

Tuning the magnetic moments and anisotropy energy of CoRh nanoparticles

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While the magnetism of monometallic transition-metal (TM) clusters has been largely investigated in past years, very little is known at present about the behavior of binary-metal particles or magnetic nanoalloys. Is it possible to tune the magnetic properties of clusters, in particular the MAE, by alloying as it has been done in the bulk? Can one microscopically design very hard or very soft nanomaterials in a controlled way? What is the role played by the spatial distribution of the chemical species within the particle on the magnetic behavior?

In order to investigate this problem we have determined experimentally and theoretically the spin moments, orbital moments and magnetic anisotropy energy (MAE) of $\text{Co}_x\text{Rh}_{1-x}$ alloy nanoparticles (NPs) as a function of size, structure and composition. The NPs are synthesized by chemical decomposition of organometallic precursors under hydrogen atmosphere and in the presence of a polymer matrix. The magnetic properties are determined using SQUID, Mössbauer spectroscopy, and X-ray magnetic circular dichroism (XMCD). Self-consistent calculations are performed in the framework of a realistic *spd*-band tight-binding Hamiltonian by treating the redistributions of the spin- and orbital-polarized density, as well as the spin-orbit (SO) interactions, on the same electronic level and from a local perspective.

Enhanced values of the average magnetic moment per CoRh unit and of the MAE are observed in alloy NPs, which indicate a significant induced polarization on the Rh atoms. These results are well reproduced by theory and were also confirmed by independent XMCD measurements of the spin and orbital Rh moments. A local theoretical analysis shows that the moments at the CoRh interface are largely responsible for the increase of the average magnetization and MAE. Comparison between theory and experiment suggests that the most likely chemical arrangement is a Rh core covered by a Co shell, with a moderate degree mixing at the interface. Experiment also shows a remarkable non-monotonous dependence of the MAE on Co concentration x with an optimum Rh content that increases with decreasing size. This novel behavior is theoretically explained as the result of the geometrical and chemical environment dependence of the induced Rh moments and the associated enhancement of SO interactions. The *4d* magnetic moments predicted by theory are confirmed by XMCD experiments at the Rh edge. These results not only demonstrate the optimization of the blocking temperature and the dominant role played by *4d* magnetism in *3d-4d* nanoalloys, but they also provide new physical insight on the subtle microscopic mechanisms responsible for the MAE of these systems, that should be very useful as a guide to microscopic material design. Controlling the concentration profile in nanoalloys, for example, by manipulating the kinetics of the synthesis process, opens therefore a variety of new routes in nanomagnetism.