Field dependence of Magnetocaloric effect identifies 1st order magnetic phase transition

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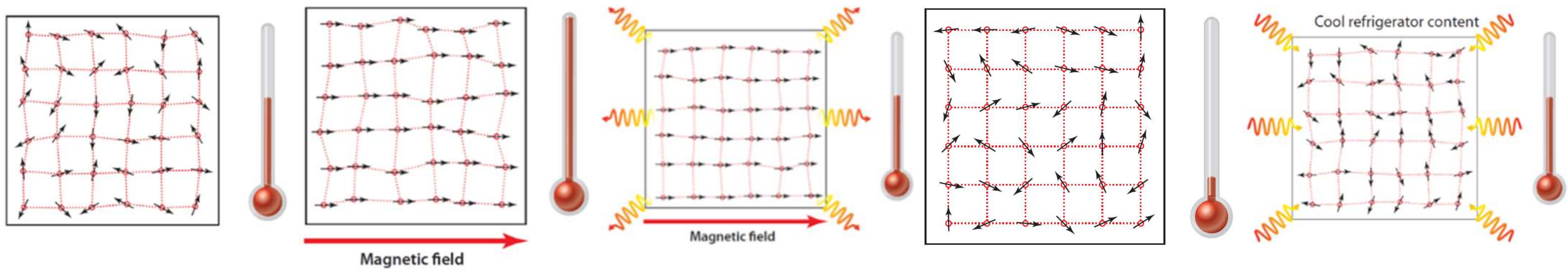
Magnetocaloric effect

refers to **adiabatic ΔT of** magnetic material when subjected to an **adiabatic varying** magnetic field

4 stages of

Magnetic Refrigeration Cycle



Adiabatic magnetization | Heat removal | Adiabatic demagnetization | Load cooling

Magnetocaloric effect ≡ ΔT or ΔS_T

Prog. Mater. Sci. **93** (2018) 112-232
Annu. Rev. Mater. Res. **42** (2012) 305–42

Magnetocaloric materials
are typically classified into two categories

According to the order of magnetic phase transitions they undergo

Classification of Magnetocaloric materials

to their phase transitions exhibited

So **AN IDEAL magnetocaloric material**

Lays in between these two types,

i.e. **critical point of SOPT**

First-order phase transitions

Exhibits

- Magnetostructural / Magnetoelastic phase transition

Examples

- $Gd_5(Si,Ge)_4$, $La(Fe,Si)_{13}$, MnFe(P,Si), Ni-Mn-X-Heusler (X=Sn / In / Sb)

MCE

- Larger ΔS_T over a narrow T_{range}
- At the expense of hysteresis, rate dependent behavior
- Phase coexistence

Second-order phase transitions

- Magnetic phase transition
- Gd
- Smaller ΔS_T over a broad T_{range}
- Thermal hysteresis absent

So,

the determination of the order of magnetic phase transition

is crucial for the evaluation of MCE materials

Outline
of the talk

INTRODUCTION

RESUTS

- **Applying them to an alloy series**
  with 1st → 2nd order phase transitions
- **Our proposed method + quantitative**
- **Numerical simulation results**
- **Is the proposed method for general use?**
  Other experimental examples

CONCLUSIONS

Typical ways to characterize them:

- **Direct MCE methods**
- **Indirect MCE methods**

Calorimetric method

- Not broadly extended in our research field
- Measurement technique can affect the data results thus **not** all suit FOPT characterization

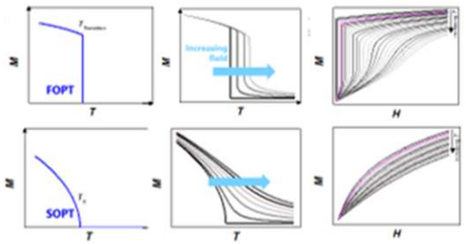
Magnetization method

- Commercially available
- More accessible

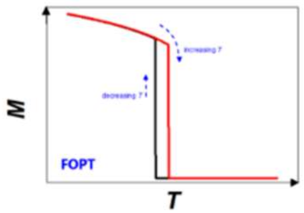
Existing ways to identify the types of magnetocaloric materials

only magnetization method

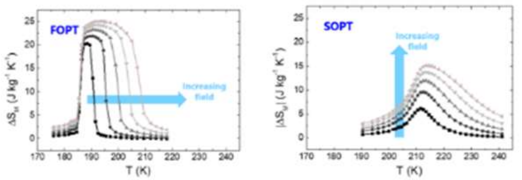
Shape of Magnetization curve



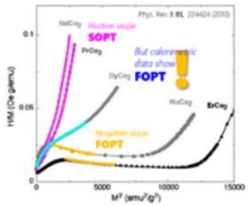
Hysteresis



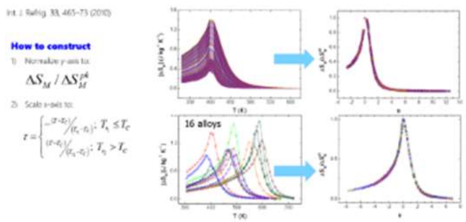
Shape of MCE curve



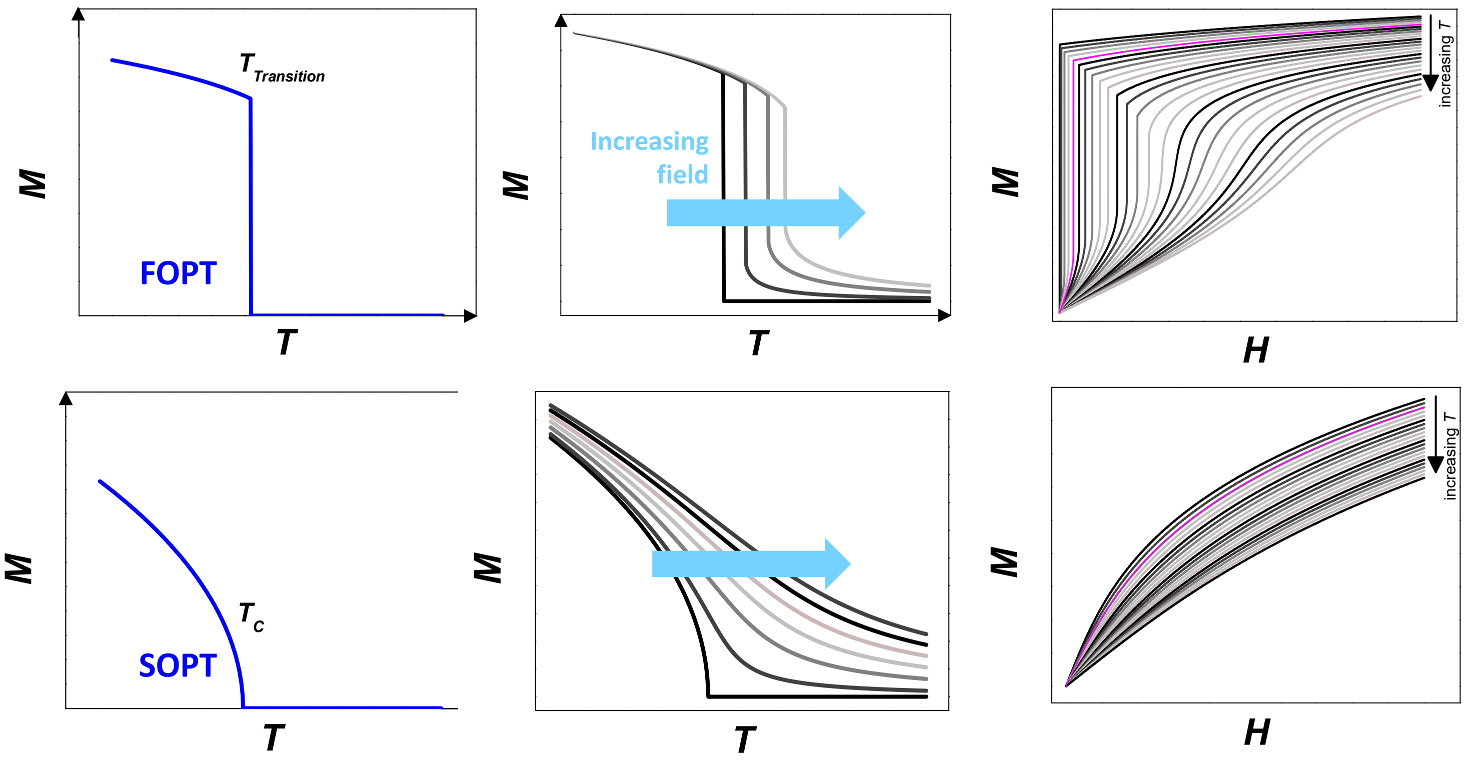
Banerjee´s criterion



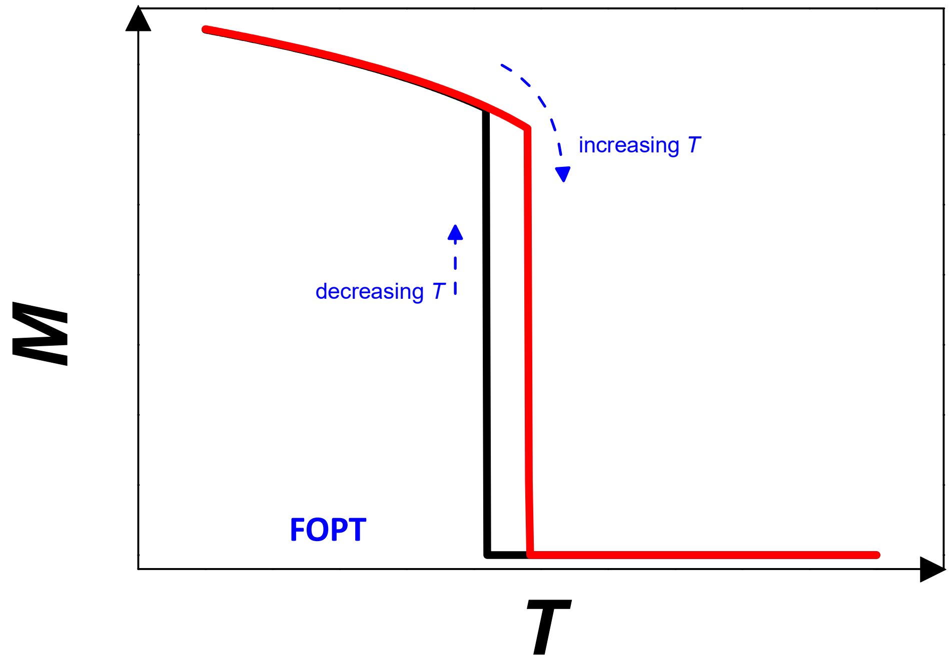
Universal Curves



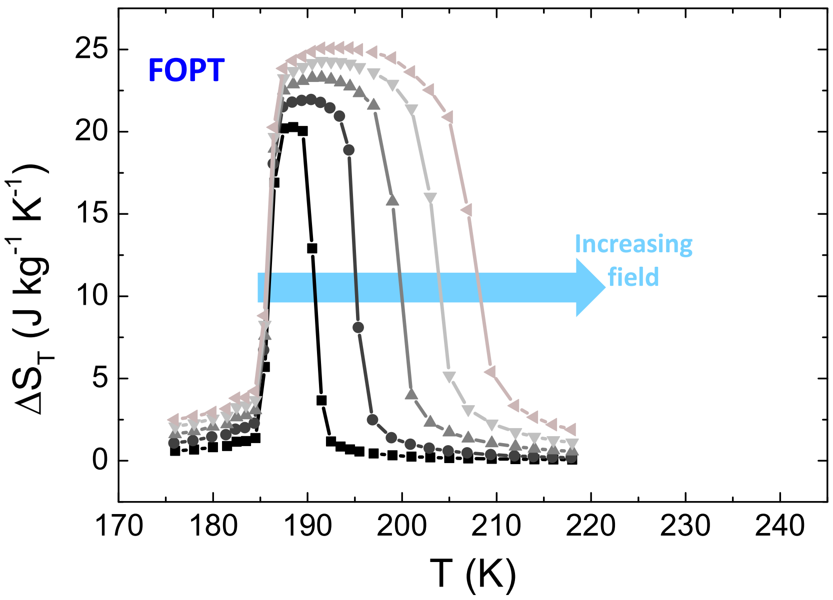
Shape of magnetization curve

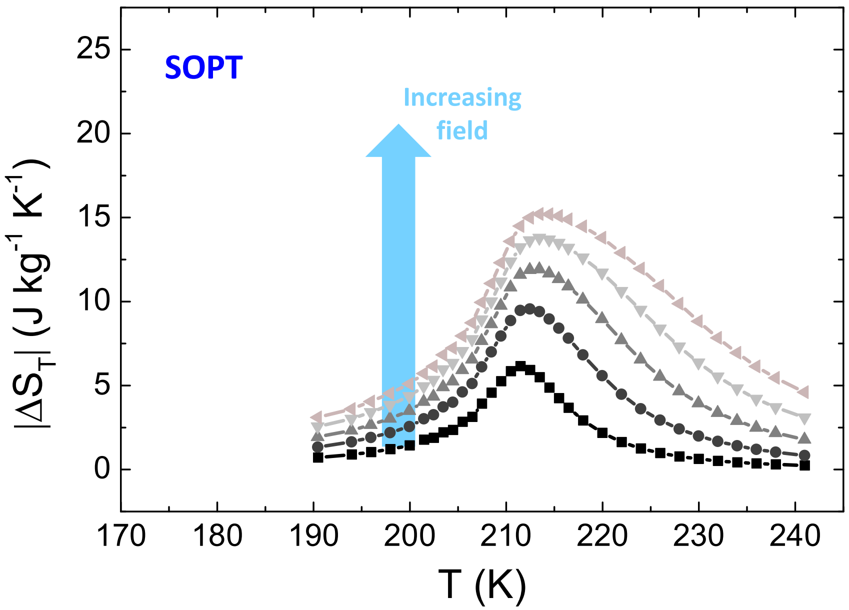


Hysteresis



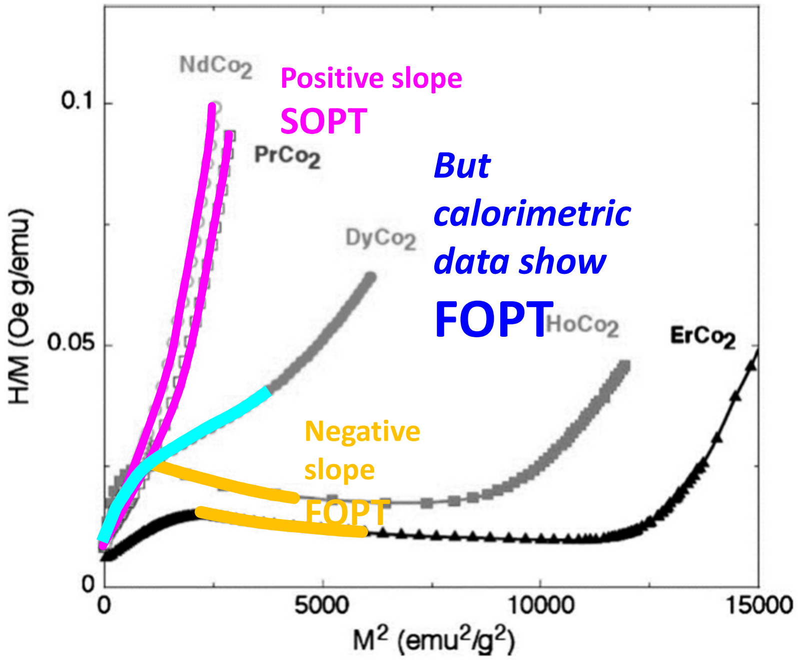
Shape of MCE curve





Banerjee´s criterion

Phys. Rev. B 81, 224424 (2010)



Universal curves

Int. J. Refrig. 33, 465–73 (2010)

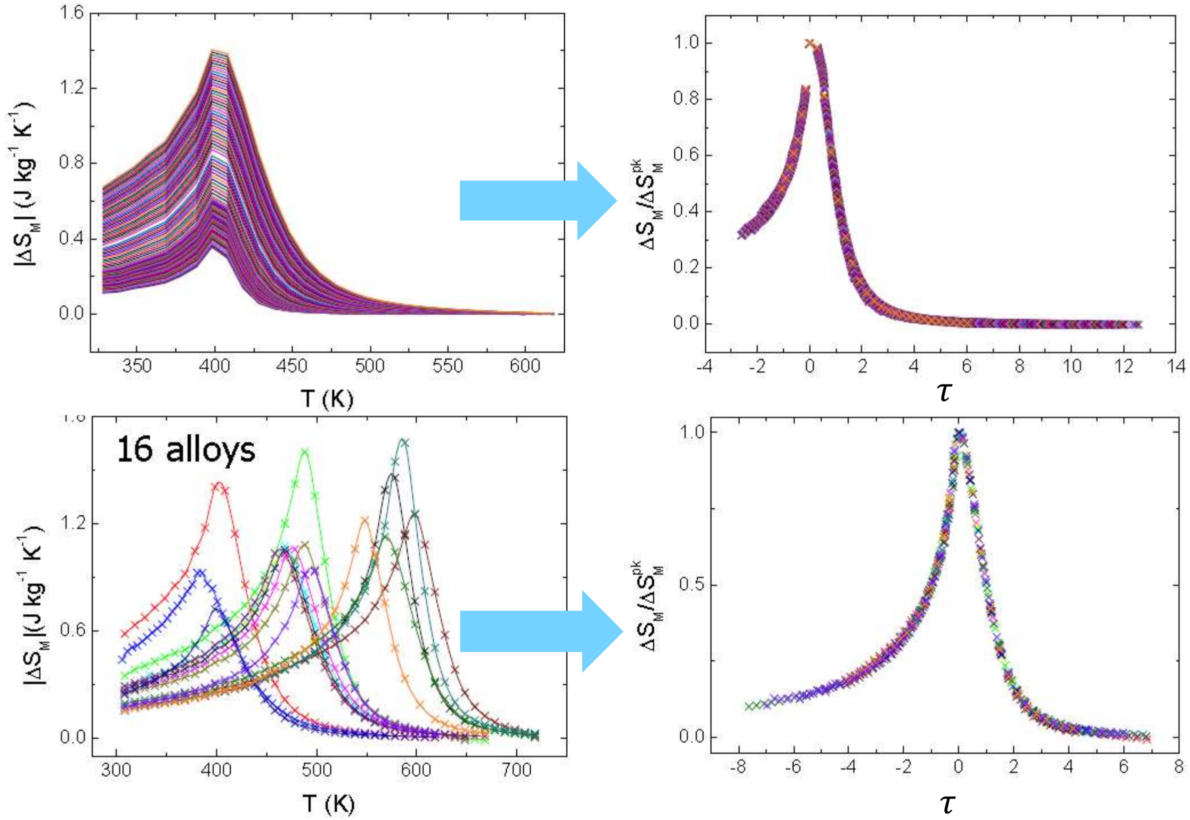
How to construct

1) Normalize y-axis to:

$$\Delta S_M \,/\, \Delta S_M^{pk}$$

2) Scale x-axis to:

$$\tau = \begin{cases} -\dfrac{(T-T_C)}{(T_{r_1}-T_C)};\ T_{r_1} \le T_C \\ \dfrac{(T-T_C)}{(T_{r_2}-T_C)};\ T_{r_2} > T_C \end{cases}$$



Universal curves

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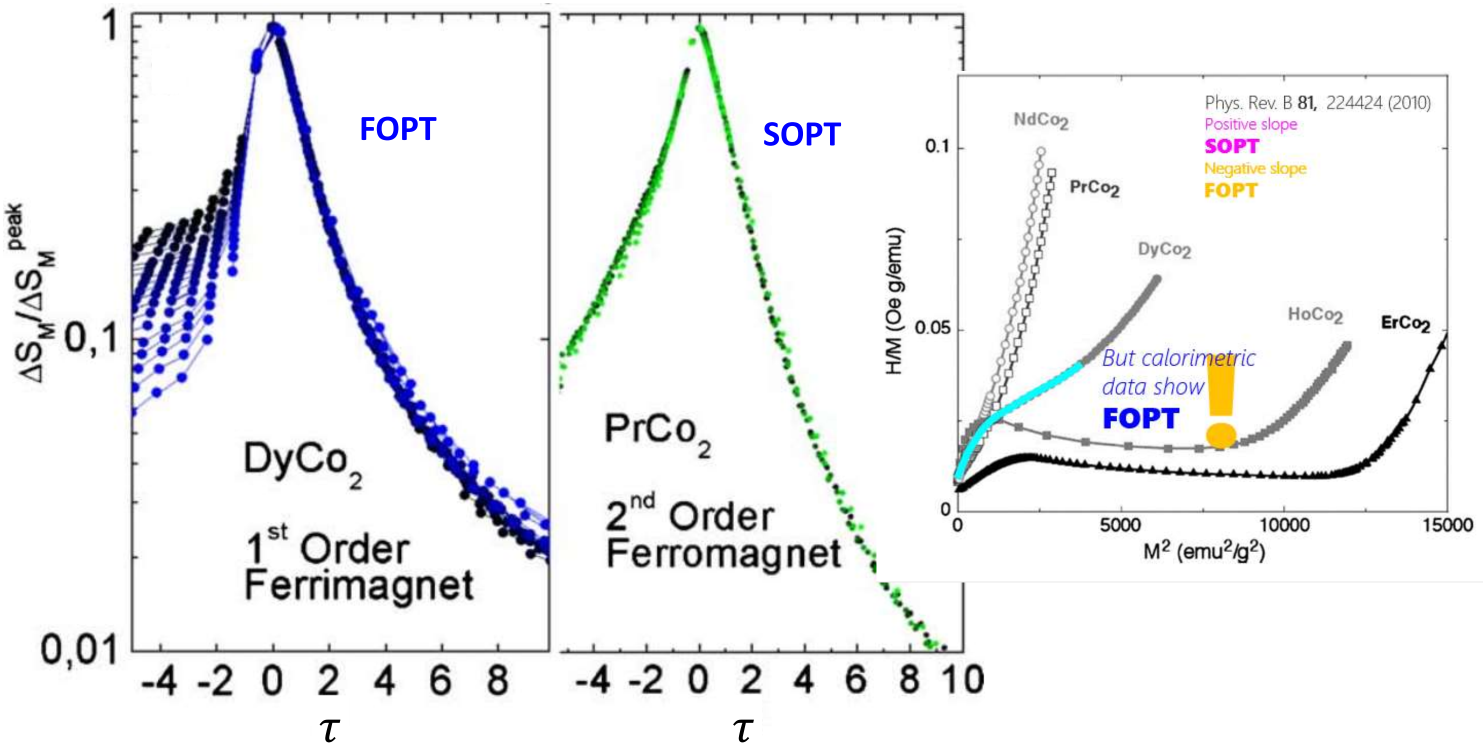


first case study

La (Fe, Si)$_{13}$ magnetocaloric materials

Magnetization Characterization Protocol

Two measurement protocols in VSM:

1) Temperature sweeping at different magnetic fields

2) Discontinuous isothermal protocol:

sample heated in zero field above transition → cooled to measurement temperature in zero field → measured in increasing field

↓

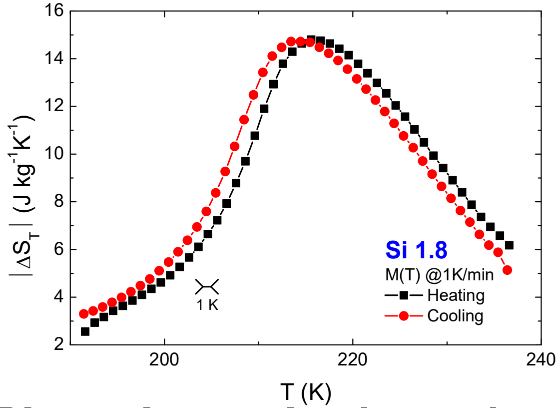
also in decreasing field

Two measurement protocols
in VSM:

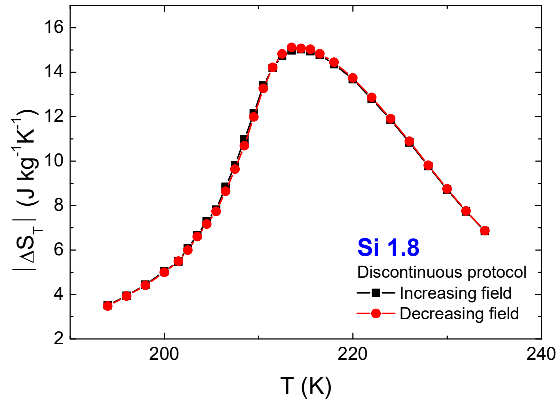
- $M(T)$ has small extrinsic lag → misleading results
- Discontinuous protocol shows no difference between increasing and decreasing field branches

J. Phys. D: Appl. Phys. 50, 414004 (2017)

1. Temperature sweeping at different magnetic fields

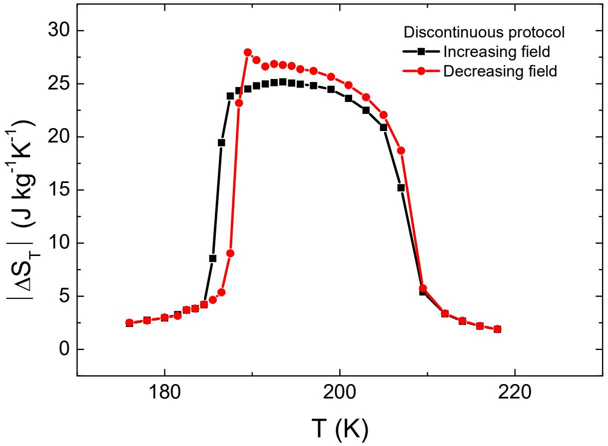


2. Discontinuous isothermal protocol

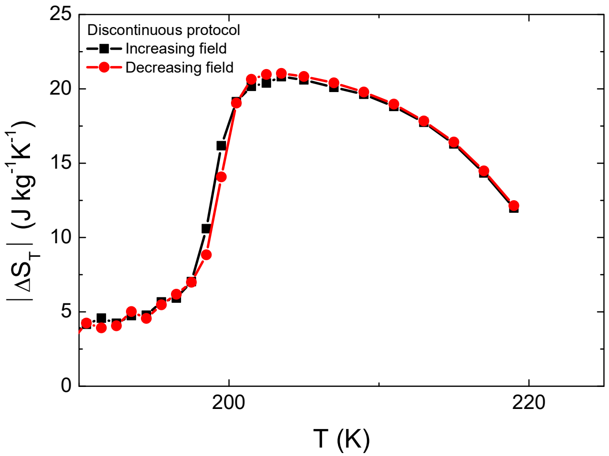


Hysteresis ?

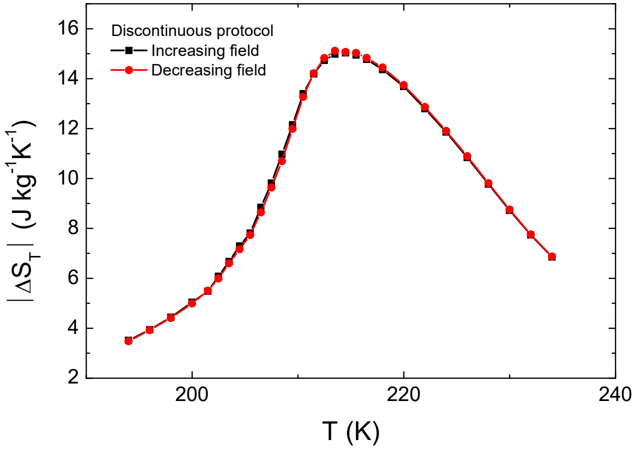
Si 1.4



Si 1.6



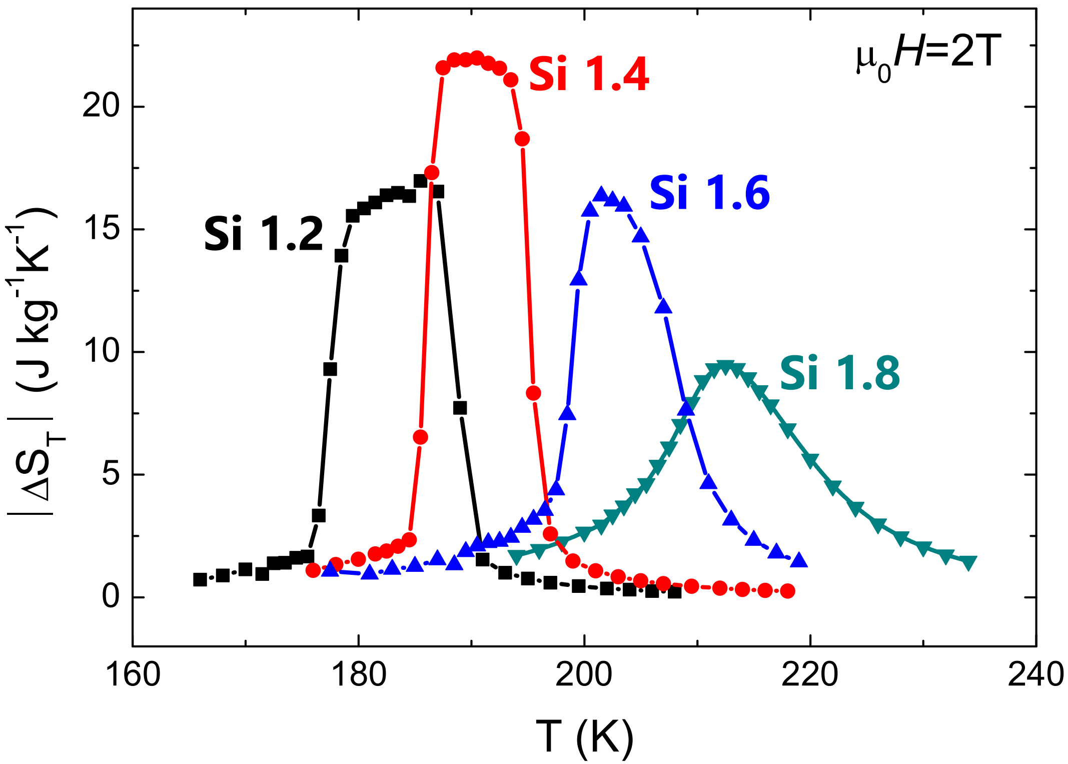
Si 1.8



$LaFe_{13-x}Si_x$

with x = 1.2 – 1.8

Denoted by their Si content

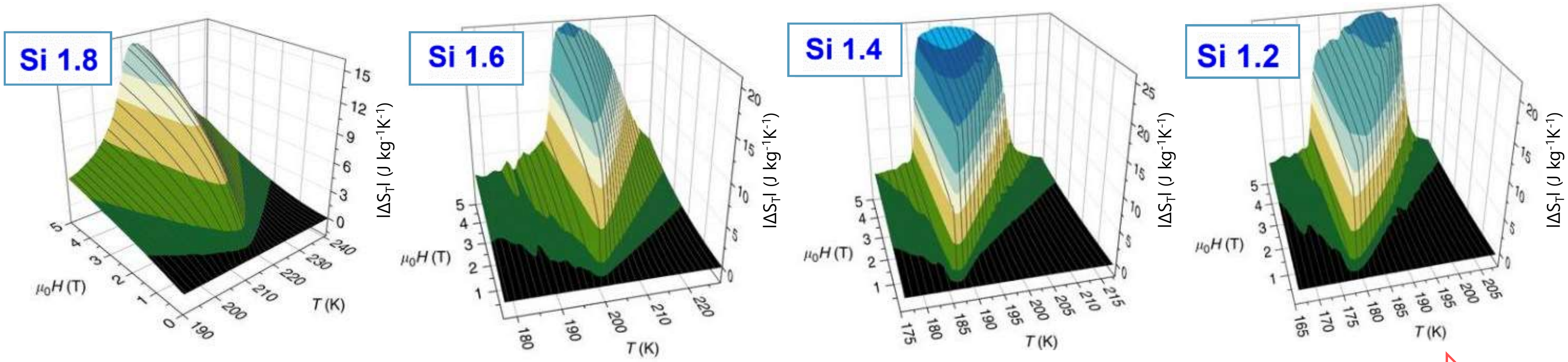


can we identify

their MCE type

from shapes of their MCE curves?

Curve Shape ?



Caret-type MCE
SOPT

Abrupt MCE ?
FOPT
or SOPT

Abrupt MCE
FOPT

Nature Communications 9, 2680 (2018)

- $LaFe_{13-x}Si_x$ alloys are examples of magnetocaloric materials with the weak FOPT
- The transition from
  FOPT→ SOPT is *gradual* and the hysteresis associated with the FOPT is low

$LaFe_{13-x}Si_x$

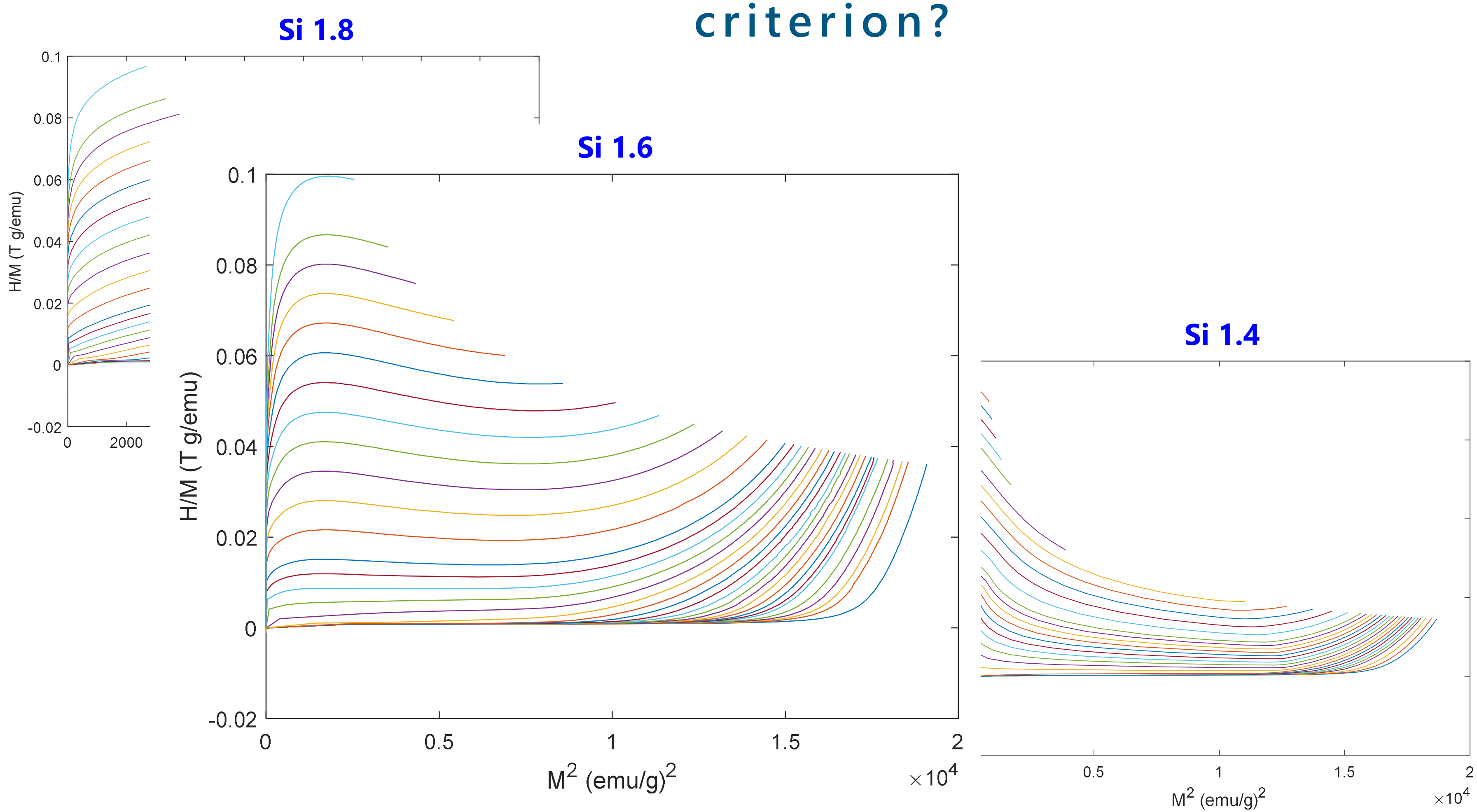
Next Technique

can we identify

their MCE type

from their Arrott plots?

Banerjee´s criterion?



$LaFe_{13-x}Si_x$

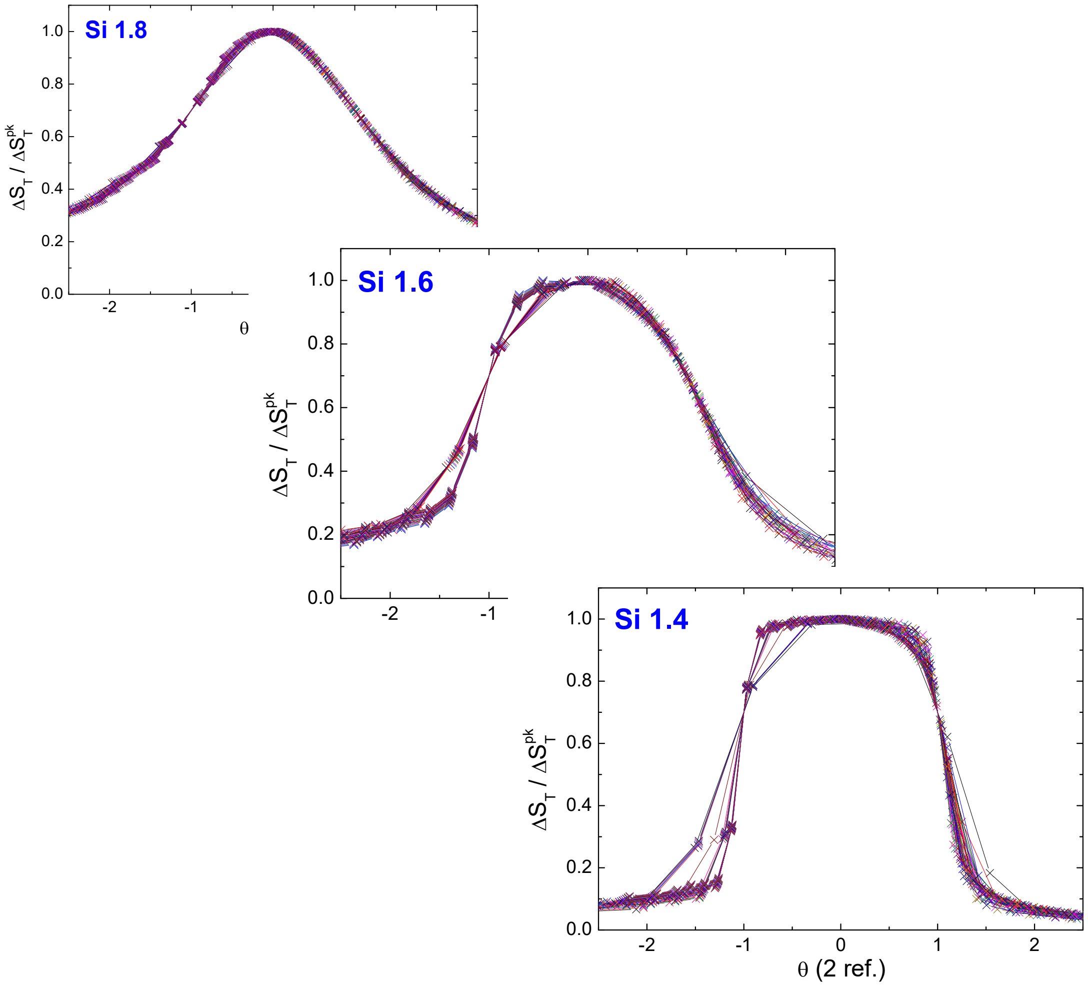
Next Technique

can we identify

their MCE type

from universal curves?

J. Phys. D: Appl. Phys. 50, 414004 (2017)



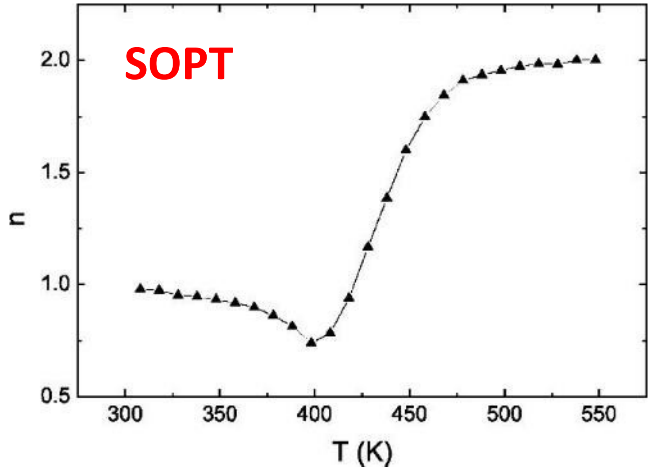
Magnetic field dependence

Int. J. Refrig. 33, 465–73 (2010)

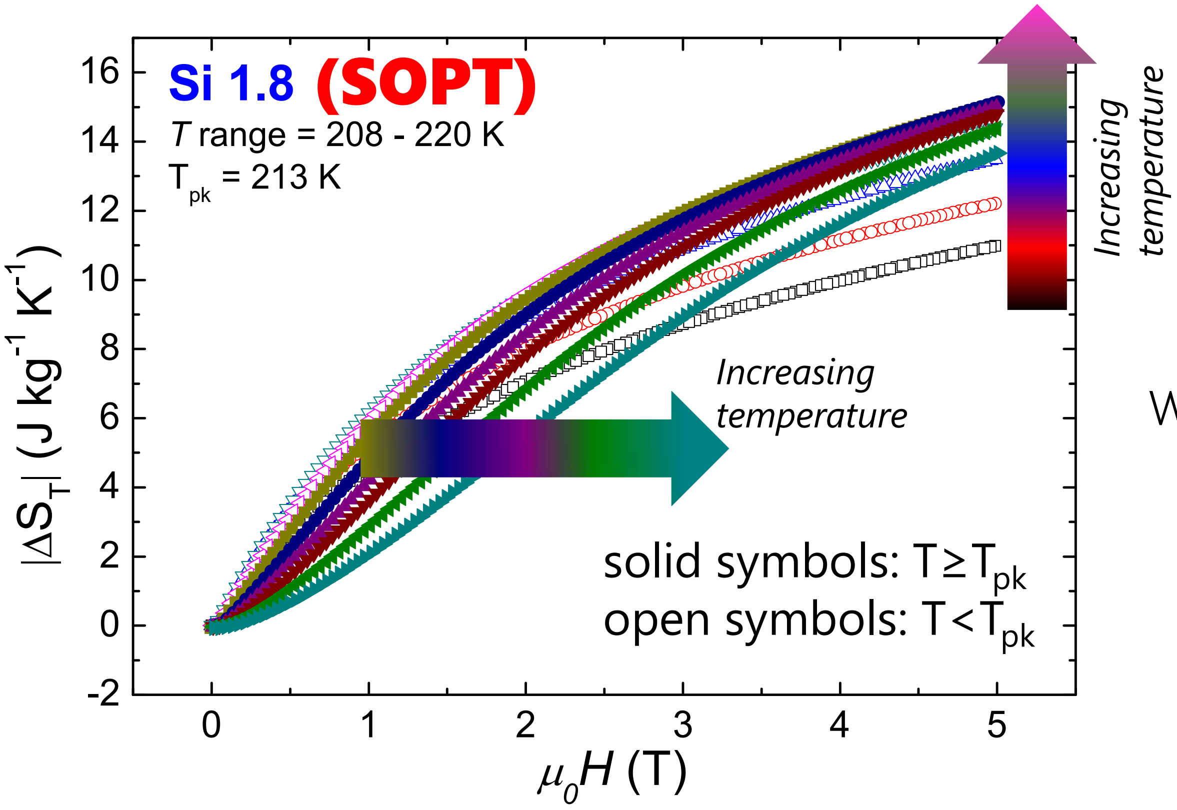
$$\Delta S_T \propto H^{n}$$

where n depends on temperature and field

$$n = \frac{dln|\Delta S_T|}{dlnH}$$

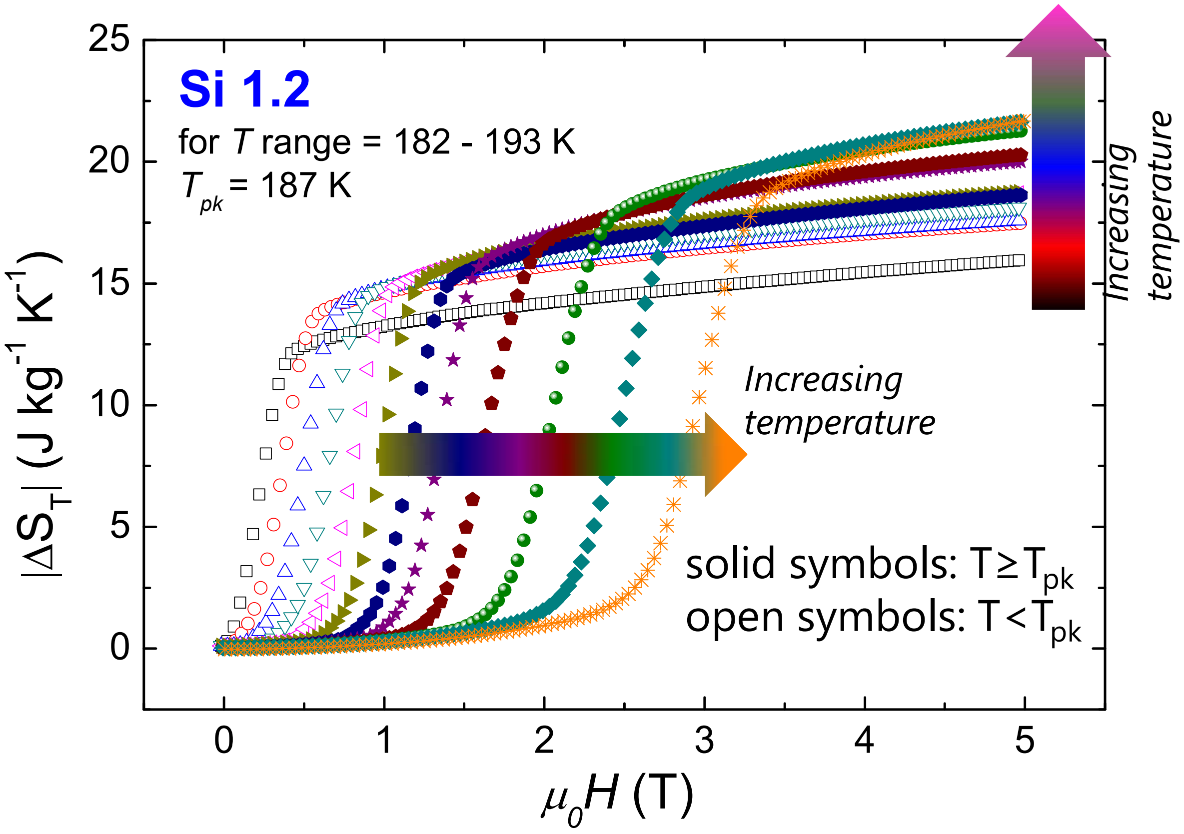


Magnetic field dependence of ΔS_T

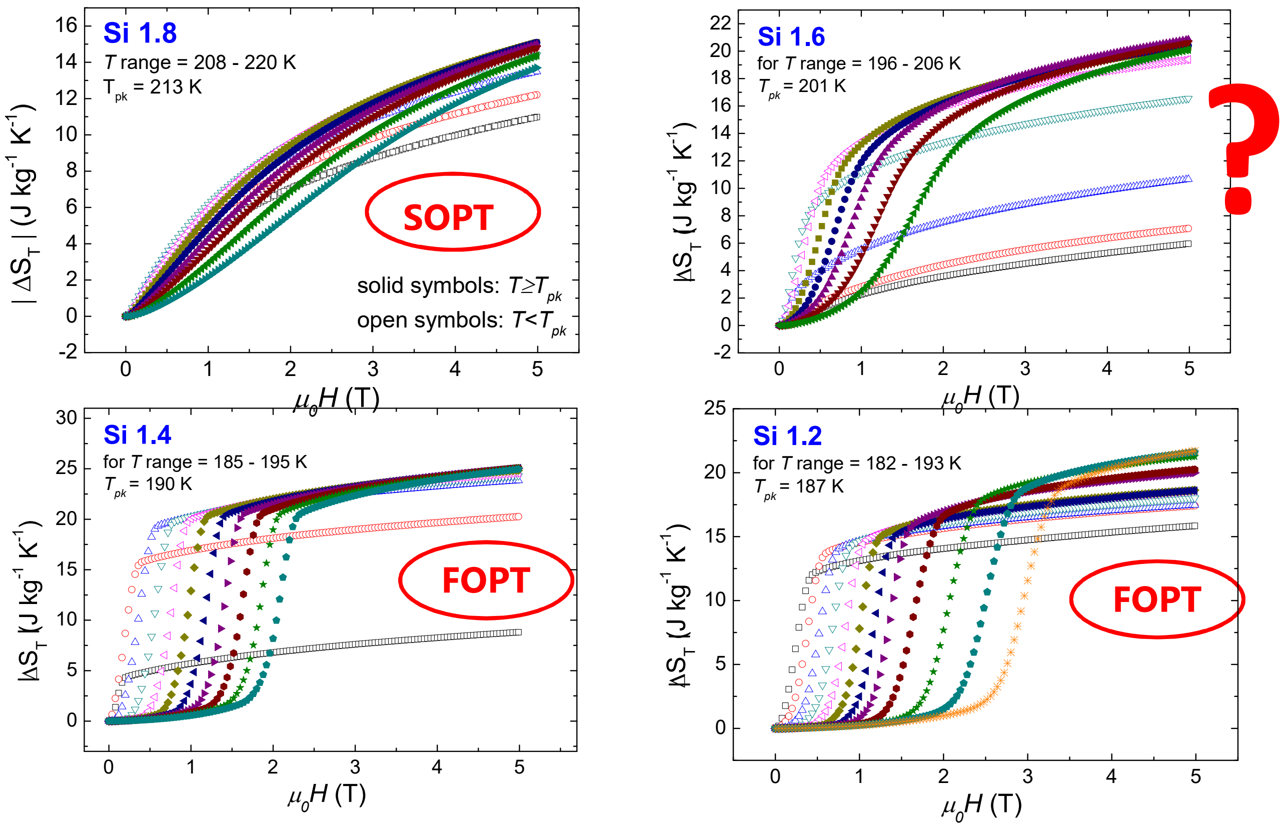


What about for sample with **FOPT?**

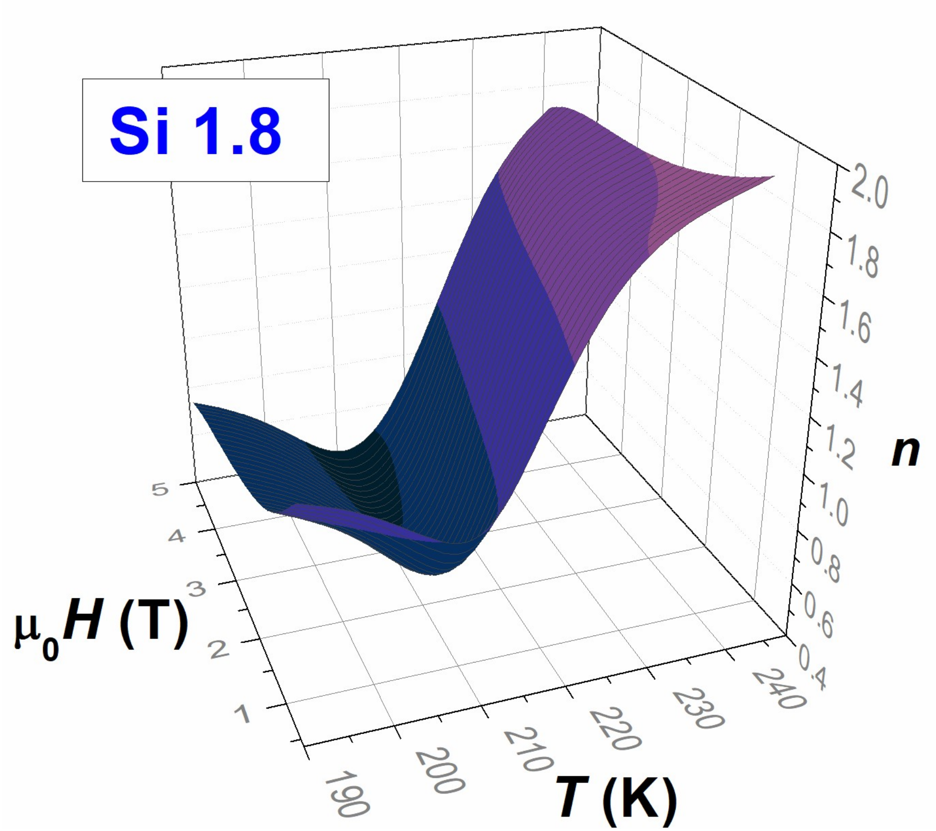
Magnetic field dependence of ΔS_T

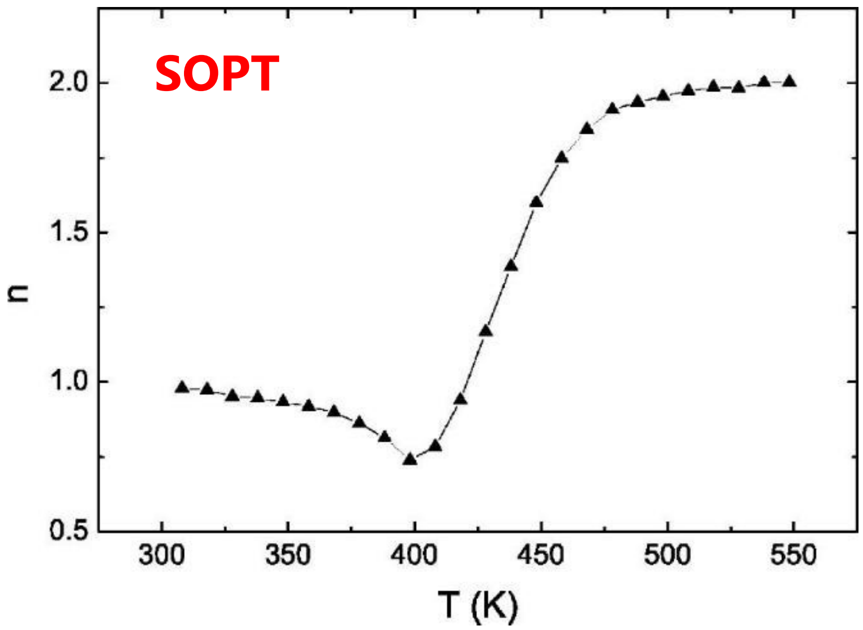


$\Delta S_T \propto H^n$?



Magnetic field dependence of *n*





Int. J. Refrig. 33, 465–73 (2010)

Exponent $n \propto H^n$?

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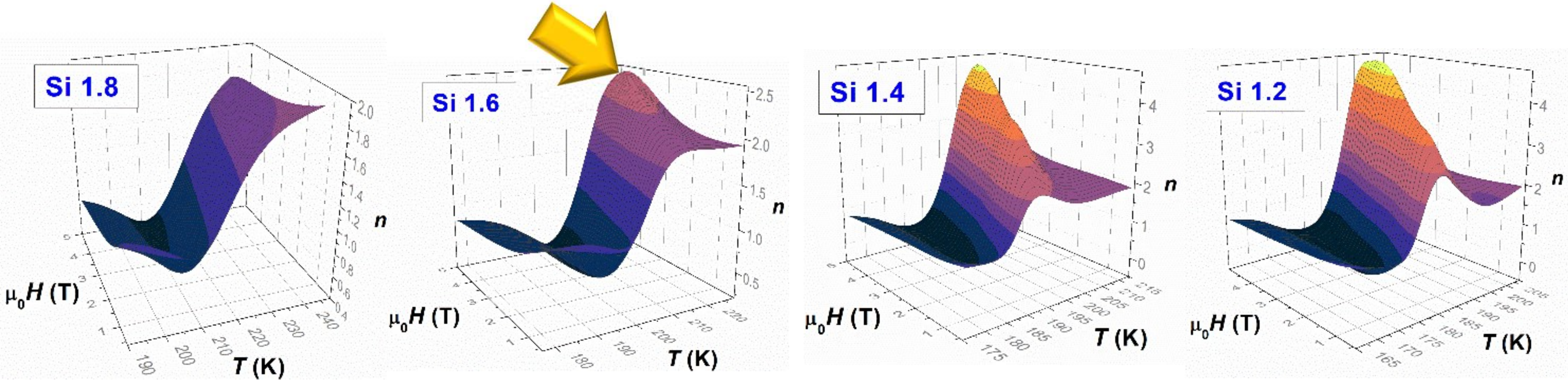


Now we can clearly see

Si 1.6 is FOPT

material

Is this in agreement with theory?

Using Bean and Rodbell model

To simulate from: 1st → 2nd order thermomagnetic phase transitions

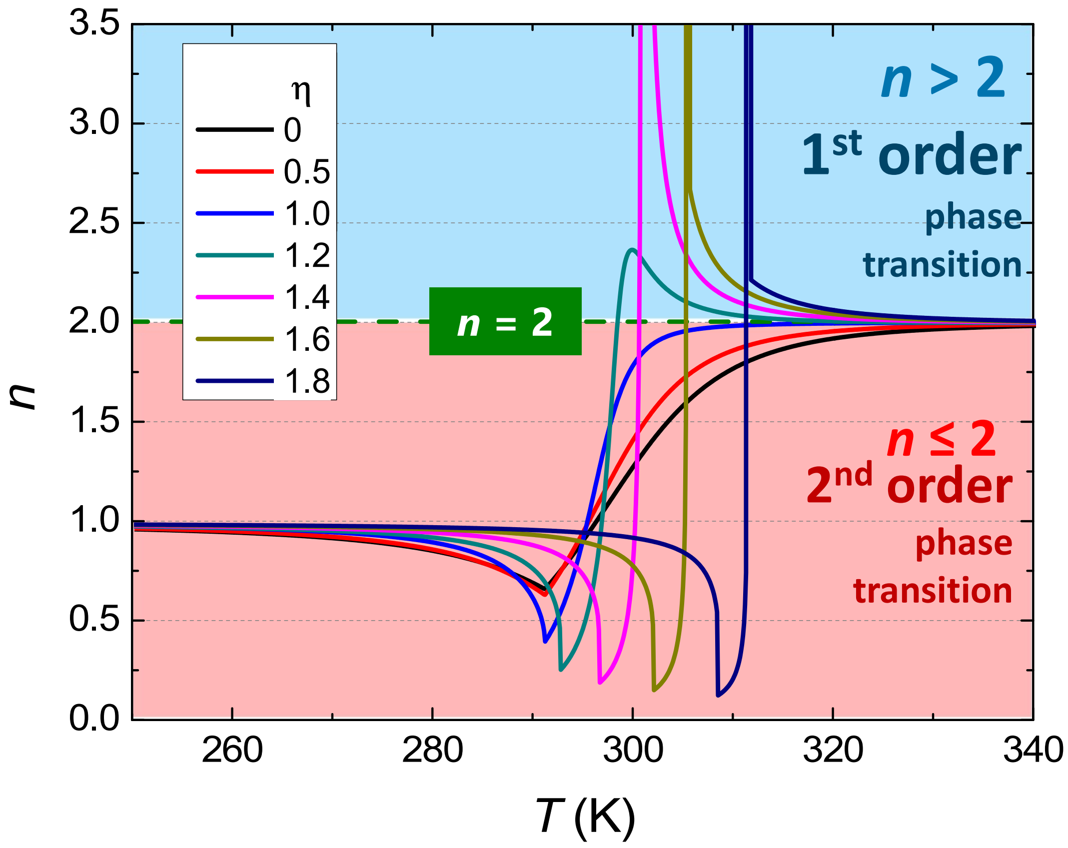
- η is used as the parameter governing the nature of the magnetic phase transition

  for $0 \leq \eta < 1$: 2nd order phase transition

  for $\eta = 1$: critical point of SOPT

  for $\eta > 1$: 1st order phase transition

Phys. Rev. B **126**, 104 (1962)
Nature Comm. 9, 2680 (2018)



Multiphase composites

$La(Fe,Mn,Si)_{13}H_{1.6}$

(FOPT)

with distribution of transition temperatures

- **Case 1:** single sample (but distributed transition *T* from various grains) embedded in epoxy matrix
- **Case 2:** Pellet of mixed samples with distributed transition *T*

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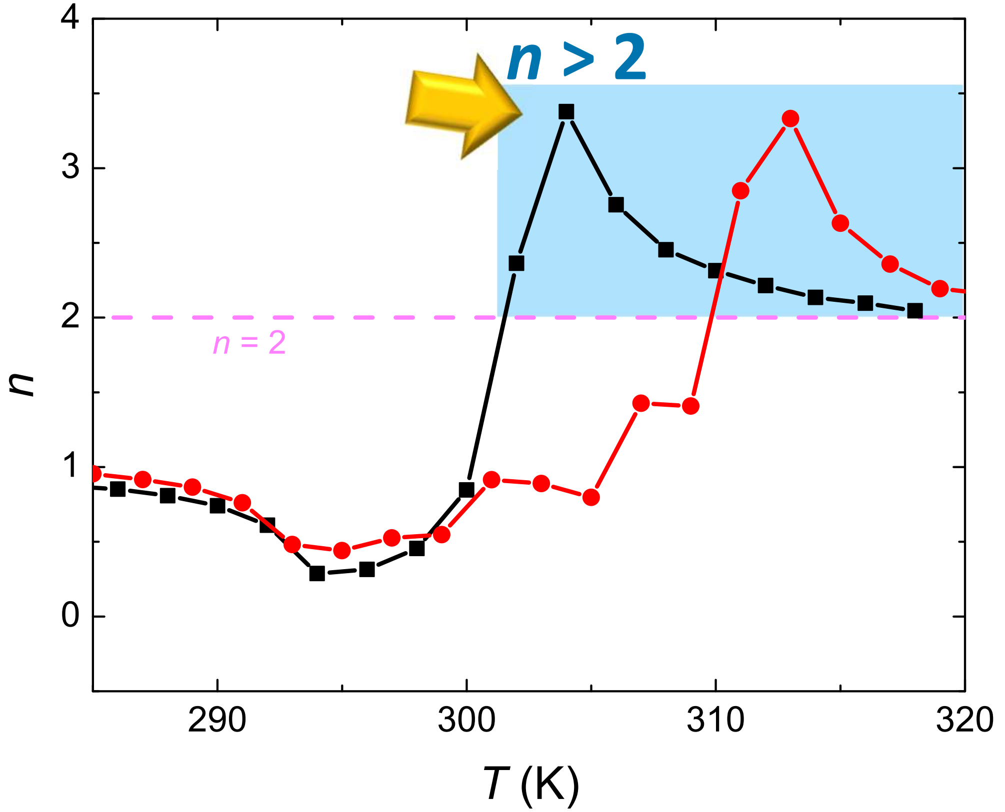
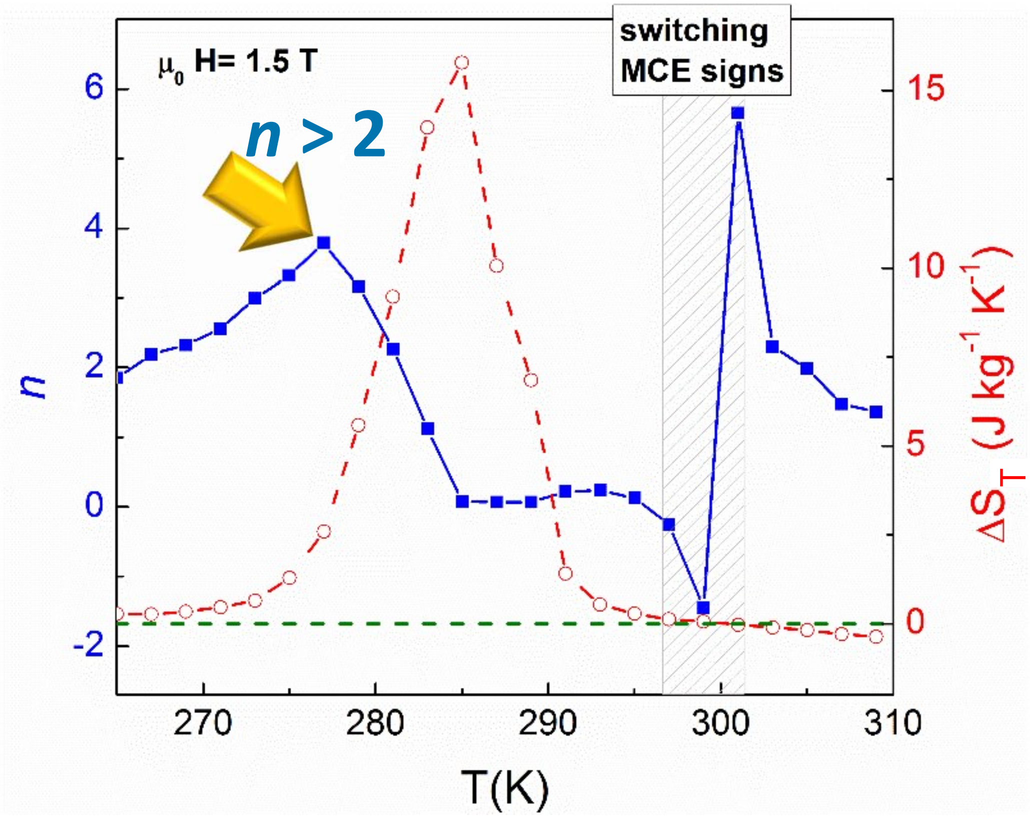


Heusler-type



$Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$

Heusler alloy

- Low *T*: Inverse MCE
- High *T*: Conventional MCE

Nature Communications 9, 2680 (2018)

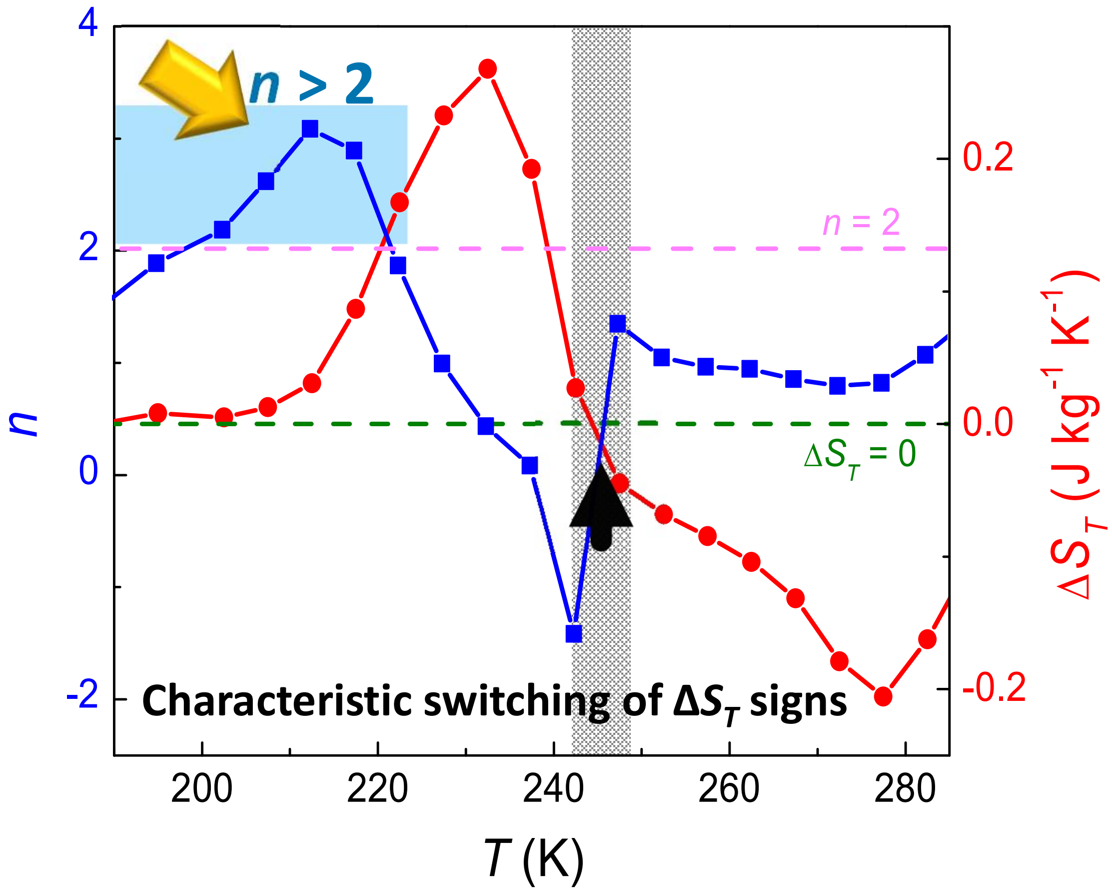
Cobaltites

$GdBaCo_2O_{6-\delta}$

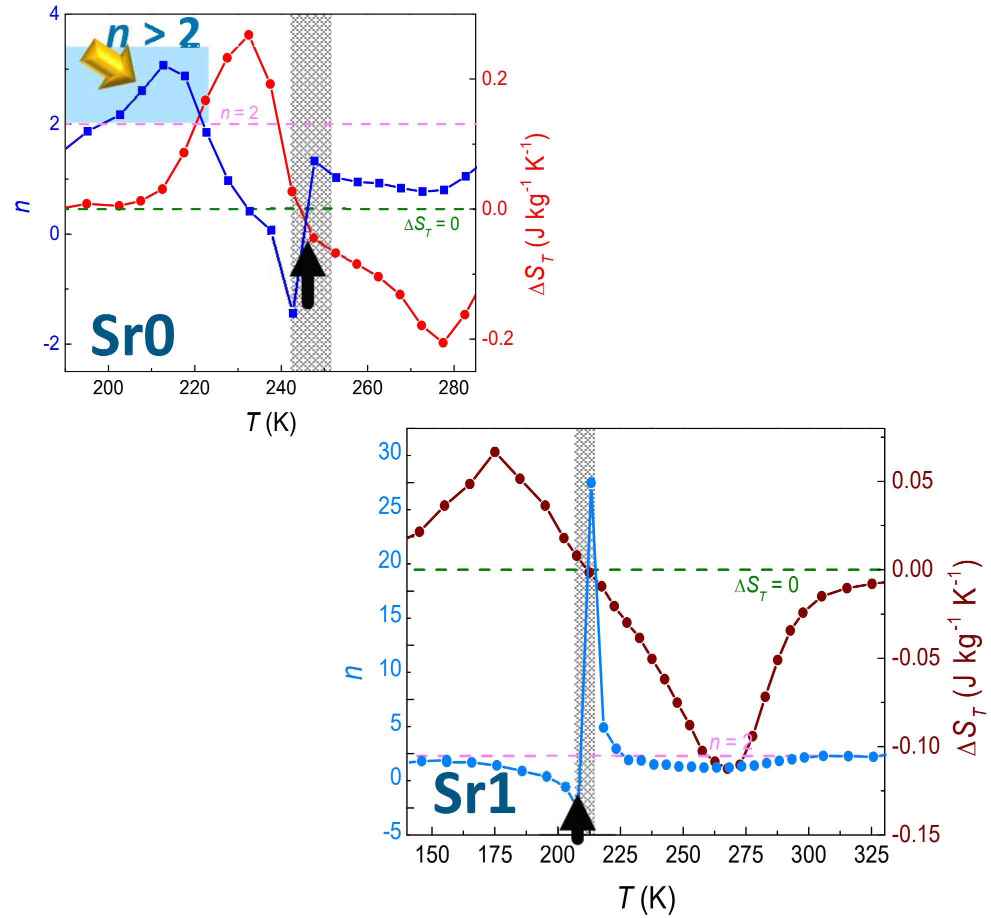
perovskite cobaltite

- Low *T*: AFM-FM
- High *T*: FM-PM

J Alloys Compds. 777, 1080 (2019).



Cobaltites



$GdBa_{1-x}Sr_xCo_2O_{6-\delta}$

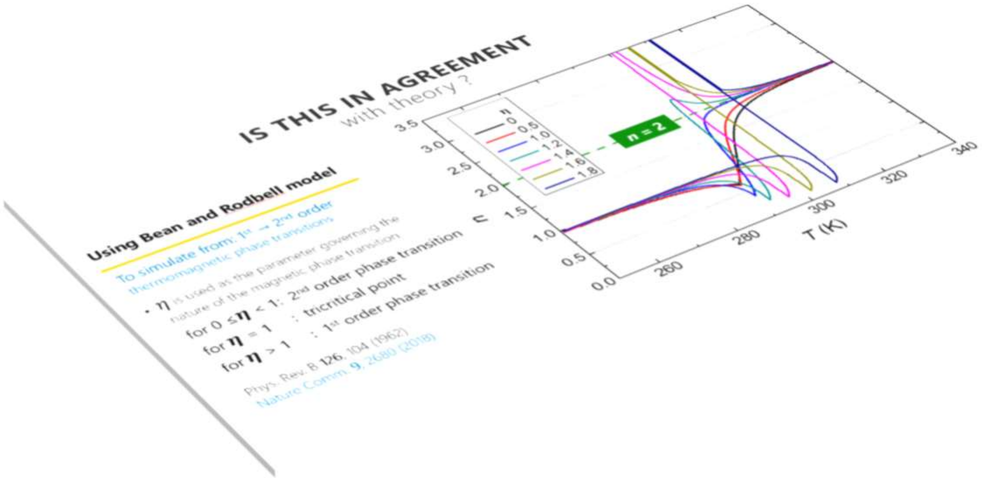
perovskite cobaltite

- Low *T*: AFM-FM
- High *T*: FM-PM

J Alloys Compds. 777, 1080 (2019).

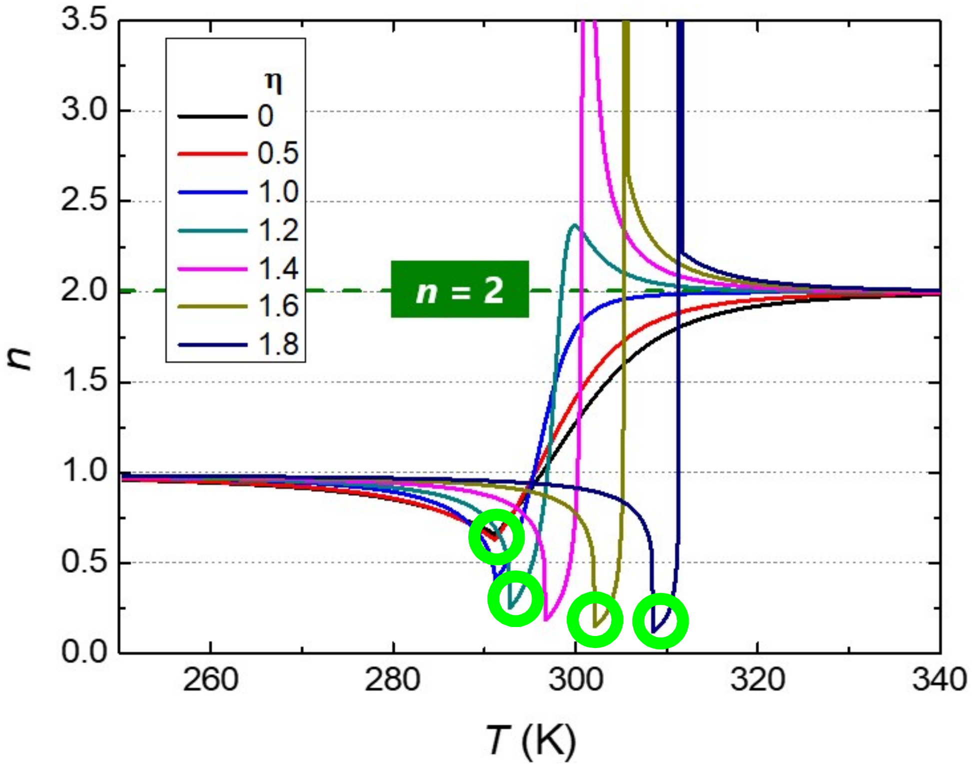
Field dependence exponent *n*

Can they do more?



Field dependence exponent *n*

Can they do more?



Field dependence exponent *n*

Can they do more?

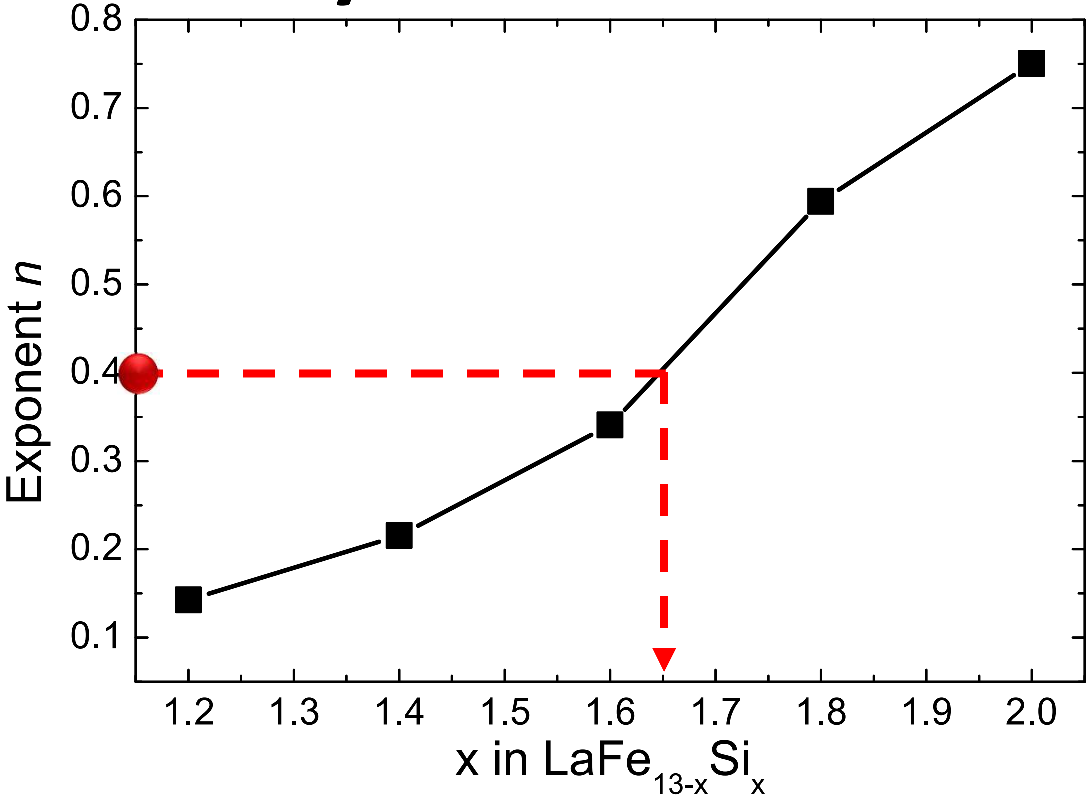
$\eta > 1$: 1st order phase transition (FOPT)

$\eta = 1$: critical point of SOPT where exponent $n = 0.4$

$0 \le \eta < 1$: 2nd order phase transition (SOPT)

J. Phys. D: Appl. Phys. 50, 414004 (2017)

Phys. Chem. Phys. Chem. 19, 3582-95 (2017)



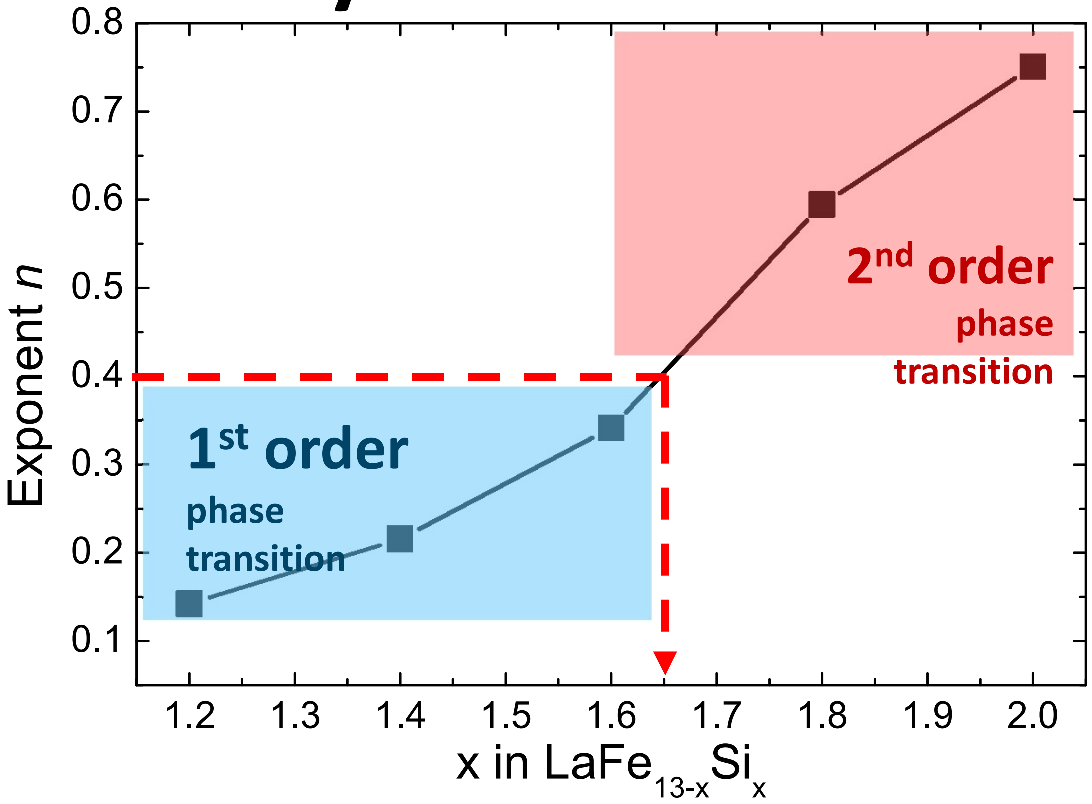
Field dependence exponent *n*

Can they do more?

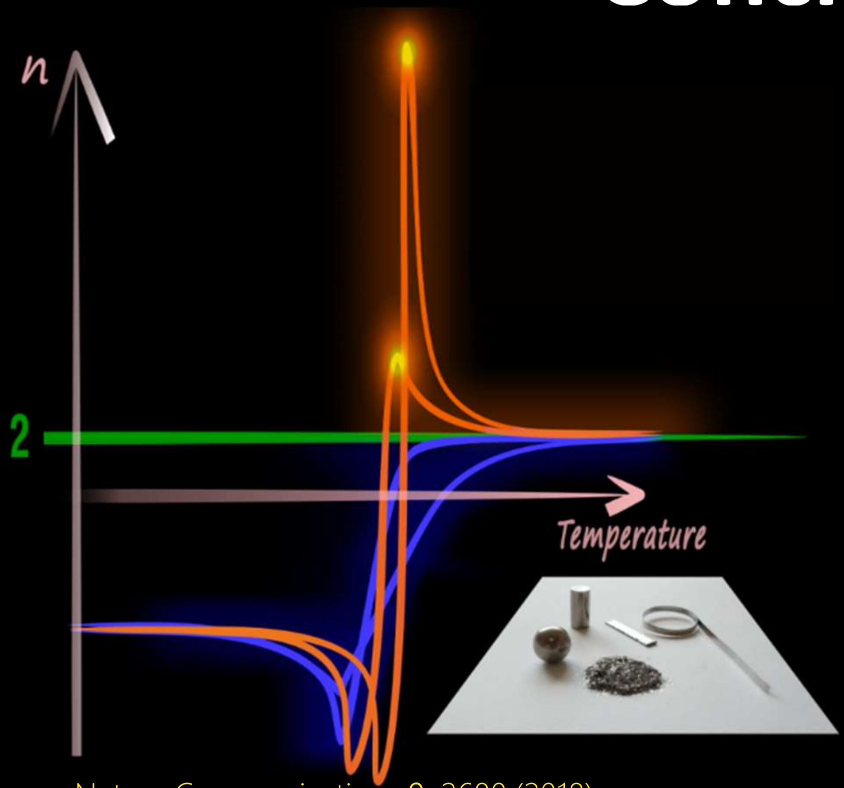
Predicts the critical composition

J. Phys. D: Appl. Phys. **50**, 414004 (2017)

Phys. Chem. Phys. Chem. **19**, 3582-95 (2017)



Conclusions



Nature Communications 9, 2680 (2018)

exponent *n* > 2
near the transition
is a fingerprint of 1st order phase transition

This constitutes a
quantitative method
to identify the order of thermomagnetic phase transition
and is a method that is
GENERAL

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