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# Structural and magnetic study of bimetallic $\text{Co}_{1-x}\text{Rh}_x$ particles

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## Abstract

We studied the structural and magnetic properties of cobalt-rhodium nanoparticles dispersed in a polymer matrix. It is shown that the structure depends on the composition, high cobalt content leading to a non-periodic structure. Magnetic measurements confirm the dispersion, particle size, and bimetallic character of the particles. Evidence is given of enhanced magnetisation for the composition  $x = 0.5$ . © 2002 Elsevier Science B.V. All rights reserved.

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Size reduction in metals is well known to modify their physical properties, in particular their magnetism. Indeed surface atoms, whose proportion is important relatively to bulk atoms, will behave differently since their coordination number is reduced. For example, it has been shown that a 4d metal can become ferromagnetic (FM) in nanoscale particles. This effect was evidenced in rhodium clusters including less than 50 atoms. In general, the 4d elements (Rh, Ru, Pd) can also present a small spin polarisation in bulk materials when they are alloyed with a FM 3d element [1,2]. Thus the question is now, how will the magnetism of FM intermetallics 3d–4d materials evolve at the nanometer scale? If size reduction and alloying effects are playing a cooperative role, then a higher electronic polarisation on the 4d elements is expected.

At these small sizes, the magnetic properties of such nanomaterials will be strongly influenced by the atomic arrangement within the particle. A fine description of the structure is therefore essential to model accurately the magnetic properties in order to synthesise particles with optimised properties.

We studied the structure and magnetism of bimetallic cobalt–rhodium particles stabilised in a polymer. Magnetism was measured by SQUID magnetometry in steady fields up to 5 T, and in pulse magnetic fields up to 30 T. The structure was investigated by high resolution transmission electron microscopy (HRTEM) and wide angle X-ray scattering (WAXS). HRTEM gives information on the size, morphology and the projected crystallographic structure of the individual particles observed. On the other hand, WAXS gives global information on the entire sample through the radial distribution function (RDF) which provides a set of accurate interatomic distances defining a characteristic signature of the three-dimensional structure. The combination of these two techniques gives complementary information to resolve the structure.

The particles were synthesised by solution chemistry following a method already used with success for others mono- and bi-metallic particles like PtRu or CoPt [3] with well controlled composition. For CoRh, two organometallic precursors ( $\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\eta^4\text{-C}_8\text{H}_{12})$  and  $\text{Rh}(\text{acac})(\eta^4\text{-C}_8\text{H}_{12})$ ) were simultaneously decomposed in the presence of a solvent (tetrahydrofuran, THF) and a polymer (polyvinylpyrrolidone, PVP). The reaction was carried out at room temperature and under a 3 bars dihydrogen pressure. The relative ratio of the precursors leads to the same cobalt/rhodium ratio in the

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particles. The different nominal compositions studied are  $\text{Co}_{0.5}\text{Rh}_{0.5}$ ,  $\text{Co}_{0.75}\text{Rh}_{0.25}$  and  $\text{Co}_{0.25}\text{Rh}_{0.75}$ . They were controlled at the end of the synthesis process by chemical microanalysis. HRTEM specimens were prepared by slow evaporation of droplets of diluted solution deposited on a copper grid covered by a thin carbon film. WAXS samples consisted of a dried powder sealed in a Lindemann glass capillary. All the samples for the structural studies were prepared under a controlled atmosphere, only microscope grids were shortly exposed to air just before entering the microscope.

Bulk rhodium is face centred cubic (FCC) with a first metal–metal distance of 0.269 nm, bulk cobalt is hexagonal at room temperature and FCC at high temperature with practically the same first interatomic distance of 0.25 nm. The bulk alloy is hexagonal for rhodium concentrations up to 49.5 at% and FCC for higher rhodium content, with cell parameters varying linearly with the composition [4]. Nanoparticles of rhodium and cobalt prepared from the same precursors, according to an identical process, have already been studied in our group. For sizes around 2 nm, Rh retains the FCC structure of the bulk metal whereas Co adopts a non-periodic structure [5]. It is noteworthy that no report on structural determination for CoRh nanoparticles appears in the literature.

HRTEM observations show particles well dispersed in the polymer matrix (see Fig. 1), excepted for the high cobalt concentration sample, in which they are packed in circular groups. For  $\text{Co}_{0.5}\text{Rh}_{0.5}$ , two different concentrations for the metal precursors were used ((a), 20 wt% and (b), 10 wt%), leading to different mean diameters

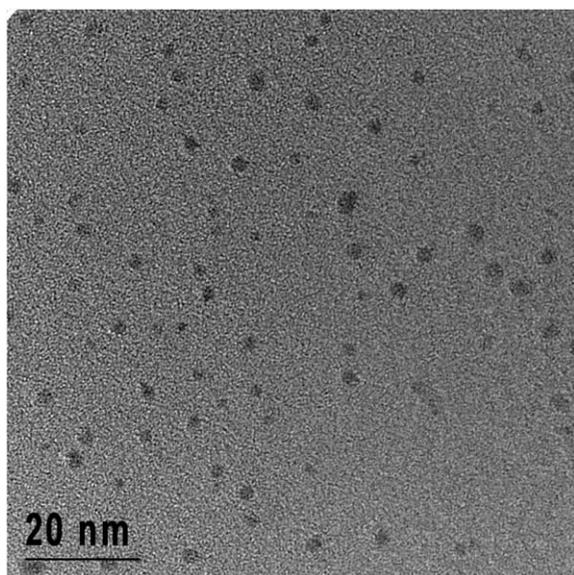


Fig. 1. Particle dispersion in the  $\text{Co}_{0.5}\text{Rh}_{0.5}$  sample.

(2.7 and 1.75 nm, respectively). Particles do not appear crystallised. The RDFs obtained by WAXS point to the same first metal–metal distance of 0.265 nm, close to the one for bulk rhodium (see Fig. 2). The pattern cannot be related to an FCC or a hexagonal phase, or even to a combination of both, and it denotes the presence of some disorder, more important for the smallest particles (b). The coherence lengths of 2 nm (a) and 1.5 nm (b), which provide a minimum value of the particles mean size, are significantly shorter than the diameter obtained by HRTEM and are another indication of disorder. After annealing under controlled atmosphere of the preparation (a), the same metal–metal distance is observed but the pattern is better defined and closer to a hexagonal structure.

For the composition  $\text{Co}_{0.75}\text{Rh}_{0.25}$ , the mean diameter found is 2.2 nm. The particles are not crystallised except some oxidised ones in the  $\text{Co}_3\text{O}_4$  structure. This is clearly caused by air-sensitivity of the particles on the microscope grid since WAXS measurements do not show any oxidation. The RDF displays a broad pattern indicating a disordered structure. The first metal–metal distance is the same as for  $\text{Co}_{0.5}\text{Rh}_{0.5}$  but the next peaks are shifted to shorter distances consistently with a higher proportion of cobalt in the particles. The coherence length of 1.3 nm, much shorter than the diameter observed by HRTEM, is another sign of disorder as in the case of  $\text{Co}_{0.5}\text{Rh}_{0.5}$ .

Particles in the  $\text{Co}_{0.25}\text{Rh}_{0.75}$  preparation have a mean size of 2.5 nm. From HRTEM, they appear well crystallised and some of them polycrystalline. This preparation is also sensitive to oxidation but leads to

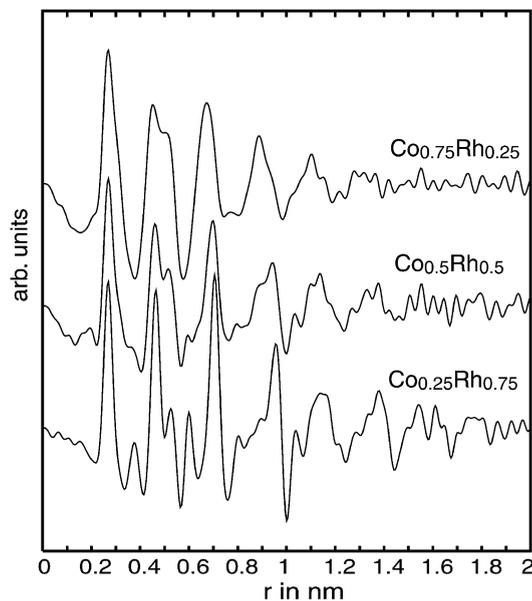


Fig. 2. Experimental RDFs of the three preparations.

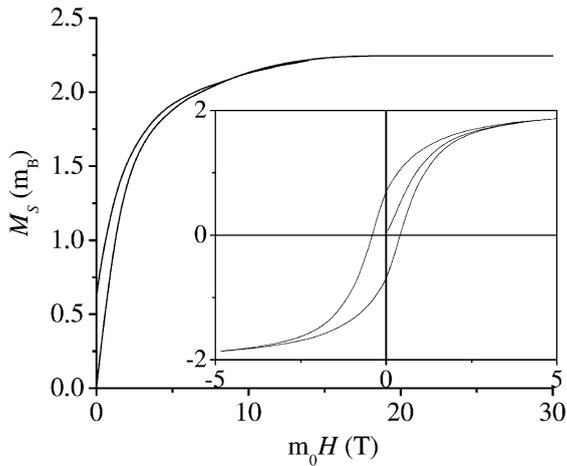


Fig. 3.  $\text{Co}_{0.5}\text{Rh}_{0.55}$  sample (a): high-field magnetisation measured at 4.2 K.

particles in the  $\text{Rh}_2\text{O}_3$  structure. We also find FCC particles with the parameters of bulk rhodium. The first metal–metal distance is the same as for the other compositions, but peaks are significantly sharper and the general pattern is closer to an fcc one. Peaks are observed out to 1.9 nm.

Concerning the magnetic measurements, zero-field-cooling field-cooling (ZFC/FC) magnetisation curves were performed in a low magnetic field on encapsulated samples. For the concentrations  $\text{Co}_{0.5}\text{Rh}_{0.5}$  (a), and (b)  $\text{Co}_{0.25}\text{Rh}_{0.75}$ , the magnetic susceptibilities are characteristic of non-interacting superparamagnetic particles with blocking temperatures  $T_B = 13.5$ , 10.9 and 6.9 K, respectively (see Fig. 3), whereas it shows interactions between superparamagnetic particles in the preparation  $\text{Co}_{0.75}\text{Rh}_{0.25}$  ( $T_B = 16.2$  K). By fitting these curves, one can deduce the particle size distribution and the effective anisotropy. The particle size distributions are consistent with the HRTEM and WAXS results.

For the systems  $\text{Co}_{0.5}\text{Rh}_{0.5}$  (a) and (b), the spontaneous magnetisation reaches a value of  $2.38 \mu_B$  per Co

site if one considers that Rh does not carry any magnetic moment. This corresponds to a huge enhancement of the magnetisation, two times bigger than usual values of bulk materials. The spontaneous magnetisation is strongly dependent on the temperature, which indicates, with the enhanced anisotropy field as compared to monometallic Co, the bimetallic and alloying character of the particles. Further magnetic measurements are planned in order to determine with more accuracy the evolution of the magnetic properties as a function of the composition.

In summary, the structure of these particles depends on their composition. The RDFs show a structure increasingly disordered with cobalt content, degrading from a structure close to FCC until a non-crystalline arrangement (see Fig. 2). Element specific methods (e.g. EXAFS) are however necessary to further characterise these samples, especially to better define the respective locations of the two metals in the alloy. Magnetic measurements generally confirm the dispersion, the average size and the bimetallic and alloyed characters of the particles. The first results show a huge enhancement of the magnetisation as compared to the bulk phases for the  $\text{Co}_{0.5}\text{Rh}_{0.5}$  preparations, probably due to the nanoscale size.

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