

Atomic relaxation effects on magnetism in CoPt nanoalloys

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Abstract. We describe the magnetism of CoPt clusters upon annealing-driven transition to chemically ordered L1₀-like phase. In one hand, X-ray magnetic circular dichroism (XMCD) investigations at each L_{2,3} edge, revealed a significant increase of both spin and orbital of Co and Pt magnetic moments after thermal ordering transition. In the other hand, reversely to the bulk alloys, a limited Magnetic Anisotropy Energy (MAE) enhancement has been obtained from SQUID magnetometry measurements on the same chemically ordered CoPt nanomagnets samples. In this paper, we relate such magnetic behaviour to element-specific dependence of the local atomic relaxations in nanoalloys, described from extended x-ray absorption fine structure (EXAFS) experiments.

1. Introduction

Magnetic nanoalloys attract a lot of attention because they offer the possibility to tune the magnetic moment and the magnetic anisotropy energy (MAE) probably up to the ultimate density storage limit. In particular, an extremely high magnetocrystalline anisotropy is expected from the stacking of pure Co (or Fe) and Pt atomic planes in the (001) direction for CoPt (or FePt) bulk alloys in the chemically ordered L1₀ phase. Nevertheless, even if a well chemical order can be observed at nanosize, the achievement of a consequent MAE enhancement without any coalescence after annealing-driven transition, remains so far absent^[1, 2, 3, 4]. The MAE determines the low-temperature orientation of the magnetization with respect to the structure of the system. It determines also the energy barrier that fixes the superparamagnetic limit at which the system loses its magnetic memory, a limit that is of crucial importance in non-volatile magnetic memory. The atomic structure and magnetic moment of CoPt and FePt nanoparticles have been experimentally observed to differ from the corresponding bulk materials in a positive way or not, due to small size effects as peculiar symmetry^[5], partial chemical ordering^[6], surface segregation^[7],... Numerous theoretical works have been performed to try to explain exotic structures^[8, 9, 10, 11] or electronic properties^[12,13] observed in nanoalloys by integrating a great number of parameters. In this paper, we relate atomic relaxation effects on magnetism in CoPt nanoalloys.

2. Experimental procedures

2.1. Sample Synthesis

Bi-metallic clusters are performed in the gas phase thanks to a laser vaporization source working in the Low Energy Clusters Beam Deposition (LECBD) regime^[1]. Recently our apparatus is equipped with a



quadrupolar electrostatic mass-deviator allowing us to deposit mass-selected clusters in an UHV deposition chamber^[5] allowing a gaussian size distribution with a relative standard deviation close to 8 %. We have focused our attention on 3 nm CoPt nanoparticles (NPs) embedded in an inert carbon matrix, in order to preserve and investigate the intrinsic cluster surface properties. We have synthesized size-selected CoPt clusters assemblies, 1%-diluted in volume in C-matrix to quite avoid magnetic interaction among NPs. The idea was to study structure and magnetism of CoPt NPs before and after an optimum annealing of 2 hours at 750 K under high vacuum without any coalescence. First of all, High Resolution TEM-observations and simulations on CoPt NPs revealed that upon annealing a transition occurred up to 2 nm in diameter from as-prepared A1 fcc-structure to a tetragonal chemically ordered L1₀ phase with quasi perfect order parameter and truncated octahedron shapes^[14].

2.2. EXAFS experiments

The geometrical arrangement has been quantitatively determined from Extended x-ray absorption fine structure (EXAFS) experiments performed in the fluorescence mode on as-prepared and annealed CoPt samples, at both Co-K and Pt-L edge, respectively on the CRG-FAME and ID12 beam lines of the european synchrotron radiation facility (ESRF) at Grenoble^[15]. Data were simulated after a 1.2–3.2 Å Fourier-window filtering (distances uncorrected from phase shift). The fits then return the number of nearest neighbors to the absorbing Co or Pt atom for each element N , their average distances R , and their Debye-Waller factors, which are related to the bond-length dispersion. In the Fig. 1a, one can see at Co-K edge, a remarkable enhancement in Fourier Transform (FT) intensity upon annealing of the peak located at 2 Å corresponding to the first metallic nearest-neighbors. From FEFF Fit simulations, we clearly show that the Co-Co/Co-Pt coordination ratio changes upon annealing from 1 to 2 as expected for the A1 to L1₀ transition with contracted lattice parameters related to the bulk phase^[15]. The best simulation has been obtained for a perfect chemically ordered CoPt packing (L1₀ like-phase) with a unique Co-Pt first neighbour distance at both edges but surprisingly two different Co-Co and Pt-Pt distances for CoPt clusters^[15].

2.3. XMCD experiments

X-ray magnetic circular dichroism (XMCD) signal has been measured on as-prepared and annealed bimetallic nanomagnets CoPt at the Co L-edge on SOLEIL – DEIMOS. Moreover, because induced magnetic moments resulting from 3d-5d proximity effects are expected in non magnetic metal, we also performed (XMCD) measurements at Pt-L edge on ID12 - ESRF beam line on the same samples. In table I, the mean orbital and spin magnetic moments (μ_L and μ_S) per Co and Pt atom, have been determined using the well-known sum rules^[16, 17] where the numbers of hole per Co and Pt atoms has been estimated from theoretical band structure calculations ($n_h \text{ Co} = 2.628$ and $n_h \text{ Pt} = 2.369$)^[18].

2.4. SQUID measurements

The magnetic behavior of the cluster-assembled films has been studied using SQUID magnetometry (Superconducting Quantum Interference Device). An accurate analysis has been reached using our recently developed “triple fit” method where the ZFC/FC curves and a room temperature magnetization loop are simultaneously adjusted using a semi-analytical model^[19]. By fitting simultaneously the entire magnetic curves, we can reach a reliable and accurate determination of the particle magnetic size distribution and MAE^[20]. So, we have found the average magnetic diameter (D_m) is equal to the observed TEM one and remains constant upon annealing. The main difference comes from the MAE evolution between the as-prepared and annealed CoPt sample where the median effective anisotropy constant (K_{eff}) increased and its corresponding dispersion ω_K slightly decreased (see Fig. 1c). This last dispersion decrease is well explained by the appearance of the chemical order at nanosize^[21]. But, the MAE value is one order of magnitude smaller that what is expected for the L1₀ CoPt bulk.

3. Discussion and conclusion

As a summary, in one hand, we found a significant increase of Co and Pt magnetic moments for the chemically ordered L1₀-like clusters structures from X-ray magnetic circular dichroism (XMCD) investigations on CoPt clusters upon annealing. In the other hand, the magnetic anisotropy energy (MAE) of the annealed sample determined from SQUID magnetometry only increased of 50 % compared to the as-prepared sample, i.e. one order of magnitude smaller to what is expected for the L1₀ bulk phase. We will try to relate to these specific magnetic results to the element-specific local atomic relaxations in CoPt clusters determined by EXAFS measurements.

First of all, notice that the average spin moment is very sensitive to the numbers of hole per Co and Pt atoms, and to the clusters size but depends weakly on the local atomic distortion. It is the reason why we found an enhancement of both μ_S (Co) and μ_S (Pt) in 3nm-CoPt clusters compared to the one for bulk L1₀ phase. Concerning the behavior of the average μ_L (Co) which is generally related to the MAE, we found both that it is more pronounced than the one found for the bulk hcp Co (0.107 μ_B /at.) and also at Co surface film (0.12 μ_B /at.). In fact, the MAE is controlled by the spin-orbit (SO) coupling between occupied and empty electronic states. Since the SO interactions are very sensitive to the position and degeneracy around the Fermi level, significant contributions to the MAE should be expected even if small variations in the local atomic environment are observed. ^[22]

Table 1. Median magnetic size diameter (D_m), maximum susceptibility (T_{max}), effective anisotropy constant (K_{eff}) and relative dispersion (ω_K) determined from SQUID measurements. Co and Pt spin (μ_S) and orbital (μ_L) magnetic moments from experimental XMCD measurements

	As-Prepared	Annealed CoPt
D_m	3.1 nm	3.1 nm
T_{max}	15 K	22 K
K_{eff}	218 KJ/m ³	293 KJ/m ³
ω_K	37 %	28 %
μ_S (Co)	1.67 μ_B /at.	1.98 μ_B /at.
μ_L (Co)	0.13 μ_B /at.	0.20 μ_B /at.
μ_S (Pt)	0.47 μ_B /at.	0.52 μ_B /at.
μ_L (Pt)	0.07 μ_B /at.	0.10 μ_B /at.

In order to explain the 3 different distances obtained from EXAFS simulations, we applied to perfect CoPt clusters in the same size range, spin-polarized density-functional calculations using the Vienna *ab initio* simulation package (VASP) ^[15]. In contrast to the bulk structure, the Co and Pt layers appear to relax independently from each other. In particular at cluster surface, the Co atoms show a clear in-plane tetramerization in the uppermost (001) Co layer, which does not match the underlying Pt layer. So, despite the strong CoPt cluster hybridization, we also found 3 different calculated relaxed mean distances for Co-Co, Co-Pt and Pt-Pt with gaussian shape distributions, in very good agreement with EXAFS experimental values. In conclusion, while in the bulk L1₀ phases, an equal Co-Co and Pt-Pt Dirac distance distribution is expected, a strong Co-Co distance (d_{CoCo}) dispersion is predicted and experimentally observed for relaxed clusters even in the chemically ordered phase (see Fig. 1.b).

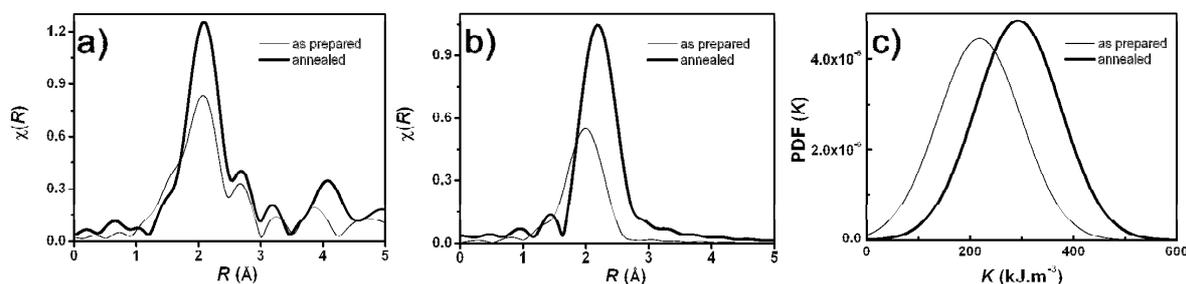


Figure 1. Experimental Fourier Transform $\chi(R)$ at Co-K edge for first metallic nearest-neighbors (a), Co-Co first-neighbor contribution to the $\chi(R)$ from its best FEFF simulation (b), and magnetic anisotropy constant K_{eff} dispersion (c) for mass-selected CoPt sample before and after annealing.

In a previous paper^[23], we have shown that the MAE dispersion in pure Co clusters essentially comes from the effect of additional facets and is relatively small. But in nanoalloys, the size and shape dispersion is not the unique source of MAE dispersion. Indeed, since the anisotropy enhancement in as-prepared CoPt compared to pure Co clusters is due to the presence of Pt atoms, the dispersion of the magnetocrystalline anisotropy (which depends on the neighborhood of each Co atom) increases with the number of possible chemical arrangements. It is the reason why the MAE of chemically disordered CoPt particles is quite large even if mass-selected clusters have a small size dispersion (8%) and a highly symmetrical shape (regular truncated octahedron)^[2]. As long as a well-defined and high enough degree of chemical order can be reached, the multiplicity of atomic configurations is strongly reduced and the MAE dispersion decreases while its median value increases^[14, 21]. But at the same time, the relaxation dispersion increases due to the stress between alternating Co and Pt planes (see figure 2 in^[24]). In ref^[22], by investigating different relaxations, it is shown using semi-empirical model, that the existence of nonuniform pattern of interatomic distances in 3d transition metal (TM) clusters can cause appreciable changes in the magnitude of the MAE. In particular, it is shown that negative and positive values for local MAE at different clusters sites can lead to an almost vanishing of the global MAE in magnetic clusters due to the cancellation of all these local contributions.

So we claim that we have obtained new experimental insights on the correlation between magnetic properties and short- or long-range chemical order in nanoalloys. We evidenced that specific finite size and more specifically strong relaxation effects are certainly related to the low MAE results obtained even on nearly perfect chemical ordered bimetallic nanoparticles assemblies.

To go further, non-collinear calculations, including the spin-orbit coupling in order to quantitatively access to the MAE values are to be done for such relaxed nanoalloys (Ab-initio+ tight-binding calculations).

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