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Magnetic nanostructures of mixed cobalt–samarium clusters

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Abstract. We synthesized Co−Sm mixed clusters from a $SmCo_5$ solid target mounted in a laser vaporization source. We studied both pure nanostructured $SmCo_5$-cluster-assembled films and the same isolated clusters embedded in a matrix. The supported cluster size distribution centered around 3 nm was determined from transmission electron microscopy observations. Mass spectra obtained on the photoionized clusters in the gas phase and Rutherford backscattering spectrometry analyses performed on 100-nm-thick films confirm the conservation of the compound-target stoicheiometry in both free and deposited clusters. However, X-ray photoemission spectroscopy measurements seem to indicate a segregation of samarium at the cluster surface. This segregation effect could explain the low values of the magnetization and coercive fields obtained from magnetometry measurements with respect to those in the bulk $SmCo_5$ crystallized phase.

PACS. 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 75.50.Tt Fine-particle systems

1 Introduction

A laser vaporization source capable of producing intense beams of nanosize clusters has been developed to synthesize original nanostructured materials using the low-energy cluster beam deposition technique (LECBD). Previous results, on pure transition-metal cluster films (Fe, Co, and Ni) [1, 2] prepared by this method and Co clusters embedded in a silver matrix [3], clearly emphasize the competition between the intrinsic cluster properties and the cluster interactions for influencing the magnetic behavior. In the case of pure cluster assembled films, supported clusters interact by direct contact. The magnetic behavior of such systems was well described in the framework of the random anisotropy model previously developed by E. Chudnowsky [4] for amorphous magnetic materials, where we use a scale law for the basic entity. The local order is not defined by the distance between atoms but by the grain size. In the case of nanosize clusters embedded in a matrix, the role and possible control of the interactions between clusters have been clearly shown to lead to a characteristic giant magnetoresistance (GMR) effect observed in the Co−Ag system as a function of the cluster concentration [3]. Unfortunately, the magnetocrystalline anisotropy of pure nanosize transition metal particles is rather low, leading to blocking temperatures (T_B) in the range 20–30 K, incompatible with potential applications in the fields of high-density memory devices and spin electronics [5, 6]. To prepare magnetic nanostrutures useful for such practical applications, it is necessary to have a system with a large magnetic moment at room temperature as well as a high local anisotropy, so that it behaves in a magnetically ordered way up to room temperature. For example, one way to reach such an objective may be the synthesis of nanocrystallized particles from a mixture of a $3d$ transition metal and a rare earth element [7]. Among various techniques for producing these mixed clusters [8, 9], the one consisting of the laser vaporization of an alloy target in an inert gas condensation source is attractive. For our experiments, we have chosen a $SmCo_5$ target (commonly used as a hard permanent magnet) because of the very large magnetic anisotropy characteristic of the gas phase, which we would like to conserve in the corresponding clusters. In this paper we report first the mixed Co−Sm cluster preparation and characterization in the gas phase. The structural properties and the magnetic behavior of pure $SmCo_5$ cluster assembled films prepared by the LECBD technique, and $SmCo_5$ clusters embedded in a silver matrix are reported in the second part of this paper.

2 Results and discussion

Nanosize Co−Sm mixed clusters were prepared in the gas phase from a $SmCo_5$ solid target mounted in a laser vaporization source described in detail elsewhere [10]. The mass abundance spectra of photoionized free clusters were characterized in a time-of-flight mass spectrometer (see Fig. 1) prior to depositions on various substrates at room temperature by the LECBD technique. In the gas phase, we observe a series of intense peaks corresponding to Co_n clusters (Fig. 1b (*)). A second series, the peaks of which consist of groups of seven lines (because of the existence of

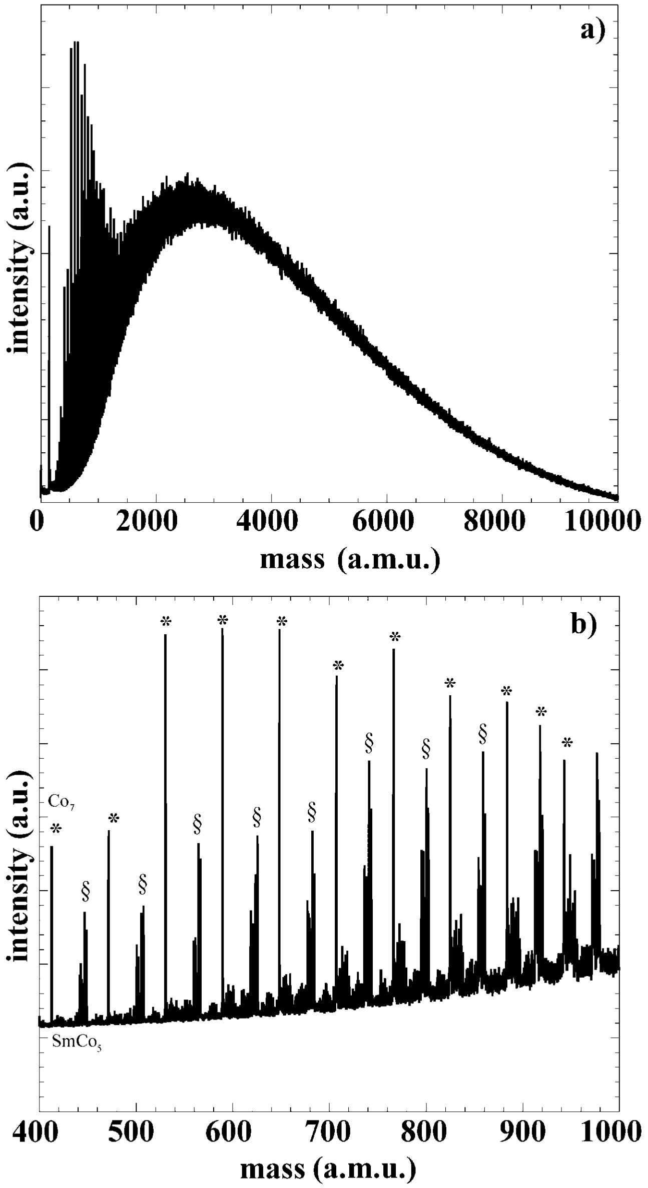

Fig. 1. Mass abundance spectra of photoionized Sm−Co mixed clusters measured in the time-of-flight mass spectrometer before deposition. (a) A complete view of the spectrum showing the Log-normal shape of the cluster size distribution. (b) A zoom in on a part of the spectrum, showing some details on the mixed character of the free clusters. (*) corresponds to the Co$_n$ series and (§) to the SmCo$_n$ series.

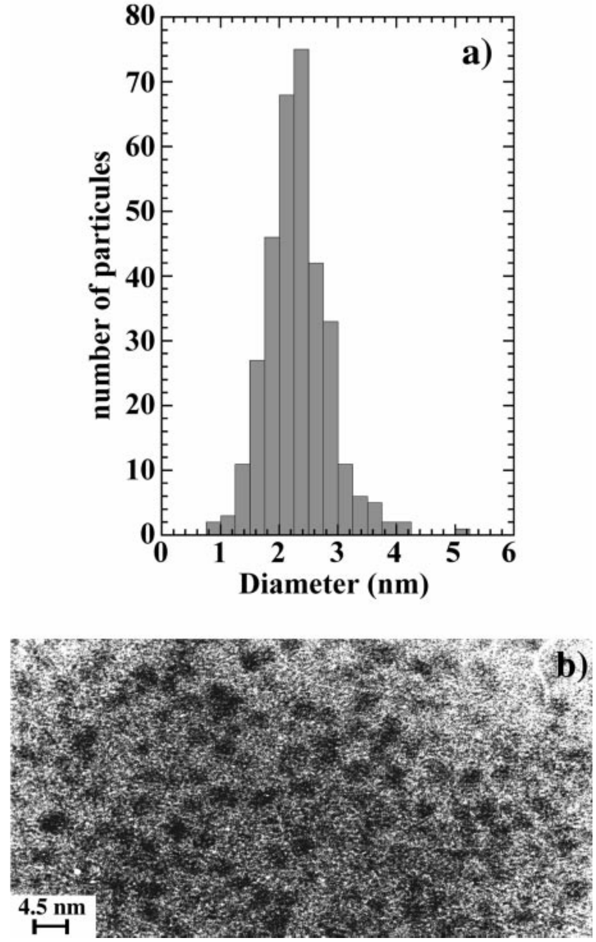

Fig. 2. Size distribution of supported Sm−Co clusters and a corresponding TEM image of the film deposited at room temperature on an amorphous carbon coated grid.

seven Sm isotopes), correspondence to Co$_n$Sm-mixed clusters is also observed (Fig. 1b (§)). The third series of peaks, less visible because of the low intensity of the components, is attributed to the presence of Co$_n$Sm$_2$ mixed clusters. Finally, the best fit of the mass spectrum is obtained from a multinomial distribution, where the nucleation rate is simply governed by the relative concentration of each Sm and Co component (SmCo$_5$ in our case).

After the first stage of cluster study in flight, the complete distribution of neutral Co−Sm clusters (Fig. 1a) was directly deposited on various substrates at room temperature or embedded in a silver matrix simultaneously deposited from an evaporation cell mounted in the deposition chamber. Both types of films were prepared with thicknesses up to a few hundred nanometers. The composition of the samples were measured using the Rutherford backscattering spectrometry (RBS) technique. The conservation in the films of the SmCo$_5$-target stoichiometry is confirmed. The size distribution of the supported clusters, obtained from transmission electron microscopy (TEM) observations (Fig. 2), is centered around 3 nm, with a rather narrow size dispersion. The X-ray photoemission spectrometry (XPS) measurements show the presence of the characteristic peaks of the pure Co phase and those of the Sm$_2$O$_3$ phase [11]. Because the only oxidized element is samarium, a possible structure for the supported clusters could be a core of pure Co surrounded by a skin of Sm oxide. The segregation of Sm atoms at the surface of the mixed clusters could be explained from the large differences between the radii of the Co and Sm atoms (Co: 0.074 nm, Sm: 0.104 nm) as well as between the surface energies of Co and Sm (Co: 2550 mJ/m^2, Sm:$<$ 1100 mJ/m^2) [12], since it is known that the element with the lower surface energy is inclined

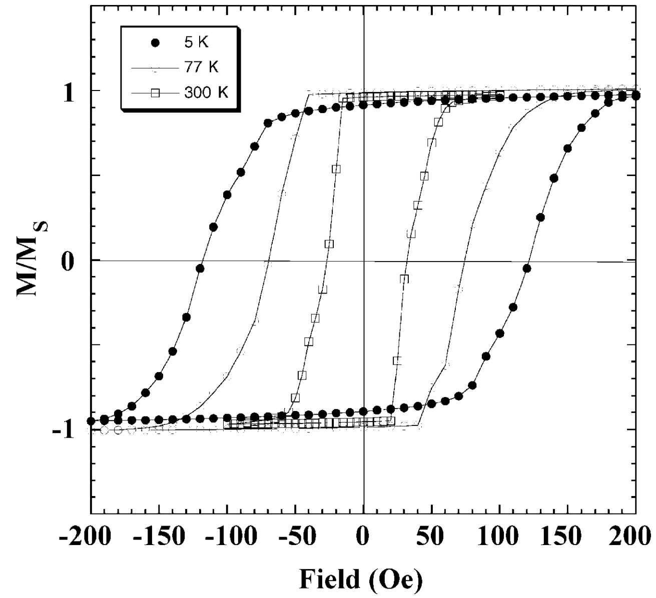

Fig. 3. Hysteresis loops performed at different temperatures on a pure 60-nm-thick $SmCo_5$ film deposited on a kapton substrate at room temperature. $M_S = 1300\,emu/cm^3$.

to segregate at the surface to minimize the total energy of the system.

The magnetic properties of the films were studied using a commercial superconducting quantum interference device (SQUID) magnetometer at the Laboratoire de Physique du Solide in Nancy, France. The classical hysteresis loops presented in Fig. 3 are obtained at different temperatures with the pure $SmCo_5$ sample. A comparable magnetic behavior was observed previously in the case of pure Co-cluster films [2] and can be interpreted in the framework of the random anisotropy model developped by E. Chudnowsky [4] for amorphous magnetic materials, but with a local order extended to the grain size; in amorphous materials, the local order is limited to the first coordination sphere. The estimated value of the saturation magnetization Ms has been found around 1300 emu/cm^3 , where only the Co-atom contribution is taken into consideration. This value is close to those obtained for pure Co-cluster films [2] with the Co grains having the same size (≈ 3 nm). Consequently, we can assume that in the Sm−Co mixed cluster films, the magnetic phase comes mainly from the pure Co core of the clusters; the samarium oxide skin at the grain surface behaves like a magnetically dead layer.

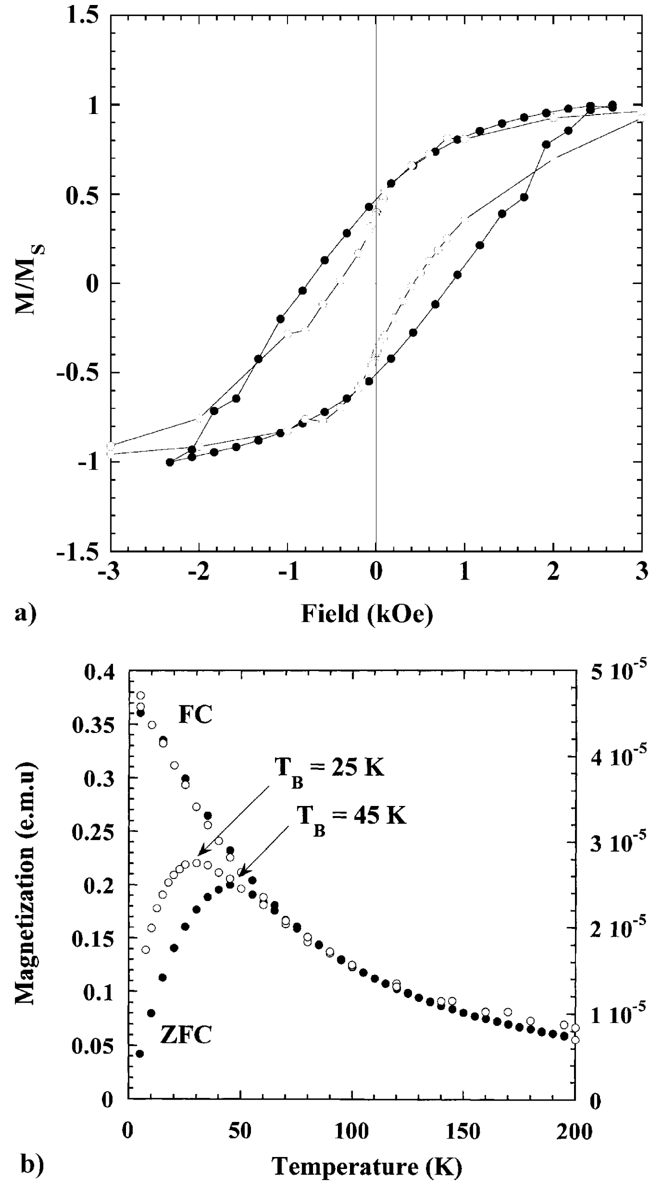

Fig. 4. (a) Hysteresis loops measured at 5 K. (b) ZFC–FC diagrams at 50 Oe for films of pure Co clusters embedded in an Ag matrix (open circles and left scale), and $SmCo_5$ mixed clusters (20 nm) embedded in an Ag matrix (filled circles and right scale), with a volumetric concentration of 10% in both cases, $M_S = 500\,emu/cm^3$. Note that this concentration is lower than those corresponding to the 3D percolation threshold (≈ 20%); this leads to a film morphology with isolated clusters randomly distributed in the silver matrix.

Two types of measurements were performed on the sample containing (volumetrically) 10% of $SmCo_5$ clusters embedded in a silver matrix ($SmCo_5-Ag$): classical hysteresis loops (Fig. 4a) and zero-field-cooled field-cooled (ZFC–FC) diagrams (Fig. 4b). The saturation magnetization M_S has been found to be around 500 emu/cm^3 [13], which is reduced, compared to the first sample, because of the lower quality of the vacuum in the codeposition chamber (where $SmCo_5$ clusters and Ag matrix are simultaneously deposited.). To analyze the effect of samarium, we compare the properties of the $SmCo_5-Ag$ sample with those of the previous Co−Ag ones [3]. We observe that the hysteresis loop of the $SmCo_5-Ag$ sample completely loses the square shape previously observed for the pure $SmCo_5$-cluster assembled film (Fig. 3), and that the Co−Ag film tends to the characteristic shape of a system with higher anisotropy [14]. The coercive field is of the order of 0.8 KOe for the $SmCo_5-Ag$ sample compared to 0.4 KOe for the Co−Ag one. The ZFC–FC diagrams for these samples (Fig. 4b) exhibit the same characteristic superparamagnetic behavior ($M \alpha\, 1/T$) above the blocking temperature T_B. However, the main result is an increase of this blocking temperature for the $SmCo_5-Ag$ sample (45 K) with respect to the $Co-Ag$ one (25 K).

3 Conclusion

The preliminary results reported in this paper seem to confirm a slight increase of the magnetic anisotropy in the mixed $SmCo_5$-cluster films compared to the pure Co-cluster ones. Unfortunately, the heterogeneous structure of the mixed clusters related to the samarium segregation towards the surface does not allow one to reach the expected high magnetocrystalline anisotropy as in the bulk $SmCo_5$ phase. Further experiments are in progress to improve the cluster structure directly, from the source, in the gas phase, or after deposition on the substrate.

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