Estimation of second order phase transition temperature of the orthorhombic phase of $Gd_5(Si_xGe_{1-x})_4$ using Arrott plots

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$Gd_5(Si_xGe_{1-x})_4$ for $0.41 \leqslant x \leqslant 0.5$ is orthorhombic and ferromagnetic at lower temperature, monoclinic and paramagnetic at higher temperature, and shows a first order magnetic-structural phase transition between the two. Magnetic moment versus magnetic field (MH) isotherms were measured just above the first order transition temperature for $Gd_5Si_{1.95}Ge_{2.05}$ and $Gd_5Si_2Ge_2$ samples and the field-induced coupled phase transition from paramagnetic/monoclinic to ferromagnetic/orthorhombic phase was observed. Using the method developed by Arrott [Phys. Rev. **108**, 1394 (1957)], the ferromagnetic portions of the MH isotherms were used to project the second order magnetic phase transition temperature of the orthorhombic phase, a region where the transition does not occur due to the first order transition at a lower temperature. These data points fall on the extrapolated line of the second order phase transition, drawn from the Si-rich region of the phase diagram. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2841728]

I. INTRODUCTION

$Gd_5(Si_xGe_{1-x})_4$ exhibits the largest known giant magnetocaloric effect near its coupled first order magnetic-structural phase transition.[1] This effect can be utilized for energy efficient refrigeration. The energy conversion efficiency of these refrigerators can reach as high as 60% of Carnot efficiency, which is much larger than the 30% achieved in conventional liquid/vapor refrigeration. An adiabatic temperature change of 17 °C can be obtained in magnetic fields of 5 T.[1] This first order magnetic-structural phase transition also involves a colossal magnetostriction of the order of 10 000 ppm (Ref. 2) and a giant magnetoresistance change ($\Delta R/R$) of about 25%.[2]

The $Gd_5(Si_xGe_{1-x})_4$ phase diagram can be divided into three regions with three different types of magnetic and structural behavior. The transition temperature of $Gd_5(Si_xGe_{1-x})_4$ increases with increasing Si content.[3] In the silicon-rich region ($0.575 \leqslant x \leqslant 1.0$) the transition from ferromagnetic phase to paramagnetic-magnetic phase is a second order magnetic phase transition with no associated structural transition. In the germanium-rich region ($0 \leqslant x \leqslant 0.31$) the transition is a first order magnetic-structural transition from Gd_5Si_4-type orthorhombic ferromagnetic to Sm_5Ge_4-type orthorhombic paramagnetic.[4] In the middle region ($0.41 \leqslant x \leqslant 0.503$) there is a first order structural phase transition from orthorhombic ferromagnetic to monoclinic paramagnetic.

This transition represents the first order magnetic/structural phase transition from ferromagnetic/orthorhombic phase to paramagnetic/monoclinic phase. If the first order structural phase transition from orthorhombic to monoclinic could be suppressed, then the orthorhombic phase would show a second order phase transition from ferromagnetic to paramagnetic phase at a higher temperature, which would be the Curie temperature of the orthorhombic phase. It is not possible, however, to directly measure this second order phase transition temperature since the first order structural phase transition occurs at a lower temperature, thereby obscuring the second order transition. In this paper we determine the projected second order phase transition temperature of the orthorhombic phase (i.e., the temperature at which it would transform from ferromagnetic to paramagnetic if there were no change in structure).

II. EXPERIMENTAL PROCEDURE

Two $Gd_5(Si_xGe_{1-x})_4$ samples with $x=0.4875$ and $x=0.5$ were prepared using 99.996% pure (weight basis) gadolinium, 99.9999% pure silicon, and 99.999% pure germanium. A polycrystalline $Gd_5Si_{1.95}Ge_{2.05}$ sample was prepared by arc melting, and a single crystal $Gd_5Si_2Ge_2$ sample was prepared by the Bridgman method at Ames Laboratory, IA. The samples were annealed at 2000 °C for 1 h and withdrawn from the furnace at 4 mm/h.

Magnetic moment versus temperature was measured for the $Gd_5Si_{1.95}Ge_{2.05}$ and $Gd_5Si_2Ge_2$ samples using a superconducting quantum interference device magnetometer with an applied field of 100 Oe (7.96 kA/m) (see Fig. 1 for $Gd_5Si_{1.95}Ge_{2.05}$, for example). The transition temperatures were determined from the inflection point of the plot and were found to be 263 K for $Gd_5Si_{1.95}Ge_{2.05}$ and 269 K for $Gd_5Si_2Ge_2$. Magnetic moments versus magnetic field isotherms were measured for various temperatures from 265 to 291 K for both samples. As an example, Fig. 2 shows the results for $Gd_5Si_{1.95}Ge_{2.05}$. Since applied magnetic field shifts the first order transformation temperature the field-induced transition from monoclinic/paramagnetic to orthorhombic/ferromagnetic phase occurred at different applied fields for different temperatures. The field required to induce this transition is larger for higher temperature. Isotherms above 289 K did not show any field-induced transition because the field required to induce any transition would

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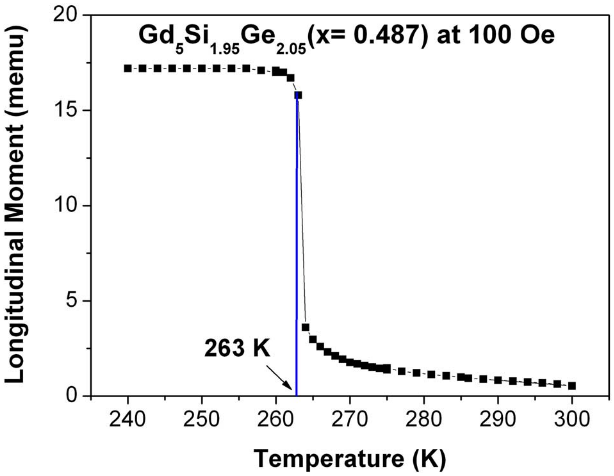

FIG. 1. (Color online) Dependence of magnetic moment on temperature under a field of 100 Oe (7.96 kA/m) for $Gd_5Si_{1.95}Ge_{2.05}$. The first order transition temperature is shown.

be more than 50 kOe (3.98 MA/m) which was above the field range of the superconducting magnet used. We expect that the first order field-induced transition will not occur above the second order phase transition temperature of the orthorhombic phase. Any amount of field applied above this temperature should not be able to induce the first order transition to orthorhombic phase as the orthorhombic phase should be paramagnetic above this temperature.

III. RESULTS AND DISCUSSION

In order to determine the second order phase transition temperature of the orthorhombic phase we use the Arrott plot technique.[5] This technique is based on a Weiss–Brillouin treatment of molecular field theory,[5,6] and it connects magnetization and magnetic field with the Curie temperature through the equation proposed by Arrott:

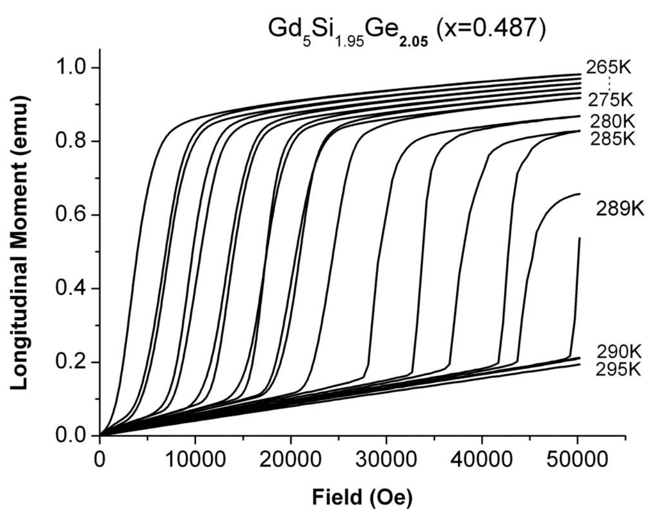

FIG. 2. Dependence of magnetic moment on magnetic field at different temperatures for $Gd_5Si_{1.95}Ge_{2.05}$.

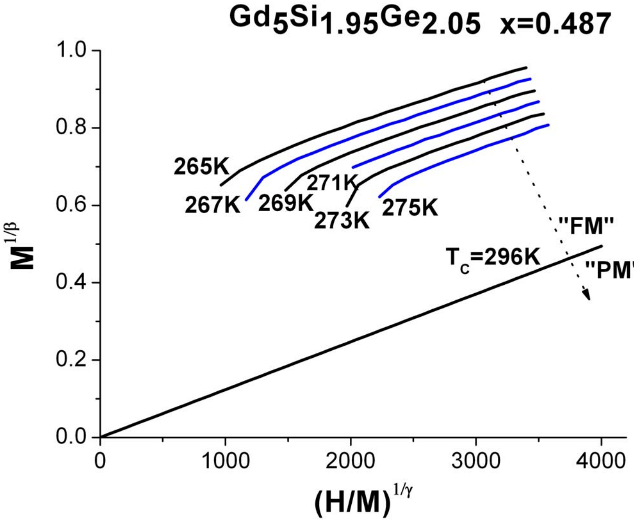

FIG. 3. (Color online) Arrott plot for $Gd_5Si_{1.95}Ge_{2.05}$. Ferromagnetic sections of the *MH* curves of Fig. 2 were used to construct the parallel isotherms. The line passing through the origin (which represents the transition temperature) was extrapolated from the known isotherms. The second order transition temperature was estimated to be 296 K.

$$\left(\frac{H}{M}\right)^{1/\gamma} = \frac{T - T_C}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta},$$

where M_1 and T_1 are constants, γ and β are treated as variable parameters to obtain the best fit to the data, and T_C is the Curie temperature (critical temperature) of the second order phase transition. In order for this technique to work, the measurements have to be made near the critical temperature.

For the correct γ and β, a plot of $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$ for each *MH* isotherm is a straight line and the plot for all of the MH isotherms is parallel to each other. For an ordinary ferromagnetic material, i.e., one which exhibits a second order transition from the paramagnetic to the ferromagnetic state, the isotherm that passes through the origin of the Arrott plot corresponds to the transition temperature. In order to use this technique for our samples, only the *ferromagnetic* parts of the *MH* isotherms (i.e., where the sample is in the orthorhombic phase) should be used. For our samples, only the isotherms below 275 K were used to construct the Arrott plots, because for higher temperatures the useful ferromagnetic part of the curves is small due to the limit of the available magnetic field (see Fig. 2).

The Arrott plot for the $Gd_5Si_{1.95}Ge_{2.05}$ sample is shown in Fig. 3. It was found that the selected (ferromagnetic) parts of the isotherms were straight lines and were parallel to each other for $\gamma = 0.9$ and $\beta = 2.2$. It is noticeable that the ends of the straight sections of these isotherms have curvature going down out of the ferromagnetic region. Projecting the parallel isotherms to higher temperatures, we constructed an isotherm which is parallel to them and passes through the origin. The distance of this isotherm from the others was measured and the second order transition temperature of the orthorhombic phase was thus determined to be 296 K for $Gd_5Si_{1.95}Ge_{2.05}$. The same procedure was applied to the $Gd_5Si_2Ge_2$ sample and determined the second order transition temperature to be 301 K.

When the calculated second order phase transition tem-

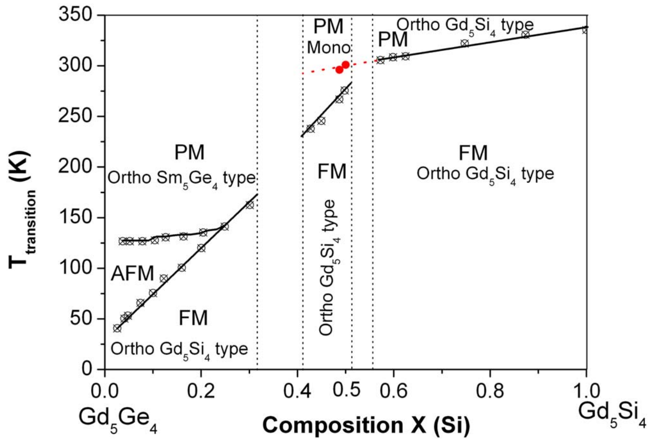

FIG. 4. (Color online) Phase diagram of $Gd_5(Si_xGe_{1-x})_4$, (Ref. 4), plotted together with the second order phase transition temperatures of the orthorhombic phase of $Gd_5Si_{1.95}Ge_{2.05}$ ($x=0.487$) and $Gd_5Si_2Ge_2$ ($x=0.5$), and the projected line of the orthorhombic second order transition.

peratures of $Gd_5Si_{1.95}Ge_{2.05}$ and $Gd_5Si_2Ge_2$ are plotted on the phase diagram as shown in Fig. 4, they appear to lie on the projected line of the Gd_5Si_4-type orthorhombic phase second order magnetic transition, extended from the Si-rich region of the phase diagram. This suggests that the Arrott plot technique may be used to calculate and project the occurrence of a second order magnetic phase transition temperature in a material even if it is suppressed by a first order phase transition so that the second order transition never actually occurs in practice.

IV. CONCLUSION

The Arrott plot method that is normally used to determine the Curie temperature of materials which exhibit a second order phase transition has been applied to a material in which the second order phase transition is suppressed by a first order magnetic-structural phase transformation. It has been shown from this that the projected second order phase transition can be determined even though it does not actually occur in practice. In the case of $Gd_5Si_{1.95}Ge_{2.05}$ it should occur at 296 K and in the case of $Gd_5Si_2Ge_2$ this should occur at 301 K. This method of estimating the projected second order phase transition temperature could be applied to other complex magnetocaloric materials such as $(Dy_xEr_{1-x})Al_2$, $Mn(As_{1-x}P_x)$, and $Ni_2(Mn_{1-x}V_x)Sn$ in which a first order phase transition suppresses the occurrence of second order phase transition.[7]

ACKNOWLEDGMENTS

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