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Understanding the role played by Fe on the tuning of magnetocaloric effect in $\text{Tb}_5\text{Si}_2\text{Ge}_2$

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In this letter, it is shown that when replacing Ge by Fe in $\text{Tb}_5\text{Si}_2\text{Ge}_2$ the structural transition still occurs and enhances the magnetocaloric effect (MCE) (up to 66%) with maximum of MCE at a critical Fe amount where the magnetic and structural transitions become fully coupled. It is observed that Fe concentration is able to mimic the effect of external pressure as it induces a complex microstructure, that tunes long range strain fields. This knowledge is crucial for the development of strategies toward materials with improved performance for efficient magnetic refrigeration applications. © 2011 American Institute of Physics. [doi:10.1063/1.3567920]

Refrigeration technologies are essential for modern society, especially those which are highly efficient and environmental friendly.^{1–3} Motivated by the potential for magnetic refrigeration applications at room temperature, the tuning of the properties of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (GSG) is being exploited to increase its critical temperature while simultaneously maintaining or improving the magnitude of the giant magnetocaloric effect (MCE). The first work toward this goal was performed by Pecharsky and Gschneider in 1997,² by studying the effect of alloying many 3d-metal and p-element in GSG, where it was observed a reduction in the MCE, indicating changes in the thermodynamic nature of the magnetic phase transition. Afterwards, it was found that substitution of Ge by Pb and Sn in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ enhances the MCE by ~11% leading, however, to only a slight increase in the critical temperature ($T_{\text{max}}=274$ and 281 K, respectively).^{4,5} In the course of this research, a large improvement was obtained for compounds with a small amount of Ge (5 at. %) replaced by Fe. Here a drastic reduction in the hysteretic losses, an increase in the critical temperature and an improvement of the magnetic refrigeration efficiency were observed.⁶ However, a decrease in the MCE value was observed and attributed to a possible suppression of the structural phase transition.⁶ Similar results were obtained through the incorporation of other chemical elements (namely, first row transition metals) in the Si/Ge network of GSG-based compounds, leading to similar results.⁵ Nevertheless, the physical origin of these effects is not clear. Unlike the case of the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, where the monoclinic (M) crystallographic phase is always found in the paramagnetic state, the $\text{Tb}_5\text{Si}_2\text{Ge}_2$ compound presents a M structure which is already in the ferromagnetic state⁷ also presenting a considerable MCE.⁸ The slight decoupling of the magnetic and structural

transitions [$T_S=100$ K and $T_C=110$ K (on cooling)] (Ref. 7) offers a unique scenario ideal to study the impact of Fe replacement on the structural and magnetic transitions, being this is the main objective of the work presented herein.

The polycrystalline samples here studied were synthesized by the traditional arc-melting method. Further details about preparation can be found elsewhere.⁹ The microstructure studies were performed by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). Low-field dc magnetization measurements and linear thermal expansion (LTE) were carried out simultaneously, in a modified commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer. The high resolution x-ray diffraction experiments were performed on the 11-D-C instrument ($\lambda=0.1066$ Å), at the Advanced Photon Source at Argonne National Laboratory (USA) in the temperature range of 10–250 K. In support information, the neutron diffraction (ND) experiments were carried out on the high intensity powder diffractometer D1B ($\lambda=2.52$ Å) at the Institut Laue-Langevin in Grenoble (France). The crystallographic characterization of the samples was made by Rietveld refinement of the x-ray synchrotron diffraction (XRS) and ND patterns using the FULLPROF software package.¹⁰

Magnetization measurements show that the systematic substitution of Ge by Fe in $\text{Tb}_5\text{Si}_2\text{Ge}_{2-y}\text{Fe}_y$ leads to an increase in T_C [Fig. 1(a)]; measured on heating from 112 to 123 K for $y=0$ and 0.20, respectively. A similar increase is observed on T_S indicating the existence of the structural phase transition as observed by LTE and XRS data [Figs. 1(b) and 2]. The LTE measurements show a considerable change in the $\Delta L/L$ at T_S [see Fig. 1(b)]. In the case of XRS data, Rietveld refinements indicate a complete conversion of the O(I) phase to M phase (on heating). This can be followed in Figs. 2(a) and 2(b), namely, through the appearance upon heating of the characteristic reflections of the M phase [(-1

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FIG. 1. (Color online) (a) Temperature dependence of the magnetization for $\text{Tb}_5\text{Si}_2\text{Ge}_{2-y}\text{Fe}_y$ compounds with $y=0, 0.075, 0.10, 0.15$ and 0.20 normalized at $M(T)/M(T=70 \text{ K})$ for $H_{\text{ap}}=50 \text{ Oe}$. (b) Temperature dependence of LTE normalized as $\frac{\Delta L}{L} = [LTE(T) - LTE(T=80 \text{ K})] / [LTE(T=140 \text{ K}) - LTE(T=80 \text{ K})]$.

3 2), (0 4 2), and $(-1 \ 4 \ 2)$] and through the disappearance of the characteristic ones of the O(I) phase [(1 3 2), (1 5 1) and (2 4 1)]. A large thermal hysteresis is observed in LTE and XRS data corresponding to the coexistence of the M and O(I) phases (bright zone in Fig. 2) in accordance with the results reported in Ref. 7. It is noteworthy that the increase in the Fe concentration also leads to an increase in the reflection at about 2.41° . This corresponds to the (2 1 1) reflection of the $\text{Tb}_5(\text{Si,Ge})_3$ secondary phase (5:3 phase; Mn_5Si_3 -type). The presence of this impurity phase is further sustained by SEM and EDS analysis of the samples, displayed in Fig. 2, showing typical Widmanstaetten-type plates (linear microstructure) already for low Fe concentration [$y=0.05$, Fig. 2(a)] (Refs. 11 and 12) with the amount of these plates increasing with the Fe content. The EDS results reveal a systematic absence of Fe in the main phase (5:4), meaning that iron is primarily accumulated in the secondary 5:3 phase and also incorporated in $\text{Tb}(\text{Si,Ge})\text{Fe}$ (1:1:1) (found in our samples in trace amounts). In addition, EDS results indicate that the 5:4 phase is systematically enriched with Ge (meaning that silicon is preferentially located on the precipitates of the secondary phases). This is in agreement with the Rietveld refinements, that reveal an slightly increase in the unit cell volume of the 5:4 phase upon the increase in the Fe content. From the same refinements one also obtains a linear increase

FIG. 2. (Color online) Temperature dependence of XRS data with $\lambda=0.1066 \text{ \AA}$, in the 93–135 K temperature range (on heating) for (a) $y=0$ and (b) $y=0.20$. (c) backscattered electron SEM micrographs of samples with $y=0.05, 0.075$ and 0.15 .

in the percentage of the 5:3 phase with a maximum of 23% for the $y=0.20$ composition. The amount of 1:1:1 phase can be considered negligible ($<1\%$ amount). The magnetostructural (y, T) phase diagram is shown in Fig. 3(a), where the values of the transition temperatures were determined from the maxima of the derivative of the thermal dependence of the corresponding macroscopic properties. Both T_S and T_C shift linearly with Fe concentration to higher temperatures (Fig. 3). Notice that dT_S/dy is steeper than dT_C/dy , revealing that the substitution by Fe is directly influencing the structure. Above $y \sim 0.19$, a fully coupled magnetic-crystallographic transformation $[\text{M}, \text{PM}] \rightarrow [\text{O(I)}, \text{FM}]$ takes place as can be seen in the inset of Fig. 3(a), which displays the simultaneous occurrence of the magnetic and structural transition (through the $dLTE/dT$ and dM/dT curves). This result is reinforced by ND experiments performed on compound with $y=0.15$ (see Ref. 13).

Figure 3(b) presents the temperature dependence of the magnetic entropy change (ΔS_m), obtained from the traditional Maxwell relation, on the Fe content for a magnetic

FIG. 3. (Color online) (a) Magnetostructural phase diagram of $\text{Tb}_5\text{Si}_2\text{Ge}_{2-y}\text{Fe}_y$ determined from magnetization and LTE data (for clarity only the values upon heating are displayed). Inset: dM/dT and $dLTE/dT$. (b) MCE for $H=50 \text{ kOe}$.

field variation of 50 kOe (no significant difference is observed in ΔS_m values when the magnetic field is increasing or decreasing).¹⁴ A drastic enhancement of the MCE up to $y=0.15$ is observed. The observed values of the MCE results the sum of the conventional magnetic entropy-driven process arising from the magnetic transition, ΔS_{mag} , plus the difference in magnetic entropy of the two crystallographic structures, ΔS_{st} .¹⁵ At higher concentration a fully coupled magnetic and structural transition occurs with a decrease in the magnetic entropy.

There is an intriguing parallelism between the effect of the substitution of Ge by Fe and the application of an external pressure on $\text{Tb}_5\text{Si}_2\text{Ge}_2$, previously reported by Morellonet *al.*¹⁵ In that Letter, it was shown that for a sufficiently high external pressure, a full coupling between the magnetic and structural transitions occurred in a tricritical point leading to the corresponding enhancement of ΔS , in accordance with our present results. Unfortunately no data of the MCE was obtained well above the tricritical point in this pressure study. However, the decrease in the MCE with the application of an external pressure was already observed in the fully coupled magnetostructural transition of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (similarly to the present case after the fully coupled transitions) and in the MnAs.^{16,17}

The features found here seem to be directly related to the complexity of the microstructure observed in the samples strongly influencing the first order magnetostructural transition (FOMT). The presence of quenched thin plates of 5:3 phase on the FOMT of $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds has been the subject of several studies,^{11,12,18,19} and it was found that an “epitaxial” interface with an angle of 7° between the (1 0 0) and (0 0 0 1) reflections of the 5:4 phase and of the 5:3 plates, respectively, was created. This gives rise to long-range strain fields in the grain boundaries (on the interface) providing a similar effect as external pressure. The aforementioned mechanism has been suggested in Ref. 20 to explain the first-order $[\text{PM}, \text{M}] \rightarrow [\text{FM}, \text{O}(\text{I})]$ transition in $\text{Gd}_5\text{Ge}_2\text{Si}_2$ single crystal, where it was inferred that long-range strain fields, arising from complex platelet/matrix interface [(5:3)/(5:4) phases, respectively], are the source of strain. They also showed that this persistent local strain promotes the $\text{PM} \rightarrow \text{FM}$ transition but not the inverse.²⁰ In conclusion, the discovery that Fe substitution in $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds operates similarly to external pressure, reinforcing the magnetostructural coupling via internal strain, opens wide perspectives for materials engineered with optimized properties for magnetic refrigeration applications.

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