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Antiferromagnetic exchange coupling measurements on single Co clusters

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This paper reports on single-cluster measurements of the angular dependence of the low-temperature ferromagnetic core magnetization switching field in exchange-coupled Co/CoO core-shell clusters using a micro-bridge DC superconducting quantum interference device (μSQUID). It is observed that the coupling with the antiferromagnetic shell induces modification in the switching field for clusters with intrinsic uniaxial anisotropy depending on the direction of the magnetic field applied during the cooling. Using a modified Stoner-Wohlfarth model, it is shown that the core interacts with two weakly coupled and asymmetrical antiferromagnetic sublattices.

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I. INTRODUCTION

The exchange coupling of a ferromagnet (F) with an antiferromagnet (AF) induces changes in its magnetic properties[1] with the strongest effects observed in Co/CoO core-shell (CS) clusters, where the increase in anisotropy enhances significantly the superparamagnetic transition temperature.[2] This strong effect is due in part to the high surface to volume ratio. It has moreover been recently pointed out that with clusters the coupling manifests differently depending on the balance between (1) the AF shell and (2) the F core total anisotropy, and on (3) the strength of the interface exchange coupling.[3] When the shell anisotropy energy is much higher than that of the core, the AF is pinned and the exchange coupling induces the bias of the F magnetization. On the opposite if the shell anisotropy is smaller than that of the core, its magnetization can rotate under applied field and no exchange bias should be observed, although the anisotropy of the core can still be modified due to the coupling. As CoO has a very high bulk anisotropy compared to that of fcc Co, it is generally found that a very small amount of oxide is sufficient to induce strong exchange bias. Some observations, however, indicate that at the onset of oxidation the shell has poor magnetic properties, which can be improved if the shells of neighboring clusters are in contact. This can be obtained by direct contact between clusters,[4] through a CoO substrate,[5] or a CoO matrix.[2]

Otherwise, for isolated core-shell clusters it is observed that a small number of uncompensated moments with weak coupling to the AF lattice dominate the exchange interaction.[6] These weakly bound moments have a distribution of blocking temperature ranging from the lowest temperatures up to 100 K. Similar observations have been made with ferrite clusters where surface spin disorder was attributed to variation in the coordination of surface atoms resulting in a distribution of exchange fields.[7]

All the experimental results on the exchange coupling of clusters published up to now were obtained with assemblies of particles (for a review, see Nogués *et al.*[8]). The details of the interface structure and magnetic properties are generally deduced from the thermal properties or the response of the system to various field coolings. In this paper we present exchange coupling measurements for individual nanometer-sized clusters. By measuring the critical field for the switching of the F magnetization, it is possible to discriminate between the intrinsic cluster anisotropy and the exchange-induced contribution.

II. EXPERIMENTAL DETAILS

We report on magnetization switching field measurements with Co and Co/CoO CS clusters deposited on CoO and Al_2O_3 sputtered thin films. Cobalt clusters, with mean diameter of 5.5 nm, were made by sputtering gas-aggregation[9] and deposited *in situ* under high vacuum. The core-shell structure was obtained by exposing the clusters to O_2 gas in the deposition chamber leading to the formation of a 1 nm antiferromagnetic shell.[10] They were covered with Nb from which the micro-bridge DC superconducting quantum interference device (μSQUID) was patterned by electron beam lithography.[11] The measurement procedure begins with cooling from room temperature down to 40 mK with no applied magnetic field. The zero field-cooled (ZFC) switching fields are measured within the μSQUID plane with applied fields up to 4.2 kOe. Subsequent measurements were carried out after heating up the sample and cooling down again with in-plane applied field [field cooled (FC)] along the $\pm x$ (10 kOe) or $\pm y$ direction (5 kOe).[12]

III. MEASUREMENTS

A. Co clusters

A preliminary study was made with Co clusters deposited on alumina. Typical switching field measurements are presented in Fig. 1. Results on 120 individually studied clusters agree with the Stoner-Wohlfarth model for coherent rotation of uniaxial magnetization with astroid-shaped critical curves[13,14] and easy axis randomly oriented within or close to the measurement plane. Three examples are given in Fig. 1(a). The uniaxial anisotropy constants K_u range from 0.4×10^6 up to 4×10^6 erg/cm^3, which is in agreement with measurements on assembly of similar clusters.[15] It is also verified that the critical curves are exactly the same upon field cooling, indicating that there is no unintentional oxidation of the clusters. However, in contrast to this large set of

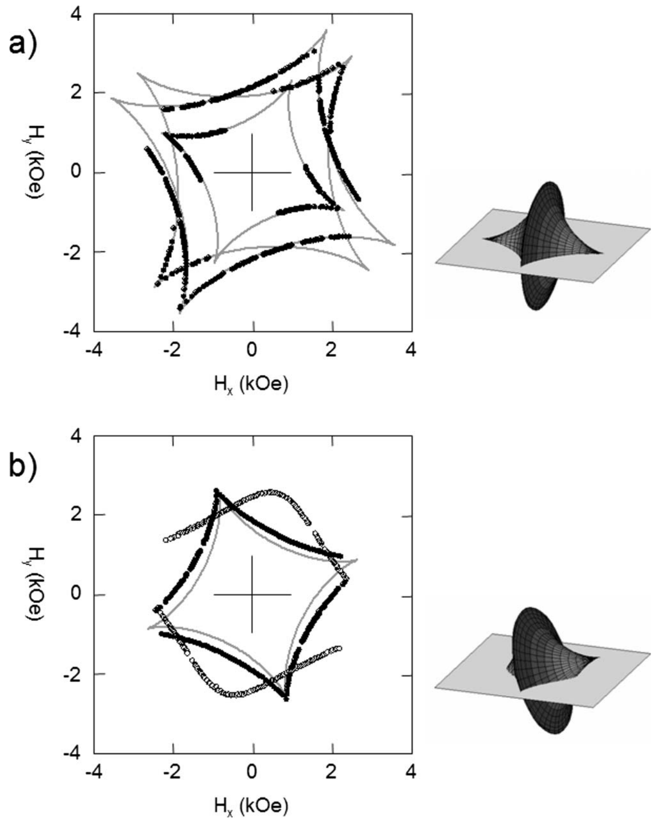

FIG. 1. Critical curves of clusters deposited on alumina. (a) Measurements of clusters in the same μSQUID (dots) and fitted astroids (gray line). The anisotropy is uniaxial with the easy-axis orientation within the measurement plane as schematically shown in the drawing at the right. (b) Switching fields for a cluster where the main anisotropy axis is out of plane (open dots) as shown in the drawing and for a cluster with deviation from the pure uniaxial case (closed dots).

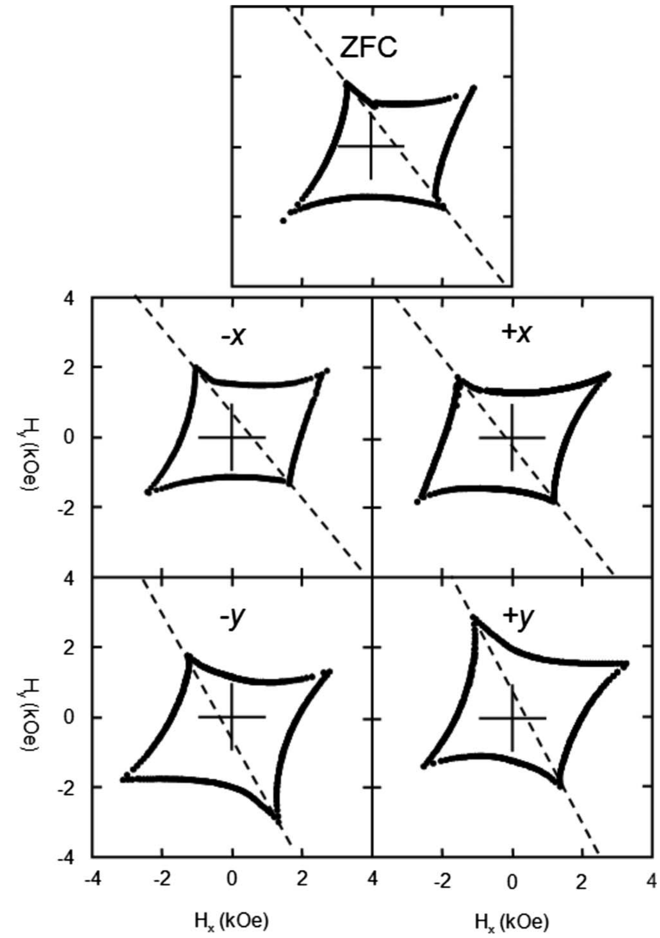

FIG. 2. Critical curves for cluster A. The top diagram is the zero field-cooled measurement. The direction of the cooling field is indicated in other diagrams. The dashed line indicates the approximative uniaxial easy-axis direction measured with the μSQUID direct mode.

observations, for some clusters the axis is out of plane, resulting in the rounding of the critical curve along the easy direction [Fig. 1(b), open dots]. For other clusters, although the main anisotropy axis is in the plane, a departure from the uniaxial anisotropy is clearly observed [Fig. 1(b), closed dots].

Subsequent measurements were made with Co clusters on CoO showing anisotropy fields and shape of the critical curves similar to those of clusters on alumina. Although the uniaxial anisotropy amplitude and orientation do not vary before and after field cooling, close examination reveals that the centers of the astroids for both FC and ZFC measurements are slightly shifted, hence revealing exchange coupling. The shift is small, never exceeding 30 Oe, while the typical anisotropy field is 3 kOe. It is randomly oriented in ZFC clusters, and for FC clusters, it is most of the time in the direction opposite to that of the cooling field. For a given cluster there is no correlation between the direction of the uniaxial easy axis and that of the FC or ZFC bias. The fact that the bias is weak for clusters deposited on CoO has been already observed for assemblies of clusters[15] and is attributed to the small contact surface with the AF substrate. This is probably also the reason why we do not observe modifications in the shape of the critical curve due to the coupling with the substrate.

B. CS clusters

In order to observe sizeable exchange coupling effects we performed a third set of measurements with Co/CoO core-shell clusters on CoO. In this case the critical curves vary significantly from one cluster to the other with a deviation from the Stoner-Wohlfarth behavior and a field-cooling-dependent anisotropy. Results for two clusters, labeled as A and B, are shown in Figs. 2 and 3. The anisotropy is not uniquely uniaxial—although four cusps are visible in each case—and some higher-order anisotropy contribution might be present especially in the ZFC measurement for cluster A.[11,16] When the cooling field is applied in the $\pm x$ direction the critical curve for this cluster resembles an astroid stretched along one of its hard directions, and the two curves are identical upon rotation. When the cooling field is applied in the $\pm y$ direction the astroid is squeezed along an easy direction with the two curves again identical upon rotation. Cluster B shows less symmetrical critical curves—the $\pm x$

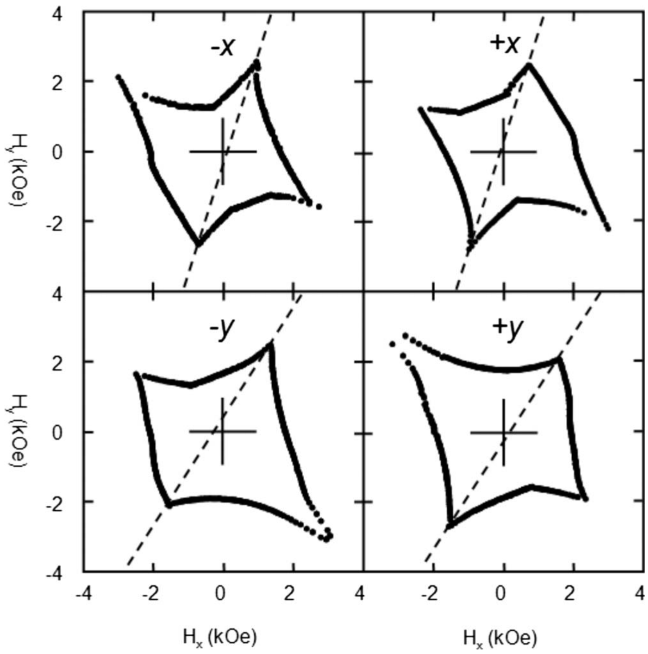

FIG. 3. Critical curves for cluster B labeled as in Fig. 2. For this cluster the ZFC critical curve was not measured.

and $\pm y$ field coolings giving rise to a deformation along the principal directions with curves that are again identical upon rotation. As a result of its asymmetry each critical curve is off centered in a direction that is not that of the cooling field. This bias is, however, misleading and must not be confused with the exchange bias that would be measured from the shift in the coercive field. Since the switching field may differ from the coercive field, for instance when measured close to a hard direction for a uniaxial cluster, their biases are not necessarily similar.

IV. MODEL AND CALCULATION

There are three characteristic features of the critical curves resulting from the exchange coupling: (i) they are not symmetrical relative to their center; (ii) the shape changes according to the direction of the cooling field; and (iii) the field cooling does not induce a significant shift from the origin. In this section we show that this behavior can be explained with an extension of the Stoner-Wohlfarth model, taking into account the exchange coupling of the F core with two AF sublattices. The reduced energy we consider is the following:

$$E = -\vec{\mathrm{F}} \cdot \vec{H} - K_u(\vec{\mathrm{F}} \cdot \hat{e}_{\mathrm{F}})^2 - \sigma_{ex}[x\overrightarrow{\mathrm{AF}}_1 \cdot \vec{\mathrm{F}} + (1-x)\overrightarrow{\mathrm{AF}}_2 \cdot \vec{\mathrm{F}}] - \alpha_1 x\overrightarrow{\mathrm{AF}}_1 \cdot \hat{e}_{\mathrm{AF}} - \alpha_2(1-x)\overrightarrow{\mathrm{AF}}_2 \cdot (-\hat{e}_{\mathrm{AF}}). \quad (1)$$

In agreement with the results with Co clusters the core is treated as a uniaxial macrospin $\vec{\mathrm{F}}$. The first term is its Zeeman energy and the second term is its anisotropy energy with in-plane easy axis $\hat{e}_{\mathrm{F}}$. The third term is the exchange coupling energy with two $\mathrm{A}\vec{\mathrm{F}}_1$ and $\mathrm{A}\vec{\mathrm{F}}_2$ sublattices, which are also treated as macrospins, with x and $(1-x)$ as their relative proportions and σ_{ex} as the positive interface coupling parameter. The last two terms are the AF sublattice energies with $\hat{e}_{\mathrm{AF}}$ as their in-plane easy directions. These effective energies, having the form of exchange energies with parameters α_1 and α_2, represent the coupling of the AF interface spins with the rest of the shell and the CoO substrate (Fig. 4). Magnetization curves were calculated by energy minimization under applied field with $\vec{\mathrm{F}}$, $\overrightarrow{\mathrm{AF}}_1$, and $\overrightarrow{\mathrm{AF}}_2$ bound to rotate in the plane and all other parameters free. The switching fields were determined by locating the associated jumps in $\vec{\mathrm{F}}$.

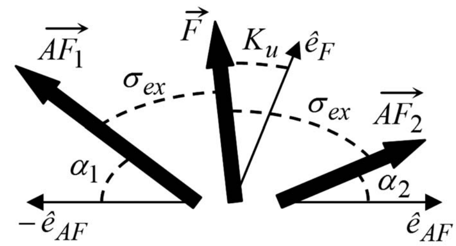

FIG. 4. Schematic representation of the model used for the energy calculation. Parameters are described in text.

Despite its simplicity this model for the AF shell can describe some very different situations. In the case where $x=1$ it corresponds to the picture described by Meiklejohn and Bean with the F core exchange coupled with an uncompensated AF lattice. If in addition we suppose that the AF magnetization is rigid ($\alpha_1 \gg K_u$), the calculated critical curve is a shifted astroid in the direction opposite to that of the coupling.[1] For partially compensated rigid AF sublattices ($x \neq 1,\ \alpha_1 = \alpha_2 \gg K_u$), the critical curve is again a shifted astroid in the direction opposite to the net AF magnetization with an amplitude given by $\sigma(2x-1)$. In this case of rigid AF magnetizations the exchange coupling has no effect on the anisotropy of the F cluster in the sense that the anisotropy field and orientation of the astroid are uniquely defined by K_u and $\hat{e}_{\mathrm{F}}$.

Looking back at the experimental curves in Figs. 2 and 3 it can be noticed that they are only slightly off centered. This rules out the coupling with only one rigid AF sublattice and indicates that there might be nearly or completely compensated AF sublattices or that the coupling with the AF might be weak. But because in the latter case the deformation to the critical curve would also be small, the former situation is considered the most plausible one.

As it was found by calculation, skewed critical curves similar to those observed only arise when the nearly compensated AF sublattices have relatively low and *different values* for the anisotropy. In this situation, where the AF magnetizations are free to depart from their equilibrium position with no applied field, the shape of the critical curve depends on the complex field-dependent energy landscape for the three coupled magnetization. In the following discussion we will only focus on the qualitative overall switching behavior of the core depending on the relative values for the model parameters.

Critical curves with deformations matching those of cluster A shown in Fig. 2 are obtained considering rather strong coupling ($\sigma_{ex}=1.2,\ K_u=1.0$) with compensated ($x=0.5$) and

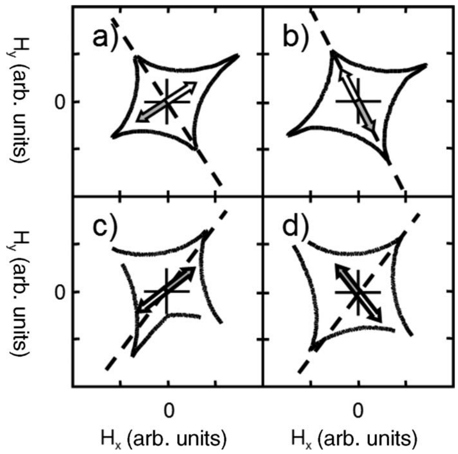

FIG. 5. Calculated critical curves for a F cluster coupled with two AF sublattices. The dashed line indicates the F easy axis. White arrow: AF1; gray arrow: AF2. Top row $x=0.5$, $\sigma_{ex}=1.2$, $K_F=1.0$, $\alpha_1=1.8$, and $\alpha_2=3.0$; (a) $\hat{e}_{AF}$ perpendicular with $\hat{e}_F$; (b) $\hat{e}_{AF}$ parallel with $\hat{e}_F$. Bottom row $x=0.6$, $\sigma_{ex}=0.8$, $K_F=1.0$, $\alpha_1=1.0$, and $\alpha_2=2.0$; (c) $\hat{e}_{AF}$ at 165° from $\hat{e}_F$; (d) $\hat{e}_{AF}$ at 75° from $\hat{e}_F$. All figures are rotated to match the experimental measurements in Figs. 2 and 3.

asymmetrical weakly bounded AF sublattices ($\alpha_1=1.8$, $\alpha_2=3.0$) [results are shown in Figs. 5(a) and 5(b)]. The difference in the FC curves are entirely accounted for by rotating the AF easy direction by 90°. Keeping all other parameters equal and having $\hat{e}_{AF}$ perpendicular with $\hat{e}_F$ stretches the astroid along one of its hard directions [Fig. 5(a)] while in the $\hat{e}_{AF}$ parallel with $\hat{e}_F$ configuration the critical curve is squeezed along one of its easy directions [Fig. 5(b)].

For cluster B, features similar to those observed in Fig. 3 are obtained with slightly uncompensated AF magnetization ($x=0.6$), weaker coupling ($\sigma_{ex}=0.8$, $K_u=1.0$), and again dissimilar AF energy parameters $\alpha_1=1.0$ and $\alpha_2=2.0$ [Figs. 5(c) and 5(d)]. Deformations of the critical curve with different FC are again obtained by rotating the AF easy direction by 90°. Having $\hat{e}_{AF}$ at 75° stretches the astroid along one of its hard directions [Fig. 5(d)], while with $\hat{e}_{AF}$ at 165° the critical curve is closer to a square with a kink in one of its sides [Fig. 5(c)].

As already mentioned the key elements to obtain critical curves matching the experimental ones are the low and dissimilar energies for the AF sublattices. This finding is coherent with the observation that the AF shells in core-shell clusters are defective and poorly coupled to the core.[4] For such small systems it is reasonable to assume that the two sublattices are not equivalent due for instance to unequal number of defects in the shell or to the small contact surface with the substrate. It must be mentioned in addition that qualitatively similar critical curves can be calculated with the same model if two different values are chosen for the exchange coupling energy σ between the core and the sublattices instead of two α anisotropy values. Obviously, the qualitative model we use constitutes an oversimplification for the CS system—the complexity of which could only be taken into account with a full microscopic calculation. But despite its simplicity it is nevertheless sufficient to assert that the asymmetrical critical curves result from the coupling with an AF with low anisotropy and a structure more complex than that of an antiferromagnet with two equivalent sublattices.

The calculation also indicates that the effect of the cooling field is to switch the AF sublattices between two sets of easy directions with $\hat{e}_{AF}$ more or less parallel or more or less perpendicular to $\hat{e}_F$. However, due to the small values of the energy parameters α_1 and α_2 the AF sublattices may depart significantly from their easy directions. For cluster A, in the case where $\hat{e}_{AF}$ is perpendicular with the F easy axis [Fig. 5(a)] with no applied field, the equilibrium configuration is with $\vec{AF}_1$ and $\vec{AF}_2$ tilted, respectively, 3° and 22° toward the $\vec{F}$ easy direction. In the case where $\hat{e}_{AF}$ is parallel with the F easy axis [Fig. 5(b)] with no applied field, the equilibrium configuration is with all three magnetizations along their easy direction. As expected, the spin-flop perpendicular configuration has an overall lower energy. Note, however, that in our calculation the canting of the AF magnetizations is not frozen, and the AF equilibrium configuration has to be calculated for every value of the applied field. Because cooling fields were not applied along other directions during measurements it is unfortunately not possible to say if there are other stable configurations for the AF magnetizations.

Regarding the low AF anisotropy it has been proposed that in the case where the rotation is irreversible, it can increase the anisotropy in addition to the exchange bias.[17–19] In our measurements such an irreversible rotation of the AF, independently of the core, can be definitely ruled out since it would induce discontinuities in the switching curve that were not observed.

One last remark regarding the experimental results is that in measuring the critical curve, the magnetization of the cluster is switched back and forth at each angle value of the applied field. For each measured cluster the critical curve was identical even after cycling the magnetization a few hundred times. This indicates that even though the AF magnetizations are not rigid, the magnetic configuration and exchange coupling are extremely robust.

V. CONCLUSION

We have developed a modified Stoner-Wohlfarth model in order to account for a large data set obtained with the μSQUID technique on core-shell cobalt clusters. This model describes characteristic features of the observed critical curves as the asymmetry of these curves with respect to the center—the shape changes associated with different cooling field directions and the relative small shift from the origin. The description of the interaction involves the coupling of the F core with two AF sublattices. Skewed critical curves are accounted for with nearly compensated sublattices of low and dissimilar anisotropy energy. It is shown that with this minimal set of assumptions, a wide range of experimental results can be described, which could not be explained with the simple picture of a unique and rigid AF lattice. The model is a step toward better understanding of the magnetic behavior of core-shell clusters, where it is known that the AF shell is often defective and poorly coupled to the core.

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