A Peltier cell calorimeter for the direct determination of the entropy change in magnetic materials

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Outline

1 Motivation: need for measurements of the magneto-caloric effect under well defined conditions

2 Description of the setup for a direct isothermal ΔS measurement

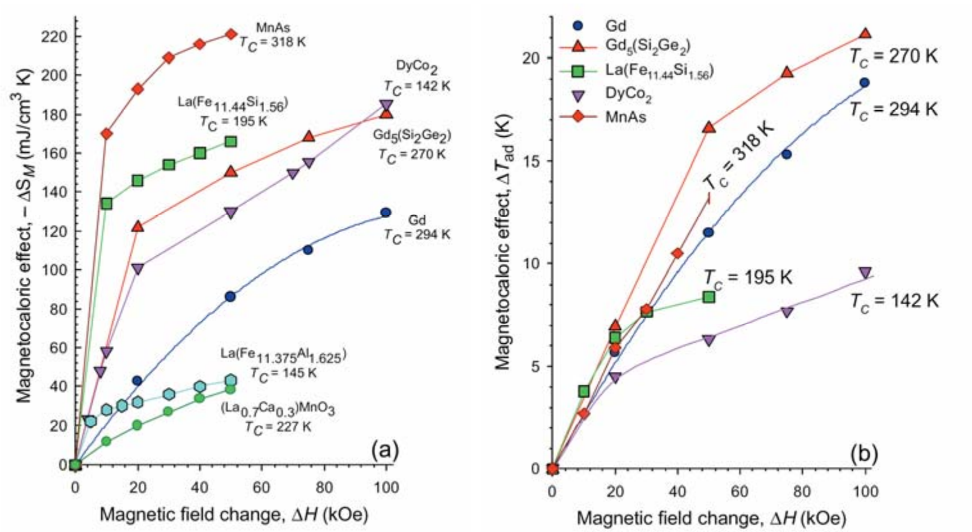
3 Peltier cells as heat sensor and actuator (theoretical description, calibration)

4 Digital control for isothermal condition

5 Test measurements of Gadolinium and GdSiGe compound

6 Future developments

Motivation



Gschneidner et al., Rep.Prog.Phys. 68, 1479, 2005

Figure 2. The isothermal entropy change as a function of the magnetic field change for $DyCo_2$ [48–50], $Gd_5(Si_2Ge_2)$ [51], $La(Fe_{11.44}Si_{1.56})$ [52], $La(Fe_{11.375}Al_{1.625})$ [53], Gd [54], $(La_{0.7}Ca_{0.3})MnO_3$ [55] and MnAs [56]. The data points for $DyCo_2$ at 4, 8 and 10 kOe were taken from [48], the data points at 20, 50, 75 and 100 kOe from [49] and that at 70 kOe from [50]. The highest values of $-\Delta S_M$ for $Gd_5(Si_2Ge_2)$ and the two highest values for Gd are unpublished results of the authors (*a*). The adiabatic temperature rise as a function of the magnetic field change for $DyCo_2$ [49], $Gd_5(Si_2Ge_2)$ [51], $La(Fe_{11.44}Si_{1.56})$ [52], Gd [7] and MnAs [56]. The highest value of ΔT_{ad} for $Gd_5(Si_2Ge_2)$ is an unpublished result of the authors (*b*).

classification of materials

measurements

standardized measurement method

Measurement principles

- ΔS isothermal entropy change
- ΔT adiabatic temperature change
- C_p heat capacity in magnetic fields

cooling power

in reversible processes quantities are related :

$$dQ = TdS = T\frac{\partial S}{\partial H}dH + C_p(T,H)dT$$

thermodynamic Maxwell's relations:

$$\left.\frac{\partial S}{\partial H}\right|_{T=\text{const}} = \left.\frac{\partial m}{\partial T}\right|_{H=\text{const}}$$

$$\Delta S(H,m) = \int_{H_1}^{H_2} \frac{\partial m(T,H)}{\partial T} dH$$

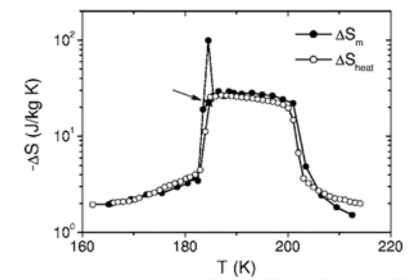
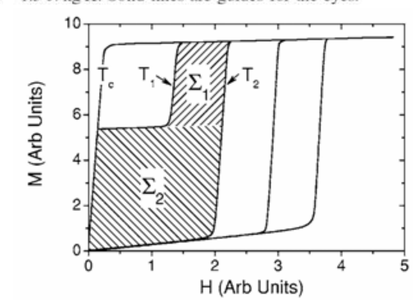


FIG. 2. Temperature-dependent entropy changes of $La_{0.7}Pr_{0.3}Fe_{11.5}Si_{1.5}$ calculated from magnetic data (solid circles) and heat capacity (open circles). The peak value drops from ~99 to ~22 J/kg K if only the contributions from the metamagnetic transition are considered (marked by an arrow). Δ has been set ~1.5 J/kg K. Solid lines are guides for the eyes.

in irreversible processes: $dQ = Td_eS = TdS - Td_iS$



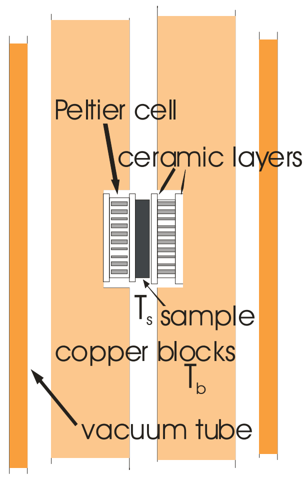
problem: systems with hysteresis in T and/or H

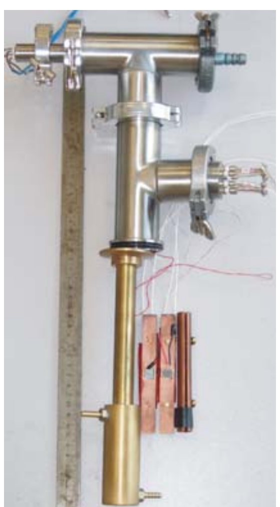
magneto-structural phase transitions

G.J.Liu et al., APL 90, 032507, 2007

Isothermal measurement of entropy change

setup scheme





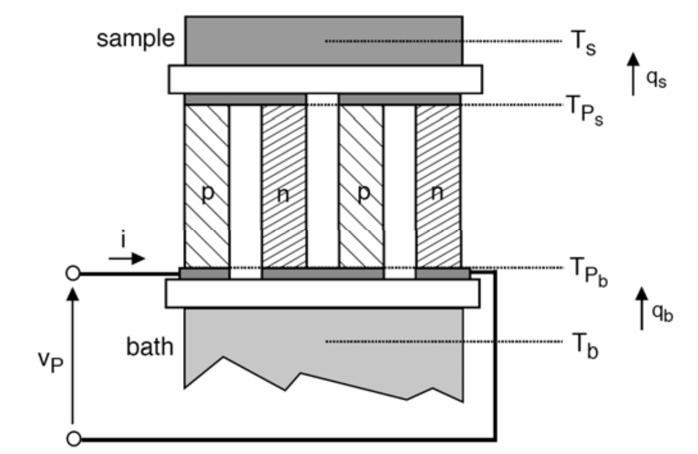
- Peltier cells are used as heat flux sensor and actuator for heating/cooling the sample simultaneously
- symmetric setup minimizes heat losses
- the temperature of the thermal bath can be changed between -30°C and 100°C by using liquid nitrogen and electric heaters
- setup in vacuum in order to avoid heat loss by convection of air and change of temperature
- magnetic field produced by electromagnet up to 1.5T

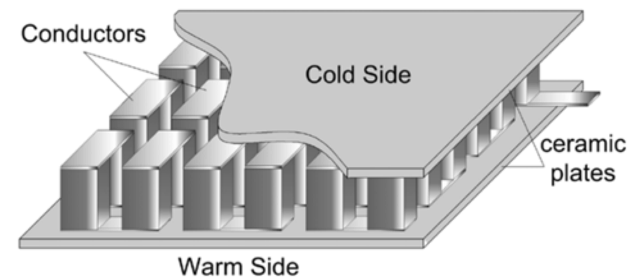
principle of the isothermal measurement

Isothermal conditions are maintained by a digitally controlled (PI type) current supply of the Peltier cells. (temperature control of the sample)

At the same time the Peltier cell voltage is measured and related to the heat flux from the sample to the bath. (heat flux sensor)

Peltier cell equations





time independent relations between current, voltage and heat flux of a thermo-electric material:

$$v_P = \epsilon\,(T_{P_s} - T_{P_b}) + R\,i \qquad (1) \quad \text{Seebeck effect}$$

$$q_s = \Pi\,i + \frac{1}{2}Ri^2 - K(T_{P_s} - T_{P_b}) \qquad (2) \quad \text{Peltier effect}$$

during measurement time dependence plays a role due to finite heat capacity of the cell and the sample

Assumption:

for small variations of the quantities in time (small T difference, slowly time varying magnetic field) , the equations 1 and 2 can be applied, introducing cell dependent parameters

Peltier cell equations

$$T_s - T_b = \frac{1}{\epsilon_P}(v_P - R_P i)$$

$$q_s = \Pi_P i - \frac{1}{S_p}(v_P - R_P i) + \frac{1}{2} R i^2$$

$$v_P = \epsilon_P (T_s - T_b) + R_P i$$

$$q_s = \Pi_P i + \frac{1}{2} R i^2 - K_P (T_s - T_b)$$

$$S_P = \epsilon_P / K_P$$

for a simplified case the cell parameters can be determined:
e.g. neglecting the heat capacity of the cell and setting the temperatures of bath and sample constant

$$\Pi_P = \Pi \frac{K_P}{K} \quad \epsilon_P = \epsilon \frac{K_P}{K} \quad R_P = R + \left(1 - \frac{K_P}{K}\right) \frac{\epsilon \Pi}{K} \quad K_P = \frac{K\, K_l}{K + K_l}$$

parameters include effects of heat conductivity (inclusively contact resistances)

time dependence taken into account by measured Peltier voltage (vp=vp(t)), i.e. heat capacities

calibration procedure necessary!

Calibration

Based on the equations 3 and 4, a calibration at constant temperature of the thermal bath is performed in three steps:

$$T_s - T_b = \frac{1}{\epsilon_P}(v_P - R_P i) \quad (3)$$

$$q_s = \Pi_P i - \frac{1}{S_p}(v_P - R_P i) + \frac{1}{2} R i^2 \quad (4)$$

- calibration of S_P

$$q_s = q_0;\ i = 0;\ \Delta T \neq 0$$

$$q_s = -\frac{1}{S_P} v_P$$

passive configuration = Peltier cell used as heat sensor

- calibration of R_P

both sides of cell in contact with thermal bath

$$q_s \neq 0;\ i = i_0;\ \Delta T = 0$$

$$R_P = \frac{v_P}{i}$$

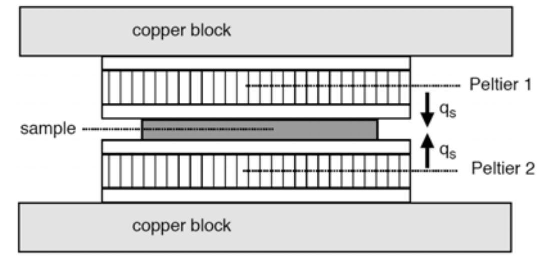
- calibration of Π_P

with sample in measurement configuration

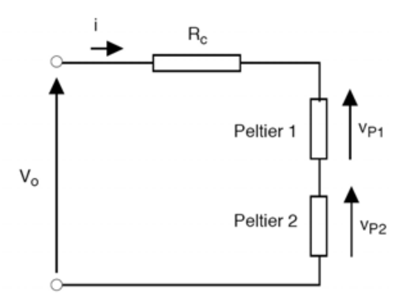
$$q_s = 0;\ i = i_0;\ \Delta T \neq 0$$

$$\Pi_P = \frac{1}{S_P}\left(\frac{v_P}{i} - R_P\right) - \frac{1}{2} R i$$

a. thermal

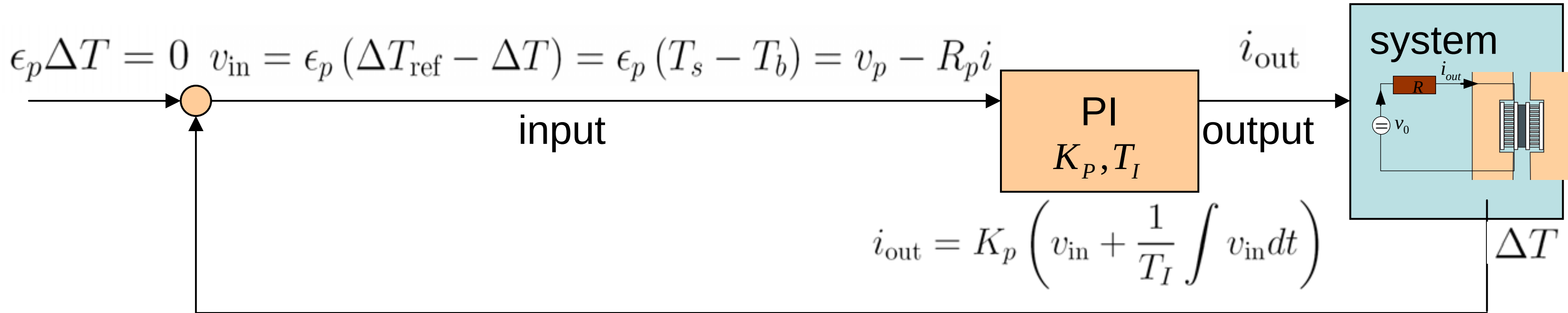


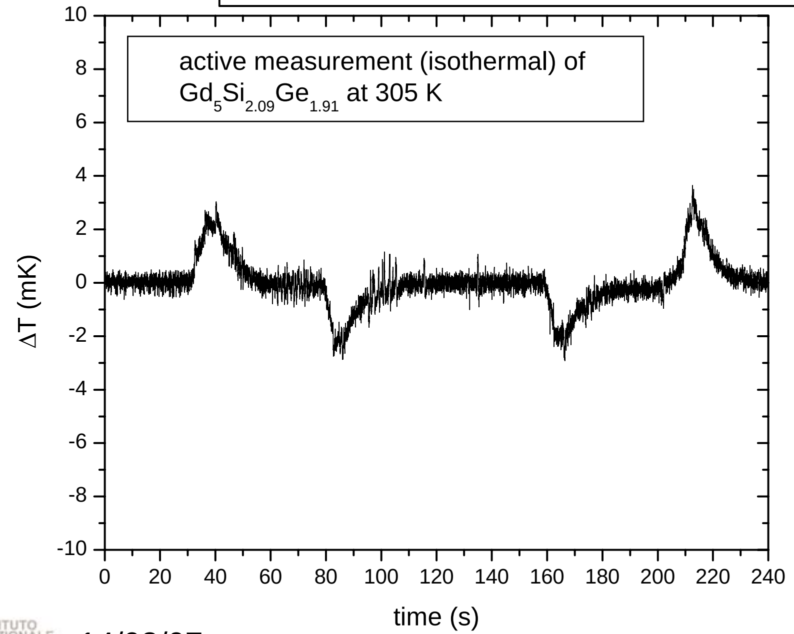
b. electric



Digital control for isothermal conditions

The PI control changes the Peltier cell current in order to minimize the temperature difference between sample and bath:





isothermal within 10mK

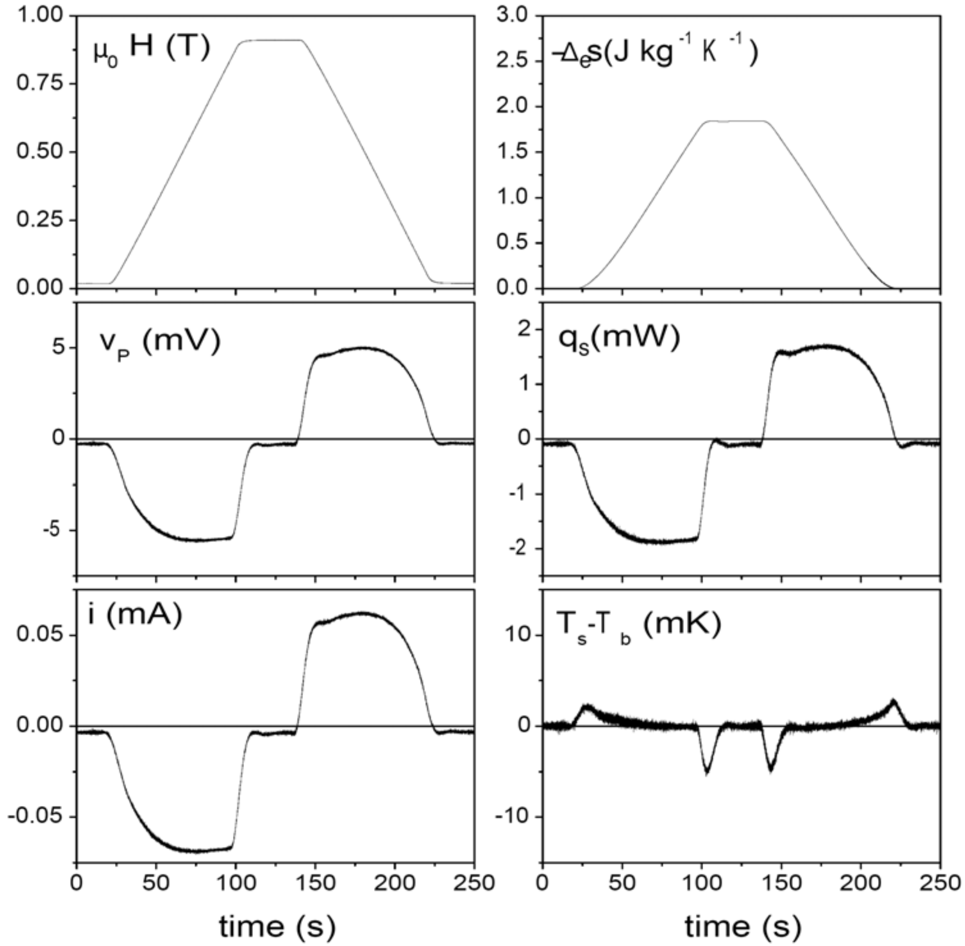
limit: noise

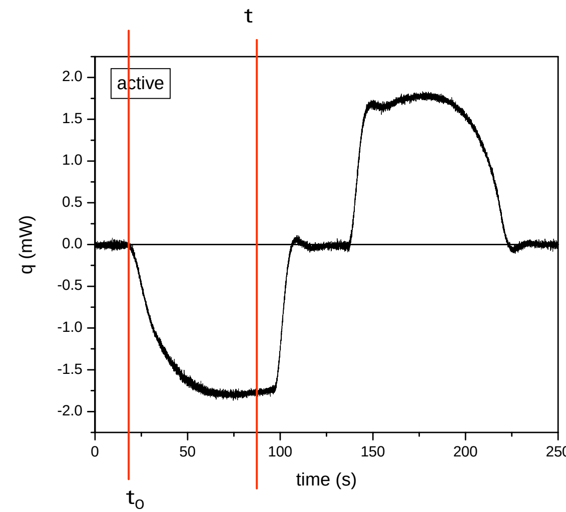
new approach: loop-to-loop control instead of real time control

Test measurement

Gd sample (sheet of 5x5x1mm):

maximum field 0.9T, rate 11mT/s
296K



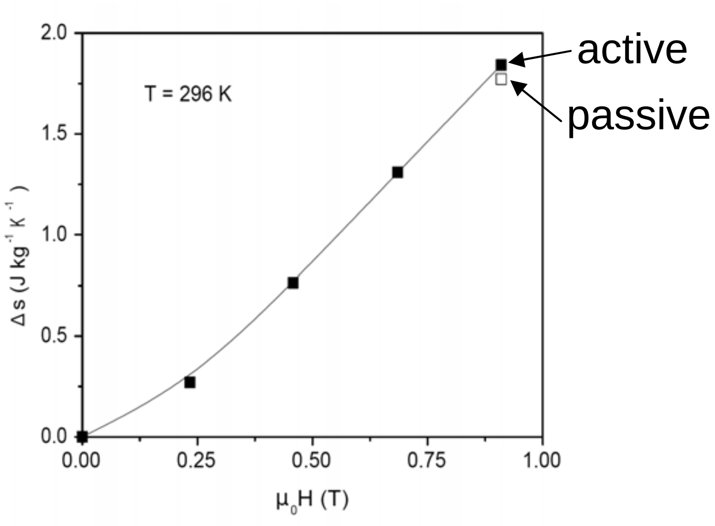


$$\Delta S = S(0) - S(H) = \frac{1}{T}\int_{t_0}^{t} q\, d\tau$$

$$\oint dS = \oint (d_e S + d_i S) = 0$$

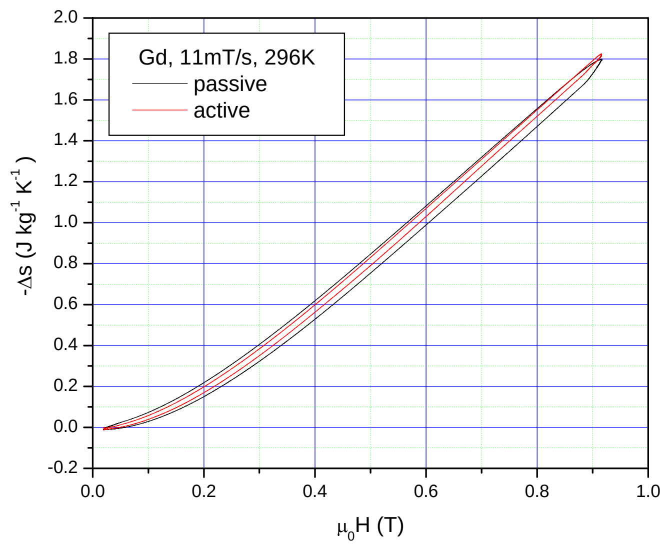
Field dependence

field dependence



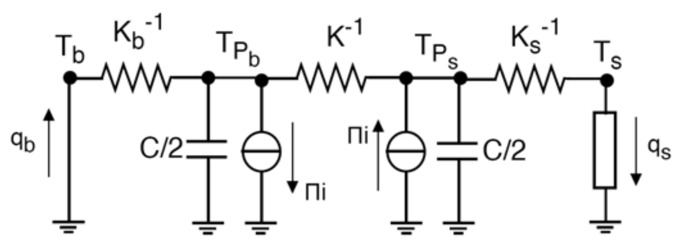
aim higher fields, superconducting magnet

influence of magnetic field on Peltier cells!



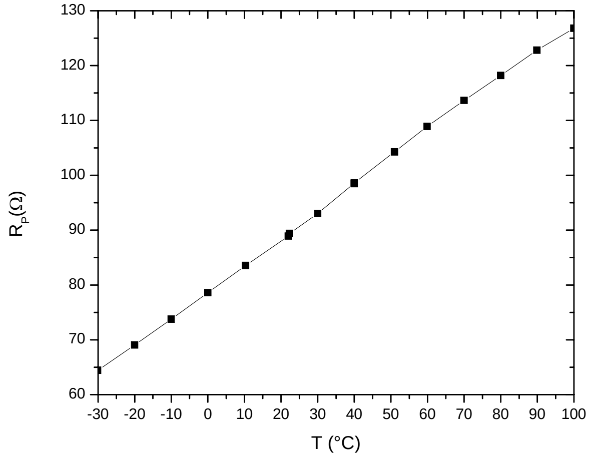
dynamic model of the Peltier cell describing heat diffusion in the cell

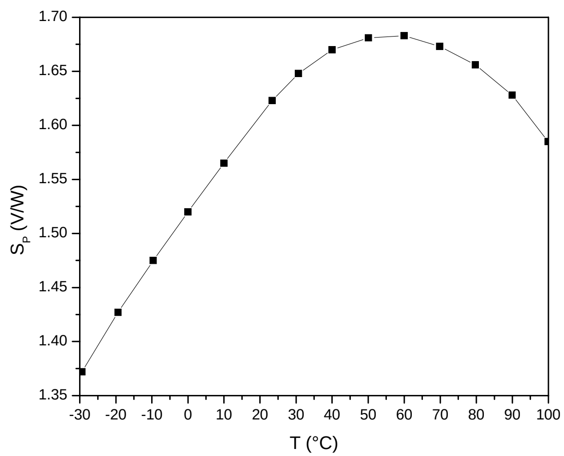
lumped parameter method

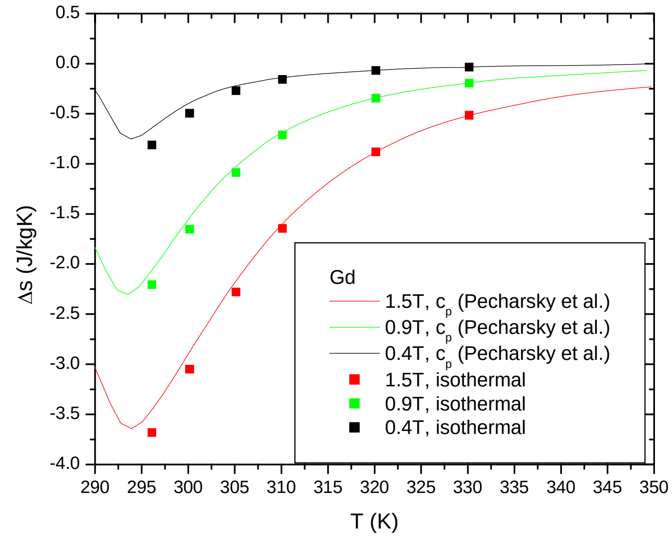


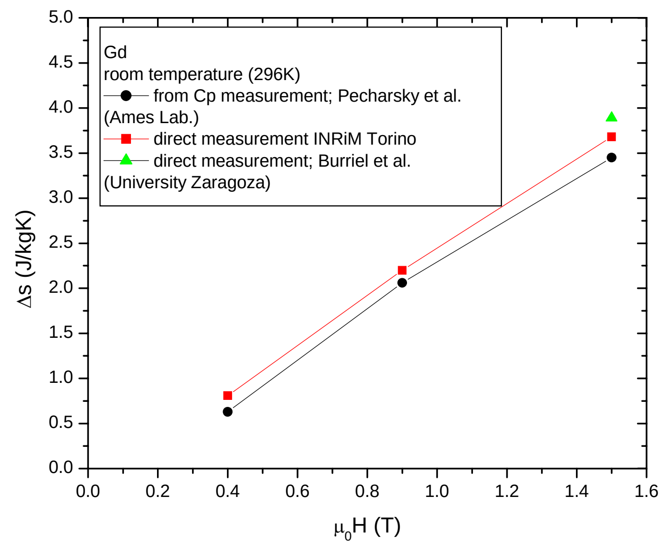
Temperature dependence

temperature dependence of calibration parameters has to be taken into account



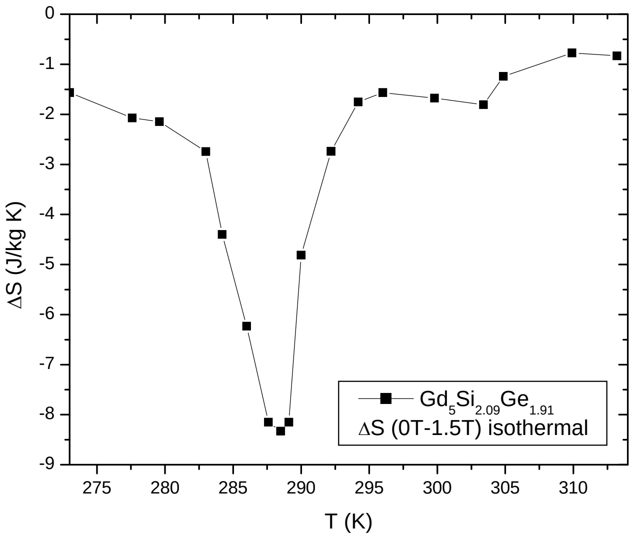




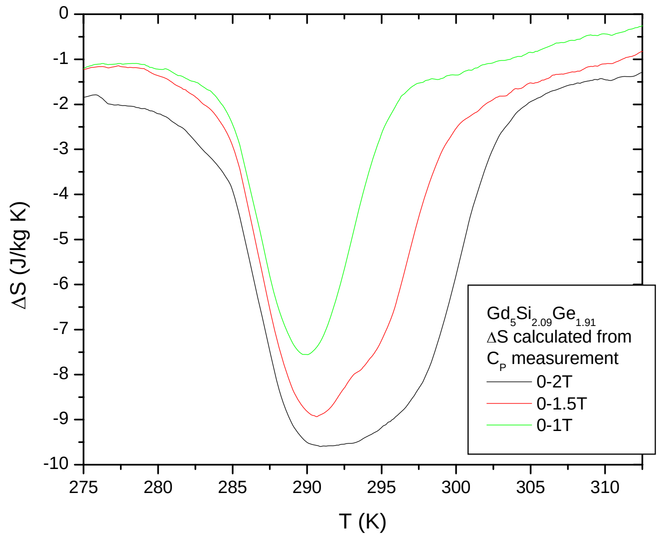


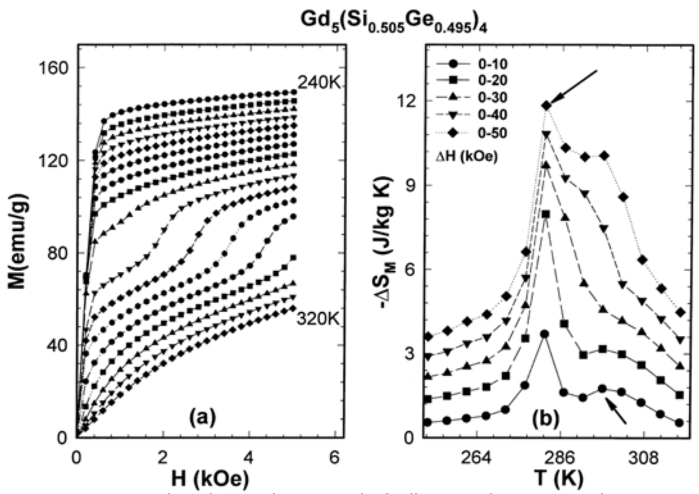
Measurements of $Gd_5Si_{2.09}Ge_{1.91}$

direct entropy measurement

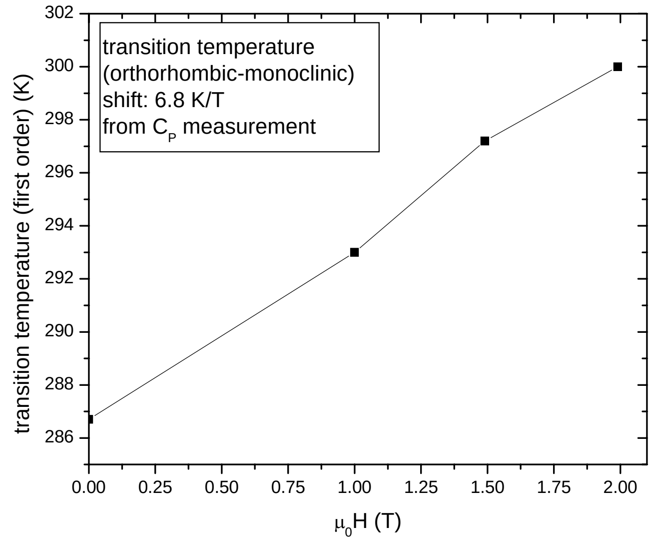


measurement of heat capacity

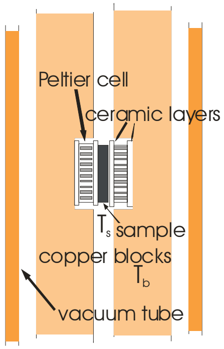




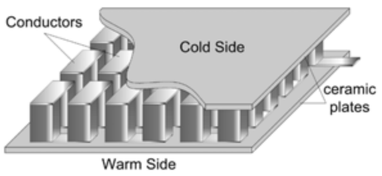
A.O.Pecharsky et al., Journal of Alloys and Compounds, 2002



Conclusion



simple setup



Peltier cells

accurate calibration

actuator and sensor

test measurement of Gd showed good results

direct entropy and C_P measurement of GdSiGe: differences have to be analyzed

further developments: fields up to 7T, cryostat

adaptation of setup for ΔT measurement

direct measurement of entropy change

measurements of magnetocaloric materials and magnetic materials with hysteresis