

Direct observation of the magnetic-field-induced entropy change in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ giant magnetocaloric alloys

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Direct observation of the entropy change in a first-order phase transition is obtained by using a differential scanning calorimeter in which the transition is field-induced under the application of an external magnetic field. This procedure enables direct evaluation of the magnetocaloric effect in materials showing first-order magnetostructural phase transitions. Results for $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ giant magnetocaloric alloys are reported. Calorimetric curves sweeping the field through the transition reveal a unusual increase of the entropy change with cycling. This increase is accounted for by considering both the structural and magnetic contributions to the total entropy change. © 2005 American Institute of Physics. [DOI: 10.1063/1.1968431]

Nowadays, there is a great deal of interest in using the magnetocaloric effect (MCE) as an alternative technology for refrigeration. The magnetic refrigeration offers the prospect of an energy-efficient and environment friendly alternative to the common vapor-cycle refrigeration technology in use today.¹ The MCE is the adiabatic temperature change or the isothermal entropy change that arises from the application or removal of a magnetic field H in a magnetic system. Systems undergoing first-order field-induced magnetostructural transitions with a large entropy change are promising candidates for magnetic refrigeration, since they are expected to display a giant MCE. Among these materials, $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$,²⁻⁴ $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$,^{5,6} and MnAs -based^{7,8} alloys show the largest MCE values.

Direct techniques to evaluate the MCE are based on the measurement of the temperature change in a sample while varying the magnetic field, in adiabatic conditions.^{9,10} Indirect evaluations can be performed using magnetization or heat capacity measurements. In the former case, the application of the Maxwell relations yields the isothermal entropy change.^{11,12} The heat capacity C_p as a function of temperature at constant magnetic fields provides isofield entropy curves, from which the adiabatic temperature change and the isothermal entropy change can be evaluated. However, this evaluation is less reliable in the vicinity of a first-order transition, since the value of C_p is not well defined due to the release or absorption of latent heat.

Differential scanning calorimeters (DSCs) are particularly suited to study first-order structural phase transitions since in these systems heat flow is directly measured while it is absorbed or released through the transition. Integration of the calorimetric signal yields the latent heat L and the total entropy change ΔS of the transition. Recently, we reported a new high-sensitivity DSC operating under an applied magnetic field.¹³ Here, we show that this new calorimeter enables a direct evaluation of the MCE by recording calorimetric

curves while the magnetic field is swept at a constant temperature.

In this letter, direct determination of ΔS for a $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloy by field-inducing the first-order phase transition is reported. Besides, calorimetric curves sweeping H through the transition reveal the evolution of ΔS with cycling. This is relevant for the applicability of these materials for magnetic refrigeration, since cycling could degrade the MCE. Our results show an increase of ΔS with cycling. This increase is interpreted taking into account the behavior of the magnetic and structural contributions to the total ΔS .

A $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ sample with $x=0.05$ was prepared by arc melting under a high-purity argon atmosphere, then cut into slices and thermally treated for 9 h at 920 °C under a vacuum of 10^{-5} mbar in a quartz tube. After annealing, the quartz tube was quickly taken out of the furnace to room temperature. The crystallographic structure of the sample was studied at room temperature with x-ray diffraction. The sample displayed the expected room-temperature Sm_5Ge_4 -type orthorhombic phase.^{3,4} DSC measurements were carried out up to 5 T. Neither the thermometry nor the heat flow sensors were affected by H .¹³

DSCs are usually designed to sweep the temperature continuously while the heat flow, $\dot{Q}(t)$, and $T(t)$ are recorded. Thus, the first-order transition is thermally induced, which yields a release or an absorption of heat. In the particular case of field-induced transitions, the temperature T_i corresponding to the peak of the transition in the calorimetric curve is tuned by H and, consequently, the field dependence of ΔS can be obtained. Our DSC has been designed to operate at constant temperature whilst sweeping the field. Fixing a temperature T above $T_i(H=0)$, and increasing H enables us to induce the first-order transition. A direct determination of the MCE is thus possible by this procedure. To our knowledge, this is the first time that ΔS in a field-induced transition has been directly evaluated. In this method, $\dot{Q}(t)$ and the field $H(t)$ are recorded as a function of time. L and ΔS are given by

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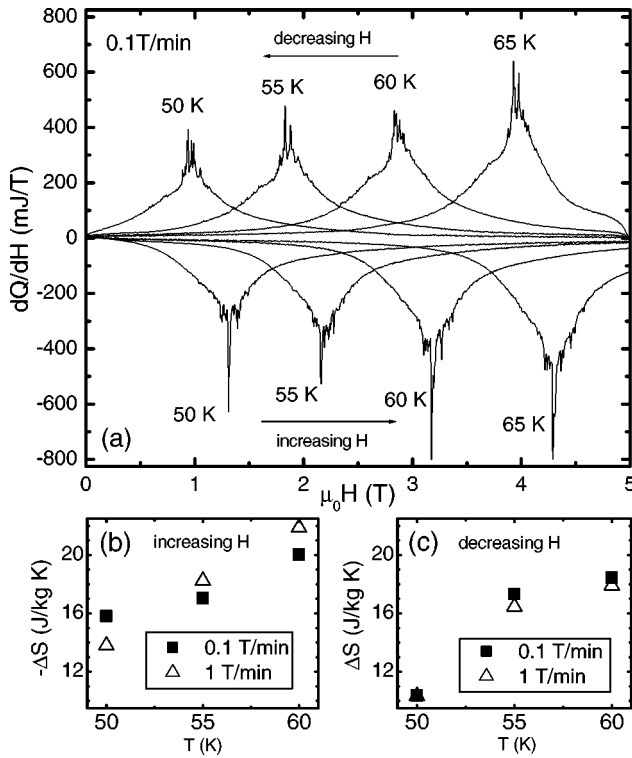


FIG. 1. (a) Calorimetric curves recorded sweeping the field (increasing and decreasing H at 0.1 T/min) in a $\text{Gd}_5(\text{Si}_{0.05}\text{Ge}_{0.95})_4$ sample at selected temperatures. (b) and (c) show the entropy change as a function of temperature increasing and decreasing H , respectively, at different field rates (0.1 and 1 T/min).

$$L = \int_{H_s}^{H_f} \frac{dQ}{dH} dH; \quad \Delta S = \frac{L}{T}, \quad (1)$$

where H_s and H_f are, respectively, fields below (above) and above (below) the start and finishing transition fields on increasing (decreasing) H .

Figure 1(a) shows an example of the calorimetric curves recorded on increasing and decreasing H for a $\text{Gd}_5(\text{Si}_{0.05}\text{Ge}_{0.95})_4$ sample at selected temperatures above the zero-field transition temperature [$T_t(H=0) \approx 45$ K]. The transition field, estimated as the peak position in dQ/dH curves, increases linearly with T , with a slope 0.20 ± 0.01 T/K, in excellent agreement with values obtained from both DSC in T -sweeping operating mode and magnetization curves.¹⁴ In Fig. 1(a), curves at $T=50, 55,$ and 60 K show the total completion of the transition, which enables a proper integration of the transition peak. This is in contrast with $T=65$ K, for which it is clear that the maximum available field of 5 T is not high enough to complete the transition. ΔS increases with T , as shown in Figs. 1(b) and 1(c), in agreement with the values obtained through DSC in T -sweeping operating mode.¹⁴ Curves at selected magnetic field rates \dot{H} (0.1 and 1 T/min) for the same T yield the same values of L and ΔS , within the experimental error, showing that these values do not depend on \dot{H} .

It is worth noting that calorimetric curves show a jerky character, which indicates the avalanche-type dynamics of the transition. Within this context, an avalanche is defined as an irreversible jump associated with the nucleation and/or growth of domains of the new phase that take place during the first-order phase transition. The dynamics of the transi-

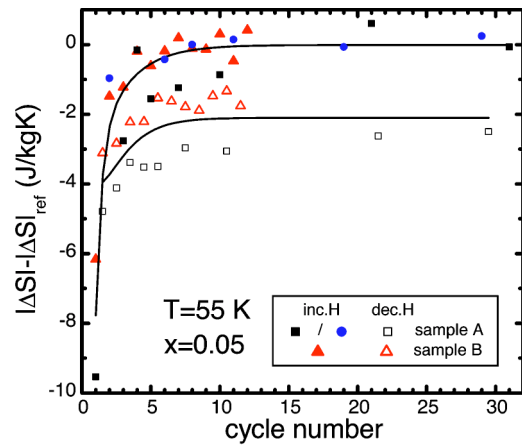


FIG. 2. (Color online) The change in $|\Delta S|$ with respect to the stationary value $|\Delta S|_{\text{ref}}$, obtained from DSC measurements at $T=55$ K in samples A and B ($x=0.05$), as a function of the cycle number. An integer is used for a cycle increasing H and the integer-and-a-half for the same cycle decreasing H . The field rate used is 0.1 T/min, except for solid (blue) circles, corresponding to 1 T/min. The stationary values for samples A and B, increasing H , are 16.64 and 17.35 J/kg K, respectively. Solid lines are fits using two exponential decays, for increasing and decreasing H .

tion may be characterized from the study of the statistical distribution of size of these avalanches.¹⁵

Another relevant effect to the dynamics of a first-order magnetostructural transition is the fact that some properties vary when the system is repeatedly cycled through the transition. Changes in the resistance^{16,17} and thermopower¹⁸ were reported for $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys when they were thermally cycled. If ΔS change with cycling, this could affect the efficiency of the MCE in magnetic refrigeration.

In order to study ΔS while cycling through the transition in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys, we used two different virgin samples (A and B). Both samples were cut from the same $x=0.05$ button. Calorimetric curves were measured by sweeping H at a constant T ($=55$ K) for different field rates (0.1 and 1 T/min). The shape of the first calorimetric curve (increasing H) for all samples was clearly different from subsequent cycles, showing a much lower area than subsequent measurements. The change in $|\Delta S|$ with cycling is displayed in Fig. 2 as a function of the cycle number (for the sake of clarity, only 31 of 90 measured cycles are shown). Three features observed for both samples are to be noted. First, $|\Delta S|$ increases strongly between the first and the second cycles and tends rapidly to a stationary value, which is reached around the fifth cycle. Second, the evolution of $|\Delta S|$ does not depend on the field rate, even when \dot{H} is increased by a factor of 10 (see solid squares and circles for sample A in Fig. 2). Third, $|\Delta S|$ for increasing H is systematically larger than $|\Delta S|$ for decreasing H .

The first feature is unusual in first-order structural transitions (martensitic-like), such as in Cu–Al–Mn, in which $|\Delta S|$ has been found to decrease with cycling.¹⁹ In martensitic materials, the evolution has been interpreted as a learning process in which the system seeks an optimal path that tends to avoid high-energy barriers that separate local metastable states.^{19,20} Therefore, it is assumed that increasing thermal cycling reduces metastability. In standard martensitic transitions, the low-temperature phase is obtained by shearing the high-temperature (cubic) phase. On the contrary, in $\text{Gd}_5(\text{Si}_{0.05}\text{Ge}_{0.95})_4$, it is the high-temperature (Gd_5Ge_4 -type

orthorhombic) phase that is obtained by shearing the low-temperature (Gd_5Si_4 -type orthorhombic) phase, yielding a breaking of $\text{Ge}(\text{Si})\text{--Ge}(\text{Si})$ bonds.⁴ Therefore, it is expected for this material that the structural entropy of the low-temperature phase must be larger than the structural entropy of the high-temperature phase. In other words, the structural and magnetic contributions to the total ΔS should have opposite signs. Accordingly, a decrease with cycling of the (absolute value of the) structural contribution to ΔS should lead to an increase of the corresponding total ΔS if we assume that the magnetic contribution remains constant. A more detailed study of these two contributions to ΔS will be published elsewhere.²¹

The fact that $|\Delta S|$ does not depend on \dot{H} indicates that the experiment is not affected by the field rate and that the same initial and final states are reached at any \dot{H} . Finally, differences between the results corresponding to increasing and decreasing H are related to the existence of hysteresis in the transition, which means that the corresponding $|\Delta S|$ are evaluated through pathways with different initial and final states.

Interestingly, the avalanche-type structure of the transition is not observed in calorimetric measurements for samples with higher Si content x , as the transition occurs at higher temperatures. The avalanche behavior is still appreciable for $x=0.1$ [$T_r(H=0) \approx 72$ K] but is apparently completely smoothed out for $x=0.49$ [$T_r(H=0) \approx 268$ K]. This is consistent with the fact that thermal activation is effective at high temperature, as shown in Ref. 22. However, even in this case, acoustic emission measurements (which is a more sensitive technique) reveal the existence of tiny avalanches.²¹ Moreover, for $x=0.49$, we have not observed any evolution of the total ΔS with cycling.

In conclusion, direct measurement of the entropy change ΔS by field-inducing the first-order phase transition with a differential scanning calorimeter operating under magnetic field is reported. This technique enables the direct evaluation of the MCE in systems showing first-order magnetostructural phase transitions, as in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys. Our results show that $|\Delta S|$ increases with cycling, reaching a stationary value after ~ 5 cycles. This shows that the efficiency of the

MCE is slightly enhanced with cycling through the transition, at least at the scale of $\sim 10^2$ cycles.

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