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Experimental report on Proposal HE2719

The role of Pt induced magnetic moments in the magnetic anisotropy energy of Co_xPt_{1-x} nanoparticles

Scientific background

Binary alloy nanoparticles composed of Co and Pt are excellent candidates to achieve the Magnetic Anisotropy Energy (MAE) increase necessary for room temperature applications[1]. Anisotropic chemical local order, $L1_0$ or $L1_2$ like, plays a key role in enhancing the volume anisotropy as compared to the isotropic chemically disordered FCC structure. This comes from the largely directional chemical bonding of Co atoms to Pt. At the Pt sites, induced magnetic moments originate from the hybridization of the Pt 5d orbitals with the Co spin-polarized 3d states. Due to the fairly large spin-orbit coupling of the Pt 5d electrons[2] the orbital moment contribute largely to the total moment on the Pt sites. These moments may be observed by XMCD experiments[3]. Owing to the high surface-to-volume atomic ratio, segregation effects may induce large changes in the surface anisotropy[4]. So, the investigation of the alloying and ordering processes and, eventually, of the core-shell nanoparticles formation are clues to the comprehension of the magnetic properties and to the optimization of the material for applications.

Our samples are prepared from nanoparticles pre-formed in the gas phase and then co-deposited in UHV with the matrix. Adjusting independently the deposition rate of the nanoparticle and matrix beams, very dilute (< 5% of nanoparticles in volume) nanoparticle assembled films, with quite negligible magnetic interaction among nanoparticles, are obtained. By coupling an electrostatic quadrupole deflector to the setup, one is able to deposit mass-selected CoPt clusters. The relative size dispersion, which is around 40% without mass selection, can be lowered to about 7% with the mass selection**.** We focus our attention to matrices with a weak influence on the interface magnetic anisotropy, like Ag and C, in order to preserve and investigate the intrinsic surface properties.

Sample preparation and characterizaton

Nanoparticles embedded in Ag and C matrices have been prepared with different compositions: Co, Co3Pt, CoPt, $CoPt_3$, and Pt. The as-cast carbon coated mixed nanoparticles were characterized using high resolution transmission electron microscopy (HRTEM) and x-ray techniques. For all compositions, the nanoparticles presented a mean diameter of about 2.5 nm and crystallize in the FCC chemically disordered phase. Post-annealings are compulsory to generate ordered phases and segregation (core-shell effects). For all the non mass-selected samples, two identical samples were prepared and one of them was systematically annealed up to 400°C to 500°C.

Previously, XMCD measurements at the Co $L_{2,3}$ edge were performed on assemblies of Co_xPt_{1-x} nanoclusters embedded in various matrices, together with complementary SQUID magnetization measurements. These experiments revealed a global rise in the blocking temperature and the spin magnetic moment per Co atom, for the annealed nanoparticles[5]. The origin of such an enhancement, which amplitude varies with the cluster composition and the matrix, is still an open question but should be closely related to the induced moments at the Pt sites.

Experimental concerns

In the first experimental session of this proposal, we performed XANES and XMCD measurements on as cast and annealed samples of binary CoPt and CoPt3 2.5 nm-particles embedded in a C matrix. In

[1] Jong-II Park et al, J.Am.Chem.Soc. **126**, 9072-9078 (2004)
[2] V.N. Antonov et al., Phys. Rev. B **64** 024402 (2001)
[3] W. Grange et al., Phys. Rev. B **58** (1998) 6298 & Phys. Rev. B **62** (2000) 1157
[4] M. J. Munoz-Navia et al, J. Phys.: Condens. Matter **16**, S2251 (2004) and Computional Materials Science **35**, 302 (2006)
[5] F. Tournus et al. Phys. Rev. B **77** (2008) 144401

the second experimental session we completed the study with the third composition Co3Pt on C and studied the Co K edge XMCD on a mass-selected CoPt sample. The induced Pt magnetic moments were measured at a temperature close to 7 K and under a magnetic fields up to 0.6 T. The magnetic moment per Pt atom and the orbital to spin moment ratio were obtained by applying the sum rules. Our samples are very diluted (about 1 to 2 monolayers equivalent) within the matrix and the high brilliance of the ID12 beamline was essential: getting a reliable full XMCD spectrum at the L2 and L3 Pt edges took about 20 hours of acquisition time. All spectra were recorded in partial fluorescence yield using the 35-channel silicon drift detector. During the first experimental session, we got some problems with the detection system and a pretty large bunch of time were used to fix this instrument. To compensate for that and to complet, at least part of our proposal, we were given an additional slot of beamtime by the end of August/beginning of September.

Experimental results

In the first part of this study, we measured three different compositions (CoPt, CoPt3 and Co3Pt) of as-cast and annealed nanoparticles within C matrices. The Pt L-edge measurements revealed that in the case of the CoPt the orbital contribution increases under annealing. On the other hand, for both CoPt3 and Co3Pt compositions there is a decrease in the orbital contribution under annealing, which is an unexpected result. This outcome could possibly be related to segregation. It has also been observed that there is an evolution of the near edge features that might be correlated to structural local changes. Such behavior within the C matrix could be either enhanced or reversed within the Ag matrix, which is supposed to favor nanoparticle ordering. We intend to complement our study by measurements on similar samples within Ag matrix.

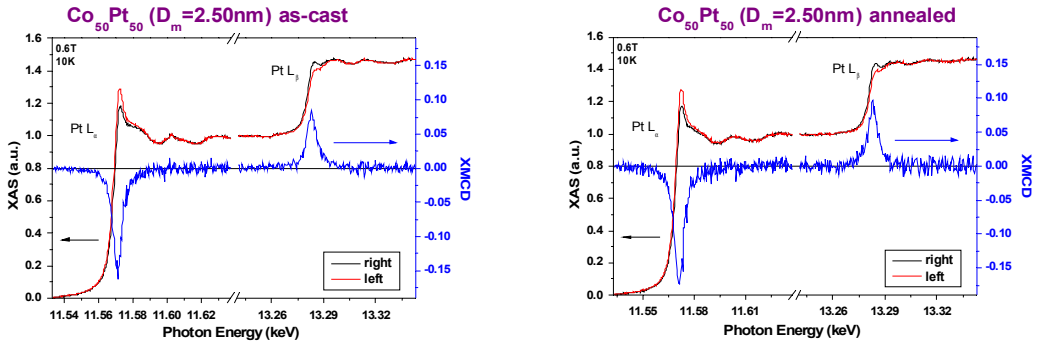

Figure 1: XMCD at the Pt L2,3 edges for CoPt as-cast (a) and annealed (b) samples.

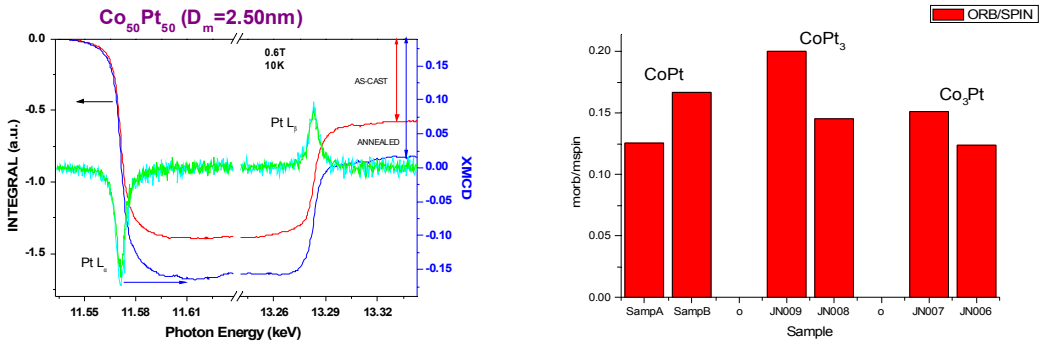

Figure 2: (a) XMCD and integrals at the Pt L2,3 edges for CoPt as-cast and annealed samples. (b) Ratio of orbital and spin moments obtained by applying the XMCD sum rules.