Magnetic Enhancement in Nanoscale CoRh Particles

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The influence of size reduction on the magnetism of CoRh has been studied on a system of isolated nanometric spherical bimetallic ultrafine particles embedded in a polymer matrix. Pulsed fields up to 30 T were used in order to approach the magnetic saturation (M_S). Particles with a mean diameter of 1.65 (± 0.1) nm display a value of $2.38\mu_B$ per CoRh unit strongly enhanced compared to values calculated or measured on a bulk alloy. These results were interpreted as the first evidence of the cooperative role of both alloying and size reduction to the enhancement of M_S in this system associating a $3d$ FM metal with a $4d$ metal.

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One of the most active research topics of the past few years is the investigation of finite size effects in magnetic materials. Technological developments require more and more magnetic nanomaterials of controlled properties taking advantage of their small size. With decreasing the size of magnetic particles occurs a transition from poly domain to single domain systems, and the apparition of superparamagnetism [1]. The modification of the electronic band structure of magnetic materials of nanometer size, at the border of the molecular and metallic states, induces unusual magnetic properties. As a consequence, an enhanced magnetic moment is predicted for nanoparticles of $3d$ ferromagnetic (FM) metals [2]. Such effects have been first demonstrated in the case of Fe, Co, and Ni metal clusters containing less than 1000 atoms, using molecular beam deflection measurements in high vacuum [3]. Recently, the case of $4d$ metal has been addressed. Bulk $4d$ metals do not display any FM behavior. However, a spin polarization can be induced by a very small perturbation of the lattice parameter, by elaborating layered structures with a FM material [4], and more efficiently by alloying with a $3d$ FM metal [5,6]. Size reduction also induces the appearance of FM in species at the border of FM as demonstrated by molecular beam deflection measurements for Rh nanoparticles up to 34 atoms [7,8], in agreement with theoretical calculations. As a consequence, one can expect unusual magnetic behaviors in Rh based alloys with $3d$ FM species, where the size reduction should play an important role on the electronic spin polarization.

As far as we know, the magnetism of bimetallic $3d$-$4d$ particles in the nanometer range (1–3 nm) has not been reported. The synthesis of bimetallic nanoparticles or clusters is far from easy, since it necessitates the control of both the particle stoichiometry and the surface state. Classical chemical methods have been demonstrated to be very efficient for the high yield synthesis of nanomaterials, but with a more or less good control of the surface chemistry, which may alter or cancel many of the unconventional properties resulting from the outer shells. In the past few years, we have developed a new chemical elaboration process based on the decomposition in mild conditions of an organometallic precursor in the presence of a stabilizing polymer. This approach, applied for the elaboration of Co nanoparticles in polyvinylpyrrolidone (PVP), interestingly produces a nanomaterial which displays the same enhancement of magnetic moment per atom as that observed for gas phase aggregates, an enhancement of the anisotropy and an unusual polytetrahedral crystalline structure [9–11]. These results illustrate the weak character of the interaction of the particle surface with this polymer. Furthermore, using a similar approach, bimetallic isolated magnetic particles of $Co_{1-x}Pt_x$ of nanometric size and adjustable composition have been obtained. They evidence a strong influence of the Pt concentration on the anisotropy, in connection with the formation of new crystalline phases [12,13].

In this Letter, we present the first synthesis and magnetic study of bimetallic CoRh nanomaterials and their magnetic characterization. Two systems of well isolated CoRh particles with sizes near 1.65(± 0.1) and 2.3(± 0.1) nm, embedded in the organic polymer PVP, have been synthesized using the organometallic approach mentioned here above. Their magnetic data clearly demonstrate the bimetallic nature of the CoRh nanoparticles, with reduced exchange energy with the nearest neighbors and larger magnetic anisotropy. The main result concerns the saturation magnetization of this system. Spectacularly, high fields up to 30 T are not sufficient to fully saturate the magnetization of the smaller nanoparticles system which reaches a value twice as large as the predicted bulk value of the CoRh alloy, suggesting a huge influence of the particle size reduction.

The particles were synthesized using a chemical procedure based on the simultaneous decomposition of two organometallic precursors $Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})$ and

Rh(acetylacetonate) (η^4-C_8H_{12}) in a tetrahydrofuran solution containing PVP. The homogeneous solution of the two precursors was submitted to a dihydrogen pressure of 3 bars. The chemical reduction of the olefins and the metals was complete after 20 h of vigorous mixing at room temperature. The black colloidal solution was first precipitated at −80 °C. Further colloid precipitation was obtained upon addition of methanol. Two initial concentrations of metal precursors were used corresponding to 10 wt % and 20 wt % initial metal/polymer weight ratios, with, in both cases, the atomic Co/Rh ratio kept equal to 1. The final atomic composition of the isolated samples was determined by chemical microanalysis. This procedure led to two bimetallic systems of respective composition, $Co_{0.47}Rh_{0.53}$ and $Co_{0.55}Rh_{0.45}$, for the samples containing initially, respectively, 10 and 20 wt % of total metal.

Figure 1 shows a low magnification transmission electron microscopy (TEM) image of the 10 wt % colloid showing nanoparticles homogeneous in size with a mean diameter of $\phi = 1.8$ (± 0.2) nm (colloid 1). Increasing the initial metal precursors content (20 wt %) leads to slightly bigger particles of $\phi = 2.6$ (± 0.2) nm (colloid 2). Both systems consist of isolated nanoparticles displaying a narrow size distribution. When observed in the high resolution TEM (HRTEM) mode, neither colloids 1 nor 2 display a well defined crystalline order (see Fig. 1 inset for colloid 1). The lattice fringes spaced by 0.22 nm observed in some particles do not provide enough elements to decide in favor of a particular phase. Both radial distribution functions (RDF) obtained from wide-angle x-ray scattering (WAXS) experiments display a broad pattern, which does not correspond to the conventional periodic crystalline phases. The coherence lengths closed to 1.5 nm (2.0 nm) for colloid 1 (colloid 2) are slightly smaller than the mean diameter observed by TEM. For both colloids, the first peak in the RDF is sharp enough to exclude significant distance dispersion and clearly indicates the metallic (i.e., nonoxidized) character of the scattering pattern. The first metal-metal distance ($d_{\text{M-M}}$), respectively, 0.270 nm and 0.265 nm for colloid 1 and colloid 2, are larger than those found in the bulk CoRh alloy (cubic parameter: 0.262 ± 0.001 nm). Colloid 1 displays a $d_{\text{M-M}}$ very close to that of bulk rhodium (cubic parameter: 0.269 nm) [6]. Definitely, the RDF obtained for the two colloids do not correspond to the crystalline phases of the bulk materials. Furthermore, the atomic arrangement in colloid 1 particles appears very similar to the nonperiodic one observed for other systems of nanoparticles (Co, CoPt) [12].

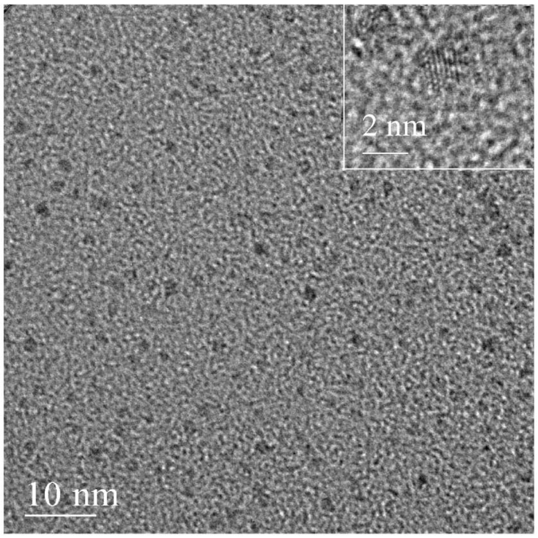

FIG. 1. Low magnification TEM micrograph of colloid 1. The inset shows an HRTEM micrograph of one particle of 1.9 nm diameter.

The magnetic properties have been investigated in steady field up to 5 T with a commercial SQUID magnetometer. The high field magnetization measurements up to 30 T have been performed using long pulsed fields (see Ref. [9]). In the following, for convenience, the magnetization data have been normalized according to the Co contents. This value also corresponds to the magnetization per CoRh unit.

Figure 2a shows a typical zero-field-cooled field-cooled (ZFCFC) magnetization vs temperature (T) curve measured in a low magnetic field of 1 mT for the smallest particles (colloid 1). It evidences a typical superparamagnetic (SP) behavior with a blocking temperature $T_B = 10.9$ K. The inverse of the magnetization vs (T) shown in the inset of Fig. 2a does not follow the classical Curie law. Colloid 2 displays the same behavior with $T_B = 13.5$ K. The origin of the discrepancy with the Curie law can be attributed to dipolar interactions between the particles and/or to the temperature dependence of the spontaneous magnetization (M_S). In the presence of dipolar interactions, the magnetic susceptibility in the SP state (χ_{SP}) for a system of identical particles of volume v is proportional to $M_S^2(T)v/3k_B(T - \theta)$, where θ is an effective temperature arising from the dipolar interactions. The quantity $\sqrt{\chi_{\text{SP}} \times (T - \theta)}$ vs T gives the temperature dependence of M_S. In both samples, M_S follows a conventional law

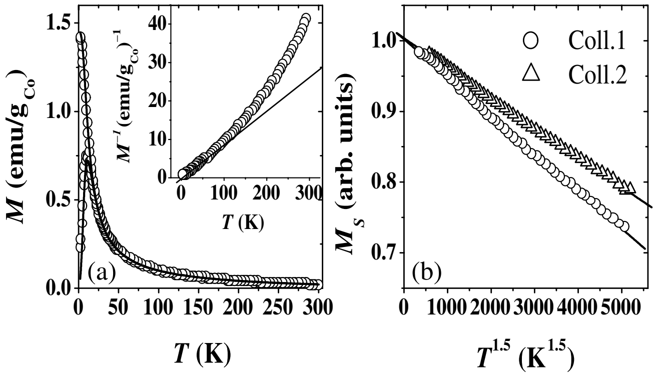

FIG. 2. (a) ZFCFC magnetization of colloid 1 (symbol) and the best fit obtained (solid line). The inset shows the departure from the Curie law (solid line) of the inverse ZFCFC magnetization of colloid 1 (symbol). (b) Variation of the normalized M_S vs $T^{3/2}$ for both colloids which are following Bloch laws.

$M_S(T) = M_S(0)[1 - \alpha T^n]$, where $n = 3/2(\pm 0.1)$, with $\theta = 0$ (± 2) (see Fig. 2). Other (θ, n) parameters corresponding to stronger dipolar FM or antiferromagnetic interactions do not fit the experimental data. The dipolar interactions are therefore very weak in agreement with the regular dilution of the particles in the PVP observed by TEM. The α coefficients of the Bloch law are given in Table I for each sample. In contrast, the M_S value of monometallic Co nanoparticles displays the opposite behavior where M_S reaches a maximum for T in the range of 300–400 K before vanishing [3]. The introduction of a different metal in a Co crystal is known to result in a decrease of T_C, and thus a weak exchange coupling between first nearest neighbor spins (J). The temperature dependence of M_S is thus a clear indication of the bimetallic nature of the particles.

Knowing the M_S vs T dependence, both the particle size distribution (ϕ: mean diameter; σ: standard deviation) and anisotropy (K_{eff}) can be determined by fitting the ZFCFC magnetization considering a system of noninteracting SP particles and a log-normal size distribution [14]. Figure 2a shows the result of the fitting procedure for colloid 1 using the parameters listed in Table I. The average magnetic size based on a model of bimetallic CoRh particles lies between the ones deduced from WAXS and HRTEM experiments. We can consider that these results are consistent since HRTEM overestimates the particle sizes, the larger particles being more easily observed. On the contrary, WAXS experiments which are sensitive to the crystalline order give an estimation of the lowest limit of the particle size. The low size dispersion allows one to consider these systems as monodisperse. Thus, the magnetic properties can be connected to the statistical average of the individual properties of randomly oriented nanoparticles having 100 ± 15 (350 ± 50) Co atoms and 110 ± 15 (300 ± 50) Rh atoms per particle for colloid 1 (colloid 2).

The low field magnetic moment per CoRh formula (μ_{CoRh}) is found to be nearly identical for both samples [$(1.9 \pm 0.1)\mu_B$]. K_{eff} is found to be larger than in monometallic Co particles, reaching the value of $1.0(\pm 0.1) \times 10^6$ J/m^3 for colloid 1. Isothermal magnetization measurements vs applied magnetic fields [$M_T(H)$] above T_B do not display hysteresis effects, confirming the SP behavior. Below T_B, the $M_T(H)$ curves have the expected hysteristic behavior of blocked FM nanoparticles. Figure 3 insets show the hysteresis loops measured in steady fields up to 5 T at 2 K. In both cases, 5 T were not sufficient to saturate the magnetization. The magnetization values at 5 T are roughly identical, around 1.9 $(\pm 0.05)\mu_B$ per CoRh. The coercive fields and the high field differential susceptibilities are larger for colloid 1 than for colloid 2. Both samples still display hysteretic behavior up to 5 T. In order to get more information about the saturation magnetization, pulsed high field magnetization measurements were undertaken up to 30 T at 4.2 K. Figure 3 shows the first magnetization and remanence curves of both colloids. The magnetization saturates for the larger particles in fields above 15 T, while a vanishing differential susceptibility persists for colloid 1 even in high fields. Unusual irreversibility phenomena are occurring in high fields up to $\mu_0 H_{\mathrm{irr}} = 13$ T (8.2 T) for colloid 1 (colloid 2) up to 6 times larger than for monometallic Co nanoparticles. Their magnitude remains constant even when changing the magnetic field sweeping rate, allowing us to discard possible dynamic effects. The difficulty to reach the magnetic saturation can be explained by the small size of the particles combined to the reduced exchange interaction J and a large on site anisotropy (K). In the case of uniformly magnetized FM nanoparticles, recent micromagnetic simulations have shown the presence of strong irreversibility in the magnetization process and effects of noncollinearity of the surface spins as the on site J/K ratio decreases [15]. They are enhanced by size reduction. At 30 T, the average magnetic moments per CoRh unit are 2.38 $(\pm 0.05)\mu_B$ and 2.3 $(\pm 0.05)\mu_B$ for colloid 1 and colloid 2. These values are larger than those measured for monometallic Co using the same experimental setup, $2.1\mu_B$ and $1.9\mu_B$ per Co atom for particles with an average number of atoms of 150 and 300, respectively [9]. More spectacularly, these values are twice as large as the predicted bulk value for a CoRh alloy (theoretical value: $1.17\mu_B$ per CoRh formula) [16].

This set of magnetic data opens new questions concerning the influence of the size on the magnetism of this $3d$-$4d$ FM bimetallic compound. These original magnetic properties should be related to the particles' size and their atomic organization. Since the crystal structure is not identified, three hypotheses can be proposed. The first one consists of CoRh alloyed particles with a nonperiodic crystal structure. The other ones are based on segregated particles with a core shell structure, namely, Co at the core and Rh in the outer shell and vice versa. Let us first discuss these segregated models. Considering M_S, both hypotheses are possible: Co should possess a high magnetic moment due to the small size of the core or to the small thickness of the outer shell, and an induced spin polarization on the Rh sites in contact with Co can be predicted as

TABLE I. Parameters of the two colloids (see text).

Sample		ϕ^a (nm)	$\phi(nm)^b$ (nm)	σ^b	T_B (K)	$K_{\mathrm{eff}}{}^b$ (10^6 J/m^3)	μ_{CoRh} (5 T) (μ_B/Co)	μ_{CoRh} (32 T) (μ_B/Co)	α (K$^{1.5}$)
Colloid 1	$Co_{47}Rh_{53}$	1.8	1.65	0.14	10.9	1	1.91	2.38	5.32×10^{-5}
Colloid 2	$Co_{55}Rh_{45}$	2.6	2.3	0.15	13.5	0.6	1.88	2.3	4.5×10^{-5}

[a] Deduced from HRTEM micrographs. [b] Deduced from ZFCFC magnetization curves.

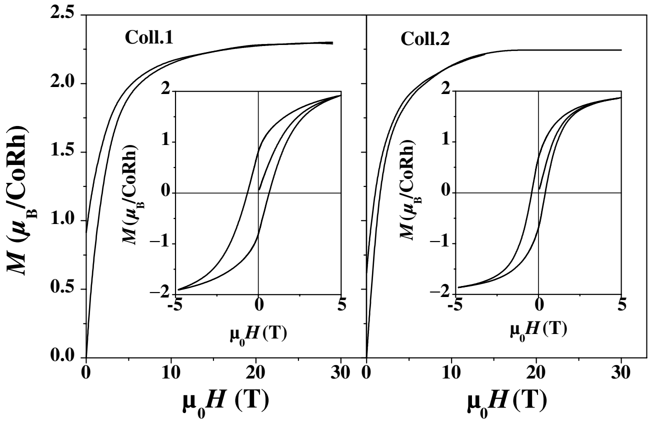

FIG. 3. First magnetization and remanence curves measured in pulse fields at 4.2 K for both colloids. The insets show the hysteresis loops measured in steady fields at 2 K.

in the case of multilayer systems. However, the first hypothesis of a Co core can be easily rejected, since it would lead to a very small size compared to the coherence length of the systems. Moreover, in segregated nanoparticles, the surface sites should be occupied by the element with the lower surface energy, namely, Co in the present case [17]. Furthermore, the value of $d_{\text{M-M}}$ deduced from the WAXS studies is larger than the expected values for the CoRh alloy and close to those of Rh. Thus, the hypothesis of segregation favors the occurrence of a Rh rich core surrounded by a Co shell. If so, most of the magnetization should be carried by the outer surface atoms. Their low coordination number would induce a faster decrease of $M_S(T)$ as a function of T^n with n well above $3/2$, in contradiction with our experimental results [18].

In fact, the hypothesis of a closed frontier between the two elements may not be suitable at these sizes with three to five atomic layers. WAXS spectra evidence a coherence length just below the magnetic size, indicating that the particles are rather homogeneous in composition with an original crystal structure and possibly some surface disorder. A regular distribution of the magnetization within the particles is the only one in agreement with a regular decrease of M_S vs $T^{3/2}$. The enhanced K_{eff} value in comparison to monometallic Co particles can be understood considering the contribution of the large spin-orbit coupling of Rh. In such an alloyed system, the M_S values measured here are twice as large as the bulk one. If one assumes that the bulk ratio $\mu_{\text{Rh}}/\mu_{\text{Co}}$ theoretically determined by Moraïtis *et al.* is still valid at these sizes [16], we estimate $\mu_{\text{Co}} = 2.02\mu_B$ and $\mu_{\text{Rh}} = 0.32\mu_B$ for colloid 1. With such crude assumptions, μ_{Co} is similar to that found for monometallic particles and unaffected by the alloying of Rh even at 50% contrarily to bulk phases. Size reduction induces strongly enhanced magnetism. However, the real distribution of the magnetism across each particle should be more complex, depending on the local structural order, and the atomic location (inner or surface). Refinements are necessary to identify the origin of the enhanced M_S values, including the precise magnetic moment (spin and orbital contribution) on each metal. A definitive answer cannot be given at this point and is challenging from both experimental and theoretical points of view. Element sensitive techniques such as extended x-ray fine structure and x-ray magnetic circular dichroism may give some important precisions on the local properties [19] and will be carried out in the future.

In conclusion, we report in this Letter the first preparation of cobalt/rhodium nanoparticles. The bimetallic character of the particles was demonstrated by both structural and magnetic studies which reveal the strong influence of size reduction. We observe a strong enhancement of the magnetization, up to twice the value of the bulk alloy. The main conclusion is that the size reduction and the association with a $3d$ FM compound play a cooperative role that leads to a probable enhanced induced electronic spin polarization on the Rh atoms and preserve the Co magnetism.

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