PHYSICAL REVIEW B **69**, 020407(R) (2004)

Field-induced magnetization steps in intermetallic compounds and manganese oxides: The martensitic scenario

V. Hardy,[1,2] S. Majumdar,[1] S. J. Crowe,[1] M. R. Lees,[1] D. McK. Paul,[1] L. Hervé,[2] A. Maignan,[2] S. Hébert,[2] C. Martin,[2] C. Yaicle,[2] M. Hervieu,[2] and B. Raveau[2]

[1]*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*

[2]*Laboratoire CRISMAT, UMR 6508, Boulevard du Maréchal Juin, 14050 Caen, France*

(Received 15 September 2003; published 23 January 2004)

Field-induced magnetization jumps with similar characteristics are observed at low temperature for the intermetallic germanide Gd_5Ge_4 and the mixed-valent manganite $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$. We report that the field location—and even the existence—of these jumps depends critically on the magnetic field sweep rate used to record the data. It is proposed that, for both compounds, the martensitic character of their antiferromagnetic-to-ferromagnetic transitions is at the origin of the magnetization steps.

DOI: 10.1103/PhysRevB.69.020407 PACS number(s): 75.60.Ej, 81.30.Kf, 75.80.+q

The $Gd_5(Si_xGe_{1-x})_4$ pseudobinary system has attracted growing interest in recent years[1–9] owing to the wealth of interesting physical properties it displays including a giant magnetocaloric effect[1] and a colossal magnetostriction.[2] These striking phenomena are related to a strong interplay between the magnetic and structural features in this system. These compounds have a layered structure made up of subnanometric slabs connected via covalentlike bonds.[7] The degree of interslab connectivity not only depends on x but also on the magnetic state. For instance, with $x=0$, the slabs are completely interconnected in the ferromagnetic (FM) state, whereas all the bonds are broken in both the antiferromagnetic (AF) and paramagnetic (P) states.[6]

Recently, Levin *et al.*[8] have reported an intriguing phenomenon for Gd_5Ge_4. After zero-field cooling (ZFC), the field-increasing branch of $M(H)$ curves recorded at low T exhibit an extremely sharp, irreversible magnetization step. It has been proposed that this behavior is related to the strongly anisotropic exchange interactions present in this material. One should note, however, that the observation of such sharp steps in polycrystalline samples is quite unusual for conventional metamagnetic transitions.

Interestingly, similar magnetization steps were recently observed for mixed-valent manganese oxides with the general formula $Pr_{1-x}Ca_xMn_{1-y}M_yO_3$ (with $x\sim0.5$, $y\sim0.05$, and where M is a cation used to destabilize the Mn sublattice).[10–12] The Mn-site substitutions weaken the robust CE-type AF ordering of the parent compound $Pr_{1-x}Ca_xMnO_3$ ($x\sim0.5$), and favor the development of a phase separation between FM and AF domains. Owing to the collective orbital ordering (OO) accompanying the AF spin ordering, the unit cell of the AF phase is strongly distorted with respect to that of the FM phase. Therefore, as a magnetic field is applied, competition develops between the magnetic energy promoting the development of the FM phase and the elastic energy associated with the strains created at the AF/FM interfaces, which tends to block the transformation.[13] The martensitic nature of this transformation has led us to propose that the magnetization step corresponds to a burstlike growth of the FM component when the driving force overcomes the energy barriers associated with the strains. Remarkably, it turns out that Gd_5Ge_4 is also a system in which FM and AF domains can coexist, and the transformation between these two phases has a pronounced martensitic character.[6,8] This is due to the collective shear movement of the slabs at the AF/FM transition which produces a considerable distortion of the unit cell. For the closely related $Gd_5(Si_{0.1}Ge_{0.9})_4$ compound, Morellon *et al.*[3] reported that the cell parameter a decreases by 1.6%, while b and c increase by 0.7% and 0.3%, respectively, at the AF/FM transition (*Pnma* space group for both phases).

This set of features has prompted us to undertake a precise comparative study between Gd_5Ge_4 and a Mn-site-substituted manganite, with a particular focus on the influence of the magnetic field sweep rate on the field-induced transformations. Our goal was to further investigate the similarity of the magnetization steps in these two systems and the relevance of the martensitic scenario to both of them.

The Gd_5Ge_4 sample was prepared by arc melting a stoichiometric mixture of 99.9 wt % pure Gd and 99.99 wt % pure Ge. The synthesis was carried out under a high-purity argon atmosphere, turning the sample several times to ensure a good homogeneity. The Gd/Ge ratio was checked by energy dispersive spectroscopy (EDS) to be equal to the nominal composition to within the accuracy of this technique. No impurities were detected by x-ray powder diffraction, which showed that the system has an orthorhombic structure at room temperature (*Pnma* space group) with lattice parameters [$a=7.68(1)$ Å, $b=14.80(1)$ Å, and $c=7.77(1)$ Å] in line with the literature.[6] The manganite chosen to compare with Gd_5Ge_4 is $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$, hereafter denoted as [PrCa40]Ga4%. This compound exhibits a phase separation similar to that of Gd_5Ge_4, and it is less sensitive to training effects than most of the manganites.[11] A [PrCa40]Ga4% ceramic sample was synthesized by solid-state reaction according to a process described previously.[10] It also has a room-temperature *Pnma* orthorhombic structure with $a=5.4293(3)$ Å, $b=7.6443(4)$ Å, and $c=5.4097(3)$ Å. Magnetic measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer and a vibrating sample magnetometer (VSM). All the $M(H)$ curves were recorded after the samples were ZFC from the paramagnetic state at 300 K.

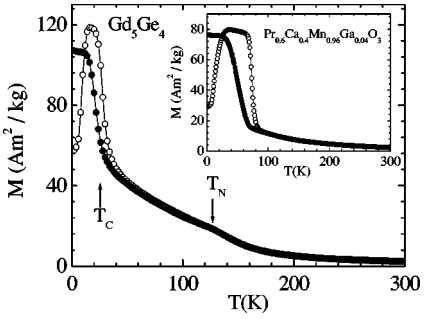

FIG. 1. dc magnetization curves recorded for Gd_5Ge_4 (main panel) and $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$ (inset) in a field of 1.2 T. The open and solid symbols correspond to the zero-field-cooled and field-cooled-cooling modes, respectively. Arrows and labels on the main panel denote the Néel temperature ($T_N \sim 127$ K) and Curie temperature ($T_C \sim 25$ K) of Gd_5Ge_4.

The main panel of Fig. 1 shows the ZFC and FCC (field-cooled-cooling) dc magnetization (M) curves as a function of temperature for Gd_5Ge_4. These curves were recorded in a field of 1.2 T to be comparable with those of Ref. 8. The inset shows the same data sets for [PrCa40]Ga4%. The $M(T)$ curves of Gd_5Ge_4 exhibit the same general features as those reported by Levin *et al.*[8]: (i) a kink at $T_N = 127$ K and (ii) an increase of M at low T, which is associated with the onset of a FM ordering. There is a pronounced hysteresis at low T that points to the first-order character of this ferromagnetic transition, the inflection point on the ZFC and FCC curves being at ~ 28 and ~ 21 K, respectively. As in Ref. 8, one can also observe that the maximum value of $M(T)$ is larger for the ZFC data than for the FCC data and that there is a steep rise of the ZFC $M(T)$ on the low-T side of the peak. It should be noted that this last feature is quite unusual for standard ferromagnets in a field as large as 1.2 T. It suggests that the onset of the FM phase is hindered when zero-field-cooling this compound down to very low temperature. In addition, note that the difference between the values of the magnetization for the ZFC and FCC curves around 20 K may be related to the large magnetostriction present in this material. A Curie-Weiss fit of the paramagnetic regime for $T > 240$ K gives $\theta_{CW} = (115.2 \pm 0.5)$ K and $\mu_{eff} = (7.85 \pm 0.01)\mu_B$/Gd, the latter value being close to the theoretical expectation ($\mu_{eff} = 7.94\mu_B$/Gd). This set of parameters is also consistent with the previous study of Gd_5Ge_4 which reported $\theta_{CW} \sim 94$ K and $\mu_{eff} \sim 7.45\mu_B$/Gd.[8] A closer look at the data of Fig. 1 reveals some differences from the sample studied by Levin *et al.*,[8] in particular a $M(T \rightarrow 0)$ value of the ZFC curve that is larger by $\sim 25\%$ in our case.

The inset of Fig. 1 shows that the $M(T)$ curves of [PrCa40]Ga4% exhibit low-T features that are remarkably similar to those found in Gd_5Ge_4. This behavior was attributed to the appearance of a FM component in this manganite, while electron microscopy demonstrated the persistence, at low T, of a short-range OO associated with the CE-type AF phase.[11] The similarity between the $M(T)$ curves of Gd_5Ge_4 and [PrCa40]Ga4% in the low-T regime is consistent with the existence, in both systems, of related ground states based on phase separation between AF and FM domains.

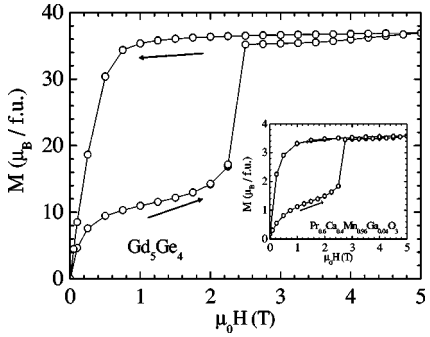

FIG. 2. Magnetic hysteresis loops recorded with a SQUID magnetometer after zero-field cooling: at 2 K for Gd_5Ge_4 (main panel) and at 3.25 K for $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$ (inset).

The main panel of Fig. 2 shows a $M(H)$ curve recorded for Gd_5Ge_4 at 2 K after ZFC. For the field-increasing branch, there is a dramatic step in the magnetization between 2.25 and 2.50 T. This jump is followed by a plateau, then a smooth tail, before finally reaching $M_{sat} = 36.6\mu_B$/f.u. at 5 T. This saturation value corresponds to $7.3\mu_B$/Gd, in good agreement with Ref. 8. The field-decreasing branch is almost flat down to ~ 1 T before going to zero. Increasing the field once again produces a curve superimposed on the reverse leg of the first loop, demonstrating the complete irreversibility of the transformation at this temperature. The overall behavior displayed in the main panel of Fig. 2 is in line with the features reported by Levin *et al.*[8] The difference, however, is that our sample exhibits a sizable FM component, as already suggested by the ZFC value of $M(T \rightarrow 0)$. In Fig. 2, this is clearly revealed by the shape of the virgin magnetization curve at low fields. It is worth noting that the behavior of the sample shown in Fig. 2 is closer to that described in Ref. 8 when it is cooled in a field of 1.2 T to assist the onset of the FM component. We suggest that the two samples may differ on a microstructural or nanostructural level (for example, grain size or local defects), and this in turn may influence the ability of the samples to accommodate the strains associated with the martensitic (FM) phase.[14–16] In addition, we note that the sample studied here may contain a higher density of nonmetallic impurities than the one discussed in Ref. 8, because of the slightly lower purity of the Gd used in its synthesis. A comparison of the present data with those of Ref. 8 suggests that interstitial impurities may favor the onset of the FM component by stabilizing the high-field Gd_5Ge_4 magnetic structure in zero magnetic field.

The inset of Fig. 2 shows a $M(H)$ curve recorded for [PrCa40]Ga4% at 3.25 K, after ZFC. This sample also exhibits a magnetization jump and all the features found for Gd_5Ge_4. For both compounds, the location of the magnetization steps in the $M(H)$ curves depends on the temperature. In order to obtain comparable data for each system, all the $M(H)$ loops recorded hereafter were recorded at 2 K for Gd_5Ge_4 and at 3.25 K for [PrCa40]Ga4%.

In manganites, one of the features supporting a martensitic scenario rather than standard metamagnetism was the influence of the field spacing used to record the $M(H)$ curves by SQUID magnetometry.[13] It was found that smaller field

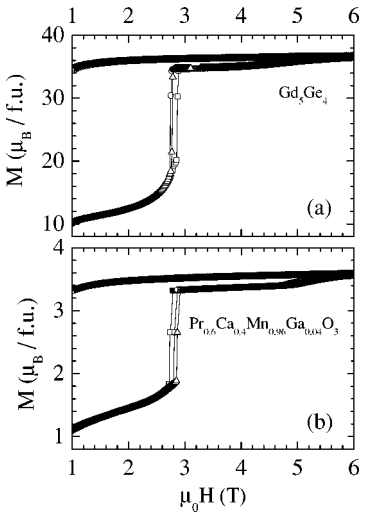

FIG. 3. Enlargements of three successive hysteresis loops recorded with a VSM, after zero-field cooling in each case: (a) Gd_5Ge_4 at 2 K, (b) $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$ at 3.25 K. The magnetic field sweep rate is 1 T/min.

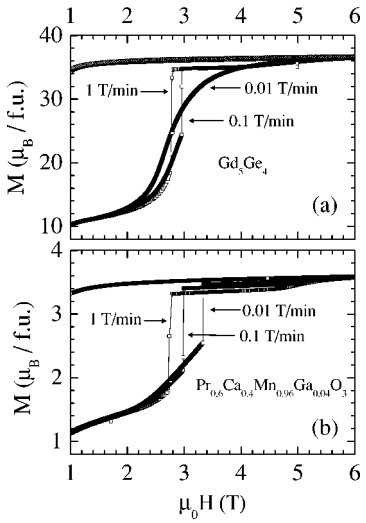

FIG. 4. Enlargements of hysteresis loops recorded with a VSM using different magnetic field sweep rates, after zero-field cooling in each case: (a) Gd_5Ge_4 at 2 K, (b) $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$ at 3.25 K.

increments can delay the magnetic instability, pushing the steps to higher field values. With SQUID measurements such a field-spacing effect can be related to the average magnetic field sweep rate. In the present study, we have used a VSM which is more suited to properly address this issue, since the data can be recorded while ramping the field. For each of the compounds investigated, we have first checked the reproducibility of the step field value for repeated measurements using the same magnetic field sweep rate.

Figure 3 shows enlargements of three successive ZFC $M(H)$ loops recorded on Gd_5Ge_4 and [PrCa40]Ga4%. One can observe small variations from run to run in the value of the step field, which is found to be 2.78 ± 0.08 T in both cases. Additional ZFC loops recorded in the case of Gd_5Ge_4 showed that the step field always lies within this range. The difference between these data and the measurements made using a SQUID magnetometer (shown in Fig. 2) will be discussed below. Even though attention has been paid to the reproducibility of the experimental conditions in which the VSM measurements were performed, we cannot rule out the possibility of small variations in some of the experimental parameters (for example, the effective cooling rate or the value of the trapped field in the superconducting coil during zero-field cooling). These variations may account for the observed scatter in the location of the step field. On the other hand, it should be noted that the existence of such a history dependence may also be regarded as a training effect; such effects are often encountered for martensitic transformations. In any event, the scatter between successive runs remains small enough to allow a reliable investigation of the influence of the magnetic field sweep rate on the magnetic state of both Gd_5Ge_4 and [PrCa40]Ga4%.

Figure 4 shows enlargements of $M(H)$ loops recorded on Gd_5Ge_4 and [PrCa40]Ga4% with three magnetic field sweep rates $dH/dt = \dot{H}$, ranging over two orders of magnitude. *In both systems, the magnetization step is found to be profoundly affected by the value of* $\dot{H}$. This result confirms that these step fields cannot be regarded as true critical fields for metamagnetic transitions. It appears that the influence of $\dot{H}$ is similar in both systems; as $\dot{H}$ is reduced, the smooth upturn of $M(H)$ starts at lower fields, whereas the step in the magnetization is pushed to a higher field. For Gd_5Ge_4, this effect is so pronounced that there is no longer a step for $\dot{H} = 0.01$ T/min. A similar disappearance of the step as $\dot{H}$ is decreased was also observed for [PrCa40]Ga4% at 3.5 K for 0.1 T/min (not shown). The influence of the magnetic field sweep rate on the magnetization steps is a feature that can be accounted for within a martensitic scenario. Indeed, for isothermal martensitic transformations, it is known that the rate of variation of the driving force (here the magnetic field) can affect the development of the transformation. For instance, Pérez-Reche *et al.*[17] have recently reported a significant influence of the cooling rate dT/dt on the temperatures of the peaks displayed on the acoustic emission spectra of $Cu_{68.4}Al_{27.8}Ni_{3.8}$. In our case, the effect is found to be more systematic and pronounced. We suggest that using a smaller $\dot{H}$ can facilitate the progressive accommodation of the martensitic strains, resulting in an upward shift of the step field and even its disappearance. It should be noted that the unusual magnetic dynamics related to the presence of martensitic strains has been previously pointed out by Levin *et al.*[8] for Gd_5Ge_4 on the basis of abnormally sluggish isothermal relaxation of the magnetization in an undercritical field.

Let us now return to the comparison between the SQUID magnetometer and VSM data. According to the systematic influence of $\dot{H}$ shown by the VSM data, the locations of the step field in the SQUID data point to an effective sweep rate close to or even slightly larger than 1 T/min. For the SQUID measurements of Fig. 2, the average sweep rate (including the pause and measurements at each field) is ~ 0.05 T/min, while the transitory sweep rate when charging the magnet is

$\sim$2 T/min. Our results suggest that (i) the average sweep rate is not a relevant parameter for characterizing the dynamics when the magnetic field has to be stabilized prior to each measurement and (ii) using a fast sweep rate for the field installations can play an important role in determining the response of these martensitic systems.

The present paper demonstrates that the magnetization steps recently reported for Gd_5Ge_4 have features very similar to those found in manganites such as [PrCa40]Ga4%, including a huge influence of the magnetic field sweep rate on the field-induced transformations. Such a feature is inconsistent with a standard metamagnetic transition whereas it can be qualitatively accounted for within a martensitic scenario. In the case of Gd_5Ge_4, previous studies have already emphasized the determining role of the martensitic strain on the magnetic properties.[6,8,18] Although they belong to completely different classes of materials, both Gd_5Ge_4 and [PrCa40]Ga4% turn out to be phase-separated systems, in which FM and AF domains having very different unit cells can coexist. Therefore, for both systems, the field-induced AF-to-FM transition at low T must be regarded as a martensitic transformation. Such transformations are well known to be discontinuous, and they can show burstlike effects. Accordingly, we propose that the similarity of the low-T properties found in Gd_5Ge_4 and [PrCa40]Ga4% is not coincidental and that the magnetization steps are manifestations of the martensitic nature of the transformation in both systems. In this scenario, the magnetization jump corresponds to a burstlike growth of the FM component within an essentially AF matrix.

We acknowledge the financial support of the EPSRC (UK) for this project.

[1] V.K. Pecharsky and K.A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).

[2] L. Morellon, P.A. Algarabel, M.R. Ibarra, J. Blasco, B. García-Landa, Z. Arnold, and F. Albertini, Phys. Rev. B **58**, R14 721 (1998).

[3] L. Morellon, J. Blasco, P.A. Algarabel, and M.R. Ibarra, Phys. Rev. B **62**, 1022 (2000).

[4] J. Stankiewicz, L. Morellon, P.A. Algarabel, and M.R. Ibarra, Phys. Rev. B **61**, 12 651 (2000).

[5] E.M. Levin, A.O. Pecharsky, V.K. Pecharsky, and K.A. Gschneidner, Jr., Phys. Rev. B **63**, 064426 (2001).

[6] E.M. Levin, V.K. Pecharsky, K.A. Gschneidner, Jr., and G.J. Miller, Phys. Rev. B **64**, 235103 (2001).

[7] A.O. Pecharsky, K.A. Gschneidner, V.K. Pecharsky, and C.E. Schindler, J. Alloys Compd. **338**, 126 (2002).

[8] E.M. Levin, K.A. Gschneidner, Jr., and V.K. Pecharsky, Phys. Rev. B **65**, 214427 (2002).

[9] J.B. Sousa, M.E. Braga, F.C. Correia, F. Carpinteiro, L. Morellon, P.A. Algarabel, and M.R. Ibarra, Phys. Rev. B **67**, 134416 (2003).

[10] S. Hébert, V. Hardy, A. Maignan, R. Mahendiran, M. Hervieu, C. Martin, and B. Raveau, J. Solid State Chem. **165**, 6 (2002); Solid State Commun. **122**, 335 (2002).

[11] A. Maignan, S. Hébert, V. Hardy, C. Martin, M. Hervieu, and B. Raveau, J. Phys.: Condens. Matter **14**, 11 809 (2002).

[12] R. Mahendiran, A. Maignan, S. Hébert, C. Martin, M. Hervieu, B. Raveau, J.F. Mitchell, and P. Schiffer, Phys. Rev. Lett. **89**, 286602 (2002).

[13] V. Hardy, S. Hébert, A. Maignan, C. Martin, M. Hervieu, and B. Raveau, J. Magn. Magn. Mater. **264**, 183 (2003).

[14] Z. Nishiyama, in *Martensitic Transformation*, edited by M. Fine *et al.* (Academic, New York, 1978).

[15] *International Conference on Martensitic Transformations* (ICOMAT 95), Lausanne, 1995, edited by R. Gotthardt and J. Van Humbeeck (Editions de Physique, Les Ulis, 1995).

[16] V. Podzorov, B.G. Kim, V. Kiryukhin, M.E. Gershenson, and S.-W. Cheong, Phys. Rev. B **64**, 140406(R) (2001).

[17] F.J. Pérez-Reche, E. Vives, L. Mañosa, and A. Planes, Phys. Rev. Lett. **87**, 195701 (2001).

[18] C. Magen, L. Morellon, P.A. Algarabel, C. Marquina, and M.R. Ibarra, J. Phys.: Condens. Matter **15**, 2389 (2003).