Evidence for coexistence of exchange bias and exchange spring effects in oxidized Co nanocluster assembled films

A N Dobrynin, M J Van Bael, K Temst and P Lievens

Laboratorium voor Vaste-Stoffysica en Magnetisme and INPAC—Institute for Nanoscale Physics and Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium
E-mail: peter.lievens@fys.kuleuven.be

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Abstract. We present the observation of a double hysteresis loop behavior in oxidized Co nanocluster assembled films. These films consist of ferromagnetic Co clusters of about 2 nm diameter, embedded in a thin antiferromagnetic CoO matrix. Magnetization measurements after zero field cooling from 300 to 5 K show this double loop behavior, with remanent magnetization of the sample determining the point of loop separation. Such magnetization behavior is related to the presence of two ferromagnetic parts with antiparallel orientations of their magnetization vectors. While the loop shifts are provided via the exchange bias mechanism, the alignment of randomly oriented magnetization vectors of Co clusters in either of two directions suggests the presence of an exchange spring effect in the system.

1 Present address: Institut Néel, 25, Rue des Martyrs Bat D, BP 166, F-38042 Grenoble Cedex 9, France.
2 Present address: Instituut voor Kern-en Stralingsfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium.
3 Authors to whom any correspondence should be addressed.
Studies of hybrid magnetic nanostructures are of key importance for the understanding of magnetism. The dimensions of such systems are comparable to the relevant length scales, such as magnetic domain wall thickness or exchange correlation length. A large surface-to-volume ratio in the nanostructures makes the interfacial interactions dominant in the system, and, therefore, attractive for exchange spring [1, 2] and exchange bias [3–5] studies. The concept of exchange spring magnets was introduced by Kneller and Hawig [1] as a way to increase the energy product of permanent magnets by combining soft and hard magnetic materials. The idea behind it is an alignment of magnetization vectors of the soft magnetic phase by those of the hard magnetic phase via the exchange coupling at the interface [6]. Exchange bias is a shift of the magnetic hysteresis loop along the field axis, showing up in hybrid ferromagnetic–antiferromagnetic (F–AF) systems after field cooling through the Néel temperature of the AF part. When cooling down, the antiferromagnet adopts the structure providing the minimum energy, which in many cases is with its spin sublattices collinear to the neighboring F spin lattice [7]. The F–AF interfacial exchange favors aligning the F and the AF spins in such a way that it is easier to rotate the F spins in the cooling field direction, than in the opposite direction [8, 9]. While for isolated F-core AF-shell nanoparticles, a critical size for exchange bias exists [10], the assemblies of such clusters may be considered as zero dimensional F clusters embedded in a thin (two-dimensional) AF matrix, and exchange bias is observed in such systems [11].

Double hysteresis loops have been observed for antiferromagnetically coupled F multilayers [12–15]. This behavior manifests itself as a separation of the hysteresis loop in two parts, shifted with respect to each other both vertically and horizontally. In this paper, we report on a double hysteresis loop behavior observed in magnetization measurements on oxidized Co nanocluster assembled films. The double loop behavior was observed previously in exchange biased bilayers [16, 17], although their structure is quite different from ferromagnet/normal metal/ferromagnet layers, where AF coupling may appear. The double hysteresis loop assumes the presence of F regions (e.g. layers), which are oriented antiparallel. Brück et al [18] and Roshchin et al [19] have shown that for ferromagnet/antiferromagnet bilayers such a configuration is possible in the case of lateral mismatch of AF and F domain sizes, when antiparallel F domains are biased in opposite directions. Low temperature magneto-optical Kerr effect magnetometry was used to measure local hysteresis loops from several spots on the surface of the ferromagnet/antiferromagnet bilayer [19]. It was shown that the local hysteresis loop is shifted to either one or the other side, depending on the mutual orientation of AF and F domains. If there are several F domains (with antiparallel magnetization orientation), corresponding to one AF domain, this leads to establishing of local exchange anisotropies of the opposite sign in neighboring F domains. Thus, although not antiferromagnetically coupled, the F domains are held antiparallel by means of the exchange coupling to the AF layer.

The case of F nanoparticles embedded in an AF matrix is different from ferromagnet/antiferromagnet bilayers, since there is no F domain structure present, and orientations of the easy axes of magnetocrystalline anisotropy of the clusters are random. In other words, the orientations of magnetization vectors of the F clusters in the ground state are either not correlated or weakly correlated, with a characteristic length much shorter than the dimensions of the sample [20, 21]. In spite of the random orientation of the magnetization vectors of Co clusters, we observed the double hysteresis loop in a large number of oxidized Co cluster assembled films.

The clusters were produced in a laser vaporization source [22] and deposited at low energies (< 0.1 eV atom⁻¹) on an amorphous SiO₂ substrate in an ultra high vacuum.
Figure 1. Time of flight mass spectrum of Co clusters.

deposition chamber [23]. The cluster size distribution was monitored with time-of-flight mass spectrometry. A typical mass spectrum of Co clusters is presented in figure 1. While individual peaks are not observed here because of the limited resolution of the spectrometer, the ‘hump’ in the spectrum appears due to the overlap of the neighboring peaks, and reflects the cluster mass distribution. Since the cluster size scales as a power of 1/3 of the number of atoms, the cluster size distribution is significantly narrower than the mass distribution, plotted in figure 1.

For a number of earlier studies of cluster assembled films prepared in the same setup in similar conditions, detailed structural investigations were carried out. In particular transmission electron microscopy showed that FePt and Co cluster films largely consist of spherical clusters with for Co an average diameter of 2.3 ± 0.6 nm. This size is very similar to the values obtained from the gas phase mass spectrometry and implies that the clusters keep their size and shape after deposition [24, 25]. In addition, the highly porous character of the film was evidenced by Rutherford backscattering spectroscopy [11].

The Co cluster films are oxidized by exposing them to air. Because of the highly porous character of the films, oxidation through the volume of the sample leads to the formation of a thin Co oxide matrix with embedded Co clusters. There is however limited structural information on the oxide matrix. Electron energy loss spectroscopy provided qualitative information on the degree of oxidation of different films, and these findings were corroborated by detailed analysis of Rutherford backscattering spectra [11].

The available magnetic information supports the structural model of an oxide matrix with embedded clusters. In this work, we consider two typical oxidized Co cluster films, samples A and B, that both show the double hysteresis loop behavior. The preparation conditions were similar for both samples, both have a thickness of the order of 30 nm, and both were oxidized by exposing to air. The double hysteresis loop behavior was not observed for all produced oxidized Co cluster samples. In particular, we reported in [11] on oxidized Co cluster samples, which did not show a double loop behavior. For those samples we did however observe hysteresis loop features corresponding to a non-oxidized, F part of the film, which was taken as evidence for inhomogeneous oxidation. In contrast, for the samples showing the double loop behavior, such features corresponding to a non-oxidized part were not observed. This provides evidence,
Figure 2. Magnetic hysteresis loops of the sample A, taken at 5 K after cooling down from 300 K. (a) FC at 10 kOe, TL; (b) ZFC after saturation in a positive field and TL. (c) ZFC from a partially demagnetized state, and TL.

albeit indirect, that these samples are oxidized throughout, and that an AF CoO matrix with embedded Co nanoparticles is formed. These arguments do not exclude the situation where a few clusters are coupled, while separated from other clusters or cluster agglomerates by the oxide matrix. However, this situation would not alter the structural model nor the conclusions of our study.

In order to verify the magnetic domain structures, magnetic force microscopy of the samples was performed at room temperature for both magnetized and demagnetized states. No magnetic domain structure (and no contrast at all) was found in either case. It is noteworthy that the samples are not superparamagnetic at room temperature, and show a hysteretic behavior.

The magnetization measurements were performed using a vibrating sample magnetometer at 5 K after cooling down from 300 K. The field was always applied parallel to the film plane. Both field cooled (FC) (in a field of 10 kOe) and zero field cooled (ZFC) hysteresis loops were measured. In figure 2(a) the FC hysteresis loop and training loop (TL) [7, 26] for sample A are shown. The subsequent TLs are not much different from the first TL. In figure 2(b), the ZFC hysteresis loop and the TL after saturation in a positive field at 300 K are shown. The difference in the exchange bias value in the case of FC and ZFC is negligible, while the coercivities are slightly different. This difference disappears in the TLs, which are almost identical both for FC and ZFC cases. It is noteworthy that the magnetization reversal goes rather abruptly (especially after field cooling), which indicates that this is a collective effect, and not a rotation of magnetization vectors of individual particles.
Figure 3. ZFC from different remanent magnetization states for sample B: (a) $M_r = 0.36M_S$; (b) $M_r = -0.44M_S$; (c) $M_r = 0.67M_S$; (d) $M_r = -0.57M_S$. The measurements are performed at 5 K.

Figure 2(c) shows a hysteresis loop, taken after zero field cooling from a partially demagnetized state. The double loop behavior is well pronounced here. The loop consists of two parts, shifted with respect to each other both vertically and horizontally. The virgin magnetization curve (0–1 T) was not measured for this sample, so the upper right part presents the TL. At the bottom left side both ZFC and TL hysteresis loops are present, and the values of the bias and the coercivity correspond to that shown in figure 2(b).

In figure 3, there are hysteresis loops for sample B, taken after zero field cooling from different remanent magnetization states. It is clear that the point of separation of the loops is determined by the remanent magnetization. The direction to which the field was first applied when measuring the hysteresis, does not influence the double loop behavior (see figure 3(d)).

As was discussed earlier, the double loop behavior assumes the presence of two antiparallel F parts in a sample. In the case of cluster assembled films the orientations of magnetization vectors of clusters are random. In figure 4(a), a schematic drawing of F clusters embedded in a paramagnetic (above the Néel temperature) matrix is shown. The orientation of paramagnetic spins in the vicinity of clusters is correlated with the F spin orientations due to dipole–dipole and exchange interactions. When an AF order is established in the matrix, there are three possibilities.

The first possibility, as illustrated in figure 4(b), assumes the establishment of a continuous (single-domain or with collinear domain structure) AF matrix in a sample, while embedded F clusters keep the orientation of their magnetization vectors. This situation will not lead to the double loop behavior, because of the random orientation of cluster magnetization vectors.

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Moreover, this is possible only in the case of very weak interfacial exchange interaction, which should be lower than the cluster magnetocrystalline anisotropy energy. Since the exchange interaction energy is proportional to the scalar product of the interfacial spin magnetic moments, such configuration may lead only to very low ZFC exchange bias values for a small fraction of clusters, showing up as smooth shoulders in the hysteresis loop. In addition, since such spin configuration assumes a very low interfacial exchange interaction energy, it may not show a significant exchange bias after field cooling either. Our data are not consistent with this situation.

The second possibility is the formation of either a discontinuous AF matrix or an AF matrix consisting of several non-collinear domains. In this case local AF structures, collinear to the neighboring F cluster spin structures, are established, and the double loop behavior is also not possible. The reason for this is that the F magnetic moments stay randomly oriented, rather than aligned in either of two directions, which is necessary for the double-loop behavior. A discontinuous CoO matrix could be formed, e.g. in the case of post-deposition oxidation of cluster films with low porosity, when the oxide regions are not connected to each other. This also assumes that non-oxidized Co parts would be present, which is consistent with the results, reported in [11].

In the third case, a continuous AF matrix is formed, and interfacial exchange is significant, leading to the alignment of the F spins by the AF spins. The orientation of the AF spin lattice is determined by the total remanent magnetization vector of the F part. This alignment, in fact, is an exchange spring effect, where the AF matrix plays the role of the hard magnetic phase, aligning the soft magnetic clusters. This way the cluster spin orientation is set either ‘up’ or ‘down’, depending on the sign of the scalar product $\mathbf{M} \cdot \mathbf{L}$, where $\mathbf{L}$ is the AF vector, and $\mathbf{M}$ is the cluster magnetization vector. The exchange bias directions are opposite for the ‘up’ and ‘down’ parts. The remanent magnetization determines the amount of ‘up’ and ‘down’ clusters, and, therefore, the point of the loop separation. This spin configuration is illustrated in figure 4(c). Thus, after zero field cooling, the positively magnetized part (the part with magnetization below the remanent value of the sample, see figure 3) is shifted to the left, while the negatively magnetized part (the part with magnetization above the remanent value) is shifted in the right direction.

Such an alignment assumes that the interfacial F–AF exchange energy exceeds the anisotropy energy of F clusters. In the ideal case of spherical clusters the interfacial exchange
energy can be written as $\sigma 4\pi r^2$, and the anisotropy energy $K 4\pi r^3/3$ (in case of uniaxial anisotropy). Here $\sigma$ is the interfacial exchange coupling constant, $K$ is the magnetocrystalline anisotropy constant, and $r$ is the cluster radius. Therefore, the condition $3\sigma > Kr$ has to be satisfied for the F clusters to be aligned by the AF matrix. The value of $2.5 \times 10^6 \text{erg cm}^{-3}$ was reported for the anisotropy constant of 3 nm Co clusters, and this value is proportional to the surface-to-volume ratio [27]. Therefore, we can assume that $K = 4 \text{erg cm}^{-3}$ for our case of 2 nm clusters, and $Kr/3 = 0.13 \text{erg cm}^{-2}$, which is more than an order of magnitude lower than the typical exchange coupling constant in the Co/CoO system of 3 erg cm$^{-2}$ [28]. This means that alignment of the F clusters by the AF matrix indeed is a valid assumption.

In this paper, we have argued that the double hysteresis loop behavior observed in samples consisting of F clusters embedded in an AF matrix may be due to a combination of exchange spring and exchange bias effects in one system. The magnetization vectors of F clusters are aligned by a continuous AF matrix, yielding only two possible antiparallel cluster spin orientations. The hysteresis loops of clusters with oppositely oriented magnetization vectors are biased in opposite directions, leading to the double loop behavior. The point of the loop separation may be adjusted by cooling down from different remanent magnetization states.

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