Entropy change and magnetocaloric effect in $Gd_5(Si_xGe_{1-x})_4$

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(Received 15 May 2002; published 3 September 2002)

Isothermal magnetization curves up to 23 T have been measured in $Gd_5Si_{1.8}Ge_{2.2}$. We show that the values of the entropy change at the first-order magnetostructural transition, obtained from the Clausius-Clapeyron equation and the Maxwell relation, are coincident, provided the Maxwell relation is evaluated only within the transition region and the maximum applied field is high enough to complete the transition. These values are also in agreement with the entropy change obtained from differential scanning calorimetry. We also show that a simple phenomenological model based on the temperature and field dependence of the magnetization accounts for these results.

The magnetocaloric effect (MCE) is the adiabatic temperature change that arises from the application or removal of a magnetic field. MCE is associated with the isothermal entropy change due to the field variation. Recently, a great deal of interest has been devoted to searching for systems showing first-order magnetostructural transitions with large entropy change, since they are expected to display giant MCE. Among these materials, $Gd_5(Si_xGe_{1-x})_4$ (Refs. 1–5) and Mn-As-based[6,7] intermetallic alloys are the most promising candidates.

The correct evaluation of the entropy change related to the MCE is a controversial issue and has lately aroused much discussion.[1,8–12] For $Gd_5(Si_xGe_{1-x})_4$, Giguère *et al.*[8] showed that the use of the Maxwell relation to calculate the entropy change overestimates (at least ~20%) the value obtained from the Clausius-Clapeyron equation that the authors[8,11] claimed to be the correct procedure due to the first-order nature of the transition in these alloys. According to them, the entropy change in the magnetostructural transition is not associated with the continuous change of the magnetization as a function of T and H, but rather with the discontinuous change in the magnetization due to the crystallographic transformation. They claimed that Maxwell relations do not hold since magnetization is not a continuous, derivable function in that case. In contrast, Gschneidner, Jr. *et al.*[9] argued that the Maxwell relation is applicable even in the occurrence of a first-order transition, except when this transition takes place at a fixed T and H, giving rise to a steplike change of the magnetization (*ideal* case). Besides, they claimed that Clausius-Clapeyron equation would imply an H-independent adiabatic temperature change, which however, is not consistent with the experimental observations.[8] Moreover, Sun *et al.*[10] showed that the entropy change calculated from the Maxwell relation is indeed equivalent to that given by the Clausius-Clapeyron equation, provided the magnetization M is considered T-independent in whichever phase the transition involves, and M is a step function with a finite jump at the transition temperature. They also suggested that the two procedures may yield different results, since the

Clausius-Clapeyron method does not take into account the reduction of spin fluctuations by an applied field. Recent measurements using a differential scanning calorimeter under applied magnetic field have shown that the Clausius-Clapeyron equation leads, within the experimental error, to the correct values of the entropy change at the magnetostructural transition in $Gd_5(Si_xGe_{1-x})_4$ alloys.[13]

Here we present a detailed analysis of the different contributions to the entropy change arising from the application of a magnetic field, in order to account for the discrepancies previously discussed. For this purpose, magnetization isotherms on $Gd_5(Si_xGe_{1-x})_4$ were measured up to very high fields. The values of the entropy change obtained from Clausius-Clapeyron and Maxwell methods are compared and analyzed within the framework of a simple phenomenological model based on the temperature and field dependence of the magnetization.

$Gd_5Si_{1.8}Ge_{2.2}$ ($x=0.45$) was prepared by arc-melting admixtures of the pure elements in the desired stoichiometry under an argon atmosphere. The sample was placed in a water-cooled copper crucible. The weight losses after arc-melting were negligible. As-prepared button was thermally treated for 4 h at 950 °C under a vacuum of 10^{-5} torr, in an electrical resistance furnace, by heating the sample in a quartz tube. After annealing, the quartz tube was quickly taken out of the furnace to room temperature. The quality of the sample and its crystallographic structure were studied by room-temperature x-ray diffraction (XRD). The ac susceptibility (77–300 K; $\nu=111$–3330 Hz; $H_{ac}=1.25$ Oe) was used to check that the temperature of the first-order phase transition was in agreement with values in the literature.[2–4] The material displayed the expected room-temperature monoclinic structure ($P112_1/a$), with unit-cell parameters $a=7.586(1)$ Å, $b=14.809(1)$ Å, $c=7.784(1)$ Å, and $\gamma=93.14°(1)$, in agreement with Refs. 3 and 4. Both XRD and ac susceptibility suggested the existence of minor amounts of a secondary orthorhombic phase ($Pnma$) for the as-prepared sample. From the small anomaly appearing at $T=294.5\pm0.5$ K in the ac data and the fitting of the unit-
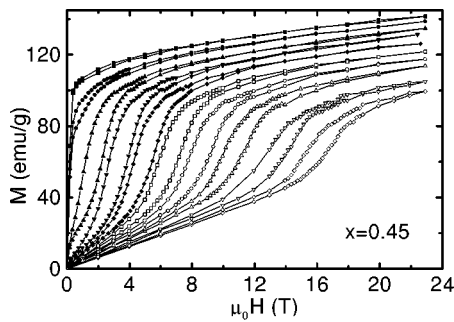
FIG. 1. Selected magnetization isotherms of $Gd_5Si_{1.8}Ge_{2.2}$ increasing and decreasing field for 231.0 K (top), 239.3 K, 247.2 K, 255.0 K, 262.5 K, 270.0 K, 278.5 K, 286.5 K, 297.3 K, and 307 K (bottom).

cell parameters, the secondary phase mostly corresponded to $x \sim 0.51-0.53$.[3,4] This secondary phase almost disappeared with annealing. The magnetization measurements were performed at the Grenoble High Magnetic Field Laboratory. $M(H)$ curves were recorded up to 23 T, both in increasing and decreasing H, from 4.2 to 310 K with a temperature step of 3 K.

$M(H)$ isotherms are shown in Fig. 1. These curves exhibit a jump ΔM at the magnetostructural transition that spreads over a field range $\mu_0 \Delta H_t \sim 4$ T for most of the temperatures, increasing to $\sim 5-6$ T for temperatures above ~ 297 K. The transition field H_t is defined as the field corresponding to the inflection point within the transition region. $\mu_0 H_t$ varies from 0 ($T = 236$ K) to 17 T ($T = 307$ K). ΔM has been estimated as the difference in the magnetization at H_t between the linear extrapolations of $M(H)$ well above and below the transition region. A linear behavior of $H_t(T)$ with a slope $\alpha \equiv dT/d(\mu_0 H_t) = 4.5 \pm 0.2$ K/T is found, which is in agreement with that obtained from calorimetric data.[13] Since ΔM also shows a linear dependence on T (decreasing with increasing temperature), it is deduced from
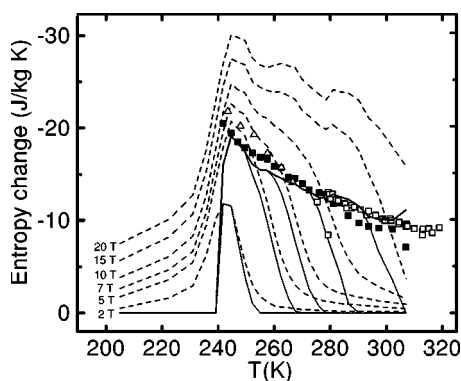

FIG. 2. Entropy change for $Gd_5Si_{1.8}Ge_{2.2}$ ($x = 0.45$) calculated from (i) Maxwell relation integrating up to H_{max} (dashed lines), (ii) Clausius-Clapeyron equation (solid squares represent this work and open squares are for $x = 0.5$ from Ref. 8), (iii) DSC measurements (open triangles), and (iv) Maxwell relation integrating within ΔH_t (solid lines). H_{max} is labeled beside each dashed line, and also stands for the solid lines on increasing the field from left to right.

the Clausius-Clapeyron equation $\Delta S = -\Delta M \, d(\mu_0 H_t)/dT = -\Delta M/\alpha$ that the transition entropy change ΔS must also vary linearly with T (see Fig. 2).

Figure 2 shows the entropy change for $x = 0.45$ (dashed lines) obtained from the $M(H)$ isotherms using the Maxwell method, $\Delta S(0 \rightarrow H_{max}, T) = \int_0^{H_{max}} \mu_0 (\partial M/\partial T)_H dH$. These curves display the typical behavior previously reported.[1,8] First, a rapid increase at low T, then a maximum value at about $T_t(H=0)$, followed by a plateaulike behavior, and finally a sharp decrease at high T. $T_t(H)$ stands for the field dependence of the transition temperature. Figure 2 also shows the values of the entropy change at the transition, ΔS, obtained from the Clausius-Clapeyron equation for $x = 0.45$ (present data) and $x = 0.5$ (taken from Ref. 8), and differential scanning calorimetry (DSC) data.[13] Note that the maximum value of the entropy change achieved using the Maxwell relation can be above or below ΔS depending on H_{max}. This can be understood by taking into account the fact that the Maxwell method includes the following contributions:

$$\Delta S(0 \rightarrow H_{max}, T) = \int_0^{H_a} \left(\frac{\partial M}{\partial T} \right)_H \mu_0 dH + \int_{H_a}^{H_b} \left(\frac{\partial M}{\partial T} \right)_H \mu_0 dH$$
$$+ \int_{H_b}^{H_{max}} \left(\frac{\partial M}{\partial T} \right)_H \mu_0 dH, \quad (1)$$

with $H_a = H_t - \Delta H_t/2$ and $H_b = H_t + \Delta H_t/2$. The first and the third integrals give the entropy change that arises from the field and temperature dependence of the magnetization in each phase. Only the second term accounts for the contribution to the entropy change of the magnetostructural transition. This is indicated by the fact that the plateaulike behavior of the solid lines in Fig. 2 [computed using the second integral in Eq. (1)] perfectly matches the ΔS values given by the Clausius-Clapeyron equation and by calorimetry. Note also that when H_{max} is less than ΔH_t, which is the minimum field needed to complete the transition, the maximum value of $\Delta S(0 \rightarrow H_{max}, T)$ is lower than ΔS (see, for instance, the curve corresponding to $\mu_0 H_{max} = 2$ T in Fig. 2). Moreover, for $H_{max} \gtrsim \Delta H_t$, the plateaulike region extends over the temperature range for which $H_{max} \gtrsim H_b(T)$. Consequently, as $H_b(T)$ increases with T, the abrupt decrease from the plateaulike region at higher T is due to the truncation of the second integral at H_{max}.

To account for the behavior described above, we propose a simple phenomenological model. The magnetization curves are considered to be of the form

$$M(T, H) = M_0 + \Delta M F \left(\frac{T - T_t(H)}{\xi} \right), \quad (2)$$

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 $\xi \rightarrow 0$ corresponds to the ideal first-order transition (F is then the Heaviside function). Using the Maxwell relation and

assuming a linear field dependence of the transition temperature, the entropy change is given by

$$\Delta S(0 \rightarrow H_{max}) = \Delta S \left[F\left(\frac{T - T_t(H_{max})}{\xi} \right) - F\left(\frac{T - T_t(H=0)}{\xi} \right) \right]. \quad (3)$$

It is worth stressing that when the transition temperature is not field dependent, $\Delta S(0 \rightarrow H_{max}) = 0$ irrespective of the value of ΔS. In general, $\Delta S(0 \rightarrow H_{max})$ is a fraction of the transition entropy change ΔS that depends on the magnitude of the shift of T_t with the magnetic field, and reaches its maximum value, ΔS, for high enough applied field. Results are even valid in the limit $\xi \rightarrow 0$, for which $\Delta S(0 \rightarrow H_{max}) = \Delta S$ for all H_{max}. Pecharsky *et al.*[14] recently arrived at basically the same conclusion using a different approach.

A simple analytical picture is provided by assuming that F is a linear function of temperature which extends within the temperature range $\Delta T_t = \alpha \Delta H_t = \xi$. Results are shown in Fig. 3. The general trends compare very well with results in Fig. 2 obtained by integrating the Maxwell relation within the transition range [second term of Eq. (1)]. Note that within the scope of the present model, a true plateau is obtained since ΔM has been assumed to be T independent, in contrast with the experimental results (Fig. 1), where ΔM decreases linearly with T. It is also observed that when H_{max} is not high enough to complete the transition ($H_{max} < \Delta H_t$), then $\Delta S(0 \rightarrow H_{max}) = (H_{max}/\Delta H_t)\Delta S$ is smaller than ΔS. Accordingly, $(H_{max}/\Delta H_t)$ is the fraction of the sample that has been transformed.

In conclusion, the magnetocaloric effect arising from a field variation $0 \rightarrow H_{max}$ can be properly evaluated through the entropy change obtained from the Maxwell method, even when an ideal first-order transition occurs. When the Maxwell relation is evaluated over the whole field range, the T and H dependences of the magnetization in each phase outside the transition region yield an entropy change larger than that of the transition. It has been shown that the Maxwell relation, the Clausius-Clapeyron equation, and the calorimetric measurements yield the entropy change of the first-order magnetostructural transition, provided (i) the Maxwell relation is evaluated only within the field range over which the transition takes place and (ii) the maximum applied field is high enough to complete the transition. The transition tem-
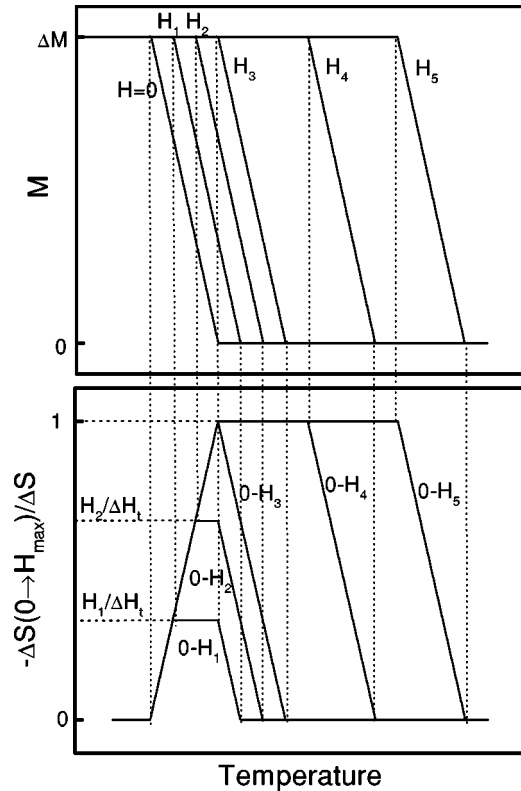

FIG. 3. Upper panel shows the temperature dependence of the magnetization across the transition region at different fields, assumed in the model described in the text. Lower panel shows the corresponding entropy change $\Delta S(0 \rightarrow H_{max})$ calculated from the Maxwell relation. In this figure, ΔS stands for the entropy change of the transition, obtained from the Clausius-Clapeyron equation.

perature must significantly shift with the applied field, in order to achieve a large MCE taking advantage of the entropy change associated to the first-order transition, as also suggested in Ref. 14.

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