Derivation of the heat capacity anomaly at a first-order transition by using a semi-adiabatic relaxation technique

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- Large MC effects (« colossal ») ↔ magnetostructural transition ↔ FOT

  It is the case for Gd5(Si,Ge)$_4$, La(Fe,Si)$_{13}$, MnAs etc…

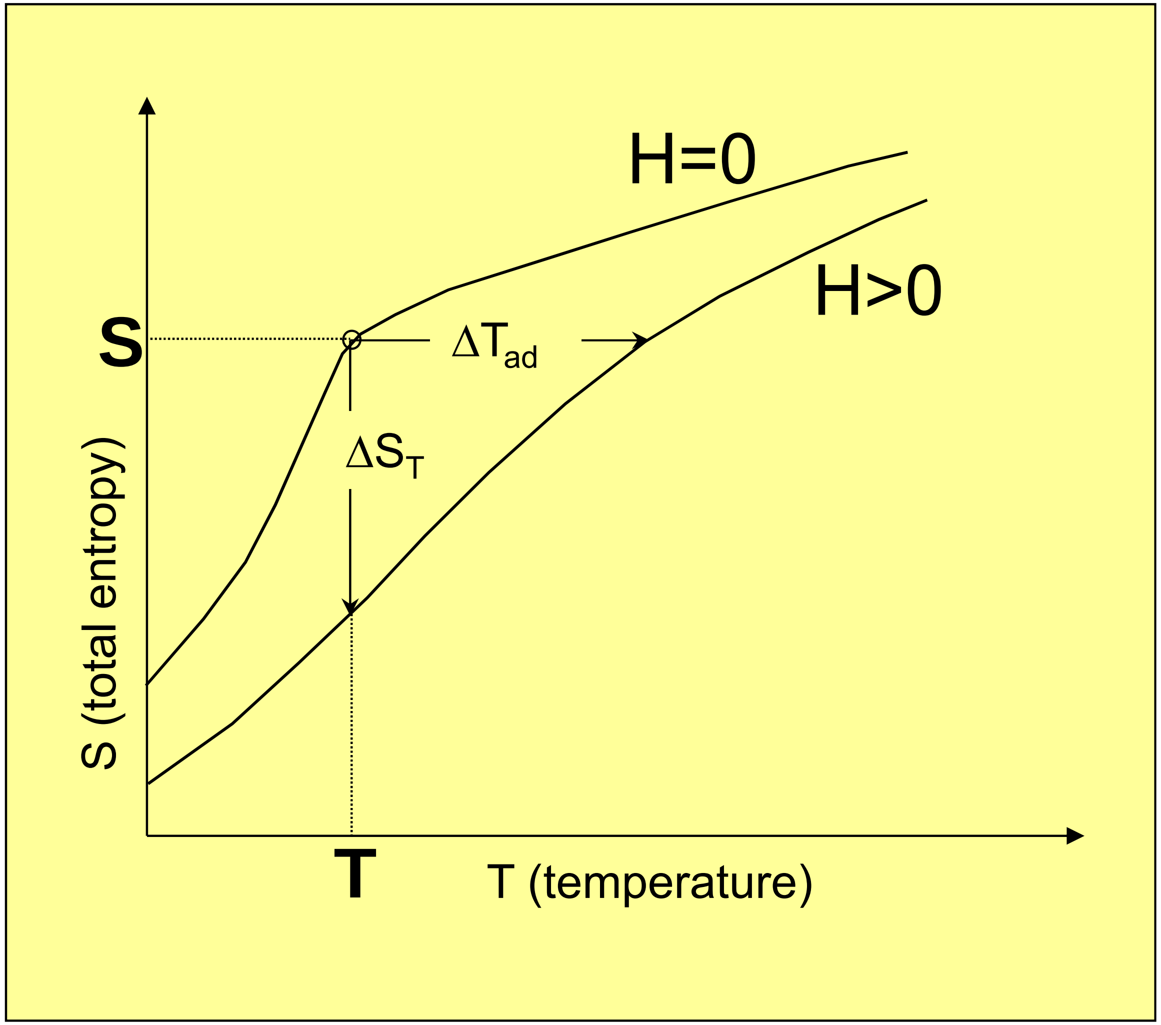
- $C_H(T)$ curves | can be used for ΔS_T / are necessary for ΔT_{ad}

  ⇒ **Reliable way to record the FOT peak on C(T) is required**

- A lot of the C(T) data nowadays are recorded by means of « semi-adiabatic » methods (in particular the PPMS from QD)

- Clues of possible problems when studying a new series of oxides having large MC effects : spinel vanadates

Magnetocaloric effect : MCE



ΔS_T : isothermal entropy change

ΔT_{ad} : adiabatic temperature change

MCE characterization

ΔS_T

Heat Capacity

$$C_H(T) \Rightarrow S_H(T) = \int_0^T \frac{C_H(T)}{T} dT$$

puis $\Delta S_T(T; 0 \to H) = [S_H(T) - S_0(T)]_T$

Magnetization

$\underline{\text{SOT}}$: *Maxwell*

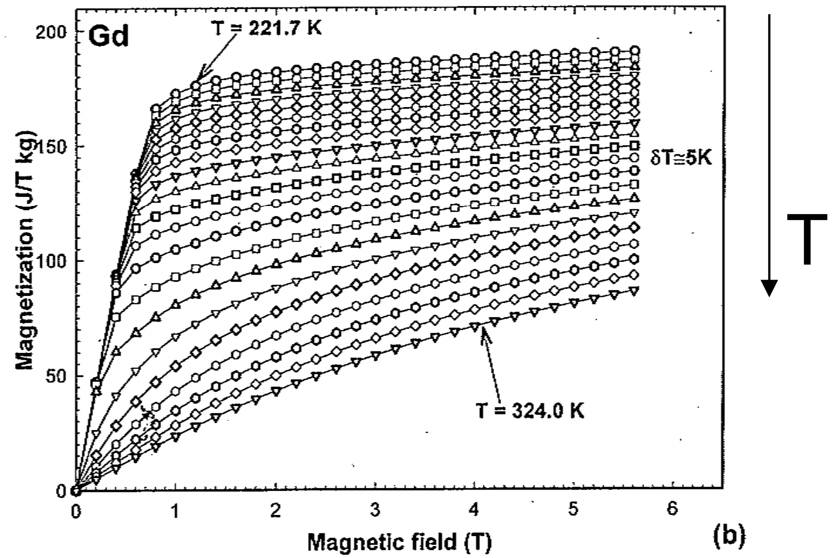
$$\Delta S_T(T; 0 \to H) = \mu_0 \int_0^H \left[\frac{\partial M(T,H)}{\partial T} \right]_H dH$$

$\underline{\text{FOT}}$: *Clausius – Clapeyron*

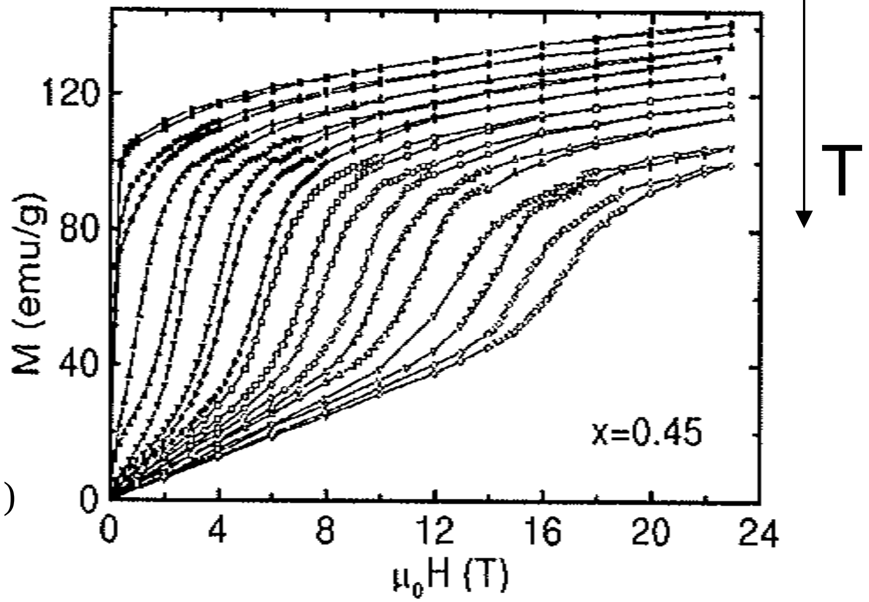
$$\Delta S_T^{\max}(T; 0 \to H) = -\mu_0 \, \Delta M(T) \times \left[\frac{\partial H_t}{\partial T} \right]_T$$

[pour $H > H_t(T)$]

SOT : Gd



FOT : $Gd_5Si_{1.8}Ge_{2.2}$



ΔT_{ad}

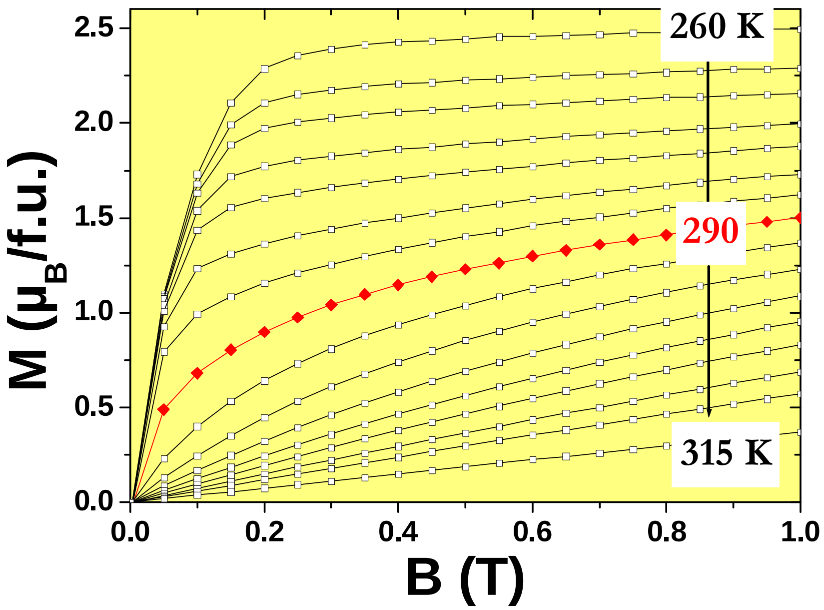
Direct $\Delta T_{ad}(T;0 \to H) = T^*[H] - T[0]$

Heat capacity $\Delta T_{ad}(T;0 \to H) = [T_H(S) - T_0(S)]_{S(T)}$

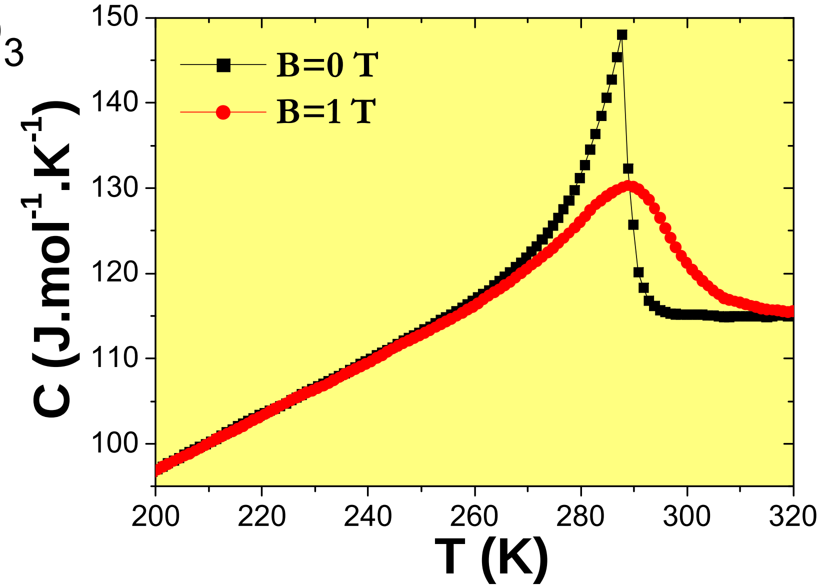
M + C_p $\Delta T_{ad}(T;0 \to H) \approx -\frac{T}{C_0(T)} \Delta S_T(T; 0 \to H)$

No problem in case of a Second Order Transition

$Pr_{0.66}Sr_{0.34}MnO_3$

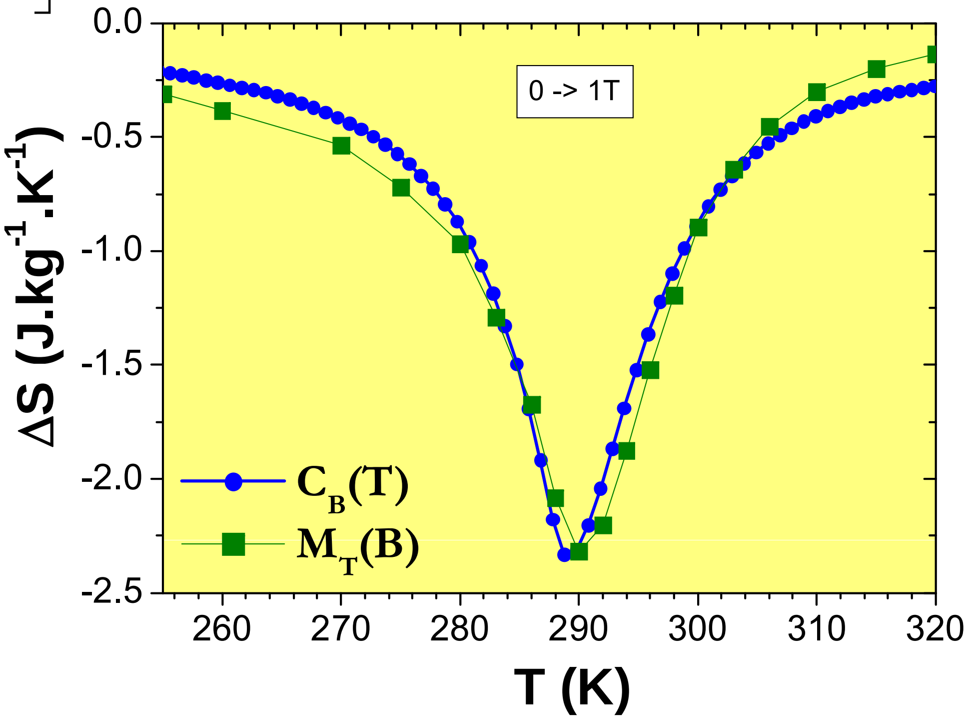


$$\Delta S(T;0\rightarrow B)=\frac{\partial}{\partial T}\left[\int_0^B M_T(B)dB\right]$$

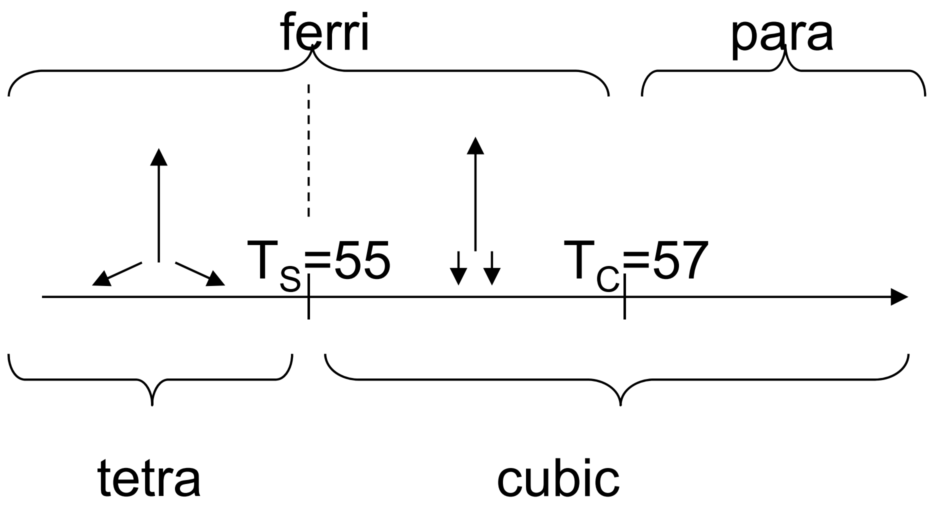


$$S(T,B)=\int_0^T \frac{C(T;B)}{T}dT$$

$$\Delta S(T;0\rightarrow B)=\left[S(T,B)-S(T,0)\right]$$

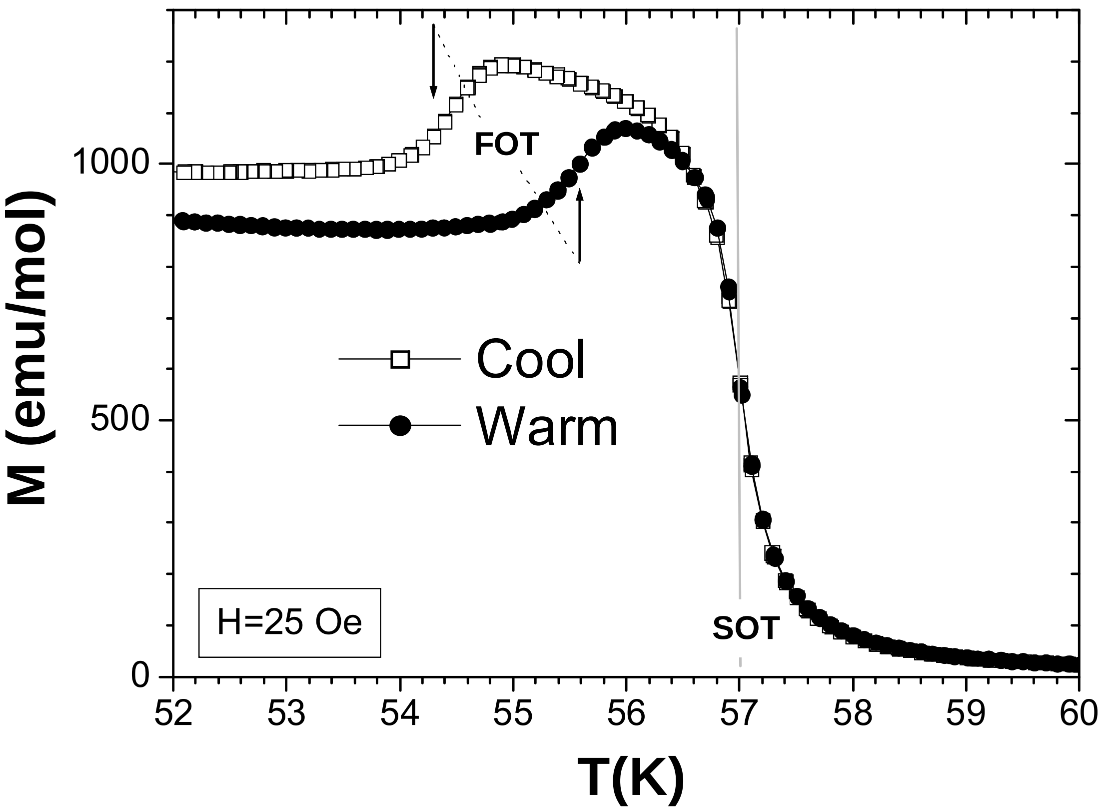


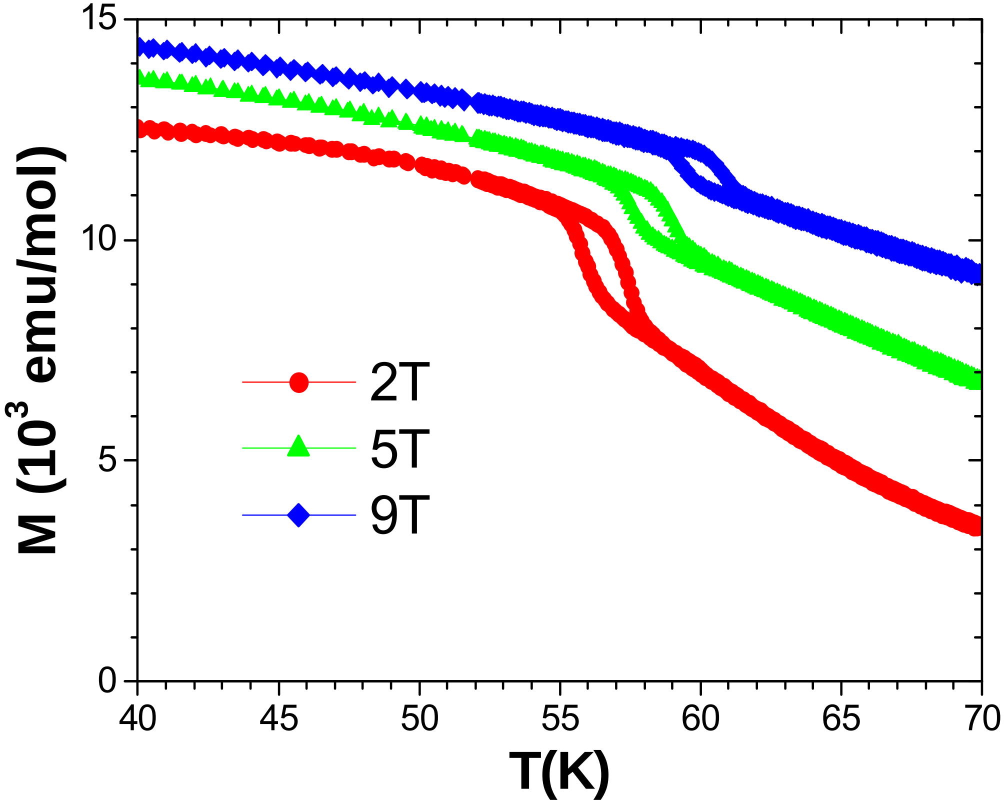
MnV_2O_4



FOT: First Order Transition

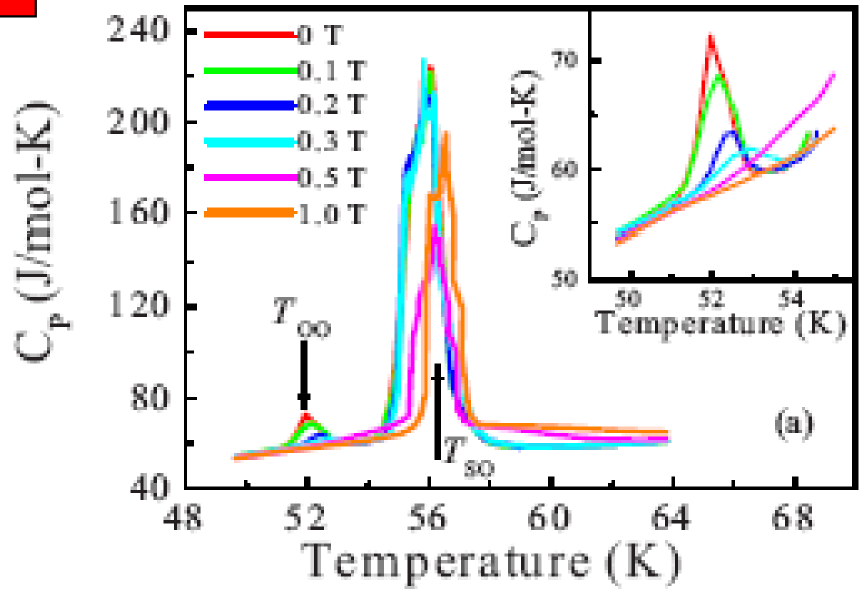
SOT: Second Order Transition





Controversial C(T) curve

- Zhou et al. PRB (2007)

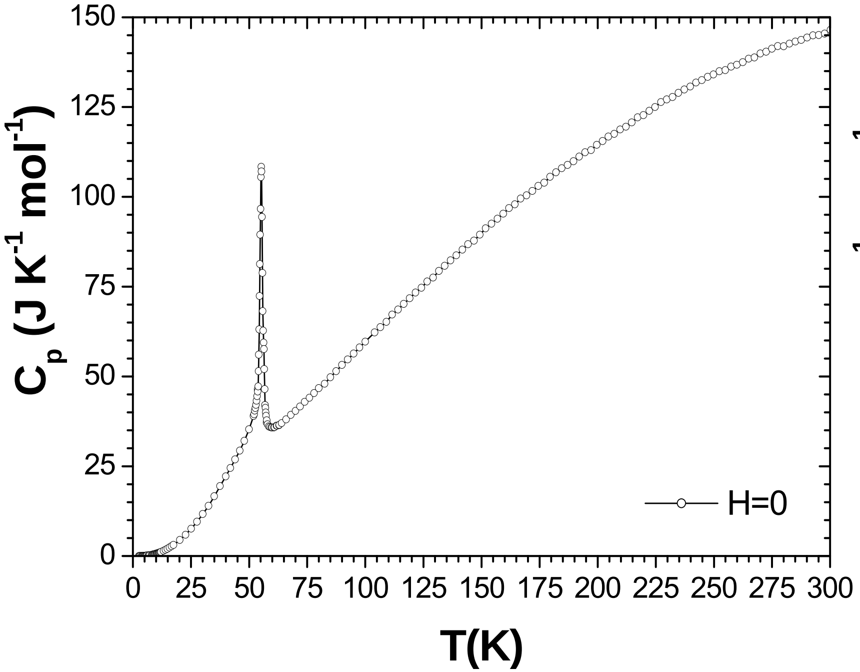


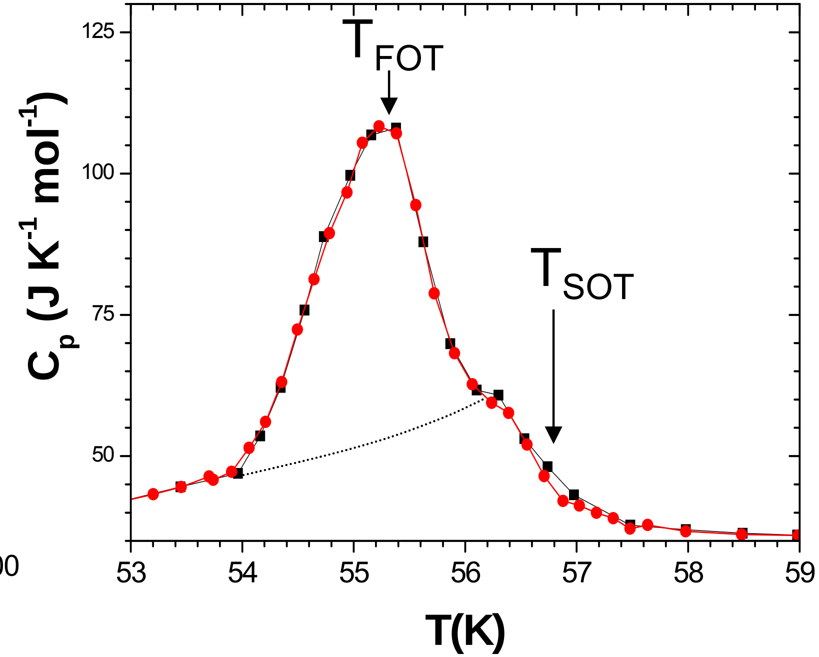
Peak FOT < Peak SOT ?

FOT vanishes in fields ?

PPMS

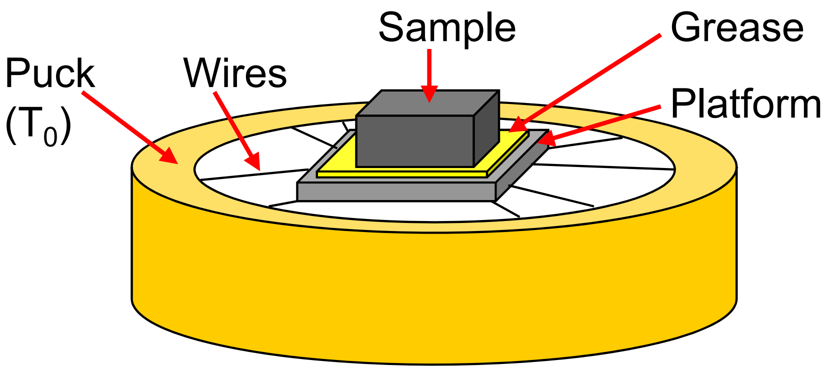
- Caen PRB (2008)

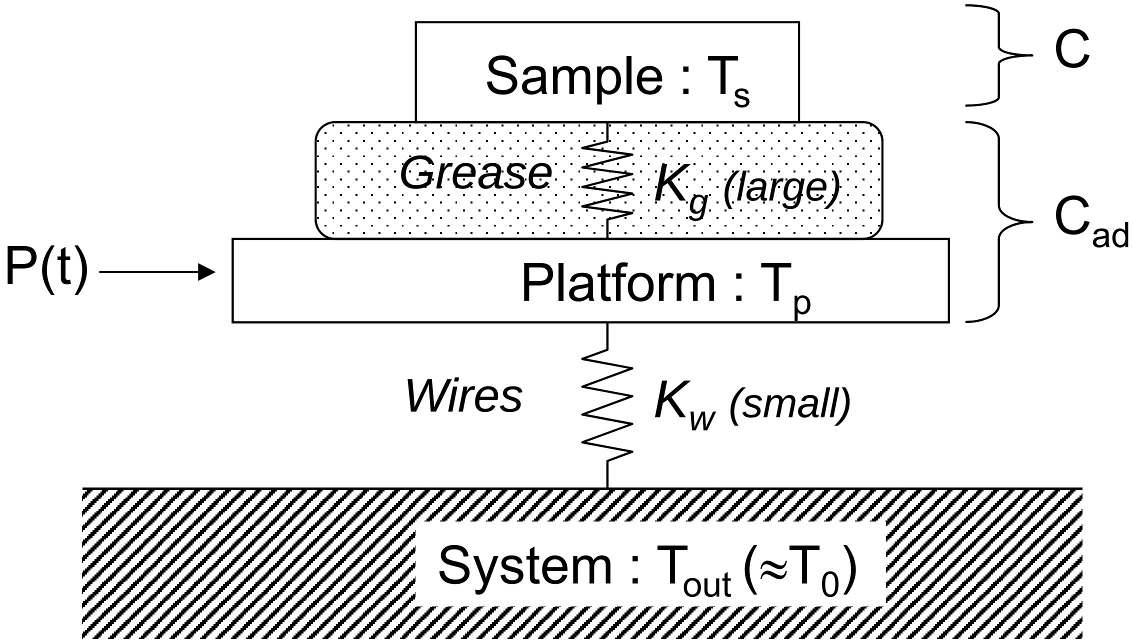


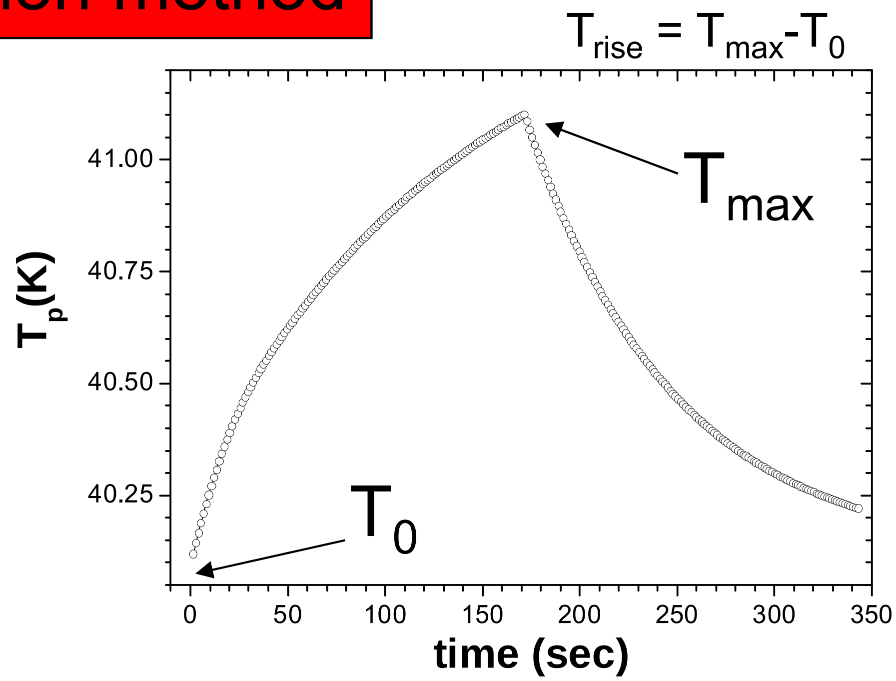


FOT can be problematic owing to their :Steepness / Latent heat / Hysteresis

Semi-adiabatic relaxation method







2 τ model

$$
\begin{cases}
0 = C\dfrac{dT_s}{dt} + K_g(T_s - T_p) \\
P = C_{ad}\dfrac{dT_p}{dt} + K_w(T_p - T_{out}) + K_g(T_p - T_s)
\end{cases}
$$

(1) Addenda (Platform + Grease)
→ $C_{ad}(T)$

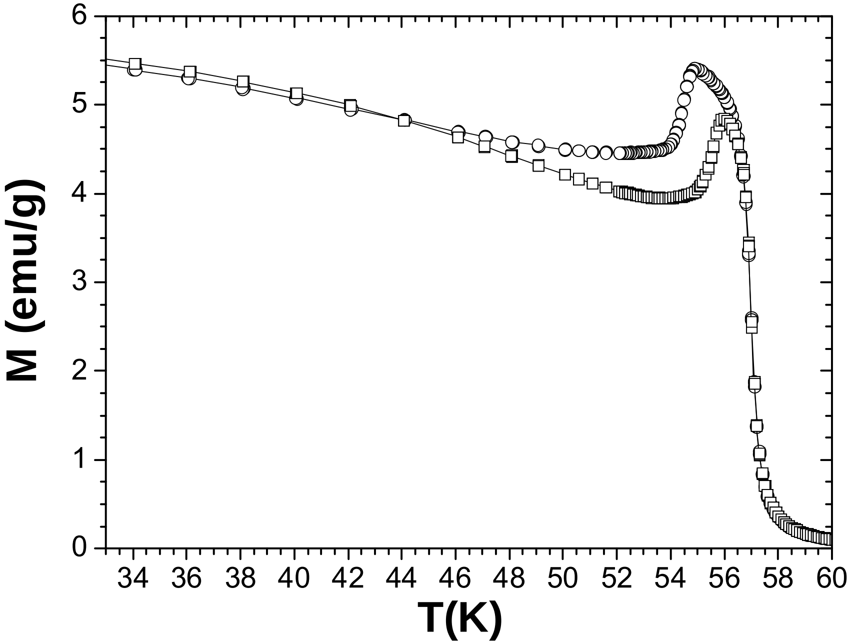
(2) Platform + Grease + Sample
→ 2 τ Fitting $T_p(t)$ & $C_{ad}(T)$
→ C(T)

CAUTION !

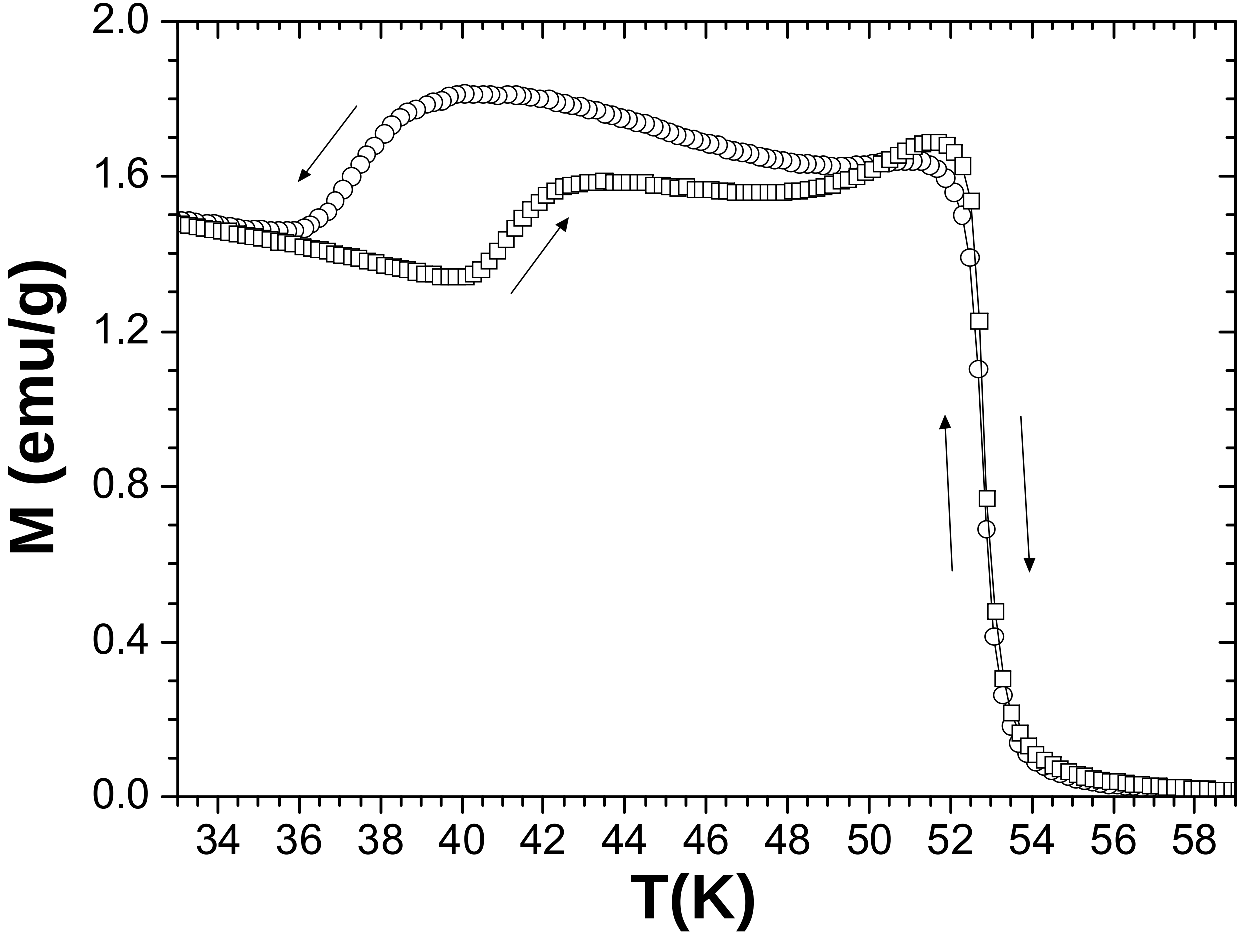
* analysis of both branches together
* averaging over T_{rise}

In order to get FOT and SOT clearly separated from each other …

MnV_2O_4

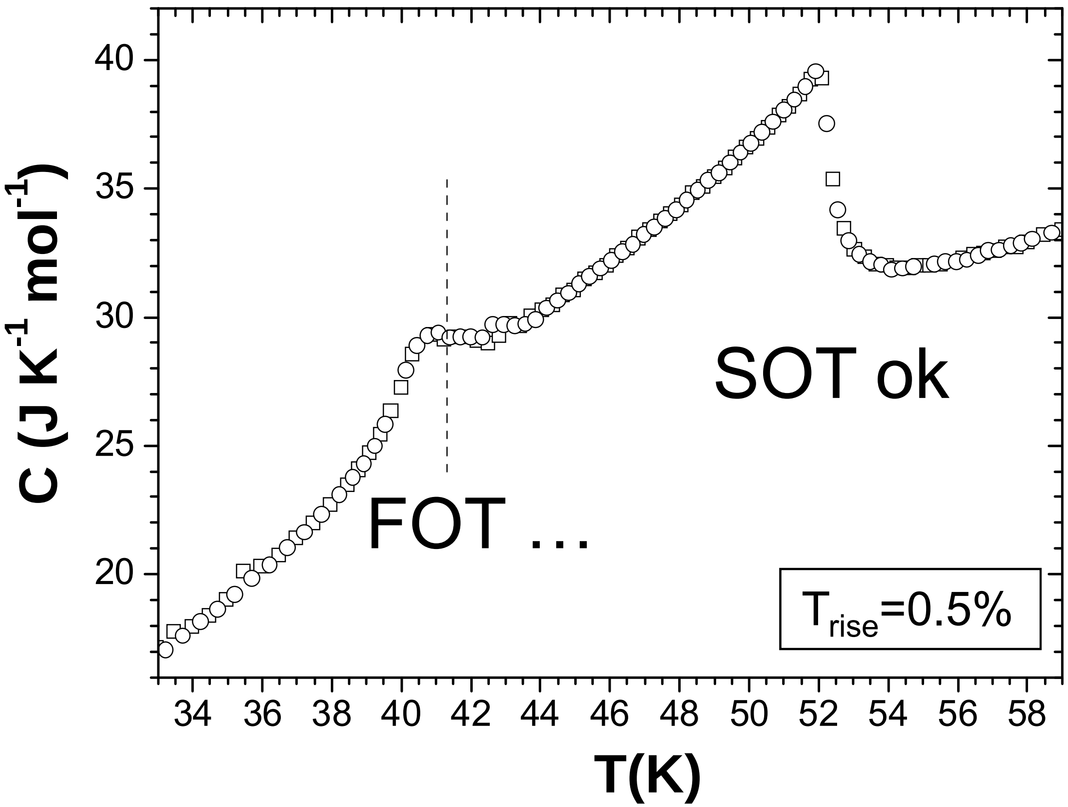


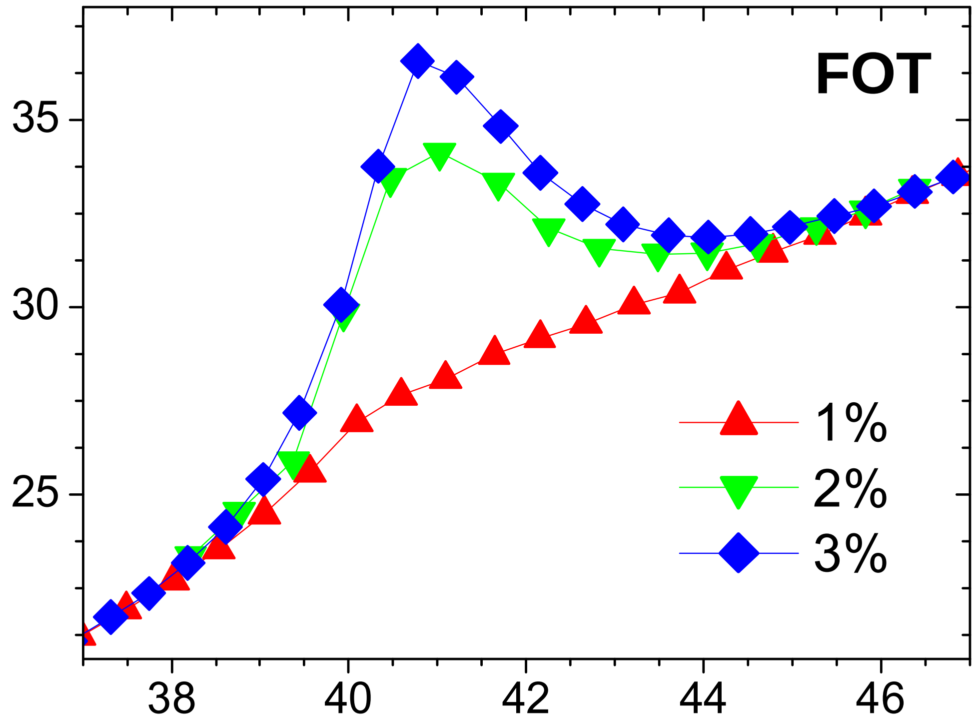
$Mn_{0.95}Zn_{0.05}V_2O_4$

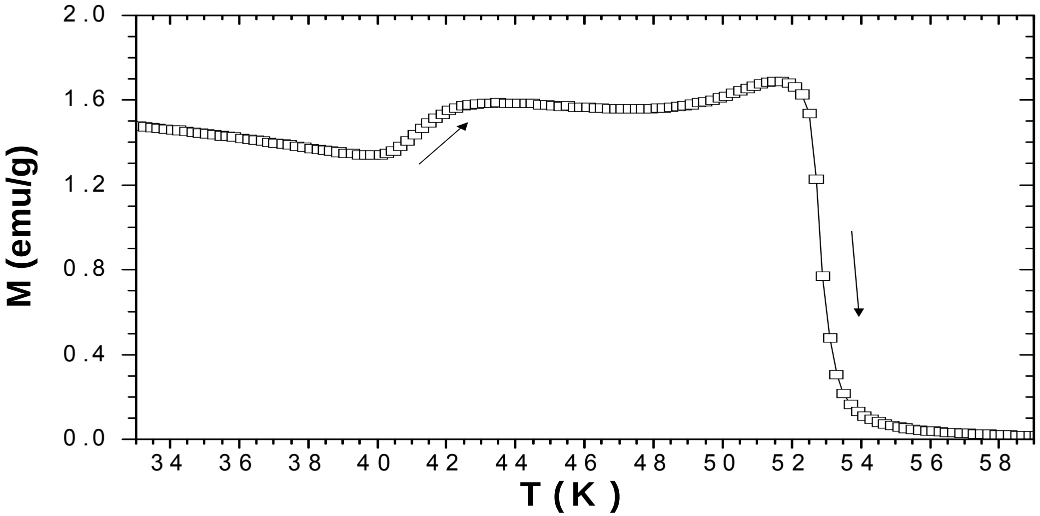


$Mn_{0.95}Zn_{0.05}V_2O_4$

QD analysis







Effect of T_{rise}

↓

Problem !

First series of improvements :

#Hysteresis ⇒ separate « warm » from « cool »

#Steepness ⇒ no averaging ⇒ point-by-point analysis

<u>2 τ model</u>

$$\begin{cases} 0 = C\dfrac{dT_s}{dt} + K_g(T_s - T_p) \\ P = C_{ad}\dfrac{dT_p}{dt} + K_w(T_p - T_{out}) + K_g(T_p - T_s) \end{cases}$$

Assuming $T_s \equiv T_p \equiv T$

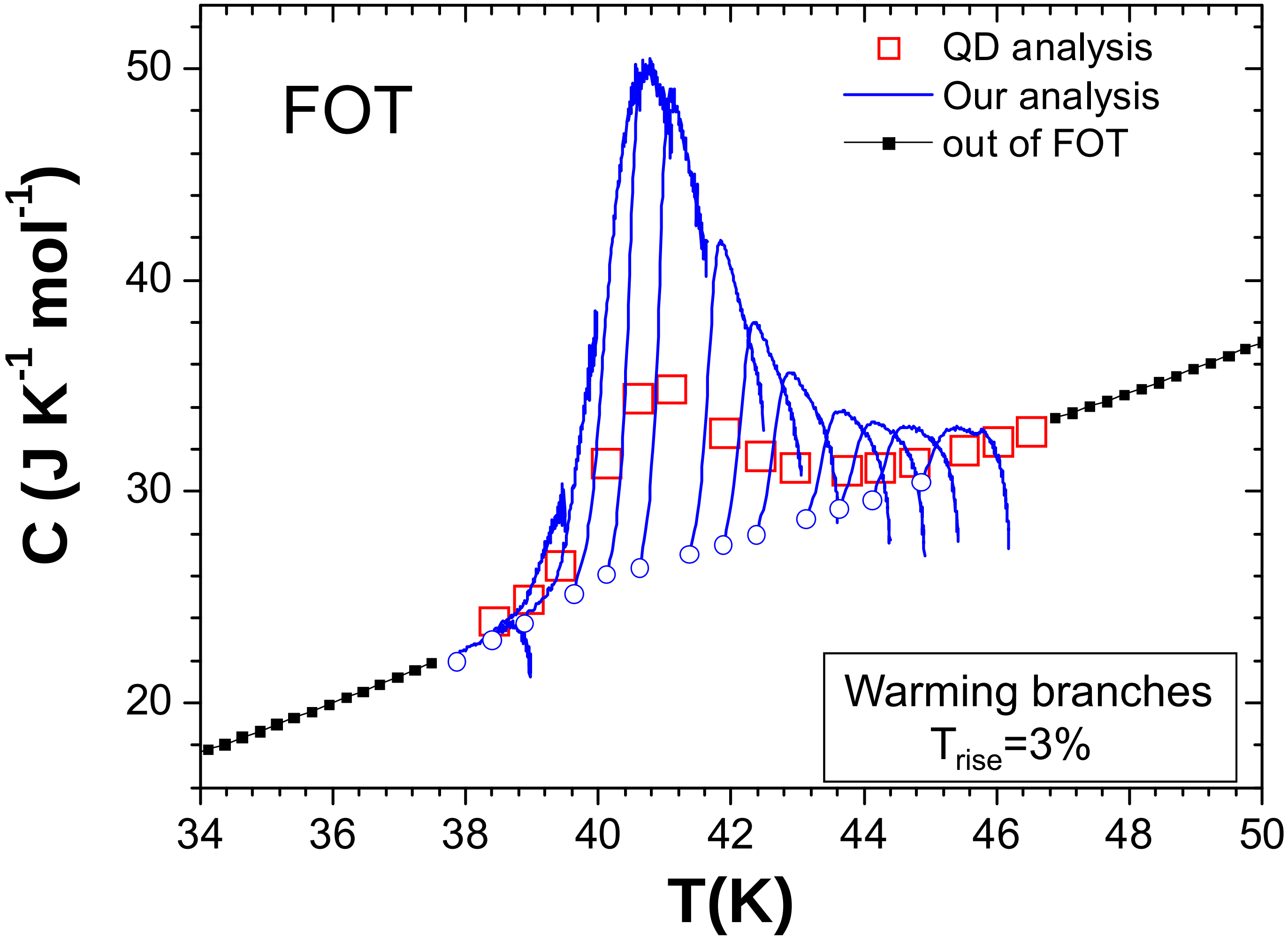
→ <u>1 τ model</u>

$$P = (C + C_{ad})\frac{dT}{dt} + K_w(T - T_{out})$$

⇓

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

$$\begin{cases} C_{ad}(T)\ \&\ K_w(T) \quad \text{from} \quad \text{Addenda} \\ \text{T(t)}\ \&\ \text{P(t)} \rightarrow \dfrac{\text{dT}}{\text{dt}}(T)\ \&\ P(T) \\ T_{out} = T_0 \end{cases}$$



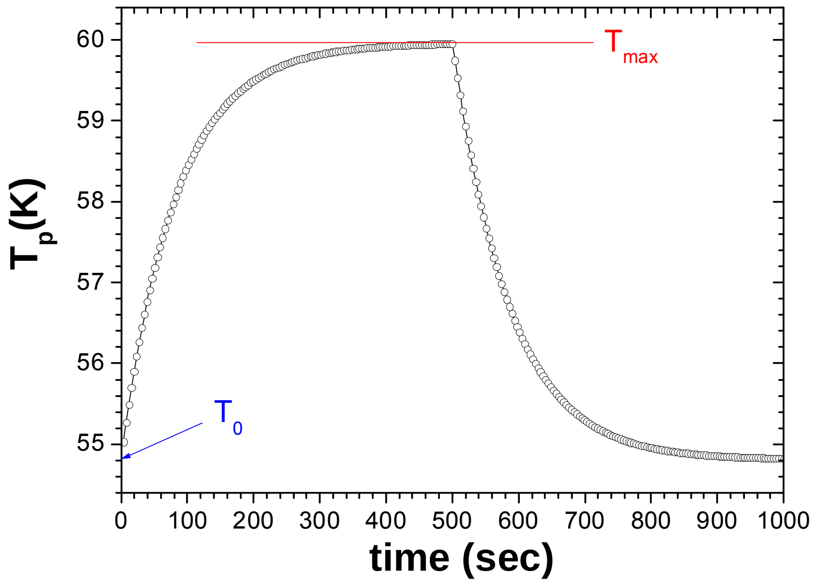
→ $C(T_0)$ ~background ?... ⇒ hidden latent heat

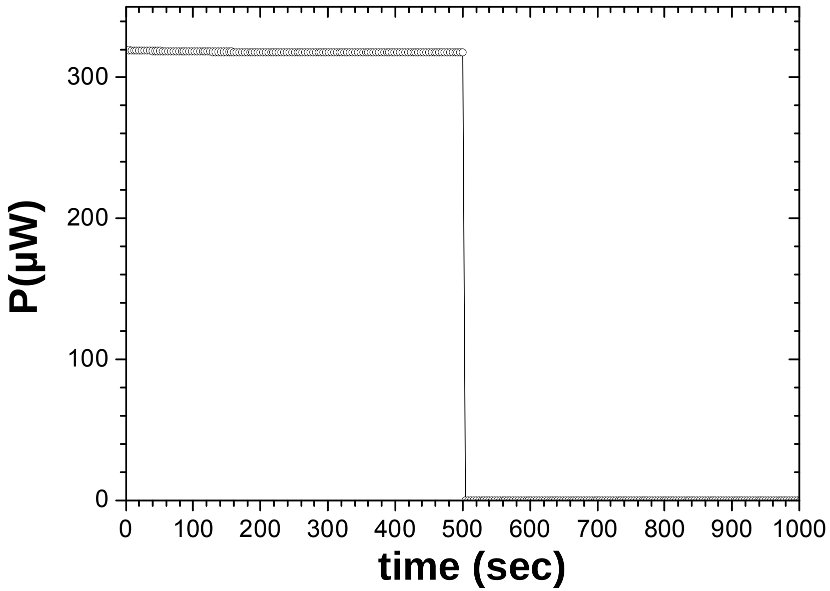
→ divergence at ~ T_{max} ?...⇒ drift in T_{out}

Second series of improvements :

#Latent heat $\Rightarrow T_0$ out of the FOT region $\Rightarrow$ large T_{rise}

#Temp. Drift $\Rightarrow$ correction T_{out}



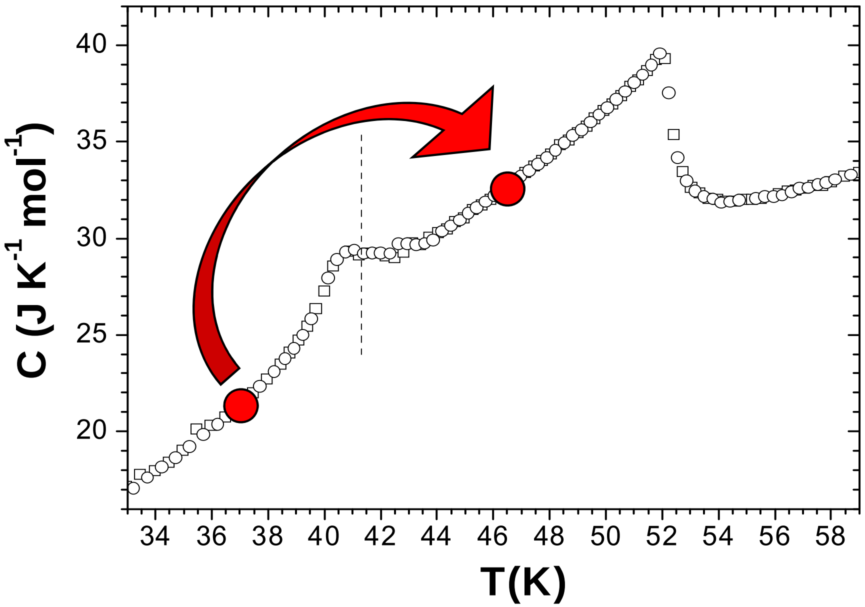


$$\left.\begin{array}{l} T_{out} = T_0 + y(T - T_0) \\ P = (C + C_{ad})\dfrac{dT}{dt} + K_w(T - T_{out}) \end{array}\right\} \quad \frac{dT}{dt} \approx 0 \Rightarrow T_{\max} - T_{out}(T_{\max}) = P(T_{\max})/K_w(T_{\max})$$

$$\Rightarrow \quad y = 1 - \left[P(T_{\max})/K_w(T_{\max})\right]/(T_{\max} - T_0)$$

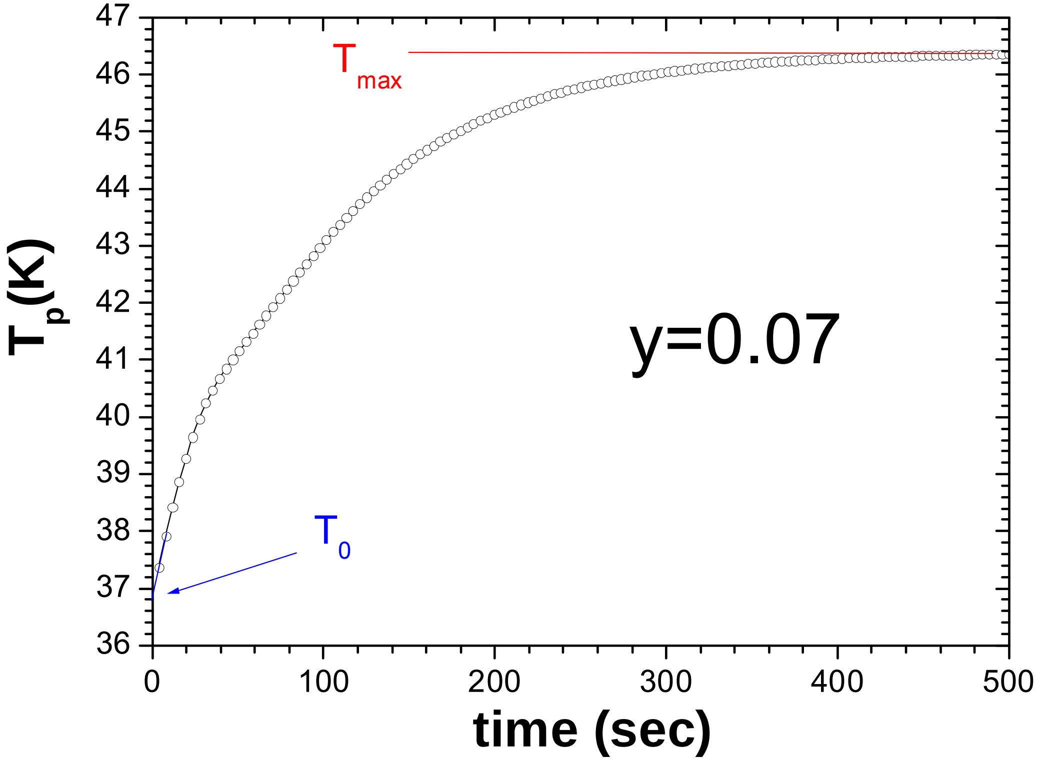
$$\boxed{C(T) = \left[\frac{P(T) - K_w(T)(T - T_0)(1 - y)}{\dfrac{dT}{dt}(T)}\right] - C_{ad}(T)}$$

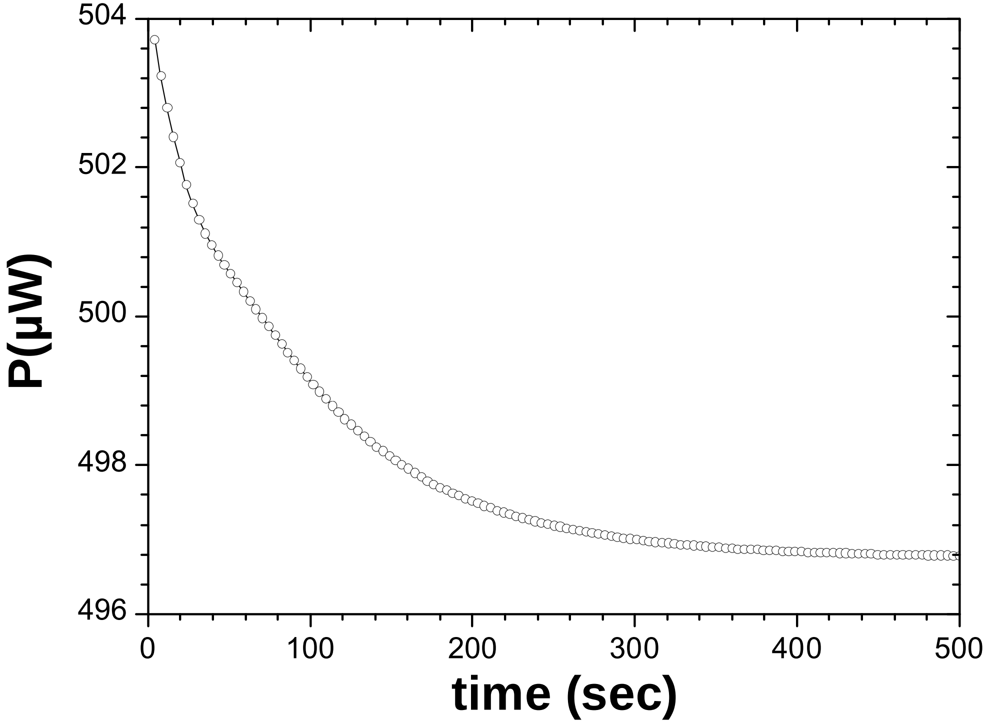
One-shot process



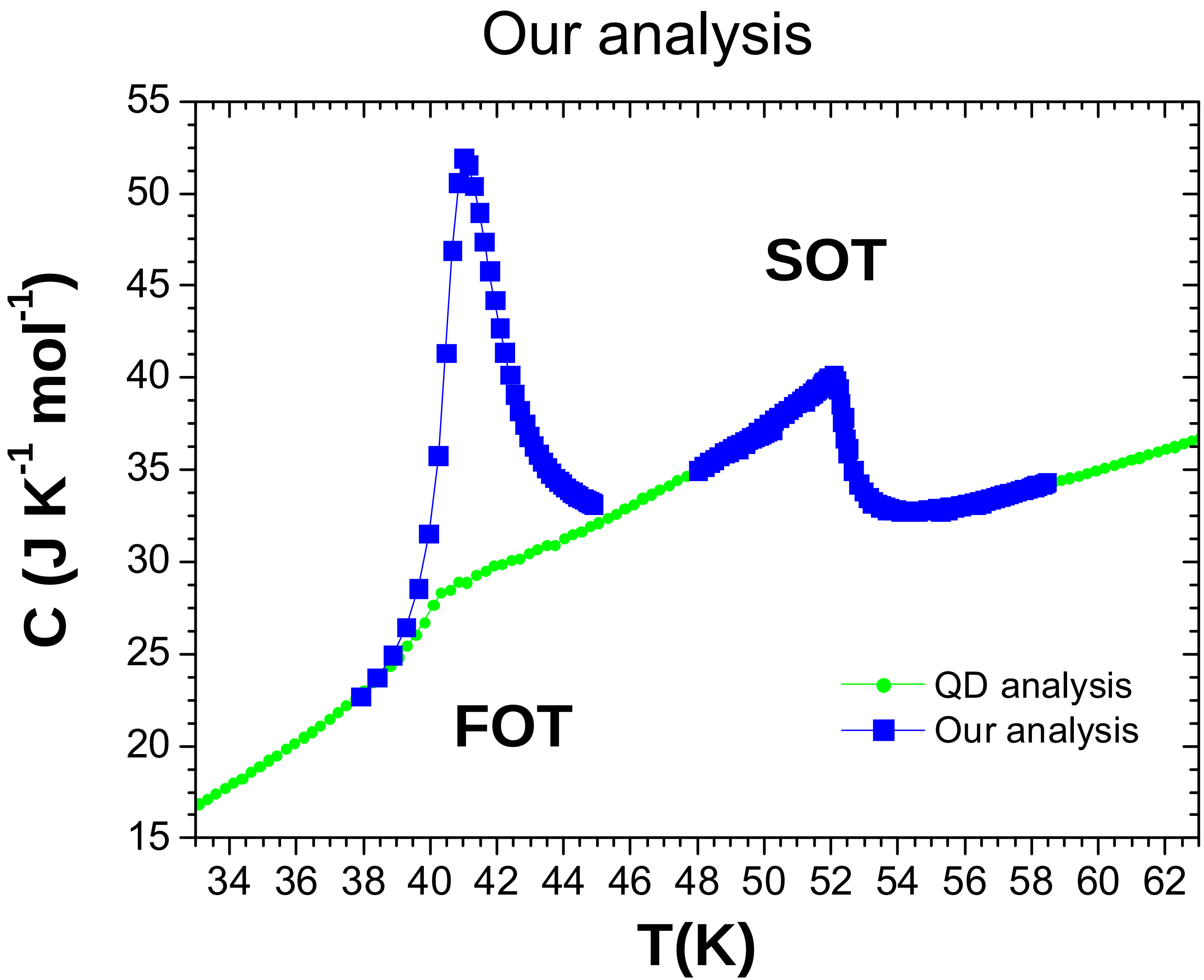
T_{rise}=10K

Δt=1000 sec



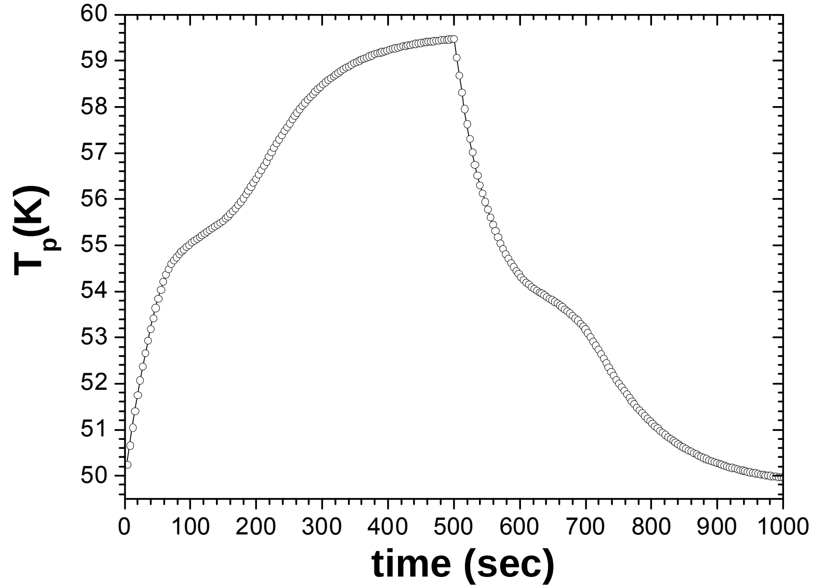


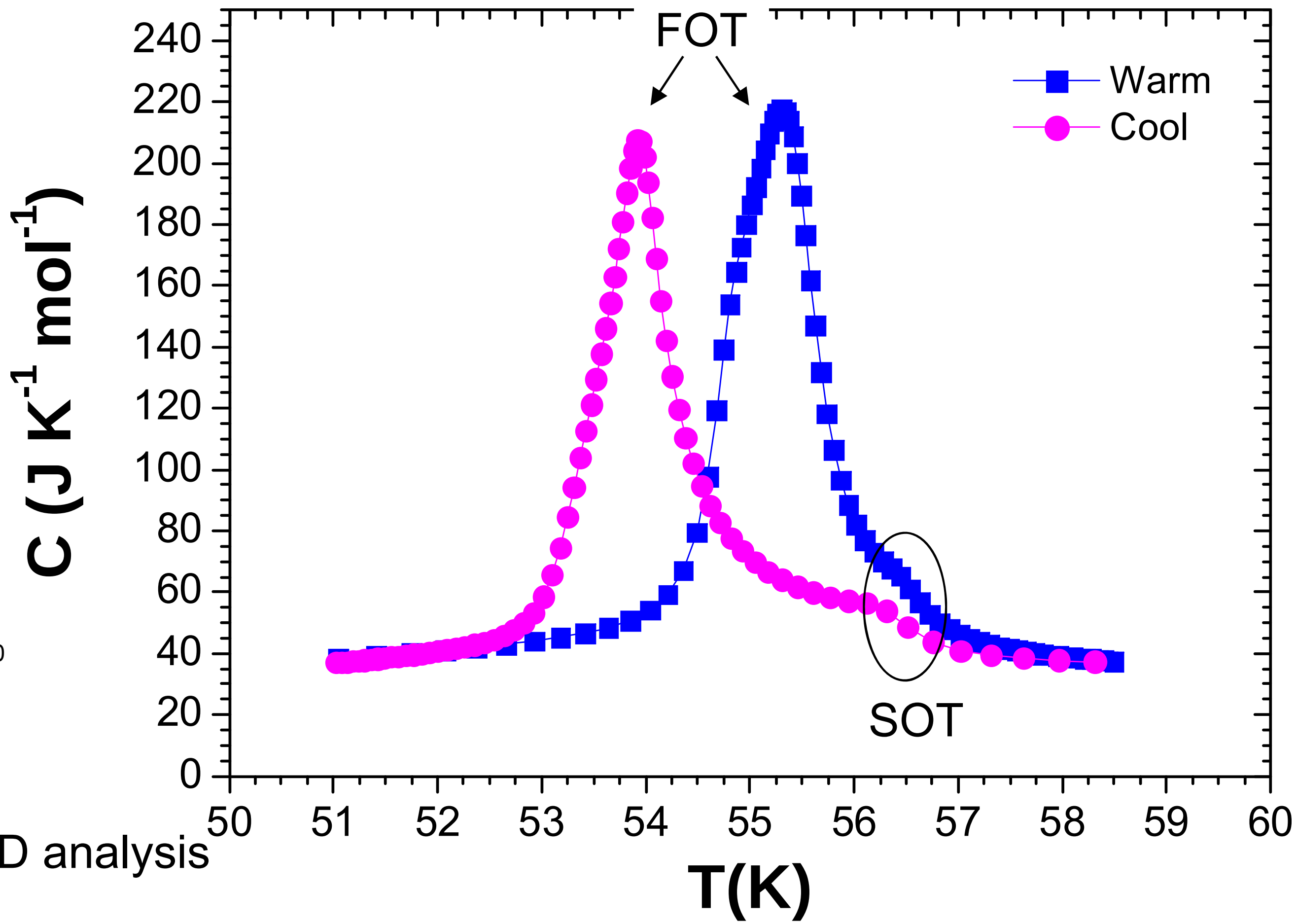
$Mn_{0.95}Zn_{0.05}V_2O_4$



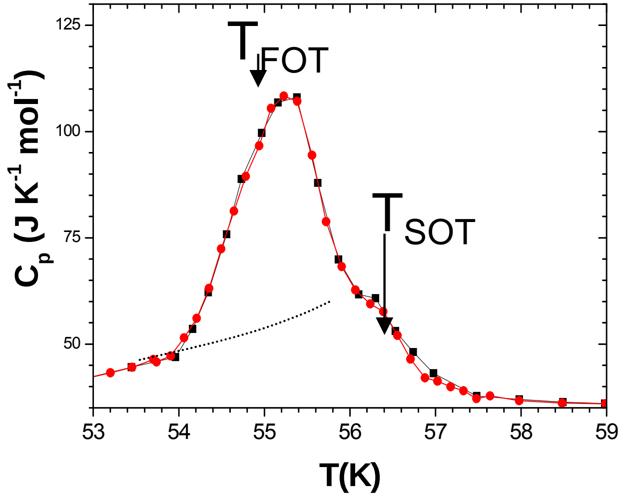
Peak FOT > Peak SOT !

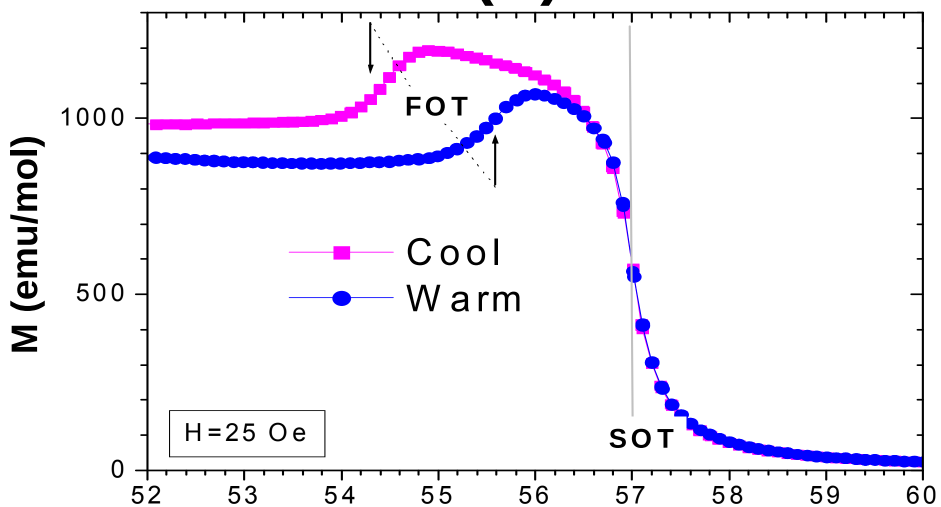
Going back to MnV_2O_4





C values higher than with standard QD analysis





MCE in MnV_2O_4