Structure and magnetocaloric properties of the Fe-doped HoTiGe alloy

V. Provenzano,[a] B. Baumgold, R. D. Shull, and A. J. Shapiro
Magnetic Materials Group, National Institute of Standards and Technology, 100 Bureau Drive, MS-8552, Gaithersburg, Maryland 20899

K. Koyama and K. Watanabe
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

N. K. Singh and K. G. Suresh
Department of Physics, Indian Institute of Technology, Bombay, Mumbai 400076, India

A. K. Nigam and S. K. Malik
Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400005, India

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The structure and magnetocaloric properties of the Fe-doped HoTiGe compound were investigated by means of scanning electron microscopy (SEM), energy dispersive spectroscopy, x-ray diffraction, magnetometry, and calorimetry. As with the early studies on the undoped compound, the Fe-containing alloy exhibited an antiferromagnetic-to-paramagnetic transition and a magnetocaloric effect peak at 90 K. The magnetization (M) versus temperature (T) data showed peaks at 10 and 90 K, while M versus field (H) curves showed the presence of a field-induced transition for all $T < 120$ K; additionally, for all $T < 60$ K, open hysteresis loops at the magnetic transitions were observed. XRD measurements between 10 and 60 K under various magnetic fields up to 3184 kA/m (40 kOe) showed that the hysteresis was not accompanied by any change in crystallography. The magnetization derived entropy change $-\Delta S_m$ vs T plot also showed the presence of two peaks, at 20 and 90 K; but below 15 K, $-\Delta S_m$ increased steeply with decreasing temperature. It is believed that the minor phases in the Fe-doped alloy give rise to the magnetization-derived $-\Delta S_m$ peak at 20 K. The heat-capacity-derived $-\Delta S_m$ vs T plot for the Fe-doped alloy also showed the presence of two peaks at 20 and 90 K. However, the heat-capacity-derived $-\Delta S_m$ did not show a rapid rise with decreasing temperature below 15 K. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2159396]

INTRODUCTION

Recent research on cooling has been focused on finding refrigerant materials with large magnetocaloric effects ($-\Delta S_m$) at the specific temperature range for the intended application. For space cooling and hydrogen liquefaction, magnetic refrigerants exhibiting large $-\Delta S_m$ effects below 30 K are highly desirable, whereas for natural gas liquefaction and near-room-temperature refrigeration, materials having large $-\Delta S_m$ effects above 100 K are sought. Equiatomic ReTiGe intermetallic compounds (where Re stands for a rare-earth element) exhibit interesting antiferromagnetic (AF)-to-paramagnetic (PM) transitions accompanied by large magnetocaloric peaks.[1–3] Of particular interest is HoTiGe, in which a field-induced magnetic transition is accompanied by hysteresis losses with the hysteresis width decreasing as T increases and vanishing for $T \geqslant 60$ K. The field-induced transition, however, persists up to 120 K. Similar field-induced magnetic transitions, attributed to crystallographic transformations, accompanied by large magnetocaloric effects have also been observed in the $Gd_5Ge_2Si_2$compound.[4] For this latter compound, the hysteresis was eliminated by doping with Fe.[5] The present study was initiated in order (1) to determine whether the field-induced magnetic transition in the HoTiGe compound involves a crystallographic phase change and (2) to determine whether Fe doping will eliminate the hysteresis losses in the HoTiGe compound as it did for $Gd_5Ge_2Si_2$.

EXPERIMENTAL DETAILS

The undoped and the Fe-doped HoTiGe samples used in this study were prepared by arc melting. The purity of the starting constituents was 99.9% mass fraction or better, and the targeted alloy composition was $HoTi_{0.9}GeFe_{0.1}$ (approximately 3 at. % Fe). Throughout the paper we shall refer to the undoped HoTiGe as the "HoTiGe compound," whereas HoTiGe with the iron addition will be referred to as the "Fe-doped HoTiGe alloy." The crystal structure of both the compound and the alloy was characterized by Cu $K\alpha$ x-ray diffraction (XRD) analysis at 300 K; low temperature XRD was also conducted on the Fe-doped alloy while under an applied magnetic field. Hysteresis loops as well as the magnetic isotherms for calculating the magnetocaloric effect were obtained by measuring the sample's magnetization M as a function of temperature T and applied magnetic field H in a superconducting quantum interference device (SQUID) magnetometer. All samples for magnetic measurements were in bulk form, except for one M vs H loop measured at 10 K on a powder sample of the Fe-doped alloy for assessing magnetic texture effects. The entropy change (magnetization-

[a]Electronic mail: virgil12@nist.gov

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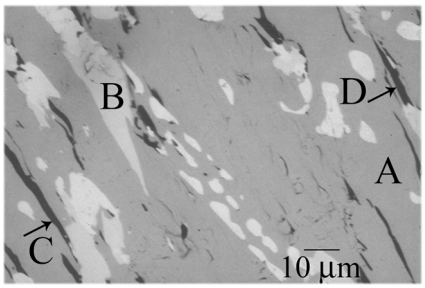

FIG. 1. Backscattered SEM micrograph of the $HoTi_{0.9}GeFe_{0.1}$ alloy. (A) HoTiGe is the majority matrix phase and, (B) $Ho_{58}Ti_5Ge_{36}Fe$, (C) $Ho_3Ti_{58}Fe_2$, and (D) $Ho_3Ti_{47}Ge_{13}Fe_{37}$ are the minority phases. The 300 K x-ray diffraction spectrum shown in Fig. 2 is consistent with the features shown in Fig. 1.

derived $-\Delta S_m$) was calculated from the magnetization data using the integrated form of the Maxwell relation:

$$\Delta S_m(T,\Delta S) = \int_0^{H'} \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (1)$$

To complement the characterization of the magnetocaloric properties obtained from the magnetic data (M vs H and $-\Delta S_m$ vs T plots), $-\Delta S_m$ data values were also computed from heat capacity data using the following equation:

$$\Delta S_m(T,H) = \left[\int_0^{T'} \frac{C(T',H) - C(T',0)}{T'} dT'\right], \quad (2)$$

where $C(T',H)$ and $C(T',0)$ are the heat capacities of the Fe-doped HoTiGe alloy measured at temperature T' and under respective applied fields of H and 0.

RESULTS AND DISCUSSION

Figure 1 shows the typical microstructure of the Fe-doped alloy ($HoTi_{0.9}GeFe_{0.1}$). Figure 1 shows that the microstructure consists of a majority matrix phase (HoTiGe) and three minority phases, having different amounts of Fe. Although not shown here, the microstructure of the HoTiGe compound was single phase.[1–3]

Though slightly shifted, most of the peaks match those of the HoTiGe majority phase; the remaining peaks are most likely associated with the Fe-containing minority phases (see Fig. 2). The M vs T data measured during heating at a fixed field of 398 kA/m (5 kOe) (Fig. 3) show an AF-to-PM transition peak centered at about 90 K, similar to that previously observed for the HoTiGe compound.[2,3] However, the M vs T plot for the Fe-doped alloy exhibits an additional AF-to-PM transition centered at 10 K. This low temperature transition was not seen in the undoped compound, implying that it is associated with the Fe doping. Specifically, the 10 K peak must be related to one of the three Fe-containing minor phases observed in Figs. 1(b) and 1(c).

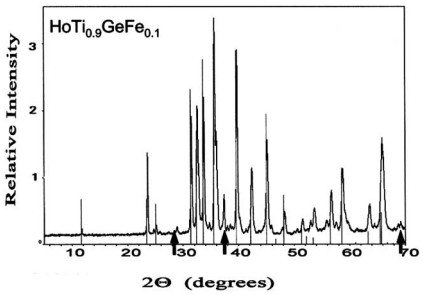

FIG. 2. Cu $K\alpha$ x-ray powder diffraction pattern, collected at room temperature, for $HoTi_{0.9}GeFe_{0.1}$. Most of the peaks match those of the HoTiGe majority phases (indicated by solid lines in the spectrum), while the remaining peaks (indicated by arrows) are most likely associated with the Fe-containing minor phases.

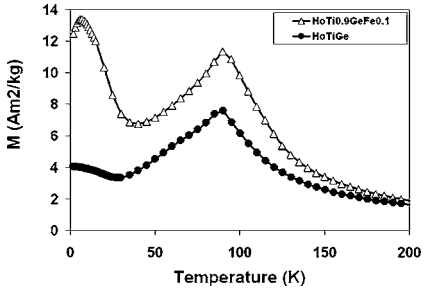

FIG. 3. M vs T data measured at 398 kA/m (5 kOe) constant field for (A) the Fe-doped alloy (open symbols) and (B) the undoped compound (filled symbols).

Figure 4 shows several representative M vs H loops for the Fe-containing alloy. In each loop the field was cycled between zero and 3980 kA/m (50 kOe) while the temperature was kept constant. The loops clearly show the following: (1) the presence of a field-induced phase transition and (2) large hysteresis losses which are associated with this field-induced transition. In addition, note that the width of the hysteresis loops decreases with increasing T, becoming zero at 60 K and above. Also, the field-induced transition is triggered by smaller field values as the temperature is increased. The hysteretic behavior of the Fe-doped alloy between 2 and 60 K is very similar to that of the compound without the iron addition. However, the Fe-doped alloy shows the presence of a remnant magnetization whose value decreases with increasing T. By contrast, in the same 2 to 60 K temperature range, no remnant magnetization was observed in the undoped compound.[1–3] Though not shown here, the M vs H loops for the doped alloy at higher temperatures (up to 120 K) show no hysteresis, similar to the 60 K loop.

The x-ray spectra of the alloy at 10 K taken under various applied fields are shown in Fig. 5. Note that the XRD patterns for the alloy remain the same when the applied field is varied from zero to 3980 kA/m (50 kOe). These x-ray results clearly show that the primary field-induced transition seen in both the doped alloy and in the HoTiGe compound does not involve a crystallographic phase change, contrary to that observed in $Gd_5Ge_2Si_2$.[4,6,7] The magnetization-derived $-\Delta S_m$ vs T plot for the Fe-doped alloy, computed from the magnetic data, using the integrated form of the Maxwell re-

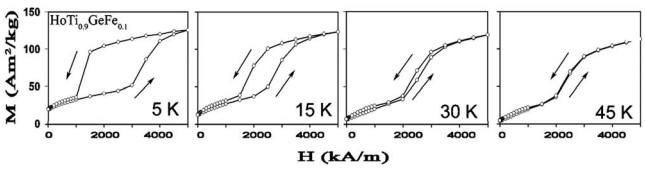

FIG. 4. Magnetization vs field loops for the Fe-doped HoTiGe alloy, taken at the indicated temperatures.

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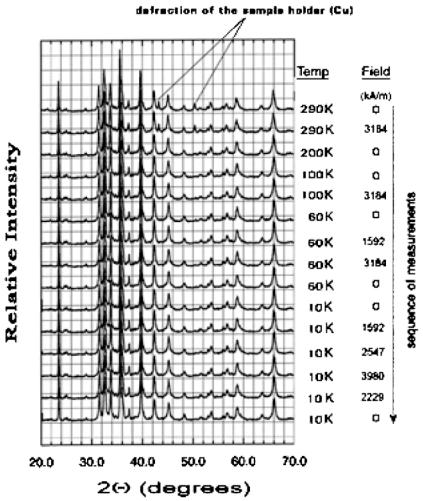

FIG. 5. X-ray diffraction patterns for the Fe-doped HoTiGe alloy, measured at the various indicated temperatures in the presence of the indicated magnetic fields. All the spectra at any temperature were first measured before cooling to the next lower T. Note that there is no change in the spectra with T or H.

lation [Eq. (1)], is presented as the filled symbols in Fig. 6. Consistent with the corresponding $-\Delta S_m$ vs T plot for the undoped compound, the plot shows the presence of a peak, centered at 90 K. However, different from the undoped compound,[1–3] the magnetization-derived $-\Delta S_m$ vs T plot for the Fe-doped alloy hints at the presence of a second higher peak, centered near 20 K, and a steeply rising $-\Delta S_m$ with decreasing T below 15 K. Figure 6 also shows the heat-capacity-derived $-\Delta S_m$ vs T plot (open symbols) determined for the Fe-doped alloy. This latter plot shows the presence of a large magnetocaloric peak centered around 20 K and a broad smaller peak centered in the vicinity of 90–120 K. This broad peak is most certainly due to the HoTiGe majority phase (Fig. 1) since it appears also in the undoped compound. However, the larger 20 K peak is most likely associated with one of the minor Fe-containing phases.

Comparison of the $-\Delta S_m$ vs T plots, respectively, computed from the M and C_p data (Fig. 6), provides valuable insight concerning the validity of the magnetic entropy change values computed from the magnetization data, using the integrated form of the Maxwell relation [Eq. (1)] in the presence of large hysteresis losses. As discussed previously, the magnetization-derived $-\Delta S_m$ shows the presence of two peaks (one at 20 K and the other at 90 K, Fig. 6, filled symbols) and a steeply rising value of $-\Delta S_m$ as T decreases below 15 K. By contrast, the equivalent plot computed from the heat capacity data shows the presence of a larger (well defined) peak at 20 K but no steeply rising value of $-\Delta S_m$ below 15 K (Fig. 6, open symbols). Note also that the Mvs H loops presented in Fig. 4 also clearly show the presence of rather large hysteresis loops below 15 K.

When hysteresis losses are present, M is no longer a single-valued function of H; the value of M at a fixed field value depends on the magnetic history. Consequently, the

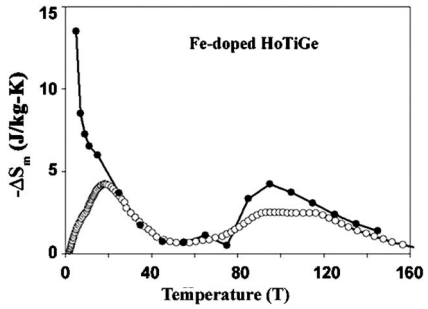

FIG. 6. $-\Delta S_m$ vs T plots, computed from magnetization data (filled symbols) using Eq. (1) and from heat capacity data (open symbols) using Eq. (2), for the Fe-doped HoTiGe alloy subjected to an applied field change (ΔH) of 3980 kA/m (50 kOe).

computed values of magnetization-derived $-\Delta S_m$, using Eq. (1), wherein M is expressed as a single-valued function of H, cannot be correct.

As the computation of the M-derived ΔS_m employs an integral of the M vs H relationship, the bigger the area enclosed in the hysteresis loop (i.e., the wider it is), the bigger the discrepancy will be between the values of magnetization-derived $-\Delta S_m$ and the heat-capacity-derived $-\Delta S_m$. Note again that the hysteresis loop width increases with decreasing temperature in the Fe-doped alloy. The heat-capacity-derived values of $-\Delta S_m$ do not suffer from hysteresis effects since they are determined directly from measured heat capacity data. Thus, heat-capacity-derived $-\Delta S_m$ values do not rely upon a specific M vs H relationship. Based on the forgoing discussion, we conclude that the steeply rising value of M-derived $-\Delta S_m$ below 15 K, but not seen in the C_p-derived $-\Delta S_m$, is a computational artifact.

CONCLUSION

Despite the similarities in the magnetization data between the HoTiGe and $Gd_5Ge_2Si_2$ compounds, they are magnetically quite different. The field-induced magnetic transition in HoTiGe is an AF-to-PM transition on increasing field while the field-induced transformation in $Gd_5Ge_2Si_2$ is a crystallographic transformation between two structures with different magnetic characters. Consequently, Fe doping the HoTiGe compound did not eliminate its hysteresis like it had done for $Gd_5Ge_2Si_2$. However, Fe-doped HoTiGe does possess another crystallographic phase, which possesses a very large magnetocaloric effect near 20 K.

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