ESRF	**Experiment title:** **X-ray absorption and Moessbauer investigation of the initial precipitation phase: structure and dynamics of Co clusters**	**Experiment number**: **08-01-162**
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Report:

Aims of the experiment

Clusters of metallic species present many intriguing properties: we mention the interesting magnetic properties such as the giant magnetoresistance (G.M.R.) effect, exhibited by clusters of magnetic material, and by alternating magnetic / non-magnetic multilayers; furthermore, nonlinear optical behaviour and in general quantum size effects are expected to manifest themselves in the smallest metallic clusters. The metallic nanosystem which we have chosen to study, Co/Ag, forms magnetic clusters and feature a fascinating nucleation process for studying quantum size effects and lattice dynamics effects.

We studied the initial phases of Co precipitation in Ag, corresponding to lower Co concentrations, where smaller clusters start forming. We have recently initiated a study of the dose dependence of the different sites taken up by Co in Ag, starting from 0.05 at.% corresponding to a kind of reference situation where essentially the substitutional site is populated . The nucleation of very small clusters sets in from approx. 1 at.%. These intriguing particles remain superparamagnetic for Mössbauer observation down to very low temperatures, below which they feature an interface magnetic hyperfine field, which is about 15 % lower than the bulk value. The latter observation deserves a deeper investigation. We expected EXAFS to contribute in a significant manner. At the intermediate concentration range, around 0.5 at. %, we have observed an unexpectedly strong population, up to 75%, of the smallest aggregates, namely Co dimers The complementary structural and lattice dynamical information that we can extract from EXAFS is of paramount importance.

A major challenge in this study consists in preparing a sample with a sufficiently high areal density of dimers. At the somewhat larger concentration range, we want to perform a full structural characterization of the nano-clusters in terms of the mean coordination number and nearest neighbor distances, in view of unraveling the interface structure as well as the crystal structure. Recent N.M.R. results on **Co clusters in Ag** point towards a h.c.p. structure, while there is also conflicting evidence favouring the f.c.c. structure. At the same time, we want to complement the few (because of the very long times involved) experimental Θ_D(Co<u>Ag</u>) values and compare them to theoretical values which we could recently obtain in M.D. calculations. One of our goals is also to compare both the structural and dynamical information for this case of ion implanted samples to that of samples prepared by co-sputtering, where we expect to observe important differences in the interface quality and therefore in the Θ_D values.

Results

XAS experiments were performed at the beamline Gilda (ESRF-Grenoble) during the period 26 April - 1 May 1999, on Co/Ag samples in the range 7500-9000 eV . We observed the following samples: A) Co/Ag [6 at% Co], Co implanted at 80 KeV on an evaporated Ag layer;

B) Co/Ag [0.56 at% Co], Co and Ag coevaporated in multiple layers by MBE;
C) Co/Ag [0.15 at% Co], " " " " " " " ;
D) Co/Ag [6 at% Co], " " " " " " " ;

+ a Co metal foil 5μm thick for reference spectra.

EXAFS spectra were collected in fluorescence by an ultrapure Ge multidetector, at 77 K for the as-prepared samples and for sample B also at 148 K and 218 K. For samples A) and D) spectra were collected also after an annealing at 350C [30 min].

The analysis of the spectra gave the following results:

► the samples at the lowest concentrations (B and C) have shown the presence of small clusters into the Ag matrix; the average coordination can be attributed to a narrow distribution of Co nano-clusters (dimers, trimers, tetramers and pentamers) with different weights.

► the sample D (as-prepared) showed evidence of an uniform distribution of 8-atom clusters (on the average).

► the sample A (as-prepared) showed larger size Co clusters (about 20 atoms/cluster).

The average coordination and nn distance for the I, II, III, coordination shell have been calculated.

The spectra obtained for the samples A and D after the annealing at 350 C, confirmed the growth of large clusters (size in the order of 100 atoms/cluster) where the contribution of the surface with respect to the volume is relatively reduced.

The absorption spectra taken near the edge (XANES) permitted to detect the chemical shifts and the fine structural modifications of the Co threshold in the configurations due to different clustering of cobalt atoms in the silver matrix.

Theoretical simulations of the EXAFS spectra were performed by the FEFF code and compared to the experimental data by the usual Fourier Transform. The Co clusters were simulated in a mixed configuration within the Ag lattice and the fitting procedure allowed to determine the Co-Co and the Co-Ag distance, the relative coordination numbers and the Debye-Waller factors for each coordination shell.

We compared the XANES regions for our samples: we noted a shift between the features of samples with small clusters and the evolution towards the larger agglomerates. For comparison also the Co foil XANES was reported in the full paper.

We reported the Fourier Transform of some EXAFS spectra together with the theoretical simulation obtained using the best fit parameters of table I. The agreement is often excellent and the uncertainty of the coordination and distance for the first shell is quite small; somewhat larger for the higher shells.

The present analysis is still in progress and a full paper will be published very soon. An invited talk on this subject will be presented by G. Faraci at the Int. Workshop "The Physics of low dimensions" Oaxaca, Mexico 16-20 Jan. 2000 and published in the Conference proceedings.

Finally I would like to remark the excellent performance of the Beamline, the energy stability and the very good control of the data acquisition. Very appreciated also the bright collaboration of the entire staff of the beamline.