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XMCD study of CoPt nanoparticles embedded in MgO and amorphous carbon matrices

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ABSTRACT

We report the synthesis and characterization of CoPt nanoparticles, using X-ray magnetic circular dichroism (XMCD) at the Co $L_{2,3}$ edges. Clusters are produced in ultra-high vacuum conditions, following a physical route, and embedded in non-metallic matrices: MgO and amorphous carbon (a-C). In MgO, Co atoms are partially oxidized, which goes with a μ_L/μ_S enhancement. On the contrary, a-C appears as a very suitable matrix. In particular, annealing of CoPt cluster embedded in a-C is able to promote L 1_0 chemical order, without alteration of the sample. This transformation, which has been directly evidenced by transmission electron microscopy observations, is accompanied by a striking augmentation of μ_S, μ_L and the μ_L/μ_S ratio of Co. The presence of Pt leads to an enhanced Co magnetic moment, as compared to Co bulk, even for the chemically disordered alloy. Moreover, the high value of 1.91 μ_B/at. measured for μ_S is unusual for Co and must be a signature of chemical order in CoPt alloy nanoparticles.

1. Introduction

CoPt nanoparticles have been widely studied during the last decade [1–17], as they represent one of the best candidates for ultra-high density magnetic storage applications [18]. Indeed, this particular alloy can crystallize in a chemically ordered phase, labelled $L1_0$, which shows a huge magnetocrystalline anisotropy [19,20]. However, CoPt nanoparticles are usually synthesized in the chemically disordered phase, labelled A1, and chemical ordering is in general obtained by post-annealing. Most of the times, this goes with problems of pollution or coalescence, difficult to avoid [5,21–24]. As far as applications are concerned, CoPt nanoparticles cannot remain isolated: they are necessarily in interaction with their environment (ligands for chemically prepared particles, substrate or matrix). In this view, when clusters are embedded in a matrix, the latter should display the following features: without deteriorating the clusters genuine magnetic properties, it must act as a good particle spacer (in particular during annealing, where it must prevent cluster coalescence), and protect clusters from pollution.

In this paper, we report the magnetic characterization, using X-ray magnetic circular dichroism (XMCD) at the Co $L_{2,3}$ edges, of CoPt nanoparticles produced following a physical route. Clusters assemblies, embedded in two different non-metallic matrices (MgO and amorphous carbon) have been investigated. After a brief description of the samples studied, we will discuss the impact of the matrix and of annealing on the Co magnetic moment.

2. Sample preparation and characterization

CoPt nanoparticles are synthesized using a physical route, as opposed to chemical synthesis of colloidal particles. We use the Low Energy Cluster Beam Deposition (LECBD) technique [25,26] that allows us to grow thin films of nanoparticles deposited on a substrate. We will give a short description of this original approach.

Clusters are produced in a laser vaporization–gas condensation source similar to that developed by Smalley, De Heer and Milani [27,28]. Briefly, a plasma created by the impact of a Nd:YAG (Yttrium Aluminium Garnet) laser beam focused on a rod is thermalized by injection of a continuous flow of helium at low pressure (typically 30 mbar) inducing cluster growth. Clusters are subsequently stabilized and cooled down in the supersonic expansion taking place at the exit nozzle of the source. A low energy cluster beam is then obtained, with clusters of different sizes, enabling the growth of thin cluster films on a substrate.

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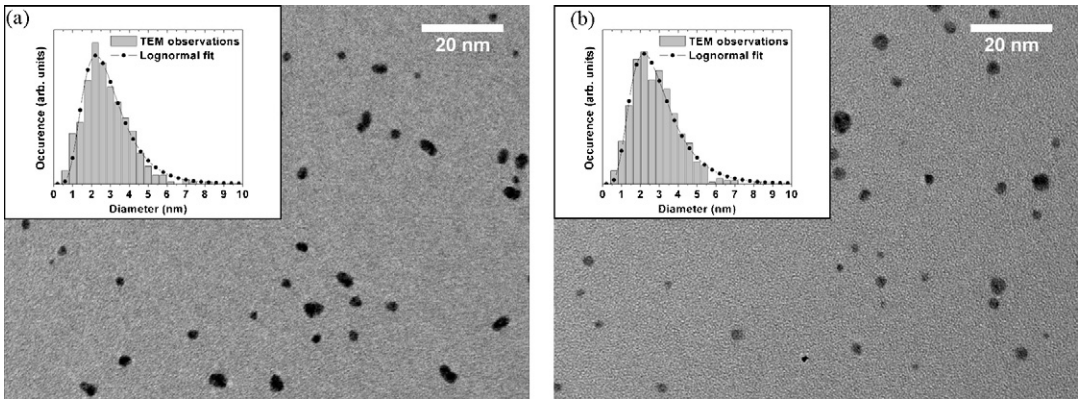

Fig. 1. TEM images of a 2D film of CoPt clusters embedded in amorphous carbon, as-prepared (a) and after annealing (b). The size histograms deduced by TEM images analysis, together with the best fits corresponding to a lognormal size distribution, are shown in inset. The fit parameters (see Eq. (1)) are $d_m = 2.58 \pm 0.10$ nm, $w = 0.42 \pm 0.05$ and $d_m = 2.67 \pm 0.10$ nm, $w = 0.47 \pm 0.05$, respectively, for as-prepared and annealed clusters.

The main key points of this technique are the following. Samples are produced under ultra-high vacuum conditions (base static pressure of 10^{-10} mbar, and around 10^{-8} mbar during deposition, due to the use of helium as carrier gas). Moreover, the experimental setup allows us to co-deposit a matrix in order to grow diluted thin films of embedded clusters. It is important to note that the clusters' composition is determined by that of the target used for laser vaporization. This means that the particles' stoichiometry can easily be adjusted by simply changing the target. In the present case, we use an equiatomic CoPt rod, leading to nanoparticles with a composition very close to $Co_{0.5}Pt_{0.5}$ [29]. Another important feature of the LECBD technique is that clusters arrive on the substrate in a soft-landing regime, following a random deposition scheme. Consequently, as long as there is no significant diffusion on the substrate, which is the case in this study, the inter-particle distance is entirely controlled by the cluster density: the surface density for two-dimensional (2D) samples or the volume density for three-dimensional (3D) samples where clusters are embedded in a matrix. This allows us to adjust the strength of inter-particle interactions and, by synthesizing highly diluted samples, to obtain thin films of clusters behaving as nearly isolated nanoparticles.

The size distribution of the deposited clusters slightly varies with the experimental conditions. It is relatively sharp and corresponds to a lognormal curve (see Fig. 1):

$$f(d) = \frac{1}{w\sqrt{2\pi}} \frac{1}{d} \exp\left\{ -\frac{1}{2}\left[\frac{\ln(d/d_m)}{w} \right]^2 \right\} \quad (1)$$

where d_m is the median diameter, and w is the dispersion.

While CoPt clusters embedded in MgO (CoPt:MgO sample) are produced by co-deposition, samples of CoPt clusters embedded in amorphous carbon (CoPt:aC) are made of a large number of clusters layers (28 successive 2D cluster depositions) separated by carbon layers (a few nanometers thick). In both cases, the cluster concentration [30] is low enough to ensure that magnetic interactions between neighboring particles can be neglected.

As mentioned above, there is a double advantage of using a matrix to embed the clusters: it prevents clusters to come into contact both during the thin film growth and during an eventual post-deposition annealing; and it protects clusters from pollution and oxidation, allowing us to expose the samples to air without any alteration of the CoPt particles properties. In addition, the use of a non-metallic matrix presents the advantage of minimizing RKKY interaction between particles. Moreover, the MgO matrix, which is interesting for tunnel electronic transport experiments, has previously been studied. It appears that this oxide matrix leads to a magnetic anisotropy energy (MAE) increase [13], probably due to a core–shell interface effect (exchange anisotropy between the ferromagnetic core and the antiferromagnetic shell).

On the other hand, the choice of amorphous carbon (a-C) as embedding matrix appears to be sound. Carbon is indeed immiscible with Co and Pt, it is an efficient protection against oxidation, and most of all, it is transparent enough to electrons so that direct TEM observations are possible. a-C is really attractive because it is a light element and it is amorphous (contrary to nano-crystalline metallic or oxide matrices): having a direct observation of embedded clusters is of great help to ensure that the samples are made of well-separated nanoparticles of well-known size, and that these characteristics are preserved upon annealing.

Following the widely used procedure, CoPt clusters embedded in a-C were annealed in order to promote $L1_0$ chemical order in nanoparticles. Two hours annealing periods were performed at a 650 °C temperature and under high vacuum, with or without a preliminary air exposure. As it can be seen in Fig. 1, there is almost no clusters coalescence: the size distribution is nearly the same, as well as the cluster density. In addition, high resolution TEM (HRTEM) images show that both as-prepared and annealed clusters are well crystallized.

For annealed samples, we have been able to successfully observe nanoparticles in different orientations revealing a $L1_0$ type contrast (see Fig. 2). This is a direct signature of the chemical order inside CoPt clusters after annealing [the $L1_0$ structure corresponds to successive pure Co and pure Pt atomic planes in the (0 0 1) direction]. At the opposite, for as-prepared samples, we have not been able to observe any $L1_0$ contrast in HRTEM images. It shows that annealing is needed to promote chemical order in the nanoparticles, and that they are being produced in the chemically disordered fcc A1 phase.

3. XMCD measurements

XMCD measurements were performed at the UE56/2-PGM-2 beamline of the BESSY synchrotron (Berlin), at the Co $L_{2,3}$ edges. We used a collinear geometry where the applied magnetic field is parallel to the incident photon beam. The X-ray absorption spectroscopy (XAS) signal was monitored using the total electron yield detection mode. The magnitude of the applied field was 5 T, which is high enough to fully saturate the sample magnetization, as it has been verified by acquiring hysteresis loops (see Fig. 3).

The CoPt:MgO sample displays an oxide contribution in its XAS spectra (see Fig. 3: Co oxidation results in a typical multiplet structure [31–33,11] for the L_3 peak, manifesting itself here as a shoulder around 779 eV in the CoPt:MgO XAS spectra), which remains weak