Change in entropy at a first-order magnetoelastic phase transition: Case study of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ giant magnetocaloric alloys

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The change in entropy, $\Delta S$, at the first-order magnetoelastic phase transition in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys for $x \leq 0.5$ has been measured with a high-sensitivity differential scanning calorimeter with built-in magnetic field, $H$. Scaling of $\Delta S$ is achieved by changing the transition temperature, $T_t$, with $x$ and $H$ from 70 to 310 K. $T_t$ is thus the relevant parameter in determining the giant magnetocaloric effect in these alloys. The calorimetric determination of the change in entropy is also in agreement with the indirect calculation obtained from the magnetization curves measured up to 23 T using both the Clausius–Clapeyron equation and the Maxwell relation. A simple phenomenological model based on the magnetization curves accounts for these results. © 2003 American Institute of Physics. [DOI: 10.1063/1.1556274]

The magnetocaloric effect (MCE) may be defined as the adiabatic change in temperature or the isothermal change in entropy that arises from the application/removal of a magnetic field, $H$. Recently, a great deal of interest has been devoted to searching for systems that show first-order magnetoelastic phase transitions, since they are expected to display giant MCE. Among these materials, Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ (Refs. 1 and 2) and MnAs-based alloys are the most promising. The aim of this article is to study the change in entropy in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys, which is a controversial issue. The use of the Maxwell relation at the non-ideal first-order transition $^{1,4}$ has been opposed to the use of the Clausius–Clapeyron equation. $^5$ In order to clarify this controversy, in this article we discuss the origin of the difference between the change in entropy related to latent heat at the first-order transition $\Delta S$, and the total change in entropy due to variation of the field from $H_1$ to $H_2$ at a given $T$, $\Delta S(H_1\rightarrow H_2,T)$.

The giant MCE in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ originates from the first-order transition that appears in two compositional ranges. For $0.24 \leq x \leq 0.5$, the transition occurs from a high-temperature paramagnetic (PM) phase to a low-temperature ferromagnetic (FM), Gd$_2$Si$_2$-type orthorhombic (O–I) phase, at temperatures ranging from 130 ($x = 0.24$) to 276 K ($x = 0.5$). $^{1,2}$ For $x \approx 0.2$, the transition takes place from a high-temperature antiferromagnetic (AFM), Gd$_2$Ge$_4$-type orthorhombic (O–II) phase to the low-temperature FM/O–I phase, whose temperature varies linearly from 20 ($x = 0$) to 120 K ($x = 0.2$). $^{1,2}$ A second-order PM–AFM transition occurs at $T_N$ (from $\sim 125$ K for $x = 0$ to $\sim 135$ K for $x = 0.2$) in the O–II phase.

Differential scanning calorimetry (DSC) under $H$ is the most suitable method by which to obtain the $H$ dependence of latent heat and change in entropy at a first-order phase transition, since DSC measures the heat flow, in contrast to quasidiabatic calorimetry, where determination of the heat capacity is uncertain due to the release of latent heat. In this article, DSC measurements of $\Delta S$ as a function of $T$ and $H$ are reported for Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys. Scaling of $\Delta S$ was suggested, where the scaling variable, $T_s$, is the temperature of the first-order magnetoelastic transition. $^6$ New DSC data under $H$ are given in order to confirm the scaling plot. We also show that DSC values of $\Delta S$ are in agreement with the indirect values obtained from the magnetization curves $M(H)$ using the Clausius–Clapeyron equation and the Maxwell relation. $^6$ Both indirect methods for increasing and decreasing $H$ are analyzed.

Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys were prepared by arc melting under argon. As-cast buttons were cut into slices and some were annealed for 4 h at 950 °C under 10$^{-5}$ Torr vacuum. $M(H)$ curves were recorded up to 230 kOe for $x = 0.18$ and 0.45 from 4.2 to 310 K. Calorimetric data were recorded using a high-sensitivity DSC. $^6$ Heating and cooling runs were performed in 4.2–300 K under fields up to 50 kOe.

The $M(H)$ isotherms measured for $x = 0.45$ and 0.18 exhibit the field-induced nature of the transition that spreads over a field range, $\Delta H_t$, which is $\sim 4$ T for our sample $x = 0.45$. The transition field $H_t$ is defined at each $T$ as the inflection point of the $M(H)$ curve. A linear relation between $H_t$ and $T$ is obtained for $x = 0.45$, which yields $M = dH/d(\mu_0H^2) = 4.5 \pm 0.2$ K/T. For $x = 0.18$ two linear ranges are observed: $\alpha = 3.66 \pm 0.07$ K/T for $T \leq 120$ K and $\alpha = 2.28 \pm 0.02$ K/T for $T \geq 120$ K.

DSC data for $x = 0.18$ (Fig. 1) also reveal the first-order nature of the AFM–FM transition and the second-order nature of the PM–AFM transition. The first-order transition

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shows a large peak in $\dot{Q}/T = dQ/dT$ ($\dot{Q}$ is the recorded heat flow and $T$ is the heating/cooling rate) and significant field dependence of $T_i$, which is estimated as the temperature at the maximum of the peak. DSC data confirm the linear relation between $H$ and $T_i$, and yield $\alpha = 4.8 \pm 0.1$ K/T for $x = 0.45$ and $\alpha = 3.64 \pm 0.05$ K/T for $x = 0.18$, in agreement with values obtained from $M(H)$. The second-order transition is observed as a small $\lambda$-type jump in the $dQ/dT$ baseline.

The absolute value of $\Delta S$ as a function of $T_i$ is shown in Fig. 2. Since $T_i$ corresponds to the transition temperature of the first-order transition for each $x$ and $H$, this allows one to sweep $T_i$ from $-70$ to $-310$ K. $\Delta S$ was calculated by numerical integration of $(dQ/dT)/T$ throughout the first-order DSC peaks, and from the $M(H)$ isotherms using the Clausius–Clapeyron equation $\Delta S = -\Delta M(dH_i/dT_i)$.

$\Delta M$ is determined from the jump in magnetization at the transition. $\Delta S$ for $x = 0.5$ taken from Ref. 5 is also displayed. Because $T_i$ is tuned by both $x$ and $H$, this enables one to derive a scaling of $|\Delta S|$ with $T_i$ for compositions $x \leq 0.5$, thus proving the equivalence of magnetovolume and substitution-related effects.

Three different trends are shown in Fig. 2. For $0.24 \leq x \leq 0.5$, $|\Delta S|$ associated with the PM–FM transition monotonically decreases with $T_i$, while, for $x \leq 0.2$, $|\Delta S|$ either decreases or increases depending on $T_i$. As $H$ shifts $T_i$, it is possible to observe both the AFM/O-II→FM/O-I transition at $T_i$ and, when the first-order transition overlaps the second-order one at high enough $H$ [$T_i(H) > T_N$], a PM/O-II→FM/O-I transition. For that reason, $x = 0.18$ has two different values for $\alpha$, depending on $T_i$. For the AFM–FM transition, $|\Delta S|$ increases monotonically with $T_i$, while for the PM–FM transition, $|\Delta S|$ decreases with $T_i$. Consequently, $|\Delta S|$ is maximum for each composition at $T_i = T_N$. The fact that $T_N$ slightly decreases with $H$ and increases with $x$ gives rise to different maxima (labeled in Fig. 2).

$\Delta S$ values obtained at each temperature from DSC and from the Clausius–Clapeyron equation are coincident within experimental error for $x = 0.45$ and 0.5, and for $x = 0.18$ in the temperature range where the AFM–FM transformation takes place (Fig. 2). Deeper inside, Fig. 3(a) shows these values of $\Delta S$ upon heating and upon a decrease in $H$ for $x = 0.45$ and 0.5 (scattered symbols), and also the change in

![FIG. 1. DSC data for $x = 0.18$ upon heating under $H$.](image1)

![FIG. 2. Scaling of $|\Delta S|$ at the first-order transition. Connected symbols correspond to values obtained from $M(H)$. Closed and open diamonds are data from Ref. 5. Symbols labeled/not labeled with $H$ correspond, respectively, to DSC data with/without $H$.](image2)

![FIG. 3. (a) Change in entropy for $x = 0.45$ calculated from the Maxwell relation integrating from $H_{max}$ to 0 (dashed lines), Clausius–Clapeyron relation integrating from $H_{max}$ to 0 (dashed lines), and Maxwell relation integrating within $H_{max}$ (solid lines). $H_{max}$ is labeled beside each dashed line, and it also represents the maximum applied field in the solid lines for which $H_{max}$ increases from left to right. (b) Change in entropy $\Delta S(H_{max} ~0)$ calculated from the Maxwell relation using a simple phenomenological model. $\Delta S = -\Delta M/\alpha$ is the value obtained from the Clausius–Clapeyron approach.](image3)
The temperature range $\Delta T = \alpha \Delta H = \xi$. The results are shown in Fig. 3(b). The general trends compare very well with experimental results in Fig. 3(a) obtained by integrating the Maxwell relation only within the transition range. It is observed that when $H_{\text{max}}$ is not high enough to complete the transition ($H_{\text{max}} < \Delta H$), then $\Delta S(H_{\text{max}} \rightarrow 0) = (H_{\text{max}}/\Delta H) \Delta S$ is smaller than $\Delta S$, and $(H_{\text{max}}/\Delta H)$ is the transformed fraction of the sample.

In summary, DSC under $H$ was used successfully to measure the change in entropy at the first-order magnetoelastic phase transition for Gd$_5$(Si$_2$Ge$_{1-x}$)$_x$ for $x \approx 0.5$. The change in entropy at the transition scales with $T_1$, since $T_1$ is tuned by $x$ and $H$, and the scaling is thus expected to be universal for any material showing strong magnetoelastic effects. The scaling proves that the magnetovolume effects due to $H$ are of the same nature as the volume effects caused by substitution. Calorimetric values of $\Delta S$ match those from the Clausius–Clapeyron equation and the Maxwell relation provided the latter is evaluated only within the range of field in which the transition takes place, and the maximum $H$ is high enough to complete the transition. The $T$ and $H$ dependences of $M$ in each phase outside the transition region yield an additional change in entropy, also accounting for the giant MCE.

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