

Magnetic Anisotropy of a Single Cobalt Nanocluster

M. Jamet,¹ W. Wernsdorfer,² C. Thirion,² D. Mailly,³ V. Dupuis,¹ P. Mélinon,¹ and A. Pérez¹

¹*DPM-Université Claude Bernard-Lyon 1 et CNRS, 69622 Villeurbanne, France*

²*Laboratoire Louis Néel-CNRS, BP 166, 38042 Grenoble, France*

³*L2M-CNRS, 196 avenue H. Ravera, 92220 Bagneux, France*

(Received 4 December 2000)

Using a new micro-SQUID setup, we investigate magnetic anisotropy in a single 1000-atom cobalt cluster. This system opens new fields in the characterization and understanding of the origin of magnetic anisotropy in such nanoparticles. For this purpose, we report three-dimensional switching field measurements performed on a 3 nm cobalt cluster embedded in a niobium matrix. We are able to separate the different magnetic anisotropy contributions and evidence the dominating role of the cluster surface.

DOI: 10.1103/PhysRevLett.86.4676

PACS numbers: 75.30.Gw, 75.50.Tt, 81.07.-b

Magnetic nanostructures are subjects of growing interest because of their potential applications in high density magnetic recording media [1] and their original magnetic properties [2]. Because of the limited sensitivity of conventional magnetic characterization techniques [3], most of the experimental studies on nanosized grains were carried out on large assemblies of particles [4], where distributions of particle sizes, shapes, and defects rendered the interpretations quite difficult. From a fundamental point of view, we present in this Letter the first magnetization reversal measurement performed on individual cobalt clusters containing about 1000 atoms. A new micro-SQUID setup [3] measures the three-dimensional (3D) diagram of the magnetization switching fields which is described with a uniform rotation model. We deduce the magnetic anisotropies of such individual nanoparticles which are dominated by surface anisotropy.

In bulk magnetic materials (3D), magnetostatic and bulk magnetocrystalline energies are the main sources of anisotropy, whereas in low-dimensional systems such as thin films (2D), wires (1D), or clusters (0D) strong interfacial effects are expected [2,5,6]. Only experiments on a single cluster can provide information on the different contributions to the magnetic anisotropy. Here we present the first magnetic measurements on individual cobalt clusters of 3 nm in diameter. High resolution transmission electron microscopy (HRTEM) performed on Co clusters deposited on carbon coated copper grids showed that they are well crystallized in the fcc structure (Fig. 1a) with a sharp size distribution (3–4 nm). Similar cobalt clusters are then embedded in a thin niobium film for magnetic measurements, and x-ray diffraction measurements showed that embedded clusters keep their fcc structure. Clusters mainly form truncated octahedrons [7,8]. Faceting is thermodynamically favorable to minimize the surface energy [9] leading to an equilibrium shape in the truncated octahedron form. Such perfect polyhedrons contain 1289 or 2406 atoms for diameters of 3.1 or 3.8 nm, respectively. As previously observed for free and deposited metallic clusters (Co, Ni, Al) [10,11], the growth of a polyhedron to one

which is one layer larger occurs by the filling of successive facets. This result has also been theoretically predicted using molecular dynamics [12]. In the first stage, atoms have a high probability ($\approx 80\%$) to participate to the growth of a close-packed (111) face, which will be the first covered. In a second stage, atoms will fill an adjacent (111) or (100) face (Fig. 1b). The magnetic signals of such particles are at least a thousand times smaller than those of previously studied nanoparticles [13,14] deposited onto the micro-SQUID device. In order to achieve the needed sensitivity, Co clusters were directly embedded into the junctions of the micro-SQUID (Fig. 2).

A laser vaporization and inert gas condensation source is used to produce an intense supersonic beam of nano-sized Co clusters which can be deposited in various matrices in UHV conditions. In such a low energy deposition regime (LECBD: low energy cluster beam deposition), clusters do not fragment upon impact on the substrate [15]. The niobium matrix is simultaneously deposited thanks to a UHV electron gun evaporator [16]. As prepared, 20-nm-thick niobium films containing a

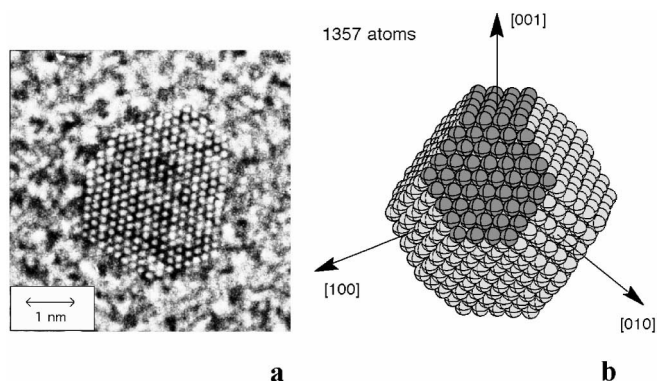


FIG. 1. (a) High resolution transmission electron microscopy observation along a $[110]$ direction of a typical 3 nm cobalt cluster exhibiting a fcc structure. (b) A characteristic cluster simulated for our magnetic calculations with light atoms belonging to the 1289-atom truncated octahedron basis and dark atoms to the (111) and (001) added facets.

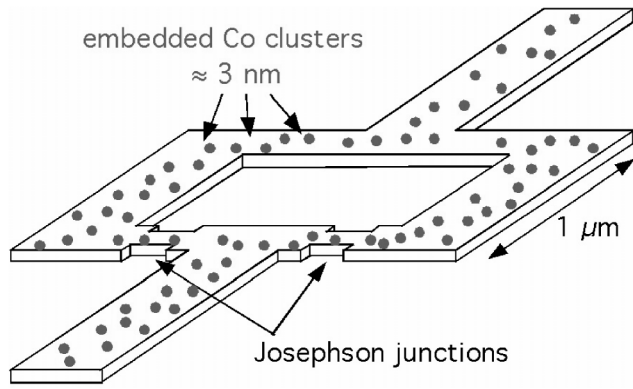


FIG. 2. Schematic drawing of a micro-bridge-dc-SQUID which is patterned out of a 20-nm-thick superconducting niobium film containing a low density of 3 nm cobalt clusters (dots).

very low concentration of cobalt clusters ($<0.1\%$) are electron beam lithographed to pattern micro-bridge-dc-SQUIDs [17] (Fig. 2). The later ones allow us to detect the magnetization reversal of a single Co cluster for an applied magnetic field in any direction and in the temperature range between 0.03 and 30 K. However, the desired sensitivity is only achieved for Co clusters embedded into the microbridges, where the magnetic flux coupling is high enough. Because of the low concentration of embedded Co clusters, we have statistically between 0 and five noninteracting particles in a microbridge ($300 \times 50 \text{ nm}^2$). In most cases, only one cluster gave a measurable signal. For cases with several signals, a precise three-dimensional study allowed us to show that each signal corresponds to an independent cluster. Indeed, studying precisely the intersection of two Stoner-Wohlfarth astroids allows one to find interactions between clusters. We found no interaction between particles and a random orientation of the easy magnetization directions.

For cobalt, the exchange length is 7 nm which is larger than the 3 nm particle size [18]. In this case, we can use to a good approximation the Stoner and Wohlfarth model [19,20] describing the magnetization reversal by uniform rotation. This model supposes that the exchange interaction in the cluster couples all the spins strongly together to form a giant spin for which the direction is given by the unit vector $\mathbf{m}$. The magnetization reversal is described by the potential energy,

$$E(\mathbf{m}, \mathbf{H}) = E_0(\mathbf{m}) - \mu_0 \nu M_s \mathbf{m} \cdot \mathbf{H}, \quad (1)$$

where ν and M_s are the magnetic volume and the saturation magnetization of the particle, respectively, and $\mathbf{H}$ is the external magnetic field. $E_0(\mathbf{m})$ is the magnetic anisotropy energy given by

$$E_0(\mathbf{m}) = E_{\text{shape}}(\mathbf{m}) + E_{\text{surface}}(\mathbf{m}) + E_{\text{ME}}(\mathbf{m}) + E_{\text{MC}}(\mathbf{m}). \quad (2)$$

E_{shape} is the magnetostatic energy related to the cluster shape. E_{surface} is due to the symmetry breaking and surface strains. In addition, if the particle experiences an external stress, the volume relaxation inside the particle induces a magnetoelastic (ME) anisotropy energy, E_{ME} . E_{MC} is the cubic magnetocrystalline anisotropy arising from the coupling of the magnetization with the fcc crystalline lattice as in the bulk. All these anisotropy energies can be developed in a power series of $m_x^a m_y^b m_z^c$ with $p = a + b + c = 2, 4, 6, \dots$ giving the order of the anisotropy term. Shape anisotropy energy contains only second order terms. Surface and magnetoelastic energies begin with second order terms, whereas the cubic magnetocrystalline anisotropy starts with fourth order terms.

At $T = 0 \text{ K}$ and $\mathbf{H} = \mathbf{0}$, $\mathbf{m}$ is aligned along an easy magnetization axis which is a minimum of E . When a magnetic field $\mathbf{H}$ is applied, the position of the minima in E changes continuously with $\mathbf{m}$ following the position of a minimum. However, there are particular fields where this minimum disappears, leading to a discontinuous variation of $\mathbf{m}$ with a jump to another minimum of E . The corresponding fields are called the switching fields of the magnetization. The micro-SQUID technique measures the switching fields for any direction of $\mathbf{H}$ [14] allowing us to determine the magnetic anisotropy energy E_0 of a single cluster. The magnetization switching is detected using the *cold mode* [3]. In the superconducting state, the SQUID is biased close to the critical current. The magnetization reversal of the particle then triggers the transition of the SQUID to the normal state. The three-dimensional switching field measurements and the studies as a function of temperature were done using a three step method (*blind mode*) [14]. First, the magnetization of the particles is saturated in a given direction (at $T = 35 \text{ mK}$). Second, a field is applied at a temperature between 35 mK and 30 K which may or may not cause a magnetization switching. Finally, the SQUID is switched on (at $T = 35 \text{ mK}$) and a field is applied in the SQUID plane to probe the resulting magnetization state. This method allows us to scan the entire field space. Figures 3a and 3c display a typical three-dimensional switching field distribution for a 3 nm Co cluster at $T = 35 \text{ mK}$. This surface is directly related to the anisotropy involved in the magnetization reversal of the particle. The experimental results in Figs. 3a and 3c can be reasonably fitted with the Stoner and Wohlfarth model [21] to obtain the following anisotropy energy:

$$E_0(\mathbf{m})/\nu = -K_1 m_z^2 + K_2 m_y^2 - K_4 (m_x^2 m_{y'}^2 + m_x^2 m_{z'}^2 + m_y^2 m_{z'}^2). \quad (3)$$

K_1 and K_2 are the anisotropy constants along z and y , the easy and hard magnetization axes, respectively. K_4 is the fourth order anisotropy constant, and the $(x'y'z')$ coordinate system is deduced from (xyz) by a 45° rotation around the z axis with $z' = z$. We find $K_1 = 2.2 \times 10^5 \text{ J/m}^3$, $K_2 = 0.9 \times 10^5 \text{ J/m}^3$, and $K_4 = 0.1 \times 10^5 \text{ J/m}^3$. The

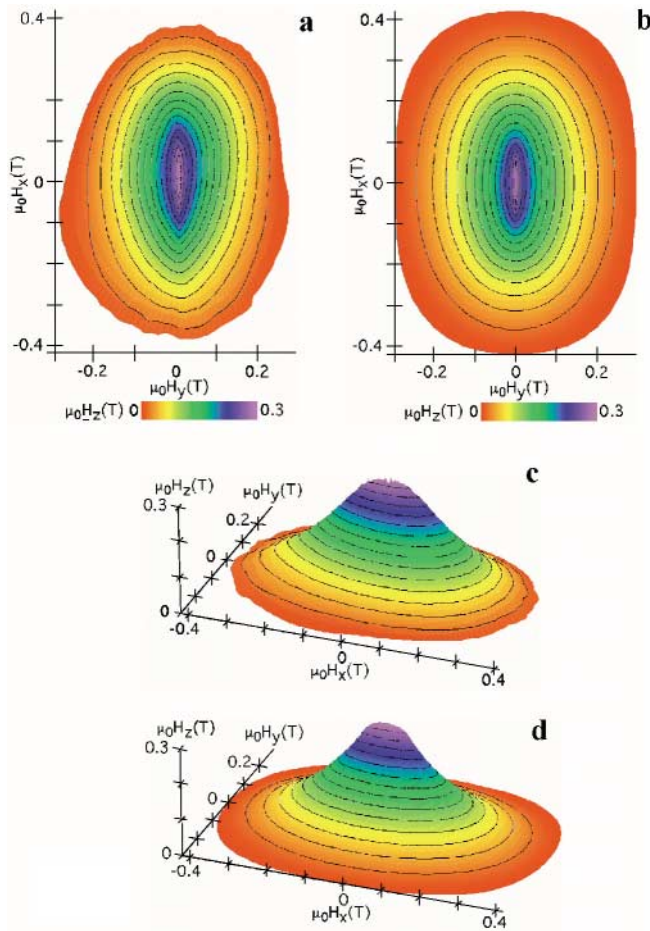


FIG. 3 (color). (a),(c) Top view and side view, respectively, of the experimental three-dimensional angular dependence of the switching field of a 3 nm Co cluster measured with the micro-SQUID. This surface is symmetrical with respect to the H_x - H_y plane and only the upper part ($\mu_0 H_z > 0$ T) is shown; it corresponds to almost 2000 measuring points. Continuous lines on the surface are contour lines on which $\mu_0 H_z$ is constant. (b),(d) Top view and side view, respectively, of the theoretical switching field surface considering only second and fourth order terms in the anisotropy energy.

corresponding theoretical surface is showed in Figs. 3b and 3d. Furthermore, we measure the temperature dependence of the switching field distribution (Fig. 4). We deduce the blocking temperature of the particle $T_B \approx 14$ K leading to an estimation of the number of magnetic atoms in this particle: $N \approx 1500$ atoms [22]. Detailed measurements on about 20 different particles showed similar three-dimensional switching field distributions with comparable anisotropy [$K_1 = (2.0 \pm 0.3) \times 10^5$ J/m³, $K_2 = (0.8 \pm 0.3) \times 10^5$ J/m³, and $K_4 = (0.1 \pm 0.05) \times 10^5$ J/m³] and size ($N = 1500 \pm 200$ atoms).

In the following, we analyze various contributions to the anisotropy energy of the small Co clusters in view of the experimental results reported above. Fine structural studies [16] showed that niobium atoms penetrate the cluster surface to almost two atomic monolayers because cobalt

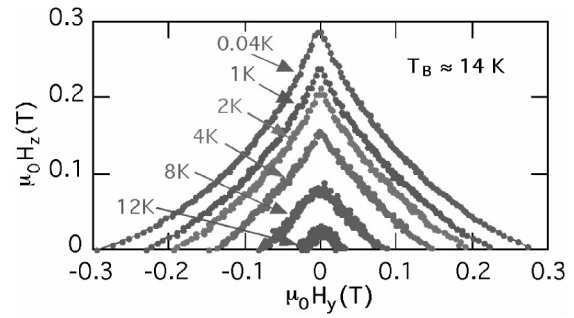


FIG. 4. Temperature dependence of the switching field measured in the H_y - H_z plane in Fig. 3. An extrapolation of the switching fields to zero gives the blocking temperature $T_B = 14$ K [22].

and niobium are miscible elements. Further magnetic measurements [16] showed that these two atomic monolayers are magnetically dead. For this reason, we estimate the shape anisotropy of the typical, nearly spherical, deposited cluster in Fig. 1b after removing two atomic monolayers at the surface. By calculating all the dipolar interactions inside the particle assuming a bulk magnetic moment of $\mu_{at} = 1.7 \mu_B$, we estimate the shape anisotropy constants: $K_1 = 0.3 \times 10^5$ J/m³ along the easy magnetization axis and $K_2 = 0.1 \times 10^5$ J/m³ along the hard magnetization axis. These values are much lower than the measured ones, which means that E_{shape} is not the main cause of anisotropy in the cluster.

We expect that the contribution of the magnetoelastic anisotropy energy E_{ME} coming from the matrix-induced stress on the particle is also small. Indeed, by using the codeposition technique, niobium atoms cover uniformly the cobalt cluster creating an isotropic distribution of stresses. Therefore they cannot give rise to second order terms in the magnetic anisotropy energy. In addition, stresses would relax preferably inside the matrix and not in the particle volume since niobium is less rigid than cobalt. HRTEM and x-ray diffraction measurements performed on niobium films containing cobalt clusters showed that niobium is nanocrystallized with a typical 10–20 nm grain size. This is direct evidence that strains have relaxed inside the matrix. Moreover, we verified that possible strains induced by an epitaxial growth of niobium on cobalt can be ruled out. Indeed we initiated the growth of niobium on a fcc cobalt film [grown on a single Cu(100) crystal] by molecular beam epitaxy (MBE) at room temperature. *In situ* reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED) measurements showed unambiguously that there is no epitaxy of niobium on cobalt. We believe therefore that only interface anisotropy $E_{surface}$ can account for the experimentally observed second order anisotropy terms. Niobium atoms at the cluster surface might enhance this interface anisotropy through surface strains and magnetoelastic coupling.

Quantitative information on surface anisotropy is only available in the case of a cluster-vacuum interface using the Néel anisotropy model. This phenomenological model is based on a simple atomic picture. In a first approximation, the magnetic energy of a pair of atoms can be written as $L \cos^2(\theta)$, where L is an atomic interaction and θ is the angle between the atomic bond and the magnetization. L depends on the fcc cobalt magnetoelastic constants and, at low temperature, $L = -1.5 \times 10^7 \text{ J/m}^3$ [23]. Summing over all the nearest neighbors in the fcc cobalt cluster in Fig. 1b, this interaction vanishes, except at the cluster surface where the cubic symmetry is broken. As a result, this interaction is proportional to the number of surface atoms (N_S). We have contributions from (111) and (100) facets with in-plane anisotropy and from edges with an easy direction along their axes. Apices give no contribution to the anisotropy since locally the cubic symmetry is not broken. After removing two atomic dead layers at the cluster surface and dividing the corresponding energy by the number of atoms in the particle (N_{tot}), one finds: $K_1 = 2.5 \times 10^5 \text{ J/m}^3$ along the easy direction and $K_2 = 0.5 \times 10^5 \text{ J/m}^3$ along the hard magnetization axis. K_1 and K_2 are proportional to the surface-to-volume ratio (i.e., N_S/N_{tot}). It is interesting to mention that the Néel surface anisotropy involves very large anisotropy constants in thin films (10^7 J/m^3), whereas, in clusters, symmetries reduce this anisotropy to a value close to our experimental result. The fourth order term K_4 gives the cubic magnetocrystalline anisotropy in the fcc cobalt cluster. x' , y' , and z' correspond to the crystallographic directions [100], [010], and [001], respectively. Thus, [111] directions are weak easy magnetization axes. Note that this anisotropy constant is smaller than the one reported in previous papers [23,24].

In conclusion, we have shown that the micro-SQUID technique combined with the LECBD is a powerful method to investigate the magnetic properties of nanosized magnetic particles. It allows one to measure in three dimensions the switching field of individual grains, giving access to its magnetic anisotropy energy. Furthermore, the temperature dependence of the switching field is measurable and allows one to probe the magnetization dynamics. In the case of nanosized cobalt clusters embedded in the niobium film of the micro-SQUID, it seems that the cluster-matrix interface provides the main contribution to the magnetic anisotropy.

The authors are indebted to B. Pannetier, A. Benoit, F. Balestro, and J.P. Nozières from CNRS-Grenoble for their contributions to the improved micro-SQUID technique, and to G. Guiraud from DPM-Villeurbanne for his

contribution to the cluster deposition. We thank B. Barbara for his constant support of this research. Part of this work has been supported by DRET, Rhône-Alpes, and the MASSDOTS ESPRIT LTR-Project No. 32464.

-
- [1] D.J. Sellmyer, M. Yu, and R.D. Kirby, *Nanostruct. Mater.* **12**, 1021 (1999).
 - [2] J.L. Dormann, D. Fiorani, and E. Tronc, in *Advances in Chemical Physics*, edited by I. Prigogine and Stuart A. Rice (Wiley, New York, 1997), Vol. XCVIII.
 - [3] W. Wernsdorfer, D. Mailly, and A. Benoit, *J. Appl. Phys.* **87**, 5094 (2000).
 - [4] R.H. Kodama, *J. Magn. Magn. Mater.* **200**, 359 (1999).
 - [5] N. Nakajima *et al.*, *Phys. Rev. Lett.* **81**, 5229 (1998).
 - [6] J. Dorantes-Davila and G.M. Pastor, *Phys. Rev. Lett.* **81**, 208 (1998).
 - [7] J. Tuaillon *et al.*, *Philos. Mag. A* **76**, 493 (1997).
 - [8] F. Parent *et al.*, *Phys. Rev. B* **55**, 3683 (1997).
 - [9] J. Buttet and J.P. Borel, *Helv. Phys. Acta* **56**, 541 (1983).
 - [10] M. Pellarin *et al.*, *Chem. Phys. Lett.* **217**, 349 (1994).
 - [11] T.P. Martin, U. Nher, and H. Schaber, *Chem. Phys. Lett.* **199**, 470 (1992).
 - [12] S. Valkealahti and M. Manninen, *Phys. Rev. B* **57**, 15 533 (1998).
 - [13] W. Wernsdorfer *et al.*, *Phys. Rev. Lett.* **78**, 1791 (1997); *Phys. Rev. Lett.* **79**, 4014 (1997).
 - [14] E. Bonet *et al.*, *Phys. Rev. Lett.* **83**, 4188 (1999).
 - [15] A. Pérez *et al.*, *J. Phys. D* **30**, 709 (1997).
 - [16] M. Jamet *et al.*, *Phys. Rev. B* **62**, 493 (2000).
 - [17] W. Wernsdorfer *et al.*, *Appl. Phys. Lett.* **78**, 7192 (1995).
 - [18] M.E. Schabes, *J. Magn. Magn. Mater.* **95**, 249 (1991).
 - [19] E.C. Stoner and E.P. Wohlfarth, *IEEE Trans. Magn.* **27**, 3475 (1991).
 - [20] A. Thiaville, *J. Magn. Magn. Mater.* **182**, 5 (1998).
 - [21] A. Thiaville, *Phys. Rev. B* **61**, 12 221 (2000).
 - [22] The blocking temperature T_B is defined as the temperature for which the measuring time τ_{mes} becomes equal to the relaxation time τ of the particle magnetization at $\mathbf{H} = \mathbf{0}$. Using an Arrhenius-like law, this can be written as $\tau_{\text{mes}} = \tau = \tau_0 \exp(K_{\text{at}} N_{\text{tot}} / k_B T_B)$, where τ_0^{-1} is the attempt frequency typically between 10^{10} and 10^{11} Hz. K_{at} is an atomic effective anisotropy energy and k_B is the Boltzmann constant. We use the expression of the switching field at $T = 0 \text{ K}$ in the easy magnetization direction, $\mu_0 H_{\text{sw}} = 2K_{\text{at}} / \mu_{\text{at}} = 0.3 \text{ T}$, and the atomic moment, $\mu_{\text{at}} = 1.7 \mu_B$, to deduce K_{at} . Finally, for $\tau_{\text{mes}} = 0.01 \text{ s}$ and $\tau_0 = 10^{-10} \text{ s}$, we find $N_{\text{tot}} \approx 1500$ which corresponds well to a 3 nm Co cluster (Fig. 1).
 - [23] D.S. Chuang, C.A. Ballentine, and R.C. O'Handley, *Phys. Rev. B* **49**, 15 084 (1994).
 - [24] C.H. Lee *et al.*, *Phys. Rev. B* **42**, 1066 (1990).