Direct Measurement of the "Giant" Adiabatic Temperature Change in $Gd_5Si_2Ge_2$

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Direct adiabatic temperature change as well as magnetic measurements were carried out on two different samples of $Gd_5Si_2Ge_2$ composition for which calculations predicted a "giant" magnetocaloric effect (MCE). While magnetic measurements well reproduce published values, serving the basis for the predictions, direct adiabatic temperature change measurements show a significantly smaller MCE. The discrepancy can be interpreted on the basis of the thermodynamics of first order magnetic transitions.

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The highest magnetocaloric effect for a second order transition known so far is produced by the rare-earth element Gd and its ferromagnetic alloys of diverse structure of composition [1–3], where the isothermal magnetic entropy change, ΔS_M, ranges up to 12 $\mathrm{J\,kg^{-1}\,K^{-1}}$ and the adiabatic temperature change, ΔT_{ad}, up to about 14 K for a 7 T applied field. The magnetocaloric effect (MCE) in these materials is related to the field dependent, gradual change of the magnetic order parameter, with no change to the magnetic order itself. The MCE is large if the field has a significant impact on the order parameter, i.e., at low temperatures in paramagnets, and near the order-disorder transition temperature in ferromagnets.

The only known material displaying magnetocaloric effects higher than Gd is the near equiatomic Fe-Rh alloy [4], where the MCE is related to a first order transition, i.e., to a change of the magnetic order itself. This transition can be induced via external magnetic field, without changing the nature (magnetic order) of the two phases involved.

On the basis of the above, significant interest was generated towards first order transition materials. The new $Gd_5(Si_xGe_{1-x})_4$; $x \leq 0.5$ alloys system [5–11] displayed "giant" magnetic entropy changes (2–5 times higher than that of pure Gd), when calculated from the magnetization curves using the Maxwell relations. The adiabatic temperature change was calculated from the total entropy curves and the values obtained were 30% higher than the magnetocaloric effect of gadolinium.

In 1995, Barclay and Liu performed a preliminary direct measurement of adiabatic temperature changes [12] on a rod-shaped $Gd_5Si_2Ge_2$ sample. (This material was prepared by Ames Laboratory via arc melting using high purity constituents [8].) The obtained adiabatic temperature changes were very similar to that of gadolinium, i.e., fairly high, but not giant. Well within experimental error, this value agreed with adiabatic temperature changes calculated from integrated specific heat data, i.e., from the entropy curves. Simultaneously, using the same methods for pure Gd resulted in adiabatic temperature changes identical to reported values [1,13]. On this basis, following the construction of a more refined device [14], direct measurements—together with detailed magnetic studies—were performed on the very same sample.

Figure 1 shows the magnetization curves in the temperature range of the transitions measured in increasing and decreasing fields using a commercial SQUID magnetometer. The magnetization curves—which are identical to those in [5] within experimental error—show a gradual transition to metamagnetism, starting at about 272 K and being complete at about 280 K. Below about 270 K the magnetization curves are characteristic of a ferromagnet without domains. Similarly, the metamagnetism gradually disappears between 310 and 320 K, giving rise to paramagnetic behavior. In the metamagnetic region, the material displays field induced transitions. The critical field for these transitions depends on the temperature as well as on the direction of the field change (increasing or decreasing fields). We believe the phenomenon is connected to different Gd sublattices with different, and/or differently ordered moments. At the critical field, the spins of at least one sublattice flip in unison toward the direction of the applied field, resulting in a near-ferromagnetic structure [15]. In decreasing fields, the ferromagnetic order collapses in lower fields than

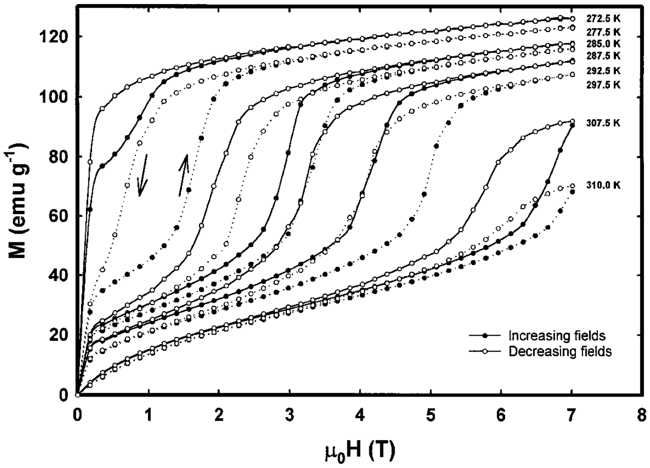

FIG. 1. Magnetization curves of a $Gd_5Si_2Ge_2$ rod, in increasing or decreasing applied fields.

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is necessary to induce the transition, resulting in a remanence-free hysteresis.

The magnetic entropy change was then calculated using the integrated Maxwell relations [16]:

$$dS = -\int \left[\frac{dM}{dT} \right]_H dH\,, \tag{1}$$

where dS, dH, dM, dT are all infinitesimal increments of either continuous functions (S, M) or independent experimental parameters (T, H). Figure 2(a) shows the calculated results for increasing fields. The behavior of ΔS_M is identical to that obtained [5–11] earlier, with a slightly higher value for the "spike" in our calculation. However, when calculating the magnetic entropy change in decreasing fields, the results become different [Fig. 2(b)]. The spike, driving the values into the giant range in increasing fields, is significantly reduced and shifted to higher temperature in decreasing fields, proving that the transition of $Gd_5Si_2Ge_2$ is not reversible. The plateau between the two spikes is stable, but it corresponds only to a moderate magnetic entropy change. This behavior, i.e., the saturation of the calculated magnetic entropy change as a function of the field, as well as the existence of the plateau, which broadens, but does not increase in height with increasing applied fields, are characteristic features of first order magnetic transitions [17].

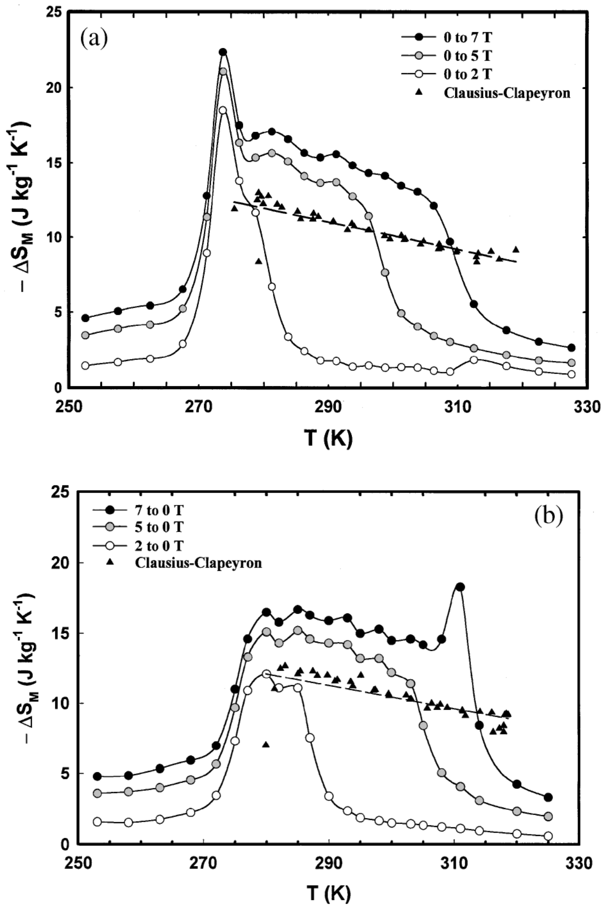

FIG. 2. Magnetic entropy change for (a) increasing and (b) decreasing fields, as calculated from the Maxwell relations (circles), or from the magnetic Clausius-Clapeyron equation (triangles), using the magnetization curves shown in Fig. 1.

Figure 3 shows the results of recent direct measurements of the adiabatic temperature change on the sample. The values obtained are quite close to results found earlier [12]. The values obtained via indirect methods [5,7,8], are about 65% larger than the values shown in Fig. 3. A significant experimental error can be excluded, as our results on high purity Gd agrees with the value of AMES laboratory [13] within 1 K (10.5 and 11.5 K, respectively, both for 5 T fields). For 7 T, our value (12 and 13 K for industrial and high purity Gd, respectively) agrees well with that of Brown (14 K, [1]).

The measurements were then repeated on a button-shaped second sample prepared by AMES laboratory via arc melting, using the same high purity starting materials as before. The adiabatic temperature change was within experimental error identical to that of the first sample as shown in Fig. 3.

To resolve the discrepancy between the direct and the indirect (calculated) results, it is necessary to review the thermodynamics behind the calculations. From now on, we will refer to the MCE in Gd type materials as "order parameter" MCE, and those in Fe-Rh or $Gd_5Si_2Ge_2$ materials as "order" MCE. The basic difference between "order parameter" and "order" MCE is the nature of the entropy change. For order parameter MCE, the gradual, continuous magnetic entropy change is related to the field-induced, gradual, continuous changes of the order parameter. The experimentally measured macroscopic magnetization well represents this order parameter [18]; thus the magnetic entropy change can be calculated from the magnetization curves using the integrated Maxwell relations [16]. This entropy change usually agrees well with the value obtained from field dependent specific heat measurements [2,13]. Simultaneously, direct measurements of the adiabatic temperature change agree well with

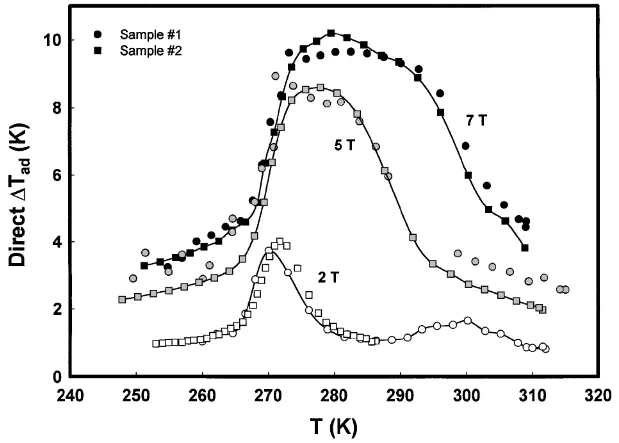

FIG. 3. Adiabatic temperature change (direct measurement) for $Gd_5Si_2Ge_2$ samples (○, rod; □, button).

values obtained from field dependent specific heat measurements [2,13] as the isentropic distance of the total entropy curves or using approximative equations [2].

On the contrary, order MCE does not involve a "magnetic" entropy change in first approximation. The sudden, discontinuous entropy change is related to the phase transition itself, and is approximately independent of the applied field. The field shifts the transition only to higher temperatures. This entropy change cannot be calculated from the Maxwell relations, for two reasons: (i) It is not a magnetic entropy change, and (ii) $M(T)$ or $M(H)$ is not a continuous, derivable function.

For first order transitions, the Clausius-Clapeyron equation offers a way to calculate the entropy change [19]. The transition occurs if the two magnetic phases have equal thermodynamic potential:

$$\left[U_1 - \frac{n_1 M_1^2}{2}\right] - \Theta S_1 + (pV_1 - HM_1) = \left[U_2 - \frac{n_2 M_2^2}{2}\right] - \Theta S_2 + (pV_2 - HM_2), \tag{2}$$

where Θ is the transition temperature at the field H, and $U_{1,2}$, $S_{1,2}$, $V_{1,2}$, $M_{1,2}$ are the internal energy, entropy, volume, and magnetization of phases 1 and 2, and nM^2 describes the molecular field contribution. Assuming the external field only triggers the transition, but does not change the value of the physical parameters (S, M, V, n) in either phase, the difference of the transition temperatures for a field change of ΔH is given as

$$\left|\frac{\Delta\Theta}{\Delta H}\right| = \left|\frac{\Delta M}{\Delta S}\right| = \text{const}, \qquad \text{on the basis of the above assumptions,} \tag{3}$$

where $\Delta M = M_2 - M_1$ is the difference between the magnetizations, and $\Delta S = S_2 - S_1$ the difference between the entropies of the two phases, and the sign depends on the sign of ΔM and ΔS.

We have to point out, that unlike the Maxwell relations, this is not a differential equation. It gives the relation between differences, not differentials. Unlike T and H in the Maxwell relations, the variables Θ and H are not independent experimental parameters. Equation (3) shows instead, that if a transition is observed at a temperature Θ_1 in an applied field H_1, the temperature will shift by $\Delta\Theta = \Delta H(\Delta M/\Delta S)$ to Θ_2, if the applied field is increased by ΔH to H_2. Similarly, if a critical field H_1 is observed on an isothermal magnetization curve at a temperature T_1, raising the temperature by ΔT to T_2 will shift the critical field by $\Delta H = \Delta T(\Delta S/\Delta M)$ to H_2. Consequently, measuring the field dependence of the critical temperature (or the temperature dependence of the critical field) will allow for the determination of $\Delta S/\Delta M$. As ΔM can be obtained from the magnetization curves with good approximation, ΔS can then be calculated from Eq. (3).

Evaluation of the $H_{\text{crit}}(T_{\text{crit}})$ curves gives the zero field transition temperature as 272.2 and 278.2 K for increasing and decreasing fields, respectively, and dT/dH equals 6.5×10^{-4} K Oe^{-1}. From this value and the experimentally observed ΔM, the entropy change can be calculated and the curves are shown in Figs. 2(a) and 2(b). The curves scale with the plateau of the Maxwell relations, but it is about 20% lower. At the zero field transition temperature the entropy change is obtained as $\Delta S = 12.5$ J kg^{-1} K^{-1}. Figure 4 displays the idealized T-S diagram for this type of material, assuming the entropy change is field and temperature independent. The figure clearly shows that if the field is not high enough to shift the transition, i.e., the nominal $\Delta\Theta < \Delta T_{\text{ad}}$, no adiabatic temperature change will be observed. Magnetization curves show that threshold field equals about 1.55 T, as discussed above. Thereafter, the value of ΔT_{ad} does not depend on the applied field, but is determined by the value of ΔS, and the slope of the curve,

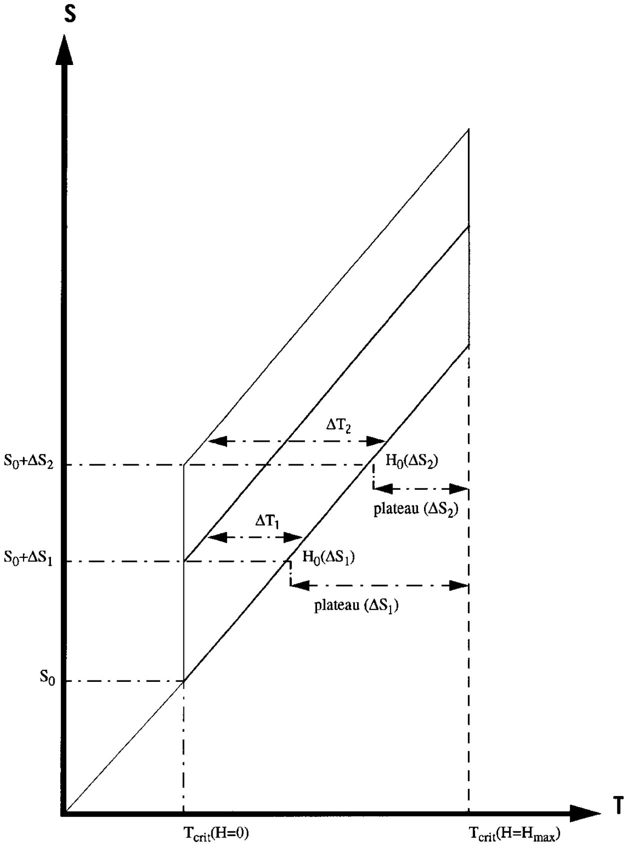

FIG. 4. Schematic $S(T)$ diagram for first order magnetic transitions, used to calculate the available ΔT_{ad} from ΔS.

which equals C_p/T at the beginning of the transition [4]. Calculating the total entropy from specific heat data, with or without magnetic field, might be difficult for a sharp transition. Using an independently obtained ΔS might be sometimes advantageous.

With ΔS calculated from the Clausius-Clapeyron method, we obtain $\Delta T = 9.9$ K, which is in excellent agreement with the direct measurement of 10 K at 7 T. From Fig. 4 we can also estimate the width of the plateau. If the experimental temperature is higher than $\Theta + \Delta\Theta$ for the maximum applied field, the adiabatic temperature change disappears as the field cannot trigger the transition anymore. For a 7 T applied field, this temperature difference equals 35 K (taking the threshold into consideration), that agrees very well with the observed width. Figure 4 also shows that increasing the value of ΔS, ΔT will also increase, as well as the threshold, which means the peak will be higher, but narrower. Using the value of the spike as obtained from Maxwell relations, yields $\Delta T_{\mathrm{max}} = 14.9$ K, which is about the value reported in Ref. [5]. At the same time, the ΔT peak is significantly narrower than the one observed in our direct measurements, in accordance with the above reasoning.

Figure 4 demonstrates that using the maximum ΔS value obtained from Maxwell relations overestimates ΔT_{ad} in case of first order transitions, and that calculations based on the total entropy curves from field-dependent specific heat measurements deliver better results [12]. The entropy discontinuity obtained from specific heat measurements can be justified by calculating the ΔS value from magnetization curves using the Clausius-Clapeyron equations [4,19].

On this basis, the magnetocaloric effect of $Gd_5Si_2Ge_2$ lies in the same range as that of Gd and its alloys.

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