Dynamics of the magnetic field-induced first order magnetic-structural phase transformation of Gd5(Si0.5Ge0.5)4

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Dynamics of the magnetic field-induced first order magnetic-structural phase transformation of $Gd_5(Si_{0.5}Ge_{0.5})_4$

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The system $Gd_5(Si_xGe_{1-x})_4$ for $0.4 \leq x \leq 0.5$ has been shown to have an unusual first order, coupled magnetic-structural phase transformation at the Curie temperature. Above the transformation temperature T_c, the material is paramagnetic with a monoclinic structure; below T_c, it is ferromagnetic with an orthorhombic structure. Another unusual feature of this phase transformation is that an applied magnetic field can increase T_c by 5 K per tesla. In this study, the magnetic-structural transformation in single crystal $Gd_5Si_2Ge_2$ was triggered by holding the sample at a temperature just above T_c, then using an applied field to increase T_c beyond the sample temperature, thereby inducing the magnetic-structural transformation. The dynamics of this field-induced phase transformation at various temperatures just above T_c were observed by measuring the magnetization as a function of time. This magnetization change is caused by the first order phase transformation which is distinctly different from the magnetization reversal which one observes in conventional magnetic relaxation experiments. The transformation could be modeled as a thermal activation process with a single energy barrier of height 4.2 ± 0.2 eV. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1687591]

I. INTRODUCTION

$Gd_5(Si_xGe_{1-x})_4$ intermetallic compounds show several highly interesting properties, including giant magnetocaloric effect, colossal magnetostriction, and giant magnetoresistance. These all occur near an unusual first order, coupled magnetic-structural phase transition. In the region $0.4 \leq x \leq 0.5$, the transition temperature T_c varies with composition, as shown in the phase diagram of Fig. 1. Near $x=0.5$, T_c occurs close to room temperature.[1] This first order magnetic-structural transition can also be induced by applied magnetic fields, since applied fields can shift T_c by ≈ 5 K per tesla.[2] For a sample maintained at a temperature just above T_c, applying a magnetic field can cause the sample to transform to the low temperature phase as T_c is increased beyond the prevailing thermodynamic temperature. Since the high temperature monoclinic phase is paramagnetic and the low temperature orthorhombic phase is ferromagnetic, a field-induced structural transformation also occurs and we can investigate the dynamics of the structural phase transition by following the change in magnetization with time after rapidly increasing the applied field, for example by using a step function increase.

II. EXPERIMENTAL METHODS

A single crystal sample of $Gd_5Si_2Ge_2$ was grown by the Bridgman method.[2] It was cut by electrical discharge machining and polished using standard metallographic techniques. A vibrating sample magnetometer, which was equipped with a liquid cooled/resistance heated sample chamber and a temperature controller, was used to measure magnetization as a function of temperature, applied field, and time. The field range was ± 600 kA/m (7.5 kOe) and the temperature range was from 253 K to 373 K. Temperature was held constant to within ± 0.1 K at eight temperatures from 275 K to 277 K. This was achieved by circulating ethanol cooled with solid CO_2 in the annular region surrounding the sample chamber and warming the chamber to the desired temperature by heating with a resistive heater operated by the temperature controller. Temperature was monitored using a K-type thermocouple.

The sample was first allowed to equilibrate at the desired temperature, then the field was rapidly ramped up to 600 kA/m (7.5 kOe) and held for the duration of the measurement. This value was chosen in order to allow a sufficiently large change in T_c. Magnetization was meanwhile recorded as a function of time. For all sample temperatures in the range investigated, the sample was either already partially in the ferromagnetic phase or it became ferromagnetic after application of the applied field. The results were then analyzed by comparing them with an exponential relaxation using Eq. (1) and a value for the relaxation time constant τ was determined at each temperature investigated:
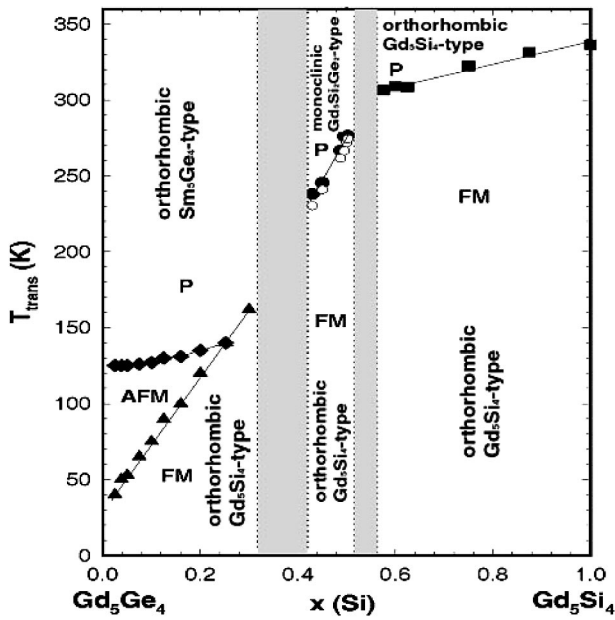
FIG. 1. Phase diagram for the $Gd_5(Si_xGe_{1-x})_4$ system (Ref. 1). P denotes a paramagnetic phase, AFM an antiferromagnetic phase, and FM a ferromagnetic phase.

$$M(t) = M_0 + M_1\left(1 - \exp\left(-\frac{t}{\tau}\right)\right), \qquad (1)$$

where M_0 is the initial magnetization at 600 kA/m and $t = 0$, and $(M_0 + M_1)$ is the asymptotic value of $M(t)$. For a constant applied field, a thermally activated process with a single barrier has a relaxation time τ related to the energy barrier ΔE given by Eq. (2),[3]

$$\tau = \frac{A}{c}\exp\left(\frac{\Delta E}{kT}\right), \qquad (2)$$

where c is an "attempt frequency," and A is a constant. The energy barrier ΔE was then determined numerically from the slope of a plot of $\ln(\tau)$ versus $1/T$.

III. RESULTS AND DISCUSSION

Examples of the data obtained at selected temperatures and solutions calculated from Eq. (1) are shown together in Fig. 2. It can be seen from this that the measured variations of magnetic moment with time follow the form of Eq. (1), which is consistent with a thermal activation process with a single energy barrier with relatively large time constant (~ 100 s). At the lower temperatures investigated, the magnetization curves took as long as 300 s to approach their asymptotic values (see inset). Results were analyzed and compared with the solutions of Eq. (2). The logarithms of the calculated values of τ were then plotted versus T^{-1}, as shown in Fig. 3, and a barrier height of 4.2 eV was obtained.

It should be noted that the two values of the time constant τ measured nearest the zero field transition temperature $T_c = 275.75 \pm 0.1$ K did not lie on the straight line in Fig. 3. A possible reason for this is that at the transition temperature, the two free energy minima representing the two different phases are equal, rather than one being lower in energy

(stable) and the other higher in energy (metastable). In addition, making measurements at a temperature so close to the transition temperature would magnify the effect of any slight compositional inhomogeneity of the sample arising from the single crystal growth process and is therefore a less useful test of the relaxation dynamics for a homogeneous material. Nevertheless, the asymptotic magnetization maxima (the magnetization for $t \gg \tau$, or equivalently the sum $M_0 + M_1$) all follow the same trend which increases steeply with decreasing sample temperature (all are below the T_c when $H_{applied} = 600$ kA/m). This can be easily understood since the further the thermodynamic temperature of the sample is below the new T_c the higher the spontaneous magnetization.[4,5]

We have suggested previously that the magnetic coupling in this material is via itinerant conduction electrons across the (Si,Ge)-(Si,Ge) covalent bonds linking the Gd-containing slabs.[6] Half of these bonds are broken when the temperature is above the magnetic-structural phase transition, and they are reformed when temperature is decreased through the magnetic-structural transition.[1] This breaking and reforming of bonds arises whether the transformation is caused by temperature reduction or by increasing applied
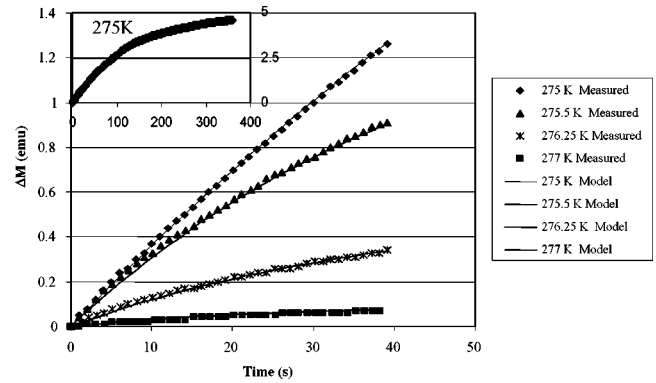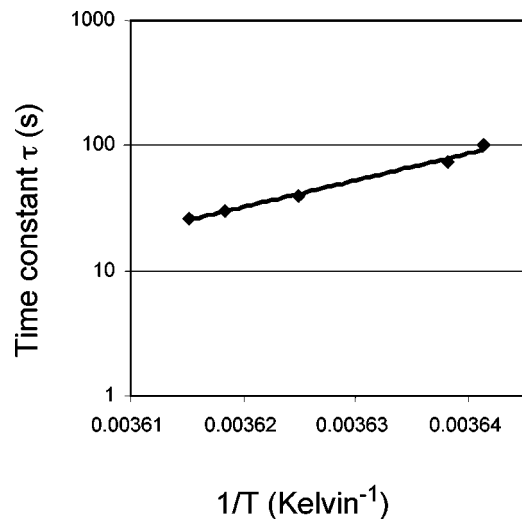

FIG. 2. Measured change in magnetization (symbols) and model calculations (lines) based on solutions to Eq. (1), for four different sample temperatures.

FIG. 3. Logarithm of time constant τ vs $1/T$, confirming the Arrhenius-type thermodynamic relationship with a single energy barrier.

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magnetic field. Thus the energy barrier can be expected to be intimately connected with the magnetic part of the electronic band structure, and the energy barrier to forming the (Si,Ge)-(Si,Ge) bonds.

It is important to remember that this phase transformation which we are investigating by the magnetic relaxation technique is a first order magnetic-structural phase transition. The relative stability of the two phases is determined by the relative heights of the energy minima. However the dynamics is determined by the height of the energy barrier separating them. Thus the 4.2 eV energy barrier height is not to be identified directly as a band structure feature or bond strength that represents the energy difference between the two phases (energy minima). Rather, we seek to identify what must happen to effect the transformation of one (paramagnetic, half-bonded monoclinic structure) to the other (ferromagnetic, fully bonded orthorhombic structure).

The hypothesis that the magnetic relaxation represents the dynamics of the magnetic-structural phase transition (and is not simply magnetic moment reorientation) is also supported by the reversibility in the process. Returning the applied field to zero and then reapplying it reinitializes the entire process, whereas in the case of irreversible moment reorientation one would expect removal and reapplication of the field in the same direction to cause much smaller changes in magnetization. Furthermore it was found that calculation of the critical domain volume for thermal fluctuation aftereffect (i.e., thermally assisted domain reorientation), by the following equation,[3]

$$\tau = \frac{1}{c'} \exp \frac{V(2K_u - M_S H)^2}{4K_u kT}, \tag{3}$$

where K_u is the anisotropy energy, c' an attempt frequency, V is the volume, and k is Boltzmann's constant, yields an unrealistically small domain volume of less than 10^{-36} m^3. Thus the energy barrier observed by magnetic measurements can be better ascribed to the magnetic-structural phase transition, and not to magnetic moment reorientation.

IV. CONCLUSIONS

The dynamics of the magnetic-structural phase transition in Gd$_5$Ge$_2$Si$_2$ have been investigated by magnetic relaxation measurements and the results have been interpreted in terms of a thermal activation model with a single energy barrier. Using this model, the energy barrier has been calculated to be 4.2 ± 0.2 eV. This energy represents not the difference between the two phases (energy minima), but rather the barrier that must be surmounted in order to effect the transformation of one (paramagnetic, half-bonded monoclinic structure) to the other (ferromagnetic, fully bonded orthorhombic structure). This energy barrier is expected to be intimately connected with the magnetic part of the electronic band structure, and the energy barrier to forming the (Si,Ge)-(Si,Ge) bonds. These experimental results show that despite the complexity of the coincident magnetic and structural transition, the transformation dynamics can still be adequately described by a simple thermodynamic model with a single energy barrier.

ACKNOWLEDGMENTS

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