Calorimetric investigation of the magnetocaloric effect in $Ni_{45}Co_{5}Mn_{37.5}In_{12.5}$

F. Guillou,[1] P. Courtois,[2] L. Porcar,[3] P. Plaindoux,[3] D. Bourgault,[3] and V. Hardy[1]

[1]Laboratoire CRISMAT, Caen [2] Institut Laue Langevin, Grenoble [3] Institut Néel, Grenoble

Ni-Co-Mn-In Heusler alloys

Martensite	Austenite	Austenite
(«nonmagnetic »)	(Ferro)	(Para)

$C_B(T)$ measurements around a broad First Order Transition by using a relaxation method

Fundings

Centre National de la Recherche Scientifique

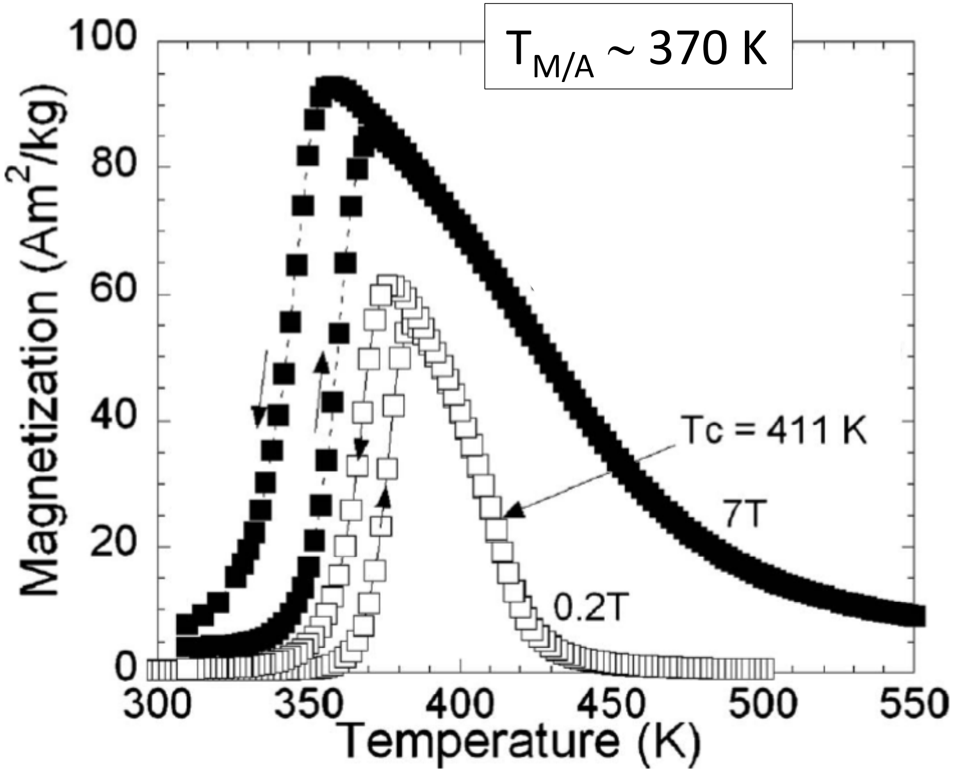
Agence Nationale de la Recherche (Project « MAGCOOL »)

$Ni_{45}Co_5Mn_{37.5}In_{12.5}$ single crystal

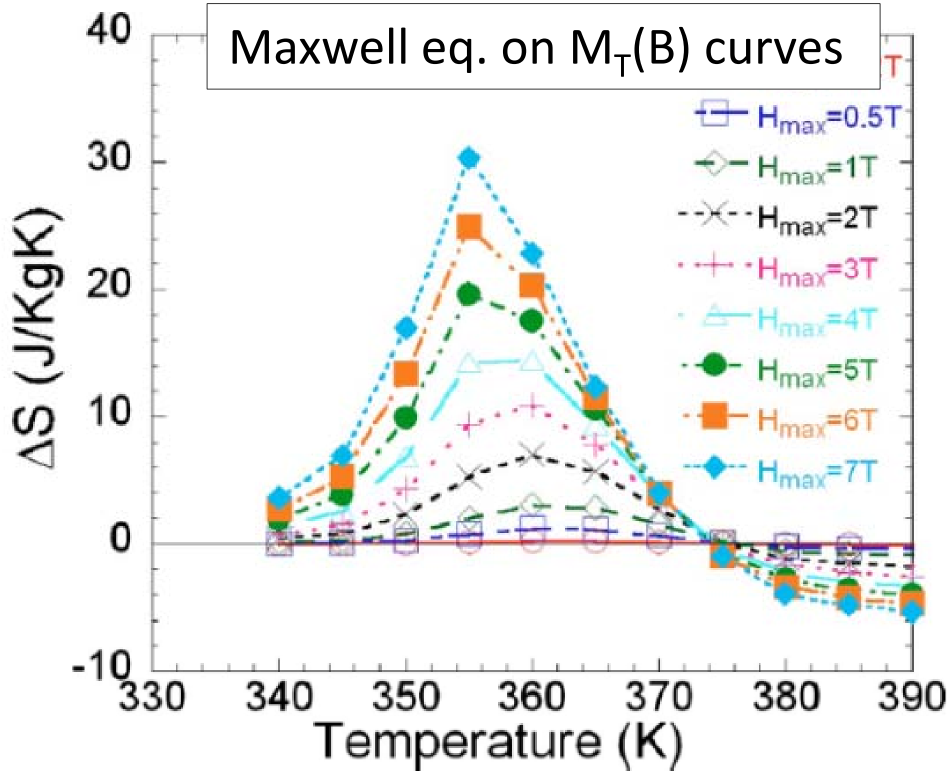
FIRST STUDY

APL 96, 132501 (2010), Bourgault *et al.* , Institut Néel & Institut Laue Langevin & CRETA, Grenoble

$T_{M/A}$ ~ 370 K



Maxwell eq. on $M_T(B)$ curves

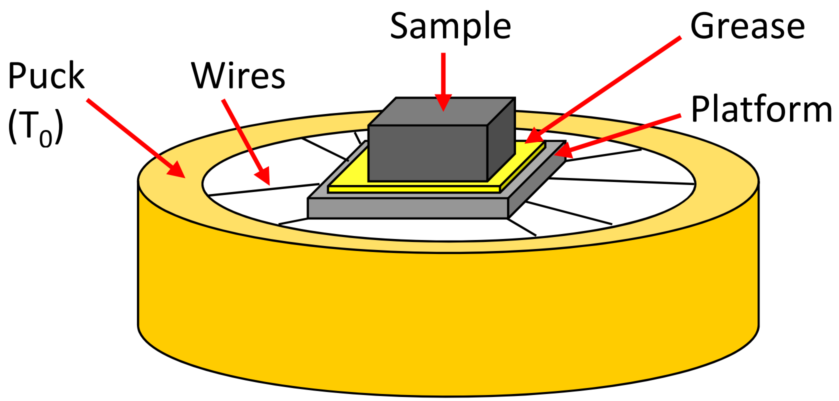


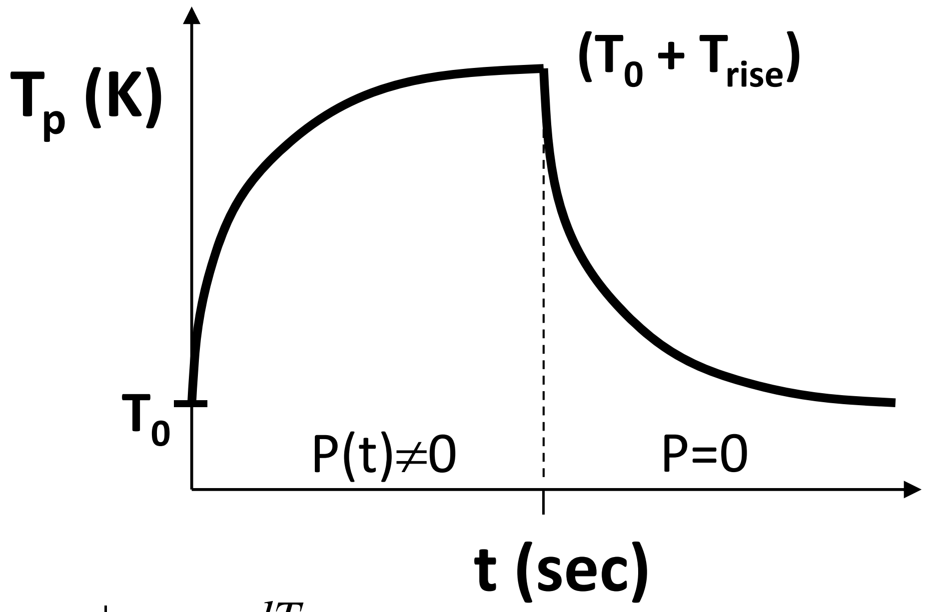
PRESENT STUDY

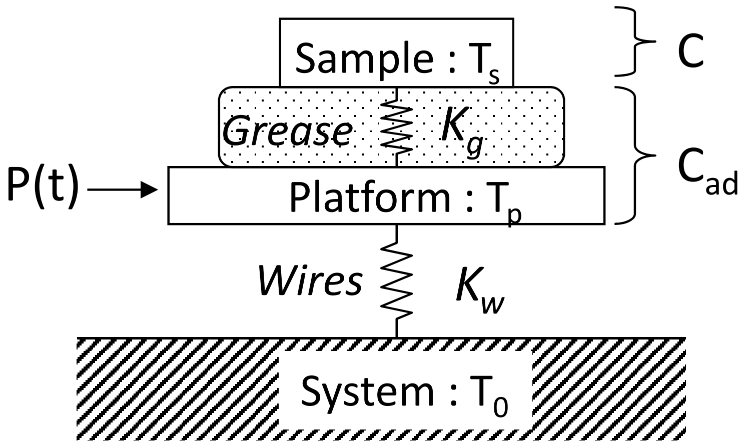
MCE from the calorimetric method : $C_0(T)$ & $C_B(T)$ → $S_0(T)$ & $S_B(T)$

- ► comparison to the magnetic method
- ► determination of $\Delta T_{ad}(T)$
- ► relationship between ΔS_{max} (MCE) and ΔS_{tr} (Jump at the Transition)

$C_B(T)$ from a relaxation technique (PPMS , Quantum Design ®)







2 τ model

$$0 = C\frac{dT_s}{dt} + K_g(T_s - T_p)$$

$$P = C_{ad}\frac{dT_p}{dt} + K_w(T_p - T_0) + K_g(T_p - T_s)$$

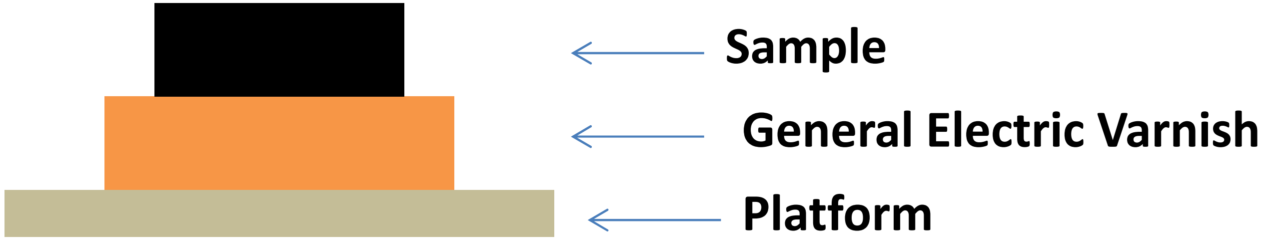
Fitting → $< C >$ over $[T_0 , T_0 + T_{rise}]$

Problems for Giant MCE around Room Temperature !

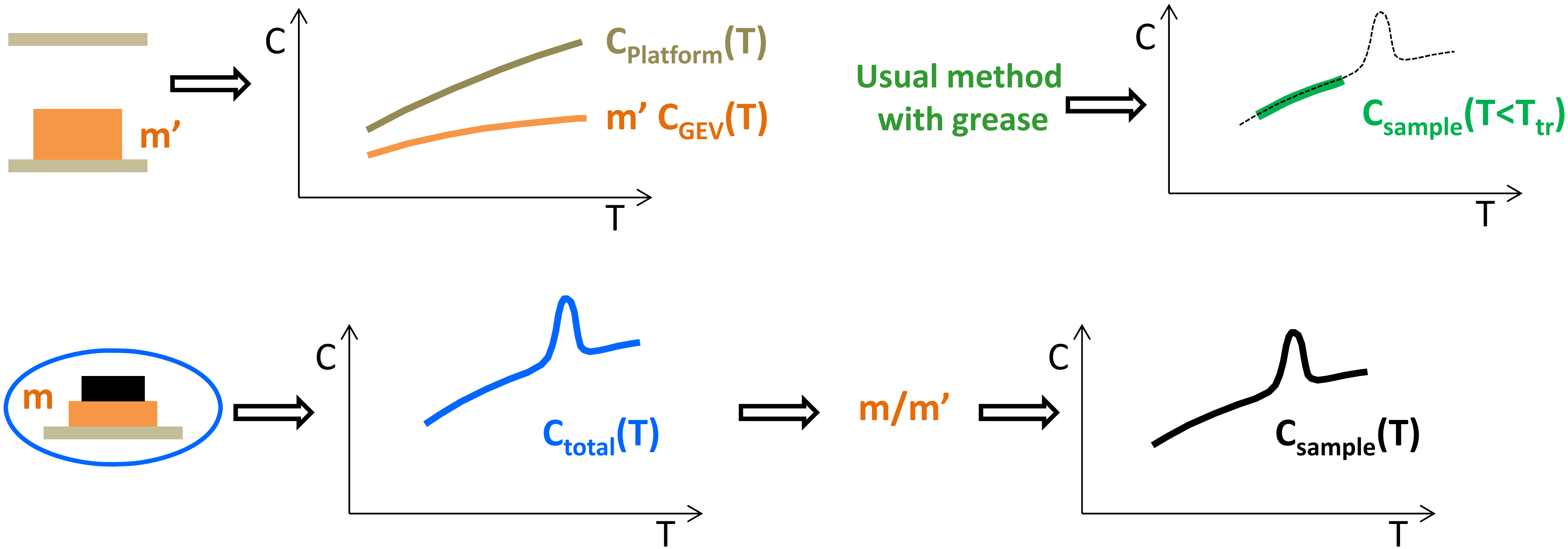
▶Practical : high T+ large M (+ presence of a field gradient) ⇒ Sample leaves the platform

▶Fundamental: for a First Order Transition ⇒ Latent Heat (always) + Hysteresis (most often)

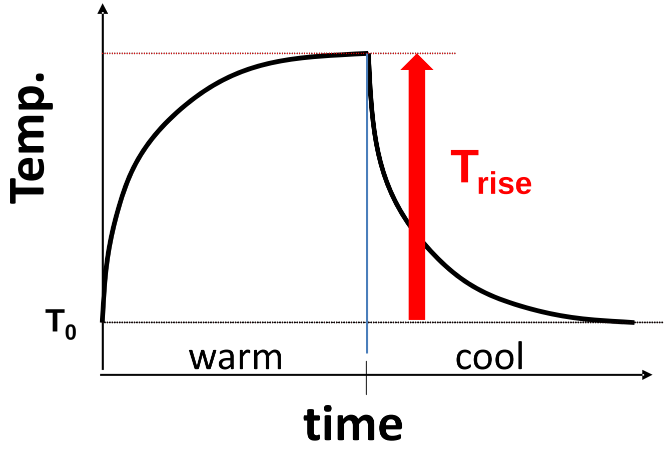
Glue the sample to the platform



… but the subtraction of the addenda (platform+paste) is not as direct as with grease …



Problems with a First Order Transition

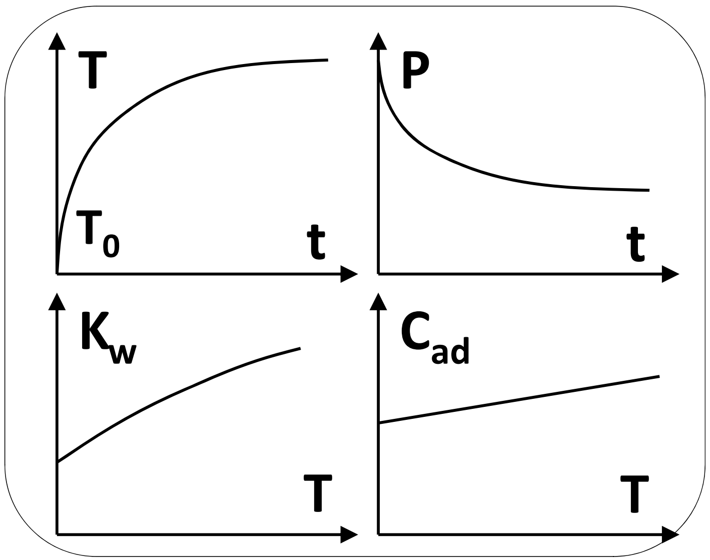


Hysteresis ⇒ Separate « warm » from « cool » ⇒ « warm » only if (hysteresis) >T_{rise}

Separate analysis of each branch ⇒ 1 τ model

$$\begin{bmatrix} 0 = C\frac{dT_s}{dt} + K_g(T_s - T_p) \\ P = C_{ad}\frac{dT_p}{dt} + K_w(T_p - T_0) + K_g(T_p - T_s) \end{bmatrix} \qquad T_s \equiv T_p \equiv T \implies P = (C + C_{ad})\frac{dT}{dt} + K_w(T - T_0)$$

K_w : thermal conductance of the wires
C_{ad} : heat capacity of the addenda

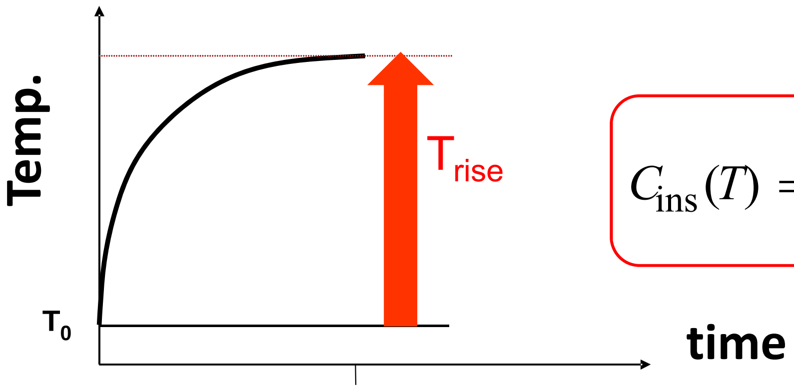


Scanning method

$$\implies C_{ins}(T) = \left\{ \frac{P(T) - K_w(T)\left[T - T_0\right]}{(dT/dt)(T)} \right\} - C_{ad}(T)$$

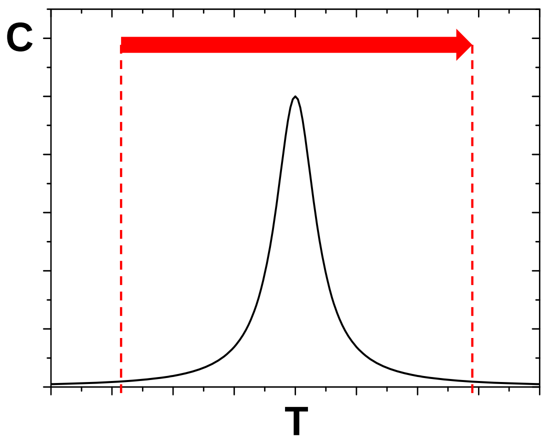
(Typical T-spacing ~ 0.05 K)

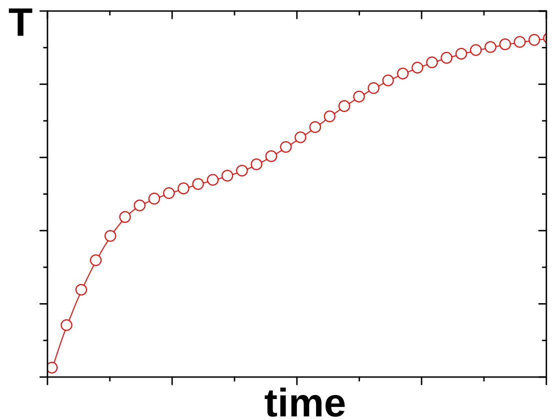
« Heating Pulse »



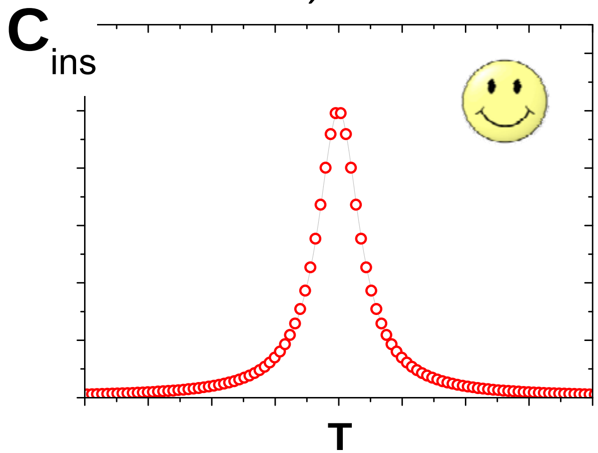
$$C_{ins}(T) = \left\{ \frac{P(T) - K_w(T)\left[T - T_0\right]}{(dT/dt)(T)} \right\} - C_{ad}(T)$$

Sharp FOT ($T_{rise} \sim \delta T_{tr}$) : direct use of $C_{ins}(T)$

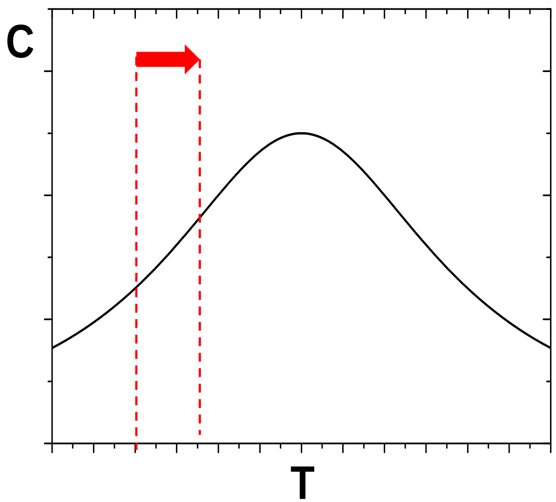




JPCM 21, 075403



Broad FOT ($T_{rise} << \delta T_{tr}$) : problem of « hidden latent heat »



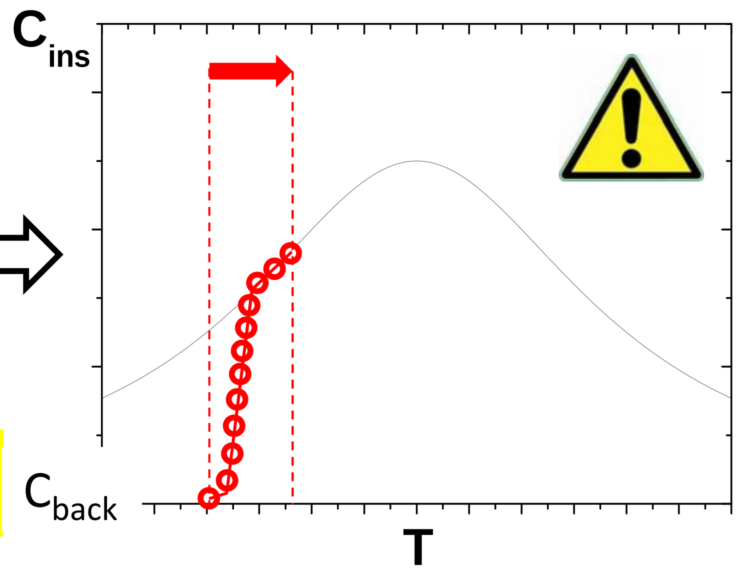
$$C \sim C_{back} + C_{tr}$$

$$\text{with} \int_{\delta T_{tr}} C_{tr}(T)\, dT \approx L$$

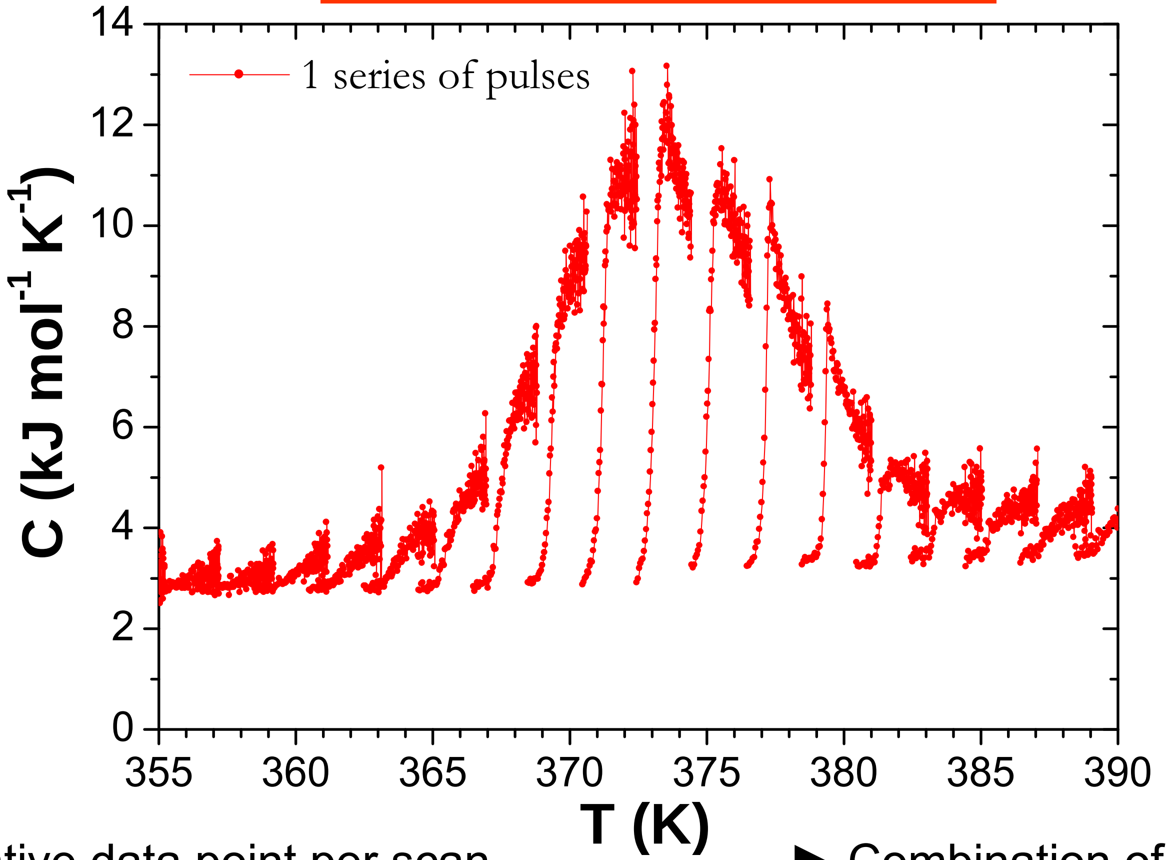
$$C_{tr}(T)\, \delta T \approx L\, \delta x$$

x : fraction of phase transformation

$$C_{ins}\,(t{\sim}0) \sim C_{back} \neq C \;\; !$$



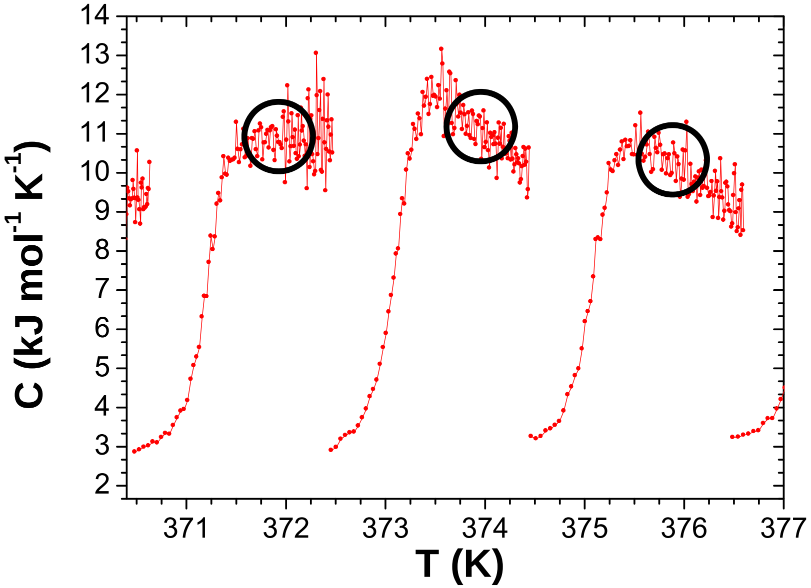
Successive Heating Pulses



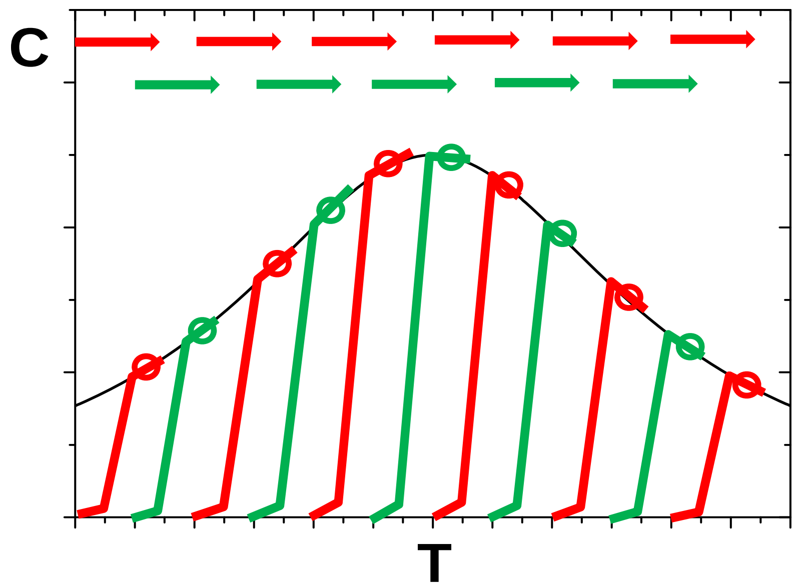
$Ni_{45}Co_5Mn_{37.5}In_{12.5}$

single crystal

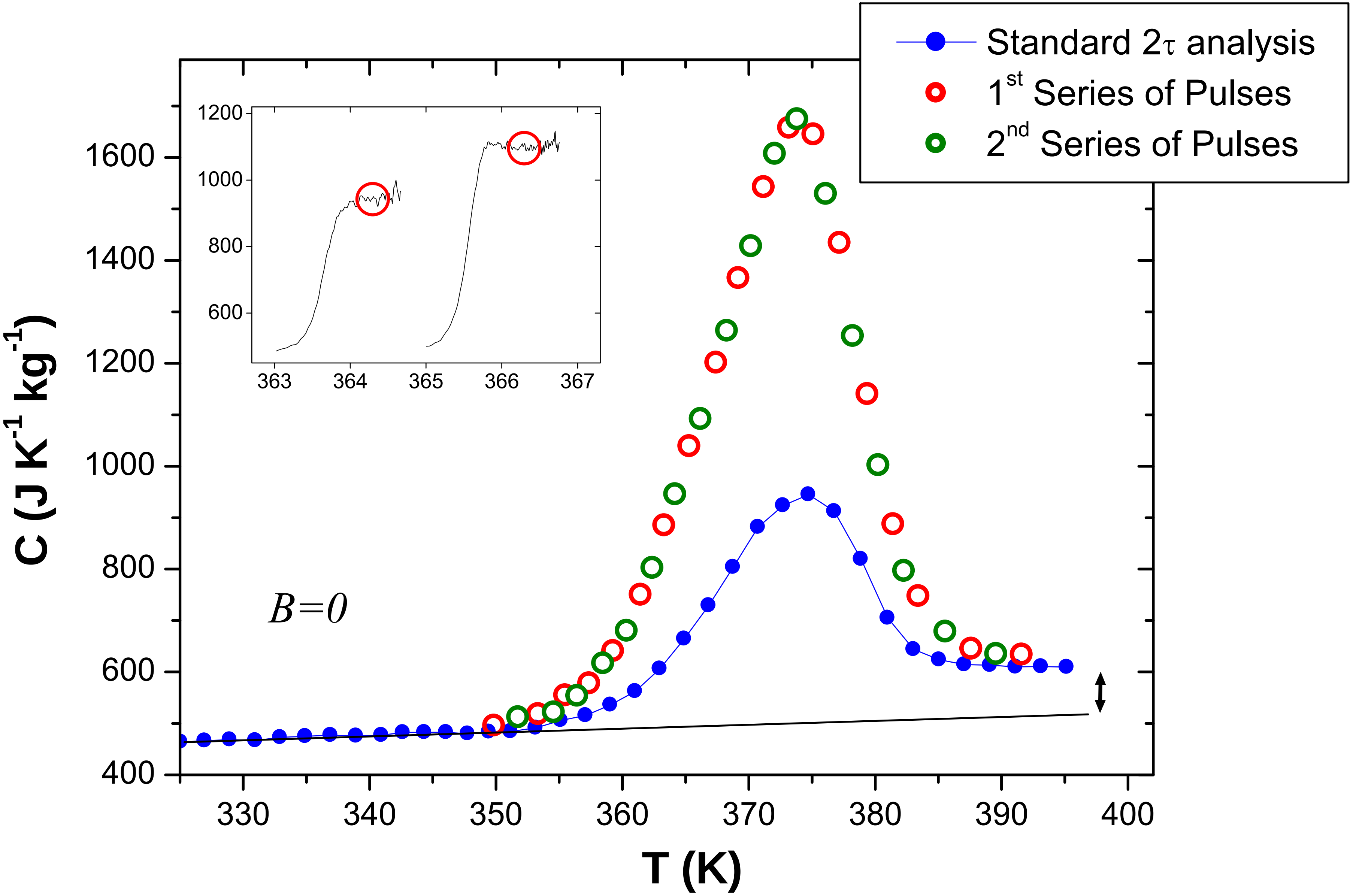
► One representative data point per scan



► Combination of several series of pulses



Comparison « Standard » versus « Heating Pulses



$\Delta C = C_A - C_M > 0$

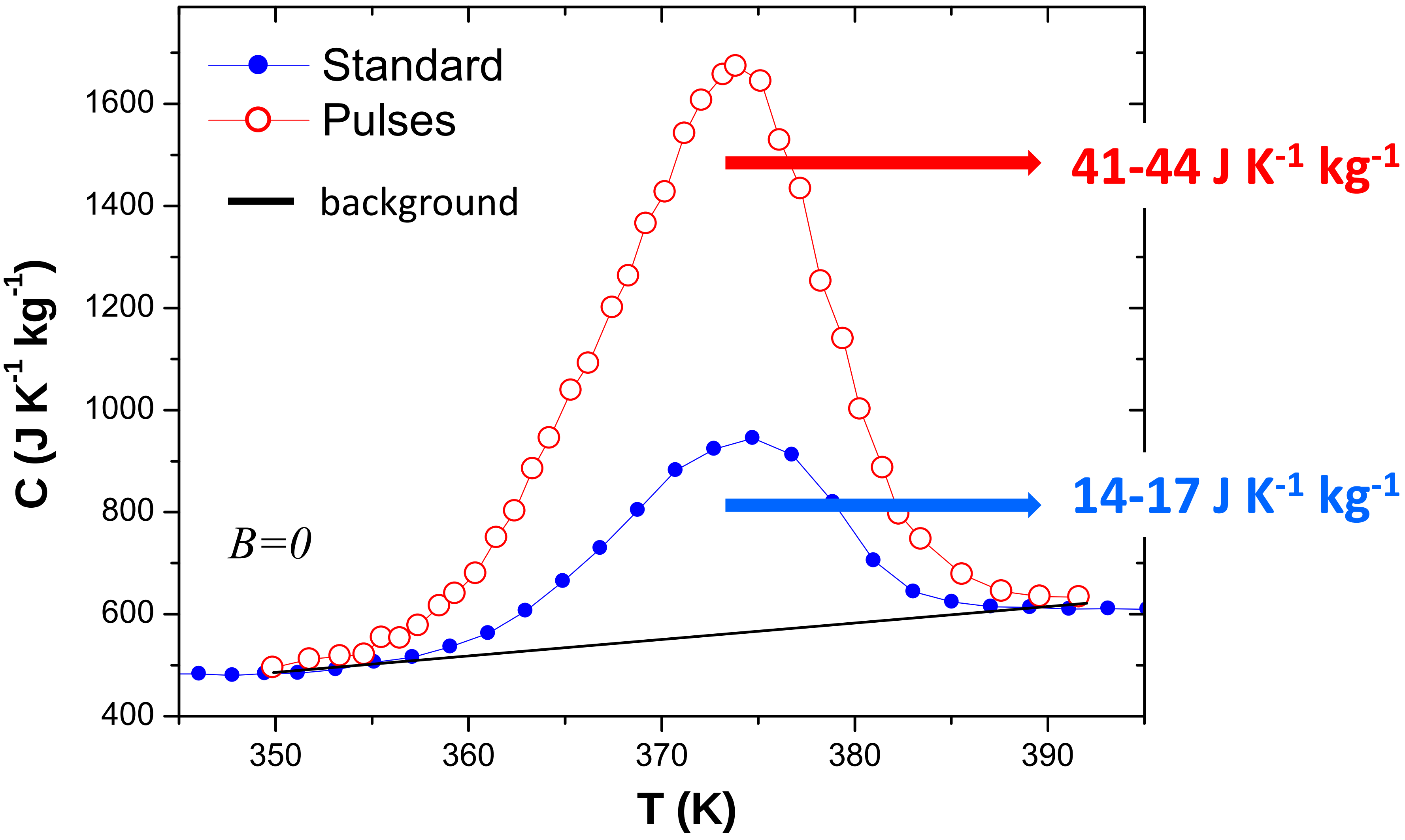
$V_A > V_M$

$\sigma_A > \sigma_M$

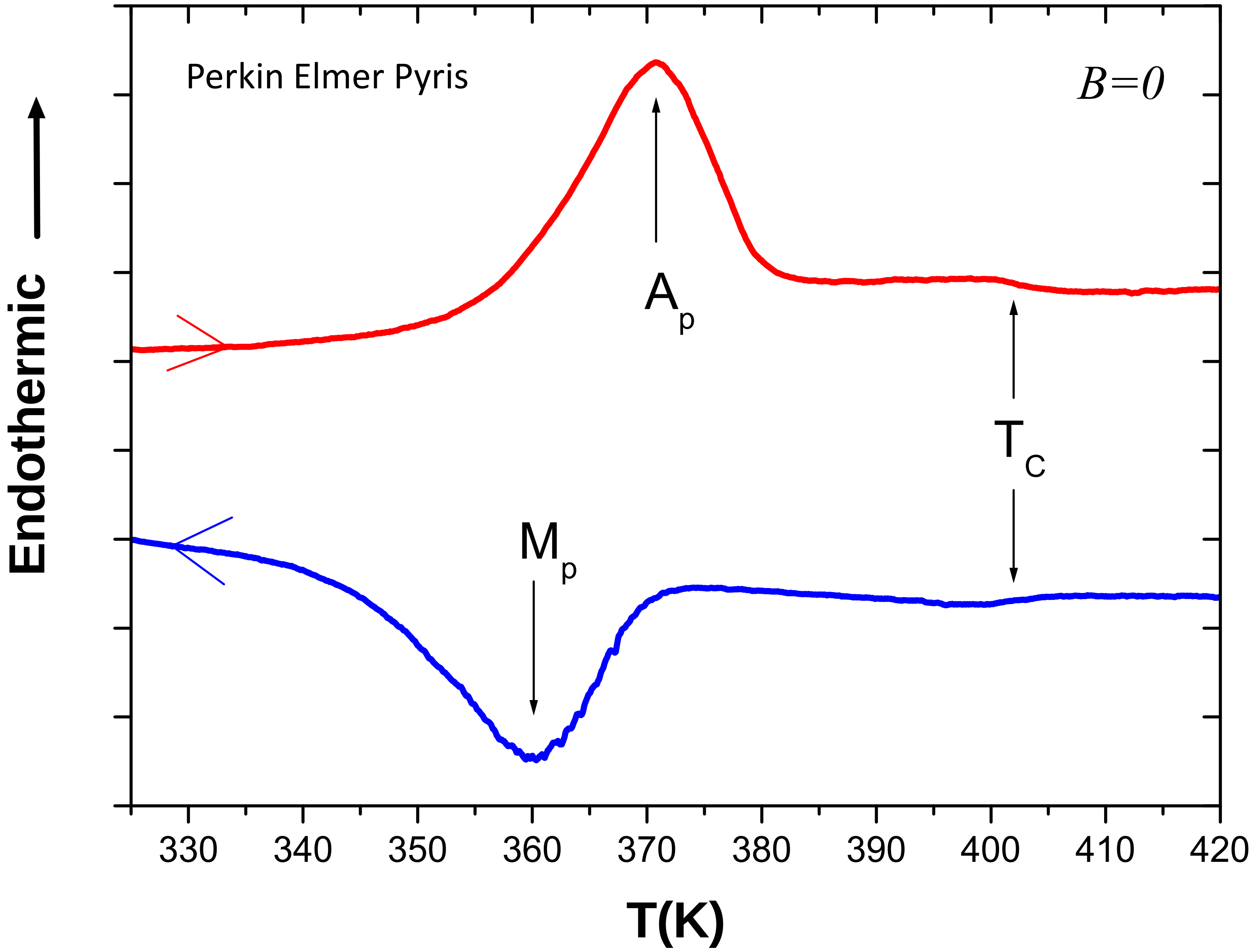
To check the reliability of the « Successive Heating Pulses » method

Evaluate ΔS_{tr} : Entropy Change at the Transition

$$\Delta S_{tr} = \int_{\delta T_{tr}} \left(\frac{C_{tr}}{T}\right) dT = \int_{\delta T_{tr}} \left(\frac{C - C_{back}}{T}\right) dT$$



Differential Scanning Calorimetry



$Ni_{45}Co_5Mn_{37.5}In_{12.5}$

single crystal

$A_p=(A_S+A_F)/2$
$M_p=(M_S+M_F)/2$

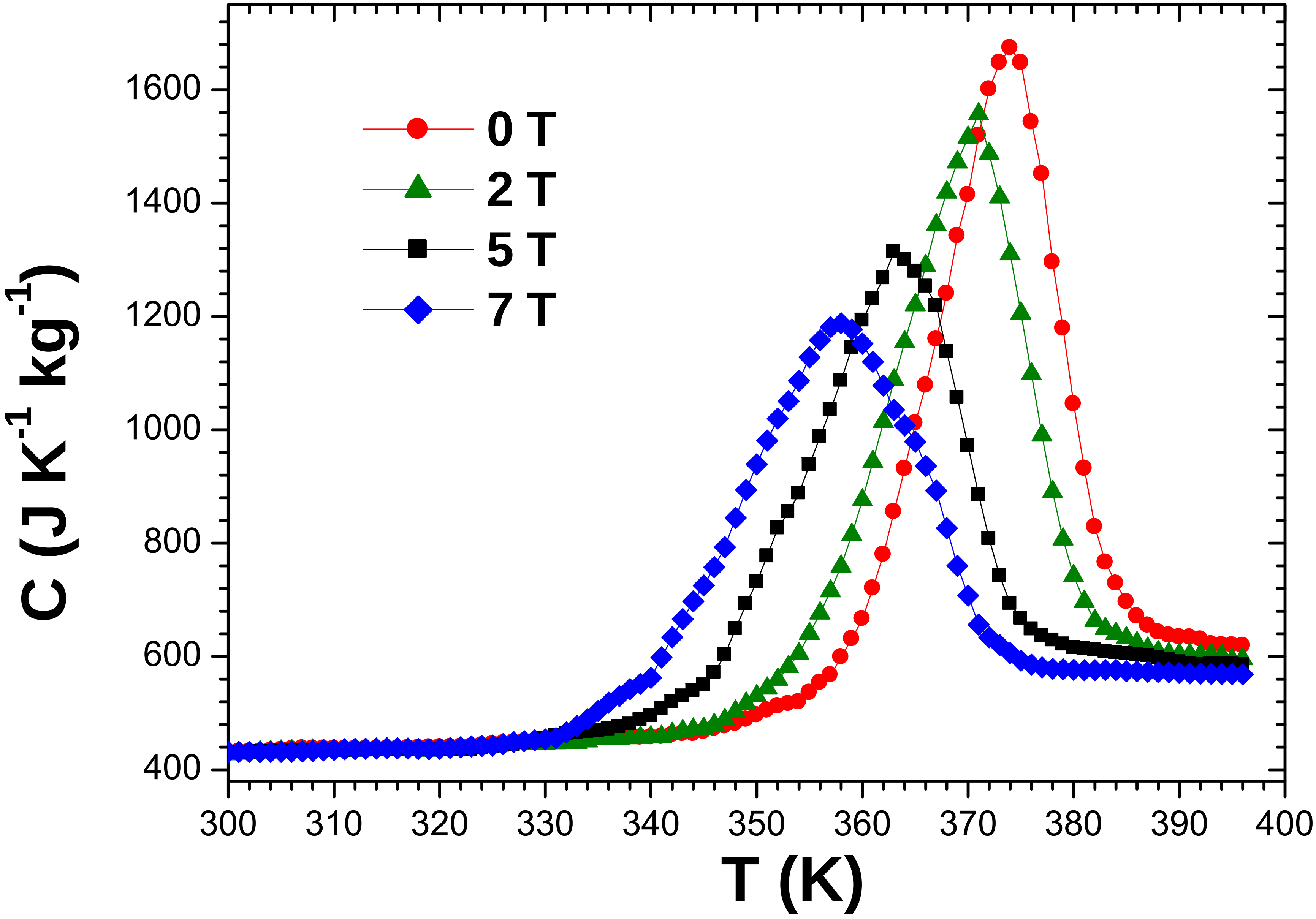
Hysteresis = A_p-M_p ~ 8K

OK with M(T)

< 3 runs @ 5K/min > : **ΔS_{tr} (DSC) ~ 45 J K^{-1} kg^{-1}**

⇒ **Well consistent with the « Heating Pulses » method (41-44 J K^{-1} kg^{-1})**

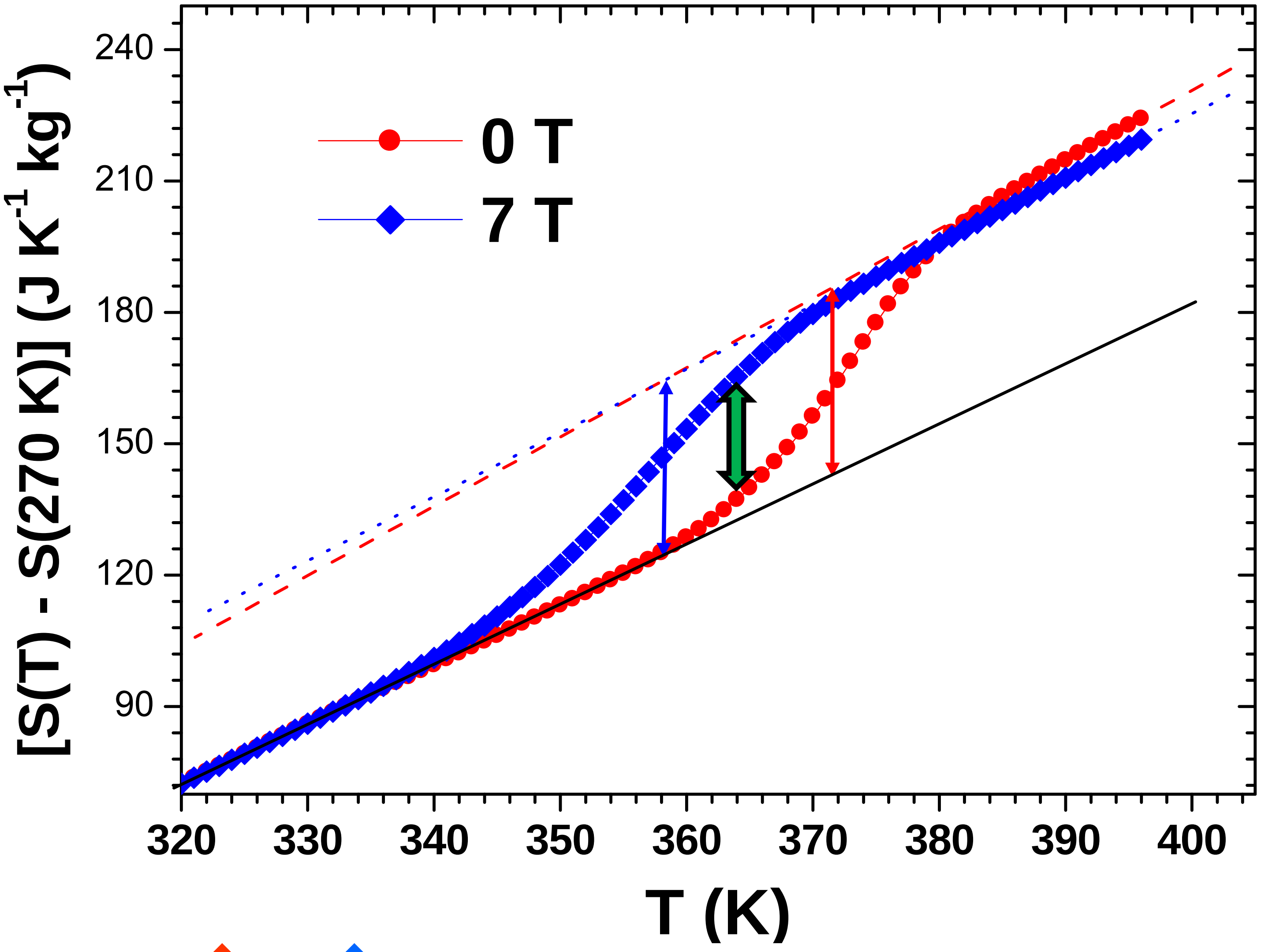
Field-dependent Heat Capacity



dT_{peak}/dB (heat capacity) = -2.35 K/T ~ dA_p/dB (magnetization)= - 2.28 K/T

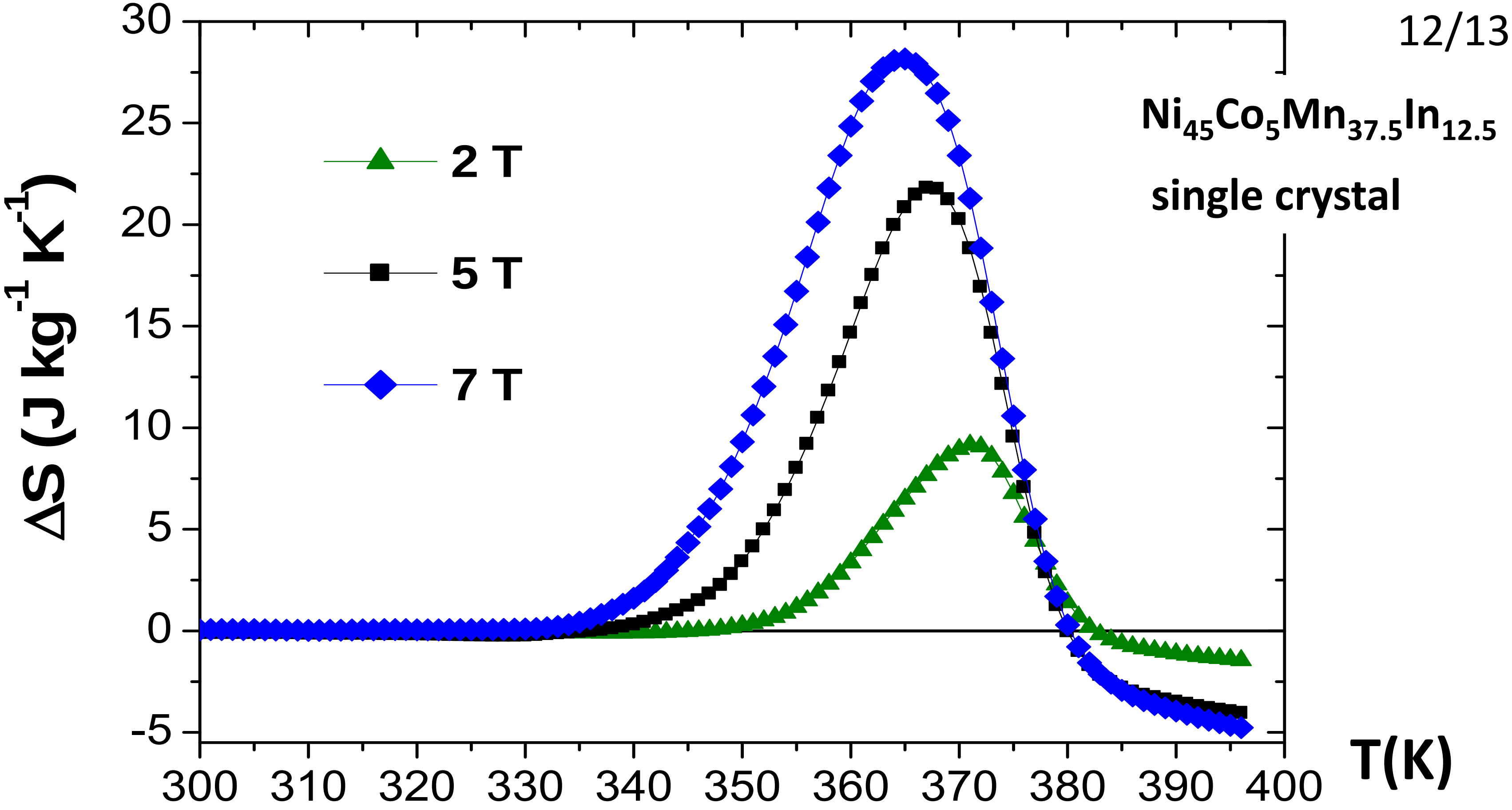
Field-dependent Entropy

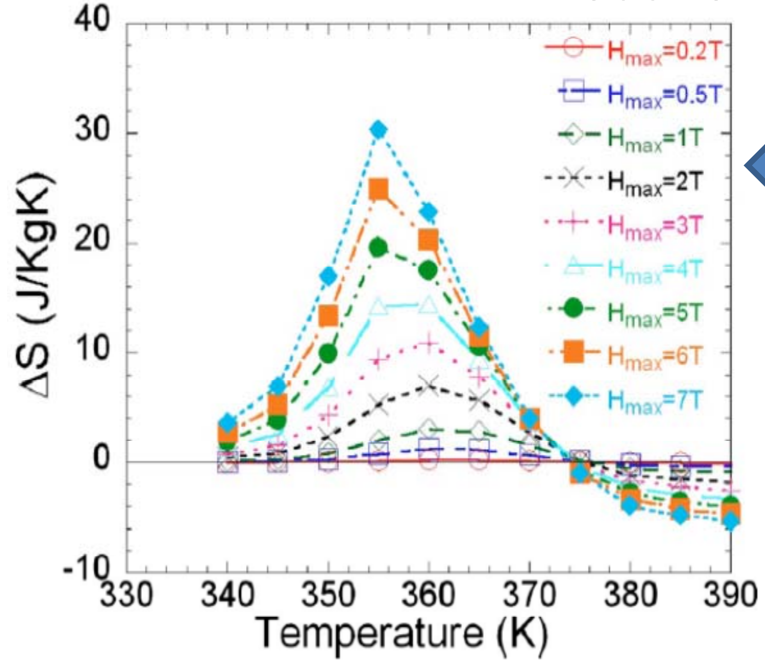
Maxwell M(B,T) : ΔS (270K) = 0 → $S(T)-S(270K)=\int_{270K}^{T}\left(C/T\right)dT$



ΔS_{tr} : ↕ ~ ↕ > ΔS_{max} : ↕ $\left(\text{as long as } B\left|\frac{dT_p}{dB}\right| < \delta T_{tr}\right)$

Isothermal Entropy Change

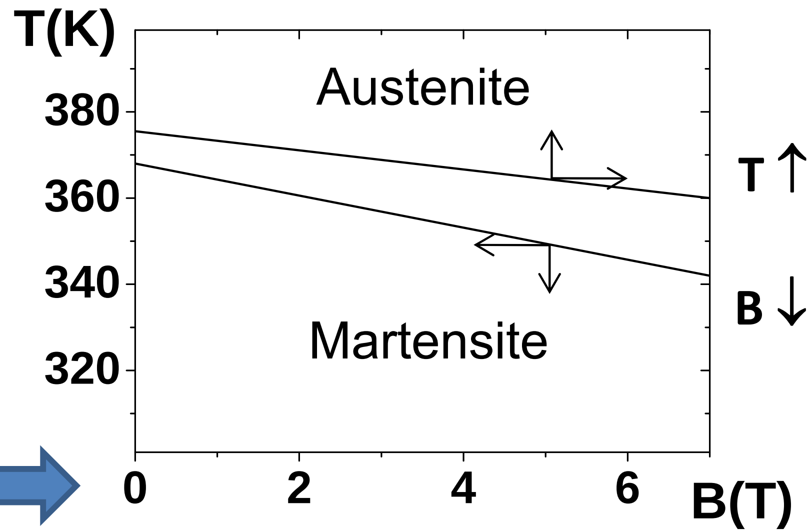




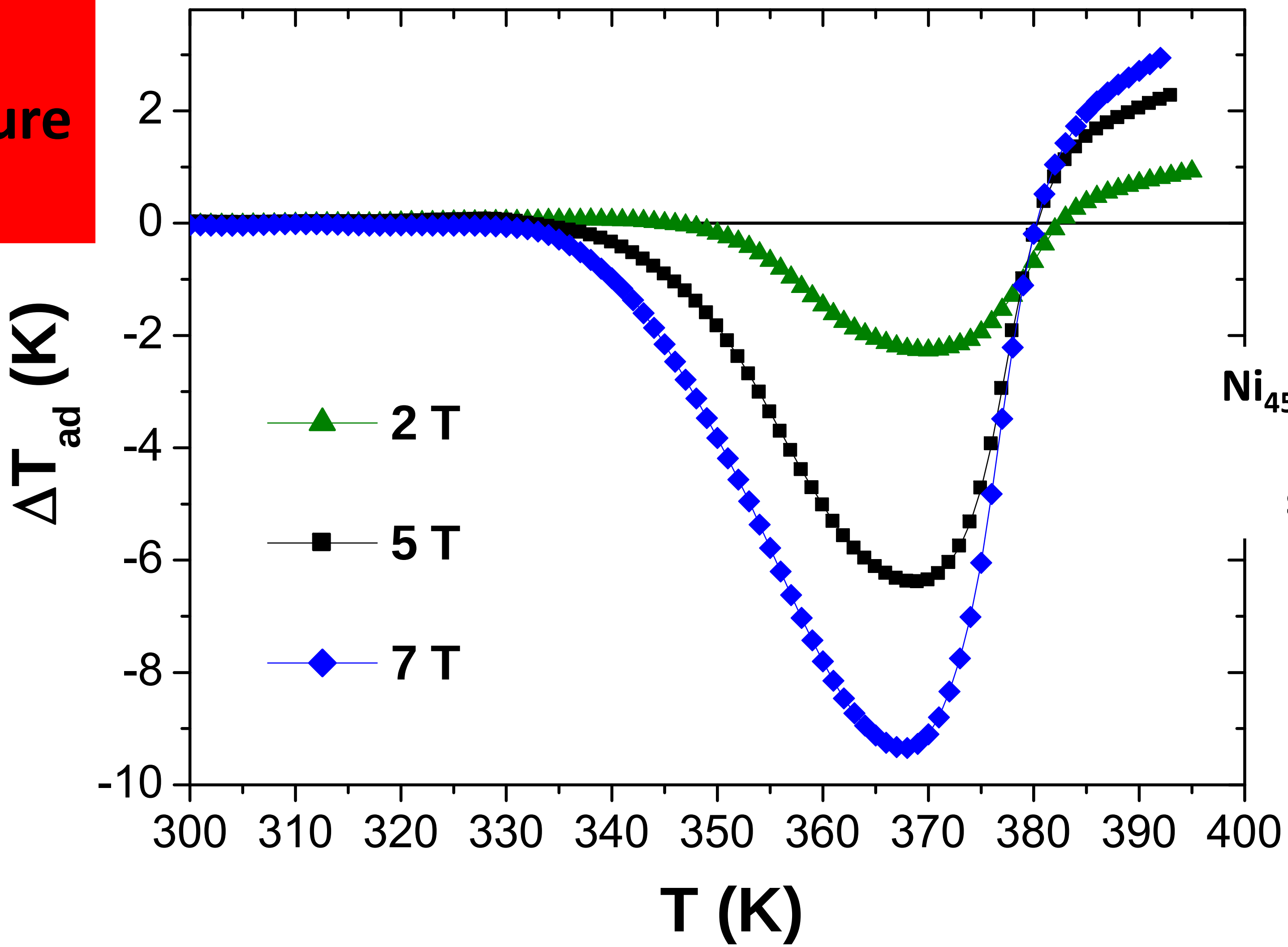
Shifted from the magnetic data ?

Maxwell eq. from $M_T(B\downarrow)$ data

Hysteresis effect !



Adiabatic Temperature Change

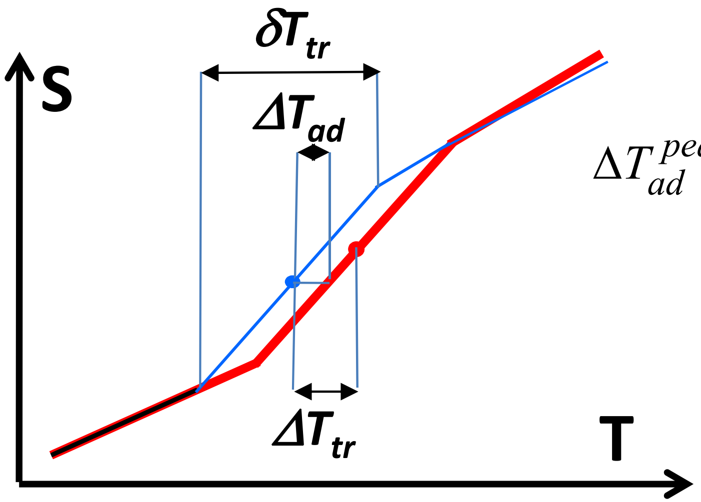


$Ni_{45}Co_5Mn_{37.5}In_{12.5}$

single crystal

$$\Delta T_{ad}^{peak} \neq \Delta T_{tr} = \left(\frac{dT_{tr}}{dB} \right) \times \Delta B$$

$$[\Delta T_{tr}(5T) \approx -2.3 \times 5 \approx -11.5 \text{ K}]$$



$$\Delta T_{ad}^{peak} \approx \Delta T_{tr} \left\{ 1 - \frac{\delta T_{tr}}{(T_{tr} / C_{back})\, \Delta S_{tr} + \delta T_{tr}} \right\}$$

δT_{tr} : width of the transition

Calorimetric investigation of the MCE in $Ni_{45}Co_5Mn_{37.5}In_{12.5}$

F. Guillou,[1] P. Courtois,[2] L. Porcar,[3] P. Plaindoux,[3] D. Bourgault,[3] and V. Hardy[1]

[1]Laboratoire CRISMAT, Caen
[2] Institut Laue Langevin, Grenoble
[3] Institut Néel, Grenoble

- « Successive Heating Pulses » is a method suitable to investigate $C_B(T)$ around broad FOT's
- Good agreement about ΔS_{max} between the Maxwell eq. and the $C_B(T)$ method
- Width of the transition δT_{tr} $\Rightarrow$ $\Delta S_{max} < \Delta S_{tr}$ & $\Delta T_{max} < |dT_{tr}/dB| \times \Delta B$
- However, good performances in terms of quantities such as $RC \approx \int \Delta S(T)\, dT$