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Determination of Curie temperature by Arrott plot technique in $Gd_5(Si_xGe_{1-x})_4$ for $x > 0.575$

R.L. Hadimani*, Y. Melikhov, J.E. Snyder, D.C. Jiles

Wolfson Centre for Magnetics, Cardiff University, Cardiff CF24 3AA, UK

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Abstract

Determination of Curie temperature by plotting magnetic moment vs. temperature curves requires a small applied field, which influences the measurement and temporarily disturbs the temperature of the sample especially for highly magnetocaloric materials. The Arrott plot technique was therefore used in order to determine the Curie temperature for a magnetocaloric $Gd_5Si_{2.7}Ge_{1.3}$ ($x = 0.675$) single crystal sample. This technique was compared with other methods such as the inflection point technique and the line projection method. The results show how applied magnetic field influences the determination of Curie temperature. Using the Arrott plot the second-order transition Curie temperature for $Gd_5Si_{2.7}Ge_{1.3}$ was determined to be 304 K.

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Keywords: Magnatocaloric effect; Curie temperature; Arrott plot

1. Introduction

The giant magnetocaloric effect exhibited by $Gd_5(Si_xGe_{1-x})_4$ near its transition temperature is due to a structural phase change coupled with the magnetic phase change. This has attracted much attention recently due to its potential application in magnetic refrigeration. The material is known to exhibit the largest observed giant magnetocaloric effect near its first-order magnetic–structural phase transition [1]. The energy conversion efficiency of magnetic refrigeration can reach as high as 60% of Carnot efficiency, which is much larger than the 30% achieved in conventional liquid/vapor cycle refrigeration. An adiabatic temperature change of 17° can be obtained in magnetic field changes of 5 T [1]. This first-order magnetic–structural phase transition is also accompanied by a colossal magnetostriction up to 10,000 ppm [2] and a giant magnetoresistance change ($\Delta R/R$) of about 25%.

The $Gd_5(Si_xGe_{1-x})_4$ phase diagram can be divided into three basic regions with three different types of magnetic and structural behavior. In the silicon-rich region the transition from Gd_5Si_4 type orthorhombic ferromagnetic phase to Gd_5Si_4 type orthorhombic paramagnetic phase is a second order magnetic phase transition. The Curie temperature of $Gd_5(Si_xGe_{1-x})_4$ increases with increasing Si content [3].

In order to study the transition temperature of $Gd_5(Si_xGe_{1-x})_4$ more accurately variety of methods described in the literature were analyzed. Methods such as the inflection point method and the line projection method give different Curie temperatures at different applied fields. It is also difficult to maintain temperature equilibrium between the inside of the sample and the temperature sensor due to magnetocaloric effects.

In this paper the Arrott plot technique [4] has been used to determine the Curie temperature of $Gd_5Si_{2.7}Ge_1$ ($Gd_5(Si_xGe_{1-x})_4$ $x = 0.675$)). This gave a value that does not vary according to the field applied.

2. Experimental details and results

The $Gd_5Si_{2.7}Ge_{1.3}$ single crystal sample ($2 \times 2 \times 2\,mm^3$) was prepared by the Bridgman method using 99.996% pure (weight basis) gadolinium, 99.9999% pure silicon and

*Corresponding author. Tel.: +44 292 087 0422; fax: +44 292 087 9538.
E-mail address: HadimaniM@Cardiff.ac.uk (R.L. Hadimani).

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99.999% pure germanium at Ames Laboratory USA. It was then annealed at 2000 °C for 1 h and withdrawn from the furnace at 4 mm/h. The cubic sample was cut by electrical discharge machining (EDM) and standard metallographic techniques were used for polishing the faces of the cube.

Magnetic moment vs. temperature curves were measured using a SQUID magnetometer with an applied magnetic field of $H = 8 \times 10^3$ A/m ($B = 0.01$ T) in the range of 250–350 K as shown in Fig. 1. The direction of the field and the axis alignment of the sample were not taken into consideration in this measurement as the second-order transition will not have any preferred direction. It can be seen from Fig. 1 that there is a transition from ferromagnetic to paramagnetic phase. Using the inflection point method Curie temperature for this measurement was estimated to be 307 K. Curie temperature for the same measurement when estimated using the line projection method was found to be 313 K.

If we try to identify Curie temperature from the measurements made under higher magnetic field for example at $H = 0.8$, 1.6 and 2.4×10^6 A/m ($B = 1$ T, 2 T or 3 T) in Fig. 2, it becomes more difficult to precisely determine the inflection point of the curves. Also, the line projection method completely fails at higher magnetic fields as the gradient of the M–H curve decreases and the line intersects the x-axis at a much higher temperature than the actual Curie point.

In order to overcome the problem of the applied magnetic field effects and the thermal effects, another method was used to identify the actual Curie point. For this, major hysteresis loops were measured at different temperatures as shown Fig. 3, and the Arrott plot technique was applied to these M–H isotherms to determine the actual Curie temperature.

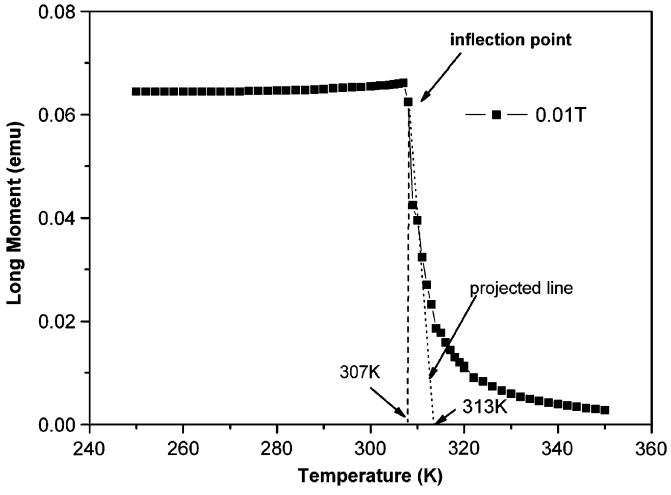

Fig. 1. Magnetic moment vs. temperature curve for $Gd_5Si_{2.7}Ge_{1.3}$ single crystal under a field of $H = 8 \times 10^3$ A/m ($B = 0.01$ T). Different Curie temperature values can be determined using either inflection point (307 K) method or line projection method (313 K).

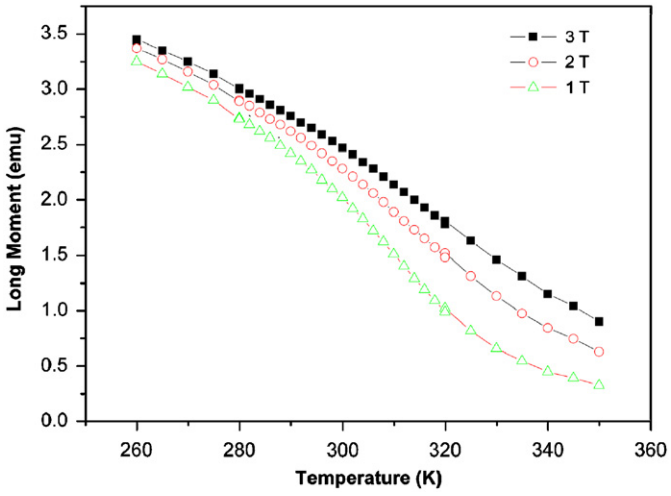

Fig. 2. Magnetic moment vs. temperature measurements for $Gd_5Si_{2.7}Ge_{1.3}$ single crystal under applied fields of 0.8, 1.6 and 2.4×10^6 A/m ($B = 1$, 2 and at 3 T) over the temperature range 250–350 K.

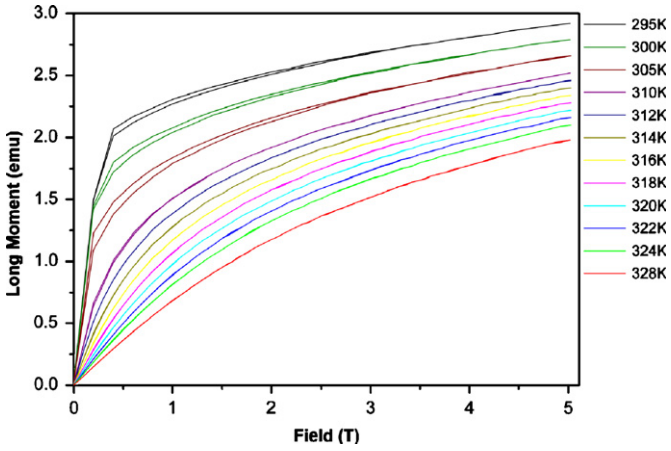

Fig. 3. Change of magnetic moment vs. magnetic field measurements for $Gd_5Si_{2.7}Ge_{1.3}$ single crystal sample for increasing temperatures from 295 to 328 K.

3. Arrott plot technique estimation of Curie temperature

Arrott plot technique is based on the Weiss–Brillouin treatment of molecular field theory [4]. Eq. (1) gives the proposed equation for magnetization as a function of both applied field and temperature [6]:

$$M = M_0 \tanh\left(\frac{\mu(H + NM)}{kT}\right) \quad (1)$$

where M_0 is the spontaneous magnetization at absolute zero, μ is magnetic moment per atom and N is the molecular field constant. Rewriting Eq. (1) as a series and assuming M/M_0 to be very small at the Curie temperature we get

$$\frac{\mu H}{kT} + N\frac{\mu M}{kT} = \frac{M}{M_0} + \frac{1}{3}\left(\frac{M}{M_0}\right)^3 + \frac{1}{5}\left(\frac{M}{M_0}\right)^5 + \ldots \quad (2)$$

ignoring higher order terms in M/M_0; differentiating and rewriting Eq. (2) we get

$$\frac{1}{\chi} = \left(\frac{kT}{\mu M_0}\right) - N \tag{3}$$

At the Curie temperature, $1/\chi = 0$, so Eq. (3) can be written as

$$T_c = \left(\frac{\mu N}{k}\right) M_0 \tag{4}$$

Substituting Eq. (4) in Eq. (3)

$$\frac{\mu H}{kT_c} = \frac{1}{3}\left(\frac{M}{M_0}\right)^3 + \frac{1}{5}\left(\frac{M}{M_0}\right)^5 + \dots \tag{5}$$

Eq. (5) can be rewritten for conditions above and below the Curie temperature as [4]

$$\frac{\mu H}{kT} = \varepsilon\frac{M}{M_0} + \frac{1}{3}\left(\frac{M}{M_0}\right)^3 + \frac{1}{5}\left(\frac{M}{M_0}\right)^5 + \dots \tag{6}$$

where $\varepsilon = T - T_c/T$.

Considering terms only up to third order and introducing the critical exponents γ and β into Eq. (6) to accommodate for deviations from the mean field approximation and also to accommodate for both polycrystalline and single crystal samples [5] we get

$$\left(\frac{H}{M}\right)^{1/\gamma} = \frac{T - T_c}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta} \tag{7}$$

where M_1 and T_1 are constants. Eq. (7) is used to identify the best values of the critical exponents γ and β under which isothermal M–H curves are straight and parallel lines. When this is done, the isotherm which passes through the origin of the plot of $(H/M)^{1/\gamma}$ vs. $M^{1/\beta}$ represents the Curie temperature. For the best estimation of Curie temperature, isothermal M–H measurements close to the Curie temperature should be used.

Isothermal M–H measurements of the $Gd_5Si_{2.7}Ge_{1.3}$ single crystal sample from Fig. 3 were re-drawn as plots of $(H/M)^{1/\gamma}$ vs. $M^{1/\beta}$ over the temperature range of 295–322 K as shown in Fig. 4. The values for γ and β needed to obtain straight lines were found to be 1.33 and 0.45, respectively. It can be seen from Fig. 4 that isotherms above the calculated Curie point are curved downwards at the end and are converging to the origin, while the isotherms below the calculated Curie point are curved upwards at the ends and are converging to the origin. The isotherm at the Curie point should not have its end curved as it should be a straight line passing through the origin. Thus, the Curie temperature was determined from Fig. 4 to be 304 K.

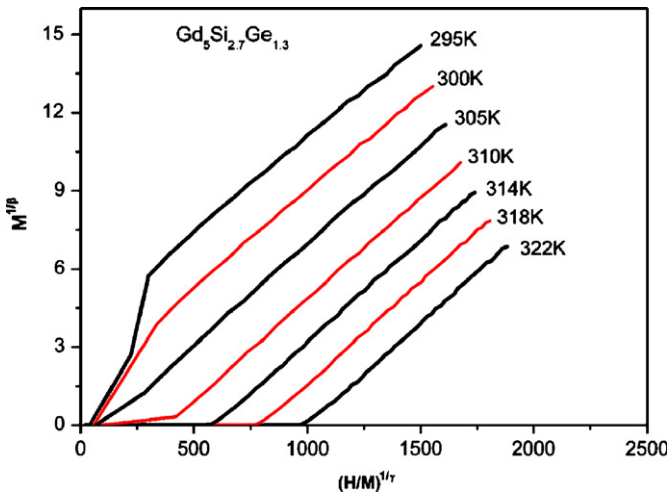

Fig. 4. Arrott plots for of $Gd_5Si_{2.7}Ge_{1.3}$ single crystal sample with the best values of the critical exponents $\beta = 0.45$ and $\gamma = 1.33$.

4. Conclusion

The Arrott plot technique can be used for determining the projected Curie temperature as it overcomes the external factors such as influence of the applied magnetic field and thermal effects. This technique is well suited for applications to magnetocaloric samples, since it uses M–H measurements at temperatures near to but not at the transition. Other methods rely on temperature measurements at the transition, which can be uncertain due to temperature difference between the magnetocaloric sample and the temperature sensor.

In this case the Arrott plot technique was successfully applied to a single crystal $Gd_5Si_{2.7}Ge_{1.3}$ sample and its Curie temperature was determined to be 304 K.

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