Eur. Phys. J. D **9**, 501–504 (1999)

**THE EUROPEAN
PHYSICAL JOURNAL D**

EDP Sciences

Magnetic properties of nanosized transition metal colloids: the influence of noble metal coating

P.M. Paulus[1], H. Bönnemann[2], A.M. van der Kraan[3], F. Luis[1,a], J. Sinzig[1], and L.J. de Jongh[1]

[1] Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands
[2] Max Planck Institut für Kohlenforschung, Postfach 101353, D-45466 Mülheim/Ruhr, Germany
[3] Interfacultair Reactor Instituut, Delft University of Technology, 2629 JB Delft, The Netherlands

Received: 1 September 1998 / Received in final form: 18 November 1998

Abstract. We present a detailed experimental study of Fe and Co colloidal particles stabilized by organic ligands. Comparison is made between the magnetic properties of pure and gold-coated particles. In all cases, evidence of superparamagnetic behaviour is found from dc susceptibility and hysteresis loops, with blocking at quite different temperatures. The magnetic anisotropy, as obtained from the blocking temperature and the coercive field, is larger for the pure particles than for the bulk material. Saturation magnetization values obtained at low temperatures are smaller than the bulk. We attribute these effects to surface pinning by the ligands. The magnetic anisotropy of the cobalt particles coated with a gold layer is found to be highly reduced, to a value very close to the bulk. By contrast, the anisotropy of iron colloids coated by gold remains larger than the bulk value, probably because of the formation of an inhomogeneous Fe/Au alloy.

PACS. 75.30.Gw Magnetic anisotropy – 82.70.Dd Colloids – 75.30.Pd Surface magnetism

The study of fine particles of transition metals can be applied to the development of materials for technological applications such as catalysis and magnetic recording. For instance, a good understanding of the physical origin of magnetic anisotropy can help to further decrease the size of the unit of information. In this paper, we study the magnetic properties of Fe and Co colloids stabilized by organic ligands. The ligands can substantially modify the anisotropy and magnetic moment of the metal atoms located at the surface of the particles. In its turn, the influence of surface pinning may be modified if the magnetic particles are coated by a noble metal layer, which separates the magnetic core from the ligand shell.

The metal colloids used in our research were prepared by reduction of a metal salt with tetraalkylammonium hydrotriorganoborates, using the method described in [1]. The long-chain tetraalkylammonium salts formed directly at the reduction center act as very effective protecting agents for preventing the particles from coalescence. In a later stage, colloids dispersed in toluene can be treated with $AuCl_3$, which slowly dissolves, according to the reaction (for the Co colloid)

$$12\,\mathrm{Co}(0) + 2\,\mathrm{AuCl_3} \rightarrow \mathrm{Co_9Au_2} + 3\,\mathrm{CoCl_2}\,. \tag{1}$$

This process is expected to coat the metal particle with Au. The magnetic signal of the paramagnetic $CoCl_2$ that is also formed during this process has been subtracted from the data (shown below). The size distribution was obtained directly from the analysis of TEM images. Magnetic measurements were performed using a commercial SQUID magnetometer. The magnetic susceptibility was obtained by the application of a field $H = 100$ Oe after the sample was cooled in either zero field (ZFC)or in the presence of the same field (FC). ^{57}Fe Mössbauer spectra were also obtained for some of the samples at several temperatures between 8 K and 200 K. The composition and sizes of the particles are given in Table 1 for the different colloids studied.

Table 1. Physical parameters of the six samples investigated. $x_{3\mathrm{d}}$ and x_{Au} stand for the concentration in mass of transition metal (Fe or Co) and gold, respectively. The size distribution has been obtained by TEM. The average diameter $\langle d\rangle$ and the width σ follow from a fit of this distribution to a Gaussian function.

Sample	$x_{3\mathrm{d}}$	x_{Au}	$\langle d\rangle$(nm)	σ(nm)
Co (A1)	0.0382	0	3.0(1)	1.0(1)
Co/Au (A2)	0.028		2.8(1)	
Fe (B1)	0.02	0	3.5(4)	1.0(4)
Fe/Au (B2)	0.0158	0.0168	2.0(1)	0.9(1)
Fe (C1)	0.58	0	5.4(2)	0.8(2)
Fe/Au (C2)	0.0138	0.0222	5.1(2)	1.8(2)

We first discuss the results obtained on two samples of pure (A1) and gold-coated (A2) Co colloids of an average of 3 nm in diameter. Magnetic susceptibility data for these

---

[a] Corresponding author.
e-mail: `fluis@phys.leidenuniv.nl`

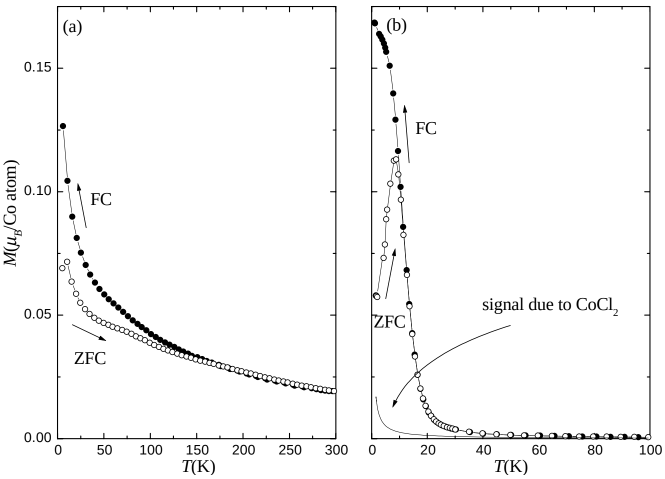

Fig. 1. ZFC and FC magnetization of the Co colloids, pure (a) and gold-coated (b), measured at $H = 100$ Oe. The contribution of the paramagnetic CoCl_2 to the total signal in (b) is also shown.

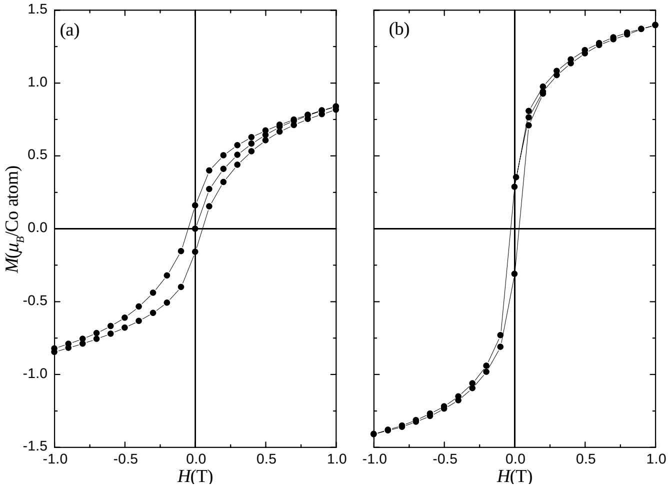

Fig. 2. Hysteresis loops measured at 5 K on the pure Co colloid (a) and the gold-coated Co particles (b).

two samples are shown in Figs. 1(a) and 1(b), respectively. At high enough temperatures, where the relaxation of the magnetic moments is faster than the characteristic experimental time, and the magnetization is linear in field, it follows Curie–Weiss' law. In the case of the pure Co colloid, the ZFC and FC curves already split at 130 K, and the ZFC susceptibility shows a shoulder at a temperature of about $T_\text{B} = 66$ K. This can be interpreted as evidence for the well-known phenomenon of blocking of the magnetic moments, which is caused by anisotropy. The upturn observed in the ZFC susceptibility at lower temperatures can be attributed to either the existence of very small particles in the sample or to a paramagnetic impurity. By contrast, the susceptibility of the Au-coated sample, A2, is dramatically different from the curve measured on the pure Co colloid, and the blocking occurs at much lower temperatures. As discussed below, this markedly different behaviour indicates that the magnetic anisotropy is highly reduced as a result of the coating with Au.

The blocking temperature T_B can be related to the average anisotropy energy barrier KV by the well-known expression:

$$k_\text{B}T_\text{B} = \alpha KV / \ln(t/\tau_o)\,. \tag{2}$$

Here V is the average volume of the particles, K the (effective) anisotropy energy density, t a characteristic experimental time (estimated about 300 s for dc experiments), τ_o an attempt time [2] which is assumed to lie between 10^{-9} and 10^{-13} s, and α a constant of the order of unity that depends on the width and shape of the size distribution in the sample [3]. Setting $\alpha = 1$ for simplicity, and taking $\ln(t/\tau_o) = 25$ (as is usually done), it follows that $K = 1.6 \times 10^7\,\text{erg/cm}^3$ for the pure colloid, whereas $K = 2.6 \times 10^6\,\text{erg/cm}^3$ for the colloid with Au. It is interesting to compare these values to the bulk anisotropy for Co, which equals approximately $2.7 \times 10^6\,\text{erg/cm}^3$; this is very close to the value that we estimate for sample A2. Apparently, the pure Co particles exhibit a large additional contribution to the anisotropy that reduces to zero when they are coated by gold. We do not think that the observed difference in T_B arises from the interaction between the particles, because both samples are quite diluted, and the organic ligand shell avoids the agglomeration of the particles. Furthermore, if we estimated the interparticle interaction energy from the quantity $k_\text{B}\theta$, where θ is the Curie temperature obtained from the high temperature susceptibility, we would find that it amounts to 2% of KV for the pure colloid and 6% for the one coated with Au. We therefore attribute the large anisotropy found for the pure colloid to the pinning of Co magnetic moments, located at the surface, by the interaction with the ligands surronding the Co cores. This interaction may act as a local electrostatic field on the Co $3d$ electrons [4].

The hysteresis loops for the Co samples measured at $T = 5$ K are shown in Figs. 2(a) and 2(b), and confirm the above interpretation in terms of a surface anisotropy. The gold-coated particles saturate at a value close to the saturation magnetization of bulk Co ($1.77\mu_\text{B}$/atom), whereas the pure colloids are much more difficult to saturate, and attain a magnetic moment of only $1.3\mu_\text{B}$ per Co atom, in a field of 5 T. We may again attribute this to the interaction with the ligands, which induce a pinning of the surface magnetic moments. The fact that both T_B and the coercive field at $T = 5$ K are reduced by the coating with gold indicates that the surface anisotropy probably also affects the moments of the inner Co atoms via the exchange interaction with those at the surface.

We performed the same type of experiment on two samples of pure Fe particles having an average diameter equal to 3.5 nm (B1) and 5.4 nm (C1), respectively, and another two samples of Fe particles, coated with Au, of about 2 nm (B2) and 5.1 nm (C2), respectively. According to the values found for θ, we roughly estimate that the interaction between particles is even weaker than for the Co colloids, except for the highly concentrated Fe colloid C1. It is possible that, for this sample, the effective anisotropy is enhanced by the effect of the interaction. The

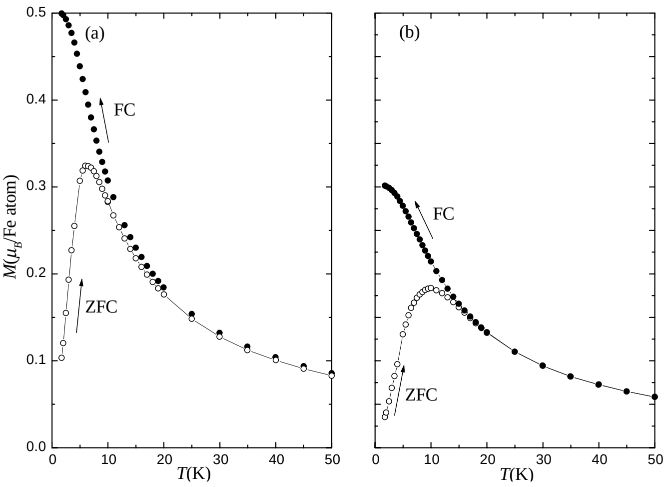

Fig. 3. ZFC and FC magnetization curves of two Fe colloids measured at $H = 100\,\mathrm{Oe}$: (a) sample B1 of pure particles; (b) sample B2 of gold-coated particles.

low field magnetization for samples B1 and B2 is shown in Figs. 3(a) and 3(b), respectively. In contrast with the result obtained for the Co colloids, we found that T_B is larger for the sample of Fe particles coated with Au, although the average volume for this sample is about five times smaller than for the pure Fe particles. Using (1) as above, we find $K = 1 \times 10^6\,\mathrm{erg/cm^3}$ for the pure and $K = 8 \times 10^6\,\mathrm{erg/cm^3}$ for the coated particles, respectively, which are both larger than $K_\mathrm{bulk} = 4.6 \times 10^5\,\mathrm{erg/cm^3}$ for bulk metallic Fe. The same method gives $K = 1.9 \times 10^6\,\mathrm{erg/cm^3}$ for the sample C1 and $K = 1.8 \times 10^6\,\mathrm{erg/cm^3}$ for C2. Thus, the addition of Au enhances the anisotropy of the smallest Fe particles, and leaves the anisotropy of the larger ones nearly unchanged.

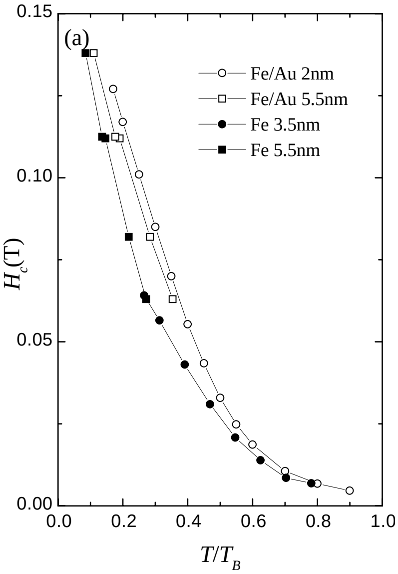

Fig. 4. Coercive field as a function of the reduced temperature T/T_B for all samples of Fe particles. T_B is the blocking temperature obtained from the peak of the ZFC susceptibility.

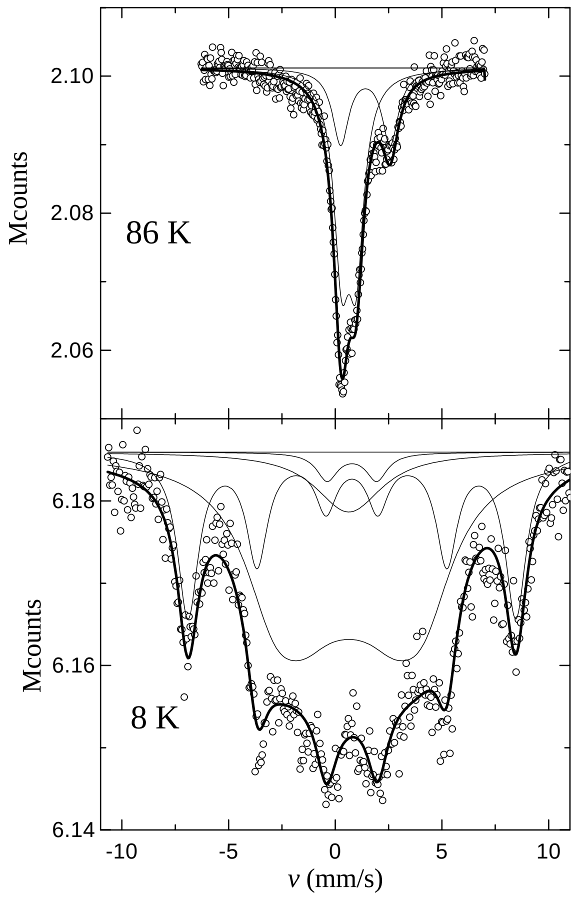

Fig. 5. ^{57}Fe Mössbauer spectra of sample C2 measured at two temperatures, above and below the blocking temperature; $T_\mathrm{B} \approx 40\,\mathrm{K}$ (T_B is the temperature where the intensity of the magnetically split part equals the unsplit contribution from the superparamagnetic particles). Thick lines represent the best fit to the experimental data obtained by a superposition of two different sites, each consisting of a magnetic sextet and a quadrupole doublet (thin lines).

A similar conclusion follows from the analysis of the magnetization curves (not shown). Although the magnetic moment per Fe atom for all the samples is smaller than the value $2.24\mu_\mathrm{B}$ for bulk Fe, the coated particles are more difficult to saturate. Correspondingly, the coercive field of the two samples of pure particles is smaller at any reduced temperature T/T_B, as is shown in Fig. 4. These results follow the same trend described before, that is, the anisotropy of the Fe colloids is not reduced when the particles are coated with Au.

The contrast between the results obtained on the gold-coated Co and Fe colloids is rather puzzling. However, we can give a plausible explanation in view of the Mössbauer data. For the sample C2 of the largest Fe particles coated with Au, the spectra can be fitted to a superposition of two subspectra (see Fig. 5). The hyperfine splittings found at 8 K equal 48 (2) T and 24 (4) T. They are both significantly different from the value ($H_\mathrm{hf} = 33\,\mathrm{T}$) for bulk Fe. We note that in previous experiments on bulk Fe/Au alloys, the presence of two phases, a phase concentrated in Fe and a diluted phase with H_{hf} larger and smaller than 33 T, respectively, has been observed [5]. Therefore, these results might indicate that, for the case of Fe colloids, the reaction (1) has produced an inhomogeneous Fe/Au alloy instead of the desired coating. Now, the increase of the anisotropy that we have found in sample B2 (Fe/Au) with respect to sample B1 (Fe) could be explained if, in this case, the Fe-rich phase had more of a tendency to lie at the surface of the colloid, giving rise to an increase of the fraction of Fe atoms that interact with the ligands with respect to the total number of Fe atoms in each particle.

In conclusion, we have shown that the interaction of the atoms that are near the surface of Fe and Co particles with shells of organic ligands induces an effective anisotropy on the magnetic moment of the total particle. For the Co colloid, this interaction appears to be reduced significantly when the particles are coated with a layer of Au. However, for the Fe colloids, the coating process seems to be ineffective, rather, it gives rise to an alloy of both metals.

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). F. L. acknowledges a grant funded by the European Commission in the frame of its TMR Marie Curie Program.

References

1. H. Bönnemann, W. Brijoux, R. Brinkmann, R. Fretzen, T. Joussen, R. Köppler, B. Korall, P. Neitler, J. Richter: J. Mol. Catal. **86**, 129 (1994)
2. L. Néel: Ann. Geophys. **5**, 99 (1949); W.F. Brown: Phys. Rev. **130**, 1677 (1963)
3. J.I. Gittlemann, B. Abeles, S. Bozowsky: Phys. Rev. B **9**, 3891 (1975)
4. A.E. Berkowitz, J.A. Lahut, I.S. Jacobs, L.M. Levinson, D.W. Forester: Phys. Rev. Lett. **34**, 594 (1975)
5. C.E. Violet, R.J. Borg: Phys. Rev. Lett. **51**, 1073 (1983)