Change in entropy at a first-order magnetoelastic phase transition: Case study of $Gd_5(Si_xGe_{1-x})_4$ giant magnetocaloric alloys

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The change in entropy, ΔS, at the first-order magnetoelastic phase transition in $Gd_5(Si_xGe_{1-x})_4$ alloys for $x \leqslant 0.5$ has been measured with a high-sensitivity differential scanning calorimeter with built-in magnetic field, H. Scaling of ΔS 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, $Gd_5(Si_xGe_{1-x})_4$ (Refs. 1 and 2) and MnAs-based[3] alloys are the most promising. The aim of this article is to study the change in entropy in $Gd_5(Si_xGe_{1-x})_4$ alloys, which is a controvertial issue. The use of the Maxwell relation at the nonideal 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 ΔS, 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 $Gd_5(Si_xGe_{1-x})_4$ originates from the first-order transition that appears in two compositional ranges. For $0.24 \leqslant x \leqslant 0.5$, the transition occurs from a high-temperature paramagnetic (PM), monoclinic (M) phase to a low-temperature ferromagnetic (FM), Gd_5Si_4-type orthorombic ($O-$I) phase, at temperatures ranging from 130 ($x = 0.24$) to 276 K ($x = 0.5$).[1,2] For $x \leqslant 0.2$, the transition takes place from a high-temperature antiferromagnetic (AFM), Gd_5Ge_4-type orthorombic ($O-$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 ~125 K for $x = 0$ to ~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 quasiadiabatic calorimetry, where determination of the heat capacity is uncertain due to the release of latent heat. In this article, DSC measurements of ΔS as a function of T and H are reported for $Gd_5(Si_xGe_{1-x})_4$ alloys. Scaling of ΔS was suggested, where the scaling variable, T_t, 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 ΔS 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.

$Gd_5(Si_xGe_{1-x})_4$ 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, ΔH_t, which is ~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 $\alpha \equiv dT/d(\mu_0 H_t) = 4.5 \pm 0.2$ K/T. For $x = 0.18$ two linear ranges are observed: $\alpha = 3.66 \pm 0.07$ K/T for $T \leqslant 120$ K and $\alpha = 2.28 \pm 0.02$ K/T for $T \geqslant 120$ 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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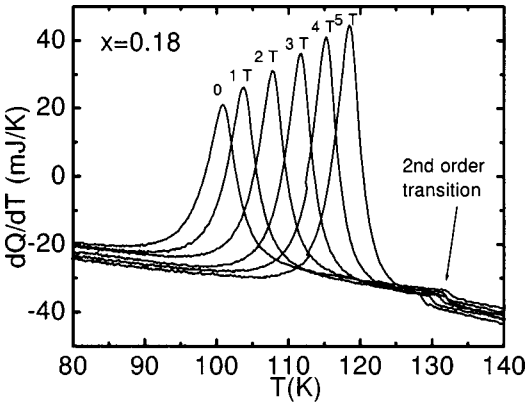

FIG. 1. DSC data for $x=0.18$ upon heating under H.

shows a large peak in $\dot{Q}/\dot{T}\equiv dQ/dT$ ($\dot{Q}$ is the recorded heat flow and $\dot{T}$ is the heating/cooling rate) and significant field dependence of T_t, which is estimated as the temperature at the maximum of the peak. DSC data confirm the linear relation between H and T_t and yield $\alpha=4.8\pm0.1$ K/T for $x=0.45$ and $\alpha=3.64\pm0.05$ K/T for $x=0.18$, in agreement with values obtained from $M(H)$. The second-order transition is observed as a small λ-type jump in the dQ/dT baseline.

The absolute value of ΔS as a function of T_t is shown in Fig. 2. Since T_t corresponds to the transition temperature of the first-order transition for each x and H, this allows one to sweep T_t from ~70 to ~310 K. ΔS 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 $\Delta S=-\Delta M(dH_t/dT_t)$.[5,7] ΔM is determined from the jump in magnetization at the transition. ΔS for $x=0.5$ taken from Ref. 5 is also displayed. Because T_t is tuned by both x and H, this enables one to

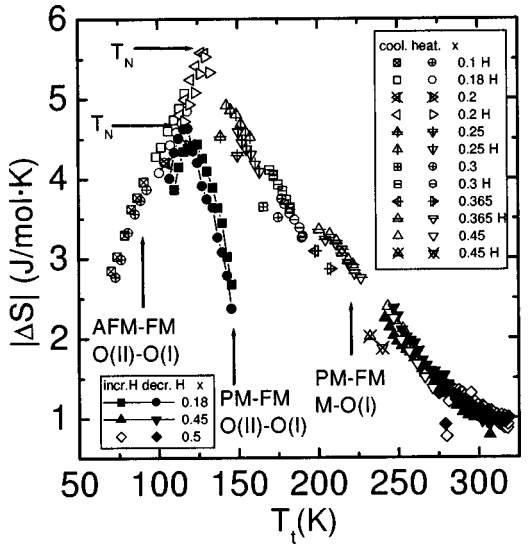

FIG. 2. Scaling of $|\Delta S|$ at the first-order transition. Connected symbols correspond to values obtained from $M(H)$. Closed and open diamonds are data from Ref. 5. Symbols labeled/not labeled with H correspond, respectively, to DSC data with/without H.

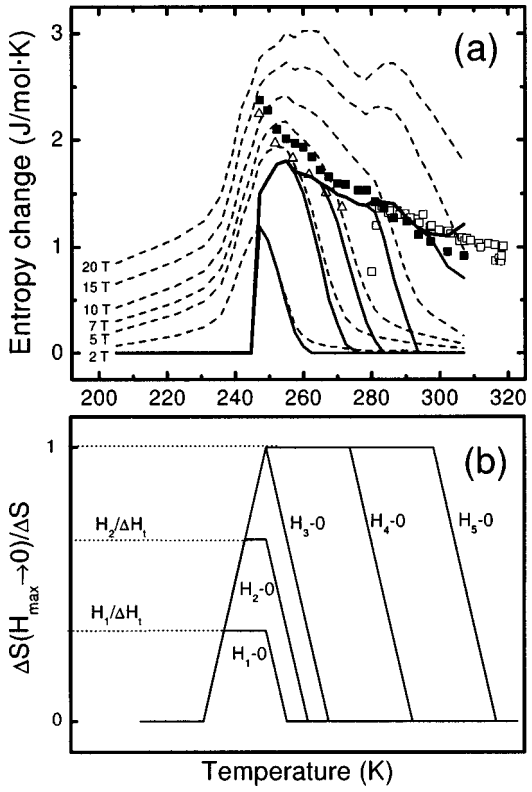

FIG. 3. (a) Change in entropy for $x=0.45$ calculated from the Maxwell relation integrating from H_{max} to 0 (dashed lines), Clausius–Clapeyron equation for decreasing H (closed squares are data in this work and open squares for $x=0.5$ are from Ref. 5), DSC measurements upon heating (open triangles), and Maxwell relation integrating within ΔH_t (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 $\Delta S(H_{max}\rightarrow 0)$ calculated from the Maxwell relation using a simple phenomenological model. $\Delta S=-\Delta M/\alpha$ is the value obtained from the Clausius–Clapeyron approach.

derive a scaling of $|\Delta S|$ with T_t for compositions $x\leqslant 0.5$, thus proving the equivalence of magnetovolume and substitution-related effects.

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

ΔS 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 ΔS upon heating and upon a decrease in H for $x=0.45$ and 0.5 (scattered symbols), and also the change in

entropy for $x=0.45$ (dashed lines) obtained from $M(H)$ using the Maxwell relation, upon a decrease in H, $\Delta S(H_{\max}\rightarrow 0,T)=\int_{H_{\max}}^{0}(\partial M/\partial T)_H \mu_0 dH$. These curves are evaluated at different temperatures and for different maximum applied fields, $H_{\max}$. They display the typical plateau-like behavior previously reported,[1,5] which can be above or below the ΔS vs T_t curve depending on the value of $H_{\max}$. If we consider that the Maxwell relation has three contributions, $\Delta S(H_{\max}\rightarrow 0,T)=\int_{H_{\max}}^{H_b}(\partial M/\partial T)_H \mu_0\, dH+\int_{H_b}^{H_a}(\partial M/\partial T)_H \mu_0\, dH+\int_{H_a}^{0}(\partial M/\partial T)_H \mu_0\, dH$, with $H_b=H_t+\Delta H_t/2$ and $H_a=H_t-\Delta H_t/2$, the first and the third integrals account for the change in entropy related to the H and T dependence of M in each phase. Only the second term gives the contribution to the change in entropy at the magnetoelastic transition. This is indicated by the fact that the plateau-like behavior of the solid lines in Fig. 3(a), computed using only the second integral, matches the ΔS vs T_t curve. Note also that when $\mu_0 H_{\max}$ is less than $\mu_0\Delta H_t\approx 4$ T, which is the minimum field needed to complete the transition, the values of $\Delta S(H_{\max}\rightarrow 0,T)$ are lower than the ΔS values [see the curve corresponding to $\mu_0 H_{\max}=2$ T in Fig. 3(a)]. Moreover, for $H_{\max}\geqslant\Delta H_t$, the plateau-like region extends over the temperature range in which $H_{\max}\geqslant H_b(T)$. Hence, as $H_b(T)$ increases with T, the abrupt decrease from the plateau-like region at higher T is due to truncation of the second integral at $H_{\max}$.

A phenomenological model is presented in order to compare the Maxwell and Clausius–Clapeyron approaches. The magnetization curves are considered to be of the form $M(T,H)=M_0+\Delta M\ F((T-T_t(H))/\xi)$, where M_0 and ΔM are assumed to be T and H independent, and $F(T)$ is a monotonously decreasing function of width ξ such that $F\rightarrow 1$ for $T\ll T_t(H)$ and $F\rightarrow 0$ for $T\gg T_t(H)$. The case of $\xi\rightarrow 0$ corresponds to the ideal first-order transition (F is then the Heaviside function). Using the Maxwell relation and assuming a linear field dependence of T_t, the change in entropy is given analytically by $\Delta S(H_{\max}\rightarrow 0)=\Delta S(F\{[T-T_t(H_{\max})]/\xi\}-F\{[T-T_t(H=0)]/\xi\})$, where $\Delta S=-\Delta M/\alpha$ is the value in the Clausius–Clapeyron approach. In general, $\Delta S(H_{\max}\rightarrow 0)$ is a fraction of ΔS, which depends on the magnitude of the shift of T_t with H, and reaches its maximum value ΔS for high enough H. The results are even valid in the limit $\xi\rightarrow 0$, for which $\Delta S(H_{\max}\rightarrow 0)=\Delta S$ for all $H_{\max}$. A simple analytical picture is provided by assuming that F is a linear function of the temperature which extends in the temperature range $\Delta T_t=\alpha\Delta H_t=\xi$. 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 $H_{\max}$ is not high enough to complete the transition ($H_{\max}<\Delta H_t$), then $\Delta S(H_{\max}\rightarrow 0)=(H_{\max}/\Delta H_t)\Delta S$ is smaller than ΔS, and $(H_{\max}/\Delta H_t)$ 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 $Gd_5(Si_xGe_{1-x})_4$, $x\leqslant 0.5$. The change in entropy at the transition scales with T_t, since T_t 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 ΔS 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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