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Thermal relaxations and phase change kinetics in LaFeSi bulk magnetocaloric material

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Abstract

Magnetic cooling (MC) is among the most promising solid-state alternative to vapor-compression refrigeration [1]. It relies on the magnetocaloric effect (MCE) which is a thermal change (i.e. temperature, entropy) induced in a magnetic material by application and removal of a magnetic field. LaFeSi-based alloys figure among the most promising refrigerant for MC because of their large MCE and their non-criticality [6]. Unfortunately, the large MCE exhibited by the LaFeSi is often associated with intrinsic hysteresis and kinetics of the transition. Both reduce the cooling power density of MC devices. Therefore the commonest approach to optimize magnetocaloric material (MCM) has been aimed at the reduction of hysteresis [1]. It needs a meticulous study of the process underlying the phase transition bringing additional

information on the energy landscape probed by the material. Here we focus on the thermal dependence of magnetic properties by studying the phase fraction relaxation, extrapolated from the measurement of magnetization as function of temperature and applied field. Moreover, we study the growth and nucleation process during transition and relaxation in the "Kolmogorov, Johnson and Mehl, and Avrami" framework [4].

Introduction

Solid-state cooling systems

Advantages

- Two century of development and optimisation.

Drawbacks

- They are bulky, complex
- Low efficiency at small scale and hard to scale down
- Harmful refrigerants

Vapor-compression refrigeration

Needs for good performance

Which parameters make a MCM attractive for MC device :

- High ΔT_{ad} to have a high temperature span
- High ΔS to have high cooling power
- Transition temperature to operate at room temperature
- Thermal conductivity
- Low hysteresis (for first-order materials)

Magnetocaloric key Materials for room temperature

- Second-Order : Gd, Gd-based alloy
- First-Order : LaFeSi-Based alloy, FeRh, MnFeP-X, GdFeSi, ...

One of the most promising

How Does Magnetocaloric Effect Work ? [2]

Field application

Paramagnetic phase High Entropy → Ferromagnetic phase Low Entropy

Magnetic moment tend to be aligned with the field and then the order in the material increase

Magnetic Entropy decreases

If we applied a field under adiabatic condition : $\Delta S = \Delta S_{mag} + \Delta S_{lattice} = 0$

Increasing of lattice entropy i.e temperature increasing (ΔT_{ad})

If we do the same under isothermal condition then we get ΔS which is the heat exchange with the thermal reservoir as $Q = T\Delta S$

Magnetocaloric Material with First-Order transition

First-Order transition ?

- Latent heat
- First derivative of the free energy with respect the temperature is discontinuous
- Metastable state
- Abrupt transition
- structural change

Second-Order transition ?

- No latent Heat
- Second derivative of the energy with respect the temperature is discontinuous
- High fluctuation and critical exponent
- Continus transition

Energetical illustration considering a bistable

Metastable state (out of equilibrium system)

Transition can occur by :

- Instability
- Thermal fluctuation

$\forall m \in [-1,1] g(m) \ll k_B T$

Ainsi $\forall m \in [-1,1] \exp\left(-\frac{g(m)}{k_B T}\right) \approx 1$

At thermal equilibrium, all states have almost the same probability. Therefore the system fluctuate at all scale

Why use MCM with First-Order transition is relevant

- They have a higher ΔS due to entropy variation associated to structural change (for example : LaFeSi transition come with 1% of deformation)

What is phase fraction relaxation

What is relaxation here ?

When a field is applied abruptly, some fraction of the material may get trapped into metastable states due to the presence of an energy barrier. Studying the subsequent relaxation towards equilibrium allows probing the energy barrier landscape that is also responsible for hysteresis.

Illustration

How locally the material switch from a state to another

Metastable state → Overcome energy barrier to reach equilibrium state

If we wait

If we increase the field

Unstable system

This switch occurs with the following transition rate :

$$f = f_0 \times \exp\left(-\frac{\Delta G_{barrier}}{k_B T}\right)$$

The evolution of the number of bistable in the PM state follows this equation :

$$\frac{dN_{bistable}}{dt} = \frac{1}{V} \int_{V_{PM}} f_{PM} dV - \frac{1}{V} \int_{V_{FM}} f_{FM} dV$$

Methodology

Measurement Device

VSM Lakeshore 7404 with thermocryostat

Experimental Protocol

- Realization of thermal hysteresis Loop M(T) – To find the transition;
- Cycle at different sweep-rate field and at different temperature;
- Relaxation at different temperature (different transition step).

Relaxation measurement

Results and discussions

Thermal hysteresis

Magnetic Hysteresis cycle

B(M) cycle at different sweep-rate field at 310.5 K

Nonmagnetocaloric contribution

Field rate at 17 mT/s

Field rate at 100 mT/s

Discussion

- Kinetic Effect is apparent
- Hysteresis area is higher for rapid rate

Discussion

- Avrami exponent = 0,89
- Constant nucleation with no growth
- Decreasing growth, no nucleation
- Different from the litterature (n=2,2) [7]
- We missed the begining of the phase relaxation

$$X = \frac{M(t) - M(t_i)}{M(t_f) - M(t_i)}$$

Perspectives

- ✓ Add thermal mass to avoid thermalization effects
- ✓ Study the effect of relaxation on hysteric loss
- ✓ Relaxation at different Temperature (to be able to probe the energy landscape)
- ✓ Relaxation after removing the Field
- ✓ Microstructure Investigation to conclude on the nature of the phase transformation
- ✓ Study the Kinetic of the transition in powders

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