ ... thermal mass of the block

- Thermal conductivity after algebraic treatment and Taylor expansion (omitting terms of second order and higher)

$$\kappa_1 = \frac{L_1}{A_{c,s}} M_1\, C_2 \left(1 + \frac{\kappa_1 L_2}{3\,\kappa_2 L_1} + \frac{C_1}{3\,C_2}\right)$$

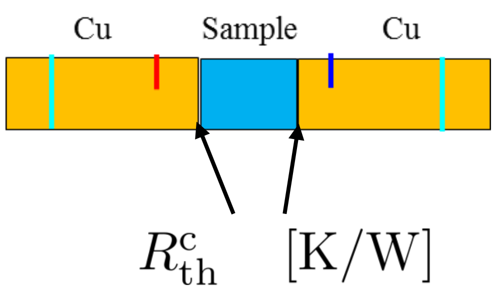
- in the example calculation less than 1% approximation error

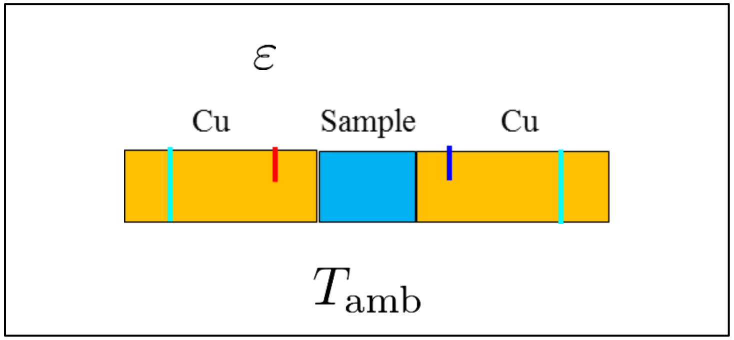
Influence factors on the relaxation time

Errors

Contact resistance at the interface

Radiation to the ambient





- Fixed values of

$$\tilde{\alpha}_{\mathrm{c}} = \left(R_{\mathrm{th}}^{\mathrm{c}}\, A_{\mathrm{c,s}}\right)^{-1} \quad [\mathrm{W/m^2\ K}]$$

- Symmetric for both side

- Emissivity ε
- Ambient temperature T_{amb}
- Significant at high T

Underestimation of κ ↔ Overestimation of κ

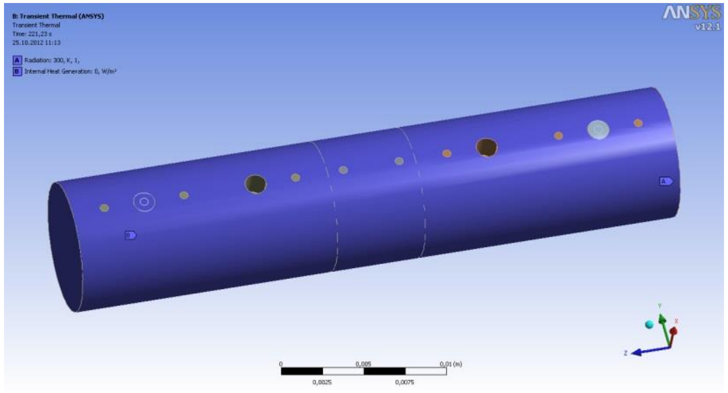
Zabrocki et al., J. Electr. Mat. 42 (7), 2402-2408 (2013)

DLR

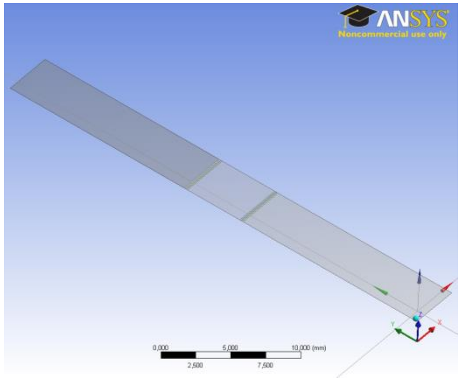
CTEM – Peltier heat

- DC current through the assembly ⇒ Peltier heat at the contacts
- At which side of the contact is the Peltier heat liberated or absorbed?

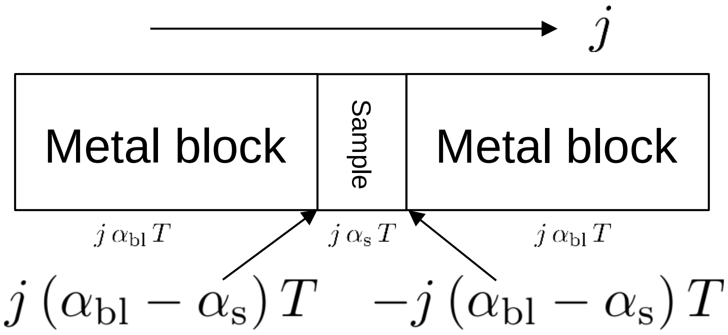
3D Simulation



2D Simulation (axisymmetric)

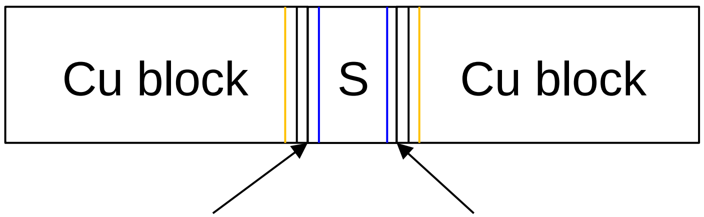


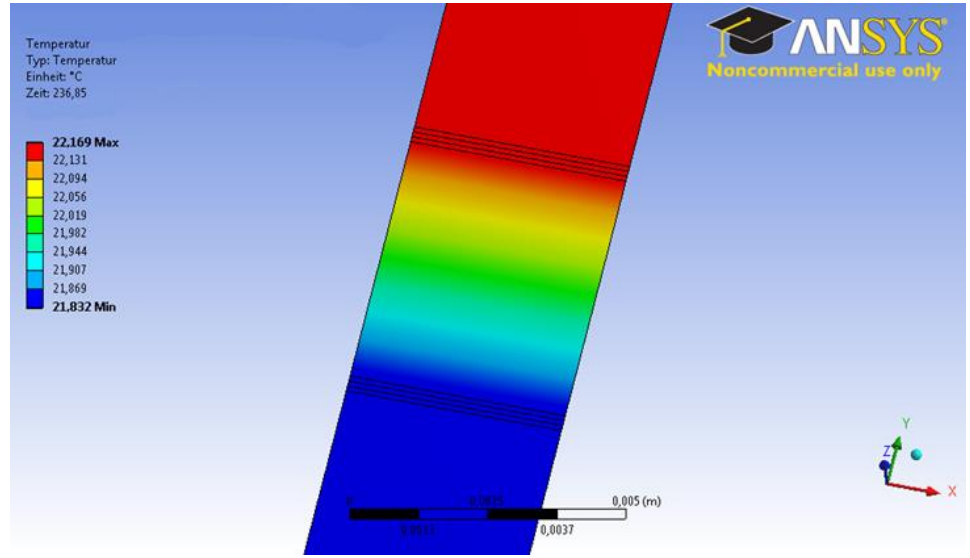
- transient thermal simulation
- No holes for thermocouples
- Heat generation in a slice
- Contacts – bulk values of a slice



Contacts as a slide

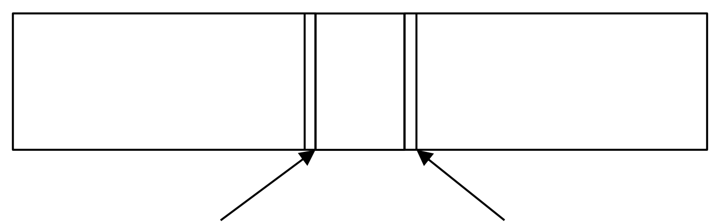
- Three thin layers:
  - Metal block
  - Contact material
  - Sample





- Contacts through bulk values

- Heat generation in the metal block or sample?



Volumetric heat generation for a certain time

- Galinstan (liquid metal solder)

$$\kappa = 16.5\ \mathrm{W/m\ K}$$

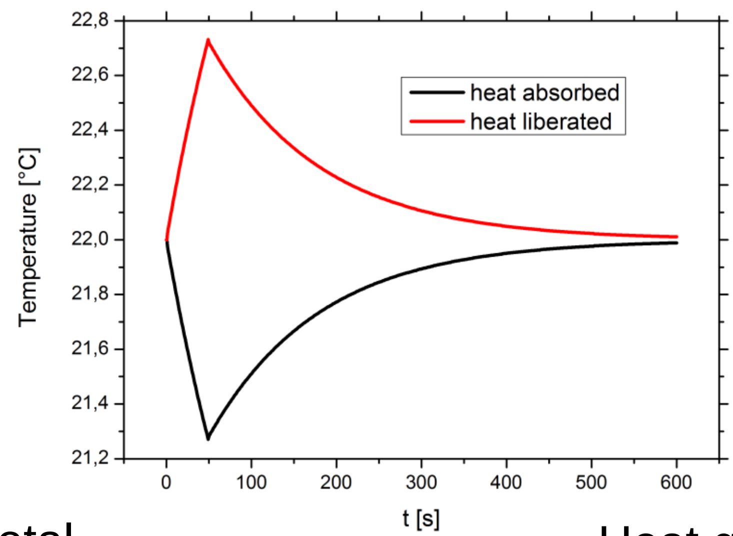
$$\rho_\mathrm{d} = 6.44\ \mathrm{g/cm^3}$$

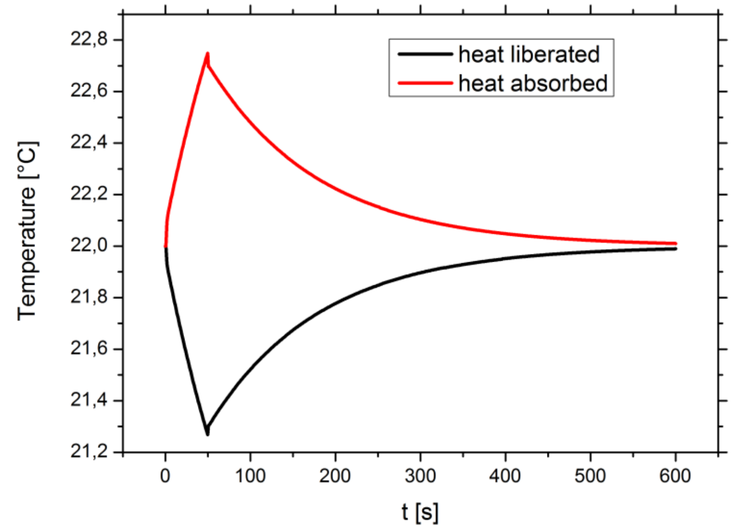
$$\sigma = 3.46 \cdot 10^6\ \mathrm{S/m}$$

$$c_p = 200\ \mathrm{J/kg\ K}$$

Peltier heat from where?

- Peltier heat liberated or absorbed at the metal side or the sample side

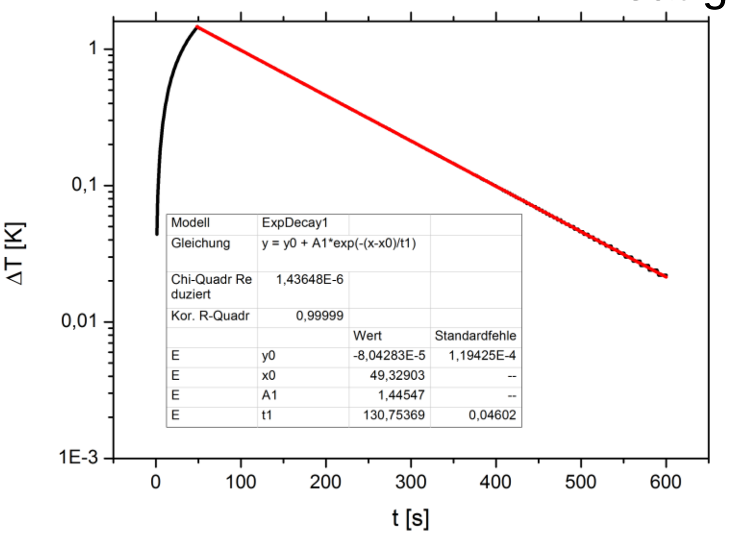


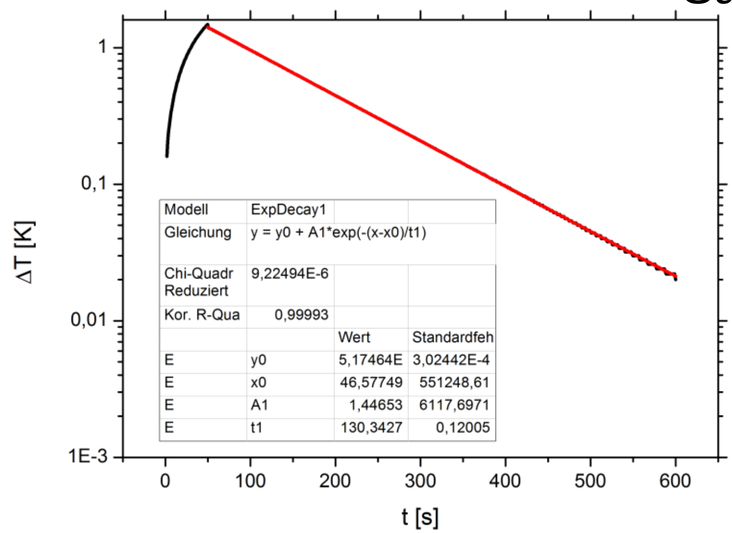


Metal

Heat generation/absorbtion

Sample

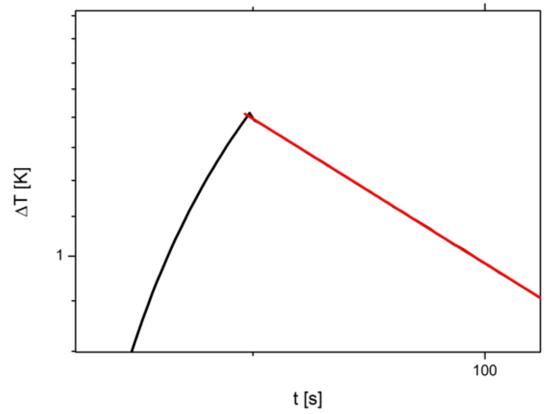




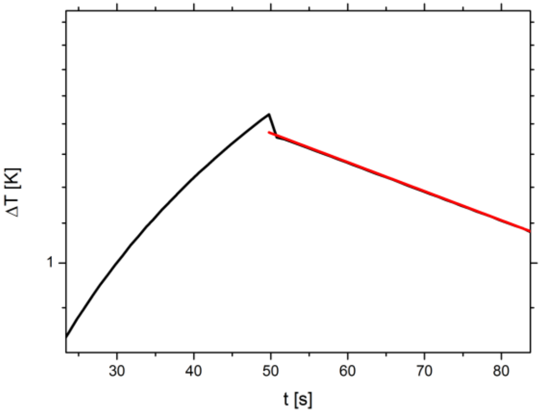
Peltier heat – Qualify contact resistance

- Peltier-heat either liberated/absorbed at metal side or sample side of the contact material ⇒ different behavior at the switch-off

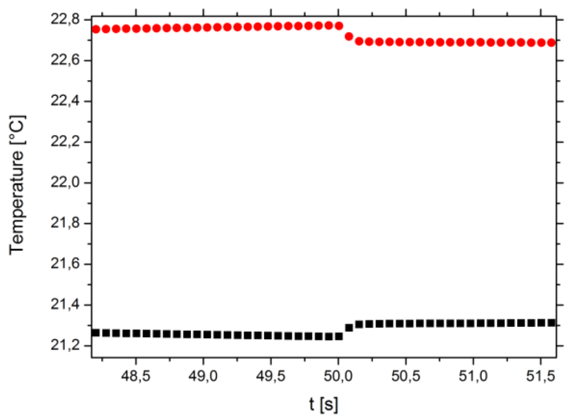
Metal

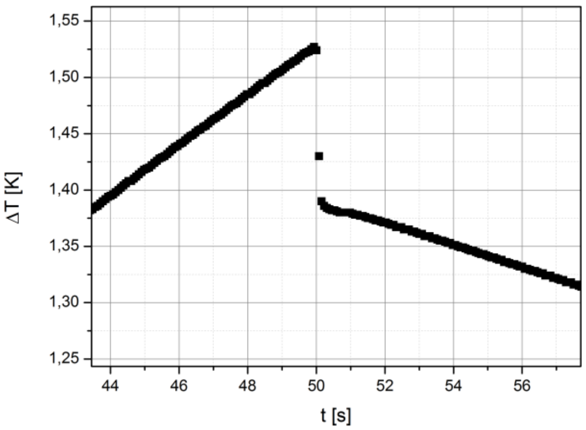


Sample



- Experimentally observed jump ⇒ Qualification of the thermal contact resistance





Summary

- Generalized heat equation in thermoelectricity for transient response
- Direct solution for the determination of the performance of TE devices
- Inverse problem: Determination of material properties from measurements of temperatures
- Dynamic measurement of the thermal conductivity – CTEM

Thank you for your attention!

DLR

The END