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Magnetic force microscopy characterization of a first-order transition: Magnetic-martensitic phase transformation in Gd5(SixGe1−x)4

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Abstract
The magnetic-martensitic phase transformation of Gd5(SixGe1−x)4 (x≈0.5), which occurs close to room temperature, has been observed for the first time using a magnetic force microscope (MFM) equipped with a heating–cooling stage. MFM images obtained from a polycrystalline Gd5(Si2.09Ge1.91) sample and single crystal Gd5(Si1.95Ge2.05)and Gd5(Si2Ge2) samples showed transition to a domain structure at low temperatures indicative of a ferromagnetic phase. Some samples exhibited complex domain structures,suggesting that Gd5(SixGe1−x)4 (x≈0.5) has a strong magnetic anisotropy. As the sample temperature increased the domain structure diminished, reflecting the transformation from ferromagnetic to paramagnetic state. On cooling the sample the domain structurereappeared, but at a lower transformation temperature than on heating. This magnetic phase transformation is highly unusual because it is an "order–disorder" phase transition, which is normally second order, but in this case the "order–disorder" (ferromagnetic to paramagnetic)transition exhibits hysteresis in temperature, indicating that it is first order. Such thermalhysteresis in phase transformation was also observed in thermal expansion experiments. The transformation temperatures obtained in the MFM study are in good agreement with those determined from thermal expansion data.

Keywords
Ames Laboratory, Magnetic phase transitions, Germanium, Phase transition, Magnetic force microscopy, Curie point

Disciplines
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Magnetic force microscopy characterization of a first-order transition: Magnetic-martensitic phase transformation in $Gd_5(Si_xGe_{1-x})_4$

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The magnetic-martensitic phase transformation of $Gd_5(Si_xGe_{1-x})_4$ ($x \approx 0.5$), which occurs close to room temperature, has been observed for the first time using a magnetic force microscope (MFM) equipped with a heating–cooling stage. MFM images obtained from a polycrystalline $Gd_5(Si_{2.09}Ge_{1.91})$ sample and single crystal $Gd_5(Si_{1.95}Ge_{2.05})$ and $Gd_5(Si_2Ge_2)$ samples showed transition to a domain structure at low temperatures indicative of a ferromagnetic phase. Some samples exhibited complex domain structures, suggesting that $Gd_5(Si_xGe_{1-x})_4$ ($x \approx 0.5$) has a strong magnetic anisotropy. As the sample temperature increased the domain structure diminished, reflecting the transformation from ferromagnetic to paramagnetic state. On cooling the sample the domain structure reappeared, but at a lower transformation temperature than on heating. This magnetic phase transformation is highly unusual because it is an ''order–disorder'' phase transition, which is normally second order, but in this case the ''order–disorder'' (ferromagnetic to paramagnetic) transition exhibits hysteresis in temperature, indicating that it is first order. Such thermal hysteresis in phase transformation was also observed in thermal expansion experiments. The transformation temperatures obtained in the MFM study are in good agreement with those determined from thermal expansion data. © *2002 American Institute of Physics.*
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I. INTRODUCTION

$Gd_5(Si_xGe_{1-x})_4$ has recently garnered much interest due to its extraordinary response in several magnetic and electronic properties during changes in temperature and magnetic field. These include colossal magnetostriction, giant magnetoresistance, and a giant magnetocaloric effect.[1] $Gd_5(Si_xGe_{1-x})_4$ undergoes a magnetic-crystallographic transformation when $x \approx 0.5$ at a Curie temperature (typically below 270 K) which is dependent on the Si to Ge ratio. During the transformation the compound exhibits changes in strain as high as $\sim 10^4$ parts per million, magnetoresistance of about 25%, and the largest magnetocaloric effect to date.[1] The phase transition is a magnetic-martensitic transformation from a paramagnetic–monoclinic crystal structure at higher temperatures to a ferromagnetic–orthorhombic crystal structure at lower temperatures, which involves shear of subnanometer atomic layers in a highly complex crystal lattice through reversible breaking and reforming of covalent Si(Ge)–Si(Ge) bonds between the layers.[1]

In this work the phase transitions in $Gd_5(Si_xGe_{1-x})_4$ ($x \approx 0.5$) have been imaged for the first time using a magnetic force microscope (MFM) equipped with a sample heating–cooling stage. The results obtained in the MFM study revealed that $Gd_5(Si_xGe_{1-x})_4$ ($x \approx 0.5$) in the ferromagnetic phase has a strong magnetic anisotropy, and that the phase transition exhibits hysteresis in temperature which is unusual for an order–disorder phase transition. For comparison the thermal expansion of the samples was measured and the results confirmed the thermal hysteresis in the phase transition. The transition temperatures measured in the MFM studies and thermal expansion experiments were found to be in good agreement.

II. EXPERIMENTAL DETAILS

One polycrystalline and two single crystal samples of $Gd_5(Si_xGe_{1-x})_4$ ($x \approx 0.5$) were fabricated from high purity elements. Their compositions are shown in Table I. The polycrystalline sample was prepared by arc-melting and the single crystal samples were grown by the Bridgman method. For the single crystal samples the *b* axis was in the sample plane for the $Gd_5(Si_{1.95}Ge_{2.05})$ sample but was perpendicular to the sample plane for the $Gd_5(Si_2Ge_2)$ sample. *In situ* MFM study of phase transformation was carried out using an atomic force microscope–magnetic force microscope equipped with a sample heating–cooling stage. The sample stage consists of a thermoelectric unit capable of varying the stage temperature from about 243 to 323 K. The sample was mounted on the stage using thermal tape to assure good thermal contact and the sample temperature was monitored using a thermocouple attached to the stage. The sample chamber was under positive pressure of argon to prevent condensation on the sample surface. During the experiments a sample was

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TABLE I. Transition temperatures (Kelvin). Transition temperatures and thermal hysteresis in phase transformation determined from the MFM studies and thermal expansion measurements for the polycrystalline and single crystal samples (measurement error is to 0.1 K).

Sample		On heating		On cooling		
		MFM	Thermal expansion measurements	MFM	Thermal expansion measurements	Average thermal hysteresis (K)
$Gd_5(Si_{1.95}Ge_{2.05})$	Single crystal	265.0	⋯	262.9	⋯	2.1
$Gd_5(Si_2Ge_2)$	Single crystal	270.1	269.1	267.4	267.5	2.2
$Gd_5(Si_{2.09}Ge_{1.91})$	Polycrystalline	285	288	280	281	6

cooled and heated through the transition temperatures. MFM images were taken at various temperatures which were held constant when taking the images. Phase transition temperatures were measured by scanning the sample surface continuously while slowly heating or cooling the sample and recording the sample temperature at which the magnetic image switched from a high to a low contrast or vice versa. This allowed the transition temperatures to be measured with a precision down to the accuracy of the thermocouple (0.1 K).

Thermal expansion measurements were made to study the phase transformations and to determine the transformation temperatures for comparison with the MFM results. The strains of the samples were measured using strain gages when the samples were cooled down and then heated up through a thermal cycle (between 200 to 300 K) in a closed-cycle helium refrigeration system.

III. EXPERIMENTAL RESULTS

The MFM images obtained from the polycrystalline $Gd_5(Si_{2.09}Ge_{1.91})$ sample provide conclusive evidence of thermal hysteresis in the phase transition. As shown in Fig. 1 a heavily branched domain structure was observed at low temperatures at which the sample was ferromagnetic. As the temperature increased the domains diminished and eventually the domain structure vanished at 285 K, indicating a transformation of the sample into a paramagnetic phase. The domain structure re-appeared on cooling but at a lower transformation temperature of 280 K. Consistent transformation temperatures were measured from the thermal expansion data (Fig. 2) which also indicate thermal hysteresis occurring during the phase transformation.

MFM images of the $Gd_5(Si_{1.95}Ge_{2.05})$ and $Gd_5(Si_2Ge_2)$ single crystal samples in the paramagnetic and ferromagnetic states are shown in Figs. 3 and 4, respectively. The former shows a stripe domain structure while the latter has an irregular domain structure with a higher contrast. The single crystal samples exhibited much sharper transitions (transitions completed within 0.1 K around the transformation temperatures) than the polycrystalline sample. The single crystal samples also exhibited hysteresis in phase transformation over a temperature range of about 2 K as shown in Table I.

IV. DISCUSSION

As shown in Fig. 4, the domain pattern observed in the $Gd_5(Si_2Ge_2)$ single crystal sample is similar to those observed in highly anisotropic magnetic materials such as NdFeB and cobalt when the easy axis is nearly normal to the surface. In such cases the surface domain structure usually consists of elliptical, closed domains with a certain level of branching depending on the sample thickness.[2] The present MFM result seems to suggest that the $Gd_5(Si_2Ge_2)$ crystal has a strong anisotropy and the easy axis is oriented close to

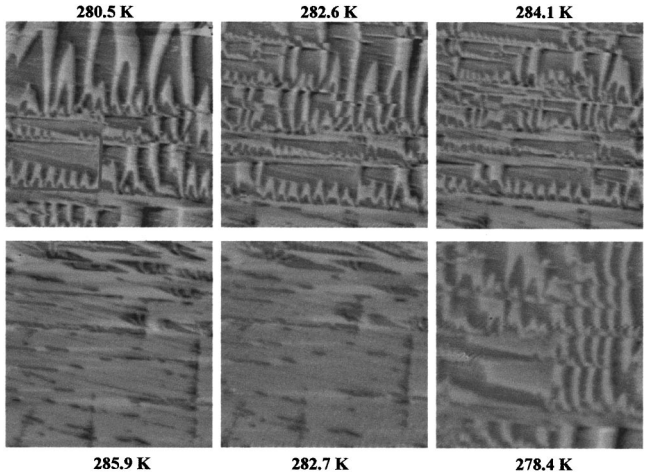

FIG. 1. MFM images showing the phase transition of polycrystalline $Gd_5(Si_{2.09}Ge_{1.91})$ sample (3° phase contrast, 20 μm scans). The straight line highlighted correspond to the crystal boundary.

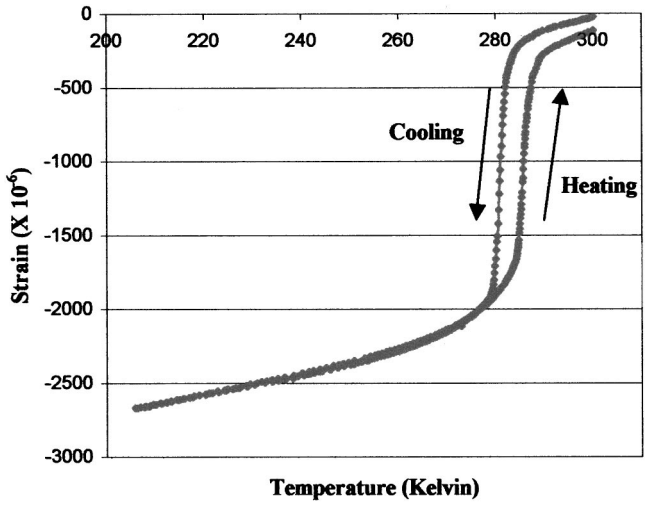

FIG. 2. Plot of the thermal expansion of the polycrystalline $Gd_5(Si_{2.09}Ge_{1.91})$ sample as a function of temperature over a thermal cycle.

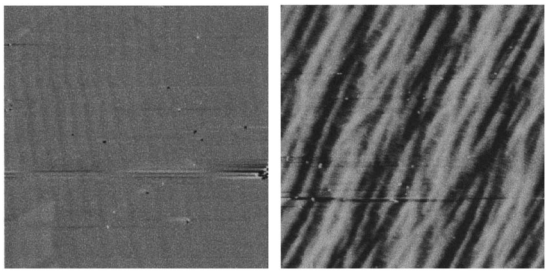

FIG. 3. MFM phase images of the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal sample with the *b* axis in plane in the (a) paramagnetic and (b) ferromagnetic phase (4° contrast, 20 μm scans).

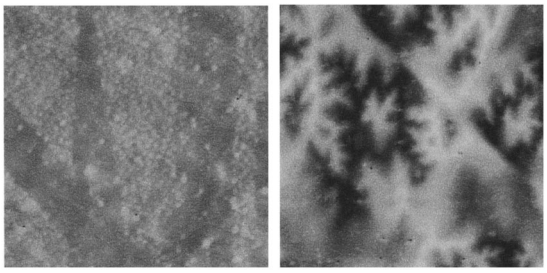

FIG. 4. MFM phase images of the $Gd_5(Si_2Ge_2)$ single crystal sample with *b* axis perpendicular to plane in the (a) paramagnetic and (b) ferromagnetic phase (5° contrast, 20 μm scans).

the *b* axis. No other direct measurement of the magnetic anisotropy of $Gd_5(Si_xGe_{1-x})_4$ has been reported in the literature yet.

One interpretation of the stripe domain structure observed in the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal sample (Fig. 3) is that the adjacent stripes have an aligned in-plane magnetization component and out-of-plane magnetization components that alternate in sign. The latter could be lying along either the *a* or *c* axis. The *a* axis, along which the strain shows the largest change during the phase transition, is inclined at an angle to the surface normal. This is confirmed by $\sim$30 μm amplitude modulations of the sample surface which were measured by monitoring the *z* position of the MFM probe when the sample was undergoing phase transformations. It can be deduced from the domain patterns observed in the single crystal samples that the easy axis of magnetization appears to be aligned close to the *b* axis and is inclined to the *a* and *c* axes. The domains in the bulk therefore have a strong magnetization component along the *b* axis and a component in the $a-c$ plane. Such domain structure is consistent with the highly branched domain pattern in the $Gd_5(Si_2Ge_2)$ single crystal sample which form to minimize magnetostatic energy of the stray field emanating from the sample surface, and the stripe domains observed in the $Gd_5(Si_{1.95}Ge_{2.05})$ sample.

The peculiar patterns observed in the high purity polycrystalline samples could also be interpreted in terms of the presence of a strong magnetic anisotropy. When the easy direction is inclined at an acute angle to surface normal the domains in the bulk have a magnetization component normal to the surface. Branched domains therefore form in the near surface layer to minimize the stray field energy. As the temperature was lowered the branched domain pattern coarsened. This is in contrast to the domain patterns observed in the single crystal samples which remained unchanged. This could be related to the results obtained in the MFM and thermal expansion studies on transition width in temperature, which indicate sharper order–disorder transitions in the single crystal samples than in the polycrystalline sample. The growth of the domain pattern in the polycrystalline sample could be caused by an increase in magnetic ordering as the temperature is lowered.

The observations made in the present MFM studies have confirmed that the phase transition in $Gd_5(Si_xGe_{1-x})_4$ where $x \approx 0.5$ shows a thermal hysteresis, which is expected of all first-order phase transitions. The thermal expansion measurements also show this thermal hysteresis in close agreement with the MFM results. Ordinarily a magnetic order–disorder phase transition would be expected to be second order, but this is no ordinary transition. The transition is a first order magnetic-martensitic phase transition which is order–disorder (ferromagnetic to paramagnetic) in magnetism, and at the same time order–order in crystal structure (orthorhombic–monoclinic), involving a larger shear in the *a* axis direction.

V. CONCLUSIONS

The magnetic-martensitic phase transition of the extraordinarily responsive $Gd_5(Si_xGe_{1-x})_4$ ($x \approx 0.5$) has been characterized through magnetic imaging using a magnetic force microscope. The results indicate that the samples have a strong magnetic anisotropy in the ferromagnetic phase, and that the order–disorder transition exhibits hysteresis in temperature, a hallmark of such a first-order transition. The transition temperatures and the extent of the hysteresis were confirmed with thermal expansion data within 1 K.

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[2] A. Hubert and R. Schäfer, *Magnetic Domains: The Analysis of Magnetic Microstructures* (Springer, Berlin, 2000).