Managing hysteresis of Gd5Si2Ge2 by magnetic field cycling

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Abstract
The influence of magnetic field cycling through the first-order magnetostructural transformation on the magnetic and magnetocaloric properties, as well as hysteresis of polycrystalline Gd5Si2Ge2, has been studied using magnetometry. The cycling has a minimal effect on the magnetic field-induced entropy change and the phase transformation temperature of the material. On the other hand, magnetic hysteresis decreases by 30% after approximately ten cycles and remains low unless the sample is moved far into the paramagnetic regime. Factors playing a role in the history dependence of hysteresis have been discussed.

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ABSTRACT
The influence of magnetic field cycling through the first-order magnetostructural transformation on the magnetic and magnetocaloric properties, as well as hysteresis of polycrystalline Gd$_5$Si$_2$Ge$_2$, has been studied using magnetometry. The cycling has a minimal effect on the magnetic field-induced entropy change and the phase transformation temperature of the material. On the other hand, magnetic hysteresis decreases by 30% after approximately ten cycles and remains low unless the sample is moved far into the paramagnetic regime. Factors playing a role in the history dependence of hysteresis have been discussed.

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INTRODUCTION
Magnetocaloric effect (MCE)—a change in a material’s temperature during adiabatic application and removal of a magnetic field—is a fundamental magnetothermal phenomenon of practical importance, e.g., in energy-efficient solid-state magnetocaloric refrigeration (MCR). Rooted in coupling of atomic magnetic moments with an external magnetic field, MCE is intrinsic to all magnetic materials, even those that are weakly magnetic or paramagnetic (PM). For instance, adiabatic demagnetization of paramagnets has been realized in commercial refrigeration systems and is employed in laboratory practice to reach ultralow temperatures. Away from absolute zero and in fields that can be sustained with permanent and/or superconducting magnets, MCEs are maximized near spontaneous magnetic phase transitions where the changes of magnetization with temperature, $[\text{d}M/\text{d}T]$, are both the largest and remain substantial as the magnetic field, $H$, increases. Continuously operating cryogenic magnetocaloric refrigeration (MCR) systems for liquefaction of hydrogen or cooling of helium below its superfluid transition temperature have been demonstrated and employed in laboratory research as well.

MCR near room temperature is complicated by the fact that lattice heat capacity of many solids is already at or approaching the fundamental limit of $3R \ J \ mol(\text{atoms})^{-1} \ K^{-1}$, where $R$ is the universal gas constant. Hence, for the majority of conventional magnetic materials, magnetic field-independent lattice entropies dominate over the magnetic field-induced magnetic entropy changes around 300 K, leading only to insignificant adiabatic temperature changes. Consequently, research activity in this temperature region was dormant until the late 1990s, although feasibility of near room temperature regenerative MCR has been demonstrated using elemental gadolinium in 1976.

Giant magnetocaloric effects (GMCEs) tunable between cryogenic and room temperatures reported in the Gd$_5$Si$_2$Ge$_2$ family showed a path forward in the design of new materials and compounds by making use of lattice entropy changes coupled with magnetic entropy changes, where both can be actuated by reasonably low magnetic fields. For example, Gd$_5$Si$_2$Ge$_2$ exhibits isothermal entropy change, $|\Delta S|$, in excess of 20 $1 \ J \ kg^{-1} \ K^{-1}$ with adiabatic temperature change, $|\Delta T_{ad}|$, reaching ~15 K between ca. 270 and 300 K when the driving magnetic field varies between 0 and 50 kOe. A number of promising materials exhibiting GMCEs were discovered, and numerous proof-of-principle MCR systems were demonstrated over the last 20 years, proving that near room temperature cooling with magnetocaloric effect has a future.

Despite exhibiting one of the largest reported $\Delta T_{ad}$, Gd$_5$Si$_2$Ge$_2$ has several drawbacks. One of the alloy components—germanium—is
rare, and when the compound is prepared from "99.9% pure" gadolinium, the material must be annealed at temperatures as high as 1570 K to realize its GMCE.7 Furthermore, this intermetallic compound is brittle and therefore has poor mechanical stability, plus its performance may be affected by measurable hysteresis. Discoveries of Fe3P- and La(Fe1−xSi)x-based materials addressed the downside related to the unfavorable chemical makeup of Gd5Si2Ge2−x, even though their synthesis is rather complicated. Poor mechanical stability, intrinsic to the majority of intermetallics, can be addressed by creating appropriate composites.31−33 Managing hysteresis and irreversibilities in Gd5Si2Ge2 and other materials while preserving the giant magnetocaloric effects, on the other hand, is quite difficult.

In principle, hysteresis in Gd5Si2Ge2 can be reduced and even completely suppressed by chemical substitutions, but a common penalty is the destruction of the first-order magnetostuctural transition responsible for GMCE, and its replacement by a second-order magnetic-only phase transformation with conventional MCE, which is lower by a factor of two or more.26,27 To make GMCE practical, materials subjected to continuous magnetizing/demagnetizing cycling near the corresponding phase transition temperatures must exhibit minimum irreversibilities, i.e., they must have low energy losses. Understanding of the factors influencing magnetic field-induced direct and reverse magnetostuctural transitions is, therefore, important to manage associated hysteresis.16,28−32

Magnetic hysteresis of approximately 5 kOe reported in Gd5Si2Ge2 single crystals when a magnetic field is cycled up and down above the Curie temperature of the compound is about half of that (ca. 10 kOe) typically reported for polycrystalline materials with the same composition.35 Assuming that the hysteresis observed in single crystals is dominated by energy barriers between the low-field monoclinic paramagnetic (PM) and high-field orthorhombic ferromagnetic (FM) phases of Gd5Si2Ge2, phase nucleation, and kinetic barriers, and therefore hysteresis, can be controlled by “training” and/or by a properly designed microstructure of polycrystals.54 The training, which consists of cycling materials through first-order transitions, is known to measurably change properties of polycrystalline Gd5Si2Ge2−x materials that undergo isosymmetric phase transitions near or below ~100 K.36−38 Since Gd5Si2Ge2 exhibits a different magnetostuctural transition, i.e., it proceeds with the change of symmetry, reversible formation of nanotwins,34,40 and is characterized by a smaller phase volume change,41 the effects of training are both of fundamental and practical interest. As far as we are aware, only one similar system, i.e., a thin film of Gd5Si1.7Ge2.7, has been examined in the past, where cycling of the film through the magnetostuctural transformation reduces its magnetocaloric effect, mostly due to lower crystallinity and a reduced fraction of the Sm3Ge9-type phase.42

**EXPERIMENTAL METHODS**

Polycrystalline Gd5Si2Ge2 material used in this study is from the same batch that was employed in an earlier investigation of its barocaloric effect.55 The sample was prepared by arc-melting of the pure elements and annealed at 1570 K for 2 h in an open tantalum container placed inside a high-vacuum induction furnace. The x-ray powder diffraction (XPD) pattern recorded at room temperature confirms that the majority of the sample crystallizes in the monoclinic phase of Gd5Si4Ge2. A minor amount (~6 vol.%) of Gd(Si1−xGe)x phase with x = 0.5 and a CrB-type structure was also detected. Backscattered scanning electron microscopy (BS-SEM) combined with electron dispersive spectroscopy (EDS) confirms that the impurity phase is indeed the Gd(Si1−xGe)x phase, which is paramagnetic in the investigated range of temperatures and magnetic fields, with stoichiometry close to Gd(Si0.6Ge0.4). (see Figure S1 and Table S1 in the supplementary material). The Bragg peaks of Silicon-rich Gd5Si2Ge2−x phase with the orthorhombic Gd5Si2-type structure, often present in minor quantities in the nominally stoichiometric Gd5Si2Ge2 alloys, were not observed, although given the complexity of the XPD pattern we cannot completely rule out its presence in a small concentration (~1−2 vol. % max). This silicon-rich phase is not discernible in the BS-SEM image due to a negligible difference in contrast when δ is small.

All magnetic measurements were performed in a DynaCool Physical Property Measurement System (PPMS, Quantum Design) using a vibrating sample magnetometer (VSM) option. A total of four samples extracted from the same batch were examined to verify the reproducibility of the results. The magnetization (M) as a function of temperature (T) was measured in a low magnetic field of 100 Oe to verify Curie temperatures, T_C, of all samples. All of them showed typical first-order magnetostuctural transitions with T_C = 265 K on heating and with thermal hysteresis of 5 K.33 The four specimens were then subjected to cyclic measurements using protocols 1, 2, and 3 described in the next paragraph. All four showed practically identical behaviors; hence, only one of the samples was fully examined further by applying protocols 4 through 7, the results of which are reported here.

Cyclic M vs H measurements were performed at 270 K (just above T_C) by sweeping the magnetic field from 0 up to 40 kOe at 100 Oe s−1 (henceforth the initial magnetization sweep) and then sweeping the field from 40 kOe down to 0 at the same rate (henceforward the return magnetization sweep). First (hereafter protocol 1), the sample was loaded in a PPMS, and its temperature was lowered to and set at 270 K. After establishing temperature stability for 20 min, isothermal M(H) measurements were performed for 80 full cycles sweeping the magnetic field from 0 to −40 kOe and back to 0. Next (hereafter protocol 2), the sample was kept at 270 K for 30 min, following which M(H) data were recorded for 40 additional full cycles. Then (protocol 3), the sample was heated to 340 K, i.e., well into the paramagnetic region (75 K above T_C), to fully remove any remaining (i.e., trapped) field-induced ferromagnetic phase, and then cooled back to 270 K in H = 0 at 10 K min−1, kept at T = 270 K for 20 min, and the isothermal magnetic field cycling was performed 40 times. Protocol 4 repeated protocol 3 except with the slower cooling rate of 1 K min−1 from 340 K to 270 K, also with H = 0. In protocol 5, the sample was heated to 340 K, then cooled down to 270 K at 10 K min−1 in a 50 kOe magnetic field, and then was held for 20 min to stabilize the temperature, subsequently slowly removing the field to 0 at 270 K and recording M(H) data for 40 full cycles. This measurement was followed by protocol 6, where the sample was cooled to 10 K, held there for 30 min, and warmed back to 270 K at 10 K min−1 (all in H = 0), where another 40-cycle measurement data set was obtained, after
establishing temperature stability for 20 min. In protocol 7, the sample was taken out of the PPMS after completing protocol 6 and stored at room temperature for 30 days, after which another set of cyclic measurements (80 cycles between 0 and 40 kOe) was recorded at 270 K, i.e., following protocol 1. In addition to the 100 Oe s\(^{-1}\) field sweep rate constant for all protocols, 40 measurement cycles were performed similar to protocol 1 but with an order of magnitude lower field sweep rate of 10 Oe s\(^{-1}\). Isothermal \(M(H)\) data recorded in protocols 1 through 5 are depicted in Figs. 1(a)–1(e).

To quantify magnetic hysteresis, one needs to define the corresponding critical fields, \(H_c\), even though both direct (during the initial magnetization sweep) and inverse (during the return magnetization sweep) magnetostructural transitions occur in Gd\(_5\)Si\(_2\)Ge\(_2\) over the range of magnetic fields. Thus, for all protocols, \(H_c\)s were assigned as magnetic fields corresponding to half of the largest magnetization recorded during the measurements, i.e., when \(M(H_c) = 0.5 M(H = 40 \text{ kOe})\). The observed magnetic field hysteresis, \(\Delta H_{\text{hyst}}\), is then defined as \(\Delta H_{\text{hyst}} = H_c - H_r\), where \(H_c\) is the critical magnetic field during the initial magnetization sweep and \(H_r\) is the critical field during the return magnetization sweep. As also follows from the data presented in Fig. 1, cycling the material through the magnetostructural transformation leads to a minor but noticeable enhancement of low-field ferromagnetism in most protocols. We quantify this by introducing initial, \(M_i\), and final, \(M_f\), magnetizations. \(M_i\) is determined by extrapolating the linear portions of \(M(H)\) data before the field-induced transitions, typically below 10 kOe, to \(H = 0\), whereas \(M_f\) is determined by extrapolating nearly linear portions of \(M(H)\) data recorded above \(\sim 30\) kOe to \(1/H = 0\).

In all protocols, the deviations from the set temperature of 270 K did not exceed \(\pm 0.25\) K. Considering that the temperature sensitivity of the critical field of the first-order phase transition in Gd\(_5\)Si\(_2\)Ge\(_2\) is 1.69(1) kOe K\(^{-1}\),\(^{33}\) the errors in the determined \(H_c\) and \(H_r\) do not exceed \(\pm 0.43\) kOe. The magnetocaloric effect was calculated using isofield \(M(T)\) measurements recorded in different applied magnetic fields,\(^{45}\) both before executing the measurements following protocol 1 and after completing protocol 7 to check whether magnetic field cycling affects the giant magnetocaloric effect and \(T_C\).

RESULTS AND DISCUSSION

The very first \(M(H)\) measurement at 270 K [Fig. 1(a), protocol 1] shows \(\Delta H_{\text{hyst}} = 8.8\) kOe, which quickly decreases as cycling continues, and hysteresis width is reduced close to 30% by the 10th cycle (Fig. 2). The reduction of the field sweep rate from 100 to 10 Oe s\(^{-1}\) does not change the observed behavior [inset in Fig. 1(a) and Fig. S2 in the supplementary material]. With further cycling, \(\Delta H_{\text{hyst}}\) continues to decrease, albeit at a much slower rate of \(\sim 20\) Oe cycle\(^{-1}\), stabilizing at \(\Delta H_{\text{hyst}} = 6.1\) kOe beyond cycle #40. In addition to lowering the hysteresis width, the cycling also reduces both critical fields: \(H_c\) from 20.9 to 17.4 kOe and \(H_r\) from 12.3 to

FIG. 1. (a)–(e) Isothermal \(M(H)\) cycling data for Gd\(_5\)Si\(_2\)Ge\(_2\) recorded at 270 K with different measurement protocols, see Experimental Methods for details, and (f) comparison of the first cycles for protocols 1 through 5. Main panels are for 100 Oe s\(^{-1}\) magnetic field sweep rate, and the inset in (a) is for 10 Oe s\(^{-1}\) magnetic field sweep rate.
During the later cycles as well, which is not the case. Finally, the temperature fluctuations in sample environment during the measurements must be considered. Given the identical behaviors of four different specimens with different mass (they ranged from 13 to 20.5 mg), rather low magnetic field sweep rates (the roughly 10 kOe field change over which the phase transformation is basically complete takes 100 s), and the fact that sample temperature is controlled by helium exchange gas, it is unlikely that self-heating (cooling) due to GMCE plays any role. Furthermore, a systematic reduction of hysteresis, especially during the first 10 cycles, is too large to be associated with minor temperature instabilities of either the sample or the measurement system. If uncontrolled temperature fluctuations are responsible, such effects will play a role during the later cycles as well, which is not the case. Finally, the same behavior is fully reproducible in the measurements under different protocols [see Figs. 1(a)–1(e)] confirming that the observed changes in $H_{ci}$, $H_{ff}$, and $\Delta H_{hyst}$ are intrinsic.

Figure 3 compares $M(T)$ data collected in a 100 Oe magnetic field before executing protocol 1 and after completing protocol 7. The temperature dependencies of magnetization before and after the cycling measurements remain practically identical near the main magnetostructural transition, and less than 1 K difference in $T_{CS}$ between the two sets of $M(T)$ is likely associated with a conventional training effect. Below 200 K, the magnetization of the cycled sample is slightly higher, likely reflecting either or both a minor magnetostrictive anisotropy (polycrystalline Gd$_5$Si$_2$Ge$_2$ often exhibits at least some texturing during solidification after arc-melting on a water-cooled copper hearth) and/or a random change of demagnetization since the specimen was an irregularly shaped piece of a polycrystalline material. A weak anomaly at 301 K reflects the presence of a small amount of the orthorhombic silicon-rich Gd$_5$Si$_{1.9}$Ge$_{2.1}$ phase not detected in XRD measurements, which has a higher Curie temperature compared to the majority monoclinic Gd$_5$Si$_2$Ge$_2$ phase.

The magnetic entropy change ($-\Delta S_M$), one of the critical parameters determining the magnetocaloric response, was calculated from isofield $M(T)$ data collected before protocol 1 (not shown) and after protocol 7 [Fig. 4(a)]. The transition remains sharp in magnetic fields up to 50 kOe, and it gradually shifts toward a high temperature with the application of a magnetic field, which are typical and well-known characteristics of the first-order magnetostructural transformation in Gd$_5$Si$_2$Ge$_2$. The $M(T)$ data show that cycling while reducing hysteresis by at least 30% has

![FIG. 2. Critical fields, $H_c$ and $H_\gamma$, the width of magnetic hysteresis, $\Delta H_{hyst}$, and $(M_f - M)/M_0$ as functions of cycle number during the measurements using protocol 1. $H_c$, $H_\gamma$, and $\Delta H_{hyst}$ are shown for every cycle from 1 through 5, and then every 5 cycles through cycle 40, and finally every 10 cycles; $(M_f - M)/M_0$ are shown for cycles 1, 2, 5, 10, 20, 30, 40, 70, and 80.](image-url)
little, if any, effect on the first-order nature of the phase transformation in the title material. Furthermore, $\Delta S_m$ remains unchanged, retaining a sizeable maximum value of $-16 \text{ J kg}^{-1} \text{ K}^{-1}$ for a 15 kOe magnetic field change [Fig. 4(b)]. Minor changes in the shape and less than 1 K displacement of the $\Delta S_m(T)$ peak are consistent with conventional training effects.

There may be several possible reasons behind decreasing the hysteresis as a result of cycling through the transition by sweeping the magnetic field up and down. One plausible explanation is the training effect, especially considering a minor yet noticeable change in the behavior of $\Delta S_m(T)$. Conventionally, training implies that the material is conditioned after each cycle to overcome kinetic and energy barriers with less resistance. It is well-known that the nucleation of the ferromagnetic phase of Gd$_5$(Si$_3$Ge$_2$) is seeded in certain locations, usually phase boundaries between the matrix and plate-like inclusions of a minor (ca. 1–2 vol.%) Gd$_5$(Si$_{1-x}$Ge$_x$) impurity phase. These boundaries act as a permanent source of strain due to different crystal structures of the matrix and the platelets and, therefore, promote the nucleation of the low-volume orthorhombic ferromagnetic phase in the bulk of the high-volume monoclinic paramagnetic matrix. The effect is asymmetric, i.e., the boundaries play little to no role during the reverse transition, where the high-volume phase must nucleate in the low-volume matrix, which typically leads to minor changes in the microstructure, the volume phase must nucleate in the low-volume matrix, which is play little to no role during the reverse transition, where the high-paramagnetic matrix. The e

FIG. 4. (a) $M(T)$ curves measured after completing protocols 1 through 7. Measurements were performed during heating in magnetic fields 0.1, 0.5, and 1.0 kOe, and then with a 2.5 kOe step between 2.5 and 20 kOe and with a 5 kOe step between 20 and 50 kOe. (b) Comparison of the magnetic entropy change, $\Delta S_m$ for $\Delta H = 15 \text{ kOe}$ calculated from the $M(T)$ data before executing measurements following protocol 1 and after the measurements following protocol 7, i.e., after a total of 320 field-up/down cycles.

... temperature (270 K) in a zero magnetic field for 30 min, there is no increase in the initial hysteresis nor there is a change in hysteresis during subsequent cycling (Fig. 1). Also for protocol 6, in which the sample was cooled down to 10 K in a zero field, brought back to 270 K, and cycled again, there was no change in hysteresis as well (data not shown).

However, when the sample is removed from the measurement system and stored at room temperature (~30 K above $T_C$ of 265 K) for a few weeks, the “training” effect disappears: the measurements performed with protocol 7 (data not shown) follow the data for protocol 1 presented in Fig. 1 with high precision. Furthermore, protocols 3 and 4 indicate that even relatively fast heating of the sample to 340 K (~75 K above $T_C$) without a magnetic field, followed by cooling down to 270 K restores the initial $H_{ci}, H_{cr}$, and hysteresis irrespective of the cooling rate. These observations suggest that the training hypothesis is not suitable to explain the observed changes in both the critical fields and hysteresis. Thus, the answer to the question of what causes the material’s return to the initial state in a warmed-up sample has to be found elsewhere.

By carefully examining the behavior of magnetization near $H = 0$ [Figs. 1(a)–1(d)], it is easy to see that a small but measurable amount of the high-field FM orthorhombic phase is retained (or trapped) after the first cycle, and its concentration continues to slowly increase in each of protocols 1, 3, and 4. In protocols 2 and 5 (as well as in protocol 6 for which data are not shown since it follows protocol 2), the amount of the trapped FM phase is already substantial during the first cycle. These observations indicate that the sample, once magnetized and demagnetized at 270 K, cooled to 10 K and warmed back to 270 K in zero field, or cooled in magnetic field from 340 to 270 K, enters the mixed-phase state, where the high-temperature, low-field PM and the low-temperature,
high-field FM phases of Gd₅Si₂Ge₂ coexist. The trapped FM phase is indeed different from the 1%–2% impurity orthorhombic Gd₅Si₂ₓ₄Ge₂₋₄ₓ phase, which has a Tₐ of ~301 K and whose concentration is unaffected by the cycling, see Fig. 3. This trapped FM phase appears to play a significant role in the progression of the direct (field-up) transformation by providing additional nucleation centers and reducing both H₁ and hysteresis already after the first magnetization-demagnetization cycle, as the field cycling continues. Storing the sample around 300 K or heating it to 340 K fully converts the trapped FM phase back to the paramagnetic monoclinic phase and has the most profound effect on restoring hysteresis.

The arguments presented in the previous paragraph are supported by how the trapped FM phase evolves with cycling. Comparing Mᵣ and Mᵢ in all protocols, except protocols 2 and 6, the FM fraction builds continuously with an increasing number of cycles and the initial increase from the 1st to the 5th cycle is the most substantial, growing slowly afterward. Furthermore, as illustrated in Fig. 2, ΔHYST and (Mᵣ−Mᵢ)/Mᵣ show qualitatively similar variations with the number of cycles, indicating a clear correlation between the amount of the trapped ferromagnetic phase and the width of hysteresis. After demagnetization at 340 K, the lack of trapped FM nucleation centers rises H₁ back to the virgin values. Once the presence of the trapped FM phase is (re)established, the hysteresis quickly decreases again. The phenomenon is fully repeatable in subsequent cycling experiments. This is further confirmed by protocol 5 where the sample was cooled down to 270 K from 340 K in the presence of a 50 kOe magnetic field. Cooling in a magnetic field also traps a certain amount of the FM phase, and ΔHYST in the first cycle of protocol 5 measurement is smaller than in other protocols [Fig. 1(f)]. We also note that (Mᵣ−Mᵢ)/Mᵣ during the first cycle is ~0.99, close to but slightly smaller than 1, confirming the presence of about 1% of the silicon-rich ferromagnetic Gd₅Si₂₁₋₄ₓGe₂₋₆ₓ impurity phase, fully consistent with its Curie temperature of 301 K seen in Fig. 3.

Our results on the macroscopic cycling behavior of Gd₅Si₂Ge₂ can be further explained considering the microscopic nature of the observed phenomena. The trapped orthorhombic ferromagnetic phase is not a thermodynamically stable second phase at 270 K, but its presence is a result of minor irreversibilities intrinsic to the martensitic-like crystallographic transformation in Gd₅Si₂Ge₂. Earlier detailed microscopic studies of the transition in both Gd₅Si₂Ge₂ and Gd₅Si₂₋₄ₓGe₂₋₁ₓ compounds using transition electron microscopy (TEM) and selected area electron diffraction (SAED) showed that a certain amount of the orthorhombic phase coexists with the monoclinic matrix within a single crystal or a grain. The formation of the monoclinic phase always involves nanotwinning along the b-axis (the longest axis of the unit-cell). The twinning minimizes internal strain caused by the substantial lateral shifts of the alternating slabs and a switch from the γ = 90° in the orthorhombic structure to γ = ~93.2° in the monoclinic structure. In a real material, nanotwinning generates stacking faults, where the lateral shift fails to occur and locally the structure remains orthorhombic, extending over a few nanometers. One may speculate that the number of such stacking errors increases substantially during the initial few cycles through the magnetostructural transition and then reaches a plateau—precisely what is also seen in Fig. 2. The phase coexistence observed experimentally by TEM was also confirmed by x-ray single crystal diffraction. Furthermore, the magnetic field dependent x-ray powder diffraction studies of Gd₅Si₂₁₋₄ₓGe₂₋₆ₓ as well as structurally similar materials, such as Gd₅Ge₄ and Tb₅Si₂₋₁ₓGe₂₋₆ₓ show that the magnetic field-induced transformations in these systems are often incomplete with two different phases retained, especially when the magnetic field is applied and removed in the vicinity of Tᵣ.

In summary, analysis of the experimental results described above together with the available literature on the microscopic mechanisms and progression of magnetostructural transformations in closely related materials indicates that the trapped FM orthorhombic phase is most likely homogeneously distributed across the material. The amount of the trapped phase may and does increase with cycling as the stacking errors accumulate during multiple transitions. This phase sets and develops rapidly during the first few cycles, and then its concentration increases at a progressively slower rate. The fact that the trapped phase is distributed evenly through the sample, and is not located at the grain boundaries only, helps to explain why the transition is occurring smoothly instead of showing multiple steps. At the same time, the formation of the trapped FM phase is a kinetically arrested, diffusionless process, which can be easily reversed by moving the sample further into the paramagnetic region.

CONCLUSIONS

Magnetocaloric performance of Gd₅Si₂Ge₂ is favorably affected by repeated cycling through the magnetostructural phase transformation with an external magnetic field. The magnetocaloric effect practically does not change after hundreds of cycles through the transition, while the initial substantial hysteresis is reduced by 30% after only 5–10 cycles. Cycling experiments performed using different protocols indicate that the ferromagnetic orthorhombic phase trapped after the application and removal of a magnetic field is responsible for the lower hysteresis. The hysteresis remains low (6 kOe) as long as additional nucleation centers in the form of the trapped ferromagnetic orthorhombic Gd₅Si₂Ge₂ phase remain intact, but it returns to the initial value (~9 kOe) when they are removed by warming the material up further into the paramagnetic regime.

SUPPLEMENTARY MATERIAL

See the supplementary material for (a) results of the backscattered scanning electron microscopy (BS-SEM) combined with electron dispersive spectroscopy (EDS) data, and (b) comparison of M (H) data measured at θ = 270 K using protocol 1 with 100 and 10 Oe s⁻¹ magnetic field sweep rates.

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related work were performed using instruments in the Sensitive Instrument Facility in the Ames Laboratory.