Dynamic response of magnetocaloric materials

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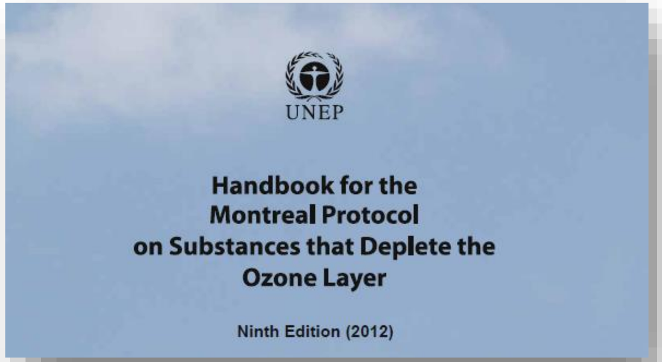
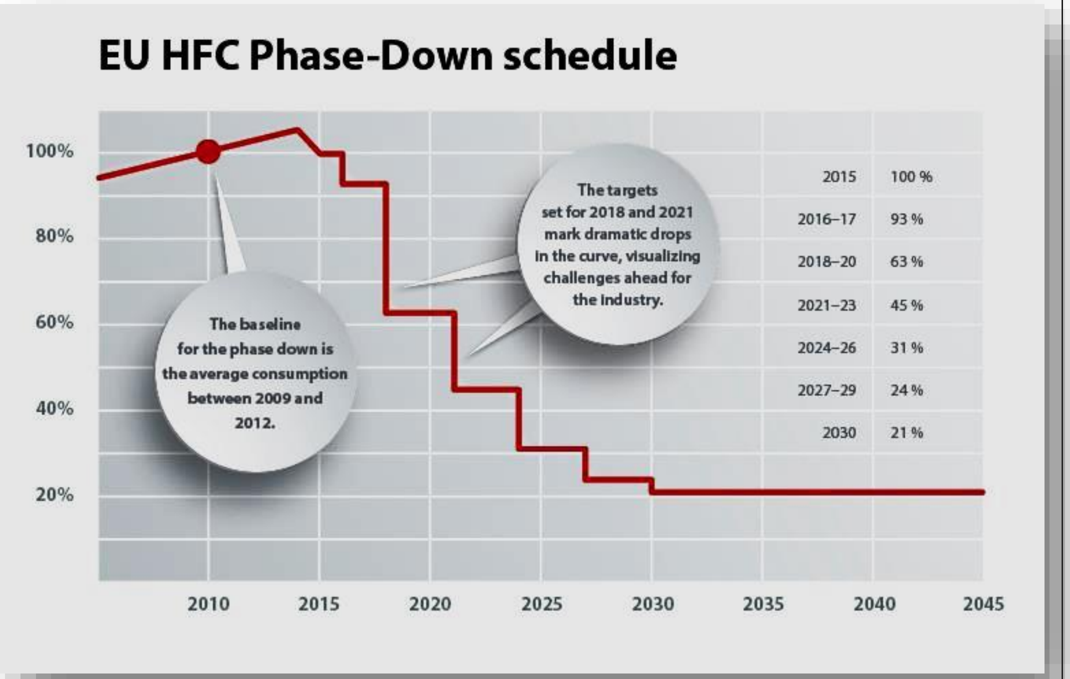
Energy and environment

- General problem of energy conversion
- Refrigeration: food conservation, household appliances
  - 25% of residential and 15% of commercial power consumption
- Constraints: Montreal (1987), Kyoto (1997) protocols
  - Present technologies: vapour compression cycles with
    - ozone depleting gases (CFCs, HCFCs)
    - greenhouse gases (CFCs, HCFCs, HFC)


UNEP

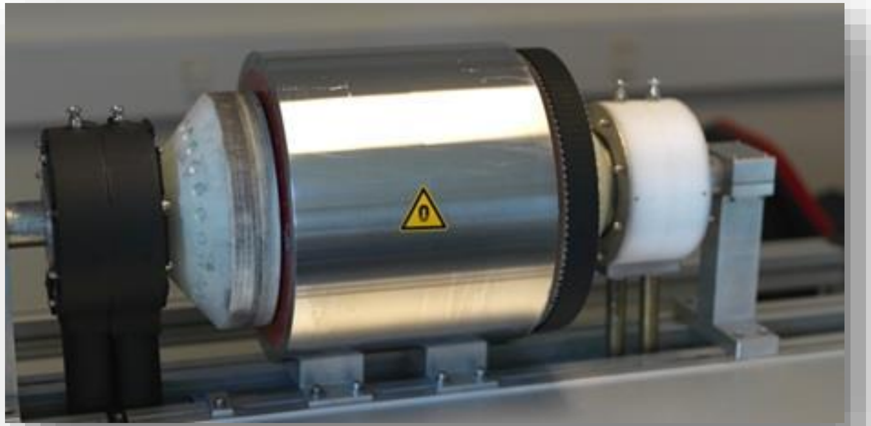
Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer

Ninth Edition (2012)



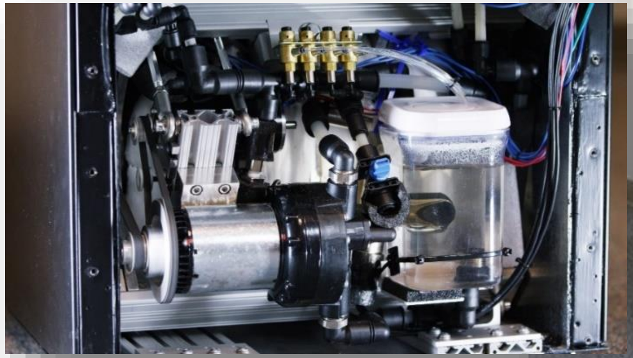
A promising alternative: a green technology

- Energy conversion (cooling) based on the magnetocaloric effect near RT:
  - No harmful gases involved, low pressure
  - Compactness (solid-state materials), low noise
  - Better efficiency? Maybe 60% theor. limit



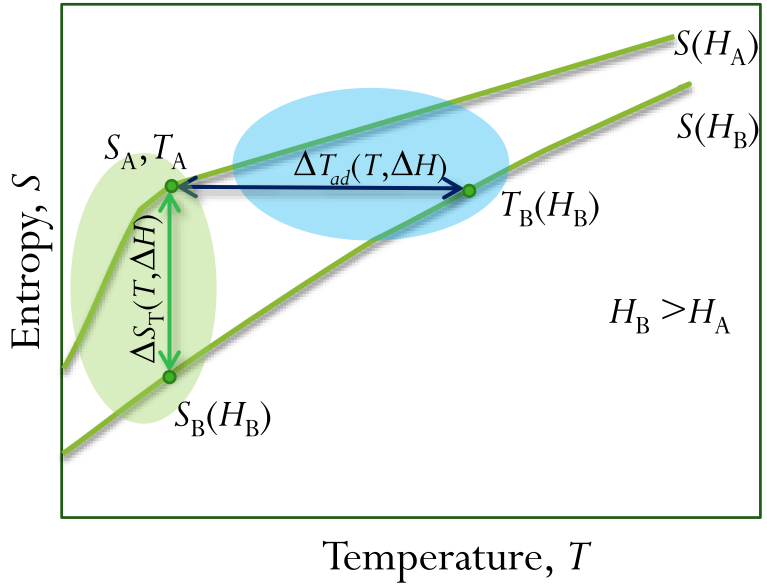
K. Engelbrecht, et al., Int. J. Refrig. 2012

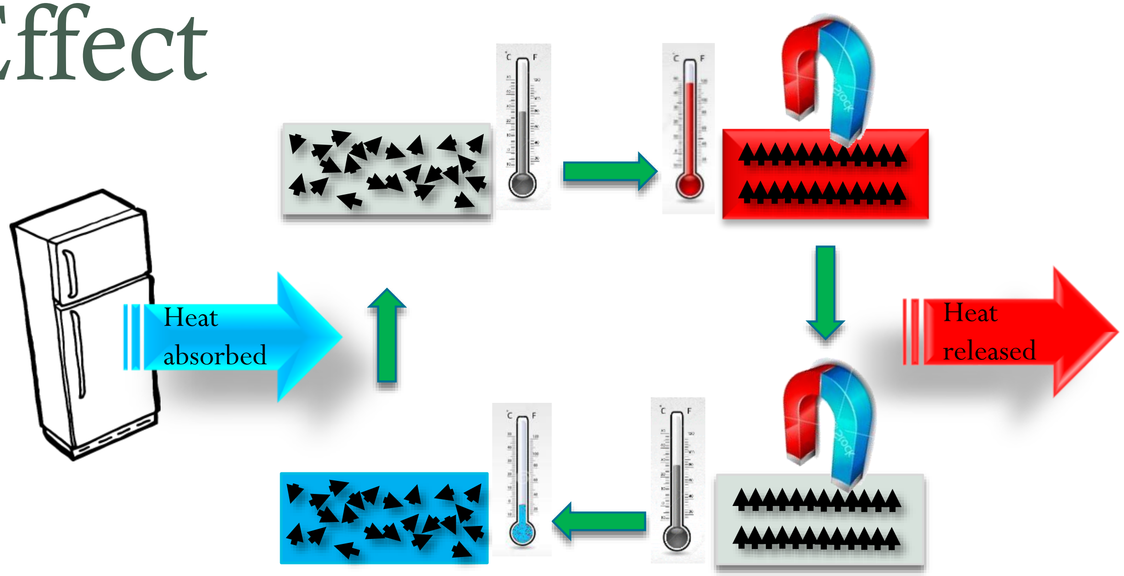
- «nearly-commercial» prototypes



Haier · BASF We create chemistry · Astronautics Corporation of America

The MagnetoCaloric Effect

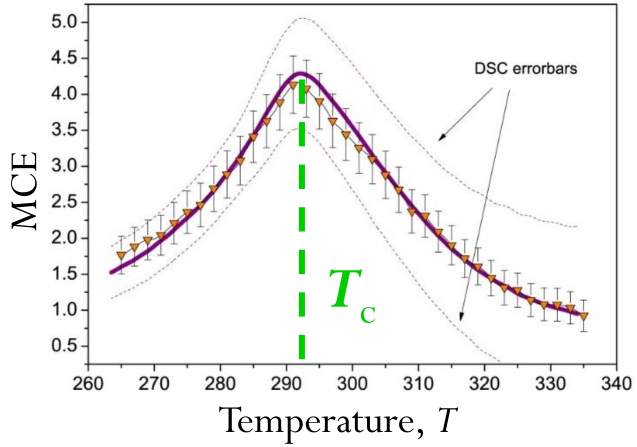




MCE

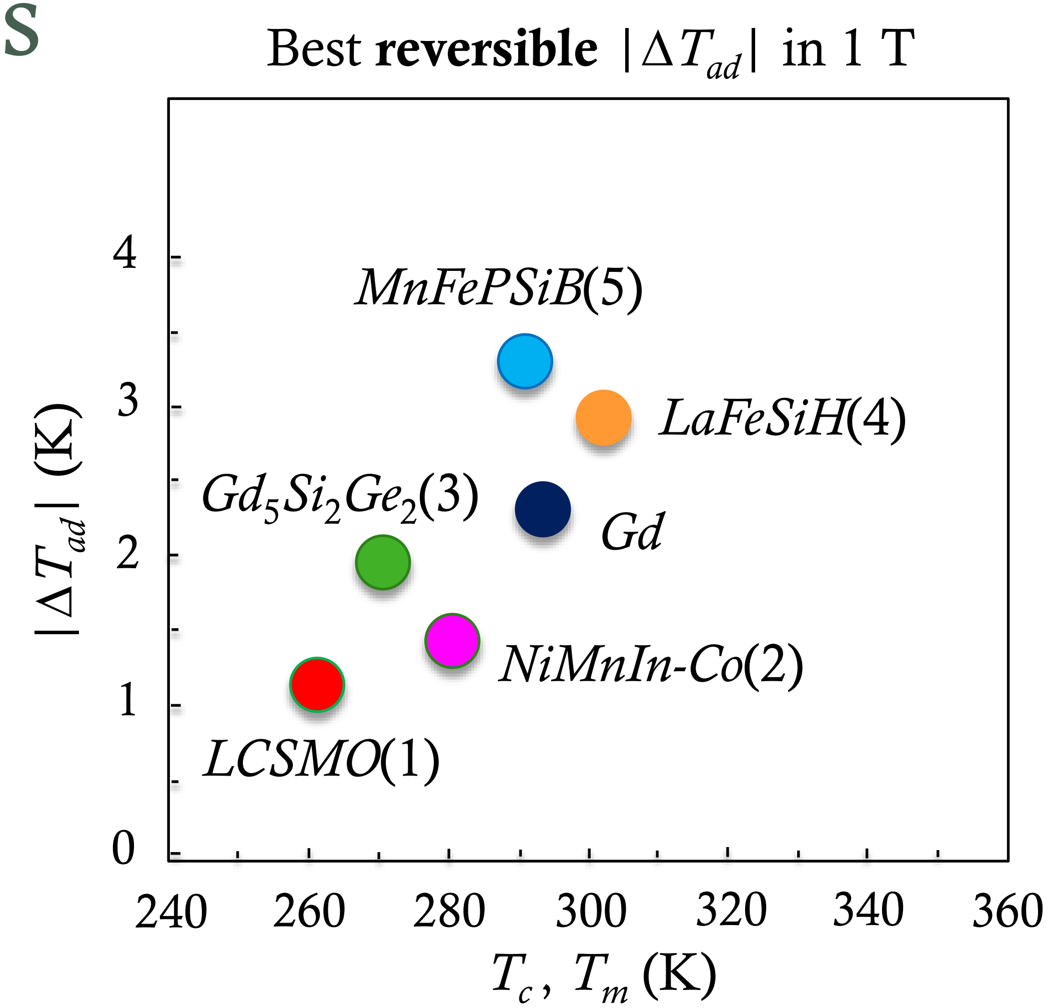
$\Delta S_T(T, \Delta H)$

$\Delta T_{ad}(T, \Delta H)$



Magnetocaloric materials

- «Classic» materials: Gd ⇒ reference
  - Curie transition
- «Giant» MC materials:
  - Magneto-structural transitions
  - 1st-order transitions
- Example of recent promising materials:



(1) Ch. Bahl, et al., Appl. Phys. Lett. 2012
(2) T. Gottschall, et al. Appl. Phys. Lett. 2015
(3) L. von Moos, J. Phys. D Appl. Phys. 2015
(4) J. Lyubina, Adv. Mater. 2010
(5) F. Guillou, et al., J. Appl. Phys. 2014

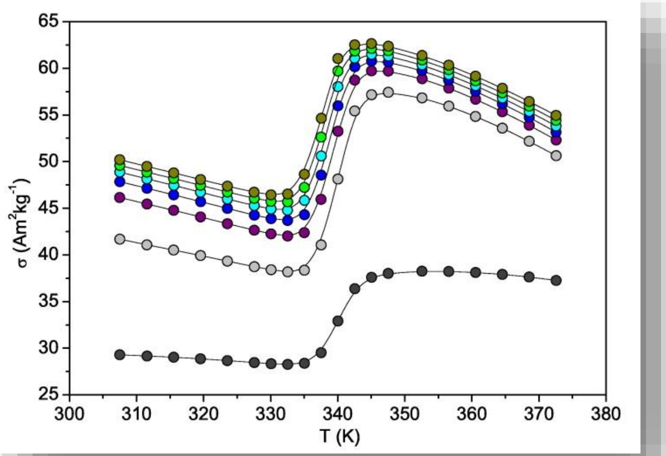
The end of the story?

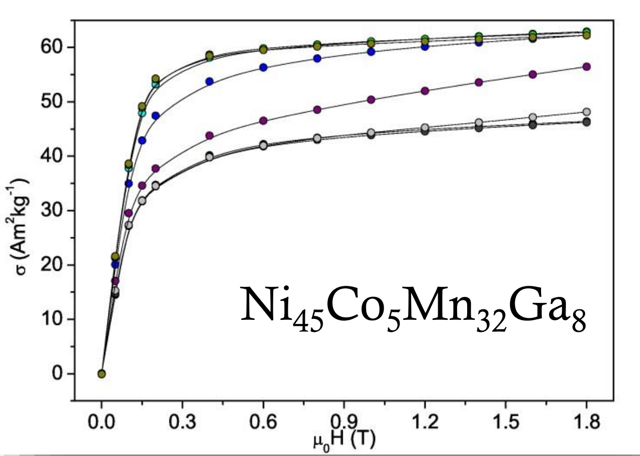
- Good materials and working devices: thus are we at the end of the story?
- No, there are many open questions:
  - Materials:
    - Hysteresis of 1st order transitions
    - Reproducibility of thermomagnetic properties
    - Thermal conductivity, mechanical stability, …
  - Devices:
    - Lower efficiency and power/temperature span, higher costs
    - ⇒ still promising but not imminent commercial applicability!

J. Steven Brown, P.A. Domanski, *Applied Thermal Engineering* 64, 252 (2014)

Characterization of the Magnetocaloric effect

- "conventional" techniques:
  - Indirect:
    - $\Delta S_T(T, \Delta H)$ from magnetization curves





Measurement protocol:
L. Caron, et al.,J. Magn. Magn. Mater. 321, 3559 (2009)

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Characterization of the Magnetocaloric effect

- "conventional" techniques:
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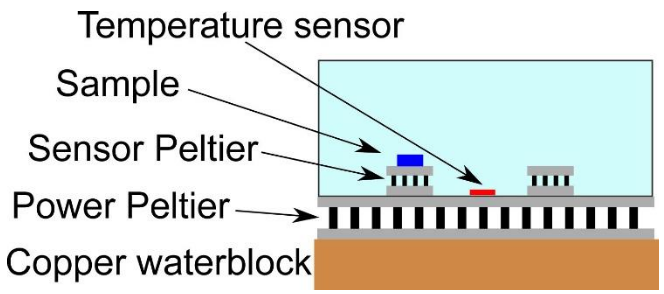
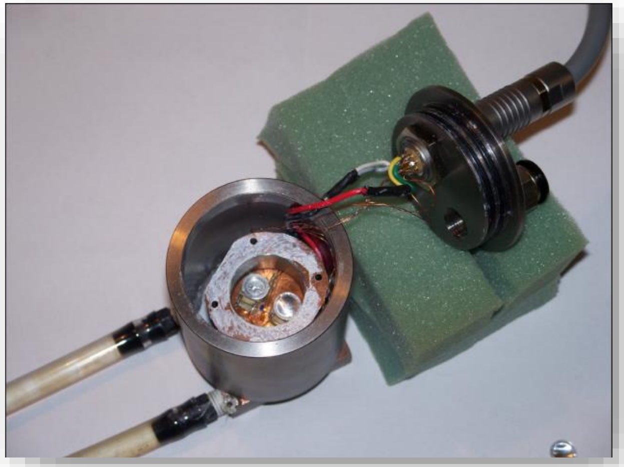
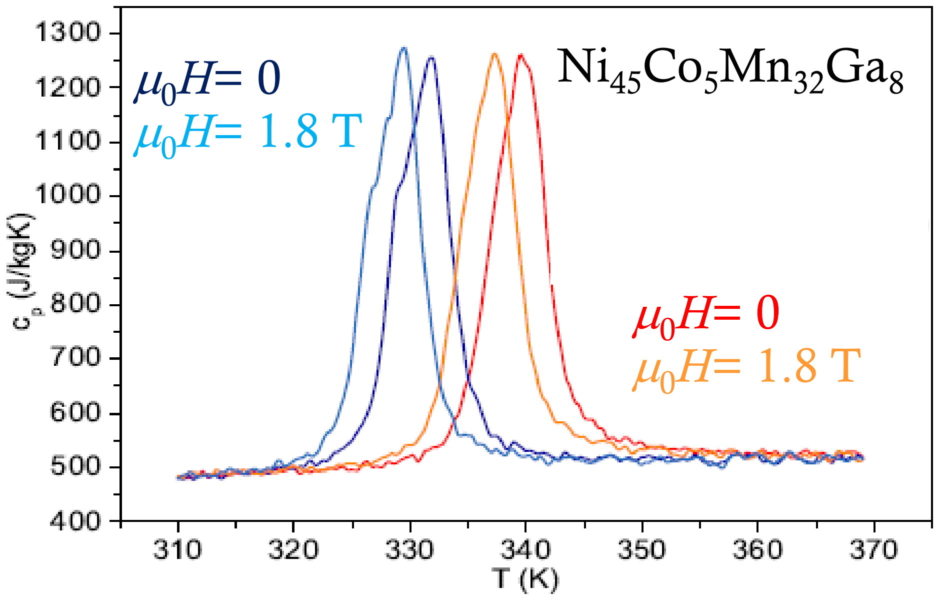
    - $\Delta S_T(T, \Delta H)$ from magnetization curves
    - $\Delta S_T(T, \Delta H)$ and $\Delta T_{ad}(T, \Delta H)$ from magnetic Differential Scanning Calorimetry



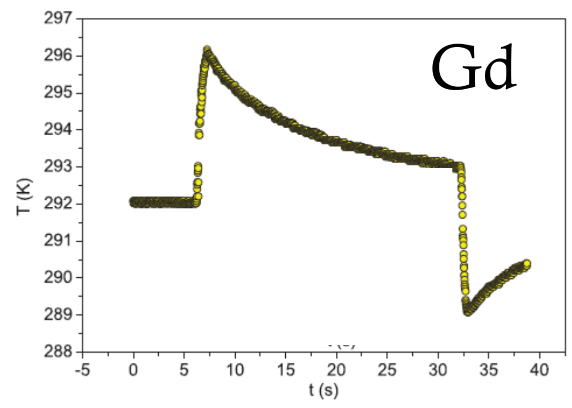


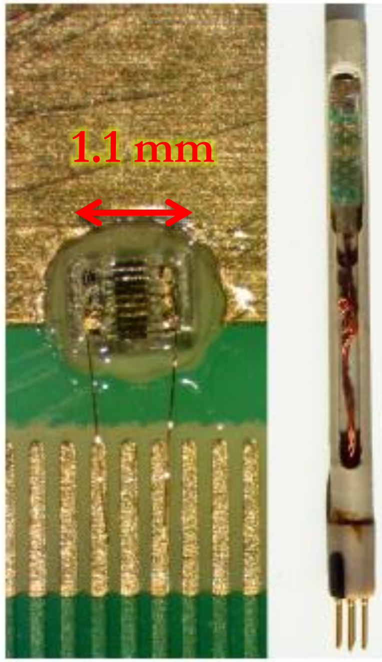


Model: S. Jeppesen, et al., Rev. Sci. Instrum. 79, 083901 (2008)
V. Basso, et al., Rev. Sci. Instrum. 81, 113904 (2010)

Characterization of the Magnetocaloric effect

- “conventional” techniques:
  - Indirect:
    - $\Delta S_T(T, \Delta H)$ from magnetization curves
    - $\Delta S_T(T, \Delta H)$ and $\Delta T_{ad}(T, \Delta H)$ from magnetic Differential Scanning Calorimetry
  - Direct:
    - $\Delta T_{ad}(T, \Delta H)$ from adiabatic temperature change measurements





G. Porcari et al., Rev. Sci. Instrum., 84, 073907 (2013)

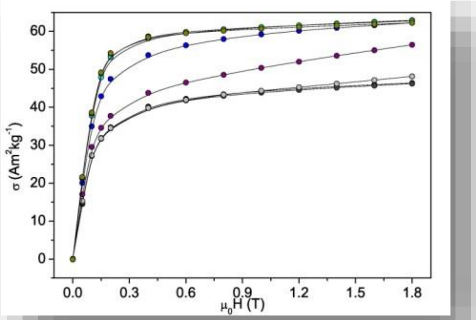
Characterization of the Magnetocaloric effect

- "conventional" techniques:
  - Indirect:
    - $\Delta S_T(T, \Delta H)$ from magnetization curves
    - $\Delta S_T(T, \Delta H)$ and $\Delta T_{ad}(T, \Delta H)$ from magnetic Differential Scanning Calorimetry
  - Direct:
    - $\Delta T_{ad}(T, \Delta H)$ from adiabatic temperature change measurements

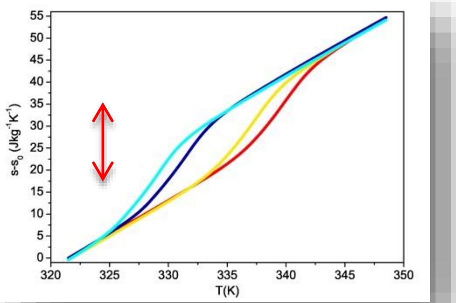
- Reproducibility of meas. for different samples (1^{st} order transitions)
  - mass, shape, micro-strains, composition …
- Importance of comparison of different techniques

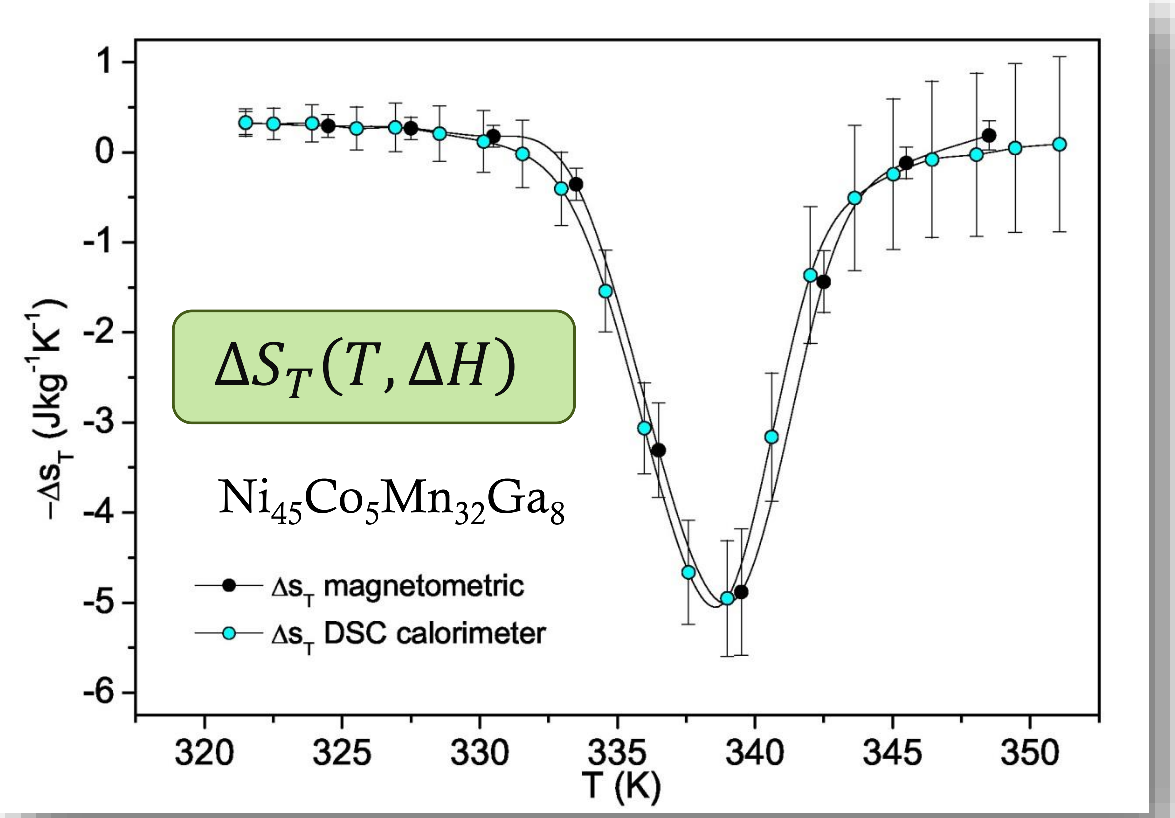
V. K. Pecharsky and K. A. Gschneidner, Jr, J. Appl. Phys., 90, 4614 (2001)

Iso-thermal entropy change: comparison



$$\Delta S_m(T_0,\Delta H)_{\Delta H} = \mu_0 \int_{H_i}^{H_f} \left(\frac{\partial M(T_0,H)}{\partial T} \right)_H dH$$

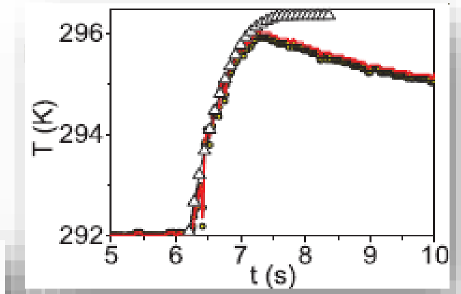


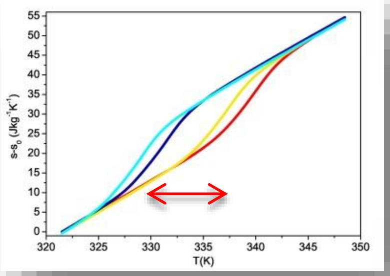


G. Porcari et al., Phys. Rev. B, 86, 104432 (2012)

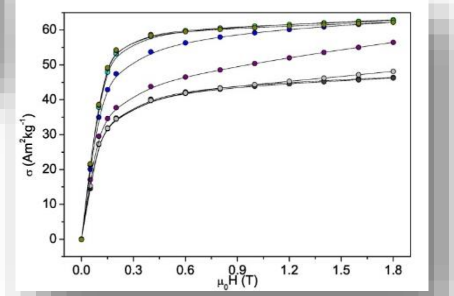
Adiabatic temperature change: comparison

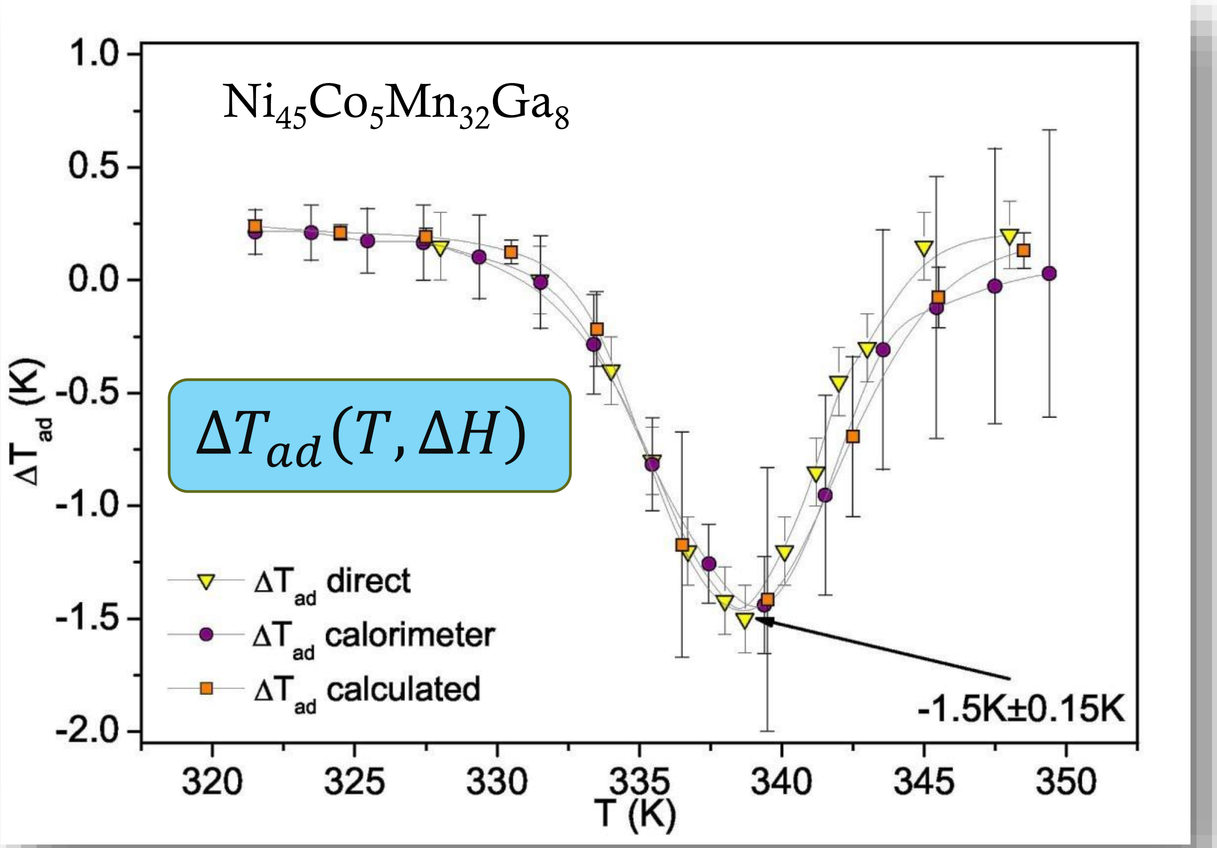
$\mu_0 dH/dt = 2$ T/s





$\mu_0 dH/dt = 10^{-3}$ T/s

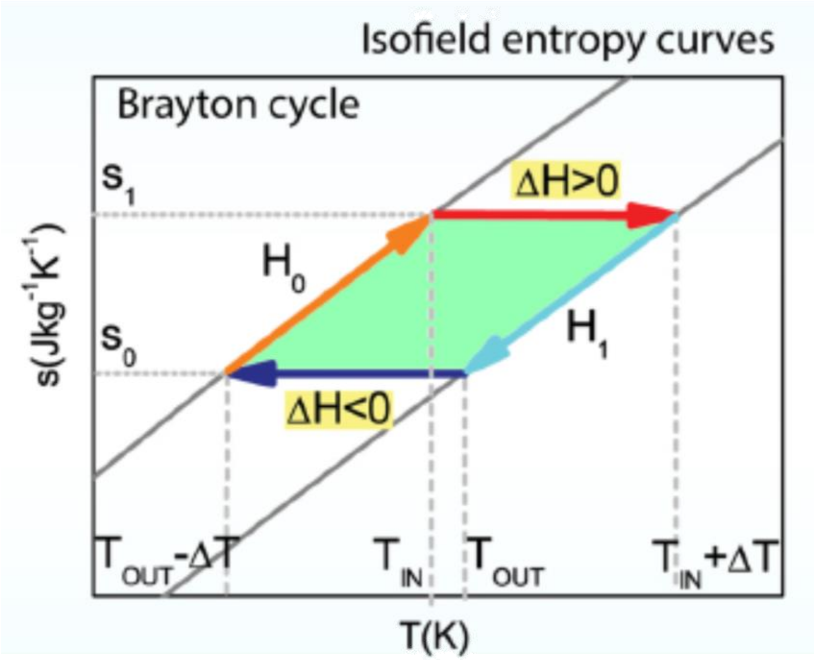


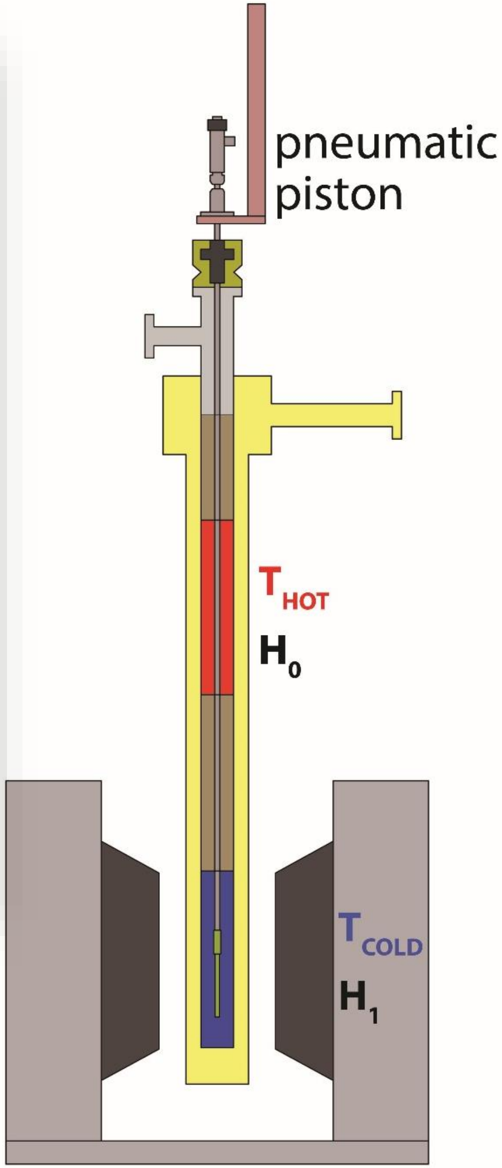


G. Porcari et al., Phys. Rev. B, 86, 104432 (2012)
G. Porcari et al., Phys. Rev. B, 85, 024414 (2012)

Thermomagnetic cycles

- Study of MCE in operating (dynamic) conditions
- Repeated thermomagnetic cycles





Pneumatic linear actuator

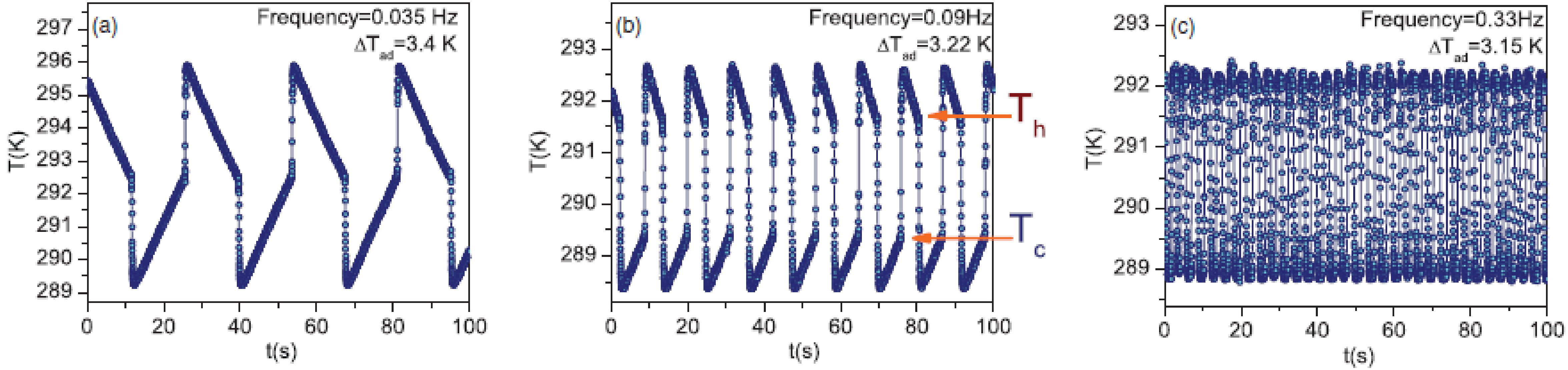
Two regions with controlled H and T

G. Porcari, et al., Rev. Sci. Instrum. **84**, 073907 (2013)

Thermomagnetic cycles

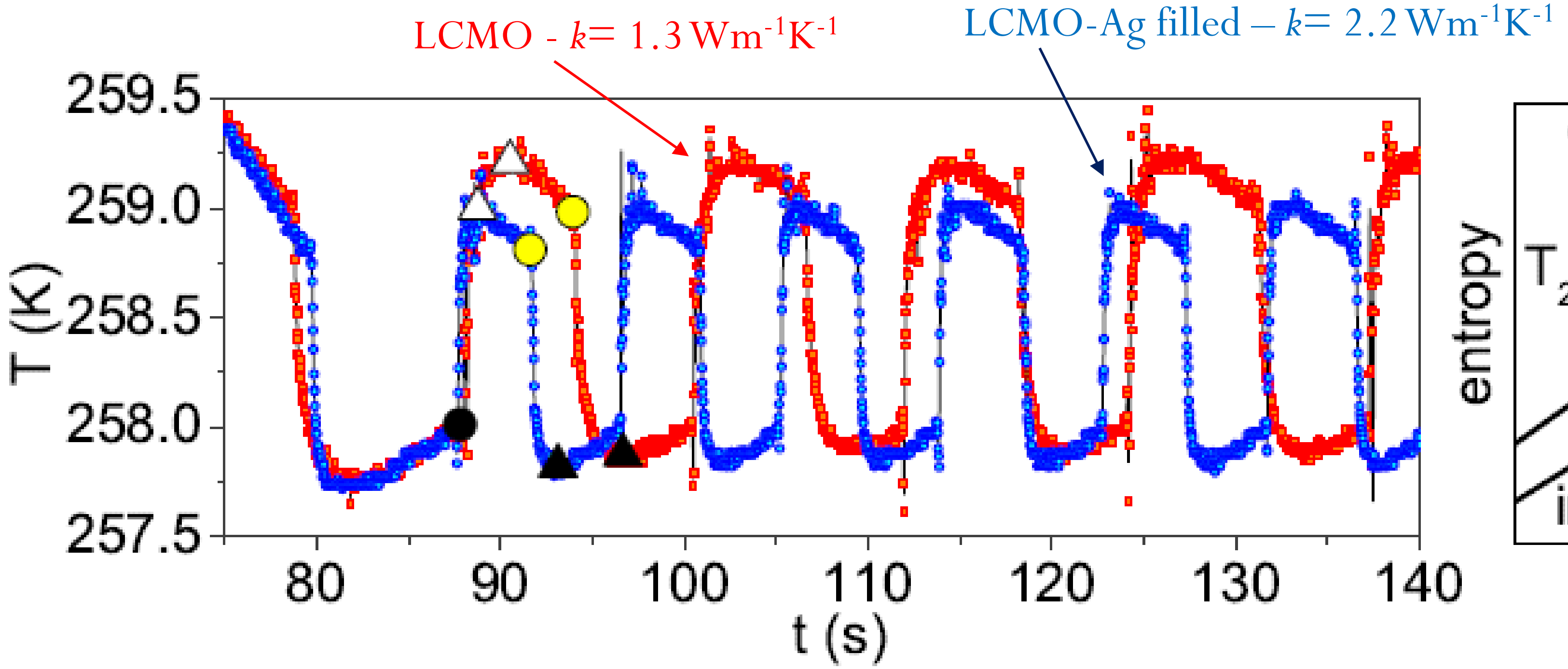
G. Porcari, et al., Rev. Sci. Instrum. **84**, 073907 (2013)

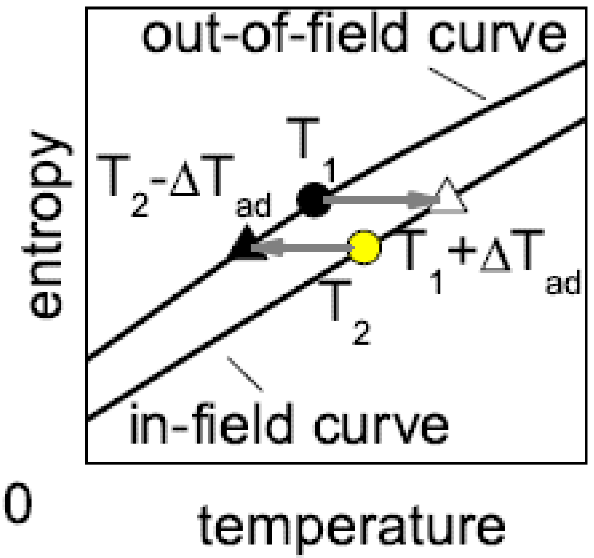
Gd polycrystalline sample



Time constant of temperature change

- Comparison of materials with different thermal conductivity: composites
  - Different magnitude of the effect and different frequency





G. Porcari, et al., Int. J. Refrig., in press (2015)

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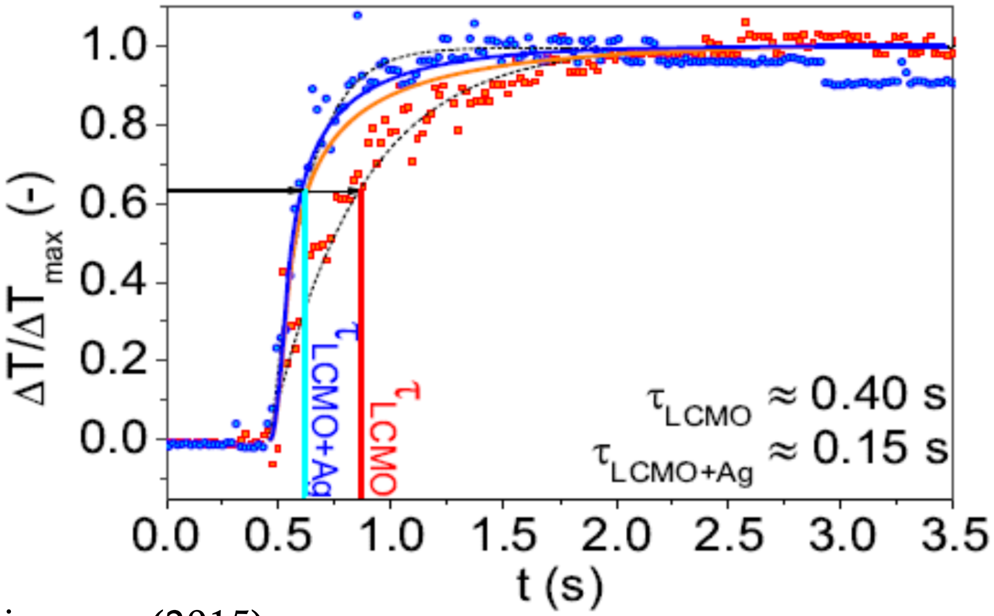
Time constant of temperature change

- Time decay of the adiabatic branch: time constant τ
- Exponential best fit + average on hundreds of cycles
- Heat-transfer simulations (FEM)



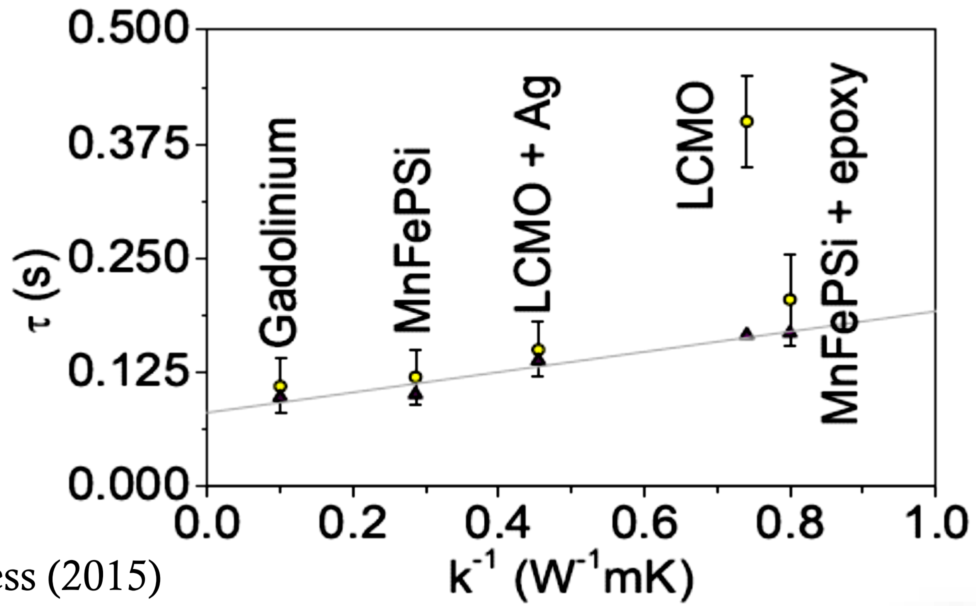
G. Porcari, et al., Int. J. Refrig., in press (2015)

Time constant of temperature change

- τ represents the dynamic response of a MC material
  - Upper bound for max operating frequency
- Indirect information on the microstructure evolution with N. of cycles
  - mechanical stability ⇔ thermal conductivity

○ experimental

▲ FEM simulations

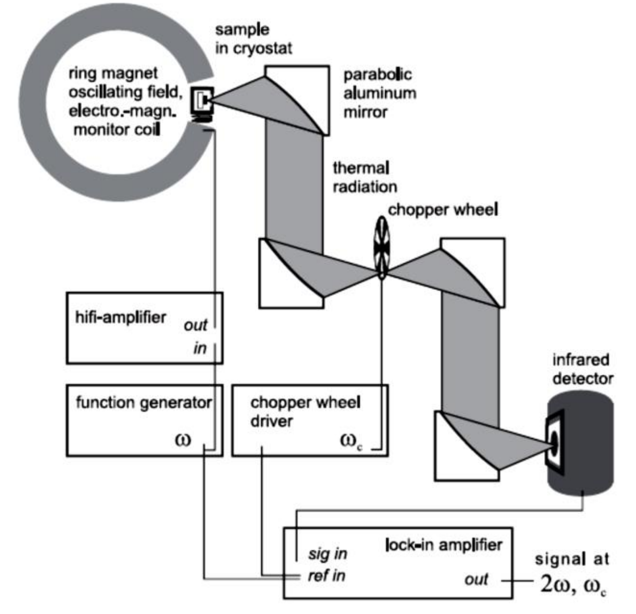


G. Porcari, et al., Int. J. Refrig., in press (2015)

Non-contact measurements techniques

- Direct methods for measuring ΔT_{ad} based on non-contact techniques:
  - nearly-ideal adiabatic conditions;
  - thermomagnetic cycles at relatively high frequency (≈10 Hz);
  - samples with reduced thickness, like as thin sheets and ribbons (→ thin films)

- Acoustic or optical detection of thermal radiation (low ac magnetic fields)



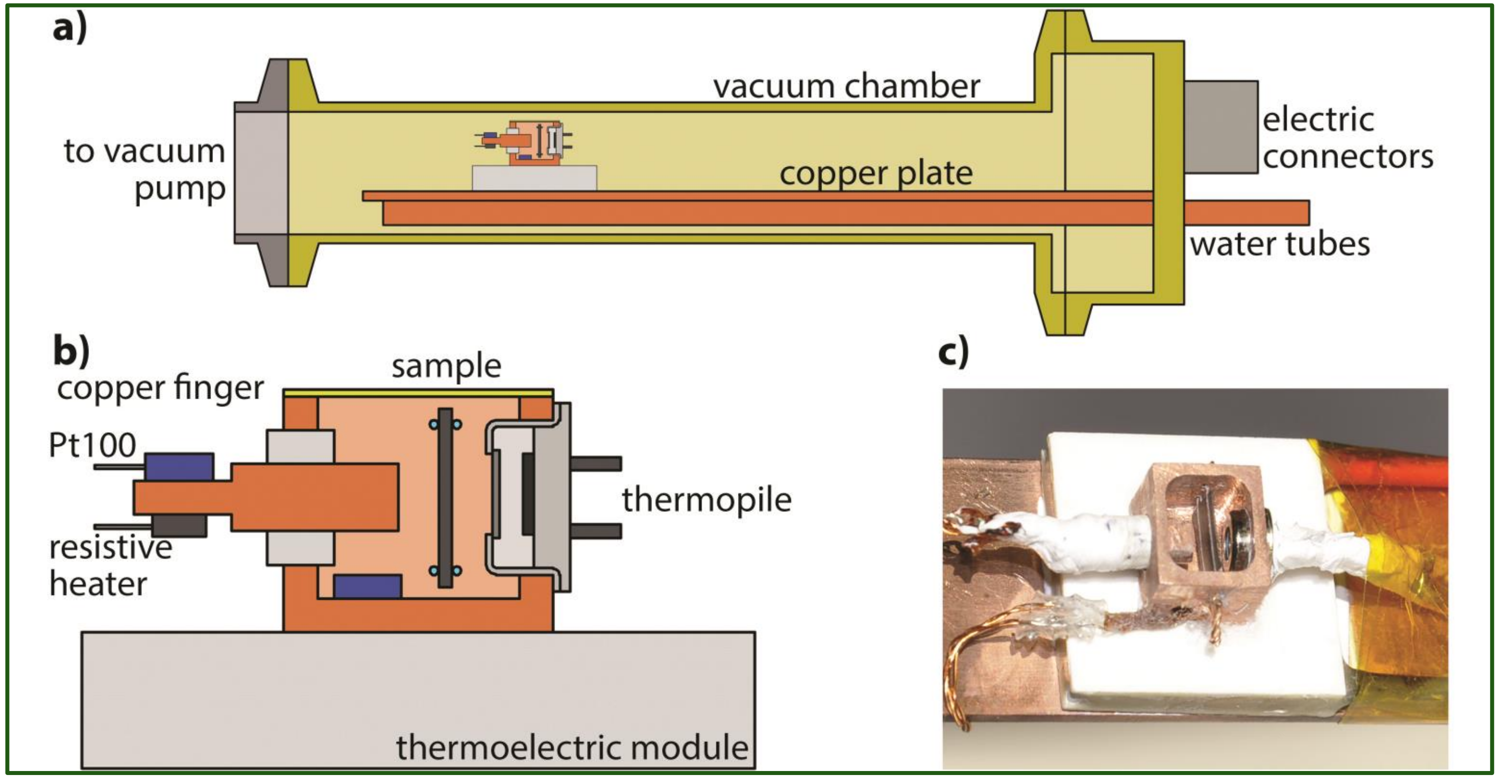
A. O. Guimarães, et al., Phys. Rev. B 80, 134406 (2009)
J. Döntgen, et al., Appl. Phys. Lett. 106, 032408 (2015)

Non-contact techniques: an example

p: 10^{-4} mbar
260K < T<350K
$\mu_0 H$ up to 2 T
τ_{magn} < 300 ms

Response time:
27 ms

Surface emissivity:
calibration



F. Cugini, et al., Rev. Sci. Instrum. **85**, 074902 (2014)

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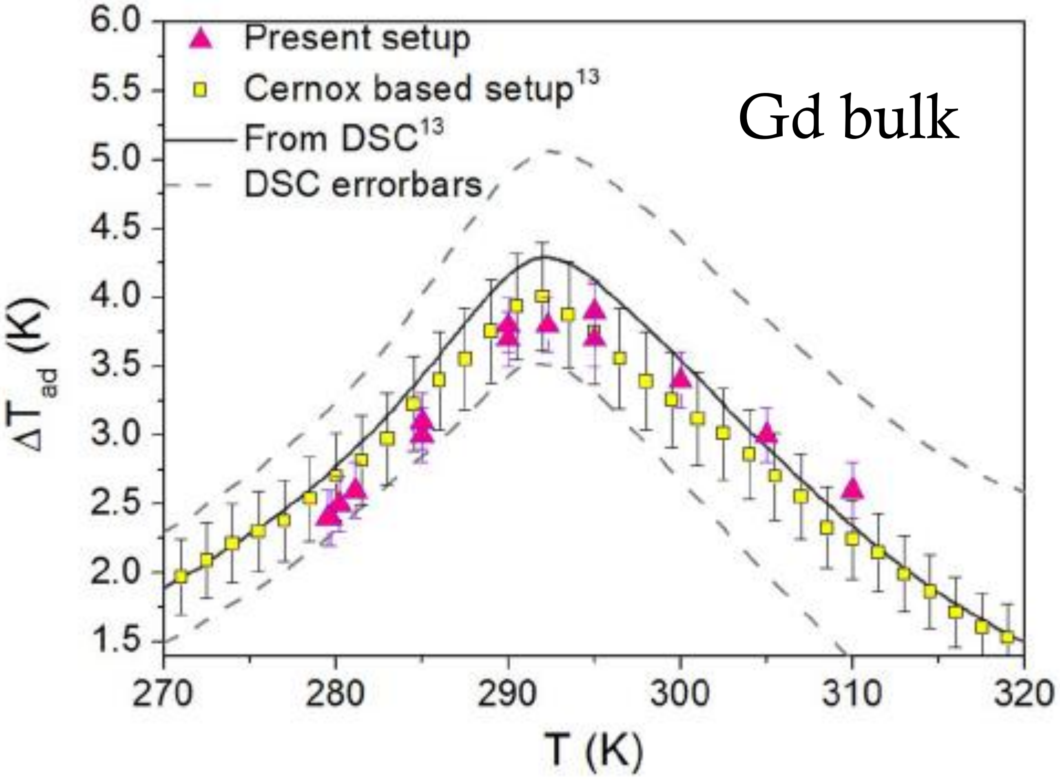
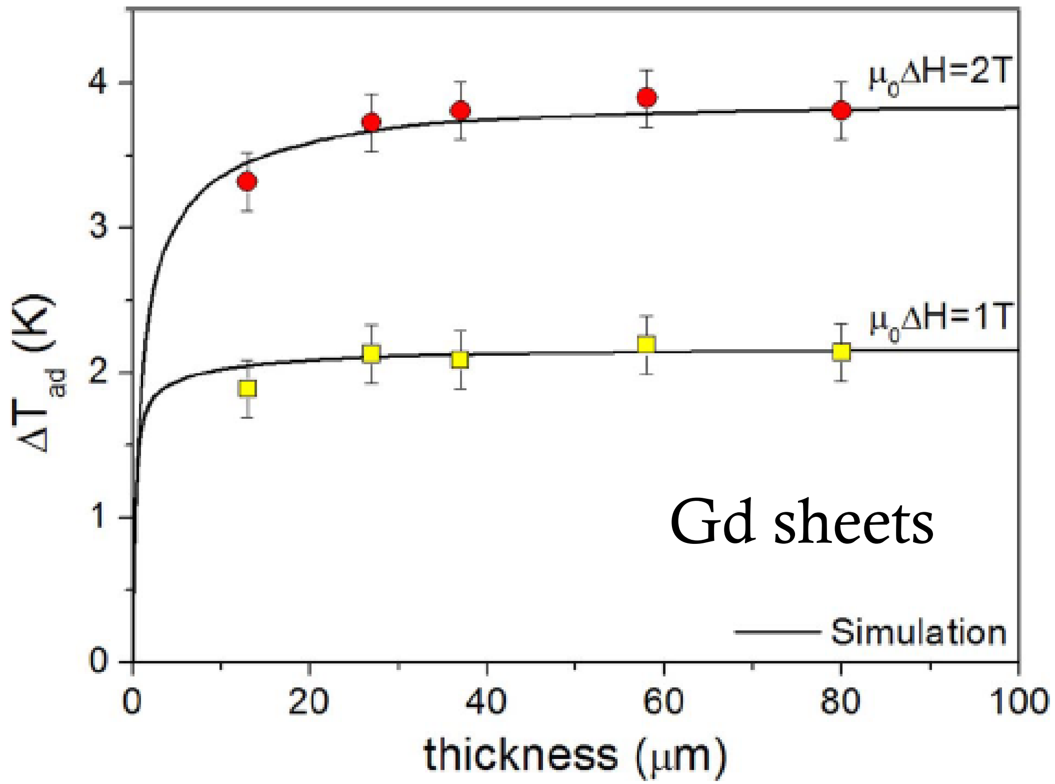
Non-contact techniques: experiments

Validation $\mu_0 \Delta H = 2$ T



Heat transfer simulations + experiments



F. Cugini, et al., Rev. Sci. Instrum. **85**, 074902 (2014)

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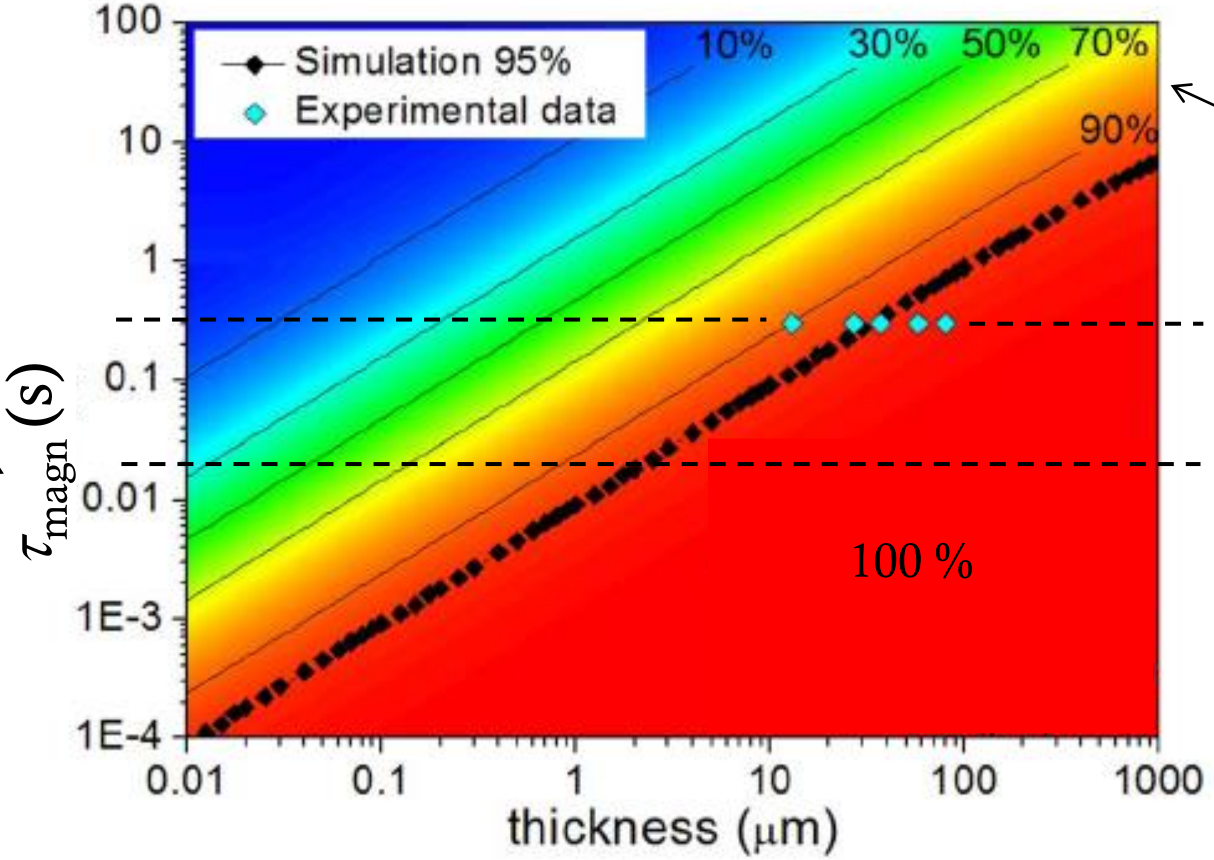
Non-contact techniques: time scale of *H* change

Gd sheets - $\mu_0 \Delta H = 1.0$ T

Magnetic field time constant



Detectable fraction of ΔT_{ad}

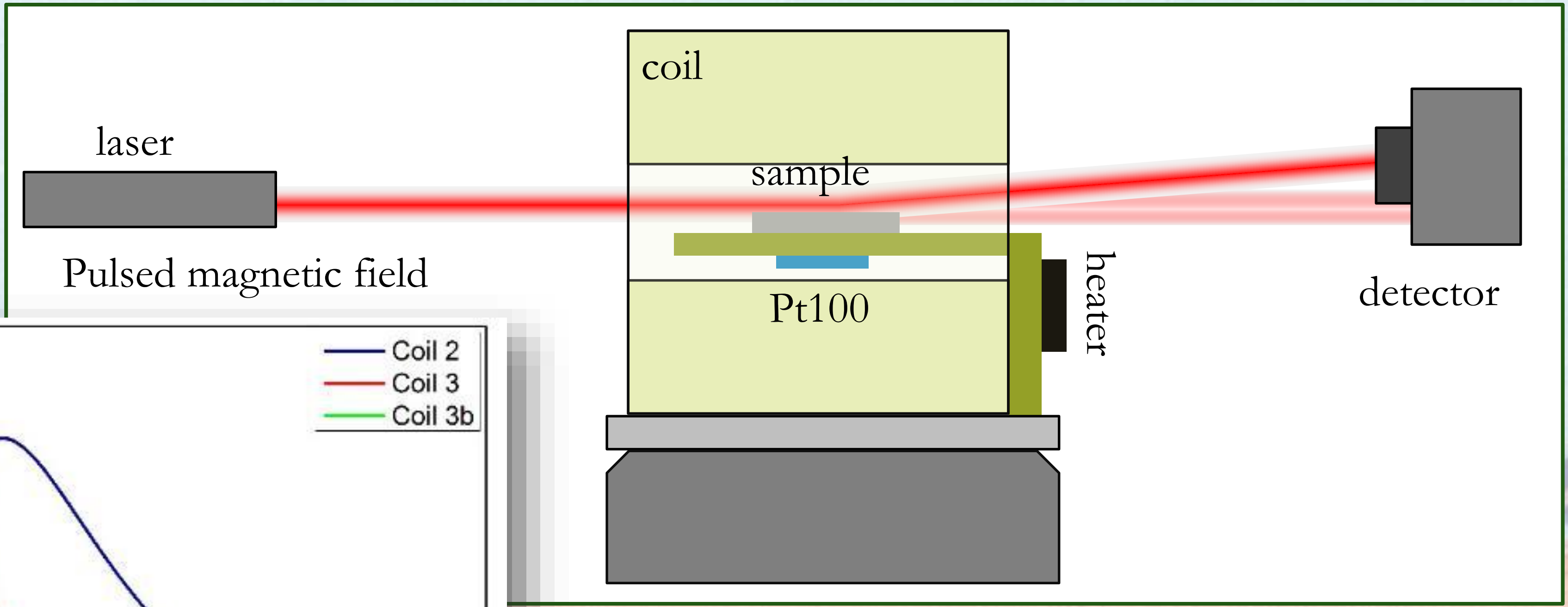
electromagnet switch on/off

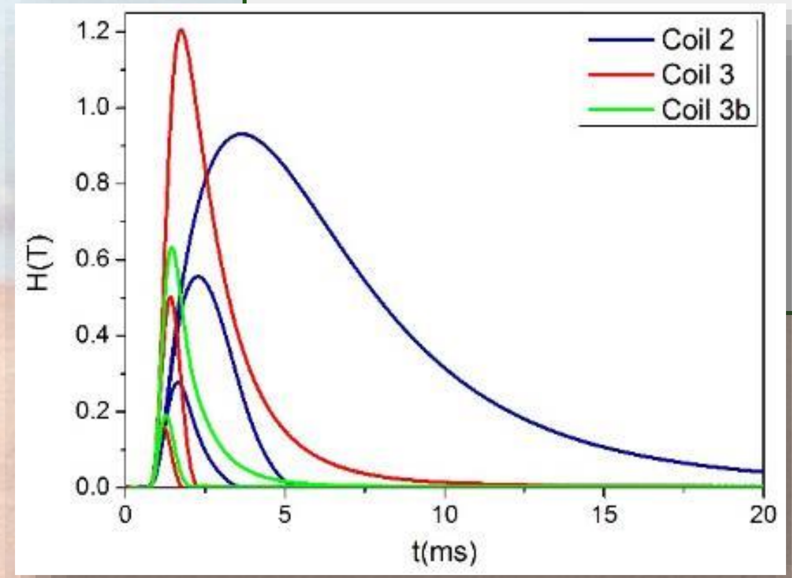
Thermopile limit

F. Cugini, et al., Rev. Sci. Instrum. **85**, 074902 (2014)

Thermal lensing (mirage effect)

Non-contact techniques: thermal lensing

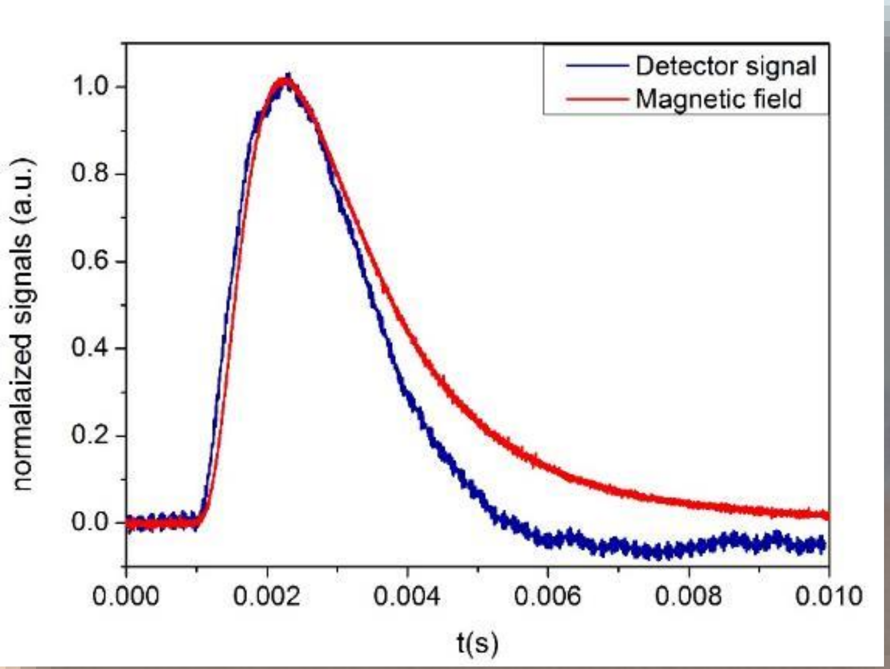




F. Cugini, et al., submitted to Appl. Phys. Lett. (2015)

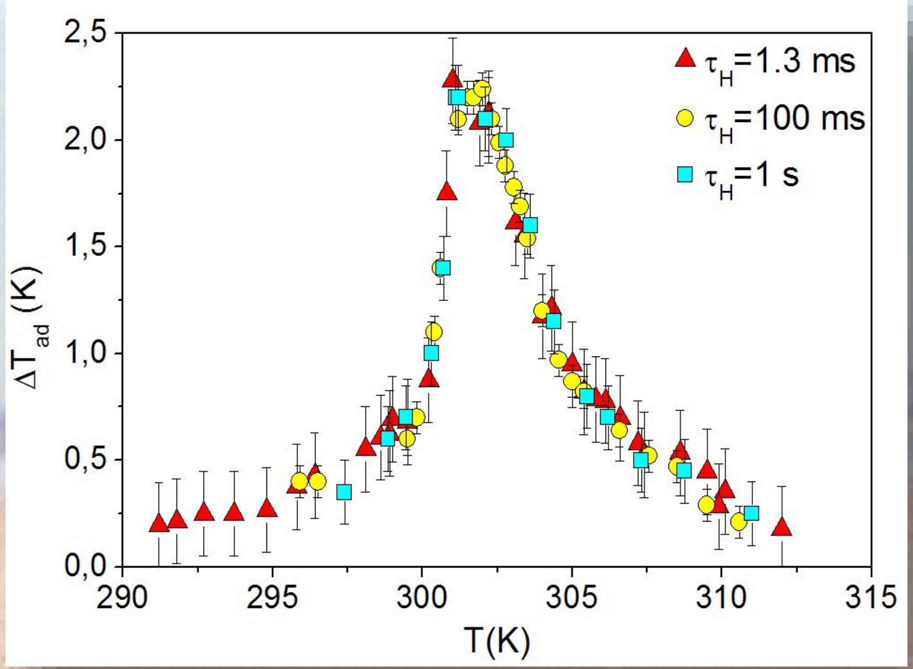
Non-contact techniques: thermal lensing

- Fast response time: < ms



F. Cugini, et al., submitted to Appl. Phys. Lett. (2015)

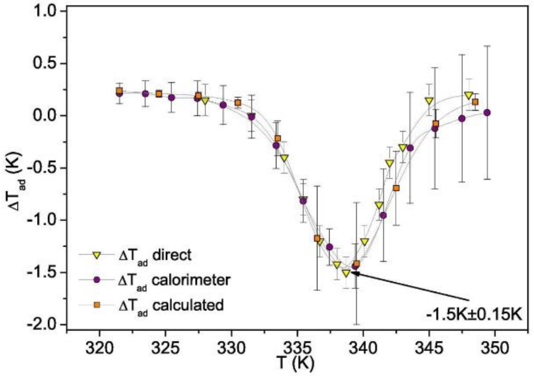
- agreement with usual techniques for measuring ΔT_{ad}

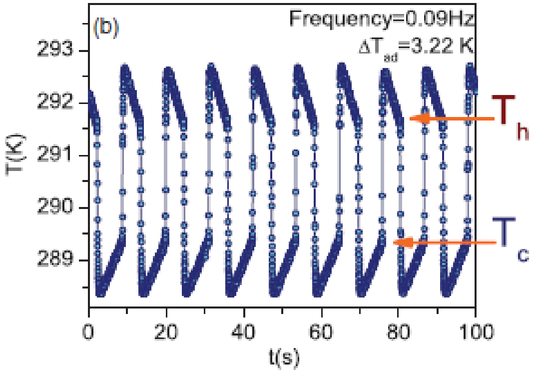


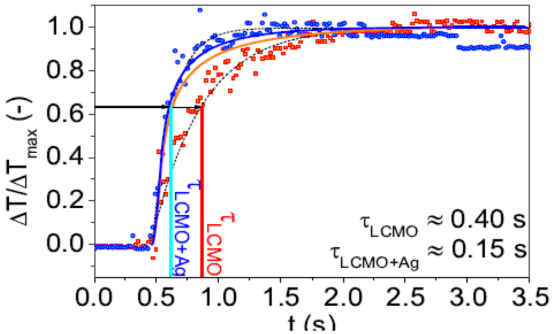
Bulk $MnFeP_{45}As_{55}$

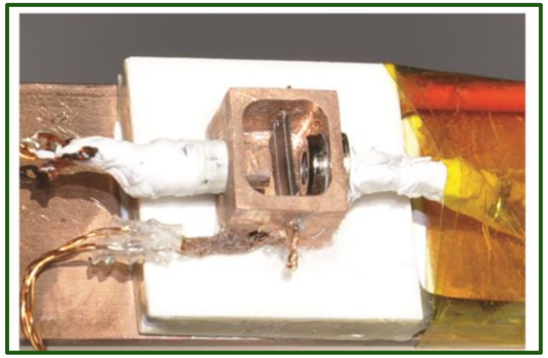
Conclusions

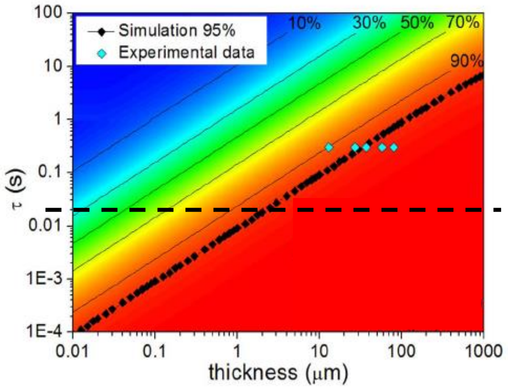
- Comparison of different techniques for characterization of MC refrigerants
- Nearly operating conditions: repeated cycles
- Dynamic response: time constant of temperature change
- Non-contact measurements: high frequency – low mass materials
- Comparison of experimental data with heat transfer simulations











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