Magnetic Relaxation of Interacting Co Clusters: Crossover from Two- to Three-Dimensional Lattices

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The influence that dipole-dipole interactions exert on the dynamics of the magnetization of nanometer-sized Co clusters has been studied by means of ac and dc susceptibility experiments. These clusters grow in a quasiordered layered structure, where all relevant parameters can be tailored and measured independently. Our data show without ambiguity that the magnetic relaxation becomes slower as the degree of interaction increases. The effective activation energy increases linearly with the number of nearest neighbor clusters, evolving from the value for a 2D layer to the fully 3D behavior, which is nearly reached for five layers. The experimental results agree quantitatively with the predictions of a simple model.

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Recent advances in magnetic nanotechnology have made it possible to fabricate high-quality samples of magnetic nanoparticles with uniform material properties [1] and even self-organized lattices of nanoparticles [2,3]. These systems have received attention for fundamental research because they are ideal systems to study the properties of single particles as well as their mutual interactions [4,5].

For applications, it is also crucial to know how magnetic dipolar interactions modify the superparamagnetic relaxation rate. The importance of this effect is evident in high density recording media [6]. Unfortunately, experiments performed until now give different and even contradictory results [7,8]. It is usually very complicated to disentangle the influence of the dipole-dipole interactions from other effects, such as size-dependent anisotropy, cluster aggregation, direct exchange interactions, etc. Theoretical models are also not free from contradictions, predicting that the reversal of magnetic moments becomes either faster [8,9] or slower [7,10,11] as the dipolar interactions are switched on. In order to solve this long debated and complicated puzzle, experiments performed on simple systems are therefore highly desirable. It is the aim of this work to fill this gap.

In contrast with other samples, self-organized lattices of magnetic clusters enable quantitative studies of interactions and an external control over the relevant parameters. For our study, we have chosen samples of nanometer-sized spherical Co clusters prepared by sequential deposition of Al_2O_3 and Co layers on a Si substrate. A nice property of these granular multilayers is that it is possible to increase either the average number of neighbors to a given cluster, by increasing the number N of Co-Al_2O_3 bilayers, or the distance between Co layers, by changing the thickness $t_{Al_2O_3}$ of the alumina layers. It was found that the clusters exhibit a well defined in-plane local order, with constant interparticle distances, and a periodical vertical organization as shown in Fig. 1, which resembles that of a close-packed hexagonal structure [3]. We have observed that the effective activation energy for the relaxation U_{eff} increases linearly with the number of nearest neighbors and that, as a result, U_{eff} shows a rapid crossover as we move from the two-dimensional layer to the three-dimensional lattice.

The diameter of the clusters can be controlled between 0.7 and 10 nm by varying the amount of Co that is deposited per layer. This amount is given as the thickness t_{Co} that the Co layer would have if it was continuous. Structural and morphological characterization of the samples revealed that the clusters are formed by pure metallic Co with the fcc crystal structure (up to a diameter of 3 nm) and that there is no binding to the Al_2O_3 matrix [12]. We denote by $\Lambda_{\parallel}$ and $\Lambda_{\perp}$ the average distance between clusters in the same layer and the periodicity of the regular packing along the direction of growth, respectively (see Fig. 1). We have prepared samples with $t_{\text{Co}} = 0.7$ nm, $t_{Al_2O_3} = 3$ nm, and $N = 1, 2, 3, 5, 7, 10, 15, 20$ under identical ambient conditions. Another $N = 20$ multilayer was prepared with $t_{Al_2O_3} = 10$ nm. Finally, a single layer of Co was deposited on a carbon grid at the same time as the $N = 1$ sample and later used for TEM studies.

Magnetic measurements were performed using a commercial SQUID magnetometer. The characteristic time for each magnetization point measurement was 170 s. The ac susceptibility was measured by applying an oscillating field of small amplitude (4.5 Oe) to the sample and using the ac detection option of the same magnetometer. The frequency $\omega/2\pi$ of the ac magnetic field was varied between 0.1 Hz and 1.5 kHz. The samples had a small diamagnetic signal arising from the silicon substrate, which was estimated by measuring under identical conditions a bare substrate of the same batch and of approximately the same dimensions as the samples. It is linear in field and independent of the temperature and was subtracted from all

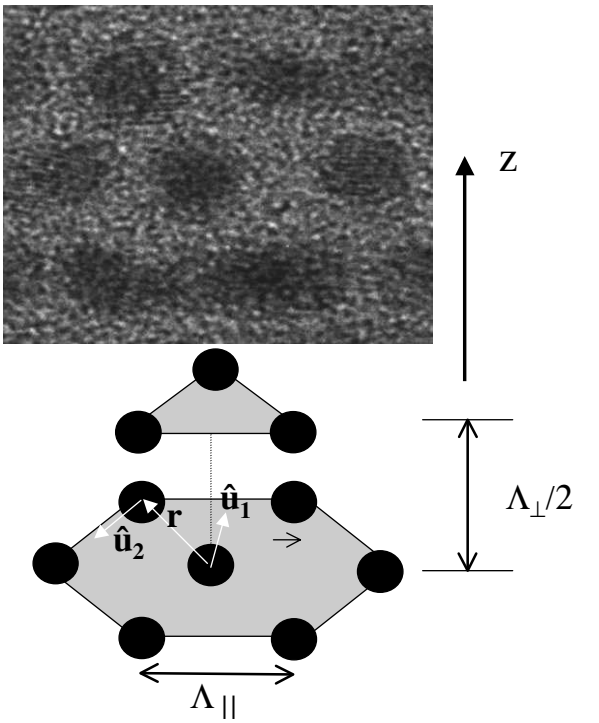

FIG. 1. Top panel: transmission electron microscopy (TEM) cross section of a multilayer, showing the quasiordered spatial arrangement of the Co clusters (dark circles). The lower panel is a schematic view of two layers shown in perspective (notice that only five of the clusters are visible in the TEM picture). In both cases, z is the direction along which the sample was grown.

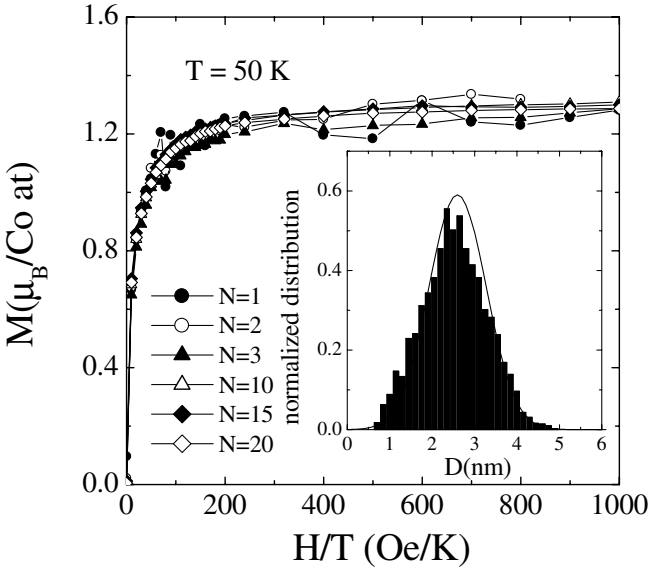

FIG. 2. Magnetization curves of some of the samples studied. The inset compares the size distribution determined from the magnetic data to the distribution directly obtained from the TEM pictures.

experimental data. In order to reduce the influence of the shape, all samples were cut with approximately the same shapes and dimensions and the magnetic field was always parallel to the layers.

The average size and the width of the size distribution can be experimentally determined by fitting the equilibrium magnetization M and susceptibility $\chi_{\rm eq}$ measured above the blocking temperatures [13]. We find that M is a function of H/T above 50 K and, as shown in Fig. 2, that data for different N fall on the same curve. The particle size distribution is moreover in good agreement with what was directly determined from the TEM pictures (see the inset of Fig. 2). The slope of the $1/\chi_{\rm eq}$ vs T curves is also the same (within the experimental uncertainties) for all samples. By contrast, the paramagnetic temperature θ increases as N increases going from 5 K for $N = 1$ to almost $\theta = 40$ K for $N = 20$. These results strongly suggest that it is possible to increase the degree of interaction between the particles while the size distribution is constant.

The ac susceptibility data show evidence for a superparamagnetic blocking at a temperature T_B, below which the magnetization curves start to show hysteresis. The blocking is caused by the progressive freezing of the magnetic moments along fixed directions. It takes place when the characteristic time τ for the reversal of the magnetic moment becomes of the order of the inverse angular frequency $1/\omega$. In Fig. 3, we show that the shift of T_B with ω is indeed well described by the Arrhenius law [15]

$$\ln(1/\omega) = \ln(\tau_0) + \frac{U_{\rm eff}}{k_B T_B}, \qquad (1)$$

where $U_{\rm eff}$ is an effective activation energy barrier that has contributions resulting from the magnetic anisotropy (U_0) and the dipole-dipole interactions with neighboring clusters ($U_{\rm int}$). We have recently studied [13] the magnetic

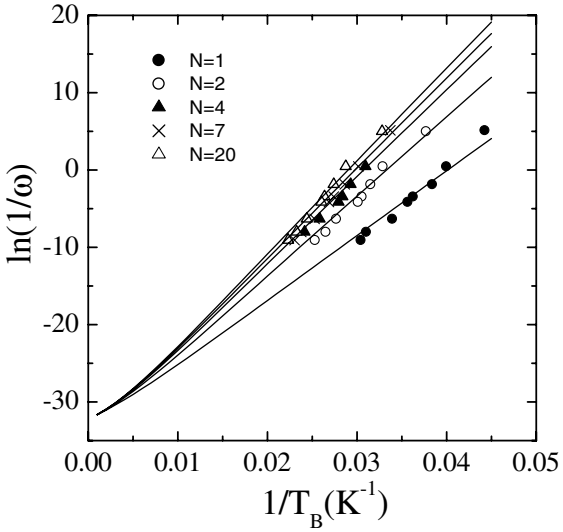

FIG. 3. Arrhenius plot of the measuring time $(1/\omega)$ as a function of the blocking temperature as obtained from χ' and zero-field-cooled dc susceptibility measurements. The lines are the results of numerical calculations made with Eqs. (3) and (4) and the parameters given in Ref. [14].

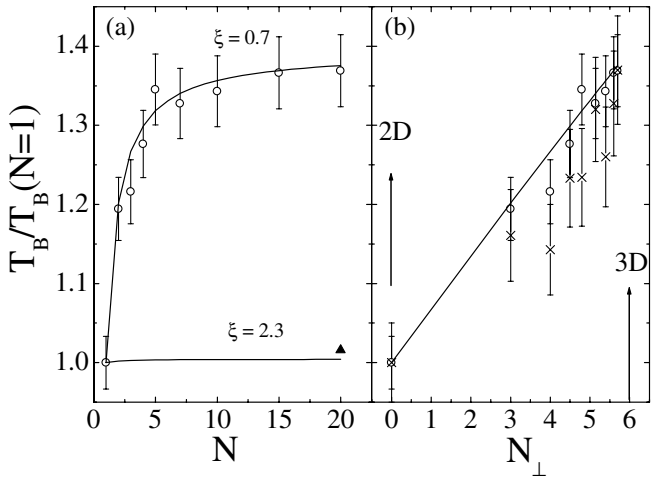

FIG. 4. (a) Variation of the blocking temperature (○, $t_{Al_2O_3} = 3$ nm; ▲, $t_{Al_2O_3} = 10$ nm) with the number of layers. T_B was obtained from χ' measured with a frequency $\omega/2\pi = 10$ Hz, and it has been normalized to the value for $N = 1$. (b) T_B [as in (a)] and the effective activation energy (×) as a function of the average number of nearest neighbors in adjacent layers. Full lines represent T_B calculated with the model described in the text (see also [14]).

anisotropy of these particles and found that it is enhanced with respect to the anisotropy of fcc Co and mainly dominated by the pinning of the atomic moments located at their surface.

In Fig. 4(a), we show how T_B varies with N. The same qualitative behavior was observed also for the dc and for the out-of-phase χ'' component of the ac susceptibility, although the uncertainty in the absolute values was larger in the latter case. T_B increases with N very rapidly for $N < 5$ and then reaches a plateau that is about 30% higher than for a single 2D layer. The rapid saturation with the number of layers indicates that the phenomenon is mainly dictated by the interaction with the nearest neighbors. This can be more clearly seen in Fig. 4(b), where we have plotted the same experimental data against the average number $N_\perp$ of nearest neighbors that each cluster has in adjacent layers. For an hcp type of arrangement (cf. Fig. 1), $N_\perp$ equals $6\frac{N-1}{N}$ and therefore saturates very rapidly to the 3D-limit value ($N_\perp = 6$) as N increases. In Fig. 4(b) we also plot U_{eff} values obtained from the best fit of Eq. (1) to the frequency dependence of T_B, shown in Fig. 3. The fact that both T_B and U_{eff} increase almost linearly with $N_\perp$ shows unambiguously that the reversal of the magnetic moments becomes slower as the strength of the dipolar interaction increases.

In Fig. 4(a) we have also plotted T_B of the sample with 20 layers separated by thicker layers of alumina. The blocking temperature is, for this case, only 2% larger than for a single layer. This supports the interpretation that dipole-dipole interactions between neighboring layers cause the observed increase of T_B with N.

In the remainder of the Letter, we try to give a more quantitative account to the observed behavior. Our approach is inspired by the theoretical model of Dormann *et al.* [7] (see also Ref. [16]). When the magnetic moment of a given cluster flips, the energy of a neighbor spin changes by an amount that equals their mutual dipolar interaction energy. Therefore, before the central spin reverses again, the magnetization of the nearest neighbors is polarized by the new local dipolar field. We write the relaxation time as for independent clusters, but modified by the interaction energy:

$$\tau_\pm = \tau_0 \exp\left(\frac{U_0 \pm E_{\text{dip}}}{k_B T}\right), \tag{2}$$

where + and − correspond, respectively, to reversal against or towards the local dipolar field created by the neighbors, which leads to either an increase or a decrease of energy by the amount E_{dip}. In our model, we simply assume that the neighbors have time to relax to their equilibrium; thus the relaxation time is always longer than for noninteracting spins. U_{int} just equals the interaction energy E_{dip} with magnetic moments, located in the same ($U_\parallel$) or in different layers ($U_\perp$), polarized by the central spin. We make the simplifying assumption that all magnetic moments rapidly precess around their *local* easy axes $\mathbf{u}$, which are randomly oriented. The model does not fix any privileged orientation in space, common to all particles, because the experimental data were measured at zero or low applied field. Using the definition of vectors given in Fig. 1, $U_\parallel$ and $U_\perp$ can be written as follows:

$$U_\parallel = N_\parallel \left\langle x \tanh\left(\frac{x}{k_B T}\right)\right\rangle, \tag{3}$$

$$U_\perp = \frac{N_\perp}{(\xi^2 + 1/3)^{3/2}} \times \left\langle x \tanh\left[\frac{x}{k_B T(\xi^2 + 1/3)^{3/2}}\right]\right\rangle + \epsilon(1/r^6), \tag{4}$$

where $x = [3(\hat{u}\hat{r})(\hat{r}\hat{u}') - \hat{u}\hat{u}']\mu^2/\Lambda_\parallel^3$, μ is the magnetic moment of a cluster, $N_\parallel \approx 6$ is the average number of neighbors in the same plane, and $\xi = \Lambda_\perp/2\Lambda_\parallel$. Averages $\langle\rangle$ are taken over random orientations of the unit vectors $\hat{\mathbf{u}}$, $\hat{\mathbf{u}}'$, and $\hat{\mathbf{r}}$ in an octant.

According to Eqs. (3) and (4), $U_\parallel$ and $U_\perp$ are proportional to $N_\parallel$ and $N_\perp$, in agreement with the experiments. Moreover, the contribution to U_{int} of the interaction with particles located in more distant layers falls off with distance as $1/r^6$ and can therefore be safely neglected. This is in agreement with the observed rapid crossover from the 2D to the 3D lattices and also with the fact that the sample with $t_{Al_2O_3} = 10$ nm remains in the 2D limit. Indeed, from Eq. (4) it follows that the interaction between layers is dominant for $\xi < 0.8$, but it must be relatively unimportant for a sample with $\xi > 0.8$. It is therefore possible to prepare densely packed layers that relax as in

the 2D limit, provided that $\Lambda_\parallel$ is smaller than the separation $\Lambda_\perp/2$ between them.

The parameters that determine $U_{\rm int}$ can be estimated from independent experiments. When the particles are not identical, as is the case for our samples, $U_{\rm eff}$ is the effective energy of those particles which contribute most to χ'. It is then usual [4] to evaluate $U_{\rm eff}$ for those particles having a volume equal to $\int V^2 g(D)\,dD / \int V g(D)\,dD$. Using the size distribution previously obtained (see Fig. 2), this expression gives a diameter equal to 3.5 nm. The surface anisotropy of these particles induces a barrier $U_0 \simeq 550{-}670$ K [13]. The analysis of the TEM pictures gives $\Lambda_\parallel \approx \langle D\rangle + 2(\pm 0.5)$ nm, where $\langle D\rangle \simeq 2.9$ nm is the average particle diameter [12]. Finally, $\Lambda_\perp$ was estimated from grazing incident small-angle x-ray scattering experiments (GISAXS), which give $\xi \simeq 0.7$ [3]. Using this value, we also estimate that $\xi \simeq 2.3$ for the sample with $t_{Al_2O_3} = 10$ nm. We have fitted our data by slightly varying U_0 and $\Lambda_\parallel$ (or equivalently $\mu^2/\Lambda_\parallel^3 U_0$) within their experimental error bars. The best agreement with the experimental results was found for $550\ {\rm K} < U_0 < 570\ {\rm K}$ and, correspondingly, $0.17 > \mu^2/\Lambda_\parallel^3 U_0 > 0.15$ [14]. In the neighborhood of T_B this gives $U_\parallel \simeq 250$ K and $U_\perp \simeq 300$ K; that is, $U_{\rm int}$ can be up to 50% of the total $U_{\rm eff}$ [17].

In Fig. 4, we compare the blocking temperatures calculated with Eqs. (1), (3), and (4) to the experimental results. As expected, the model predicts that T_B saturates to a constant value for large N and, despite its simplicity, gives a good quantitative account of the measured data. As an additional test of the model, we have also calculated the frequency dependence of T_B [14], which accounts reasonably well for the observed variation for all values of N [see Fig. (3)].

Concluding, the experiments show unambiguously that dipole-dipole interactions between magnetic nanoparticles slow down the reversal of their magnetic moments. We have found that the effective energy barrier increases linearly with the number of nearest neighbor clusters, changing from the 2D limit to the 3D value that is nearly fully realized for $N = 5$ layers. For the first time, it has been possible to tailor the relevant parameters: particle size distribution, number of neighbors, and their distances, which determine the influence of the interactions. This unique property of the samples gives the opportunity to test existing models and shows that it is possible to account reasonably well for the observed behavior.

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[17] Note that averaging over orientations of the easy axes and the thermal fluctuations [see Eqs. (3) and (4)] reduce $U_\parallel$ and $U_\perp$ significantly from their maximum values $6\mu^2/\Lambda_\parallel^3 \simeq 600$ K and $6\mu^2/(\xi^2 + 1/3)^{3/2}\Lambda_\parallel^3 \simeq 800$ K, respectively.