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Abstract

Magnetization measurements using a $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal with the magnetic field applied along three crystallographic directions, $[001]$, $[010]$ and $[100]$, were carried out as a function of the applied field (0–56 kOe) at various temperatures (~5–320 K). The magnetic field (H)–temperature (T) phase diagrams were constructed for the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal with field along the three directions. A small anisotropy was observed. The magnetocaloric effect was calculated from isothermal magnetization data, and the observed anisotropy correlates with the H–T phase diagrams. The results are discussed in connection with the magnetic field induced martensitic-like structural transition observed in $Gd_5(Si_2Ge_2)$-type compounds.

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Magnetic field induced phase transitions in Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) single crystal and the anisotropic magnetocaloric effect

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(Presented on 15 November 2002)

Magnetization measurements using a Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) single crystal with the magnetic field applied along three crystallographic directions, [001], [010] and [100], were carried out as a function of the applied field (0–56 kOe) at various temperatures ($\sim$5–320 K). The magnetic field (H)–temperature (T) phase diagrams were constructed for the Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) single crystal with field along the three directions. A small anisotropy was observed. The magnetocaloric effect was calculated from isothermal magnetization data, and the observed anisotropy correlates with the H–T phase diagrams. The results are discussed in connection with the magnetic field induced martensitic-like structural transition observed in Gd$_5$(Si$_2$Ge$_2$)-type compounds. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1556259]

I. INTRODUCTION

The Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ family of compounds has been found to display a variety of interesting physical behaviors, such as the giant magnetocaloric (GMC),[1,2] the giant magnetoresistance (GMR),[3–5] and the colossal magnetostrictive (CMS) effects.[6,7] This combination of properties is quite unique thus making the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ series of compounds a potential candidate for application in magnetic refrigeration, magnetoelectrical and magnetomechanical devices. Recent experimental results[6–9] indicate that in the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ system there is a magnetic field induced disorder–order or order–order magnetic phase transition, coupled with a crystallographic phase transition when $x \geq 0.5$. Thus, simultaneous magnetic and crystallographic phase changes appear to be responsible for the observed GMC, GMR and CMS effects.

All of the experimental data reported to date are based on polycrystalline materials with varying purity. Examination of the anisotropy, which can be done using single crystalline samples, may further clarify the underlying mechanisms responsible for unusual magnetoelastic coupling observed in these Gd-based (an S-state lanthanide ion) intermetallic compounds. However, to the best of our knowledge, the magnetic properties of the single crystals of the compounds in the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ series are not known. In the present study, we report on the isothermal magnetization, the magnetic field induced first-order magnetic phase transition, and the magnetocaloric effect as functions of the temperature and magnetic field with the field vector parallel to three major crystallographic axes of high purity single crystal of Gd$_5$(Si$_{1.95}$Ge$_{2.05}$).

II. EXPERIMENTAL DETAILS

The single crystal of Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) was grown by the Bridgman method, starting from a polycrystalline raw material with a nominal chemical composition, Gd$_5$(Si$_2$Ge$_2$). The polycrystalline stock was prepared by arc melting the high purity constituent elements in argon atmosphere, and its phase purity was confirmed by x-ray powder diffraction, see Ref. 10 for details. The nearly cubic shape single crystal with six faces parallel to (100), (010), and (001) crystallographic planes was cut from a large single-crystal grain using the spark erosion technique. The orientation of the crystallographic axes in the sample was established by using the backscattered Laue technique, and the orientations of three independent faces of the specimen were verified by diffractometry. The chemical composition [Gd$_5$(Si$_{1.95}$Ge$_{2.05}$)] was determined by comparing the Curie temperature of the single crystal (obtained from ac susceptibility results) with the composition-T_C phase diagram.[11]

The isothermal magnetization measurements were performed by using a LakeShore magnetometer (model 7225) at various temperatures in the range of 5–320 K, over a magnetic field range of 0–56 kOe. The magnetocaloric properties were evaluated from isothermal dc magnetization data (no demagnetization correction) using the Maxwell relation. The accuracy of the alignment of the magnetic field vector with the crystallographic directions of the single crystal was ±5°.

III. RESULTS AND DISCUSSION

Figure 1 shows the isothermal magnetization data for the Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) single crystal measured in the temperature range of $\sim$257 to $\sim$300 K with the magnetic field applied parallel to the [001] direction. At temperatures below $\sim$257 K, the $M(H)$ behavior is typical of a soft ferromagnet. With an increase in temperature, the $M(H)$ is indicative of mixed ferromagnetic (FM) and paramagnetic states (PM),[5,7,12] and

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J. Appl. Phys., Vol. 93, No. 10, Parts 2 & 3, 15 May 2003
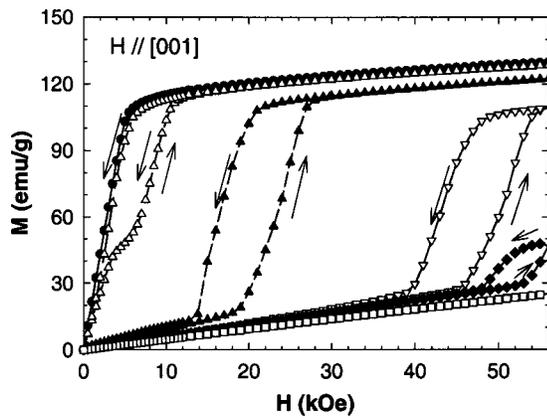
Tang *et al.*   8299

FIG. 1. Isothermal magnetization data collected during an increase and decrease in magnetic field using the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal with $H//[001]$ at (●) 256.9, (△) 258.9, (▲) 267.1, (▽) 281.4, (◆) 285.4, and (□) 299.6 K.
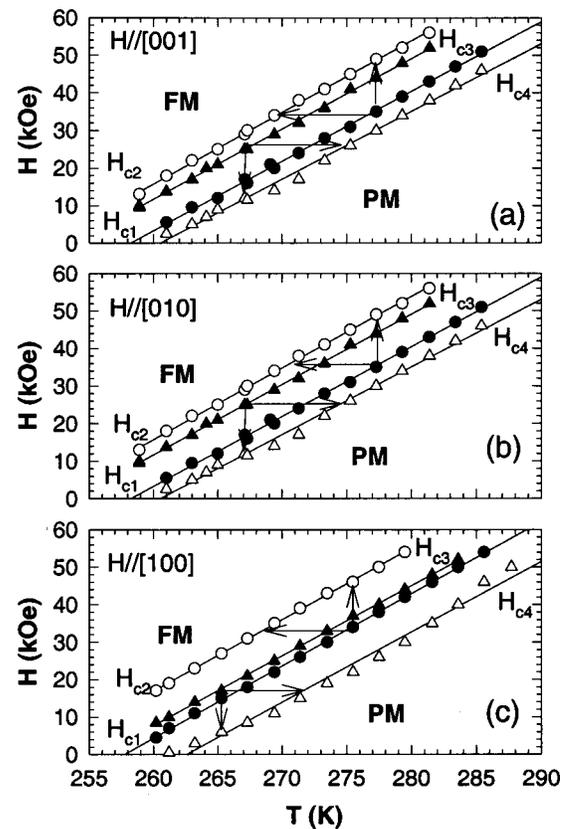
FIG. 2. $H-T$ phase diagrams for the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal: (a) $H//[001]$, (b) $H//[010]$, and (c) $H//[100]$. The points are experimental data, and the straight lines are linear least square fits to the experimental data. The closed symbols indicate the start of the particular transformation, and the open symbols correspond to the end of the same transition.

then finally of a purely paramagnetic state in zero magnetic field. The mixed state is revealed by the peculiar behavior of the isothermal magnetization at certain temperatures, e.g., the case at ~258.9 K, shown in Fig. 1. With an increase in magnetic field above the Curie temperature, a magnetic field induced PM→FM phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$ begins at a certain critical magnetic field (H_{c1}), and it is completed when the field exceeds a higher critical value (H_{c2}). With a decrease in magnetic field, a reverse magnetic phase transition FM→PM takes place at a field (H_{c3}, lower than H_{c2}), and it ends at a certain field (H_{c4}, lower than the corresponding H_{c1}). All critical fields are temperature dependent. It is obvious that there is hysteresis of ~10 kOe (calculated from the maxima of the dM/dH vs H functions) between the field-increasing and the field-decreasing $M(H)$ branches. The critical field values were determined from the beginning (H_{c1}, H_{c3}) and the end (H_{c2}, H_{c4}) of the corresponding dM/dH minima at the peak bases.

Isothermal magnetization data were also collected at various temperatures for the other two directions, [010] and [100], respectively. The magnetic field induced PM↔FM magnetic phase transitions, closely resembling those observed in the case with the field applied parallel to the [001] direction, were also observed for $H//[010]$ and $H//[100]$, and the corresponding critical field values were determined in the same way as described above. Moreover, the temperature induced PM↔FM magnetic phase transitions were characterized as first-order type from the $M(T)$ data collected at various fields, and exhibit thermal hysteresis of ~12 K between the heating and the cooling branches.

Employing the critical magnetic field values at the various temperatures obtained above, we constructed the magnetic field (H) versus temperature (T) phase diagrams for all three crystallographic directions, shown in Figs. 2(a)–2(c), respectively. The vertical and horizontal arrows indicate the start and the end of the transition in the isothermal and isofield regimes, respectively. The critical magnetic fields (H_{c1}, H_{c2}, H_{c3}, and H_{c4}) increase nearly linearly with an increase in temperature at a rate of ~1.8 kOe/K. There are three regimes in each diagram, PM, PM+FM, and FM, di-

vided by critical field lines H_{c1} and H_{c2} or H_{c3} and H_{c4}, respectively. Above H_{c2} and below H_{c4}, the system is magnetically homogeneous, FM and PM, respectively. Between H_{c1} and H_{c2} and between H_{c3} and H_{c4}, there is a mixture of PM and FM states.[5,7,12] In addition, there is hysteresis between the PM→FM and the FM→PM transitions, which is indicated by the gaps between H_{c1} and H_{c4} or between H_{c2} and H_{c3}. The coexistence of the PM and FM states in certain magnetic field and temperature ranges is similar to that reported earlier in polycrystalline samples[7,12] in this series.

There are some notable features which are worth mentioning and they may be related to either or both the intrinsic anisotropy of the crystal lattice or the anisotropy of the magnetic field induced phase transition, even though the $H-T$ phase diagrams basically look similar to one another. So the H_{c1} and H_{c2} are plotted together in Fig. 3 as functions of temperature for three directions. It is obvious that there is slight shift in the critical field boundaries when compared with each other. The gap between H_{c1} and H_{c2} (i.e., the region of coexistence of the PM and FM phases) is smallest in the case with $H//[001]$ and largest in the case with $H//[010]$. The hysteresis (not shown here but seen in Fig. 2), which is indicated by the difference between H_{c1} and H_{c4} or between H_{c2} and H_{c3}, is largest in the case with $H//[100]$. These anisotropic features may be related to the noticeable lattice distortion along the [100] direction[8,9] which occurs
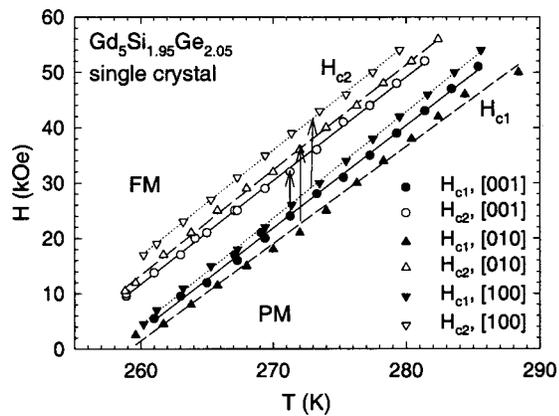
FIG. 3. Critical magnetic field values as a function of temperature of the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal with the field along different directions. Closed symbols represent H_{c1}, and open symbols represent H_{c2}.

FIG. 4. Magnetocaloric effect ($-\Delta S_{magn}$) as function of temperature for the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal, with $H//[001]$, $H//[010]$, and $H//[100]$ calculated from the isothermal magnetization data for a change in magnetic field from 0 to 50 kOe.

during the martensitic-like structural transition around the T_C.

From the isothermal $M(H)$ data at various temperatures, the magnetocaloric effect (i.e., the isothermal change of the magnetic entropy, $-\Delta S_{magn}$) was evaluated by utilizing one of the Maxwell equations $(\partial S_{magn}/\partial H)_T = (\partial M/\partial T)_H$, where T is the absolute temperature and H is the applied magnetic field.[1] The magnetocaloric effect ($-\Delta S_{magn}$) with a change in magnetic field of 0–50 kOe is plotted as a function of temperature in Fig. 4 for the single-crystal $Gd_5(Si_{1.95}Ge_{2.05})$. There are two distinct anomalies: the first is the spikes observed in three cases in the vicinity of the zero-field T_C. The second is small anisotropy in the extent of the $-\Delta S_{magn}$, i.e., the broadening of the magnetocaloric effect at higher temperature in the case with $H//[010]$. The spikes are probably numerical integration errors, which may be observed in the vicinity of the first-order PM→FM transition when $M(H)$ is discontinuous or in nonequilibrium,[13] although they were repeatable in an independent measurement. They could be verified further by magnetization measurements around the zero-field T_C at various temperature and/or magnetic field intervals. However, we need to point out that the largest spike, i.e., the highest $-\Delta S_{magn}$ value of ~ 75 (J/kg K) ($\Delta H = 0 - 50$ kOe) is obtained in the case with $H//[100]$. This feature may be intrinsic and related to the accompanying lattice distortion. Broadening of the magnetocaloric effect at higher temperature in the case of $H//[010]$ is consistent with the largest gap (the region of coexistence) between H_{c1} and H_{c2} of the magnetic field induced PM →FM transition and shifting of the respective phase boundaries towards higher temperature (see Fig. 3).

IV. CONCLUSIONS

A magnetic field induced first-order magnetic phase transition was observed in a $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal with the magnetic field vector parallel to three crystallographic directions, and was found to be slightly anisotropic. The $H-T$ phase diagrams were constructed for these cases ($H//[100]$, $H//[010]$, and $H//[001]$) based on the isother-
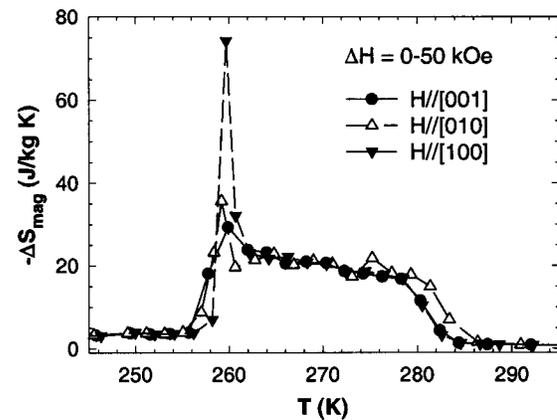
mal magnetization data, and found to be slightly anisotropic. The GMC effect evaluated from the magnetization as a function of the temperature and magnetic field is maximum in the vicinity of T_C. The small anisotropy of the GMC effect that is observed may be correlated with the nature of the crystalline anisotropy of this compound, and minor anisotropy of the magnetic field induced magnetic phase transition. The relationships between the anisotropy of the magnetocaloric effect (including the anomalous spikes at $\sim T_C$ and the anisotropy in the [010] direction at higher temperature) and the intrinsic magnetic anisotropy require further clarification.

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