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2008 J. Phys.: Condens. Matter 20 215224

(http://iopscience.iop.org/0953-8984/20/21/215224)

J. Phys.: Condens. Matter **20** (2008) 215224 (5pp) doi:10.1088/0953-8984/20/21/215224

Entropy change for magnetic phase transitions in CoNi/Gd nanolayers

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Received 25 February 2008, in final form 2 April 2008
Published 24 April 2008
Online at stacks.iop.org/JPhysCM/20/215224

Abstract
First-order magnetic phase transitions showing thermal hysteresis have been investigated in CoNi/Gd nanolayers. The phase transitions between two coexisting ordered phases are controlled by external magnetic fields (50–500 Oe). The magnetic entropy change has been calculated from isothermal hysteresis data showing two discontinuities with opposite signs as the temperature is cycled in the 20–300 K temperature interval.

(Some figures in this article are in colour only in the electronic version)

Theoretical and experimental investigations of phase transitions, as well as their practical applications, have been conducted in many different systems. When the transition is of first order, the property being measured near the transition temperature displays a sudden change in magnitude as well as thermal hysteresis and an associated latent heat. First-order derivative of Gibbs free energy (G) with respect to temperature, and therefore the entropy (S), is discontinuous. The hysteresis effect, depending on the way the region of interest is investigated can be explained by the phases coexistence in the studied system. For a second-order phase transition the second derivative of G, the heat capacity (C), is discontinuous [1, 2]. The studies on phase transitions in magnetic materials have mainly been focused on the order/disorder transitions such as ferromagnetic to paramagnetic. The isothermal magnetization of a material decreases the entropy and subsequent adiabatic demagnetization can lead to a temperature decrease [3]. The inverse effect, entropy increase, was also observed in first-order phase transitions near the ordering temperatures [4, 5] when the magnetic field is adiabatically applied. Most of the magnetic materials undergo a structural phase transition and an associated change in magnetization [6–11]. Due to this merged transition, a high entropy change (ΔS) can be observed. For detailed review see [9, 11]. Direct or indirect ΔS calculations on bulk materials have been done in pure Gd, Tb, Dy, Ho, Er or Tm and in their alloys [12–14] in large external magnetic fields. Phase transitions appear next to the Curie temperature and at lower temperatures when the spin structure changes [15–17].

In this paper, we present magnetic entropy change ΔS due to magnetic first-order phase transitions, in ultrathin multilayers of CoNi/Gd. Thermal hysteresis in transitions between two ordered states were observed in measurements of magnetic moment versus temperature, $M(T)$, in constant external magnetic field, leading to change in magnetic entropy.

Magnetic thermal hysteresis effect has been investigated by measuring the total magnetic moment versus temperature in different TM (transition metal)/RE (rare earth) (Co/Gd, Fe/Gd, CoNi/Gd) multilayers and CoGd alloys. The experimental results can be explained using a simple theoretical model [18–21]. The fundamental property of the artificial ferrimagnets is the antiferromagnetic coupling between the TM and the heavy RE such as Gd or Tb. The system has a total zero magnetic moment at the compensation temperature, T_{comp}.

The total energy, E, for the antiferromagnetically coupled layers can be expressed in terms of: Zeeman energy of the individual components, exchange coupling term dependent on the relative orientation of the two sublayers moments and the anisotropy term.

The equilibrium states of the TM/RE multilayers can be understood using a theoretical model presented in [22, 23].

For $T < T_{\mathrm{comp}}$ the system is in the RE aligned state, the RE moment dominates and is aligned with the external magnetic field where the TM moment is antiparallel to the external magnetic field. For $T > T_{\mathrm{comp}}$ the system is in the TM aligned state, the TM moment is dominant and aligned with the external magnetic field where the RE moment is antiparallel with the applied field. There can also be twisted states where the moments, of the two sublayers make angles other than 0° or 180° with the applied field.

For the TM/RE multilayers, a theoretical model with an anisotropy field, H_a, (that is temperature independent and in the same direction with the applied field) is used to explain the stability of both aligned phases (TM and RE) over a certain temperature range [18].

$$E = -H M_{TM} \cos\theta_1 - H M_{RE} \cos\theta_2 + J M_{RE} M_{TM} \times \cos(\theta_2 - \theta_1) - M_{TM} H_a \cos^2\theta_1 \quad (1)$$

H is the applied magnetic field, $M_{TM,RE}$ transition metal or rare earth magnetic moment, $\theta_{1,2}$ angle between TM or RE magnetic moment and the applied field direction, J exchange coupling constant.

Fundamentally, this new phenomenon in ferrimagnetic systems, magnetic thermal hysteresis is caused by the different temperature dependence of the magnetization for the TM and RE sublayers.

Co80Ni20 (wt%) and Gd layers were dc sputtered at room temperature on a glass substrate in 3 mTorr ultra high purity Ar gas. To prevent contamination UHV was achieved in the deposition chamber (10^{-9} Torr base pressure) and to prevent sample oxidation 20 nm of Ag was used as buffer and cap layers in all samples. The multilayers have polycrystalline structure [19]. The samples were cooled at a rate of 10 K min^{-1} from 300 to 10 K, followed by the heating process at the same rate back to 300 K, under a constant in plane-applied magnetic field. The constant external magnetic field was adjusted in the 50–500 Oe range. The thermal hysteresis $M(T)$ and field hysteresis $M(H)$ loops were measured using a SQUID magnetometer.

Figure 1 presents $M(T)$ curves for (CoNi 1.5 nm/Gd 2 nm)$_4$. The two minima observed in figure 1(a) at T_1 and T_2 in the measurement of magnetic moment as a function of temperature during the cooling and heating cycles correspond to first-order magnetic phase transition temperatures.

CoNi and Gd moments are antiferromagnetically aligned in small external fields (50–300 Oe) where the interaction is dominated by the exchange and anisotropy energy values. In figure 1(a) the sample will switch from the CoNi aligned state to the Gd aligned state during the cooling cycle (supercooling) at $T_1 < T_{comp}$, and back to the CoNi aligned state at $T_2 > T_{comp}$ during the heating cycle (superheating) under an external magnetic field of 50 Oe. As the temperature is reduced from 300 K, the Gd moment increases and dominates over the CoNi moment (assumed constant in 10–300 K temperature interval), however the anisotropy keeps the system in the CoNi aligned state through supercooling. As a result negative moments are measured between $T_{comp} = 165$ K, (the compensation temperature) and $T_1 = 100$ K (the transition temperature). Similarly negative moments were measured between $T_{comp} = 165$ K and $T_2 = 230$ K as the system is kept in the Gd aligned state through superheating. The thermal hysteresis width $\Delta T = T_2 - T_1$, represents the coexistence temperature interval for the two magnetically ordered CoNi and Gd aligned phases. At $H = 50$ Oe (as shown in figure 1(a)) $\Delta T = 130$ K and at $H = 100$ Oe (as shown in figure 1(b)) $\Delta T = 60$ K. With higher external magnetic fields, the difference in transition temperature becomes smaller and above a critical external magnetic field, it is reduced to zero. An $H = 200$ Oe external

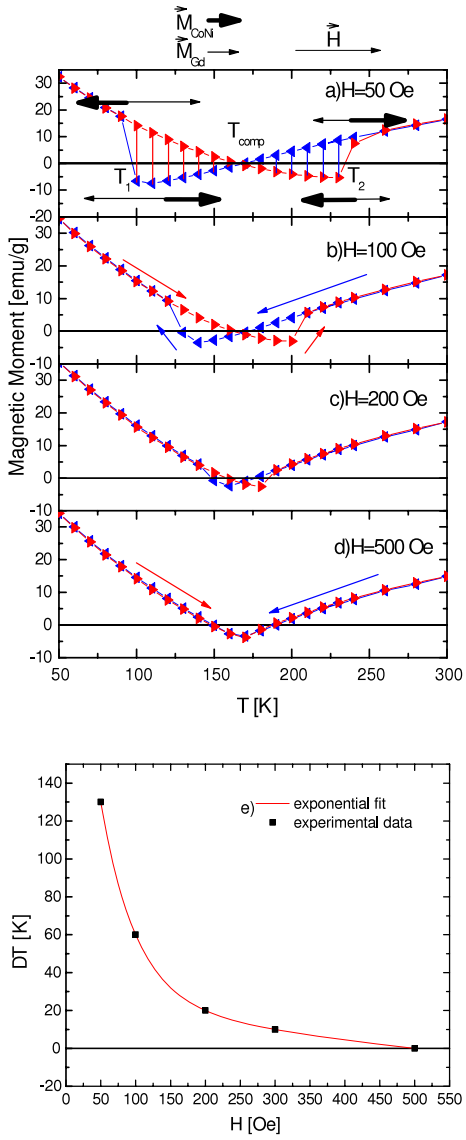

Figure 1. Temperature dependence of magnetic moment for (CoNi 1.5 nm/Gd 2 nm)$_4$ for different external magnetic fields and thermal hysteresis width as a function of the applied field. On the top of the figure, the thin and thick arrows indicate the Gd and CoNi magnetic moments respectively. In (a) magnetic moments with respect of the external field direction are presented around transition temperatures T_1 and T_2. The vertical lines illustrate the region where the two phases coexist. In (b) and (d) the arrows are used to indicate the direction during the measurement: cooling from 300 to 50 K (blue arrows and symbols online) followed by the heating process (red arrows and symbols online).

magnetic field reduces ΔT to 20 K, (as shown in figure 1(c)) and for $H = 500$ Oe (as shown in figure 1(d)) the $M(T)$ shows just the typical T_{comp} of ferrimagnetic systems with no thermal hysteresis. At 500 Oe, $M(T)$ is reversible for the heating and cooling cycles, the only minimum indicating the unique T_{comp}. The thermal hysteresis width decreases as a function of the applied field The experimental data $\Delta T(H)$ shown in figure 1(e) has an exponential fit.

The integration of Maxwell relation [3] for an isothermal hysteresis indicates that entropy change is directly proportional

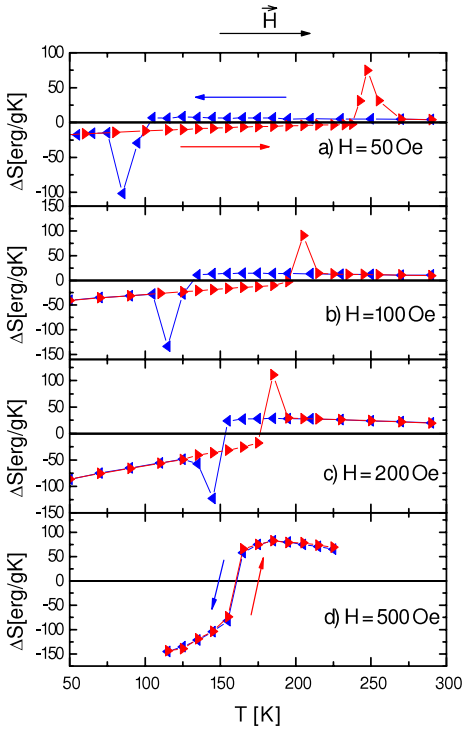

Figure 2. Entropy change as a function of temperature for (CoNi 1.5 nm/Gd 2 nm)$_4$ for different external magnetic fields. In (b) and (d) the arrows are used to indicate the direction during the measurement: cooling from 300 to 50 K (blue arrows and symbols online) followed by the heating process (red arrows and symbols online). 1 erg g K^{-1} = 10^{-4} J kg^{-1} K^{-1}.

to the magnetization derivative with respect to temperature at constant magnetic field and scales with the applied magnetic field value. The sign of ΔS as determined from equation (2) is dependent on the sign of ΔM during the heating or cooling cycle of the measurement.

$$\Delta S_m = \int_{Hi}^{Hf} \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \qquad (2)$$

The entropy change ΔS, as function of temperature is shown in figure 2. ΔS is calculated by numerically evaluating the integral in equation (2) using the isothermal hysteresis data. As the model for magnetic thermal hysteresis predicts [18], the temperature stability interval of the two phases is controlled by the magnetic field. The sudden change in magnetic moment with temperature gives a discontinuity to $\Delta S(T)$ in a narrow temperature range.

On either side of the transition temperatures, the two phases have similar symmetries. The CoNi and Gd moments are coupled antiparallel to each other; the larger of the moments aligns parallel to the external magnetic field while the smaller moment aligns opposite to the magnetic field. There is an abrupt change between these two stable states at two critical temperatures (T_1 and T_2). During the cooling, the system undergoes a phase transition from CoNi to Gd aligned state: the multilayer switches magnetization 180° and hence magnetic moment changes from negative to positive at 100 K. The anisotropy holds the system in the CoNi aligned state

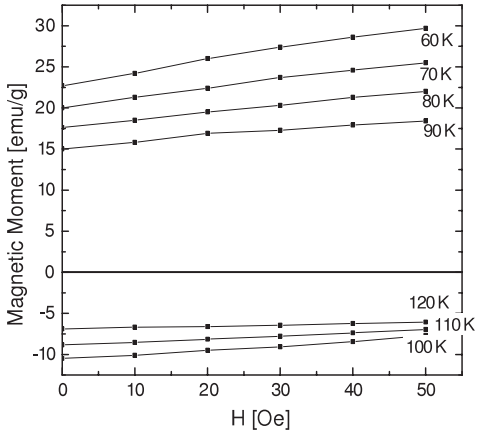

Figure 3. Selected hysteresis loops for (CoNi 1.5 nm/Gd 2 nm)$_4$ multilayer around transition temperature, T_1 = 100 K. Negative magnetic moments for (120–100) K correspond to CoNi aligned phase and positive magnetic moments (90–60) K correspond to Gd aligned phase.

down to T_1 (figure 1(a)) where the energy stored through the supercooling process is released. This transition determines the decrease in entropy observed below 100 K (figure 2(a)).

Similarly, when the system is heated up, the anisotropy holds the system in the Gd aligned state after the system passes through T_{comp} and reaches T_2 as shown in (figure 1(a)) (superheating). The system reverses the phase to the CoNi aligned phase, with a second abrupt 180° switching of the magnetic moment, reaching the favorable energetic state for high temperatures. The system now absorbs energy.The transition will now determine a second discontinuity in $\Delta S(T)$ around 250 K, while the system is heated back to 300 K as shown in figure 2(a). In figure 2(b) for H = 100 Oe similar minimum and maximum values of $\Delta S(T)$ are related with magnetic phase transitions temperatures at T_1 = 130 K and T_2 = 200 K respectively. $\Delta S(T)$ for H = 200 Oe is shown in figure 2(c).The minimum and maximum of ΔS are around 150 K and 180 K respectively.

The absolute value of $\Delta S(T)$ increases slightly with the external magnetic field value (H = 0–200 Oe), and the phase transitions collapse to a single temperature above the critical field of H = 500 Oe. In this case, the Zeeman energy will dominate the anisotropy energy at all the temperatures. This shows that the thermal hysteresis in the magnetic phase transitions is temperature controlled under small external magnetic fields. In figure 1(d) for H = 500 Oe, the system shows no hysteresis in $M(T)$ measurements and correspondingly no peaks are observed in $\Delta S(T)$ shown in figure 2(d). Figure 3 shows the magnetic hysteresis loops, $M(H)$, of (CoNi 1.5 nm/Gd 2 nm)$_4$ for temperatures around the transition temperature T_1 = 100 K. It can be seen that the magnetic moment does not change significantly with the applied field from 0–50 Oe, but it does change sign with temperature. Magnetic moment has the same negative sign observed in the thermal hysteresis between (120–100) K and then becomes positive in the lower temperature interval (90–60) K.

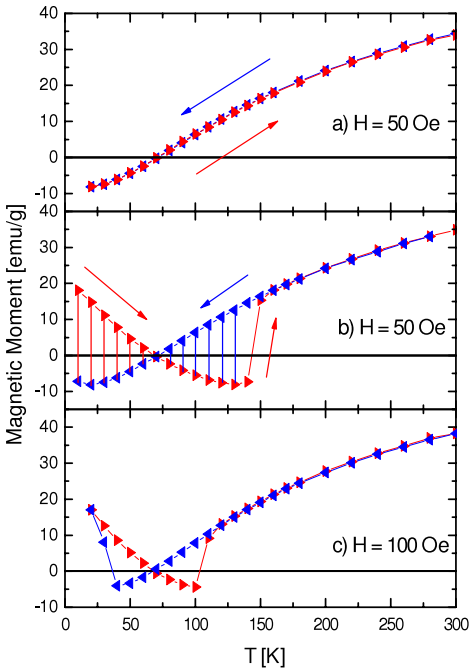

Figure 4. Temperature dependence of magnetic moment for $(\text{CoNi 2 nm/Gd 2 nm})_4$ for different external magnetic fields. The vertical lines show the region where the two phases coexist. The direction during the measurement is indicated by arrows. In (a) at $H = 50$ Oe, the starting point for measurements is 300 K and no phase transition is observed. In (b), at $H = 50$ Oe, the starting point for measurements is 10 K and first-order phase transition is observed during the heating process.

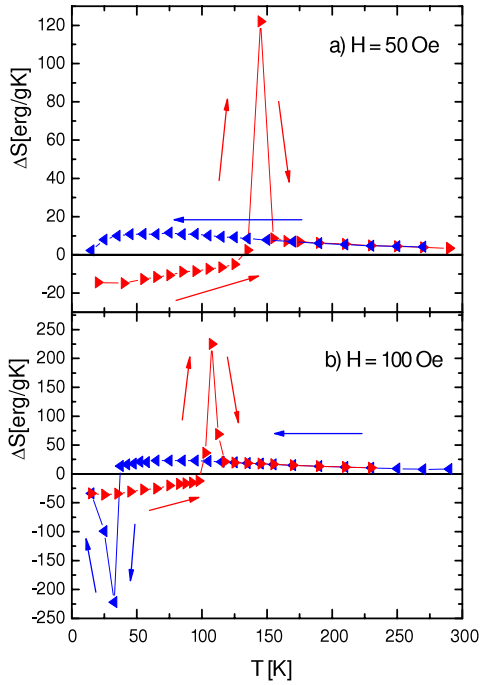

Figure 5. Entropy change as a function of temperature for $(\text{CoNi 2 nm/Gd 2 nm})_4$ for different external magnetic fields. In (a) and (b) the arrows are used to indicate the direction during the measurement: cooling from 300 to 50 K (blue arrows and symbols online) followed by the heating process (red arrows and symbols online). In (a) at $H = 50$ Oe the starting point for measurements is 10 K. Entropy change is observed just during the heating process. In (b), at $H = 100$ Oe, the starting point for measurements is 300 K. Entropy change is observed for both cooling and heating of the sample.

The change in energy between CoNi and Gd aligned phases is calculated at T_1 and T_2 based on equation (1) and [18].

$$\Delta E_{T1} = E_{\text{CoNi}} - E_{\text{Gd}} = 2H(M_{\text{Gd}}^{T1} - M_{\text{CoNi}}) > 0, \quad (M_{\text{Gd}}^{T1} > M_{\text{CoNi}}) \tag{3}$$

$$\Delta E_{T2} = E_{\text{CoNi}} - E_{\text{Gd}} = 2H(M_{\text{Gd}}^{T2} - M_{\text{CoNi}}) < 0, \quad (M_{\text{Gd}}^{T2} < M_{\text{CoNi}}). \tag{4}$$

M_{Gd}^{T1} and M_{Gd}^{T2} are Gd magnetic moments at the two transition temperatures respectively. M_{CoNi} is the CoNi magnetic moment, which is temperature independent to a good approximation in the 20–300 K interval and H is the applied magnetic field. The anisotropy term and exchange coupling terms were considered temperature independent and they canceled out in the difference.

It should be pointed out that ΔE_{T1} and ΔE_{T2} have opposite signs, which is in agreement with the signs of $\Delta S(T)$ from experimental data. At $H = 100$ Oe applied field, $\Delta S_{T1} = -102.2$ erg g^{-1} K^{-1} and $\Delta S_{T2} = 74.6$ erg g^{-1} K^{-1} as shown in table 1. The trend $|\Delta S_{T1}| > |\Delta S_{T2}|$ is observed in figure 2 and presented in table 1 for all the fields. At low temperature, more energy is required to switch larger magnetic moments even if the net magnetic moments at the transition temperatures have the same magnitude. This is due to the Gd moment temperature dependence and it is shown in figure 1(a) using the arrows. The magnitude of entropy change does not scale with the applied field like in second-order phase transitions. The nature of the transition is different in this case and the value of the applied field controls just the phase transition temperatures (figure 1(e)).

(CoNi 2 nm/Gd 2 nm) with lower T_{comp} was also investigated. The addition of more CoNi to the system makes the compensation temperature lower, $T_{\text{comp}} = 65$ K. The magnetic moment as a function of temperature is shown for this multilayer in figure 4. The difference in behavior is at the applied magnetic field of 50 Oe. This multilayer can have no phase transition or one phase transition depending on the starting point (300 K or 10 K respectively). The multilayer stays in the CoNi aligned phase during cooling from 300 to 10 K and follows the same path while heating back to 300 K. This is due to the fact that the anisotropy of the multilayer is now higher than the Zeeman energy (figure 4(a)). If the initial state is at low temperature, the Gd aligned phase, during heating to 300 K, the system undergoes a very sharp phase transition at $T_2 = 140$ K as shown in figure 4(b). On the contrary, the first multilayer studied has 2 phase transitions for this applied field of 50 Oe independent of the starting point. In figure 4(c), under a 100 Oe applied field, two phase transitions are observed. One at $T_1 = 40$ K and one at $T_2 = 100$ K, during the cooling and heating cycles respectively. The entropy change as a function of temperature, $\Delta S(T)$, is presented for this sample in figure 5. In figure 5(a), $H = 50$ Oe, starting from 20 K, and heating the sample toward 300 K, just a maximum in entropy change around 150 K is observed

Table 1. Entropy change (ΔS) at the first-order transitions for (CoNi 1.5 nm/Gd 2 nm)$_4$ for different applied magnetic fields.

H (Oe)	ΔS_{T1} (erg g^{-1} K^{-1})	ΔS_{T2} (erg g^{-1} K^{-1})
50	−102.2	74.6
100	−133.3	90.2
200	−123.0	111.0

as the system switches from Gd to the CoNi aligned phase. For the cooling cycle $\Delta S(T)$ has a monotonic temperature dependence. In figure 5(b), at $H = 100$ Oe, starting from 300 K, a minimum corresponding to the first phase transition around 40 K, and a maximum corresponding to the second phase transition around 100 K are observed in $\Delta S(T)$. These results demonstrate that at low fields one can observe no transition or one transition only depending on the starting point of $M(T)$ measurements.

Magnetic entropy change has been calculated for an artificial ferrimagnetic system of CoNi /Gd nanolayers. $\Delta S(T)$ associated with first-order magnetic phase transitions, has a minimum during the cooling cycle and a maximum during the heating cycle. The magnetic phase transitions with entropy change can be controlled over 20–300 K interval with small applied magnetic fields. The order–order magnetic phase transitions observed in $\Delta S(T)$ and $M(T)$ are explained due to the temperature dependence of the Gd moment associated with the existence of an anisotropy field in the CoNi layers. The same multilayer can show none, one, or two phase transitions by applying an external magnetic field in a small range (50–100 Oe) and by changing the starting point in the cooling/heating cycles.

Acknowledgments

This work was supported by a grant No.(Y-1215) from The Welch Foundation. The authors would like to thank Dr C Rong from UTA for help with the software to calculate $\Delta S(T)$.

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