Magnetocaloric Effect: From Energy Efficient Refrigeration to Fundamental Studies of Phase Transitions

Victorino Franco
Universidad de Sevilla
2019 IEEE Magnetics Society Distinguished Lecture
vfranco@us.es
• IEEE
  • The world’s largest technical professional organization dedicated to advancing technology for the benefit of humanity
  • Sections at different regions worldwide
  • Societies and Technical Councils
  • Student branches
  • Mentoring program
  • IEEE Collabratec

• IEEE Magnetics Society
  • Publishes IEEE Transactions on Magnetics & IEEE Magnetics Letters
  • Organizes MMM and Intermag Conferences + ...
  • Summer School for graduate students
  • Chapter activities
  • Distinguished Lecturer program
Cathedral and Giralda

World records
Largest Gothic Cathedral
3rd largest church

UNESCO World Heritage
Plaza de España
Tourists from all over the World...
and beyond
Royal Tobacco Factory

Stone-built in the XVIII century
First tobacco factory established in Europe
The most important one (produced 75% of the cigarettes consumed in Europe)
Bizet’s opera Carmen was set here
Universidad de Sevilla

Founded in 1505

~ 74,000 students; 4,500 academic staff

2nd largest in Spain in number of students

8th in Spain in scientific production

1st in Spain in international patents
MCE: Materials research & phase transitions

- **Energy**
- **What is MCE?**
- **Magnitudes**
- **Types of materials**
- **How to measure?**
- **How to compare?**
- **Phase transitions**
- **Hysteresis**
- **Nanomaterials**
Magnetic materials for energy applications

- Using non-renewable energy sources is a problem
- Non-efficient conversion is even worse
Influence on Earth? 1884-2018
MAGNETIC REFRIGERATION:
towards an increased energy efficiency

- Residential and Commercial sectors account for ~42% of the total energy consumption
  - More than 50% for HVAC

- Larger energetic efficiency
  - 60% vs. 40% of the theoretical limit

- Environmental benefits
  - No greenhouse or ozone depletion gas

- Vibration and noise
  - Special applications

Room temperature magnetic refrigeration $\rightarrow$ phase transitions
V. Franco, J.S. Blázquez, J.J. Ipus, J.Y. Law, L.M. Moreno-Ramírez, A. Conde,
Progress in Materials Science, 93 (2018) 112
What is magnetocaloric effect?

• Link to offline video
Real experiment
Real life applications

GE prototype 2014
Real life applications

Haier + Astronautics Corporation of America + BASF @ CES Las Vegas 2015
Not only fridges

- Thermomagnetic motors
- Cooling data centers
- E-mobility
- MRI switchable contrast
- Controlled drug delivery
- Transient cooling
**Characteristic parameters**

**Magnetic entropy change**

\[ \Delta S_M = \mu_0 \int_0^{H_{\text{max}}} \left( \frac{\partial M}{\partial T} \right)_H \, dH \]

**Adiabatic temperature change**

\[ \Delta T_{ad} = -\mu_0 \int_0^{H_{\text{max}}} \frac{T}{C_{p,H}} \left( \frac{\partial M}{\partial T} \right)_{p,H} \, dH \]
**Characteristic parameters**

**Magnetic entropy change**
\[ \Delta S_M = \mu_0 \int_0^{H_{\text{max}}} \left( \frac{\partial M}{\partial T} \right)_H \, dH \]

**Adiabatic temperature change**
\[ \Delta T_{\text{ad}} \approx -\frac{T \Delta S_M}{C_{p,H}} \]

**Refrigerant capacity**
\[ RC(\Delta H) = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_M(T, \Delta H) \, dT \]

Amount of heat that can be transferred between reservoirs
Dangerous to use for shallow peaks

**Coef. of Refrigerant Performance**
\[ CRP(H_{\text{max}}) = \frac{\Delta S_M \Delta T_{\text{rev}}}{\mu_0 \int_0^{H_{\text{max}}} M \, dH} \]


**Temperature averaged Entropy Change**
\[ TEC(\Delta T_{\text{lift}}) = \frac{1}{\Delta T_{\text{lift}}} \max_{T_{\text{mid}}} \left\{ \int_{T_{\text{mid}} - \frac{\Delta T_{\text{lift}}}{2}}^{T_{\text{mid}} + \frac{\Delta T_{\text{lift}}}{2}} \Delta S_M(T') \, dT' \right\} \]

TYPEs OF MCE MATERIALS

Types of MCE

SOPT

- Moderate MCE peak
- Broad temperature span
- No hysteresis
- Examples: Gd, amorphous alloys...

FOPT

- Large MCE peak
- Reduced temperature span
- Hysteresis
- Magnetostructural transitions require large field
- Examples: Gd$_5$Si$_2$Ge$_2$, La(FeSi)$_{13}$, MnFePAs, Heusler alloys
Measurement techniques

Direct

- Temperature sensor in contact with the sample
  - Thermal mass of the sensor has to be much lower than that of the sample
  - Not broadly available as commercial systems
  - Low signal for low field
- Possible options
  - AC techniques
  - Mirage effect
  - Pulsed fields
  - Recalibration of sensor measurements
Measurement techniques

- Magnetometer with variable temperature option

\[ \Delta S_M = \mu_0 \int_0^{H_{\text{max}}} \left( \frac{\partial M}{\partial T} \right)_H dH \]
Measurement techniques

- **Direct**
- **Indirect**

### Calorimeter with applied magnetic field

\[
S_H(T) = S_{0,H} + \int_{0}^{T} \frac{C_H(T)}{T} \, dT
\]

Cannot reach 0 K

\[
S_{H}^{ap}(T) \approx \frac{1}{2} C_H(T_{ini}) + \int_{T_{ini}}^{T} \frac{C_H(T)}{T} \, dT
\]
Measurement techniques

Direct

Indirect

Magnetic

Calorimetric

Specific entropy (J kg\(^{-1}\) K\(^{-1}\))

Temperature (K)

- Direct
- Indirect
- Magnetic
- Calorimetric

\[ \Delta S = \Delta T \]

\[ \Delta T_{ad} \]

\[ \Delta S_M \]
Measurement techniques

Direct

Indirect

Magnetic

Calorimetric

There is an optimal value for which we do not have to reach 0 K and prevents errors

\[ S_H^a p(T) \approx \frac{1}{2} C_H(T_{ini}) + \int_{T_{ini}}^{T} \frac{C_H(T)}{T} \, dT \]

\( T_{ini} \) plays a very important role

Beware of the measurement protocol!!!
Field dependence of $\Delta S_M(H)$
(AKA: how to compare with data from the literature)

- Data evolve differently with field for different $T$
- Usual assumption: linear behavior
Why not using a linear approach for the value of the peak?

Description of $\Delta S_M(H)$

Experimental data

$|\Delta S_M^{pl}| (J \cdot K^{-1} \cdot kg^{-1})$

$H (T)$
Description of $\Delta S_M(H)$

Why not using a linear interpolation?

Error: ~24 %
Description of $\Delta S_M(H)$

Why not using a linear extrapolation?

Error: \( \sim 30\% \)
Description of $\Delta S_M(H)$

A power law represents properly the data
TYPES OF MCE

SOPT

- Universal scaling

- Critical exponents

MATERIALS

FOPT

- How to know if it is FOPT?

- Critical point of the SOPT
Data reduction

\[ |\Delta S_M| \text{ (J kg}^{-1} \text{ K}^{-1}) \]

\[ T \text{ (K)} \]
Field dependence of $\Delta S_M(H)$

$$\Delta S_M \propto H^n \quad n = \frac{d \ln |\Delta S_M|}{d \ln H}$$

- $T \ll T_C$: $n=1$
- $T \gg T_C$: $n=2$
- $T = T_C$: $n = 1 + \frac{1}{\delta} \left( 1 - \frac{1}{\beta} \right)$

Universal curve for the field dependence?

- Different characteristic regions of $n$
- The temperature dependence of $\Delta S_M$ also changes above and below $T_C$
- Phenomenological universal curve:
  - Normalization of $\Delta S_M$
  - Rescaled temperature using 2 reference points

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C); & T \leq T_C \\ (T - T_C)/(T_{r2} - T_C); & T > T_C \end{cases}$$
“Measurements”
for different applied fields
Selection of equivalent points
(with respect to the peak)
Rescale (normalize) the vertical axis
Rescale the temperature axis

\[ \theta = \begin{cases} 
-\frac{(T - T_C)}{(T_{r1} - T_C)}; & T \leq T_C \\
\frac{(T - T_C)}{(T_{r2} - T_C)}; & T > T_C
\end{cases} \]
Experimental results

96 curves; 0.25 – 1.5 T

Spin freezing transition
in core-shell nanoparticles: field dependence

V. Franco, A. Conde, D. Sidhaye, B.L.V. Prasad, P. Poddar, S. Srinath, M.H. Phan, H. Srikanth,
MCE of different alloy series

Field dependence is eliminated
Temperature dependence is related to the critical exponents
Similar values of the critical exponents

Universal curve for $\Delta S_M$
Universal curve for $\Delta S_M$

What is this good for?
Extrapolation using the universal curve

Fe$_{91-x}$Mo$_8$Cu$_1$B$_x$ ($x=15, 17, 20$)

Overlapping magnetic phenomena: the use of $n$

$\text{Er}_{0.15}\text{Dy}_{0.85}\text{Al}_2$

Overlapping magnetic phenomena: universal curve

$\text{Er}_{0.15}\text{Dy}_{0.85}\text{Al}_2$

Noise reduction

Problem:
• Experimental data might be noisy
  • Derivatives
• Smoothing would alter the shape of the peak

Solution:
• Universal scaling?
Noise reduction

Problem:
• Experimental data might be noisy
  • Derivatives
• Smoothing would alter the shape of the peak

Solution:
• Universal scaling?
Noise reduction

Problem:
- Experimental data might be noisy
  - Derivatives
- Smoothing would alter the shape of the peak

Solution:
- Universal scaling?
Noise reduction

Problem:
- Experimental data might be noisy
  - Derivatives
- Smoothing would alter the shape of the peak

Solution:
- Universal scaling?
Noise reduction

Problem:
- Experimental data might be noisy
  - Derivatives
- Smoothing would alter the shape of the peak

Solution:
- Universal scaling?
The physics behind the universal curve: Scaling

• 2nd order phase transitions scale:
  • For a given universality class, all magnetization curves collapse
  • MCE should collapse

• Theoretician’s point of view: *if EOS and critical exponents are known, the universal curve can be calculated*

• Our point of view: *the universal curve can be found without knowing neither EOS, nor the critical exponents*
Features which are EOS-independent

- Scaling EOS

\[ \frac{M}{|t|^\beta} = m_{\pm} \left( \frac{H}{|t|^\Delta} \right) \]

- Magnetic entropy change and temperature axis scale with field

\[ \Delta S_M / a_M = H^{\frac{1-\alpha}{\Delta}} s(t / H^{1/\Delta}) \]

- By using the reference temperatures there is no need to know the critical exponents or the EOS to use this scaling

Critical Exponents

• Describe the behavior of physical quantities near continuous phase transitions.
• They are universal
  • do not depend on the details of the physical system,
  • depend only on some of its general features, e.g.
    • dimensionality of the system
    • range of the interactions
• Kenneth G. Wilson, Nobel Prize in Physics 1982 “for his theory for critical phenomena in connection with phase transitions”
\begin{array}{|c|c|}
\hline
\textbf{Magnitude} & \textbf{Exponent} \\
\hline
\Delta T_{ad}^p & 1/\Delta \\
\hline
T_r & 1/\Delta \\
\hline
T_{pk} - T_C \; \text{(not mean field)} & 1/\Delta \\
\hline
T_{pk} - T_C \; \text{(mean field)} & 0 \\
\hline
\Delta S_M \; (T = T_c) & 1 + 1/\delta \; (1 - 1/\beta) = (1 - \alpha)/\Delta \\
\hline
\Delta S_M^p & 1 + 1/\delta \; (1 - 1/\beta) = (1 - \alpha)/\Delta \\
\hline
RC_{\text{Area}} \; \text{or} \; RC_{\text{FWHM}} & 1 + 1/\delta \\
\hline
\end{array}

In the mean field case, $\alpha=0 \Rightarrow \Delta T_{ad}$ and $\Delta S_M$ would have the same field dependence

Field dependence of the reference temperature

$T_c(K)$

$H^{1/(\beta+\gamma)}$

$\text{Fe}_{78}\text{Co}_5\text{Zr}_6\text{B}_5\text{Ge}_5\text{Cu}_1$
Field dependence of the peak entropy change

\[ \Delta S_{pk}^M = A H^n \]

- \( A = -1.0434 \pm 0.0006 \)
- \( n = 0.764 \pm 0.001 \)
- \( R^2 = 0.99985 \)
Field dependence of the refrigerant capacity

\[ RC_{FWHM} \propto H^{1 + \frac{1}{\delta}} \]

The problem

• Gd$_5$Si$_2$Ge$_2$ has a structural phase transition:
  • The low temperature phase disappears before it reaches its Curie temperature.
• How to determine $T_c$?
Solution?

• Use Arrott plot only on one side
• Extrapolate to higher temperatures
• Anomalous values of the critical exponents ($\beta=2.2; \gamma=0.9$)
• Reason: A-N plots are approximately linear, even for large variations of the critical exponents

Alternative solution

• **Suppress the magneto-structural transition** by proper doping, as was done for the case of the Gd$_5$Si$_2$Ge$_2$ compound

• In the undoped compound, the low temperature phase is orthorhombic and it transforms to a monoclinic phase at temperatures above 270 K.

• In the Gd$_5$Si$_2$Ge$_{1.9}X_{0.1}$ doped alloy (with X= Al, Cu, Ga, Mn, Fe, Co) the **monoclinic phase is entirely suppressed** in the case of the first four of these metal additives, and is **mostly suppressed in the cases of the latter two of these additives**.

V. Franco, A. Conde, V. Provenzano, R.D. Shull, JMMM 322 (2010) 218
Universal curve

• Evidence of a second order phase transition
Kouvel-Fisher method

• Iterative process:
  • Arrott-Noakes plot ($M^{1/\beta}$ vs $(H / M)^{1/\gamma}$)
  • $M_0$ and $\chi_0$ via extrapolation (intersection with axes)
  • Define
    \[
    X(T) = \chi_0^{-1} \left( \frac{d \chi_0^{-1}}{dT} \right)^{-1} = \left( T - T_C \right) / \gamma
    \]
    \[
    Y(T) = M_0 \left( \frac{dM_0}{dT} \right)^{-1} = \left( T - T_C \right) / \beta
    \]
  • Extract exponents and $T_c$
  • Iterate until convergence
A fully second order case

Arrott-Noakes plot for the Al doped Gd$_5$Ge$_2$Si$_2$ alloy using the exponents extracted from the Kouvel-Fisher analysis
Scaling of MCE using K-F exponents

\[ T_r (K) = (\mu_0 H)^{1/(\beta_1)} (T^{0.69}) \]

\[ RC_{FWHM} (J/Kg) = (\mu_0 H)^{1/\beta_0} (T^{1.26}) \]
Arrott plot using exponents obtained from MCE

Exponents were extracted from the scaling of the magnetic entropy change
No qualitative difference

- Differences between critical exponents obtained in both ways are within error margin
Fe doped Gd$_5$Ge$_2$Si$_2$

Scaling with a single reference temperature does not fully hold
Fe doped Gd$_5$Ge$_2$Si$_2$

Using two reference temperatures allows the collapse $\rightarrow$ mostly second order transition
Arrott plot using exponents obtained from MCE

- K-F method could not be used due to the remaining structural transition
Reduced thermal hysteresis (mostly second order)
## Doped GdSiGe: critical exponents determination

<table>
<thead>
<tr>
<th></th>
<th>$T_c$ (K)</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Gd</td>
<td>293.3</td>
<td>0.381</td>
<td>From 1.196 to 1.24</td>
<td>Measured 3.615 Calculated* from 4.139 to 4.25</td>
</tr>
<tr>
<td>(literature)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-doping</td>
<td>295.5</td>
<td>0.38 [0.4]</td>
<td>1.15 [1.1*]</td>
<td>4.03* [3.5]</td>
</tr>
<tr>
<td>Mn-doping</td>
<td>295.6</td>
<td>0.41 [0.40]</td>
<td>1.05 [1.2*]</td>
<td>3.56* [4.1]</td>
</tr>
<tr>
<td>Ga-doping</td>
<td>289.5</td>
<td>0.34 [0.42]</td>
<td>1.17 [1.3*]</td>
<td>4.44* [4.1]</td>
</tr>
<tr>
<td>Al-doping</td>
<td>293.5</td>
<td>0.38 [0.39]</td>
<td>1.08 [1.1*]</td>
<td>3.84* [3.8]</td>
</tr>
<tr>
<td>Fe-doping</td>
<td>292</td>
<td>[0.3]</td>
<td>[0.9*]</td>
<td>[4]</td>
</tr>
</tbody>
</table>

[ ] MCE; others, Kouvel-Kisher

V. Franco, A. Conde, V. Provenzano, R.D. Shull, JMMM 322 (2010) 218
Hysteresis... who cares?

**Magnetic refrigeration**
- Requires cyclic operation (T and H)
- Thermal hysteresis reduces the cyclic response
- Rate dependent phenomena limits the speed of operation

**Thermomagnetic motor**
- Cyclic operation
- Simulations indicate that performance is enhanced with hysteresis

**Single shot operation**
- Hysteresis might prevent undesirable triggers

---

As in many other aspects of magnetism, hysteresis is not necessarily bad. Characterize it properly in order to
- Minimize it, or
- Make the most out of it

---

How to characterize hysteresis? FORC

• FORC = First Order Reversal Curves
• Initially proposed as a method to identify the Preisach model parameters
• Later extended as a model-independent technique to characterize the irreversibility in magnetic materials magnetization reversal.
Spectral decomposition of the loop using hysterons
Characteristics of a hysteron

- Rectangular loops
- Coercivity $H_c$
- Interaction field $H_u$
- Reversing at $-(H_c+H_u)$ and $(H_c-H_u)$
Determination of the FORC distribution
Determination of the FORC distribution
Determination of the FORC distribution
Determination of the FORC distribution

\[ \rho(H, H_r) = -\frac{1}{2} \frac{\partial^2 M(H, H_r)}{\partial H_r \partial H} \quad (H \geq H_r) \]
H vs T FORC

H FORC
H, H_r plane

\[ \rho(H, H_r) = -\frac{1}{2} \frac{\partial^2 M(H, H_r)}{\partial H \partial H} \quad (H \geq H_r) \]

H_c and H_u
Field sweep

T FORC
T, T_r plane

\[ \rho(T, T_r) = -\frac{1}{2} \frac{\partial^2 M(H, H_r)}{\partial T \partial T} \quad (T \geq T_r) \]

T_h and T_u
Temperature sweep

Time consuming
Heusler alloys

• Structural transition

Austenite (Fm3m)
High temperature phase

Martensite (P4/mmm)
Low temperature phase

• Our sample composition

$\text{Ni}_{45.7}\text{Mn}_{36.6}\text{In}_{13.5}\text{Co}_{4.2}$

• Non-magnetic phase at low T $\rightarrow$ ferromagnetic phase at high T
The transition can be induced by field and temperature

Ni$_{45.7}$Mn$_{36.6}$In$_{13.5}$Co$_{4.2}$

M(H) curves depend on the field and temperature history

→ USE THE APPROPRIATE MEASUREMENT PROTOCOL
Temperature FORC

The transition gets displaced for different fields FORC curves also do
FORC distribution

Obtaining the distribution requires smoothing

While there can be many $T$ values, $T_r$ is more limited

Different smoothing factor along the different axes

Procedure:

Modified Pike's algorithm: fitting to a polynomial surface

linear in $T_r$

quadratic in $T$

using a matrix of 3 data points along the $T_r$ axis and 5 along the $T$ axis.
FORC distribution

• Qualitatively similar behavior
• $T_u$ axis is referred to the center of the loop
• Cooling or heating does not play a remarkable role (asymmetry of the transition)
Existing methods to determine the order of MCE phase transitions

<table>
<thead>
<tr>
<th>Shape of Magnetization curve</th>
<th>Hysteresis</th>
<th>Shape of MCE curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qualitative</td>
<td>Very sensitive to experimental conditions</td>
<td>Qualitative</td>
</tr>
<tr>
<td>Arrott plots</td>
<td></td>
<td>Unreliable</td>
</tr>
<tr>
<td>Universal Curve</td>
<td></td>
<td>Qualitative</td>
</tr>
</tbody>
</table>
Banerjee criterion

• Landau expansion of free energy leads to

\[ H = aM + bM^3 = a'(T - T_C)M + bM^3 \]

• Second order phase transitions have a positive \( b \)

• At the Curie temperature \( a = 0 \)

• The order of the phase transition can be determined from the slope of \( \frac{H}{M} vs M^2 \)

Application to $\text{RCO}_2$

- Banerjee criterion: $\text{DyCO}_2$?

- Calorimetric measurements indicate that $\text{DyCO}_2$ is first order

Universal scaling

Why does this work?

• Banerjee criterion was based on a particular equation of state (Landau expansion)

• Universal scaling does not impose any restriction to the formulation of the equation of state
  • We only assume that second order phase transitions scale
  • The universal curve is a more general approach to determine the order of the phase transition
  • Unfortunately, it relies on qualitative features→subjective
New method for Fingerprinting the order of the phase transition

Bean-Rodbell model
\[ \Delta S_M \propto H^n \]

SOPT

FOPT

OVERSHOOT

New method for fingerprinting the order of the phase transition

\[ \Delta S_M \propto H^n \]

\( \text{SOPT} \)

\( \text{FOPT} \)

Applicable to diverse types of materials

La(FeSi)\(_{13}\)

Simulations

Heusler

A peculiar case

- **GdBaCo$_2$O$_{6-\delta}$**
- perovskite cobaltite
- Low $T$: AFM-FM
- High $T$: FM-PM

Characteristic switching of $\Delta S_T$ signs

A peculiar case

- **GdBa$_{1-x}$Sr$_x$Co$_2$O$_{6-\delta}$**
- Same crystal symmetry for $x=0$ & 1
- Unlike $x=0$, $x=1$ becomes SOPT
How to find the critical point?

**Experimental**

- $\text{LaFe}_{13-x}\text{Si}_x$ samples prepared by suction casting
  - Annealed at 1373 K for 12 h
- Microstructural characterization by XRD and SEM
- $\text{M(H,T)}$ measured in a VSM using two different protocols:
  - Temperature sweeping at different fields
  - Discontinuous isothermal protocol:
    - Heat the sample in zero field above the transition
    - Cool down to measurement temperature in zero field
    - Measure increasing field (also decreasing for control)
- Magnetic entropy change calculated from magnetization measurements
- Adiabatic temperature change measured in a custom made set-up
How to find the critical point?

- Experimental
- MCE response

![Graph showing MCE response for different compositions of La, Fe, and Si. The x-axis represents temperature (T) in Kelvin, ranging from 180 to 260 K, and the y-axis represents the magnetocaloric effect (ΔS_M) in Joules per kilogram Kelvin (J kg⁻¹ K⁻¹). The graph includes markers for different compositions: La_{1.07}Fe_{11.2}Si_{1.8}, La_{1.07}Fe_{11.4}Si_{1.6}, La_{1.12}Fe_{11.6}Si_{1.4}, and La_{1.13}Fe_{11.8}Si_{1.2}. The magnetic field H is set to 2 Tesla (μ_0 H=2T).]
How to find the critical point?

- Experimental
- MCE response
- Field dependence of MCE

![Graph showing the field dependence of MCE with different compositions and their corresponding ΔS_M^pk values.](image)
How to find the tricritical point?

1. Experimental
2. MCE response
3. Field dependence of MCE

Bean-Rodbell model

$$\Delta S_M \propto H^n$$

Scaling holds for SOPT Tricritical

How to find the critical point?

- Experimental
- MCE response
- Field dependence of MCE

High field slope: $n=2/5$ (tricritical) for $x=1.65$

\[ \Delta S_M \propto H^n \]

MCE in Nanomaterials:
a qualitatively different behavior

1D

2D

25 nm

3D
An ensemble of single domain nanoparticles

\[ \Delta S_M = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \]
Combined direct and inverse MCE

Self assembled array of nanowires

MCE in Nanocrystalline alloys:
Not as good as initially expected
Nanocrystallization of Mo-Finemet

Smaller values of the coercivity peak $\rightarrow$ More reduced dipolar interactions

MCE of nanocrystalline Mo-Finemet

- SPM better than paramagnets
- The peak is broadened due to different $T_C$ (sum rule)
- RC does not increase

MCE in Multiphase materials: is there a way of increasing RC?
Non-interacting composite (calculations)
Non-interacting composite (calculations)

\[
\Delta S_M(x, T, H_{max}) = x \Delta S_{M,A} + (1 - x) \Delta S_{M,B}
\]
Non-interacting composite (calculations)

\[ \Delta S_M (x, T, H_{\text{max}}) = x \Delta S_{M,A} + (1 - x) \Delta S_{M,B} \]
If phases have very distant $T_C$, RC diminishes

- There exists $\Delta T_{C,\text{opt}}$

The majority phase should have the largest $T_C$ ($x_{\text{opt}} > 0.5$)

Improvements of RC as large as 83% can be obtained

Optimal values are dependent on $H_{\text{max}}$

---

RC of composite: Comparison with experiments

Fe$_{88-2x}$Co$_x$Ni$_x$Zr$_7$B$_4$Cu$_1$

- Is there a shift in the data?
- Do interactions between phases play a role?

Model material

• Each phase

\[ H^\gamma = a_i (T - T_{Ci}) M^\gamma + b_i M^{\beta + 1} \]

• Composite

\[ M = xM_A + (1 - x)M_B \]

• Interactions (mean field)

\[ H_{eff} = H + \lambda M \]

• \( \Delta S_M \) calculated from Maxwell relation
Influence of interactions

- Peak temperatures are shifted with increasing interaction strength
- Table-like character is enhanced

RCI

\[ \lambda = 0 \text{ g/cm}^3 \]

\[ \lambda = 100 \text{ g/cm}^3 \]
RCI

$\lambda = 0 \text{ g/cm}^3$

$\lambda = 100 \text{ g/cm}^3$
• There is no qualitative change of the curves due to interactions
• There is a shift of $x_{\text{opt}}$ to lower values
The shift found experimentally can be ascribed to interactions between phases.

- \( \lambda \approx 50 \text{ g/cm}^3 \)
- Equivalent to fields between 0.4 T and 0.1 T between \( T_c \)’s

Multilayered structures

A way to control the field dependence of MCE
our reference: Single phase materials
Bulk Gd sample
Field dependence of $\Delta S_M$

$\Delta S_M \propto H^n$

$$n = \frac{d \ln |\Delta S_M|}{d \ln H}$$

- $T \ll T_C$: $n = 1$
- $T \gg T_C$: $n = 2$
- $T = T_C$: $n = 1 + \frac{1}{\delta} \left( 1 - \frac{1}{\beta} \right)$

- The field dependence is the lowest when the MCE signal is the largest
• Deviations from the power law at low fields due to non-saturation
our Goal: To increase the field dependence at the peak \textit{Vla nanostructuring?}
Electrodeposited samples. NiCu alloys

\[ \rho_i, \ t_i, \ w = 100 \text{ nm} \]
\[ \rho_i = \text{Current density} \]
\[ t_i = \text{Deposition time} \]

\[ \rho_i, \ 2t_i, \ 2w = 200 \text{ nm} \]
Fabrication parameters

<table>
<thead>
<tr>
<th>Order</th>
<th>$\rho$ (mA cm$^{-2}$)</th>
<th>t (s)</th>
<th>Ni content (at.%)</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>69.8</td>
<td>68</td>
<td>271</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>40.9</td>
<td>77</td>
<td>371</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
<td>19.5</td>
<td>84</td>
<td>449</td>
</tr>
<tr>
<td>4</td>
<td>6.5</td>
<td>56.5</td>
<td>70</td>
<td>293</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>27.3</td>
<td>81</td>
<td>416</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>84.2</td>
<td>66</td>
<td>248</td>
</tr>
<tr>
<td>7</td>
<td>2.6</td>
<td>122.3</td>
<td>61</td>
<td>193</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>48.4</td>
<td>73</td>
<td>326</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>108.4</td>
<td>64</td>
<td>226</td>
</tr>
</tbody>
</table>
Thermomagnetic curves
Magnetic entropy change

- Peaks are broadened due to the distribution of $T_c$’s
- Longer deposition times enhances this effect
- Overlapping of the different peaks from the different phases

R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432
Field dependece at the peak

A linear field dependence of the peak is achieved

R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432
Field dependence in an extended T range

R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432
Field dependence in an extended T range

Broad T range in which linearity is achieved

R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432
Field dependence of $n$

Difference with bulk composites (H independent)
Can we achieve something similar without compositional gradients?
Sputtered Gd/Ti multilayers: Finite size scaling

\[
\frac{[T_C(\infty) - T_C(L)]}{T_C(\infty)} = CL^{-\lambda}
\]

D. Doblas, V. Franco, A. Conde, A.V. Svalov, G.V. Kurlyandskaya, Materials and Desing 114 (2017) 214
D. Doblas, V. Franco, A. Conde, A.V. Svalov, G.V. Kurlyandskaya, Materials and Desing 114 (2017) 214
Conclusions

MCE is a promising alternative for energy efficient refrigeration

It can be used to characterize phase transitions

For SOPT materials, there is an universal curve for MCE

The order of the phase transition can be determined quantitatively

T-FORC gives valuable information about FOPT materials

There are alternative applications of MCE

Nanomaterials for MCE are less studied than bulk → interesting science
Acknowledgements

Sevilla University

IEEE Magnetics Society

Non-Crystalline Solids group

Numerous collaborators worldwide (cited)

Funding agencies

Industrial partners
Advice for the young out there

- Do not trust black boxes (experimental devices/programs)
- Apply techniques from other fields to your own research
- Attend as many talks as possible, even outside your field
- Discuss topics with colleagues from other areas
- Network with researchers, use mentoring possibilities…