Delft Days on Magnetocalorics, Delft, Netherlands, 30-31 October, 2008

Determination of the magnetocaloric parameters through magnetic and thermodynamic methods in first-order transitions

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Outline

- **Determination of magnetocaloric parameters**
  - **Calorimetric methods**
    - **Heat capacity. Practical limitations**
    - **Direct measurements of ΔT_S and ΔS_T**
  - **Magnetic methods**
    - **Magnetization. Maxwell relation**
      - **Isothermal. Isofield. Other thermal and field paths**
      - **First-order transitions. Overestimation of ΔS_T**
    - **Adiabatic pulsed field**
      - **Adiabatic and isothermal magnetization**
- **Applicability of the Maxwell relation. Hysteretic compounds**
  - **Errors with isothermal magnetization curves**
  - **Solutions**
    - **Magnetization *M(T)* at constant field**
    - **Isothermal magnetization of appropriate thermal and field history**

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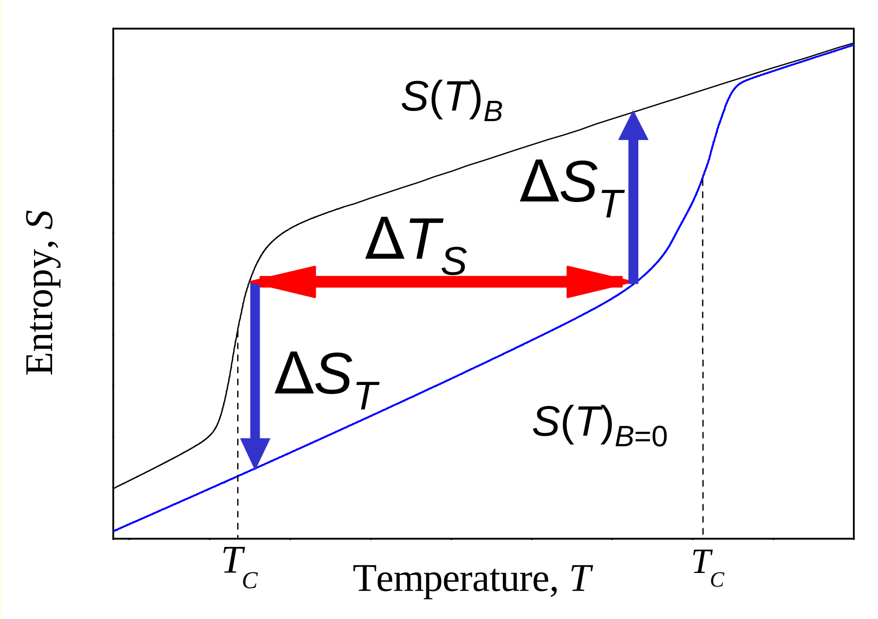
• Determination of the magnetocaloric parameters

◆ Calorimetric methods

➢ **From heat capacity**

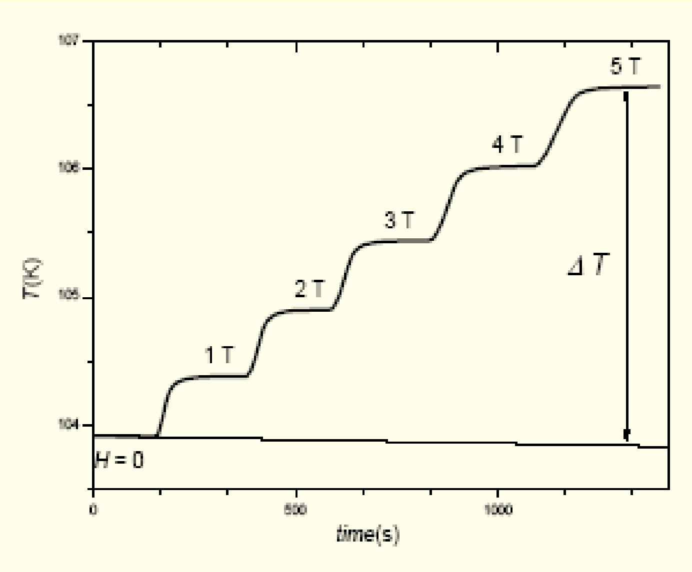


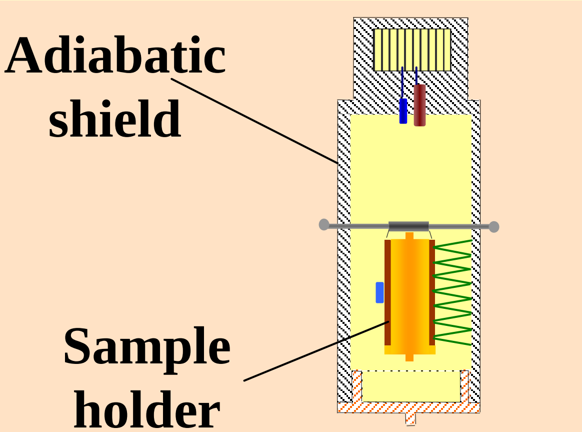
$$\boxed{\Delta T_S} = \left(T(S)_{H_2} - T(S)_{H_1}\right)$$

$$\boxed{\Delta S_T} = S(T)_{H_2} - S(T)_{H_1} = \int_0^T \frac{C(T)_{p,H_2} - C(T)_{p,H_1}}{T} dT$$

- Good at low temperatures
- Low precision at room T
- Scarce $C(T)_H$ data

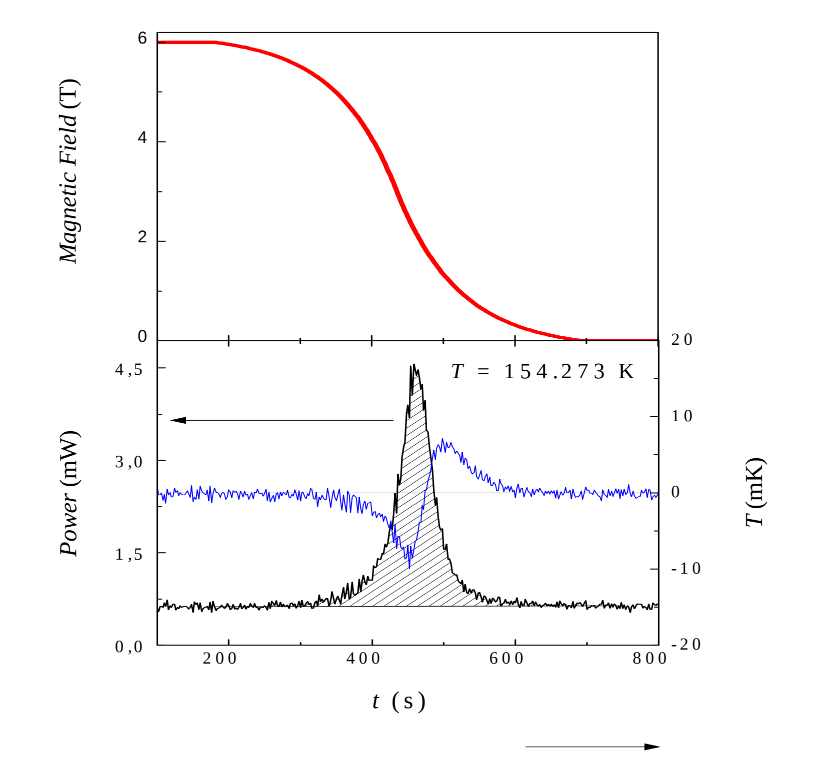
➢ From direct measurements





$$\boxed{\Delta T_S} = [T(S)_{H_2} - T(S)_{H_1}]$$

$$\boxed{\Delta S_T} = \Delta Q/T = [S(T)_{H_2} - S(T)_{H_1}]$$



L. Tocado, E. Palacios, R. Burriel
J. Magn. Magn. Mater. **290-291**, 719 (2005).

Magnetic methods

From magnetization data

Using the Maxwell relation $$\left(\frac{\partial S(T,H)}{\partial H}\right)_{p,T} = \left(\frac{\partial M(T,H)}{\partial T}\right)_{p,H}$$

$$\boxed{\Delta S_T} = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_{p,H} dH$$

$$\boxed{\Delta T_S} = \int_0^H \left(\frac{T}{C(T,H)} \times \frac{\partial M(T,H)}{\partial T}\right)_{p,H} dH$$

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- **Easy measurements**
  - **Isothermal magnetization**
  - **At constant field**
  - **Other thermal and field history**

- **Problems**
  - **Limited to ΔS_T**
    - **Calculation of ΔT_S requires $C(T, H)$**
  - **Discontinuities in first derivatives**
    - **Computational errors**
  - **Maxwell relations valid for state functions**
    - ***M(T,H)* is not a state function in first-order transitions**
    - **It depends on history (hysteresis)**

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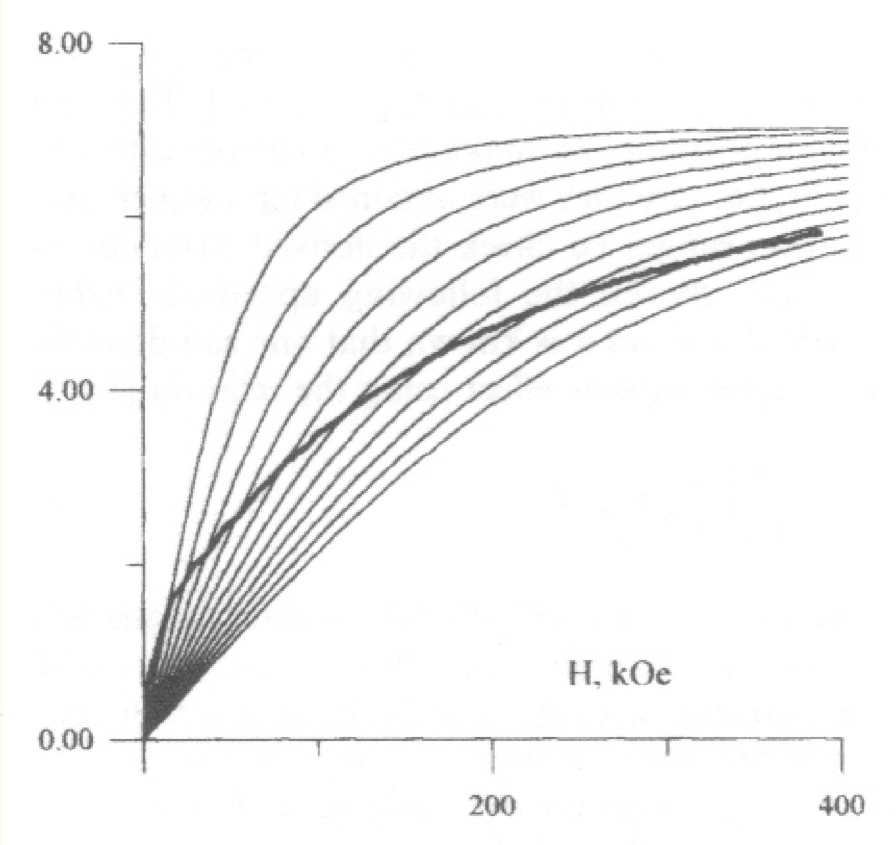
Adiabatic pulsed fields

- **Comparison of magnetization curves in adiabatic and isothermal processes**



R.Z. Levitin, V.V. Snegirev, A.V. Kopylov, A.S. Lagutin, A. Gerber
J. Magn. Magn. Mater. **170**, 223 (1997).

- **Applicability of the Maxwell relation. Hysteretic compounds**

$$dG = -SdT - MdB - Vdp$$

$$\left(\frac{\partial G}{\partial T}\right)_{B,p} = -S \Rightarrow \left(\frac{\partial^2 G}{\partial T \partial B}\right) = -\left(\frac{\partial S}{\partial B}\right)_{T,p}$$

$$\left(\frac{\partial G}{\partial B}\right)_{T,p} = -M \Rightarrow \left(\frac{\partial^2 G}{\partial B \partial T}\right) = -\left(\frac{\partial M}{\partial T}\right)_{B,p}$$

$$\left(\frac{\partial S}{\partial B}\right)_{T,p} = \left(\frac{\partial M}{\partial T}\right)_{B,p} \quad \text{Maxwell relation}$$

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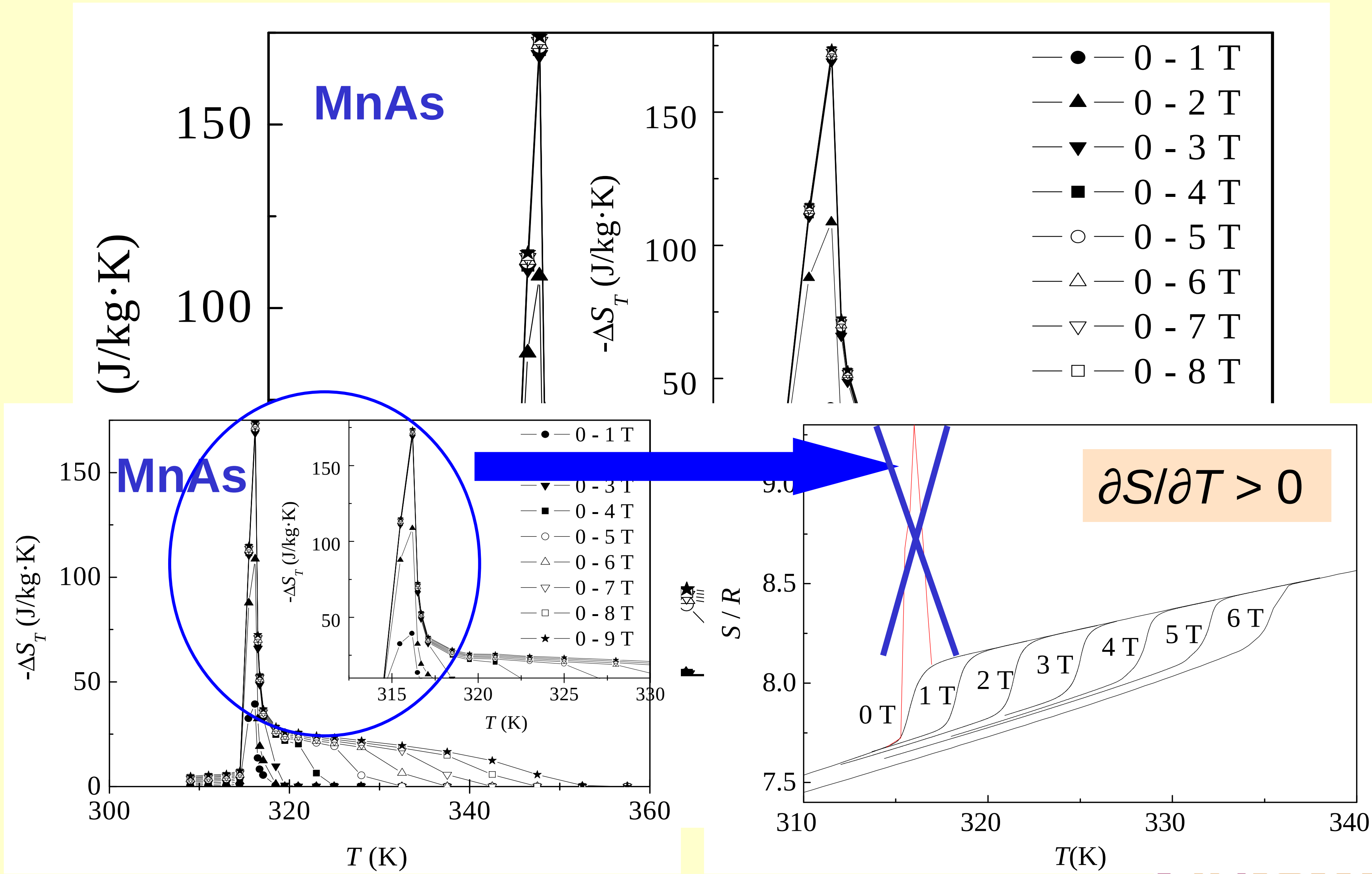
Application to MnAs



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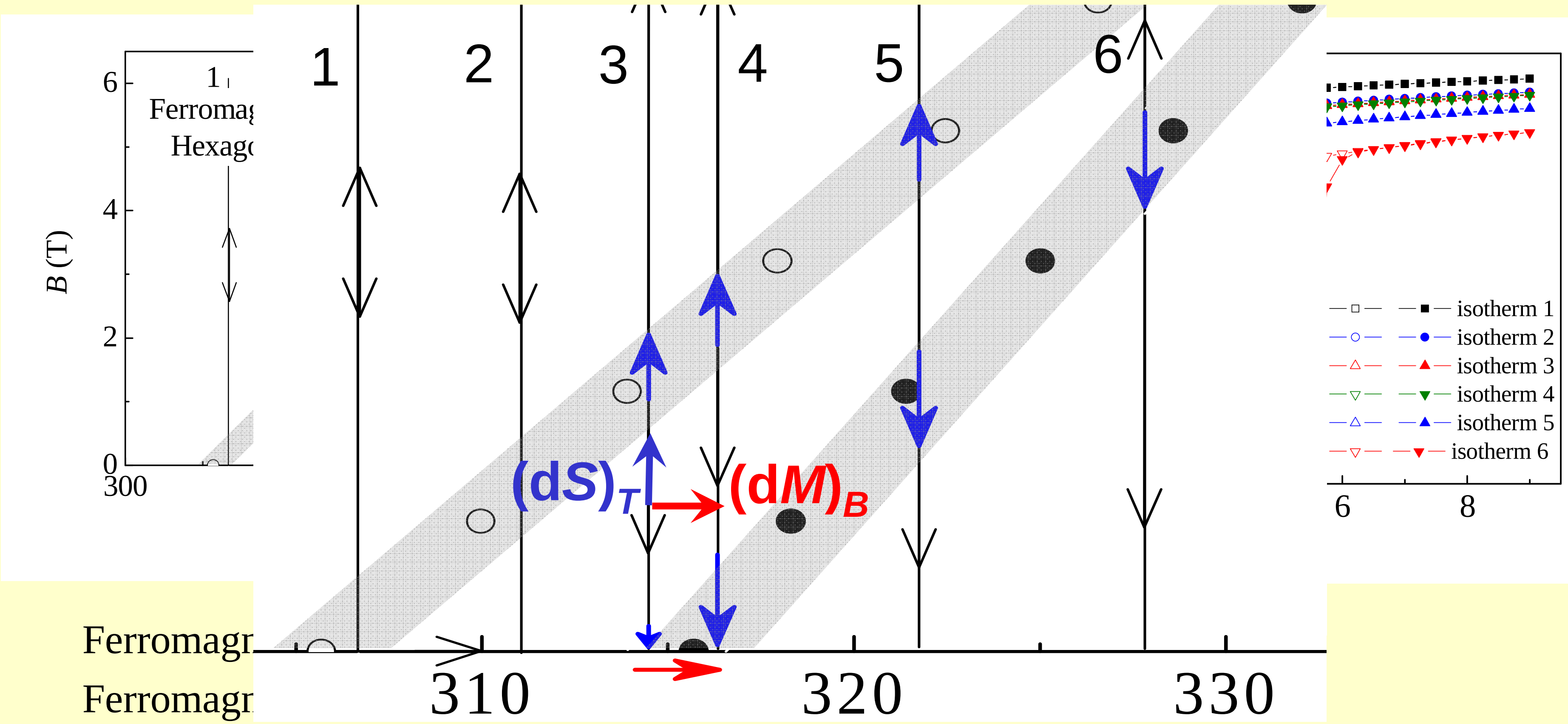
Phase diagram from M and C_p measurements

Isothermal magnetization measurements: $M(B)_T$

MnAs



Ferromagn

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Paramagnetic phase (x = 0) ➔ Isotherms 5 and 6

Calculation in a real process (isothermal magnetization)

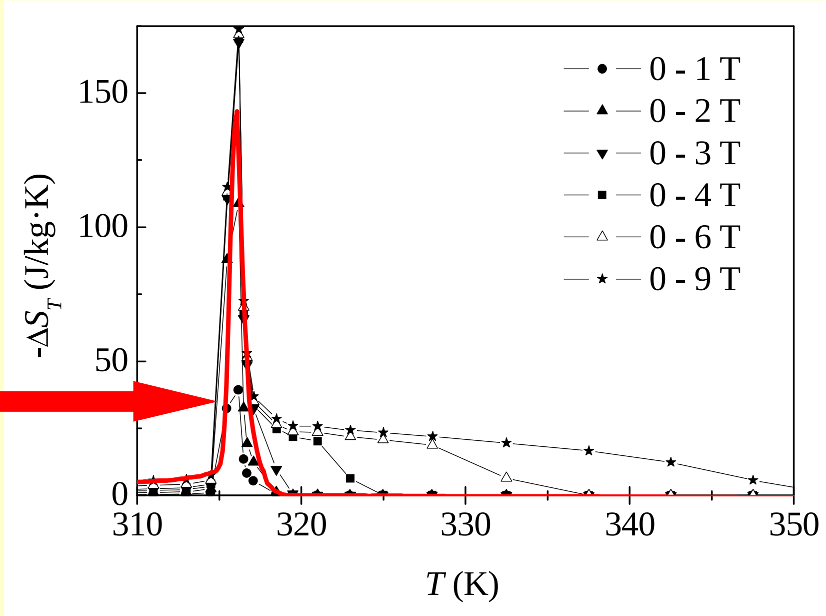
$$M = x\cdot M_F + (1\text{-}x)\cdot M_P \longrightarrow \left(\frac{\partial M}{\partial T}\right)_B = (1-x)\left(\frac{\partial M_P}{\partial T}\right)_B + x\left(\frac{\partial M_F}{\partial T}\right)_B + (M_F - M_P)\left(\frac{\partial x}{\partial T}\right)_B$$

$$dS = \left(\frac{\partial M}{\partial T}\right)_B dB \longrightarrow dS = (1-x)\left(\frac{\partial M_P}{\partial T}\right)_B dB + x\left(\frac{\partial M_F}{\partial T}\right)_B dB + (M_F - M_P)\left(\frac{\partial x}{\partial B}\right)_T dB$$

$$dS = dS' + dS_{ex}$$

$$\int_0^{Bt} (M_F - M_P)\left(\frac{\partial x}{\partial T}\right)_B dB$$

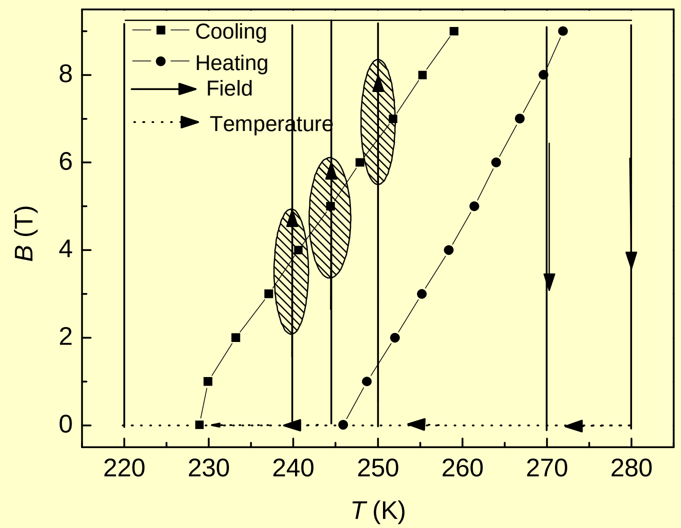
$$\left(\frac{\partial x}{\partial T}\right)_{B=0} = \frac{\left(C_{p,B=0}\right)_{anom}}{\left(\Delta H\right)_{B=0}}$$



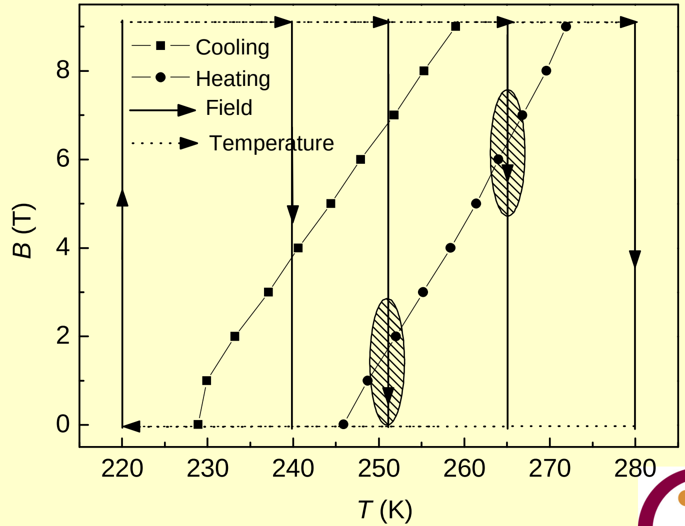
Solutions for hysteretic compounds

$Mn_{1.1}Fe_{0.9}P_{0.82}Ge_{0.18}$

- **Magnetization at constant fields** ***M(T)***

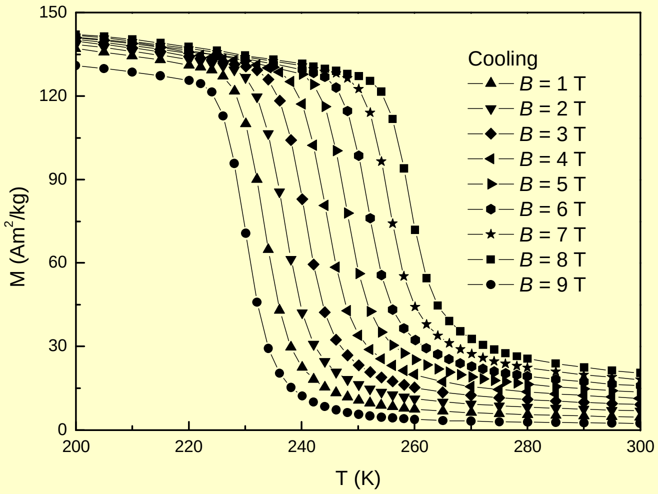


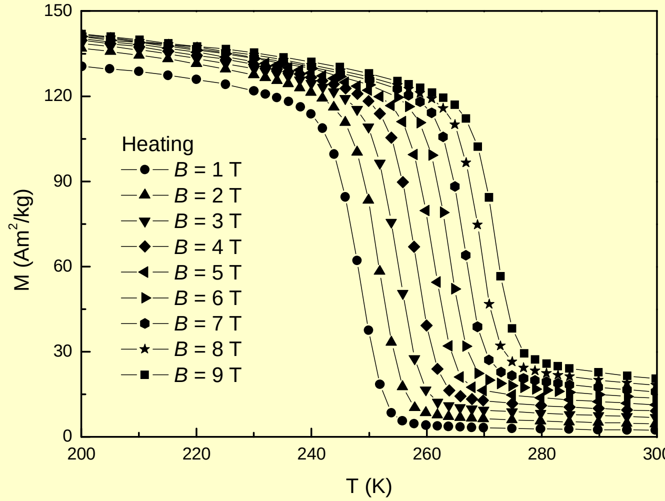
- **Isothermal magnetization (for increasing fields) after forcing the P state by heating and cooling**

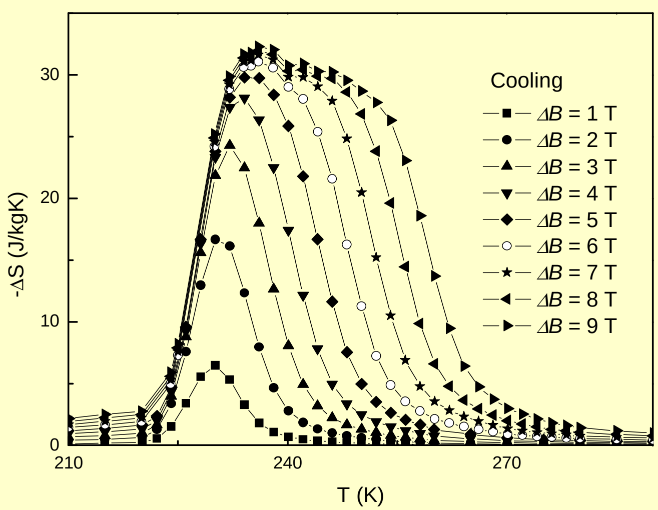


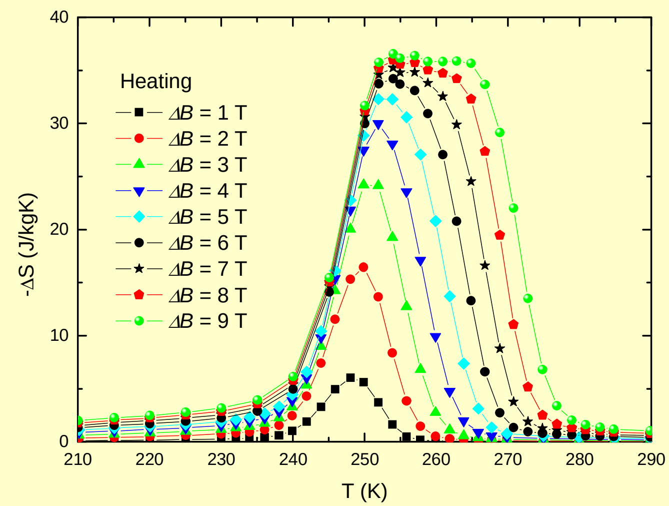
- **Isothermal magnetization (for decreasing fields) after forcing the F state by cooling and heating**

$Mn_{1.1}Fe_{0.9}P_{0.82}Ge_{0.18}$









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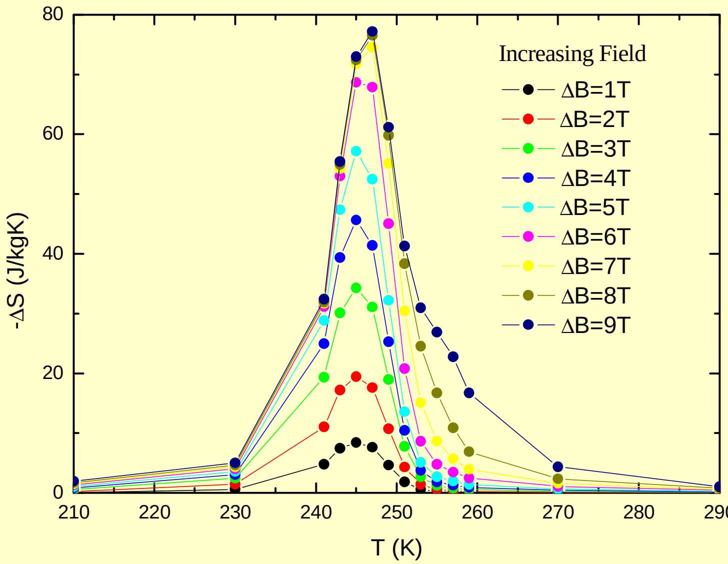
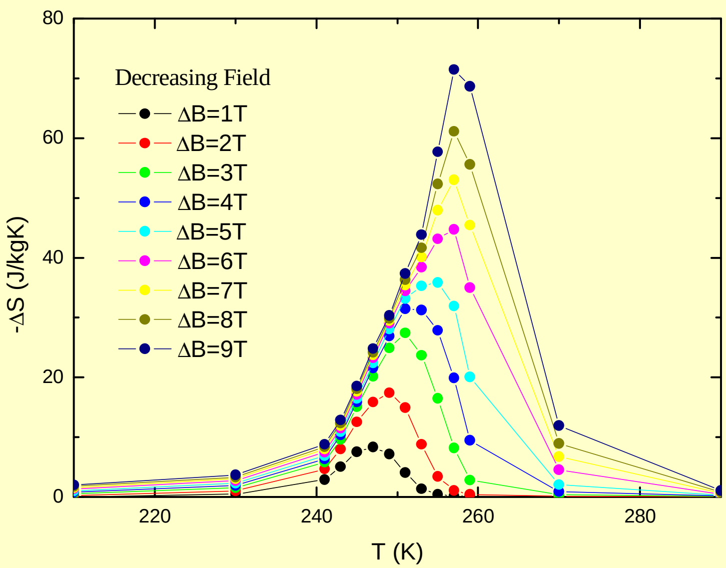
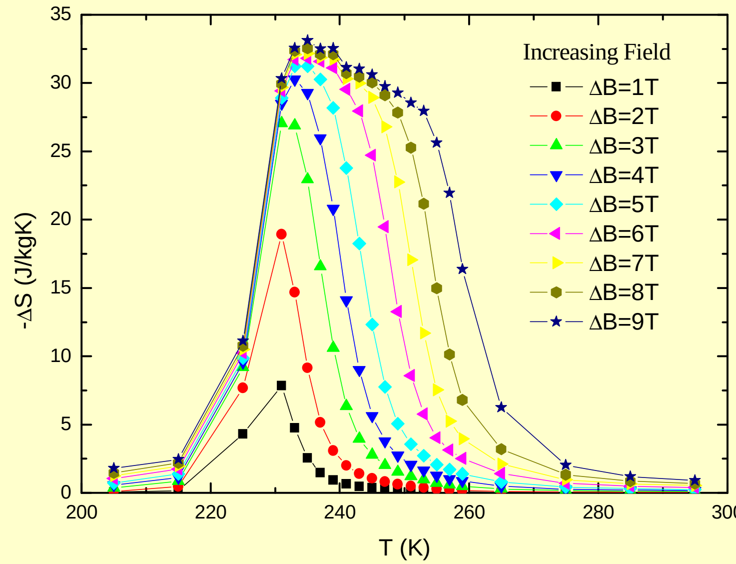
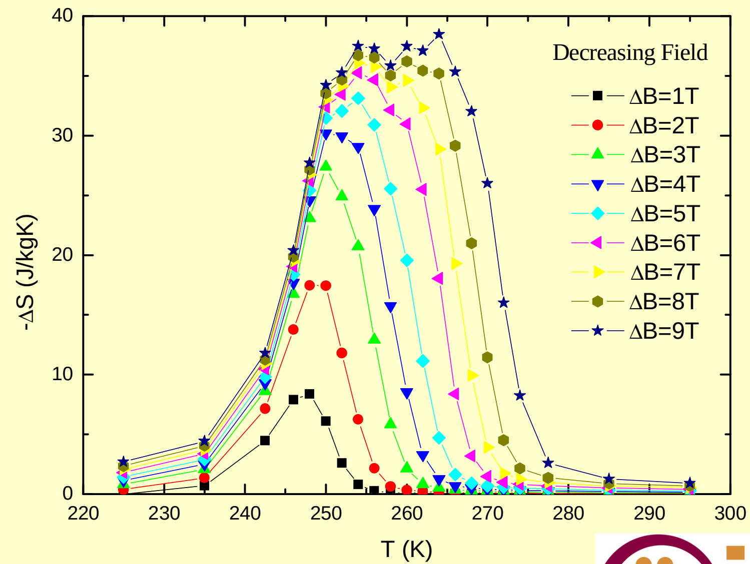
Isothermal magnetization





Isothermal magnetization from P or F state





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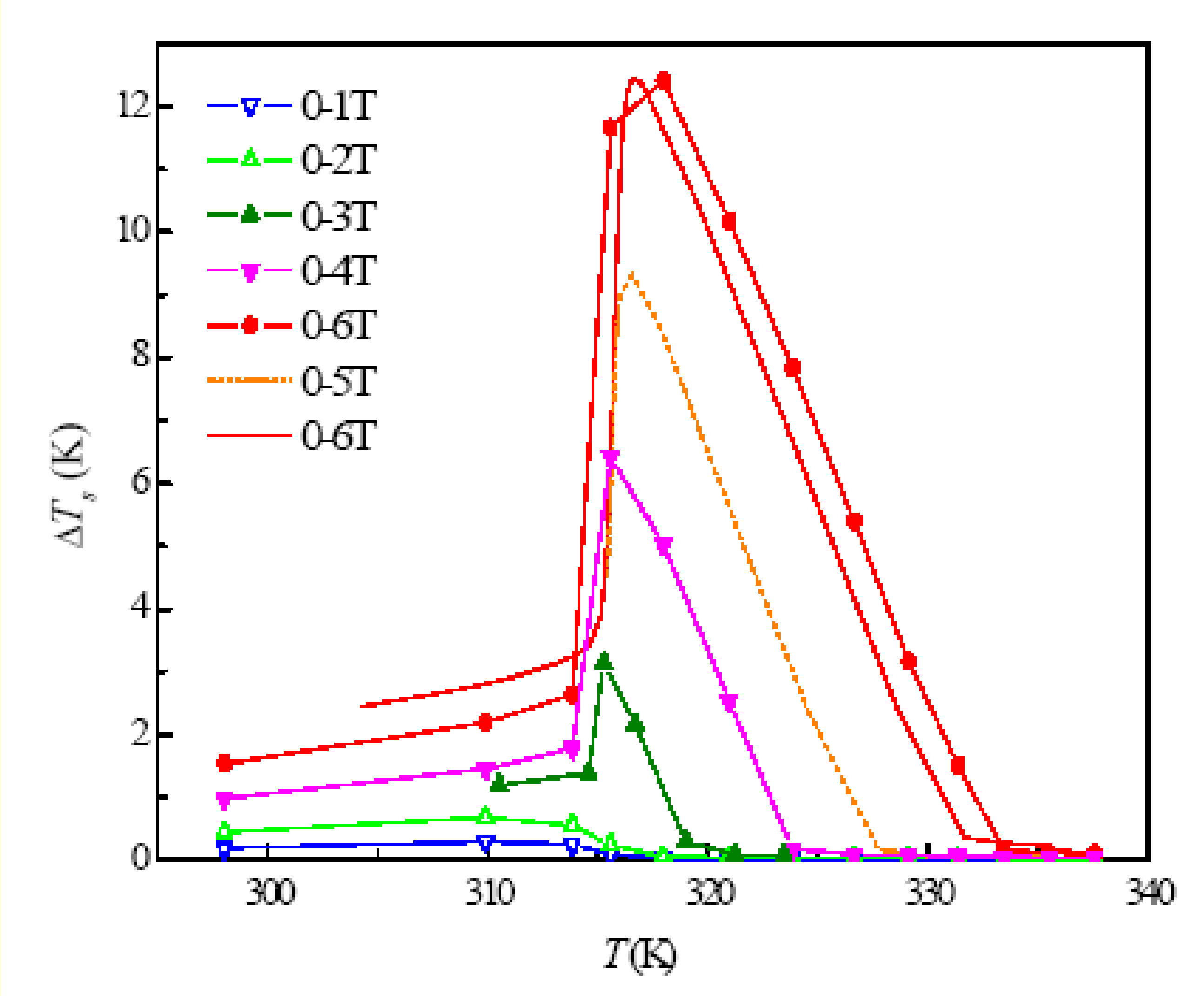
MnAs

Adiabatic temperature change for MnAs

- Direct ΔT_S (symbols)
- From C_p (lines)



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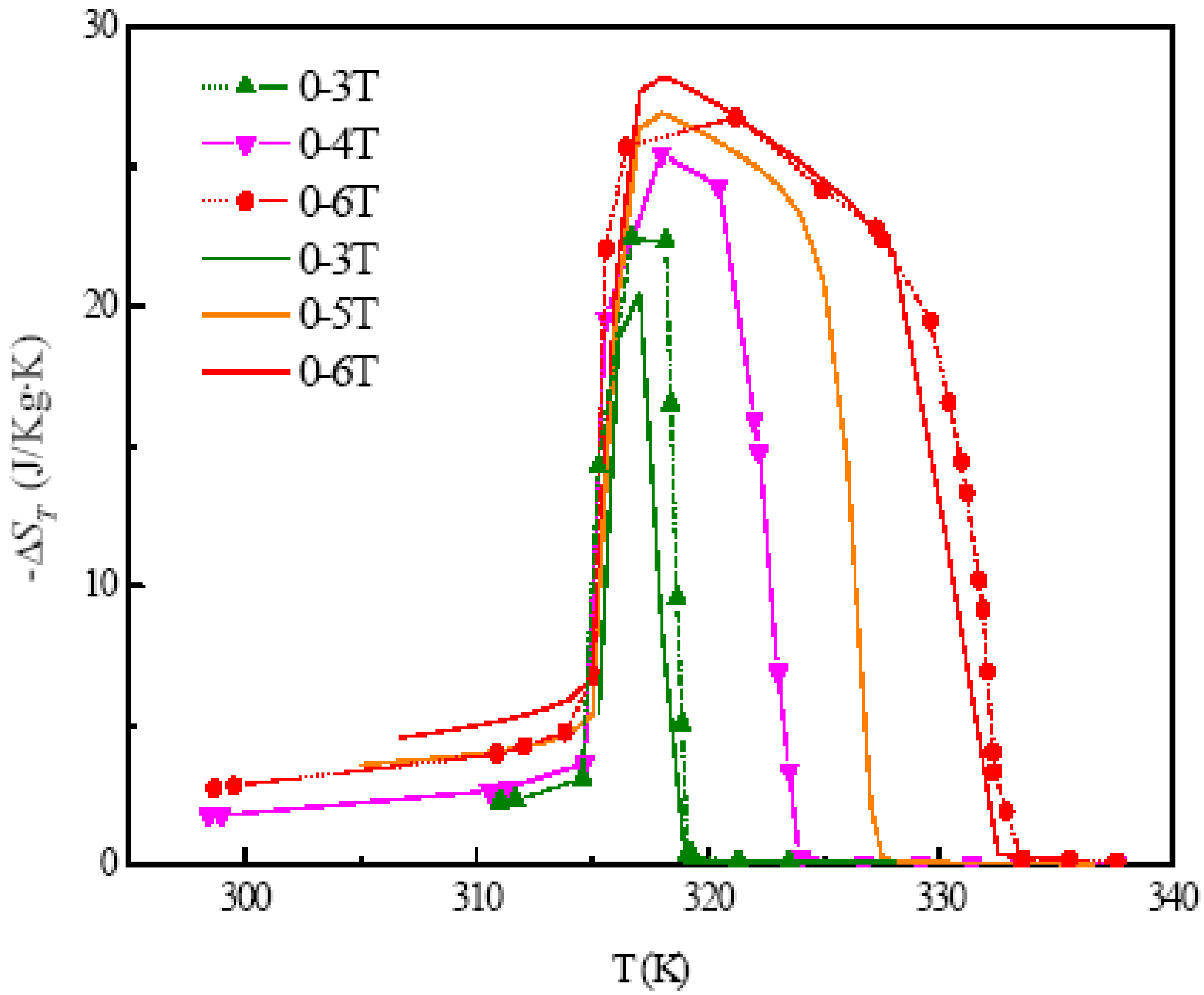

Isothermal entropy change for MnAs

- Direct results (symbols)
- From C_p (lines)

L. Tocado, E. Palacios, R. Burriel

J. Therm. Anal. Calorim. **84**, 213 (2006).

Conclusions

- **Importance of reliable estimates of ΔT_S and ΔS_T**
  - **Practical results from *M(T,H)* in paramagnets and in second order transitions**
  - **Materials with giant MCE: first-order transitions**
    - **Incorrect results from *M(T,H)***
    - **Overvalued calculations**
- **Limitations from C_p results for high temperature ΔS_T calculations**
- **Direct measurement of ΔT_S and ΔS_T**
- **Importance of thermal history in *M(H)* measurements**
- **Use of isofield magnetization curves or controlled isothermal curves**
- **Practical results in first-order transition compounds**
  - **Absence of spurious spikes, no evidence of colossal MCE**
  - **Calculation of the spurious spikes**

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