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Hysteresis of cobalt nanoparticles organized in a two-dimensional network: dipolar interaction effects

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Abstract

The hysteresis curve at very low temperature of Co nanoparticles organized in a two-dimensional network on a graphite substrate is determined both experimentally and from a numerical calculation. The Co particles are modeled as spherical particles of uniaxial symmetry and the easy axes are randomly distributed. We focus on the effect of the dipolar interactions between particles on the hysteresis loop: the magnetization curve is thus compared to the case of non-interacting particles, which corresponds to particles dispersed in solution at vanishing concentration. The magnetization curve is calculated for two orientations of the applied field: normal and parallel to the substrate surface. The ratio between the remanence magnetizations obtained with the field, normal and parallel to the surface, appears to be a convenient parameter to estimate the importance of the dipolar interactions. A satisfactory agreement with experiment is obtained for this ratio.

Keywords: Magnetism; Nanoparticles; Numerical calculations

1. Introduction

Different methods are now available to synthesize nanosized Co particles, which are then monodomain magnetic particles [1–6]. It is, moreover, possible to obtain coated Co particles, which can either be dispersed in a solvent or deposited on a substrate [1,2,5]. In particular, the synthesis in reverse micelles' solution provides a soft chemical way to obtain such particles [1–5]. When the particles are deposited on a graphite substrate, self-organized monolayers, presenting a hexagonal structure are formed [1,2,5]. For coated particles, the distance of closest approach between particles is sufficient for the interaction to be mainly of magnetostatic character. In this case, the comparison of the magnetic properties, corresponding to particles dispersed in the solvent or deposited on the substrate, is a relevant way to estimate the interactions between particles.

The influence of the interactions between nanoparticles on the magnetic properties has been studied in different situations. In three-dimensional systems, the magnetic properties, in terms of the concentration in particles, for instance, for γ-Fe_2O_3 particles embedded in a polymer, have been investigated experimentally [7–11] and theoretically. On another hand, Monte Carlo simulations for three-dimensional random dispersions of Stoner–Wohlfarth

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particles with random distribution of the easy axes are available [12–14]. In two dimensional systems, the dipolar interactions have been investigated for films including strongly oriented ferromagnetic particles (see for instance Refs. [15–17]), and a two dimensional random field Ising model including dipolar interactions, adapted to these later situations, has been developed [18].

In this paper, the magnetization curve at very low temperature (3 K) of Co particles deposited on a graphite substrate and organized in a two-dimensional network is investigated. The Co particles are synthesized from the reverse micelles technique [19] from which coated Co nanoparticles of diameter ca. 6 nm are obtained [1,2]. The system is frozen at zero field. The magnetization curves for the particles dispersed in the solvent or deposited on the substrate are measured; in the later case, the two orientations of the field, normal and parallel to the substrate, are considered. The numerical calculations are performed on a two-dimensional lattice of Stoner–Wohlfarth particles with a random distribution of easy axes. A simple analysis in terms of demagnetizing field is shown to fit well the numerical calculations, at least in the case of weak coupling between particles. The ratio of the remanence magnetizations, corresponding to the field, normal and parallel to the substrate surface, is found to be a convenient measure of the importance of the dipolar interactions, and a satisfactory agreement is obtained between the numerical calculations and the experiment.

2. Numerical calculations

We calculate the magnetization in the direction of the applied field for an assembly of particles organized on a well-defined two-dimensional lattice of either square or hexagonal structure. The surface plane is the $(\hat{x}, \hat{y})$ plane and the $\hat{z}$-axis is the normal to the surface; the applied field is either normal or parallel to the surface plane. No thermal effect is included since we focus on the very low temperature limit (3 K) of the hysteresis loop. We consider a monodisperse system of spherical particles of uniaxial symmetry (Stoner–Wohlfarth particles [20,21]). The particles are located at the sites (labeled k) of the lattice and the easy axes, $\hat{n}_k$, are randomly distributed since we model a system frozen at zero field. The case of non-interacting particles corresponds to particles randomly dispersed in the solvent at vanishing concentration. The particles are characterized by an anisotropy constant K, a bulk saturation magnetization M_s, and a volume $v_o = (\pi/6)D^3$, where D is the particle diameter. The energy of a particle located at site k is given by

$$E_k = -Kv_o\left(\hat{n}_k\,\hat{\mu}_k\right)^2 - H_{\mathrm{eff}}(k)\,\mu_k\cos(\Psi_k - \Theta_k) \tag{1}$$

where $H_{\mathrm{eff}}(k)$ is the effective magnetic field felt by the particle, $\mu_k = M_s v_o\,\hat{\mu}_k$ is the magnetic moment of the particle, Θ_k and Ψ_k are the angles $(\hat{\mu}_k, \hat{n}_k)$ and $(\hat{n}_k, \hat{H}_{\mathrm{eff}}(k))$, respectively. Here and in the following, circumflexes denote unit vectors. The effective magnetic field at site k is the sum of the applied field, H_a, and the total dipolar field

$$H_{\mathrm{eff}}(k) = H_a + \left(\frac{\mu}{d^3}\right)\sum_{j\neq k}\frac{3\left(\hat{\mu}_j\hat{\mathbf{r}}_{jk}\right)\hat{\mathbf{r}}_{jk} - \hat{\mu}_j}{\left(r_{jk}/d\right)^3}$$

$$\equiv H_a + \left(\frac{\mu}{d^3}\right)\sum_{j\neq k} h_{\mathrm{dip}}(jk) \tag{2}$$

where $\hat{\mathbf{r}}_{jk}$ is the unit vector in the direction joining particles j and k, and d is the nearest neighbor distance. For convenience, we deal with the reduced effective field

$$h_{\mathrm{eff}}(k) = \frac{H_{\mathrm{eff}}(k)}{H_K} = \hat{h}_a h_a + \alpha_d\sum_{j\neq k} h_{\mathrm{dip}}(j,k) \tag{3}$$

where $H_K = (2K/M_s)$ is the usual anisotropy field and the coupling constant α_d is given by

$$\alpha_d = \frac{\pi}{12}\frac{M_s^2}{K}(D/d)^3. \tag{4}$$

The configuration of the magnetic moments orientations $\{\hat{\mu}_k\}$ is determined from the minimization of the total energy of the system. This is done first by setting $\hat{\mu}_k$ in the plane defined by $\hat{h}_{\mathrm{eff}}(k)$ and $\hat{n}_k$, and secondly, by determining the angle Θ_k from the local equilibrium condition [20,21]

$$\frac{\partial E_k}{\partial\Theta_k} = 0; \quad \frac{\partial^2 E_k}{\partial\Theta_k^2} > 0. \tag{5}$$

This leads to either one or two solutions, $\Theta^{(u)}$ and $\Theta^{(d)}$, corresponding to the ''up'' and ''down'' states, respectively, according to the magnitude of the effective field and to the orientation of the easy axis of the site k.

The calculation is performed on a grid including N_s sites and the long-ranged character of the dipolar field is accounted for by considering eight neighboring grids deduced from the one on which the calculation is actually done by periodicity. We start from a totally saturated state, where $\hat{\mu}_k = \hat{h}_a$ for all k, and therefore, where the dipolar field is in the direction of the applied field, $\hat{h}_a$, and takes the same value for all the sites. Then, the magnitude of the applied field is decreased, all the sites are examined in a random order, and the corresponding $\hat{\mu}_k$ are determined according to Eq. (5). After each variation of the value of a moment, say $\hat{\mu}_{k_o}$ at site k_o, the dipolar fields at all the sites $k \neq k_o$ are updated. Then, the list of the sites where the deviation $\delta\hat{\mu}_k$ of $\hat{\mu}_k$ from its new equilibrium position, i.e. calculated with the updated dipolar field, such that $|\delta\hat{\mu}_k| > \varepsilon$ is updated, and we chose a new site k_o from this list. The process is performed iteratively until the maximum value of the magnitude of the deviation of the $\hat{\mu}_k$ from their equilibrium state is less than a threshold value, $\varepsilon = 10^{-3}$. We finally determine the total magnetization in the direction of the applied field per site, normalized by the saturation magnetization M_s in terms of the applied field

$$M(h_a) = \frac{1}{N_s} \sum_k \hat{\mu}_k \hat{h}_a. \quad (6)$$

The computing time of such numerical calculations is very large; accordingly, in order to perform calculations of the hysteresis loops on large systems, we have also considered a simple approximation, referred to in the following as the scalar approximation, where only the component in the direction $\hat{h}_a$ of the total dipolar field on all sites k is taken into account: then only a scalar variable namely, $\cos(\Psi_k - \Theta_k)$, has to be calculated on each site.

3. Experimental procedure

The synthesis of the Co particles is performed as described in preceding papers [1,2]. These particles are obtained by mixing two micellar solutions characterized by the same diameter (3 nm): the first one contains 10^{-2} M $Co(AOT)_2$ and the second one 2×10^{-2} M sodium tetrahydroboride ($NaBH_4$). After mixing, stable colloidal particles are formed and are then extracted from the reverse micelles under anaerobic conditions by covalent attachment of lauric acid. After this surface passivation, the cobalt particles are stable under air and could be easily redispersed in hexane [2]. The nanoparticles have been characterized by X-ray diffraction and small angles X-rays scatterings. From these analysis it is concluded that the nanoparticles are spherical and consist of metallic fcc Co [2].

Deposition of a drop of solution on a carbon grid makes it possible to observe a large coverage of particles, locally arranged in a hexagonal network [1,2]. Their average size is 5.8 nm with a narrow size distribution (11%).

At 3 K, the particles are ferromagnetic. Magnetization curves are recorded for particles deposited on a graphite substrate (HOPG) and under an external field either normal or parallel to the substrate surface.

4. Results and discussion

Fig. 1 clearly shows a change in the shape of the hysteresis loop depending on the orientation of the substrate relative to the applied magnetic field: when the substrate is parallel to the field, the remanence to saturation magnetization ratio is 0.28. The hysteresis loop is squarer (Fig. 1) than that obtained with the particles dispersed in solution. In apposition to what is observed under a parallel-applied field, the hysteresis loop is smooth when the applied field is perpendicular to the substrate (Fig. 1). The remanence to saturation magnetization ratio is 0.21. For any applied field direction, saturation magnetization is reached at 2 T and is 110 emu/g.

Under any experimental conditions, the coercive field does not change significantly and is 0.07 T. The saturation magnetization remains unchanged (110 emu/g).

The parameters needed for the calculation are the bulk characteristics of the nanoparticle materials, M_s

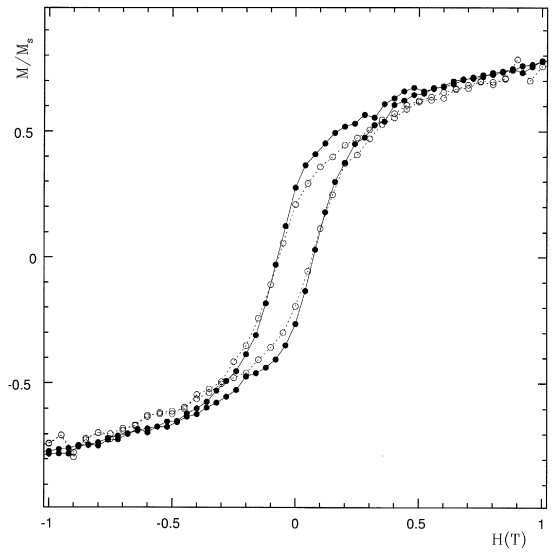

Fig. 1. Experimental hysteresis curves for the particles deposited on the graphite substrate. Solid circles: applied field parallel to the surface; open circles: applied field normal to the surface. The lines are guides for the eye.

and K, the particles diameter, D, and the nearest neighbor distance, d. We take $K = 2.5 \times 10^6$ ergs/cm^3, which has been obtained from zero-field cooled magnetization measurements [2], and is very close to the value of fcc bulk cobalt [21,22]. Moreover, this value is in agreement with the experimental results reported in Ref. [3]. The saturation magnetization of bulk fcc Co is $M_s = 162$ emu/g, leading to $\alpha_d = 0.2118(D/d)3$; in our nanoparticles, M_s takes a smaller value, and this reduces the coupling constant. The value of the mean diameter of the particles is typically $D = 5$–7 nm, and the corresponding nearest neighbor distance range is $d = 7$–9 nm. With $M_s = 162$ emu/g, we get α_d in between 0.075 and 0.10; therefore, we can consider $\alpha_d \approx 0.10$ as a maximum value for the coupling constant of such monolayers of coated Co nanoparticles. All the calculations have been performed with $N_s = 625$ sites. The convergence of the results with respect to N_s for the perfect lattice has been obtained for $N_s \geq 400$.

The hysteresis loops corresponding to $\alpha_d = 0.10$ and the two orientations of the applied field are shown and compared to the non-interacting case ($\alpha_d = 0$) in Fig. 2. At a qualitative level, the important result is that the hysteresis loop is sharper than that corresponding to the isolated particles ($\alpha_d = 0$) when the applied field is parallel to the surface, while it is smoother and tilted when the applied field is normal to the surface.

This result can be explained in terms of demagnetizing fields effects; however, since we do not deal with a uniform medium, some care must be taken. First, we introduce the effective macroscopic field, $H_M = H_a + H_d$, where $H_d = -4\pi L M_v$ denotes the demagnetizing field, L is the demagnetizing factor (for a sphere $L = 1/3$, and for a film normal to the z axis, $L_x = L_y = 0$ and $L_z = 1$) and M_v is the magnetization per volume unit. Here, H_d represents the effect of the magnetization of the system, replaced by a continuous medium uniformly magnetized. In order to approximate the field felt by a particle at a given site k, we must take into account the discreteness of the system. For this, we consider a sphere S, centered on site k, calculate the dipolar field, say Σ_{dip}, due to the particles located inside this sphere, and subtract the corresponding continuum contribution, $H_d^{(s)} = -(4\pi/3)M_v$. Notice that the sphere S must be sufficiently large for the part of the system located outside of it to be considered as a macro-

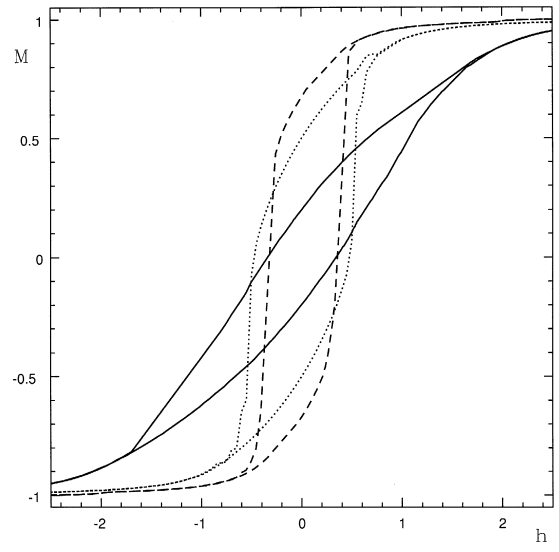

Fig. 2. Calculated hysteresis curves on an hexagonal lattice. Dotted line: $\alpha_d = 0$; solid line: $\alpha_d = 0.10$ and applied field normal to the surface; dashed line: $\alpha_d = 0.10$ and applied field parallel to the surface.

scopic medium. The effective field is then $H_{\mathrm{eff}} = H_{\mathrm{a}} - 4\pi M_{\mathrm{v}}(L - 1/3) + \Sigma_{\mathrm{dip}}$. Our system is a limiting case, where the only sphere which can be centered on a site and still included in the system is a sphere including only the considered site. Therefore, Σ_{dip} exactly vanishes and we have $H_{\mathrm{eff}} = H_{\mathrm{a}} - 4\pi M_{\mathrm{v}}(L - 1/3)$. The magnetization M_{v} per unit volume is related to the reduced magnetization per particle via the number density of sites, ρ by $M_{\mathrm{v}} = \rho M_{\mathrm{s}} v_{\mathrm{o}} M$. We assume that the monolayer is taken from a regular three-dimensional lattice; therefore, ρ is that of the sc ($\rho = 1/d^3$), and of the fcc ($\rho = \sqrt{2}/d^3$) 3-D lattices for the monolayers of square and the hexagonal structure, respectively. By taking into account only the demagnetizing field effect, we thus deduce the following simple approximation for the magnetization curve

$$M(h_{\mathrm{a}}) = M_{\mathrm{is}}\big(h_{\mathrm{a}} - 4\pi(L - 1/3)\, a\alpha_d M(h_{\mathrm{a}})\big) \quad (7)$$

where $M_{\mathrm{is}}(h)$ is the magnetization per particle of the non interacting case, $a = 1$ and $a = \sqrt{2}$ for the square and the hexagonal lattices, respectively. In Fig. 3, we compare the result of Eq. (7) to that of the complete calculation for the square lattice in the case $\alpha_{\mathrm{d}} = 0.10$. Eq. (7) is a good approximation for $M(h_{\mathrm{a}})$, at least in the weak coupling limit, and this shows that, for rather small values of the coupling constant α_{d}, the modification of the hysteresis loop due to the dipolar interactions can be explained mainly in terms of the demagnetizing field effect. However, Eq. (7) cannot reproduce the variation of the coercive field, h_{co}, with the dipolar interactions which, although rather small, is not negligible at $\alpha_{\mathrm{d}} = 0.10$. On the other hand, from the complete calculation of the magnetization curve, we get a result for the variation of h_{co} with respect to α_{d} in the case of the square lattice, comparable to those of the Monte Carlo simulations for three-dimensional random distributions of Stoner–Wohlfarth particles [13,14]; moreover, the variation of h_{co} is independent of the orientation of the applied field. In any case, for the values of α_{d} corresponding to the monolayers of Co particles, we are interested in, we expect only a very small change in h_{co}.

By using our scalar approximation, we have performed calculations on systems including $N_{\mathrm{s}} = 2500$ sites. From these calculations, we can take into account the presence of vacancies observed in the experimental samples, by introducing in the lattice a fraction, f_{d}, of unoccupied sites chosen randomly. Although we have no theoretical way for representing the effect of the vacancies, we find that the effect of f_{d}, at least for $f_{\mathrm{d}} \leq 0.30$, is very well reproduced by the introduction of an effective coupling constant given by

$$\alpha_{\mathrm{eff}} = \alpha_{\mathrm{d}}(1 - f_{\mathrm{d}}^{x}) \quad \text{with} \quad x = 1.15. \quad (8)$$

To estimate at a quantitative level the effect of the dipolar interactions on the magnetization of the system, we focus on the remanence magnetization M_{r} in terms of α_{d} for the two orientations of the field. We examine the behavior, with the value of the coupling constant α_{d}, of $M_{\mathrm{r}}/M_{\mathrm{s}}$ and of the ratio $\gamma = M_{\mathrm{r}}^{\perp}/M_{\mathrm{r}}^{\parallel}$, where $M_{\mathrm{r}}^{\perp}$ and $M_{\mathrm{r}}^{\parallel}$ are the values of the remanence magnetization for the applied field, normal and parallel to the surface, respectively. The result for γ is shown in Fig. 4. The ratio γ appears to be the relevant variable to test the importance of the dipolar interactions since it is expected to depend mainly on the value of the coupling constant α_{d} and not on the precise shape of the hysteresis loop;

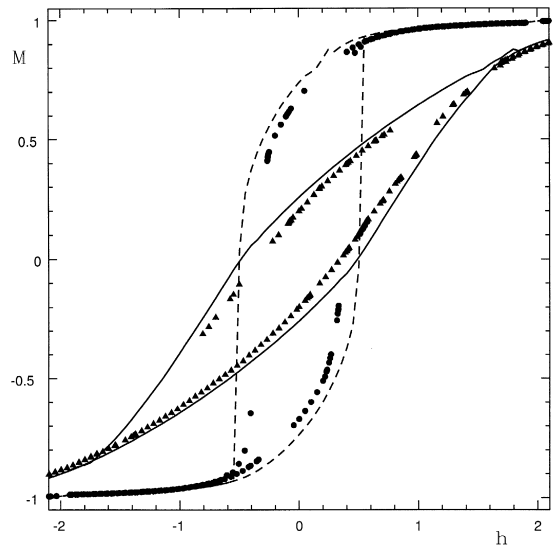

Fig. 3. Comparison of the full calculation with the approximation given by Eq. (7) for hexagonal lattice, and $\alpha_{\mathrm{d}} = 0.10$. Solid line and dashed lines: Eq. (7) with the field, normal and parallel to the lattice plane, respectively. Solid points and triangles: result of the full calculation for the field, normal and parallel to the lattice surface, respectively.

moreover, it does not depend on the value of the saturation magnetization M_s since the experimental values of $M_r^{\perp}$ and $M_r^{\parallel}$ are determined on the same sample.

The mean diameter of the particles is $D = 6$ nm, and the nearest neighbor distance is $d \approx 8.5$ nm. This leads to a coupling constant $\alpha_d = 0.035$. Assuming a fraction of vacancies of approximately $f_d = 0.20$, we obtain, from Eq. (8), an effective coupling constant $\alpha_d = 0.030$. The corresponding calculated hysteresis loops are shown in Fig. 5. Concerning the effect of the orientation of the applied field relative to the sample surface, the calculated and the experimental curves are in agreement at a qualitative level. In particular, the coercive field is found to be nearly independent of the orientation of the field. The comparison, at a quantitative level, with the experiments is not easy, since the shape of the experimental hysteresis loop does not coincide with that of the assembly of Stoner–Wohlfarth particles. Indeed, the saturation is obtained for higher fields, and the coercive field is much lower than that of the Stoner–Wohlfarth particles, for which we get $H_{co} = 0.252$ T, with $M_s = 110$ emu/g. On the other hand, the ratio γ, defined above, is a relevant measure of the effect of the deviation of the hysteresis loop due to the orientation of the applied field. For a coupling constant $\alpha_d \approx 0.030$, we expect a value $\alpha \approx 0.76$ (see Fig. 4); this is in good agreement with the experiment since the experimental value is $\gamma^{exp} = 0.75 \pm 0.08$. From another deposit of similar Co particles, also organized in hexagonal network, and characterized by: $D = 8.5$ nm, $d = 10.5$ nm, and $M_s = 120$ emu/g, $M_r^{\perp}/M_s = 0.40$ and $M_r^{\parallel}/M_s = 0.60$ have been obtained [23]. For this sample, we have $\alpha_d \approx 0.05$, leading to $\gamma = 0.60$ while $\gamma^{exp} \approx 0.66$. Therefore, we can conclude that the difference we get in the hysteresis loops with the two orientations of the applied field are mainly due to the dipolar interactions between particles.

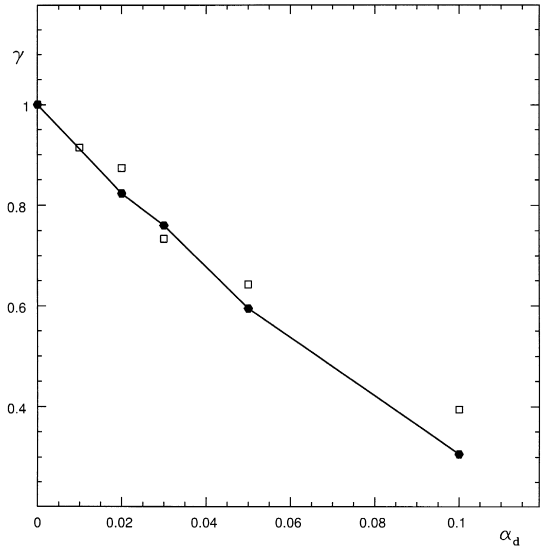

Fig. 4. Ratio γ in terms of α_d. Squares: square lattice; hexagons: hexagonal lattice. The lines are guides for the eye.

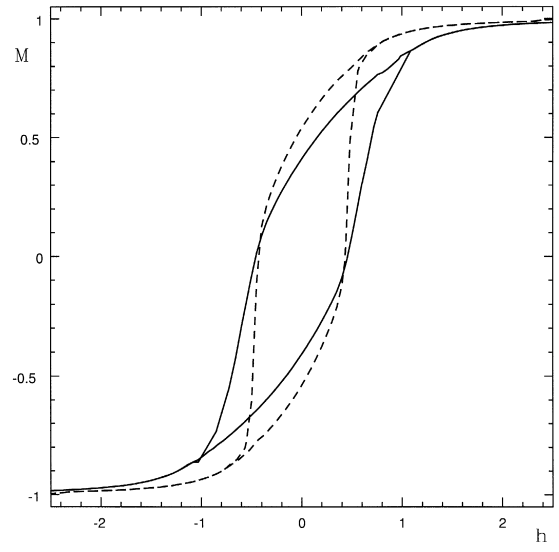

Fig. 5. Calculated hysteresis curves on a hexagonal lattice. Dotted line: $\alpha_d = 0$; solid line: $\alpha_d = 0.03$ and applied field normal to the surface; dashed line: $\alpha_d = 0.03$ and applied field parallel to the surface.

5. Conclusion

In the present work, we have studied both experimentally and theoretically the hysteresis curve of two-dimensional self-organized monolayers of nanosized Co particles. We especially focused on the effect of the orientation of the applied field relative to the sample surface. From the calculation of the hysteresis loop, we can conclude that, as a direct consequence of the random distribution of the easy

axes of the particles, the difference of the hysteresis curves as measured with an applied field parallel or normal to the sample surface is mainly due to the dipolar interactions between particles. We have shown that this can be explained in terms of demagnetizing field effects. The comparison between the experimental and the numerical results can be done through the ratio γ of the remanence magnetizations, as measured with the applied field, normal and parallel to the sample surface, respectively. For γ, we get a satisfactory agreement between the calculated and the experimental results.

References

[1] C. Petit, A. Taleb, M.P. Pileni, Adv. Mater. 10 (1998) 259.
[2] C. Petit, A. Taleb, M.P. Pileni, J. Phys. Chem. B 103 (1999) 1805.
[3] J.P. Chen, C.M. Sorensen, K.J. Klabunde, G.C. Hadjanayis, Phys. Rev. B 51 (1995) 11527.
[4] X.M. Lin, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, Langmuir 14 (1998) 7140.
[5] S. Sun, C.B. Murray, J. Appl. Phys. 85 (1999) 4325.
[6] M. Respaud, J.M. Broto, H. Rakoto, A. Fert, L. Thomas, B. Barbara, M. Verelst, E. Snoeck, P. Lecante, A. Mosset, J. Ossuna, T. Ould Ely, C. Amiens, B. Chaudret, Phys. Rev. B 57 (1998) 2925.
[7] J.L. Dormann, L. Spinu, E. Tronc, J.P. Jolivet, F. Lucari, F. D'Orazio, D. Fiorani, J. Magn. Magn. Mater. 183 (1998) L255.
[8] J.L. Dormann, R. Cherkaoui, L. Spinu, M. Noguès, F. Lucari, F. D'Orazio, D. Fiorani, A. Garcia, E. Tronc, J.P. Jolivet, J. Magn. Mgn. Mater. 187 (1998) L139.
[9] M. El-Hilo, K. O'Grady, R.W. Chantrell, J. Magn. Magn. Mater. 114 (1992) 295.
[10] S. Mørup, E. Tronc, Phys. Rev. Lett. 72 (1994) 3278.
[11] J.L. Dormann, L. Bessais, D. Fiorani, J. Phys. C 21 (1981) 2015.
[12] J.O. Andersson, C. Djurberg, T. Jonsson, P. Svedlindh, P. Nordblad, Phys. Rev. B 58 (1997) 13983.
[13] M. El-Hilo, R.W. Chantrell, K. O'Grady, J. Appl. Phys. 84 (1998) 5114.
[14] D. Kechrakos, K.N. Trohidou, Phys. Rev. B 58 (1998) 12169.
[15] J.G. Zhu, N.H. Bertram, J. Appl. Phys. 66 (1989) 1291.
[16] G. Bottoni, D. Candolfo, A. Cecchetti, J. Appl. Phys. 85 (1999) 4729.
[17] A. Magni, Phys. Rev. B 59 (1999) 985.
[18] M.P. Pileni, J. Phys. Chem. 97 (1993) 6961.
[19] E.C. Stoner, E.P. Wohlfarth, Philos. Trans. R. Soc. London, Ser. A 240 (1948) 599.
[20] H. Pfeiffer, Phys. Status Solidi A 122 (1990) 377.
[21] W. Sucksmith, J.E. Thompson, Proc. R. Soc. London 225 (1954) 362.
[22] W.D. Doyle, P.J. Flanders, in: Proceedings of the International Conference on Magnetism, Nottingham,1964, p. 751.
[23] J. Legrand, C. Petit, D. Bazin, M.P. Pileni, to be published.