

Bimetallic CoRh and CoRu nanoparticles: size induced enhanced magnetisation

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Elsevier use only: Received date here; revised date here; accepted date here

Abstract

The magnetism of bimetallic $\text{Co}_x\text{M}_{1-x}$ (M : Ru and Rh) clusters has been investigated on systems of nanoparticles with diameters smaller than 2nm embedded in a polymer obtained by means of organometallic synthesis. Whatever the composition (up to $x = 0.75$), the investigation of magnetism evidence a ferromagnetic behavior. As a consequence of size reduction, both CoRh and CoRu systems display enhanced magnetic moments and anisotropy compared to bulk values. © 2001 Elsevier Science. All rights reserved.

Keywords: nanocrystals; nanoparticles; clusters; size effect; polarisation; anisotropy.

PACS numbers: 78.67.Bf; 71.20.Be; 75.30.Gw; 75.75.+a

1. Introduction

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 as a result of surface and structure effects. Such effects have been first demonstrated in the case of Fe, Co and Ni metal clusters containing less than 1000 atoms.[1] Size reduction also induces the appearance of FM as demonstrated by molecular beam deflection measurements for Rh clusters up to 34 atoms although Ru remains non magnetic.[2] These results demonstrate that size reduction promotes in some cases an electronic polarization in species at the border of FM. Moreover, a spin polarization can be induced by a very small

perturbation of the lattice parameter, by elaborating layered structures with a FM material and more efficiently by alloying with a 3d FM metal. As a consequence, one can expect unusual magnetic behaviors in 3d FM/4d clusters, where size reduction should play an important role on spin and orbital polarization.

The synthesis of bimetallic nanoparticles requires size, composition and surface state controls. 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.[3,4] This route leads to nanoparticles of narrow size distribution that fulfill the requirements stated above, where the by-products of the synthesis do not alter the surface magnetism. This approach has been applied to the case of bimetallic CoRh and CoRu for different leading to ultrafine particles with diameters below 2nm. A FM behavior has been observed in all the cases with a strong enhancement of the magnetic moment.

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2. Magnetic properties

The synthesis and structural characterization of the samples (Co_3Rh_1 , Co_1Rh_1 , Co_1Rh_3 and Co_3Ru_1 , Co_1Ru_1 , Co_1Ru_3) have been described elsewhere.[5,6] They consist in nanoparticles assemblies well dispersed in a polymer matrix (polyvinylpyrrolidone), which prevent the magnetic dipolar couplings. The different samples have roughly the same average size between 1.6 nm and 2.3 nm with narrow size dispersion (Fig.1). They allow the investigation of the intrinsic magnetic properties at a given particle size as a function of rhodium and ruthenium content.

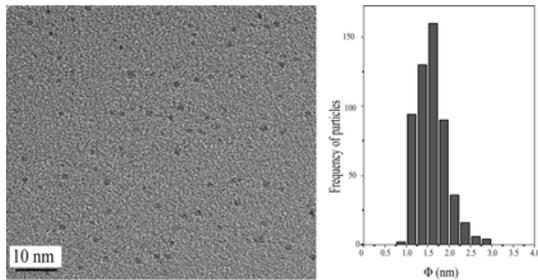


Fig.1: TEM micrograph and size histogram for Co_1Ru_3 particles with a mean size of 1.6 ± 0.3 nm.

Magnetic properties have been investigated using a commercial SQUID magnetometer. Fig. 2 displays the evolution of the hysteresis curves measured at 2K for different samples. The measurements have been calibrated according to the Co contents. All these systems display FM behaviour. As a general tendency the magnetisation does not saturate even in fields up to 5 T. Increasing the atomic 4d metal concentration considerably affects both absolute magnetisation and shape of the hysteresis loops. The magnetisation loops are irreversible over a large range of magnetic fields, and strong high field susceptibility is noticeable. Alloying with Rh or Ru induces a reinforcement of the coercive fields of the material, which indicates stronger anisotropy fields.

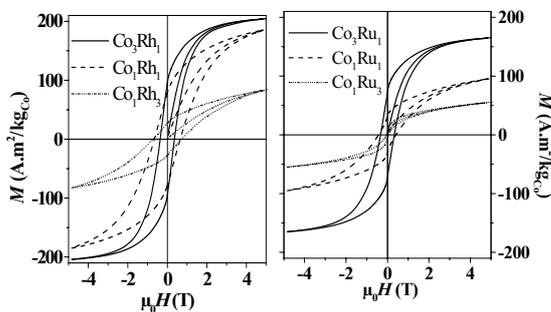


Fig. 2: Hysteresis loops measured at 2K with a SQUID magnetometer.

The magnetic moment largely exceeds the bulk value for all the compositions. For all these samples, no oxide layer has been evidenced (neither from high resolution electronic microscopy nor magnetisation measurements), and these high values of magnetisations evidence a clean surface state of the nanoparticles. This enhancement is a consequence of the size reduction. It cannot be attributed to the sole enhancement of the Co magnetic moment even in the case of very small segregated Co clusters within the nanoparticles where high spin and orbital Co contributions are expected. Therefore magnetic data point towards a large Rh contribution, which may only be reached in nanoscale alloyed systems. The CoRu system reproduces the same tendency, however with lower sensitivity. Thus, Ru may be less polarized as already observed in small clusters or in bulk alloys with cobalt.

Estimations of the effective anisotropy have been done by fitting ZFC/FC curves.[5,6]

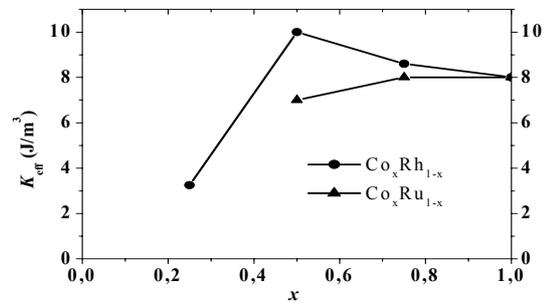


Fig.3: Effective anisotropy of $\text{Co}_x\text{Rh}_{1-x}$ and $\text{Co}_x\text{Ru}_{1-x}$ systems measured by ZFC/FC procedures at $\mu_0 H = 1.0$ mT.

The anisotropy is found to be high for all systems but does not increase as much as expected when increasing rhodium or ruthenium ratio.

3. Conclusion

The CoRh system displays a huge enhancement of magnetic moment per atom compared to the bulk value. In the CoRu system, enhancement is less spectacular but still effective. Alloying Co with 4d also induces a reinforcement of the coercive fields. The volume reduction promotes high magnetic moments, probably both on the Co and 4d metals. The quantitative analysis of the polarization induced on Rh and Ru by element sensitive techniques is currently underway in order to better understand the origin of magnetic moment enhancement.

References

- [1] I.M.L. Billas, et al., Science **265** (1994) 1662.
- [2] A.J. Cox, et al., Phys. Rev. B. **49** (1994) 1229570.
- [3] J. Osuna et al, J. Phys. Chem. **100** (1996) 14571.
- [4] M. Respaud et al., Phys. Rev. B **57**, (1998) 2925.
- [5] D. Zitoun, et al, Phys. Rev. Lett. **89** (2002) 37203.
- [6] D. Zitoun et al, J. Phys. Chem. B (in press).