Massive Magnetic-Field-Induced Structural Transformation in Gd_5Ge_4 and the Nature of the Giant Magnetocaloric Effect

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A massive magnetic-field-induced structural transformation in Gd_5Ge_4, which occurs below 30 K, was imaged at the atomic level by uniquely coupling high-resolution x-ray powder diffraction with magnetic fields up to 35 kOe. In addition to uncovering the nature of the magnetic field induced structural transition, our data demonstrate that the giant magnetocaloric effect, observed in low magnetic fields, arises from the amplification of a conventional magnetic entropy-driven mechanism by the difference in the entropies of two phases, borne by the concomitant structural transformation.

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Magnetic cooling has a potential to reduce global energy consumption, minimize the need for ozone depleting and greenhouse chemicals, and may soon become an alternative to the vapor-compression approach [1]. Instead of a working fluid undergoing a liquid-vapor transition in a conventional cooling system, a magnetic refrigerator employs a solid, which heats up when magnetized and cools down when demagnetized. These magnetic field induced temperature variations in solids are known as the magnetocaloric effect (MCE). The extent of the latter is one of the most critical parameters defining the performance of a magnetic refrigerator—the higher the MCE, the higher the efficiency of the device, all other things being equal. Although the MCE was discovered in 1881 [2], it took about 50 years to explain its origin and exploit the effect to reach sub-Kelvin temperatures [3–5]. More than half a century later, the feasibility of magnetic cooling near room temperature was demonstrated [6,7].

Discovered in 1966 [8], Gd_5Ge_4 was recently identified as one of the end members in the series of the $Gd_5(Si_xGe_{4-x})$ giant MCE materials [9,10]. The latter exhibit a factor of 2 to 4 enhancement of the magnetic field induced entropy change between ~20 and ~300 K when compared to the majority of magnetic solids. Gd_5Ge_4 orders antiferromagnetically at ~130 K [11,12], and in low magnetic fields, the antiferromagnetic state is preserved down to ~2 K [13,14]. Magnetization [12], magnetostriction [13], and electrical resistivity [14] of Gd_5Ge_4 point to a field induced structural transition (FIST) coupled with a transformation to a collinear ferromagnet below 30 K, but only when the magnetic field exceeds 10 kOe. The high magnetic field crystal structure of Gd_5Ge_4, therefore, cannot be inferred from zero field diffraction data, as was possible for other members of the series [15–17], where temperature alone triggers a seemingly identical structural change. Field dependent neutron powder diffraction [18] of Gd_5Ge_4 is impractical due to the high absorption cross section of the naturally occurring mixture of Gd isotopes. The complexity of this crystal structure [8], coupled with the presence of both the magnetic and Bragg scattering below 130 K in addition to the relatively low resolution of neutron diffraction data, would make it extremely difficult to extract reliable structural information. Hence, x-ray diffraction in the magnetic field appears to be the only viable option to provide atomic-scale details of a FIST in Gd_5Ge_4 and, therefore, to facilitate a better understanding of the giant MCE and support future development of advanced magnetocaloric materials. Although attempted in the past, x-ray diffraction in an applied magnetic field was limited to analyzing single Bragg peaks [19] or field induced texture [20]. This Letter reports on a massive FIST, which occurs in Gd_5Ge_4 below 30 K, studied by high-resolution x-ray powder diffraction in magnetic fields reaching 35 kOe. The results establish the critical role of a FIST in achieving the giant MCE and explain the nature of the phenomenon in Gd_5Ge_4 and in other materials [21–24], which exhibit strong magnetothermal responses.

Gd_5Ge_4 powder ($< 38\ \mu$m) was mixed with diluted varnish and mounted on a copper sample holder. After drying, a flat surface was formed by using a 280 grit sandpaper to both minimize the preferred orientation and improve the resolution of the pattern. The x-ray diffraction data were collected on a Rigaku TTRAX rotating anode powder diffractometer employing Mo $K\alpha$ radiation over a wide range of reciprocal space (i.e., $7^\circ \leq 2\theta \leq 42^\circ$, which is equivalent to $\sin\theta/\lambda \leq 0.5\ \text{Å}^{-1}$). The sample temperature was controlled to within ± 0.02 K below 50 K, and better than ± 0.05 K above 50 K using a helium flow cryostat coupled with a split-coil superconducting magnet. The magnet provided a uniform 0 to 35 kOe magnetic field around the sample with the magnetic field vector coplanar with the plane of the specimen. The magnetic field was applied isothermally after cooling the sample in zero magnetic field from ~300 K to the temperature of the measurement. Multiple sets of diffraction data were collected with a 0.01° step of 2θ, and each set was employed in Rietveld

refinement. Profile residuals were from 9% to 11% and derived Bragg residuals were from 6% to 7%. Changes in the three-dimensional distribution of atoms were determined with 0.01 to 0.03 Å accuracy [25]. Phase quantities were determined to within 1 mol %.

When Gd_5Ge_4 is cooled from 300 to 5 K in zero magnetic field, only lattice parameters are anisotropically reduced due to thermal contraction. A magnetic field, however, has a profound effect on the crystal structure of the material, as illustrated in Fig. 1. Isothermal exposure to an increasing magnetic field at 6.1 K results in a structural transition, which begins around 15 kOe and is nearly complete at 25 kOe [Fig. 1(a)]. The FIST in Gd_5Ge_4 is irreversible at 6.1 K as seen in the powder patterns, which barely change when the magnetic field is removed [Fig. 1(b)]. The behavior is different upon isothermal magnetic field cycling at 25 K. Just as at 6.1 K, the low magnetic field crystal structure transforms into the high magnetic field modification between 15 and 25 kOe [Fig. 1(c)]. However, when the magnetic field is reduced at 25 K, the zero field diffraction pattern is restored between 15 and 5 kOe [Fig. 1(d)] with a ~10 kOe hysteresis.

As follows from the results of the structure determination (Table I), the low magnetic field (LF) crystal structures (LF-Gd_5Ge_4) observed at 6.1 and 25 K are identical to one another within the accuracy of the technique, and so are the high magnetic field (HF) polymorphs (HF-Gd_5Ge_4). Both contain nearly identical layers of atoms arranged in a distinctly different fashion, as is shown in Fig. 2. The LF-Gd_5Ge_4 and HF-Gd_5Ge_4 relate to one another via shear displacements of the neighboring layers by more than 0.2 Å. These large shifts in opposite directions alter numerous interatomic distances and modify interactions among atoms from adjacent layers. The most prominent magnetic field induced change occurs in the interlayer Ge-Ge bonds. In the LF-Gd_5Ge_4, where the corresponding interatomic distances are $\delta_{\text{Ge-Ge}} = 3.62(1)$ Å, the bonds are weak, but in the HF-Gd_5Ge_4 they become stronger due to a 1 Å contraction [$\delta_{\text{Ge-Ge}} = 2.62(1)$ Å]. The layers undergo little change, as evidenced by small variations of the interatomic distances inside each layer. The magnetic field, therefore, triggers a martensiticlike structural transition, which results in displacements of the layers and in the breaking and the reforming of the covalentlike interlayer Ge-Ge bonds.

The FISTs observed in Gd_5Ge_4 at 6.1 and 25 K clearly correlate with the behavior of the magnetization measured at the same temperatures. As illustrated in Fig. 3(a), the fraction of the HF-Gd_5Ge_4 formed at 6.1 K by an increasing magnetic field follows the initial magnetization path, including two metamagnetic features present at ~15 and ~25 kOe. It is well established that upon removal of the magnetic field isothermally, Gd_5Ge_4

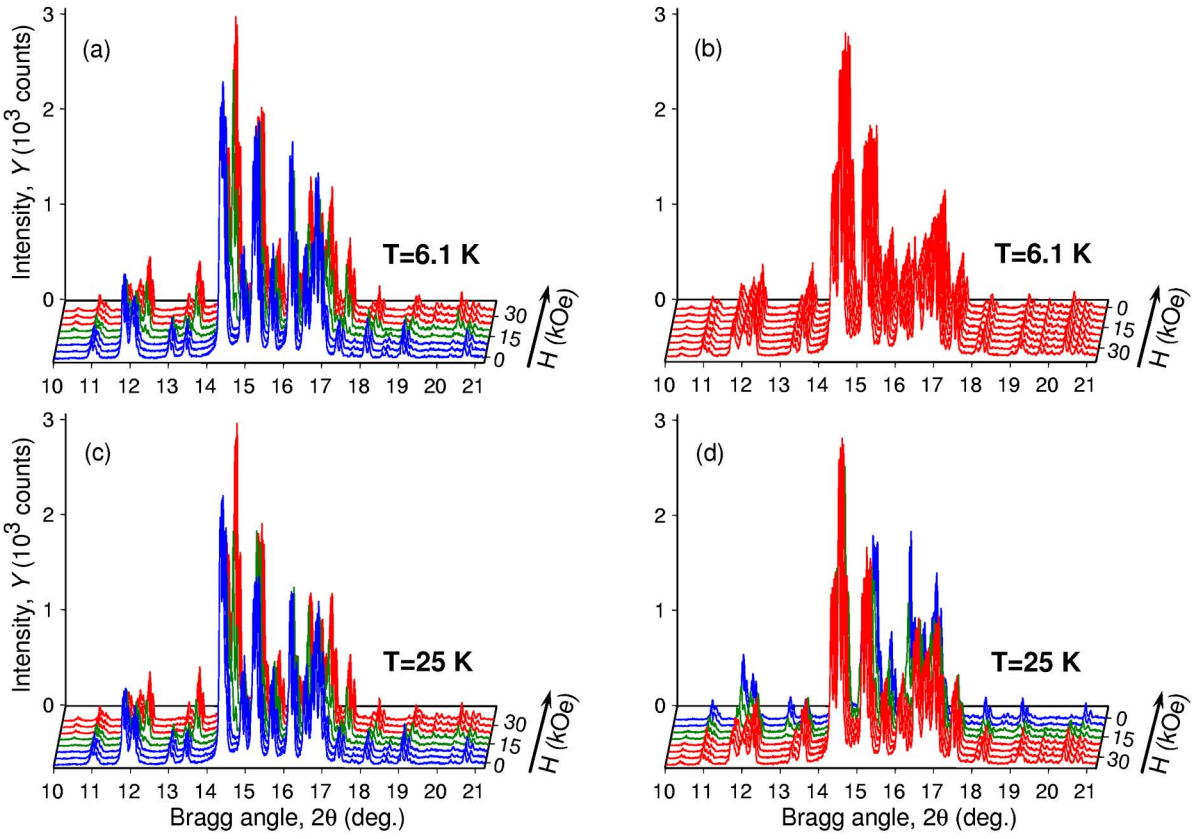

FIG. 1 (color online). The x-ray powder diffraction patterns of Gd_5Ge_4 collected at 6.1 and 25 K during increasing (a),(c) and decreasing (b),(d) magnetic fields. Only the range from 10° to 21°2θ is shown for clarity.

TABLE I. Crystal structures of Gd_5Ge_4 at 6.1 and 25 K in 0 and 35 kOe magnetic field. The space group symmetry is *Pnma* in each case.

	$T = 6.1$ K, H = 0; $a = 7.6838(2)$, $b = 14.7830(4)$, $c = 7.7628(3)$ Å			T = 25 K, H = 0; $a = 7.6841(2)$, $b = 14.7839(5)$, $c = 7.7639(3)$ Å		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Gd1	0.2926(4)	1/4	−0.0005(5)	0.2936(5)	1/4	−0.0005(5)
Gd2	−0.0303(2)	0.1022(1)	0.1776(3)	−0.0294(2)	0.1013(1)	0.1773(3)
Gd3	0.3805(3)	0.8832(1)	0.1645(3)	0.3794(3)	0.8830(1)	0.1642(3)
Ge1	0.1754(7)	1/4	0.3676(9)	0.1786(8)	1/4	0.3663(9)
Ge2	0.9139(9)	1/4	0.8855(9)	0.9188(9)	1/4	0.8850(9)
Ge3	0.2173(6)	0.9560(3)	0.4655(6)	0.2186(6)	0.9564(3)	0.4636(6)
	T = 6.1 K, H = 35 kOe; $a = 7.5399(3)$, $b = 14.8039(5)$, $c = 7.8123(3)$ Å			T = 25 K, H = 35 kOe; $a = 7.5399(3)$, $b = 14.8050(5)$, $c = 7.8125(3)$ Å		
Gd1	0.3478(5)	1/4	0.0082(5)	0.3481(6)	1/4	0.0076(5)
Gd2	0.0152(3)	0.0964(1)	0.1842(3)	0.0146(3)	0.0964(1)	0.1843(3)
Gd3	0.3213(3)	0.8784(1)	0.1776(3)	0.3216(3)	0.8787(1)	0.1757(3)
Ge1	0.2340(9)	1/4	0.3647(9)	0.2360(9)	1/4	0.3640(9)
Ge2	0.9743(9)	1/4	0.8956(9)	0.9723(9)	1/4	0.8937(9)
Ge3	0.1491(8)	0.9561(3)	0.4772(7)	0.1503(9)	0.9568(3)	0.4758(7)

remains ferromagnetic at 6.1 K [12,13]. Consistent with the macroscopic magnetism, the system preserves the HF-Gd_5Ge_4 structure, whose concentration is only slightly reduced from 93% to 86% when the magnetic field is lowered from 35 kOe to 0. At 25 K, where both the transformation and the giant MCE are reversible, the amount of the HF-Gd_5Ge_4 structure follows both the initial magnetization and the subsequent demagnetization paths [Fig. 3(b)]. The nearly quantitative correspondence between the isothermal magnetization behavior and the structural changes occurring in the material provides a direct experimental evidence of intimate coupling between the magnetic and crystal lattices in Gd_5Ge_4 and reveals the role of the FIST in the appearance of the giant MCE.

Quite unexpectedly, no more than 93 mol % of the sample has been transformed from the LF-Gd_5Ge_4 to the HF-Gd_5Ge_4 structure by a 35 kOe field at either temperature, even though at this magnetic field the magnetization is at ~99% of its saturation value ($7.5\mu_B$/Gd atom), thus indicating a nearly completely collinear spin structure. The effect of the *magnetic field* on the

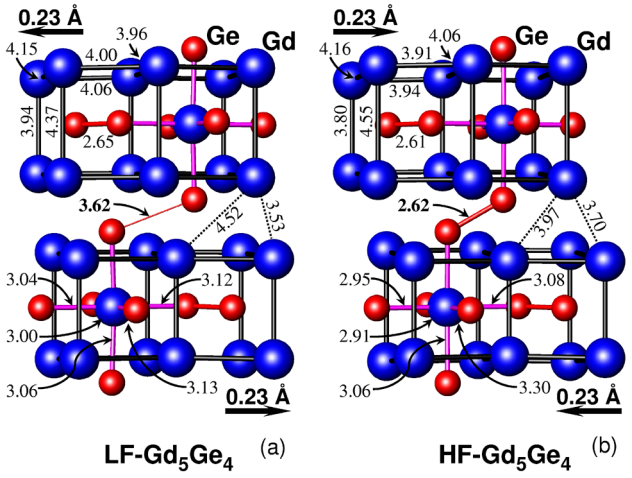

FIG. 2 (color online). Fragments of the antiferromagnetic low field (LF-Gd_5Ge_4) and ferromagnetic high field (HF-Gd_5Ge_4) crystal structures viewed along the Z axes with selected distances labeled in Å. The intralayer distances vary by a maximum of 5.%, while the interlayer distances change by as much as 27.6% during the LF to HF transformation. The short thick arrows in (a) and (b) indicate the directions and the magnitudes of the shifts of the layers during the LF to HF and HF to LF transitions, respectively.

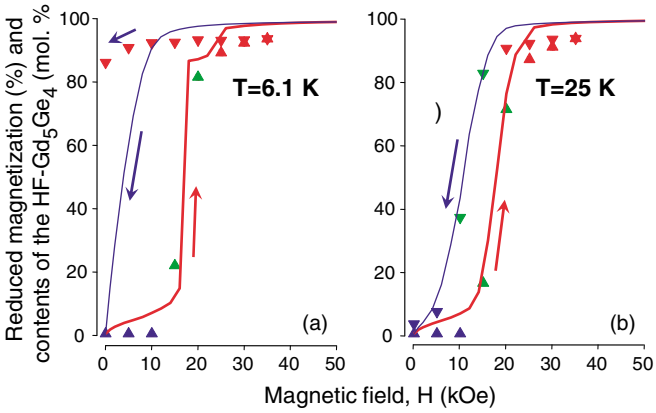

FIG. 3 (color online). The reduced magnetization of Gd_5Ge_4 (lines) measured at 6.1 K (a) and 25 K (b), and molar concentration (triangles) of the HF-Gd_5Ge_4 phase. The arrows indicate the direction of the change of the magnetic field. Up triangles correspond to the increasing magnetic field and down triangles correspond to the decreasing magnetic field.

crystallography of Gd_5Ge_4 is, therefore, different from the effect of *temperature* on the crystal structures of the related $Gd_5Si_2Ge_2$ [16] and $Gd_5Si_{0.4}Ge_{3.6}$ [17]. In the latter two systems, the respective temperature induced structural transitions are complete, while in the title compound, a small but measurable fraction of Gd_5Ge_4 retains its low field crystal structure while clearly ordering ferromagnetically.

The ability of the magnetic field to induce a structural change can be related to the coupling of the localized magnetic moments of the Gd atoms with the external field. The increasing magnetic field causes a spin-flip, and the resulting collinear or nearly collinear spin system minimizes its free energy via a martensiticlike FIST (Fig. 2). The sample remains both structurally and magnetically inhomogeneous in a certain range of magnetic fields because work performed by the magnetic field to increase bulk magnetization and work done to overcome strain created by a 1.1% change of the phase volume (see Table I) are balanced. Since magnetic work ($\mu_0 HdM$) becomes negligible near saturation ($dM \rightarrow 0$) but strain remains considerable, this can explain the presence of a small amount (7 mol %) of the ferromagnetic LF-Gd_5Ge_4 in a magnetically saturated sample.

In magnetic solids without FIST, the MCE is proportional to the rate of change of bulk magnetization (M) with temperature (T) in constant magnetic field (H) [3,4]:

$$(\Delta S_M)_T = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH;$$
$$(\Delta T_{\mathrm{ad}})_S = -\mu_0 \int_0^H \frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H dH, \qquad (1)$$

where ΔS_M and ΔT_{ad} are the isothermal magnetic entropy and the adiabatic temperature changes, respectively. The large magnetic field induced phase volume and chemical bonding changes, observed in Gd_5Ge_4, show that the giant MCE is achieved due to the concomitant change of the entropy during the structural transformation. As a result, the observed giant MCE is the sum of the conventional magnetic entropy-driven process [Eq. (1)] and the difference in the entropies of the two crystallographic modifications (ΔS_{st}):

$$(\Delta S)_T = (\Delta S_M)_T + (\Delta S_{\mathrm{st}})_T$$
$$= \mu_0 \int_0^H \left(\frac{\partial M}{dT}\right)_H dH + (\Delta S_{\mathrm{st}})_T. \qquad (2)$$

Although the second factor in Eq. (2) is a hidden parameter in conventional magnetization measurements, an estimate based on comparing the MCE exhibited by the members of the $Gd_5(Si_xGe_{4-x})$ family with and without FIST [9,10] indicates that ΔS_{st} accounts for more than a half of the total effect in magnetic fields below 2 T. Advanced magnetocaloric materials should exist in other systems where structural changes are coupled with ferromagnetic ordering and, therefore, can be triggered by a magnetic field. Considering Eq. (2), the strongest MCE should be found in materials, engineered in order to maximize the entropy of a structural transformation, ΔS_{st}. An interesting opportunity exists in solids where low- and high-field phases have different symmetries [e.g., the $Gd_5(Si_xGe_{4-x})$ system with $1.5 \leq x \leq 2.1$] because breaking the symmetry should affect the degeneracy of electronic states and may result in further increase of ΔS_{st}.

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