

Giant heat dissipation at the low-temperature reversible-irreversible transition in Gd_5Ge_4

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The heat exchanged at the low-temperature first-order magnetostructural transition is directly measured in Gd_5Ge_4 . Results show that the origin and the temperature dependence of the heat exchanged varies with the reversible/irreversible character of the first-order transition. In the reversible regime, the heat exchanged by the sample is mostly due to the latent heat at the transition and decreases with decreasing temperature, while in the irreversible regime, the heat is irreversibly dissipated and increases strongly with decreasing temperature, reaching a value of 237 J/kg at 4 K.

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Nowadays, there is a great deal of interest in using the magnetocaloric effect (MCE) as an alternative technology for refrigeration. 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.¹ Materials showing first-order field-induced magnetostructural transitions are promising candidates for magnetic refrigeration, since they are expected to display a giant MCE.¹ The largest MCE values near room temperature have been found in $\text{Fe}_{0.49}\text{Rh}_{0.51}$,² $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$,³⁻⁵ $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$,^{6,7} and MnAs-based^{8,9} alloys. At low temperatures, paramagnetic salts have been traditionally used for MCE. However, the most suitable paramagnets are intermetallic compounds or garnets such as PrNi_5 ,¹⁰ $\text{Gd}_3\text{Ga}_{5-x}\text{Fe}_x\text{O}_{12}$,¹¹ or $\text{Dy}_3\text{Ga}_5\text{O}_{12}$.¹² In order to enhance MCE at low temperatures, materials with a second-order phase transition have been investigated, such as ErAl_2 (Ref. 13) and ErNi_2 ,¹⁴ but as far as we know, MCE associated with a first-order phase transition below 20 K has not been reported.

$\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys have been extensively studied since the discovery of giant MCE in $x \leq 0.5$ compounds.³ Ge-rich compounds ($x \leq 0.2$) present a first-order structural transition ranging from ~ 20 K ($x=0$) to ~ 120 K ($x=0.2$), accompanied by a change in the magnetic ordering between antiferromagnetic (AFM) and ferromagnetic (FM) state,³⁻⁵ which gives rise to a large entropy change. In particular, the unusual magnetic behavior shown by the end-compound Gd_5Ge_4 at low temperatures has lately attracted a lot of interest.¹⁵⁻²⁴ In this alloy, the nature of the AFM ordering related to the high-temperature phase is complex, with competing AFM (between layers) and FM interactions (within layers).^{5,15-18} Moreover, due to this anisotropy in the exchange interactions, the magnetic ordering remains AFM without undergoing the structural transition after zero-field-cooling (ZFC) down to ~ 2 K.^{15,19} The application of a certain magnetic field, whose value depends on the temperature, induces the first-order AFM-to-FM transition, which is irreversible at temperatures below ~ 10 K, partially reversible from ~ 10 to ~ 20 K and fully reversible above ~ 20 K (Refs. 15, 17, 20, and 21) as in the rest of Ge-rich compounds. The irreversibility of the transition might be due to a hindrance of the kinetics of the reversed AFM-FM transition, which at suffi-

ciently low temperatures and high fields becomes arrested (i.e., structural relaxation time is larger than experimental time scales).^{21,24}

In this work, a study of the heat absorbed or released at the low-temperature irreversible and reversible first-order field-induced phase transitions is carried out in Gd_5Ge_4 . Results show that the origin and the temperature dependence of the exchanged heat varies with the reversible/irreversible character of the first-order transition. In detail, the heat exchanged by the sample in the reversible regime is majorly due to the latent heat at the magnetostructural transition, while the heat dissipation associated with the magnetic work is much smaller. In contrast, in the irreversible regime, giant heat dissipation much larger than the latent heat occurs, because of a progressive stabilization of the AFM phase at low temperatures.

Gd_5Ge_4 sample was prepared by arc-melting admixtures of pure elements (99.9 wt % Gd and 99.999 wt % Ge) in the desired stoichiometry under a high-purity argon atmosphere. The sample was placed in a water-cooled copper crucible and melted several times to ensure good homogeneity. The weight losses after arc-melting were negligible. The crystallographic structure of the sample was studied at room-temperature by x-ray diffraction (XRD). The sample displayed the expected Sm_5Ge_4 -type orthorhombic structure.^{4,5} Electron-beam microprobe analysis showed that no secondary phases were present in the sample. Magnetization measurements were carried out from 4 to 300 K and up to 50 kOe using a superconducting quantum interference device (SQUID) magnetometer. $M(T)$ curve on heating at 5 kOe after ZFC from 300 K showed a cuspid between 12 and 27 K, and the expected AFM-to-paramagnetic transition at ≈ 130 K, in agreement with previously reported results.^{15,17} A second ZFC curve, recorded on heating at 5 kOe after applying a field of 50 kOe during a few seconds at 4 K, shows a strong decrease at ~ 25 K and matches the first ZFC curve above ~ 30 K. Isothermal magnetization curves were measured while increasing and decreasing the field after ZFC from above 130 K, at temperatures $T=4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40$, and 45 K. From 4 to 20 K, the magnetization curves while increasing the field showed the expected irreversible transition between AFM and FM phases,^{15,17} the sample remaining in the FM phase after the

field was further reduced down to zero. The presence of a 22% FM component in the virgin sample^{16,22} was estimated from the saturation in the magnetization curve at 4 K, observed before the irreversible transition takes place. The FM state in the virgin sample may be stabilized by interstitial impurities in Gd used in the synthesis, as Hardy *et al.* suggested.²² The heat dissipated in a magnetization hysteresis loop Q_M was calculated as the area comprised inside the loop. Calorimetric data were measured using a differential scanning calorimeter (DSC) operating under a magnetic field H .²⁵ Measurements were carried out by recording heat flow while H was swept at 10 kOe/min at a constant temperature, which enables to obtain the heat released or absorbed by the sample as the integral of the calorimetric peak.²⁶

Calorimetric curves shown in Fig. 1 were obtained after ZFC the sample from a temperature well above 130 K (which corresponds to the Néel temperature of the material) down to a given temperature T . This procedure was carried out at temperatures $T=4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40$, and 45 K. Calorimetric curves for 4–16 K are displayed in Fig. 1(a). In this case, a peak corresponding to the irreversible AFM-to-FM transition appears at a certain value of the magnetic field, which indicates that a certain amount of heat (Q_{inc}) is released by the sample. Besides, no peak is observed while decreasing H , due to the irreversibility of the transition (for the sake of clarity, the corresponding calorimetric curves are not shown). However, calorimetric curves from 18 to 25 K, displayed in Fig. 1(b), show also a peak when H is decreased. In this case, the area of the peak corresponds to the heat absorbed by the sample (Q_{dec}), which is much smaller than that obtained while increasing H , indicating that the transition is only partially reversible. The area of this peak increases with T up to 25 K [see Fig. 1(b)], temperature above which the transition is fully reversible and the difference between Q_{inc} and Q_{dec} remains constant as a function of temperature [Fig. 1(c)]. In the partially reversible regime, the reconversion of part of the sample to the AFM phase is observed only at 18 and 20 K when H is reduced to zero (see Fig. 2), since low values of exchanged heat may not be detected by the DSC at lower temperatures.²⁷ At 25 K, the reversibility of the transition is still incomplete, in agreement with $M(T)$ measurements, which indicate that the onset of reversibility in this sample is located between 26 and 30 K.

The reproducible peak structure present in the calorimetric curves (Fig. 1) arises from the avalanche-type dynamics of the first-order transformation, which is known to be athermal for $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds with low transition temperature.^{26,28,29} In this case, the system reproduces the optimal path through the distribution of energy barriers (controlled by the presence of disorder such as dislocations, vacancies or grain boundaries) that separate the two phases.

Figure 2 shows the heat absorbed or released by the sample at the transition, obtained from the area of the calorimetric peaks^{25,26} in Fig. 1. The absolute value of this data is displayed to allow a direct comparison between negative values obtained while increasing H (released heat, Q_{inc}) and positive values obtained while decreasing H (absorbed heat, Q_{dec}). In the fully reversible regime, above 25 K, the major contribution to Q_{inc} and Q_{dec} comes from the latent heat as-

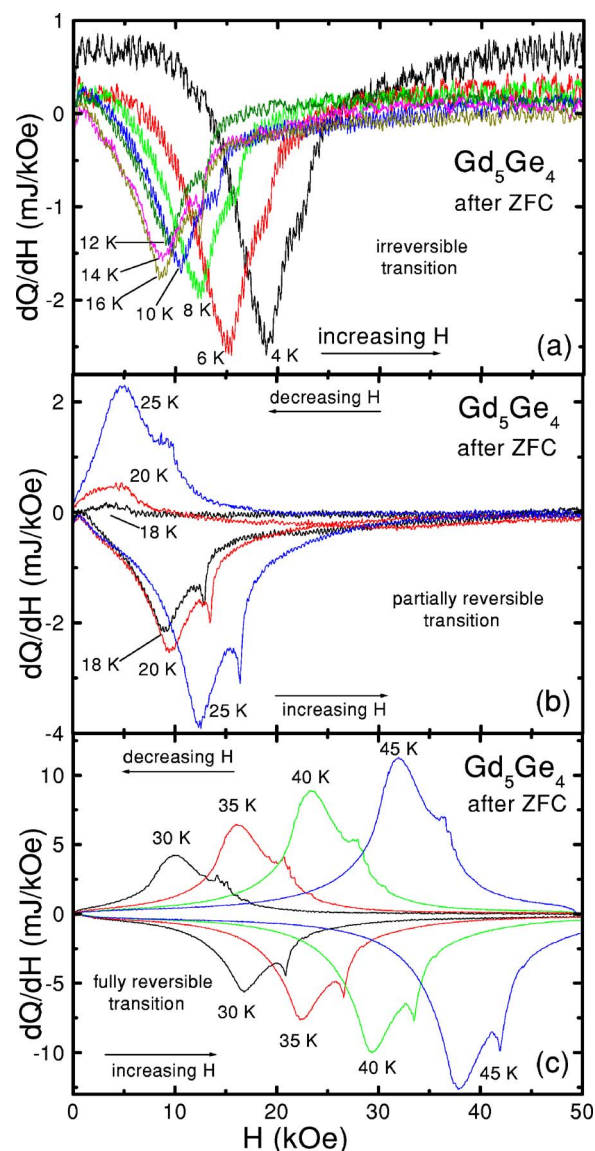


FIG. 1. (Color online) Calorimetric curves recorded while sweeping H at selected temperatures, after zero-field-cooling the sample from well above 130 K. (a) Curves at $T=4, 6, 8, 10, 12, 14$, and 16 K, measured increasing H , where only the irreversible transition is observed. (b) Curves at $T=18, 20$, and 25 K, measured increasing and decreasing H , where the partially reversible transition is shown. (c) Curves at $T=30, 35, 40$, and 45 K, measured increasing and decreasing H , for which the transition is fully reversible.

sociated with the first-order nature of the magnetostructural transition.^{30,31} The difference $|Q_{inc}| - |Q_{dec}| = Q_{diss}$ thus represents the heat that the sample releases irreversibly in a close magnetic field cycle. Figure 2 shows that Q_{diss} is almost temperature independent in the fully reversible regime and coincides with Q_M , which indicates that Q_{diss} is majorly due to the rearrangement of the magnetic domains. We note that, in this regime, Q_{diss} is much smaller than both Q_{inc} and Q_{dec} , in accordance with the well-known behavior at the reversible AFM-FM transition in Ge-rich alloys, which is exhaustively reported in Refs. 30 and 31. However, Q_{inc} and Q_{dec} decrease at low temperature because the contribution of the latent heat

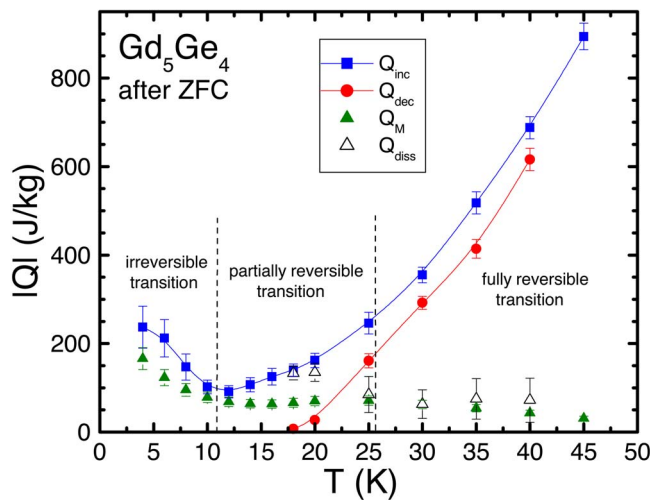


FIG. 2. (Color online) Absolute values of the exchanged heat obtained from DSC measurements while increasing and decreasing H (Q_{inc} and Q_{dec} , respectively) and of the heat dissipation in a magnetization hysteresis loop (Q_M), at selected temperatures, after zero-field-cooling the sample from well above 130 K. Q_{diss} stands for $|Q_{inc}| - |Q_{dec}|$. Solid lines are a guide to the eye.

also decreases as expected from the third principle of thermodynamics. In the partially reversible regime, Q_{inc} tends to a constant value, which corresponds to Q_{diss} since Q_{dec} tends to zero. This fact suggests that the irreversible heat dissipation takes place primarily as H is increased, since the magnetic work required to build a FM state from an AFM one is much higher than that corresponding to the inverse transition because of the relative magnetic hardness of the two phases involved. Finally, in the irreversible regime, $Q_{diss} = Q_{inc}$ follows Q_M within the experimental error indicating that the heat irreversibly dissipated by the sample is much larger than the latent heat associated with the first-order transition. Furthermore, both Q_{inc} and Q_M increase largely at low temperatures which points out that the AFM phase is stabilized as temperature decreases, since the magnetic work required to rearrange the AFM domains into FM ones increases. We note that at 4 K a value of $Q_{inc} = 237$ J/kg is obtained, which is in fact less than that expected (304 J/kg) if the whole sample were AFM in the virgin state. According to Levin *et al.*,¹⁹ thermal fluctuations of the Gd magnetic moments and/or elasticity of the lattice in the AFM phase are reduced when lowering the temperature, favoring the AFM ordering, which raises the free energy difference between AFM and FM phases. This is unambiguously shown by the increase in the heat dissipation at the transition as shown in Fig. 2 at low temperature. Consequently, when the first-order AFM-FM transition loses its reversible nature, the transition becomes dominated by the heat dissipation Q_{diss} .

Finally, various calorimetric curves were recorded at 4 K on increasing H after a thermal regeneration process at zero field, which consists in heating the sample (in the FM state) up to a given temperature (T_{max}) and cooling it again down

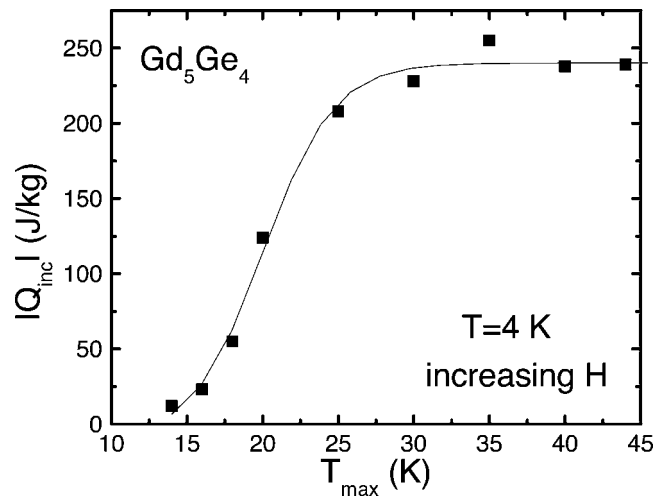


FIG. 3. Absolute value of the heat released by the sample obtained from DSC measurements while increasing H at 4 K, after the sample in the FM state was heated up to T_{max} and cooled down to 4 K at zero field. Solid line is a guide to the eye.

to 4 K. The obtained absolute values of Q_{inc} at the transition as a function of T_{max} are displayed in Fig. 3. For T_{max} between 14 and 25 K only a part of the system in the FM state transforms to the AFM state during the regeneration process, giving rise to a heat dissipation measured at 4 K that increases with T_{max} . For T_{max} equal or above 30 K, the sample is entirely regenerated and the maximum value of Q_{inc} is recovered at 4 K. For T_{max} equal or below 12 K, no heat exchange can be measured.

In conclusion, the thermal dependence of the exchanged heat varies with the reversible/irreversible character of the first-order transition present in Gd_5Ge_4 at low temperatures. In the reversible regime (above ~ 27 K), the exchanged heat mostly arises from the latent heat at the magnetostructural transition, while the heat dissipation due to the magnetic work needed to complete the AFM-FM transformation is almost temperature independent and much smaller. As the temperature is reduced, and the system progressively enters the partially reversible regime, the latent heat tends to zero and the heat irreversibly dissipated becomes dominant. In the complete irreversible regime (below ~ 12 K) the heat dissipation largely increases with decreasing temperature reaching a value of 237 J/kg at 4 K with an applied magnetic field of 30 kOe, unambiguously showing the progressive stabilization of the AFM phase. Finally, although the irreversibility of the transition in Gd_5Ge_4 does not allow a direct application in magnetic refrigeration, the large value of Q_{inc} at 4 K arises as a reference point for development of new magnetocaloric materials at low temperatures.

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