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Influence of temperature on the coercive field of non-interacting fine magnetic particles

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Abstract

The Néel model of relaxation in a two level system was used in order to study the influence of temperature on the hysteresis loops of single-domain magnetic particles presenting uniaxial anisotropy and coherent magnetization reversal. Following the same line as the work by Stoner and Wohlfarth, the dependence of the coercive field on temperature for every possible orientation of the easy axis with respect to the field was studied. This study was then extended to include samples composed of many randomly oriented particles, concluding that the thermal dependence of the coercive field in these samples is not the frequently used $T^{1/2}$ dependence, which is valid only when the easy directions of the particles are oriented parallel to the magnetic field, but $T^{3/4}$. The model also facilitates the calculation of the dependence of the coercive field on other parameters, including the size of the particles or the characteristic measuring time.

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1. Introduction

Fine magnetic particles have been a very active subject of investigation since the late 1940s, due to their scientific and technological interest. The work by Néel [1] can be considered as one of the milestones of this field. Brown [2] and more recently other authors [3,4] have made also important contributions to the field of relaxation in these systems. An excellent review of the relaxation models in fine magnetic particles can be found in Ref. [5].

In order to study the coercive field of fine magnetic particles and its dependence on temperature some simplifications must be made. This study assumes that the particles form a system of non-interacting identical single-domain particles of ellipsoidal shape and uniaxial anisotropy presenting coherent magnetization reversal. It is also to be

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assumed that the particles are fixed in a non-magnetic solid matrix and cannot rotate freely, so they cannot align the anisotropy axis with the field. This study will be based, on one side, on the classical Stoner–Wohlfarth model [6] which applies to this kind of particles at $T = 0$ K. The Stoner–Wohlfarth model does not make any reference to the temperature, nor does it speak of thermal equilibrium. In this model the direction of magnetization remains stable, but this will be true only if no external perturbation takes magnetization over the energy barrier. Thermal agitation may provide such a perturbation, the result being that over a long time (compared with the relaxation time of the sample) thermal equilibrium is reached. The problem of single-domain magnetic particles in thermal equilibrium was thoroughly studied by Bean and Livingston [7] and due to the similarities with the atomic paramagnetism it is called superparamagnetism.

Using the relaxation model by Néel, the transition between these two limiting cases will be studied, focusing on coercivity and its dependence on temperature.

In what follows H is the external applied field, K is the anisotropy constant and V the volume of the particle. If M_s is the saturation magnetization, $\mu = VM_s$ will be the total magnetic moment of such a particle. It is assumed that K, V and M_s are independent of H; this assumption is not very restrictive in moderate fields.

With ψ and θ respectively being the angles formed by the easy axis and the magnetic moment of the particle with the positive direction of H, the first angle determines what will be called the orientation of the particle with respect to the field. The free energy of a particle in an external magnetic field (omitting constant terms from the demagnetizing energy) will be

$$\mathscr{H} = 2KV\left(\frac{1}{2}\sin^2(\psi - \theta) - \frac{H}{H_a}\cos\theta\right), \tag{1}$$

where $H_a = 2KV/\mu$ is known as the anisotropy field. Since the particles cannot rotate, ψ will be constant.

Following the work of Stoner and Wohlfarth we will use reduced units. For example the reduced field h is defined by $h = H/H_a$.

In this model another important magnitude is the field at which the particles suffer an irreversible jump in their magnetization direction when decreasing the applied field. It is called *critical field* $H_k(\psi)$ and can be calculated from the condition for an inflexion point on the energy curve (first and second derivatives equal to zero) and depends strongly on the orientation of the particle. The critical field coincides with the coercive field H_c (defined as the field for which the measured magnetization changes sign) if $\psi \in [0, \pi/4]$ (rad). In particular, for $\psi = 0$, the critical field is also equal to the anisotropy field and takes the maximum theoretical value of coercivity. If $\psi \in [\pi/4, \pi/2]$ magnetization takes negative values before the field reaches its critical value, so the coercive field is smaller than the critical field.

$\psi \in [0, \pi/4]$:

$$h_c = \frac{(1 - w^2 + w^4)^{1/2}}{1 + w^2} \quad \text{with } w = (\tan\psi)^{1/3}, \tag{2}$$

$$\psi \in [\pi/4, \pi/2]: \quad h_c = \frac{\sin(2\psi - \pi)}{2}. \tag{3}$$

2. Approach to equilibrium. Temperature dependence of coercivity

A set of non-interacting particles (with or without anisotropy) in thermal equilibrium has no coercive field and no remanence. The presence of coercivity and remanence is a measurement of how far the particle is from equilibrium. The way the particles approach equilibrium is the key to understanding how the properties depend on temperature and measurement time. With the appropriate relaxation model the transition from the SW model at $T = 0$ K to the superparamagnetic model of thermal equilibrium (infinite measurement time) can be studied.

For particles without anisotropy, the SW loop has no coercive field and it is simply the limit of the Langevin function when $T \to 0$ K. There is nothing to study here.

Particles with anisotropy, out of thermal equilibrium present remanence and coercivity, according to the SW model. These parameters change

continuously during the relaxation process, decreasing to zero in thermal equilibrium as the magnetization relaxes from the value of the SW model to the value in thermal equilibrium.

For simplicity the Néel model of relaxation [1,8] has been chosen. When two different equilibrium positions exist this model considers a transition probability of $e^{-\Delta E/k_B T}$ so relaxation time will be inversely proportional to it $1/\tau = f_0 e^{-\Delta E/k_B T}$. The pre-exponential factor f_0 is considered by Néel to be constant, of the order of magnitude between 10^9–$10^{10}\,s^{-1}$. This expression can be written as follows, assuming the value of 10^9 for f_0

$$\Delta E \approx (20.7 + \ln \tau) k_B T. \tag{4}$$

Because of the rapid change of the exponential function, only if the characteristic time of measurement has the same order of magnitude as the relaxation time τ will it be possible to observe dynamical effects. At the same time, relaxation time depends very dramatically on the energy barrier. As this is a function of the external field, in a very narrow interval of fields the particle changes from one SW type behaviour to the superparamagnetic one, and this is not very far from the other branch of the SW loop. The characteristic time depends on the kind of experiment but for normal magnetometric measurements is usually around 100 s, and the temperature that satisfies this relaxation time is called the blocking temperature T_B. Substituting this time in the expression above we see that if $\Delta E < 25 k_B T$ the relaxation time will be comparable or less than the characteristic measurement time and it will be possible to observe superparamagnetic behaviour. It is then possible in this simple model, to treat the complex effects of relaxation in the first approximation by simply making the energy barrier diminish its value in $25 k_B T$ or $(20.7 + \ln c) k_B T$ in general for other characteristic times c. The irreversible jump in the Stoner–Wohlfarth loop now takes place when the new energy barrier drops to zero.

2.1. Coercivity for an aligned, non-interacting, identical particle system

In the case of particles with the anisotropy axis parallel to the applied magnetic field the energy barrier can be calculated easily:

$$\Delta E = \frac{(2KV - \mu H)^2}{4KV} = \frac{1}{2}\mu H_a \left(1 - \frac{H}{H_k}\right)^2. \tag{5}$$

Equaling the energy barrier and the thermal energy a new critical field is obtained

$$\frac{(2KV - \mu H_k(T))^2}{4KV} = 25 k_B T. \tag{6}$$

The coercive field for aligned particles is the same as the critical field, so in this case dependence of coercivity on temperature is obtained:

$$H_c(T) = H_k(T) = H_k(0)\left(1 - 5\left(\frac{k_B T}{KV}\right)^{1/2}\right). \tag{7}$$

The coercive field decreases proportionally to $\sqrt{T}$. This kind of dependence of coercivity is widely accepted for any system of identical single domain particles without interaction, but it must be kept in mind that the calculation is only valid for the specific case of aligned particles.

2.2. Coercivity for a random, non-interacting, identical particle system

The main objective of this study is to extend the previous result to every possible orientation of the particles and to obtain the thermal dependence of the coercivity of a random sample of identical particles.

For an arbitrary orientation, the energy barrier depends on the field in a more complicated way according to the quadratic law $(1 - h/h_k)^2$. In most cases, there is no analytical expression, so a numerical approach is necessary.

An orientation was fixed and the angles of the maxima $\theta_{M,h}$ and minima $\theta_{m,h}$ of the energy calculated. $\theta_{m1,h}$ is the first minimum and the one which determines the direction of magnetization and the magnetization curve, unless the energy barrier is surpassed. This process was carried out numerically for every value of h. The significative interval is $[-1, 1]$ and in that interval h is decreased in steps $\Delta h = 0.02$. The hysteresis loop is determined by h and $\cos \theta_{m1}$. Additionally, the energy barrier between the minima $\Delta e(h)$ (see Fig. 1) is also calculated.

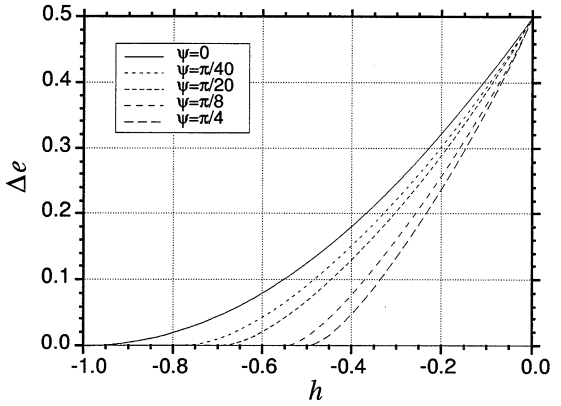

Fig. 1. Energy barrier as a function of the applied field for different particle orientations ($\psi = n\pi/40$ rad; $n = 0, 1, 2, 5, 10$). The field at which $\Delta e = 0$ is the critical field h_k.

The process had to be carried out for every orientation. In a compromise between accuracy and speed of the calculus 20 different orientations ψ were taken between 0 and $\pi/2$ at regular intervals of $\pi/40$ rad.

The effect of temperature was implemented in the way previously described. According to the model of relaxation chosen, the energy barrier Δe decreases as the magnetic field is increased in the direction opposed to magnetization. When the energy barrier equals the thermal energy factor, (chosen by us to be $25k_BT$ corresponding to the characteristic measurement time $c = 10^2$ s), the irreversible jump takes place. This means that at the jump, the energy barrier is proportional to temperature. It will be called *reduced temperature*.

$$t = \Delta e_k = \frac{\Delta E_k}{2KV} = \frac{25k_BT}{2KV} = \frac{1}{2}\frac{T}{T_B}. \tag{8}$$

This equivalence relationship between energy barrier and temperature is the main point here. Looking again at Fig. 1 we can see that we have only to invert the curve to obtain the dependence of the critical field on reduced temperature for every single orientation. The dependence of the energy barrier on field is the same for complementary angles, accordingly the thermal dependence of the critical field will be the same.

It has already been said that the critical field is not the same as the coercive field, even in the particles of this study with coherent reversal of magnetization. For $\pi/4 < \psi \leqslant \pi/2$ the coercive field begins by taking the constant value h_p. As the temperature rises the critical field diminishes until it is less than h_p. At that moment the coercive field equals the critical field and its thermal dependence is the same. The dependence for different values of the orientation is shown in Fig. 2.

Once h, Δe and the orientation ψ have been obtained, the angular dependence of the coercivity of a set of identical particles with the same orientation can be studied, including the influence of temperature. This is plotted in Fig. 3.

What happens then to the hysteresis loops? The model has been implemented by choosing a value of temperature and translating it into a reduced temperature. For every ψ the energy barrier is examined and when $\Delta e < t$ the irreversible jump takes place. The magnetization is supposed to jump from θ_{m1} to θ_{m2} (of course this is not exactly true, but the superparamagnetic value and the second branch of the reduced hysteresis loops are very close for most of the field values as has been shown previously). The value of cos θ is calculated for the rest of the loop.

To see the thermal dependence of the coercive field of a sample with a random orientation of the easy axis it is necessary to calculate the corresponding loop, integrating the individual loops obtained at the chosen temperature. In Fig. 4 some hysteresis loops at different temperatures are shown.

Extracting the new coercivities from the calculated plots the desired thermal dependence of the coercive field is obtained. This is represented in Fig. 5. The equation

$$h_c = 0.479 - 0.81t^{3/4} \tag{9}$$

fits the data very well for the whole range of temperatures.

2.3. Size dependence of coercivity. Samples presenting size distribution

Once h_c as a function of the reduced temperature t is obtained (Eq. (9)) further dependences can be studied. By working with reduced magnitudes,

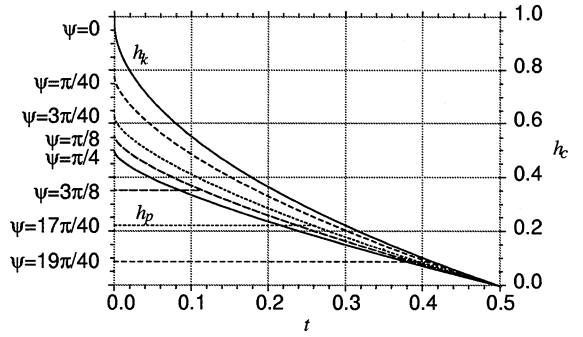

Fig. 2. Critical field (h_k) and coercivity (h_c) plotted as a function of reduced temperature for several orientations $\psi = n\pi/40$ rad; $n = 0, 1, 3, 5, 10, 15, 17, 19$. For particles with $\psi > \pi/4$ the critical field is the same as for particles oriented along the complementary angle, but the coercivity remains constant $h_c = h_p$ until the critical field becomes smaller than that value.

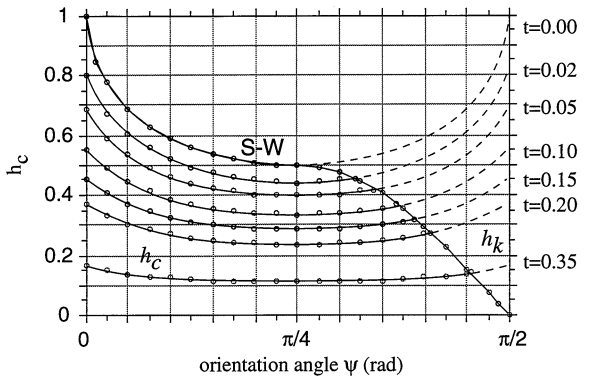

Fig. 3. Angular variation of the critical field h_k (dotted lines) and coercivity h_c (solid lines) plotted for different reduced temperatures. The thick line shows the S–W result.

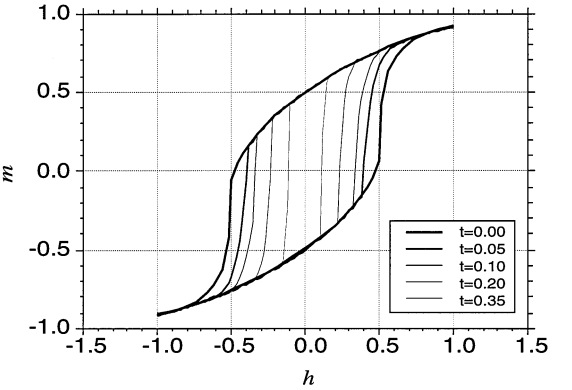

Fig. 4. Hysteresis loops of random samples at several reduced temperatures $t = 0, 0.05, 0.10, 0.20, 0.35$.

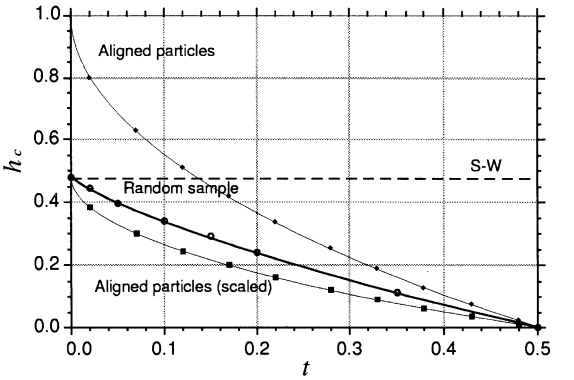

Fig. 5. Reduced coercive field for a non-interacting set of randomly oriented uniaxial particles plotted as a function of reduced temperature. The dependence of the coercivity in the case of particles aligned along the applied field is shown for comparison. For aligned samples coercivity drops linearly with $\sqrt{t}$ while for the random sample it is well expressed by $t^{3/4}$.

interesting scaling laws are obtained. Assume, for example, particles with the same anisotropy constant and the same modulus of magnetization but with different volume. The variation of coercivity with size, maintaining T constant, is obtained. This was previously done by Shirk and Buessem [9] using the same approach. Using the direct relationship between t and V given by Eq. (8),

$$V = \frac{25k_BT}{2Kt} = V_0\frac{1}{t} \tag{10}$$

and since the anisotropy field h_a is independent of V, it is only necessary to replot $h_c(t)$ as a function of $1/t$ to get the desired result, $h_c(V/V_0)$, plotted in Fig. 6. In the previous expression V_0 represents half the superparamagnetic volume at that temperature. The relation fits

$$h_c = 0.479 - 0.81\left(\frac{V}{V_0}\right)^{-3/4} \tag{11}$$

resulting from Eq. (9).

It can be seen that the SW value of 0.479 is valid only for particle sizes of 100 times the superparamagnetic value, and, at these sizes, the SW model may not apply. (See also Fig. 2 of Ref. [9].)

In the SW model size is not a relevant parameter, hysteresis loops and consequently coercivity do not depend on it. This is not true in superparamagnetism. The magnetization curves are different because the energy barriers (directly proportional to V) are different. Also in relaxation models volume plays a key role. Even assuming single-domain particles coercivity depends on volume and consequently the volume distribution becomes important when it comes to interpreting the results. For example, particles aligned along the field present a squared hysteresis loop. If we think of a discrete flat size distribution (the fraction of the total volume occupied by the particles with different sizes is the same, so their weight in the global loop is the same) we can see the resulting hysteresis loop in Fig. 7.

The resulting coercivity in this case is the mean of the coercive forces and the resulting loop is not square anymore but inclined, as if an additional demagnetizing factor had appeared.

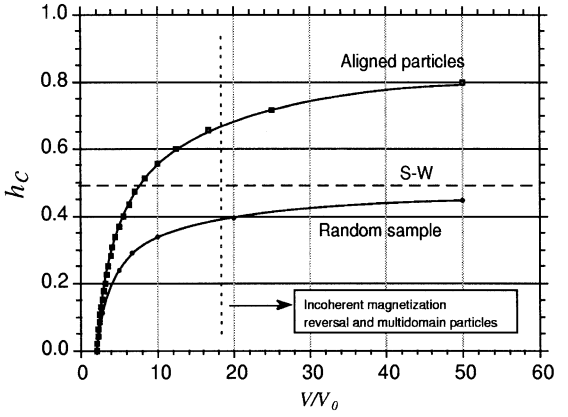

Fig. 6. Reduced coercivity of a random particle system plotted as a function of particle size at a fixed temperature. The crystalline anisotropy and the saturation magnetization of the particles are assumed to be constant. The limit is the Stoner–Wohlfarth value 0.479. The curve fits $V^{-3/4}$. The case for aligned particles (scaled to 0.479) is shown for comparison.

2.4. The effect of measurement time on coercivity

The dependence of the coercive field on the characteristic measurement time of the experiment τ_m for particles with fixed volume V and at temperature T can also be obtained. From Eqs. (4) and (8)

$$\tau_m = \exp\left(\frac{2KV}{k_B T}t - 20.7\right), \tag{12}$$

$$t = \frac{k_B T}{2KV}(\ln \tau_m + 20.7), \tag{13}$$

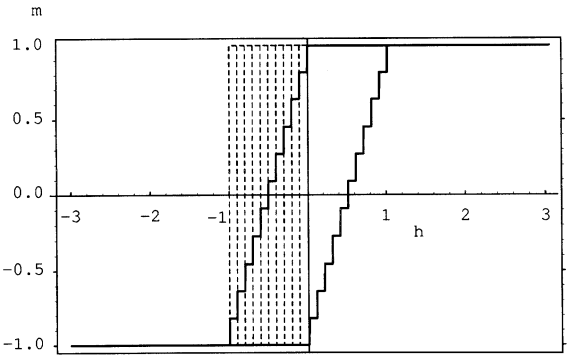

Fig. 7. Resulting loop of a set of aligned particles with a flat discrete size distribution. Although every individual loop is square the resulting loop is inclined. Coercivity in this particular case is the mean of the coercive forces for each particle size.

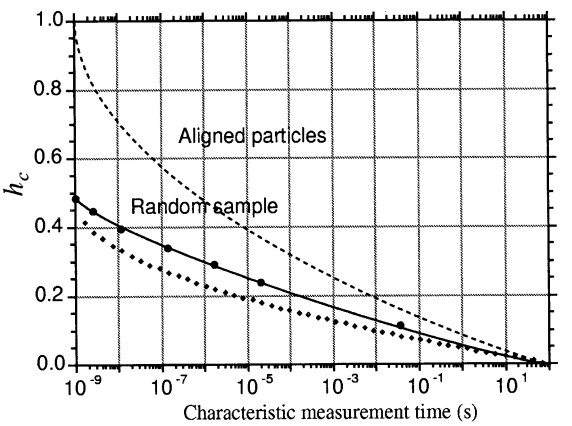

Fig. 8. Dependence of the coercive field on measurement time for the case of random easy axis orientations (assuming $t = T/2T_B = 0.5$).

and from Eq. (9)

$$h_c = 0.479 - 0.81\left(\frac{k_B T}{2KV}(\ln \tau_m + 20.7)\right)^{3/4} \quad (14)$$

plotting now h_c as a function of the new variable we obtain the desired result (see Fig. 8). In a long range of measurement times the dependence of the coercive field of the random sample is almost linear with $\log(\tau_m)$.

3. Conclusions

Combining the Stoner–Wohlfarth model with the Néel relaxation model the thermal dependence of the coercive field in a random system of identical noninteracting single-domain particles presenting uniaxial anisotropy has been calculated, generalizing the known $\sqrt{T}$ result.

The thermal dependence of coercivity varies depending on the orientation of the particles (the angle between the easy axis of anisotropy and the applied field). Particles oriented parallel to H experience a drop in coercivity proportional to $\sqrt{T}$, for $\psi \leqslant \pi/4$ the coercivity also drops continuously with temperature, but less dramatically. For bigger angles of orientation the coercive field should be practically temperature independent until the angle of orientation is such that the critical field equals the coercive field. For even bigger angles it begins to fall in the same way as it does in particles oriented to the complementary angle.

Random samples, show a decrease in coercivity with temperature, almost proportional to $T^{3/4}$ (not taking into account the intrinsic temperature dependence of basic parameters such as saturation magnetization or anisotropy constants).

At $T \neq 0$ K measured coercivity depends on the size of the particle, this is significant if the sample measured presents a size distribution. The model also allows the calculation of the dependence of coercivity with parameters like the measuring time or different kinds of anisotropies.

Lastly, we want to reiterate that both models, SW for low temperatures and the superparamagnetic for very small particles are widely used, but due to their strongly restrictive hypotheses and requirements one has to be very careful when interpreting the results using these models. Real samples can present size distributions, incoherent rotation modes and interactions between particles which can make the model inapplicable.

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