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The origin of the non-monotonic field dependence of the blocking temperature in magnetic nanoparticles

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Abstract

The dependence of the peak temperature (T_P) of the zero-field-cooled (ZFC) magnetization curves on the field in a magnetic nanoparticle system was studied using a diluted magnetic fluid composed of FePt nanoparticles. We found that the peak temperature increases with increasing applied field below 3 kOe; it then decreases when the applied field is increased further. We attribute the non-monotonic field dependence of the peak temperature to the anisotropic energy barrier distribution of the particles and to the slow decrease of high-field magnetization above the blocking temperature. Numerical simulations, based on magnetic dynamics, agree well with our experimental results.

Small magnetic particles have been studied very intensively for a long time due to their fundamental importance as well as their technological relevance [1–3]. With decreasing particle size, the magnetic stability of nanoparticles will become an important issue in technological applications due to thermal agitation [4]. A magnetic nanoparticle is generally in a single domain state with uniaxial anisotropy [2]. The relaxation time for its moment, $\mu = M_S V$, between 'up' and 'down' at zero-field is determined by the exponential law:

$$\tau = \tau_0 \exp(U/k_B T), \tag{1}$$

where τ_0 is the attempt frequency of the order of 10^{-9}–10^{-12} s [5], k_B is the Boltzmann constant, T is the temperature in kelvin and M_S and V are the spontaneous magnetization and the volume of the particle. The anisotropy energy, $U = KV$, is the energy barrier between the degenerated double-well potential, where K is the anisotropy constant. If the moment is detected by a technique with a measuring time t_m, the particle behaves superparamagnetically when $\tau < t_m$; the particle is in the blocked state when $\tau > t_m$. The blocking temperature, T_B, is then defined as $T_B = U/[k_B \ln(t_m/\tau_0)]$.

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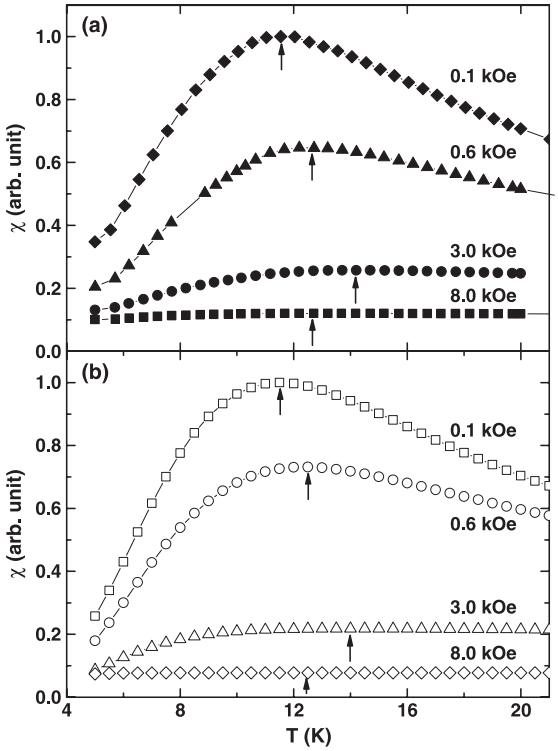

Figure 1. (a) Experimental ZFC curves measured in various fields. (b) Simulated ZFC curves. Peak temperatures are indicated by arrows.

The blocking temperature can be obtained from low-field zero-field-cooled (ZFC) curves [6, 7]. In a nanoparticle system with size distribution, the peak of the ZFC curve, T_P, is simply the average blocking temperature of the sample. It is worth noting that the applied magnetic field, H, in the ZFC magnetization measurements can significantly change the energy barrier,

$$U = KV(1 - H/H_K)^2, \tag{2}$$

where $H_K = 2K/M_S$ and is the anisotropy field. Therefore, it is expected that as H increases U will decrease monotonically for all particles. Consequently, T_P in the ZFC curve should decrease monotonically with increasing H.

However, non-monotonic field dependence of the peak temperature has been observed in a number of systems, such as Fe_3O_4 [8], γ-Fe_2O_3 [9], Fe–C [10, 11], ferritin [12–14] and M_{12}-ac [15]. In this paper, we present an observation of the anomalous behaviour in magnetic FePt nanoparticles and a model to account for it.

$L1_0$ structured FePt nanoparticles with an average diameter of 2.6 nm were fabricated following the method reported by Sun *et al* [16, 17]. The FePt nanoparticles were dispersed in hexane with a volume fraction of less than 1% to avoid inter-particle interactions. The solution was transferred to a Quantum Design SQUID magnetometer at room temperature and then a field of 50 kOe was applied to align the easy axes. After the sample was cooled to 150 K, at which point hexane froze into a solid and the particles were in a superparamagnetic state, the field was turned off. The ZFC magnetizations were then measured from 5 to 150 K in different fields. The representative ZFC curves are shown in figure 1(a). The field dependence of T_P

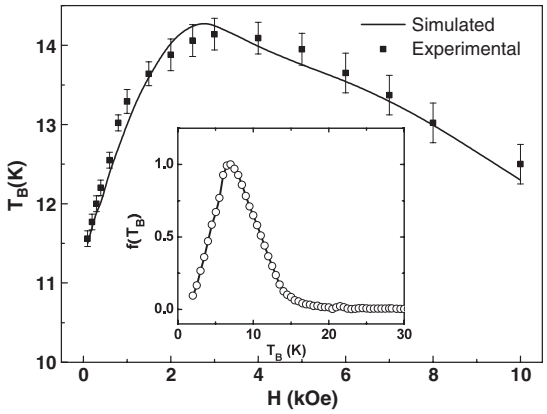

Figure 2. Experimental (open circle) and simulated (line) T_P dependences on the field. The inset displays the energy barrier distribution extracted from the ZFC–FC curves.

shown in figure 2 is non-monotonic. T_P decreases with the applied field when $H > 3$ kOe and increases with increasing H for $H < 3$ kOe.

Many models have been proposed to explain this phenomenon [8–15, 18, 19]. The periodic oscillation of the field dependence of T_P in Mn_{12}-ac has been successfully interpreted in terms of resonant spin tunnelling [19]. However, there is no conclusive explanation for magnetic particles. The Curie law has been used to describe the superparamagnetism [9]. It is well known that the Curie law is an approximation of the Langevin function and is valid only when the Zeeman energy is much smaller than the thermal energy, i.e. $\mu H \ll k_B T$. The magnetic moment of a 2.6 nm FePt particle, $\mu \sim 1000\mu_B$, is much larger than common atomic moments. As a consequence, the Zeeman energy is so large that the Curie law becomes invalid for such a large field. In figure 1, it is evident that the $M(T)$ curves decrease at a slower rate than Curie law predicts above the peak temperature. The peak in a low-field ZFC curve is the consequence of the competition between the decrease in the moments of the superparamagnetic particles and the increase in the moments of the newly relaxed larger particles. The slow decrease of magnetization essentially affects the position of T_P. Hence, the Langevin function has been adopted to describe the magnetic behaviour of unblocked particles to account for the slower decrease of the magnetization than predicted by the Curie law [10, 18]. Therefore, the anomaly could be interpreted using the Langevin function.

The Langevin function is based on isotropic magnetic moments, which have the same probability of occurring in any direction without an external field. But magnetic nanoparticles always have anisotropy, which alters their population in different directions. As we observed in Fe_8 molecular magnets, the anisotropy plays a very important role in determining the temperature- and field-dependent magnetization curves [20]. In addition, the magnetic behaviour of blocked particles should not be described using a static method, since magnetic relaxation begins as soon as the external field is applied. To avoid these problems, we started with the basic dynamics of the magnetic moment to study the non-monotonic field dependence of the peak temperature in FePt nanoparticles.

When a small field, H, is applied along the easy axes of the particles in a sample composed of N aligned, non-interacting magnetic nanoparticles, one of the degenerated (in the double-well potential) states becomes metastable due to the Zeeman energy. Consequently, the relaxation times are different for particles in different wells [1]:

$$\tau^{\pm} = \tau_0 \exp\left[KV(1 \mp H/H_K)^2/k_B T\right]. \tag{3}$$

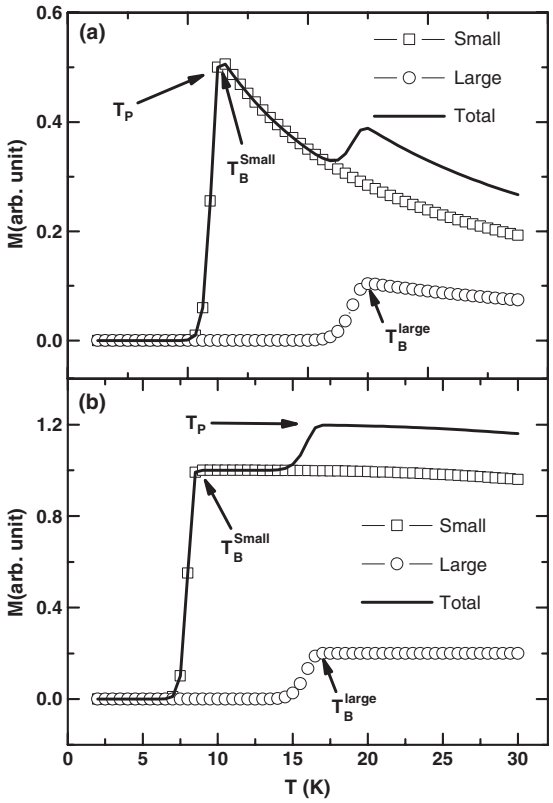

Figure 3. (a) ZFC curves of $H = 0.01H_K$ for smaller particles (open squares), larger particles (open circles) and their sum (solid line). (b) ZFC curves of $H = 0.1H_K$. The peak temperature is indicated for each curve.

And the magnetic moment of the system is determined by the difference in the number of particles parallel (N^+) or antiparallel (N^-) to the applied field. The magnetic moment of the system at time t after applying field H is given by [1]:

$$m(t) = \int NVM_S \left[\frac{\tau^+ - \tau^-}{\tau^+ + \tau^-} - \left(\frac{\tau^+ - \tau^-}{\tau^+ + \tau^-} - \frac{N_0^+}{N_0^-} \right) \exp(-t/\tau) \right] f(V)\,\mathrm{d}V \tag{4}$$

where N_0^+ (N_0^-) is the initial value of N^+ (N^-), τ is the effective relaxation time, and $1/\tau = 1/\tau^+ + 1/\tau^-$.

To clearly demonstrate why T_P shifts with H, we consider a simple barrier distribution, in which 1/10 is large and 9/10 is small. Given $T_B^S = 10$ K as the intrinsic blocking temperature for the small nanoparticles and $T_B^L = 20$ K for the large nanoparticles, the energy barrier distribution for the sample can therefore be written as $f(T_B) = 0.9\delta(T_B - 10) + 0.1\delta(T_B - 20)$. For $H = 0.01H_K$ and a temperature sweeping rate of 0.5 K min^{-1}, the ZFC curves were simulated and they are shown in figure 3(a). Both curves exhibit Curie law behaviour above their blocking temperatures. The ZFC magnetization of small, $m_S(T)$, and large nanoparticles, $m_L(T)$, peak at 10 and 20 K, respectively. The peak temperature of the whole system is 10 K, corresponding to $T_B^S = 10$ K, due to the large number of small particles. Similarly, the ZFC curves in a field of $H = 0.1H_K$ were simulated and the are shown in figure 3(b). Both T_B^S and T_B^L shift to lower temperatures, which is in agreement with

equation (2). However, the peak temperature of the total magnetization curve for the whole sample is around 17 K. That is, the T_P in the ZFC curves increases with H. The physics associated with the observation can be understood as follows. Due to the large Zeeman energy, $m_S(T)$ does not follow the Curie law and it decreases quite slowly above T_B (figure 3). At the same time, $m_L(T)$ increases sharply due to the deblocking of the large particles. As a result, the peak temperature of the whole sample shifts to a higher temperature, although the blocking temperatures of the individual particles shift to lower temperatures.

We have demonstrated, by using a very simple energy barrier distribution, that a dynamic model can account for the anomaly in the field-dependent peak temperature of particle systems. To compare the model with experimental data shown in figures 1 and 2, we used the parameters of the sample, such as the size distribution and anisotropy constant, to simulate the ZFC curves in different fields. The anisotropy constant is determined from the low-field ZFC curve to be $K = 2 \times 10^7$ erg cm^{-3}. The saturation magnetization is about 1×10^4 emu cm^{-3} [21]. The energy barrier distribution (or $f(T_B)$) can be roughly extracted from low-field ZFC and field-cooled (ZFC–FC) curves [9, 22]. The extracted energy barrier distribution is shown in the inset of figure 2, which is between the normal and lognormal distributions.

The same temperature sweep rate of 0.5 K min^{-1} as used in the experiments was employed in order to consider the relaxation effect. Examples of the calculated ZFC curves and the field-dependent T_P s are shown in figure 1(b) and figure 2, respectively, for comparison with our experimental results. The ZFC curves clearly show that the magnetization does not follow the Curie law in the high fields due to the large Zeeman energy and the magnetic anisotropy energy. It is evident in figure 2 that the numerical results are in good agreement with the experimental results. The model, which takes magnetic anisotropy and relaxation into account, explains the non-monotonic field dependence of T_P very well.

In conclusion, we have demonstrated that the non-monotonic field dependence of T_P in ZFC curves of a particle sample is due to the size distribution and the slow decrease in the magnetization above the blocking temperature in high fields. We expect that this effect should be observed in other magnetic nanoparticle systems with proper energy barrier distributions.

Acknowledgments

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References

[1] Dormann J L, Fiorani D and Tronc E 1997 *Adv. Chem. Phys.* **98** 283
[2] LesliePelecky D L and Rieke R D 1996 *Chem. Mater.* **8** 1770
[3] Kodama R H 1999 *J. Magn. Magn. Mater.* **200** 359
[4] Skumryev V, Stoyanov S, Zhang Y, Hadjipanayis G, Givord D and Nogues J 2003 *Nature* **423** 850
[5] Jonsson T, Svedlindh P and Hansen M F 1998 *Phys. Rev. Lett.* **81** 3976
[6] Zhang X X, Hernandez J M, Tejada J and Ziolo R F 1996 *Phys. Rev.* B **54** 4101
[7] Zhang X X, Wen G H, Xiao G and Sun S H 2003 *J. Magn. Magn. Mater.* **261** 21
[8] Luo W, Nagel S R, Rosenbaum T F and Rosensweig R E 1991 *Phys. Rev. Lett.* **67** 2721
[9] Sappey R, Vincent E, Hadacek N, Chaput F, Boilot J P and Zins D 1997 *Phys. Rev.* B **56** 14551
[10] Hanson M, Johansson C and Morup S 1995 *J. Phys.: Condens. Matter* **7** 9263
[11] Linderoth S, Balcells L, Labarta A, Tejada J, Hendriksen P V and Sethi S A 1993 *J. Magn. Magn. Mater.* **124** 269
[12] Gider S, Awschalom D D, Douglas T, Wong K, Mann S and Cain G 1996 *J. Appl. Phys.* **79** 5324
[13] Tejada J, Zhang X X, delBarco E, Hernandez J M and Chudnovsky E M 1997 *Phys. Rev. Lett.* **79** 1754
[14] Friedman J R, Voskoboynik U and Sarachik M P 1997 *Phys. Rev.* B **56** 10793
[15] Friedman J R, Sarachik M P, Tejada J and Ziolo R 1996 *Phys. Rev. Lett.* **76** 3830

[16] Sun S H, Murray C B, Weller D, Folks L and Moser A 2000 *Science* **287** 1989
[17] Gu H W, Zheng R K, Zhang X X and Xu B 2004 *J. Am. Chem. Soc.* **126** 5664
[18] Kachkachi H, Coffey W T, Crothers D S F, Ezzir A, Kennedy E C, Nogues M and Tronc E 2000 *J. Phys.: Condens. Matter* **12** 3077
[19] Chudnovsky E M 1998 *J. Magn. Magn. Mater.* **185** L267
[20] Zhang X X, Wei H L, Zhang Z Q and Zhang L Y 2001 *Phys. Rev. Lett.* **87** 157203
[21] Wu X W, Liu C, Li L, Jones P, Chantrell R W and Weller D 2004 *J. Appl. Phys.* **95** 6810
[22] Denardin J C, Brandl A L, Knobel M, Panissod P, Pakhomov A B, Liu H and Zhang X X 2002 *Phys. Rev.* B **65** 064422