Interpretation of thermal dependence of magnetic aftereffect for magnetic nanocomposite with slow decay rates

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(Received 9 January 2012; final version received 27 February 2012)

A new experimental characterization is presented of time-, field-, and temperature-dependent dynamic effects in magnetization of a nanocomposite which displays slow decay. Field and temperature variations of irreversible susceptibility, \( \chi_{irr} \), decay coefficient, \( S \), fluctuation field, \( h_f \), and activation volume, \( V \), have been calculated for the nanocomposite sample (Co\(_{80}\)Ni\(_{20}\)) using a recently developed modified Preisach–Arrhenius (MPA) model. The sample is composed of non-interacting nanoparticles having negligible reversible magnetization. Non-Arrhenius behavior is observed in both the maximum decay coefficient, \( S_{\text{max}} \), and the fluctuation field, \( h_f \), as a function of temperature \( T \). The peak of both temperature curves are identical and occur at a critical temperature \( T_k \) of \( \sim 50 \) K, which agrees with our experimental results. Based on the effect of a temperature-dependent chemical potential on energy barrier, \( h_f \) is studied for \( T < T_k \) and \( T \geq T_k \), respectively. A more complete MPA model that can predict the magnetization as function of time, field and temperature for a magnetic material with slow decay rates is proposed. This model uses a multi-variable analytical formula, \( m(\ln(t), H, T) \), which incorporates the characteristic parameters.

Keywords: magnetic aftereffect; fluctuation field; numerical modeling; Co\(_{80}\)Ni\(_{20}\) nanocomposite

1. Introduction

In magnetic information storage devices where a certain magnetization state must be permanently conserved, the decay of magnetization towards anhysteretic ground state with time is normally slow due to the presence of large energy barriers. However, continuous reduction of particle sizes is required in order to achieve ultra-high storage density and the reversal of magnetization has become easier as a result. Thus, magnetic aftereffects of mono-domain ferromagnetic nanoparticles with diameters in the range 10–100 nm, and exhibiting slow decay, have attracted considerable interest [1–5].

A modified Preisach–Arrhenius (MPA) model has recently been presented [6] which predicts time reliability of magnetization state in magnetic nanoparticles based on (i) quasi-equilibrium thermodynamics [7,8], (ii) the assumption that the decay rate is maximized at the field that maximizes the irreversible susceptibility [9], and (iii) experimental and artificial data on a Co\(_{80}\)Ni\(_{20}\) nanocomposite.

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The model can predict the shape of the entire magnetic aftereffect curves, for magnetic materials with slow decay rate, which cannot be observed experimentally within a reasonable time interval. It resolved problems that were attributed to the instability of the Preisach function by including a feedback parameter derived from the Moving model [10,11] and the variance–variable model [12] into the operative field.

The following analytical formula is derived from the MPA model [6],

\[
m \left( \ln \left( t \right) \right) \bigg|_{h_{ri}, T} = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n \left( \ln(\gamma) - t_k \right)^{2n+1}}{(2n + 1) n!},
\]

where \( t \) is the relative decay time, \( h_{ri} \) is the holding field within the region of interest, \( T \) is temperature, \( t_k \) is the critical time and \( \sigma_t \) is the standard deviation of decay rate. Equation (1) enables us to predict the magnetization at any time during the decay process at a given \( h_{ri} \) and a given temperature.

In this investigation, the joint presence of field-induced effects and thermal activation in magnetic aftereffect is interpreted. Both field and temperature dependence are shown in characteristic magnetic state parameters, such as coercivity, irreversible susceptibility, decay coefficient and fluctuation field, that are derived from hysteretic and aftereffect measurements. Extension of Equation (1) to a multi-variable function is proposed so that the precise nature of time, field and temperature dependence in magnetic aftereffect can be rigorously described. The accuracy of the extended model has been validated by experimental data.

2. Experimental characterization

The nanocomposite sample used in this study consists of monodispersed quasi-spherical \( \text{Co}_{80}\text{Ni}_{20} \) ferromagnetic nanoparticles with 50 nm average diameter (i.e., homogeneous in size). The nanoparticles, prepared by the polyol method, are embedded in a diamagnetic PVC polymer matrix with uniform distribution [13]. The nanocomposite contains the \( \text{Co}_{80}\text{Ni}_{20} \) nanoparticles at 0.4 wt % concentration. Hence, each nanoparticle is an isolated single-domain particle, and according to Wohlfarth [9], the activation volume of each nanoparticle is the actual particle volume. The sample also satisfies the MPA model criteria: (i) negligible reversible magnetization and (ii) negligible interaction between the magnetic nanoparticles. As shown in Figure 1, physical properites (i.e. size, shape, and distribution) of the nanocomposite sample are obtained from TEM and SEM images.

Hysteresis loops and magnetic aftereffect curves of the \( \text{Co}_{80}\text{Ni}_{20} \) nanocomposite were measured at temperatures ranging from 5 K to 300 K, using a SQUID magnetometer (Quantum Design, MPMS XL 5.0 Tesla). The diamagnetic contribution of the PVC matrix has been measured separately and substracted in the data presented.

Figure 2a shows descending hysteretic curves at selected temperatures from 5 K to 300 K over the field range –5 Tesla to 5 Tesla. As the temperature increases from 5 K to 300 K, coercivity \( H_c \) decreases monotonically from 0.095 Tesla to 0.035 Tesla (Figure 2b, shown by an arrow).

The irreversible susceptibility \( \chi_{irr} \) [14] is defined as

\[
\chi_{irr} = \frac{\partial M_{irr}}{\partial H} \bigg|_{M_{irr}}.
\]
Since the reversible magnetization is negligible for the Co\textsubscript{80}Ni\textsubscript{20} nanocomposite, $\chi_{irr}$ can be derived from the remanent magnetization curve. As shown in Figure 3, $\chi_{irr}$ is dependent on both applied field and temperature. As temperature increases from 5 K to 300 K, the value of the maximum irreversible susceptibility $\chi_{irr,max}$ (i.e. the peak of each $\chi_{irr}$ curve) increases monotonically and the location of the $\chi_{irr,max}$ shifts to lower field (shown by arrow). For any combination of temperature and field, the value of the corresponding irreversible susceptibility can be found on the three-dimensional surface in Figure 4.

3. Implementation of modified Preisach-Arrhenius model

The recently developed MPA model can predict the shape of the entire magnetic aftereffect curves for magnetic materials with slow decay rate, and thus, enables us to accurately extract the maximum decay coefficient, $S_{\text{max}}$, at a given holding field, $H$, and temperature, $T$. Figure 5 shows the predicted sigmoidal-shaped decay curve at a given temperature ($T = 50$ K) and holding field ($-0.1$ Tesla) using MPA model (solid blue). The location and value of the maximum decay slope $S_{\text{max}}$ (dotted) can be accurately calculated.

After obtaining the values of decay coefficient at any given temperature and field, the applied field dependence of decay coefficient is studied for selected temperatures within the range of 10 K to 300 K. As shown in Figure 6, the decay coefficient is dependent on both the applied field and the temperature. At each temperature, the applied field at which the maximum decay coefficient (black dot) occurs has been defined as the remanent coercivity $h_{rc}$ [15]. As the temperature increases from 10 K to 300 K, the value of $h_{rc}$ decreases monotonically, as shown by the arrow. The value of $S_{\text{max}}$, increases as temperature increases from 10 K to 50 K (dotted line) and then decreases as temperature increases further from 50 K to 300 K (dashed line). Note: $S_{\text{max}}$ reaches the maximum value when the temperature is 50 K.
Figure 2. (a) Hysteresis loops of the Co$_{90}$Ni$_{20}$ nanocomposite at selected temperatures from 5 K to 300 K after correction for the diamagnetic PVC matrix. Main panel: highlight of the hysteresis loops over field range $-0.5$ to 0.5 Tesla. Inset: hysteresis loops over the field range $-5$ to 5 Tesla. (b) Highlight of hysteresis loops in (a) over the field range $-0.2$ to 0.0 Tesla. The arrow illustrates the shift of decreasing coercivity $H_c$ (increasing $-H_c$) as the temperature increases from 5 K to 300 K.

Non-Arrhenius behavior [16] is observed in the maximum decay coefficient $S_{\text{max}}$ as a function of the temperature $T$ curve, with the peak, $S_{\text{max}}$, at the critical temperature $T_k$ of $\sim 50$ K (Figure 7). The non-Arrhenius behavior implies that the density of states in energy space is not uniform and the energy distribution of magnetic excitations obeys
Figure 3. Applied field dependence of irreversible susceptibility for the Co$_{80}$Ni$_{20}$ nanocomposite at selected temperatures from 5 K to 300 K. The maximum irreversible susceptibility $\chi_{\text{irr, max}}$ of each curve (peak value) is represented by black dot. The arrow illustrates the shift of increasing $\chi_{\text{irr, max}}$ as the temperature increases from 5 K to 300 K.

Figure 4. Applied field and temperature dependence of irreversible susceptibility for the Co$_{80}$Ni$_{20}$ nanocomposite. The color varies from light green for small values of $\chi_{\text{irr}}$ to purple for $\chi_{\text{irr, max}}$.

quantum statistics rather than Maxwell–Boltzmann statistics which are assumed in the Preisach–Arrhenius model. Bose-Einstein statistics have been proposed to explain similar non-Arrhenius behavior in nano-magnetic materials [17,18]. In Figure 8, the maximum decay coefficient is plotted, in three dimensions, as a function of both temperature and holding field. For any combination of temperature and field, the value of the corresponding maximum decay rate can be found on the surface in Figure 8.
Figure 5. Extraction of decay coefficient from decay curve using MPA model.

Figure 6. Holding field dependence of decay coefficient, $S$, for the Co$_{80}$Ni$_{20}$ nanocomposite at selected temperatures from 10 K to 300 K. As temperature increases from 10 K to 300 K, $S_{\text{max}}$ increases first from 10 K to 50 K, reaches peak value at 50 K and then decreases from 50 K to 300 K.

4. Extension to modified Preisach-Arrhenius model

The fluctuation field $h_f$, introduced by Néel [19] and expanded by Street and Brown [14] is defined as
Figure 7. Temperature dependence of the maximum decay coefficient for the Co$_{80}$Ni$_{20}$ nanocomposite. MPA model evaluated $S_{\text{max}}$ at selected temperatures are represented by red dots. The non-Arrhenius behavior is illustrated by the black fitting curve.

Figure 8. Temperature and field dependence of the maximum decay coefficient for the Co$_{80}$Ni$_{20}$ nanocomposite. The maximum decay coefficient varies from light green for small values of $S_{\text{max}}$ to dark blue for peak value of $S_{\text{max}}$.

$$h_f(H, T) = \frac{S(H, T)}{\chi_{\text{irr}}(H, T)},$$

(3)

where $S$ is the decay coefficient and $\chi_{\text{irr}}$ is irreversible susceptibility. Hence, $h_f$ can be rigorously determined from macroscopic measurements of $S$ and $\chi_{\text{irr}}$. As shown in Figures 4 and 8, both $S$ and $\chi_{\text{irr}}$ are dependent on the variation of $T$ and $H$, where $H$ is the holding field in $S(H, T)$ and the applied field in $\chi_{\text{irr}}(H, T)$. Note, the fluctuation field may also have time dependence, which can be attributed to the gradual variation in magnetic properties of the moments during the thermal relaxation process.
In Figure 9, the fluctuation field is plotted, in three dimensions, as a function of both temperature and field. Note: the generated surface (highlighted by red circle) is expected to have percent error of $\pm 0.5\%$, due to the limited amount of data obtained from measurements of $S$ and $\chi_{irr}$.

At each holding field in the region of interest, the non-Arrhenius behavior has been observed in the fluctuation field vs. temperature curves. Figure 10 shows the temperature dependence of the fluctuation field at a representative applied field of $-0.1$ Tesla, with a peak value at a critical temperature $T_k \approx 50$ K. Even though the location of the critical temperature varies at different holding fields in the range of negative saturation to positive saturation, the variation is negligible within the region of interest. Hence, for the special case of a monodispersed nanoparticulate system that exhibits slow decay, the fluctuation field, the driving force of the magnetic thermal aftereffect over the energy barrier, can be assumed to be independent of the holding field within the region of interest. Therefore,

$$h_f(H, T) |_{h_n} = \frac{S(T)}{\chi_{irr}(T)}. \quad (4)$$

Wohlfarth [9] suggested that $h_f$ can alternatively be evaluated by equating two definitions of an activation energy

$$E = \mu_0 M_S V h_f = kT. \quad (5)$$

Hence, the $h_f$ can alternatively been given by

$$h_f(H, T) |_{h_n} = h_f(T) = \frac{kT}{\mu_0 M_S(T) V(T)}. \quad (6)$$
where $\mu_0$ is the Bohr magneton, $k$ is the Boltzmann constant, $M_S$ is the saturation magnetization, $T$ is the temperature and $V$ is the activation volume \[20\text{–}22\].

Della Torre and co-workers \[16\] introduced a temperature-dependent chemical potential $\zeta$ to describe the magnetic aftereffect when the holding field is close to coercivity, i.e. the system has a substantial spin entropy $s$. The temperature dependence of the fluctuation field below and above the critical temperature can then be described separately. For $T < T_k$, the fluctuation field $h_f(T)$ can be described by Equation (6), which is directly proportional to temperature, except for weak temperature changes associated with variations in $M_S$ and $V$. For $T \geq T_k$, the effect of chemical potential on the energy barrier is not negligible and the expression of $h_f(T)$ is modified, accordingly:

$$h_f(H, T) \bigg|_{h_{ri}} = h_f(T) = \frac{kT}{\mu_0 M_S(T) V(T) (1 - E_B/\zeta(T))},$$

(7)

Figure 11 shows the joint field and temperature dependences of the fluctuation field that were evaluated using Equation (7). The difference between Figures 9 and 11 in the peak region (highlighted by red circle in Figure 9) is attributed to the inaccuracy in the measured data (±0.5%).

It is proposed to incorporate the interpretation of the temperature dependence of magnetic aftereffect into the previously developed MPA model and to extend Equation (1) to a multi-variable function, based on the behavior of fluctuation field

$$m \left( \ln(t), H, T \right) \bigg|_{h_{ri}} = \frac{2}{\sqrt{2\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n \left( \ln(t) - t_k(T) \right)^{2n+1}}{(2n+1) n!},$$

(8)

where critical time $t_k(T)$ is given by
Figure 11. Temperature and applied field dependence of the fluctuation field for the Co$_{80}$Ni$_{20}$ nanocomposite. $h_f$ were evaluated using Equation (7).

\[ t_k(T) = \frac{\bar{h}_k - c}{h_f(T)}, \]  

(9)

the standard deviation of decay rate $\sigma_i(T)$ is given by

\[ \sigma_i(T) = \frac{\sqrt{2} \sigma}{h_f(T)}, \]  

(10)

and fluctuation field $h_f(T)$ can be given by Equation (6) and Equation (7) for $T < T_k$ and $T \geq T_k$, respectively.

Note that expanding Equation (8) up to the 4th order term ($n = 4$) gives a computationally efficient approximation of the equation.

5. Conclusion

The characteristic parameters, such as irreversible susceptibility, $\chi_{irr}$, maximum decay coefficient, $S_{max}$, and fluctuation field, $h_f$, have been derived on dimensional grounds, i.e. both field and temperature variation, from hysteretic and thermal aftereffect measurements and theoretical analysis based on the MPA model. As the temperature increases, while $\chi_{irr,max}$ increases monotonically, $S_{max}$ and $h_f$ within $h_{ri}$ demonstrate non-Arrhenius behaviors, which are interpreted as follows: (i) for $T < T_k$, $h_f$, derived by equating two definitions of activation energy, is directly proportional to temperature, except for weak variations in saturation magnetization $M_S$ and activation volume $V$ with temperature, (ii) for $T \geq T_k$, a temperature-dependent chemical potential reduces the effective energy barrier, and as a result, exerts an influence on the behavior of $h_f$. These interpretations have been incorporated into the extended multi-variable analytical MPA model, which is quantitatively consistent with the presented data.
Acknowledgements
The authors thank Dr. Vázquez of CISC, Madrid, Spain for providing us with the nanocomposite sample. The authors are grateful to Prof. M. Wagner and Dr. C. Yan of The George Washington University for collaboration and to Drs. C. Dennis and V. Provenzano of the National Institute of Standards and Technology for fruitful discussions. The work is partially supported by National Science Foundation under Contract no. 0733526 and no. 1031619.

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