Evidence of a magnetic glass state in the magnetocaloric material Gd_5Ge_4

S. B. Roy,[1] M. K. Chattopadhyay,[1] P. Chaddah,[2] J. D. Moore,[3] G. K. Perkins,[3] L. F. Cohen,[3] K. A. Gschneidner, Jr.,[4] and V. K. Pecharsky[4]

[1]*Magnetic and Superconducting Materials Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India*

[2]*UGC-DAE Consortium for Scientific Research, Indore 452017, India*

[3]*Blackett Laboratory, Imperial College of Science Technology and Medicine, London SW7 2BZ, United Kingdom*

[4]*Ames Laboratory of the US DOE and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-3200, USA*

(Received 16 June 2006; published 14 July 2006)

We demonstrate the kinetic arrest of the first-order phase transition from the high-temperature antiferromagnetic state to the ferromagnetic ground state in zero and low applied magnetic fields, occurring within the experimental time scale in the magnetocaloric material Gd_5Ge_4. A magnetization study clearly reveals glasslike dynamics in the low-temperature antiferromagnetically ordered state. The observation of a glasslike magnetic state is unusual, but we expect that a similar phenomenon should exist in other magnetic systems.

DOI: 10.1103/PhysRevB.74.012403 PACS number(s): 75.30.Kz

Gd_5Ge_4 is a parent compound of the $Gd_5(Ge,Si)_4$ family of alloys, which show a large magnetocaloric effect,[1] giant magnetoresistance,[2] and large magnetostriction.[3] A combination of these interesting properties has naturally motivated many investigations of this family of compounds to understand the underlying physics. It is clear, for example, that the first-order magnetostructural phase transition (FOPT) and the associated phase coexistence (PC) across the transition play an important role in the functionality[4–6] of Gd_5Ge_4 and other magnetic systems, such as the manganites showing colossal magnetoresistance[7] (CMR), and the doped-$CeFe_2$ alloys.[8] One of the main interests in FOPT physics presently concerns the length scale[7,9] of the PC and the influence of disorder on this length scale.[5,6,8,10] This is not the subject of the present paper, however.

An important aspect of disorder-influenced FOPT is that some liquids called glass formers experience a viscous retardation of crystallization in their supercooled state.[11] In the experimental time scale the supercooled liquid ceases to be ergodic and it enters a glassy state. The dynamical picture of a glass is a liquid where the atomic or molecular motions (or kinetics) are arrested.[12,13] Using these concepts and applying them to a first-order magnetic phase transition, it has recently been suggested that in the case of the low-temperature (T)–high-magnetic-field (H) part of the phase diagram of Ru-doped $CeFe_2$ alloys there is a viscous retardation of nucleation and growth of the antiferromagnetic (AFM) phase across the ferromagnet (FM) to AFM transition;[14] that is certainly suggestive of a glasslike behavior. Further, there exists an indication of a similar frozen phase-coexistence regime in the CMR manganite compound $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ (LPCMO).[15] The similarity between these two very different classes of materials has now been highlighted in a very recent work.[16] The dynamics associated with this frozen PC regime is different from that of the usual PC observed across a disorder-broadened FOPT.[14] Here we demonstrate the generality of this phenomenon by showing that the magnetic equivalent of a glassy state exists in the Gd_5Ge_4 system, and that it can be controlled by H, in addition to T.

To date it has been accepted that Gd_5Ge_4 orders as an AFM at 128 K and remains AFM down to at least 1.8 K in zero and low applied magnetic fields ($\leqslant$10 kOe).[17,18] A FOPT to a FM state, however, takes place over a wide T region when the applied H is greater than a critical $H_M(T)$.[4,17–21] A large entropy change is observed across this AFM-FM transition,[19,20] and the $H_M(T)$ boundary has been studied in detail.[4,17–21] $H_M(T)$ decreases with decreasing T but shows an upturn below 20 K where the character of the AFM-FM transition changes markedly.[4,17–21] We show here that below 20 K $H_M(T)$ is masked by a kinetic arrest of the FOPT on the experimental time scale, i.e., from a few minutes to several hours. As a result, a magnetically long-range-ordered[22] yet clearly glasslike, nonergodic magnetic state sets in at low T instead of an equilibrium FM ground state. The onset of this nontrivial magnetic-glass state is characterized by typical dynamical features which are considered to be the hallmark of a conventional structural glass transition. Note that the magnetic-glass state reported here is quite distinct from a conventional spin-glass state in a number of clearly identifiable ways.[23]

The polycrystalline sample of Gd_5Ge_4 used here is well characterized and different samples from the same batch have been used in recent studies.[2,4,17,19–21] Magnetization measurements were made with a commercial vibrating sample magnetometer (VSM; Quantum Design). We use three experimental protocols, zero-field-cooled (ZFC), field-cooled-cooling (FCC), and field-cooled-warming (FCW) for the magnetization measurements. In the ZFC mode the sample is cooled to 3 K before the measuring H is switched on and the measurement is made while warming up the sample. The applied H is switched on in the T regime above the FM-AFM transition temperature (T_N) in the FCC mode and the measurement is made while cooling across T_N. On reaching 3 K in the FCC mode, the data are taken again in the presence of the same H while warming up the sample. This is the FCW mode.

The M versus T plots of Gd_5Ge_4 shown in Fig. 1 are obtained with ZFC, FCC, and FCW modes in H=10 kOe. The inset of Fig. 1 highlights the paramagnetic (PM) to AFM transition at $\approx$128 K. $M_{ZFC}(T)$ shows a broad peak

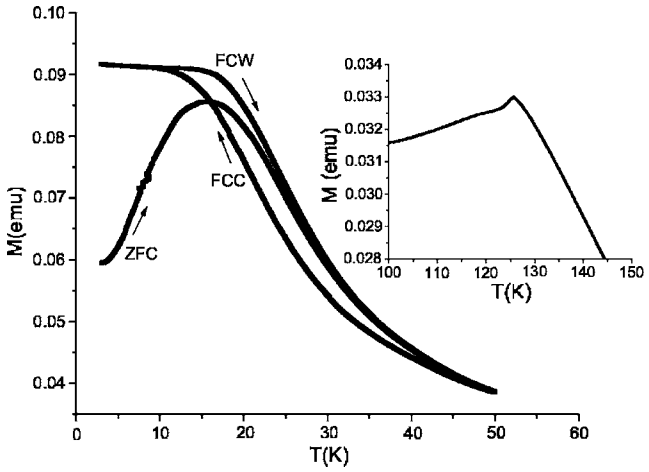

FIG. 1. M versus T plots obtained in ZFC, FCC, and FCW modes with an applied H of 10 kOe. T is varied with a sweep rate of 1 K/min and the VSM records the data in quasicontinuous manner during the T sweep. Data presented are actual discrete data points and not a continuous guideline. The inset shows $M(T)$ in the vicinity of the nonhysteretic PM-AFM transition.

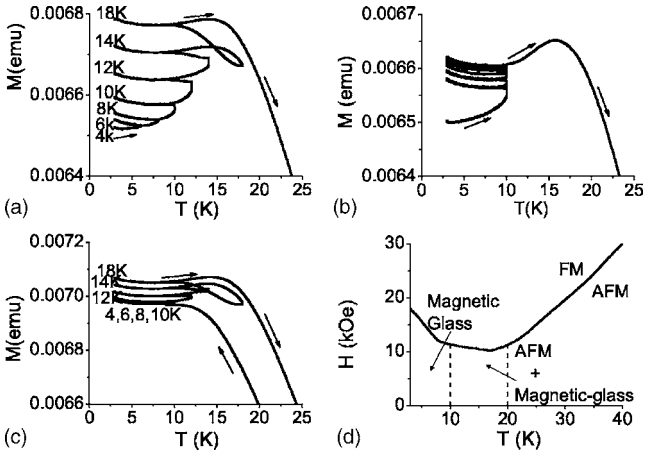

FIG. 2. M vs T plots recorded in $H=500$ Oe showing the effect of T cycling starting from $T_0=3$ K. In (a) and (b) the sample is prepared in ZFC mode, and in (c) it is prepared in FCC mode. T is varied with a sweep rate of 1 K/min and the data presented are actual discrete data points and not a continuous guideline. (d) presents the H-T phase diagram of Gd_5Ge_4 showing the low-T, low-H regime where the magnetic-glass behavior is observed. The phase boundaries are determined from isothermal M-H and isofield M-T measurements (Refs. 18 and 21).

centered around 18 K. A similar broad peak in $M_{ZFC}(T)$ with $H \leqslant 10$ kOe was attributed earlier to the possible rearrangement of a complex AFM structure in Gd_5Ge_4.[18] Although an earlier study highlighting the thermomagnetic irreversibility of Gd_5Ge_4 [i.e., $M_{ZFC}(T) \neq M_{FCW}(T)$] at low T exists,[18] a systematic study of $M_{FCC}(T)$ is lacking. We note that the $M_{FCC}(T)$ saturates below 10 K, and overlaps the $M_{FCW}(T)$ in the region $3 \leqslant T \leqslant 10$ K. Above 10 K there is a distinct thermal hysteresis between $M_{FCC}(T)$ and $M_{FCW}(T)$, which is a typical characteristic of a FOPT. All these features have been observed with various H from 10 kOe down to 500 Oe but are not shown here for conciseness.

We now show that the low-T states obtained in the ZFC and FCC modes are not equilibrium states. In Figs. 2(a)–2(c) we present effects of T cycling on M in both the ZFC and FCC modes. We start at $T_0=3$ K in $H=500$ Oe after reaching T_0 in either the ZFC or FCC mode. T is then raised to a temperature T_M and reduced back to T_0. Starting with $T_M=4$ K this T cycling is continued with $T_M=6$, 8, 10, 12, 14 and 18 K in the subsequent cycles. On the ZFC path [Fig. 2(a)], M at T_0 (M_0) clearly increases after the first T cycle. This increase in M_0 in the subsequent cycles becomes larger as T_M becomes higher. When T_M is 10 K and higher, the initial rise in M becomes nearly discontinuous. This actually reflects the highly metastable nature of the underlying magnetic state, in which M relaxes over a finite time required by the experimental system to reverse the direction of T. The effect of multiple T cycling to the same T_M is shown in Fig. 2(b). The M_0 continues to increase with every T cycle. In Fig. 2(c) we present results of T cycling from various T_M after reaching T_0 in the FCC mode. It is now interesting to note that there is hardly any effect of T cycling not only on M_0 but also on $M(T)$ as long as $T_M \leqslant 10$ K. But when T_M exceeds 10 K, M_0 begins to increase. However, M saturates again when T is lowered below 10 K but now with somewhat higher M value (M_{sat}) from that in the FCC path. This M_{sat} continues to rise in the subsequent cycles. This effect of T cycling clearly establishes the metastable nature of both the ZFC and FCC states in this low-T regime. A similar metastable magnetic response has also been observed with applied $H=10$ kOe. While thermomagnetic irreversibility (TMI), i.e., $M_{ZFC} \neq M_{FC}$, is also a characteristic of spin-glass behavior,[23] the TMI reported here is distinctly different. The spin-glass transition is not a FOPT; hence $M_{FC}(T)$ is not expected to be accompanied by any thermal hysteresis. Moreover, in contrast to the present case the FC state in spin glasses is known to be an equilibrium state.

We argue that in a zero- and low-field FCC path, the transition from the high-T AFM state in Gd_5Ge_4 to the low-T FM state is arrested between 10 and 20 K. This event can be compared with the glass formation process in a polymeric glass—polyvinylchloride—where the glassy state is reached via a heterogeneous state consisting of microcrystallites.[24] In comparison, we have here a frozen-in-time magnetic phase configuration consisting of a small number of transformed equilibrium FM islands and a metastable AFM matrix. Unlike the usual highly metastable supercooled state associated with a standard FOPT,[25] the glassy state in Gd_5Ge_4 (although metastable in nature) is much less susceptible to small energy fluctuations. Hence, the T cycling below 10 K does not really cause a drastic change of the phase configuration. However, when the T_M exceeds 10 K, the sample tends to move out of the glassy regime and the frozen metastable AFM matrix may now be gradually converted to the equilibrium FM state due to small energy fluctuations. This process is akin to the recrystallization of a glass.[12] Continuing T cycling here will convert an increasingly large phase fraction to the equilibrium FM state, and hence will give rise to higher M_0 values on each T cycling step.

Within the framework of the kinetic arrest of the FOPT, in

the ZFC path at $T=3$ K and $H=0$ we start with a magnetic-glass state with a frozen nonequilibrium AFM matrix coexisting with small islands of the transformed equilibrium FM state. Now, switching H on will not only introduce energy fluctuations it will also stimulate further spin alignment within the FM state. So the ZFC state at 3 K with H, say, 500 Oe, will be more susceptible to any T cycling than the corresponding FCC state. This profile is consistent with the T-cycling results of Figs. 2(a) and 2(b).

Figure 2(d) presents the refined H-T phase diagram in which the low-T, low-H phase region, originally designated as AFM-2,[18] is replaced with the magnetic glass. Here, below approximately $H=10$ kOe and $T=20$ K, the formation of the FM ground state is prevented and instead the sample tends to enter a nonergodic magnetic-glass state. Due to the quenched disorder in Gd_5Ge_4, the first-order AFM-FM transition boundary is actually a quasicontinuous band.[21] This broadening of the transition boundary leads to a coexistence of the equilibrium AFM phase and the magnetic-glass state in the sample over a finite T regime below 20 K before a complete glass state is achieved below ≈ 10 K. On the other hand, large amounts of disorder will act as nucleation centers for the formation of the FM phase. Indeed 15–25% conversion from the AFM to the FM state has been observed in ZFC Gd_5Ge_4 samples loaded with interstitial impurities.[26] In the sample studied here, the supercooling of the high-T AFM state (which is the precursor for glass formation) was possible because of its cleaner chemistry, and, presumably, morphology. Formation (or not) of the magnetic-glass state thus can be naturally explained by samples having different purities.

The H-T phase diagram of Fig. 2(d) provides a physical explanation of the irreversibility associated with the H-induced AFM to FM transition observed in Gd_5Ge_4 below 20 K.[17,18,21] Nonequilibrium AFM clusters, which are retained below 20 K, represent the frozen-in configuration of the high-T AFM Gd_5Ge_4. The AFM-FM transition field $H_M(T)$ of these clusters increases with decreasing T because the competing thermal energy (k_BT) is also lower. The transition boundary below 20 K thus approximates the magnetic fields above which the remaining frozen-in AFM Gd_5Ge_4 transforms into the equilibrium FM Gd_5Ge_4. Once the AFM-FM conversion is finished, the sample behaves as a soft ferromagnet on subsequent H cycles, and the virgin ZFC state may be recovered only in a new ZFC cycle initiated either from the PM state or from well inside the equilibrium AFM regime. Transformation of the frozen-in AFM Gd_5Ge_4 to the equilibrium FM state also explains the highly irreversible character of heat dissipation in this T regime.[20]

Magnetization relaxation at various T on the FCC path provides further evidence of the glasslike character of this low-T magnetic state. As the system goes below T_N and approaches the limit of supercooling or metastability, T^*,[25] the barrier between the metastable AFM state and the equilibrium FM state in the free energy curve decreases. Hence a relaxation in M with a progressively higher relaxation rate is expected. This is observed in the T regime $35>T>20$ K (data not shown here for conciseness). However, with a further decrease in T the relaxation rate decreases markedly. This is indicative of a kinetic arrest of the transition process.

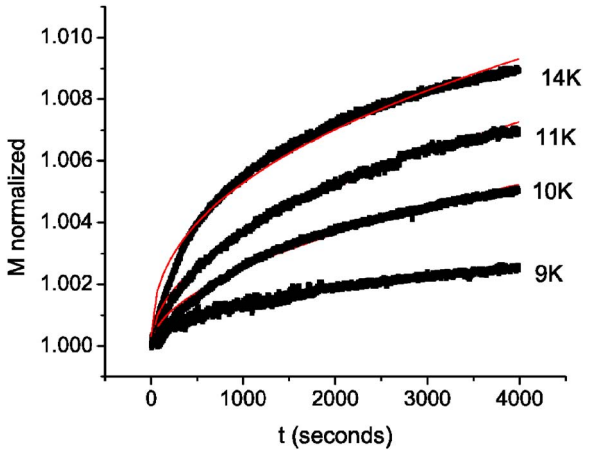

FIG. 3. (Color online) M vs t plots at the onset of the magnetic-glass regime. Data presented are actual discrete data points taken at close interval. The data below $T<14$ K fit well a KWW stretched exponential function $\Phi(t)\propto\exp[-(t/\tau)^{\beta}]$, and the actual fitted curve cannot be distinguished from the presented quasicontinuous data points at 9 and 10 K. Notable deviations of the fits from the actual data points are seen at 14 K and higher where the relaxation does not follow the KWW function.

In Fig. 3 we present M vs time (t) plots at various T below 15 K on the FCC path with $H=500$ Oe. Relaxation data can be fitted well with a Kohlrausch-Williams-Watt (KWW) stretched exponential function $\Phi(t)\propto\exp[-(t/\tau)^{\beta}]$, where τ is the characteristic relaxation time and β is a shape parameter. The value of β varies between 0.45 and 0.5, and it implies that the metastable AFM phase relaxes with a distribution of relaxation times.[12] The average τ increases markedly with the decrease in T and reaches a value of 9×10^{10} s at 9 K. The character of the M-t plots changes qualitatively below 9 K. There is no regular decay in M within our experimental resolution, and only random fluctuations are observed. All these behaviors are considered to be the hallmark of a structural glass transformation from the supercooled liquid glass-former state.[11,12]

The low-T magnetization dynamics in Gd_5Ge_4 is quite similar to that of LPCMO,[15,27–29] which also undergoes PM-AFM-FM transitions as T varies. A generalized framework of the disorder-influenced FOPT involving kinetic arrest of the first-order AFM to FM transition, provides a natural explanation to many of the observed phenomena. The same phenomenological framework can explain the formation of a nonergodic, glasslike, yet fully ordered magnetic state in other systems showing a FOPT but with an AFM ground state, namely, doped $CeFe_2$ alloys.[14] It is important to note here that the magnetoelastic coupling is a common ingredient in all of the systems mentioned above, and the magnetic transition is accompanied by an interesting strain-related behavior in doped $CeFe_2$ alloys,[30] Gd_5Ge_4,[3–5,19] and manganites.[28] This generality can be extended further with the recent discovery of strain-glass behavior in the ferroelastic martensitic system NiTi.[31] This is an interesting example of kinetic arrest of a FOPT involving a nonmagnetic crystalline phase.

In conclusion we argue that the equilibrium thermodynamic ground state of Gd_5Ge_4 is actually ferromagnetic. However, this FM ground state is avoided by a kinetic arrest of the first-order AFM-FM transition. Instead, the low-T, low-H magnetic state attains a configuration consisting of a small fraction of transformed (equilibrium) FM phase in an untransformed (nonequilibrium) AFM matrix. This phase configuration is nonergodic and the associated transformation dynamics is typical of glasses. This kind of magnetic-glass state is quite different from conventional spin glasses where the spin configuration is frozen at random on a microscopic scale. The magnetic-glass state observed here is likely to be found in many other classes of magnetic materials with first-order magnetostructural phase transitions occurring at low temperatures

We thank A. O. Tsokol for providing the sample of Gd_5Ge_4. Work at the Ames Laboratory is supported by the office of Basic Energy Sciences, Materials Sciences Division of the U.S. DOE under Contract No. W-7405-ENG-82 with Iowa State University of Science and Technology.

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997); Appl. Phys. Lett. **70**, 3299 (1997).
[2] E. M. Levin *et al.*, Phys. Rev. B **60**, 7993 (1999).
[3] L. Morellon *et al.*, Phys. Rev. B **58**, R14721 (1998); C. Magen *et al.*, J. Phys.: Condens. Matter **15**, 2389 (2003).
[4] E. M. Levin *et al.*, Phys. Rev. B **69**, 144428 (2004); Y. Mudryk *et al.*, *ibid.* **72**, 064442 (2005).
[5] J. D. Moore *et al.*, Appl. Phys. Lett. **88**, 072501 (2006).
[6] J. D. Moore *et al.*, Phys. Rev. B **73**, 144426 (2006).
[7] E. Dagotto, *The Physics of Manganites and Related Compounds* (Springer, Berlin, 2003), and references therein.
[8] S. B. Roy *et al.*, Phys. Rev. Lett. **92**, 147203 (2004).
[9] M. Uehara *et al.*, Nature (London) **399**, 560 (1999); D. D. Sarma *et al.*, Phys. Rev. Lett. **93**, 097202 (2004).
[10] K. H. Ahn, T. Lookman, and A. R. Bishop, Nature (London) **428**, 401 (2004); J. Burgy, A. Moreo, and E. Dagotto, Phys. Rev. Lett. **92**, 097202 (2004).
[11] P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).
[12] S Brawer, *Relaxation in Viscous Liquids and Glasses* (The American Ceramic Society, Columbus, OH, 1985).
[13] The general definition of glass is a noncrystalline solid material that yields broad nearly featureless diffraction pattern (Ref. 12). But it should be noted here that the dynamical behavior typical of glass formation is not necessarily restricted to materials that are positionally disordered (Ref. 12).
[14] M. K. Chattopadhyay, S. B. Roy, and P. Chaddah, Phys. Rev. B **72**, 180401(R) (2005).
[15] L. Ghivelder and F. Parisi, Phys. Rev. B **71**, 184425 (2005).
[16] Kranti Kumar *et al.*, Phys. Rev. B **73**, 184435 (2006).
[17] E. M. Levin *et al.*, Phys. Rev. B **65**, 214427 (2002).
[18] H. Tang *et al.*, Phys. Rev. B **69**, 064410 (2004).
[19] V. K. Pecharsky *et al.*, Phys. Rev. Lett. **91**, 197204 (2003).
[20] F. Casanova, A. Labarta, and X. Batlle, Phys. Rev. B **72**, 172402 (2005).
[21] M. K. Chattopadhyay *et al.*, Phys. Rev. B **70**, 214421 (2004).
[22] L. Tan *et al.*, Phys. Rev. B **71**, 214408 (2005).
[23] J. Mydosh, *Spin Glasses* (Taylor and Francis, London, 1992).
[24] D. J. Blundell, Polymer **20**, 934 (1979); A. Arbe *et al.*, J. Chem. Phys. **117**, 1336 (2002).
[25] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, U.K., 1995).
[26] C. Magen *et al.*, Phys. Rev. Lett. **91**, 207202 (2003); V. Hardy *et al.*, Phys. Rev. B **69**, 020407(R) (2004).
[27] M. Uehara and S. W. Cheong, Europhys. Lett. **52**, 674 (2000).
[28] P. A. Sharma *et al.*, Phys. Rev. B **71**, 224416 (2005).
[29] J. Sacanell, F. Parisi, J. C. P. Campoy, and L. Ghivelder, Phys. Rev. B **73**, 014403 (2006).
[30] A. Minakov *et al.*, Rev. Sci. Instrum. **76**, 043906 (2005).
[31] S. Sarkar *et al.*, Phys. Rev. Lett. **95**, 205702 (2005).