Journal of Magnetics 8(1), 1-6 (2003)

Extraordinary Magnetomechanical Coupling as a Result of a Combined Magnetic Structural Transition in a New Class of Rare Earth Compound

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(Received 10 December 2002)

The new class of $Gd_5(Si_xGe_{1-x})_4$ compounds undergoes a simultaneous magnetic/structural phase transition giving a high level of strain that can be induced either by change in temperature or by application of a magnetic field. Profound changes of structural, magnetic, and electronic changes occur in the $Gd_5(Si_xGe_{1-x})_4$ system lead to extreme behavior of the material such as the giant magnetocaloric effect, colossal magnetostriction, and giant magnetoresistance. These unique material characters can be utilized for various applications including magnetic solid refrigerants, sensors, and actuators.

Key words : Thermal expansion, Magnetocaloric effect, Magnetic refrigeration, Magnetostriction, MFM

1. Introduction

Research on the electronic, magnetic, thermal, optical, and mechanical properties of a series of intermetallic compounds, $Gd_5(Si_xGe_{1-x})_4$, has recently increased due to their unique physical properties such as: the existence of a magnetic-martensitic first-order phase transformation, the highest known room temperature magnetocaloric effect (MCE), colossal magnetostriction (~10,000 ppm), and giant magnetoresistance (~25%). The crystal structures of the $Gd_5(Si_xGe_{1-x})_4$ compounds contain 36 atoms per unit cell [1]. When the composition range is $0.24 \leq x \leq 0.5$, the crystal structures become monoclinic (space group $P112_1/a$) at higher temperatures and these compounds undergo a first order magnetic transition from a high-temperature paramagnetic/monoclinic to a low-temperature ferromagnetic/orthorhombic state [2]. In this composition range, the giant MCE is related to the first order magnetic transition. $Gd_5(Si_{\sim 2}Ge_{\sim 2})$ undergoes a magnetic-crystallographic transformation at ~280 K depending on the exact chemical composition. During transformation, a shear displacement of atomic layers of up to 1.0 Å occurs. The actual transition temperature depends on composition and the magnitude of an applied magnetic field.

The magnetic entropy change, ΔS_{mag} of $Gd_5(Si_xGe_{1-x})_4$ compounds near room temperature has been found to be two times larger than that of Gd [3]. There are a couple of advantages of this new class of compounds as magnetic refrigerant materials. The first is the fact that Curie temperature of the compounds can be varied between ~20 and ~286 K by changing the Si and Ge ratio in $Gd_5(Si_xGe_{1-x})_4$ compounds [4]. The second is the fact that the giant magnetocaloric effect in $Gd_5(Si_xGe_{1-x})_4$ compounds can be reversible, *i.e.* MCE does not disappear after the first application of the magnetic field. This material therefore holds promise for the development of magnetic refrigeration which is described in section 2.

The linear thermal expansion along the axis of single-crystal $Gd_5(Si_{1.95}Ge_{2.05})$, which was measured for the first time is described in section 3. The results showed that the sudden change in strain is due to simultaneous magnetic and martensitic phase transformations. Both temperature and magnetic field influence the phase transformation. The sudden change in strain occurs at different temperatures depending on whether the temperature is being increased or decreased. This hysteresis in temperature is characteristic of a first-order phase transformation. Furthermore both of these observations are unusual for a magnetic order/disorder transition. The temperature of the transition can be increased by the presence of a magnetic field.

As a characterization tool for a series of $Gd_5(Si_xGe_{1-x})_4$ compounds, we employed magnetic force microscope

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(MFM). MFM employs a sharp magnetic tip (typical tip radius is about 20 to 40 nm) attached to a flexible cantilever to sense the magnetic interaction between the tip and a sample. MFM provides a powerful tool that is complementary to the bulk properties measurements techniques (e.g. ac magnetic susceptibility measurements) for characterization the phase transition in $Gd_5(Si_xGe_{1-x})_4$. The results for this experiment is described in section 4.

2. Magnetocaloric effect and magnetic refrigeration

The magnetocaloric effect (MCE) is the phenomenon whereby adiabatic temperature changes can be generated in magnetic materials under the action of a magnetic field. The heat capacity of a magnetic material has three components: C_{el} (electronic), [5] C_l (lattice) and C_{mag} (magnetic) [6]. Similarly the entropy has three components S_{el}, S_l and S_{mag}. In the magnetocaloric effect only the magnetic component of the entropy is of interest. When magnetic materials are subjected to an increase in magnetic field under adiabatic conditions this leads to a decrease of the magnetic or spin entropy. In an adiabatic process this leads to the enhancement of lattice entropy S_l, thus raising the temperature of the material. From consideration of energy balance, the heat energy transfer under adiabatic conditions $C_{mag}\Delta T$ can be equated with the energy change under isothermal conditions due to a change in entropy $T\Delta S_{mag}$

$$C_{mag}\Delta T = T\Delta S_{mag} \tag{1}$$

Therefore the adiabatic temperature change ΔT is directly proportional to the field-induced change in magnetic entropy under isothermal conditions. Consequently a material with large ΔS_{mag} is needed. Furthermore the majority of the magnetic entropy change in a magnetic material occurs within 20~50 K of its Curie temperature.

The magnetic entropy change, ΔS_{mag}, can be obtained from heat transfer during magnetic phase transition. The amount of heat transferred depends on the conditions under which the process takes place, but can be written as either

$$\Delta Q = \int_{T_1}^{T_2} C dT = \int_{S_1}^{S_2} T dS_{mag}. \tag{2}$$

For small changes in entropy under a magnetic field, one can use the Maxwell relation

$$\left(\frac{\partial S}{\partial B}\right) = \left(\frac{\partial M}{\partial T}\right)_B \tag{3}$$

and therefore

$$\Delta S_{mag} = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB. \tag{4}$$

The magnetocaloric effect can be determined from magnetization or heat capacity measurements. Usually the maximum MCE occurs for ferromagnetic materials at their Curie temperatures T_C because the spin entropy change is maximum at T_C. The search for magnetic materials showing large MCE has increased because in addition to their intrinsic interest they can be used as solid magnetic refrigerant materials for magnetic refrigerators (MRs). Conventional refrigerators still use ozone-depleting volatile liquid refrigerants. MR uses a solid refrigerant and no hazardous liquid or gaseous materials for heat transfer. It uses fluids such as water, or water-alcohol solution. The basic thermodynamics energy transfer equation for a gas in a conventional refrigerator can be described by $dW = -PdV$ while the energy transfer equation for a magnetic refrigerant material in a magnetic field, H, is given by $dW = HdM$. Magnetic refrigeration offers better Carnot efficiency (60% at 5 Tesla) than vapor-cycling refrigerator (< 30%) which employs a compressor to generate pressure [7].

Therefore, a MR can be used to replace the standard gas-compression refrigerator because it offers an energy-efficient and environmentally clean operation. A magnetic material having both a large magnetic moment per atom, m, and relatively high Curie temperature, T_c, such as Gd ($m = 7.9\ \mu_B$, $T_c = 293$ K) exhibits a magnetocaloric effect that is large enough for practical applications in magnetic refrigeration systems.

3. Thermal expansion and magnetostriction

The thermal expansion measurements were conducted using the strain-gauge method in a Janis Research 2-stage closed cycle helium refrigeration system with temperature range 10~325 K. Data were collected at temperature intervals of 1 K or strain intervals of 4 ppm for the $Gd_5(Si_{1.95}Ge_{2.05})$ single crystal (5 mm × 4 mm × 1 mm) grown by the Bridgman method. The dc magnetic field was produced by a standard electro-magnet with field range of 2.5 T. Thermal expansion measurements were carried out initially without applying a magnetic field. Then, a series of thermal expansion measurements were made for different constant applied magnetic field strengths along the axis. The magnetic field was maintained constant throughout the measurement cycle. The values of the field strength used were: 0, 1.0, 1.5, 2.0, and 2.5 T. The location of the steepest point of the strain versus

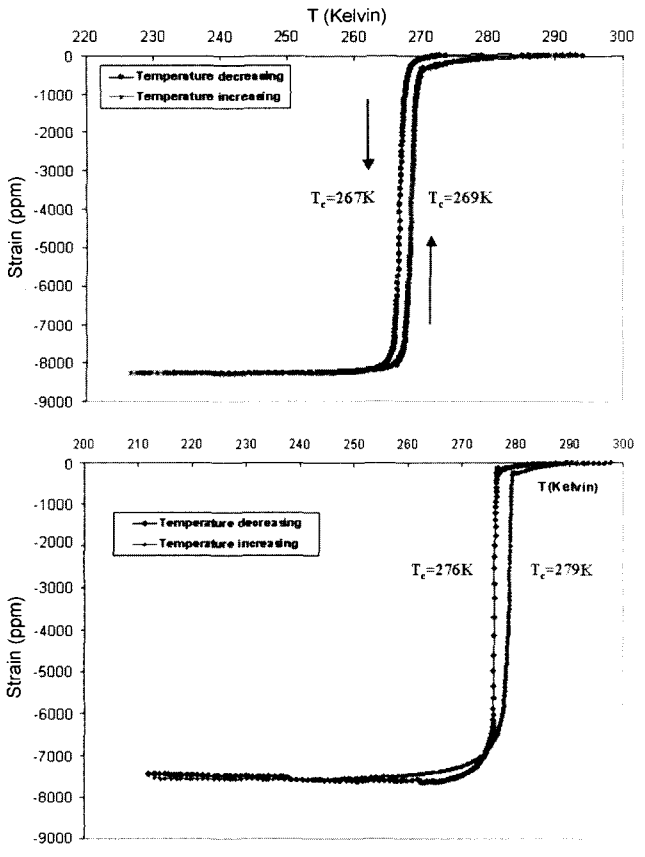


Fig. 1. (a) Thermal expansion of $Gd_5(Si_{1.95}Ge_{2.05})$ along the a-axis under zero applied field. T_c is 267 K on cooling and 269 K on heating. (b) Thermal expansion of $Gd_5(Si_{1.95}Ge_{2.05})$ along the a-axis under an applied field of 2 T.

temperature curve was taken to be the transition temperature.

Fig. 1(a) shows the linear thermal expansion measured along the axis in zero applied magnetic field. The strain λ ($\lambda = \Delta\lambda/l_o$, where l_o denotes the original length) showed an abrupt change during the cooling and heating processes due to the phase transformation. On cooling, there are two transformations that happen simultaneously at 267 K. One is the crystalline structural transition: monoclinic to orthorhombic. The other is the magnetic transition: paramagnetic to ferromagnetic. An ordinary magnetic transition between the paramagnetic and ferromagnetic states is a second order transition which is not accompanied by a simultaneous crystallographic transformation.

In this material, it was found that on heating the transition occurs at a higher temperature of 269 K. The temperature hysteresis is therefore 2 K. One of the features of a first-order phase transformation is the hysteresis in the transition temperature which is due to the latent heat at the transition temperature for a first-order transition. The dc electrical resistivity, dc magnetization, and heat capacity measurements for the same composition also show a thermal hysteresis on cooling and heating [8]. Therefore, the thermal expansion data confirm that the transformation in this material is an unusual simultaneous first-order magnetic/structural phase transformation that is magnetically an orderdisorder transition, but structurally an orderorder transition.

In these materials, the structural or crystalline phase transition can be caused either by change in temperature or change in magnetic field. Therefore, the structural transition can be induced by the presence of a magnetic field at temperatures above the normal transition temperature. An example is given in Fig. 1(b), which shows the thermal expansion of $Gd_5(Si_{1.95}Ge_{2.05})$ under an applied field of 2 T. The transition temperatures were found to be 276 K on cooling and 279 K on heating which are higher than the corresponding transition temperatures measured without any applied field. The dependence of the transition temperature of single-crystal $Gd_5(Si_{1.95}Ge_{2.05})$ on the magnetic field along the axis is shown in Fig. 2. On either cooling or heating the transition temperature increases linearly with magnetic field at a rate of 4.9 K/T (the average value of the slopes of the plots in Fig. 2).

The magnetic structure of $Gd_5(Si_{1.95}Ge_{2.05})$ is determined by two competing factors: the exchange interaction between Gd atoms which tends to order the magnetic moments, and the thermal energy which tends to disorder the magnetic moments. When the exchange energy is greater than the thermal energy the material is ferromagnetic. At the transition temperature they are equal. Above the transition temperature the thermal energy is greater and the material is magnetically disordered. Since the magnetic field is applied along one direction, in this case the a-axis, we assume that the magnetic field suppresses the randomizing effect of thermal energy of the

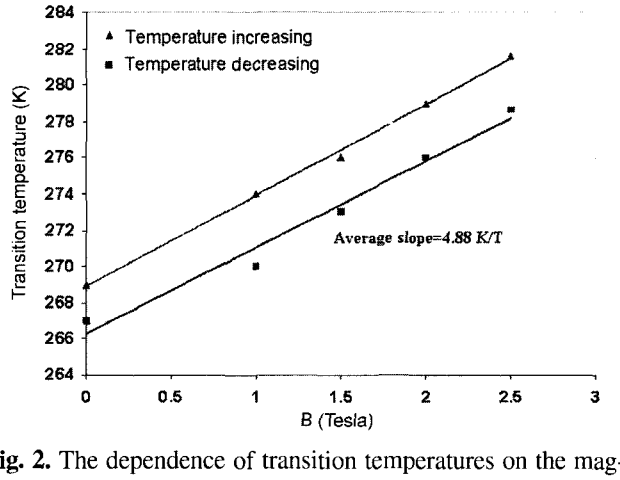


Fig. 2. The dependence of transition temperatures on the magnetic field applied along the a-axis.

Gd atoms. Therefore, in order to disrupt the magnetic order in the presence of a magnetic field, additional thermal energy is required. The result is that the transition temperature is shifted toward a higher temperature when a magnetic field is applied. The extra thermal energy for each atom of Gd required to disorder the magnetic moments is equal to the magnetic energy exerted by the external magnetic field

$$\Delta E=\frac{n}{2}k_B\Delta T \tag{5}$$

$$E_H=m\Delta B \tag{6}$$

where n is the number of degrees of freedom (DOFs), k_B is Boltzmann's constant (1.38×10^{-23} J·K^{-1}), m is the magnetic moment of the Gd atom (7.9 $\mu_B = 7.3\times10^{-23}$ A m^2). Based on this assumption the expected rate of change of transition temperature with field is

$$\frac{\Delta T}{\Delta B}=\frac{2m}{nk_B}\approx\frac{10.6}{n}K\cdot T^{-1} \tag{7}$$

The measured rate of change of transition temperature with field $(\Delta T/\Delta B)_{meas}$ is 4.9 K/T.

According to equation (7) $n=2$ would give the expected rate of change of transition temperature with field to be 5.3 K/T, which is very close to the measured value of 4.9 K/T. This suggests that the thermal energy required to overcome the effect of the applied field is equivalent to a system with only two DOFs.

4. Characterization of phase transformation using MFM

The magnetic-martensitic phase transformation of $Gd_5(Si_xGe_{1-x})_4$ ($x\approx0.5$), 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 [9, 10]. A polycrystalline $Gd_5(Si_xGe_{1-x})_4$ ($x\approx0.5$) sample was prepared by arc-melting from high purity elements. Single crystal $Gd_5(Si_xGe_{1-x})_4$ ($x\approx0.5$) samples were grown by the Bridgman method. Three single crystals were cut using electric discharge machine (EDM) to have the a-, b- and c- axis oriented normal to the largest sample plane.

Another single crystal sample was cut into a cube for vibrating sample magnetometry measurements to determine the magnetic anisotropy of $Gd_5(Si_xGe_{1-x})_4$ in the ferromagnetic state. In this work *in situ* MFM study of phase transformation was carried out using an atomic force microscope/magnetic force microscope (Digital Instrument, Inc, Model: Dimension 3100) equipped with a sample heating-cooling stage. The sample stage consists of a thermoelectric unit capable of varying the stage temperature from about 243 K to 323 K. The sample was mounted on the stage using thermal tape to ensure a good thermal contact and the sample temperature was monitored using a thermocouple attached to the stage. The sample stage utilizes an open chamber design that can be readily attached to a commercial MFM without modifying the microscopy. The sample chamber was under positive pressure of cooled argon to prevent condensation on the sample surface.

During the experiments a sample was cooled and heated through the transition temperatures. MFM images were taken at various temperatures which were held constant when taking the images. Commercial magnetic probes with magnetic coating (Digital Instrument, Inc. Model: MESP) were used. 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 (0.2 K) for comparison with those obtained in ac susceptibility and thermal expansion measurements.

The MFM images obtained from the polycrystalline samples provide conclusive evidence of thermal hysteresis in the phase transition of $Gd_5(Si_xGe_{1-x})_4$ ($x\approx0.5$). As shown in Fig. 3, a heavily branched domain structure was observed at low temperatures when the sample was ferromagnetic. As the temperature increased the domains diminished and eventually vanished at 285 K, indicating a transformation of the sample into a paramagnetic phase.

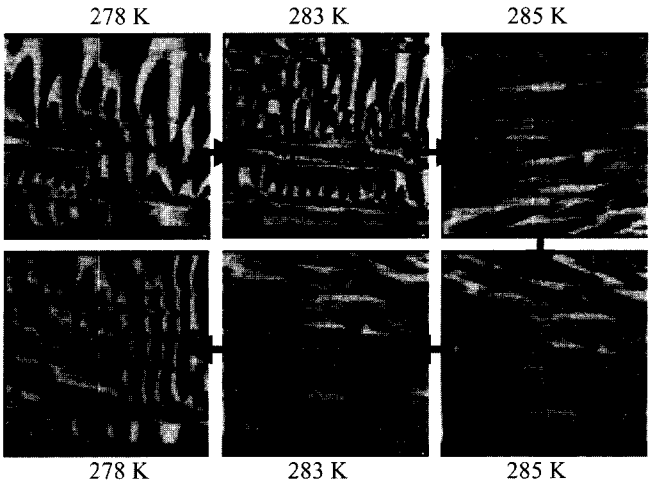
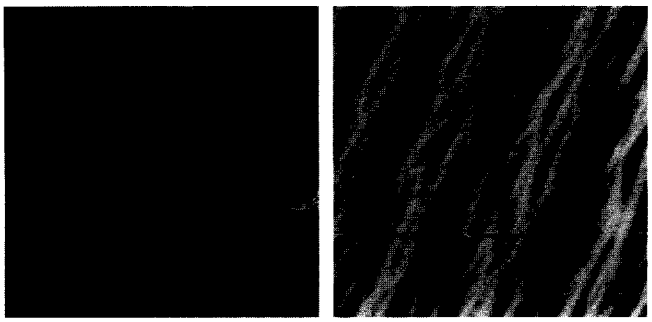
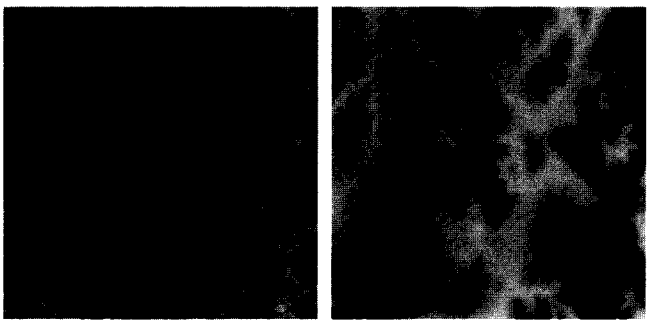


Fig. 3. A series of MFM images (20 μm × 20 μm) showing thermal hysteresis of the phase transition of polycrystalline $Gd_5(Si_xGe_{1-x})_4$ over a thermal cycle.



(a) 294K (b) 258K

Fig. 4. MFM images (20 μm × 20 μm) showing the formation of a stripe domain pattern in the single crystal $Gd_5(Si_xGe_{1-x})_4$ sample with the a-axis perpendicular to the surface when it was transformed from the (a) paramagnetic to (b) ferromagnetic phase.

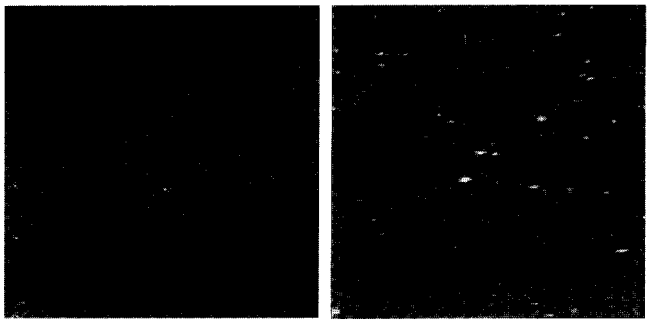


(a) 295k (b) 265K

Fig. 5. MFM images (20 mm × 20 mm) showing the formation of a rosette domain pattern in the single crystal sample with the b-axis perpendicular to the surface when it was transformed from the (a) paramagnetic to (b) ferromagnetic phase.

The domain structure re-appeared on cooling but at a lower transformation temperature of 280 K (image not shown). These transition temperatures were found to be consistent with those measured from the thermal expansion measurements, which also indicate thermal hysteresis in the phase transformation.

The MFM images obtained from the single crystal samples, each with a principal crystallographic axis perpendicular to sample plane, are shown in Figs. 4 to 6. As shown in Fig. 4, a stripe domain pattern was observed in the a-axis image, indicating an out of plane component that alternates from one domain to the next. The "floral" domain patterns in the b-axis image (Fig. 5) are characteristic of images observed in a plane perpendicular to the easy axis of highly anisotropic materials such as cobalt [11]. It has been suggested that formation of the floral pattern could result from domain branching near the surface to minimize magnetostatic energy. In contrast, the c-axis image shows no detectable magnetic contrast



(a) (b)

Fig. 6. MFM images (20 μm × 20 μm) of the single crystal sample with the c-axis perpendicular to the surface showed virtually no change in image contrast when it was transformed from the (a) paramagnetic to (b) ferromagnetic phase.

(Fig. 6).

The measurement results indicate that the b-axis is the magnetic easy axis for $Gd_5(Si_xGe_{1-x})_4$. This conclusion is further supported by the complete lack of magnetic contrast in the c-axis image shown in Fig. 6 and the stripe domain pattern in the a-axis image (Fig. 4), whose width is comparable to the size and spacing of the floral domain patterns in the b-axis image. Such stripe magnetic domain pattern is consistent with a significant (~3°) angular change of the b-axis with respect to the a-c plane from one domain to the next. After an atomic displacement in the a-axis direction, there will be a misalignment of the b-c plane in the sample surface that is sufficient for the component of the b-axis that is out of plane to provide some perpendicular anisotropy. Surface energy is then minimized by a configuration of stripe domains, where magnetization vectors alternate between orientations with components into the plane (down) and those with components out of the plane (up).

Results of the MFM study on the single crystal samples revealed a magnetic anisotropy of $Gd_5(Si_xGe_{1-x})_4$ with the b-axis being the easy axis. In order to determine quantitatively the anisotropy of $Gd_5(Si_2Ge_2)$ vibrating sample magnetometer (VSM) measurements were made on a $Gd_5(Si_2Ge_2)$ single crystal cube with the crystallographic orientataion of the cube face identified using x-ray diffractometry (XRD). During the experiments, the sample temperature was maintained below the Curie point/transition temperature using a dry ice/ethanol mixture. Hysteresis loops were measured using magnetizing field with a maximum amplitude of 600 kA/m applied along the three principal axes of the crystal.

The measured hysteresis loops, shown in Fig. 7, are consistent with those of a sample with uniaxial anisotropy. After corrections were made for demagnetizing effects

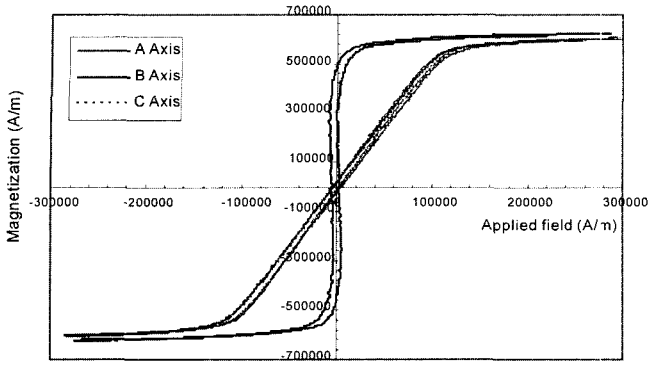


Fig. 7. Magnetization curves of the $Gd_5(Si_xGe_{1-x})_4$ ($x \approx 0.5$) single crystal sample with magnetizing field applied along the a-, b- and c-axes.

along all three directions, the magnetization curve along the b-axis loop showed the highest permeability, while those along the a- and c-axes had identical permeability. The stripes seen in Fig. 3 but not in 6 may be attributed to the lattice rotation rather than a component of spontaneous magnetization along the a-axis.

Anisotropy energy for magnetic moments aligned along each of the principal axes can be calculated from the area between the magnetization curve on the M, H plane, and the magnetization axis. In the case of uniaxial anisotropy this calculation is particularly simple, as the two harder axes show the same anisotropy energy required for domain rotation under the action of a field. The anisotropy coefficient K_0 is simply the area for the easy axis curve, while K_1, the first anisotropy coefficient, is the difference in energy between the easy and hard axis magnetization curves [12].

The anisotropy coefficients K_0 and K_1 were found to be $0.78 \pm 0.03 \times 10^4$ J/m^3 and $4.1 \pm 0.2 \times 10^4$ J/m^3 respectively. These values of anisotropy coefficients are similar to those of iron or a medium anisotropy garnet, and are an order of magnitude smaller than cobalt and an order of magnitude greater than nickel. The anisotropy coefficient measurement results confirm the inferences drawn from the MFM images that the materials have uniaxial anisotropy with the b-axis as the magnetic easy axis.

5. Summary and Conclusions

The linear thermal expansion along the axis of single-crystal $Gd_5(Si_{1.95}Ge_{2.05})$ was measured. An applied field shifts the transformation temperature by about 5 K/T. It appears, therefore, that the magnetic field suppresses the vibration of the Gd atoms so that the magnetic and structural phase transitions are moved to a higher temperature. For characterization of the phase transition in $Gd_5(Si_xGe_{1-x})$ compounds, MFM images were taken. These images offer the unique capability of imaging magnetic domain structure of materials with a high sensitivity and spatial resolution (typically 50 nm or better), and therefore the technique allows detailed examination of the magnetic structure as the material passes through phase transition, such as the homogeneity of occurrence of magnetic phase and the domain pattern that indicates the local magnetic anisotropy in ferromagnetic state. $Gd_5(Si_xGe_{1-x})_4$ compounds are promising materials for solid magnetic refrigerant because the magnetic caloric effect of them is two times larger than that of Gd known as the best MCE material so far at near room temperature.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Materials Science Division under Contract W-7405-ENG-82.

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