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Entropy change at magnetic phase transitions of the first order and second order

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ABSTRACT

Magnetocaloric properties close to first order and second order phase transitions are presented and discussed. The specific heat capacity as a function of the magnetic field and the magnetic field induced entropy change has been measured by direct heat flux calorimetry in Gd, hydrogenated La(Fe–Mn–Si)$_{13}$, La(Fe–Co–Si)$_{13}$ and the Heusler alloy Ni–Mn–Co–Sn. The resulting $s(H_a,T)$ entropy constitutive relation is compared with a model including the ferromagnetic, electronic and structural contributions to the free energy.

Changement d'entropie et transitions de la phase magnétique de premier et de second ordre

Mots clés : Effet magnétocalorique ; Gd ; La(Fe–Si)$_{13}$; Alliage de Heusler Ni–Mn–Co–Sn ; Théorie du champ moyen

1. Introduction

The possibility to develop refrigeration techniques in the solid state, is attracting numerous efforts in fields of material science and engineering (Fähler et al., 2012) by searching ferro-caloric materials in which the entropy of the system can be changed by an external action such as the magnetic field, the applied stress or the electric field. In the case of magnetic materials, the entropy state equation $s(H_a,T)$ contains all the necessary information to design thermodynamic cycles for refrigeration and derive the figures of merit of the material: the isothermal entropy change $\Delta s_{iso}(H_a,T)$ and the adiabatic temperature change $\Delta T_{ad}(H_a,T)$ (see Fig.1) (Smith et al., 2012).

By using heat flux calorimetry in magnetic field it is possible to determine experimentally the entropy state equation $s(H_a,T)$ (Basso et al., 2010). In this paper we present experimental data on selected materials: Gd, hydrogenated La(Fe–Mn–Si)$_{13}$–H, La-(Fe–Co–Si)$_{13}$ and the Heusler alloy Ni–Mn–Co–Sn. The magnetocaloric properties, i.e. the specific heat capacity as a function of the magnetic field and the magnetic field induced entropy change are interpreted and

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Nomenclature

s	specific entropy
Δs_{iso}	isothermal entropy change (specific)
s_{PM}	specific entropy in the paramagnetic state
s_M	specific entropy, magnetic contribution
$\hat{s}$	reduced entropy, magnetic contribution
T	absolute temperature
t	reduced temperature
$\dot{T}$	temperature scan rate
ΔT_{ad}	adiabatic temperature change
T_s	sample temperature
T_c	critical temperature
H	magnetic field
H_a	applied magnetic field
h	reduced magnetic field
f_L	Landau free energy (specific)
f_S	magnetic free energy (specific)
f_S	structural free energy (specific)
q_s	heat flux
R	thermal contact resistance
m_s	sample mass
c_p	specific heat capacity
c_{PM}	specific heat capacity in the paramagnetic state
c_M	specific heat capacity, magnetic contribution
c_S	specific heat capacity, structural contribution
c_{ph}	specific heat capacity, phonon contribution
c_{ele}	specific heat capacity, electronic contribution
c_{pv}	specific heat capacity, thermal expansion contribution
α_T	coefficient of thermal expansion
κ_T	isothermal compressibility
υ	specific volume
M	magnetization
m	reduced magnetization
μ_0	permeability of vacuum
W	Weiss mean field coefficient
J	total angular momentum quantum number
S	spin angular momentum quantum number
g	Lande g-factor

discussed in terms of the ferromagnetic, electronic and structural contributions to the free energy.

2. Experimental methods

In presence of phase transitions of the first kind, the methods of heat flux calorimetry (Plackowski et al., 2002; Marcos et al., 2003; Jeppesen et al., 2008; Miyoshi et al., 2008; Basso et al., 2010, 2012a) are more appropriate than relaxation calorimetry (Suzuki et al., 2010; Shi et al., 2011), because they are able to fully capture the irreversible components of the latent heat. The specific entropy variation is computed from the measured heat flux q_s, by the expression

$$s - s_0 = \frac{1}{m_s}\int_0^t \frac{q_s}{T_s}\mathrm{d}t \tag{1}$$

where m_s is the sample mass (Basso et al., 2010). The temperature of the sample T_s can be derived from the temperature measured on the thermal bath T, by taking into account the thermal contact resistance R (Airoldi et al., 1994; Price, 1995; Plackowski et al., 2002; Basso et al., 2012a):

$$T_s = T - Rq_s \tag{2}$$

The thermal contact resistance R has to be determined for each measurement because it depends on the quality of the thermal contact realized. The method to determine R consists in making temperature scans under different rates (Basso et al., 2012a). Using Eqs. (1) and (2) the entropy, s, and the temperature, T_s, are computed from the measured q_s and T. The experimental curves $s(T_s;\dot{T},R)$, measured under different rates $\dot{T}$, are found to rescale together onto the same one, only at a well specific value of R. In Figs. 2–4 are shown both the raw experimental data (with $R = 0$ and $T_s = T$) and the result of

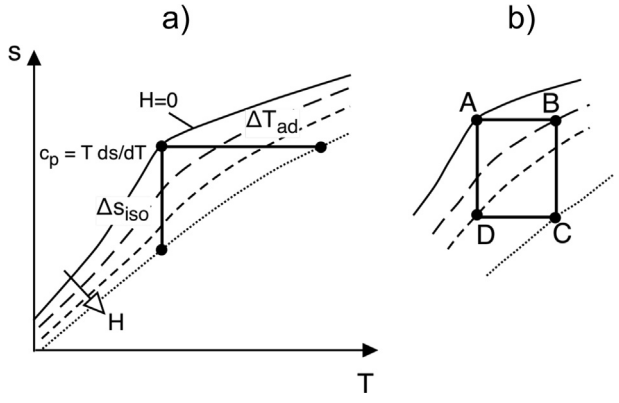

Fig. 1 – a) Entropy state equation $s(H,T)$. b) Magnetic Carnot cycle in the (s,T) diagram.

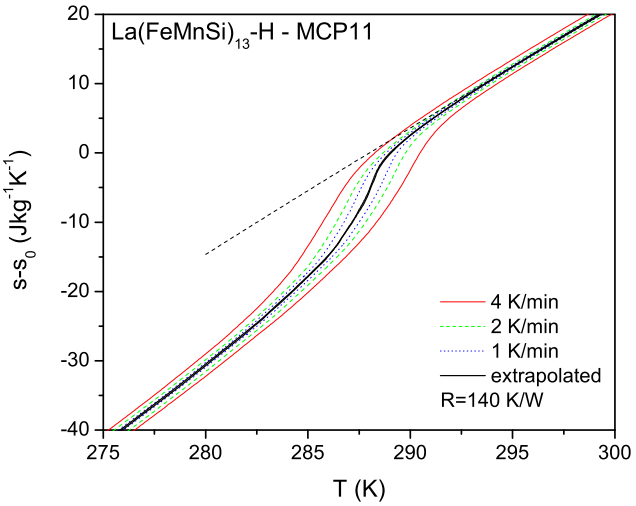

Fig. 2 – $LaFe_{11.384}Mn_{0.356}Si_{1.26}$-$H_{1.52}$ powder of mass 109.95 mg measured by heat compensation calorimetry under different rates. Sample entropy s by Eq. (1). The extrapolated curve is obtained by using T_s of Eq. (2) with $R = 140\ kW^{-1}$.