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Dispersion of magnetic anisotropy in size-selected CoPt clusters

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The magnetic anisotropy energy distribution of a diluted assembly of CoPt nanoparticles, size-selected around a diameter of 3 nm, is characterized by superconducting quantum interference device magnetometry. By comparison with unselected CoPt clusters and size-selected Co clusters, we show experimental evidence of a significant anisotropy constant dispersion, which is a nanoalloy specificity.

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Magnetic nanoparticles are extensively studied both for fundamental reasons and in view of their potential applications in the field of biotechnology, catalysis, or magnetic information storage.[1–4] One of the key quantity, especially for the last application, is the particles' magnetic anisotropy energy (MAE) E_{ani} because it controls the stability of their magnetization (with temperature, time, and magnetic field).

When surface effects are negligible, E_{ani} is expected to vary linearly with the volume V of a particle and we can simply write: $E_{\mathrm{ani}}=K_{\mathrm{eff}}V$, where K_{eff} is the *anisotropy constant*. This quantity is a characteristic of a given material in its bulk phase. In fact, it is well known that K_{eff} can be modified (usually increased) at nanometer sizes.[5–13] In order to take into account the surface effect, the MAE may be empirically written $E_{\mathrm{ani}}=K_V V+K_S S$ where S is the surface of a particle and the two constants K_V and K_S are, respectively, the *volume* and *surface* anisotropies. Nevertheless, even when such a size-reduction effect is considered, it is still assumed that the MAE is fully controlled by the size,[14] which corresponds in a general notation to $E_{\mathrm{ani}}=K_{\mathrm{eff}}(V)V$, where the anisotropy constant can vary with V.

Accordingly, the magnetic response of an assembly of particles in experimental situations where the MAE plays a role is then assumed to be directly linked to the particles' size distribution.[6,8,10,15–17] For example, for zero field-cooled/field-cooled (ZFC/FC) curves, which give a signature of the MAE distribution among the particles, the total susceptibility may be expressed as

$$\chi_{\mathrm{tot}}=\int \chi(V)f(V)\mathrm{d}V \tag{1}$$

with $f(V)$ the size distribution and $\chi(V)$ the response of a particle (or particle ensemble) of volume V, and thus a given value of E_{ani}.

However, given the physical origin of the MAE, it is clear that it will vary from one nanomagnet to another[18] in an assembly, and that it must also depend on other factors than the volume of a particle: its precise shape, for instance, or its environment. Therefore, even if the major source of MAE dispersion is generally the size distribution, there should exist an anisotropy constant dispersion reflecting the slight differences among particles of the same volume. The fact that the single $K_{\mathrm{eff}}(V)$ model can be successfully used in many cases to analyze experimental results can be explained by the dominating influence of size dispersion in magnetic nanoparticles assemblies, even for systems having a quite well-defined particle diameter. One can then wonder if such an anisotropy constant dispersion can be experimentally detected: to the best of our knowledge, this was not the case up to now.

Nanoalloys are good candidates to search for an evidence of anisotropy constant dispersion in diluted particle assemblies. Slightly different compositions or degrees of chemical order parameter can indeed correspond to significantly different K_{eff} values. In addition, recent theoretical considerations[19] have predicted the existence of a large K_{eff} dispersion in chemically disordered CoPt and FePt clusters, mainly due to the various atomic configurations statistically accessible.

In this Rapid Communication, we characterize the MAE distribution of a diluted assembly of CoPt nanoparticles, size-selected around a diameter of 3 nm. We show, by comparison with unselected CoPt clusters and size-selected Co clusters, that an anisotropy constant dispersion must be considered in order to account for the magnetic susceptibility measurements.

A thin film of CoPt cluster layers (≃0.5 Å equivalent thickness per layer) separated by 5 nm of carbon matrix has been synthesized (see supplementary information[20] for the characteristics of each sample discussed in this Rapid Communication) using the low-energy cluster beam-deposition technique described elsewhere.[21–23] Particles are produced by laser vaporization and deposited under ultrahigh vacuum conditions, after mass selection (relative diameter dispersion around 8%) with a quadrupolar electrostatic deviator.[22,24] The sample dilution (≃1 vol %) ensures that the interparticle magnetic interactions are negligible. The clusters' size distribution is determined from transmission electron microscopy (TEM) measurements [cf. Figs 1(a) and 1(b)]. We also verify from TEM measurements[16] that CoPt clusters are in the chemically disordered A1 face-centered-cubic phase with geometries corresponding to a negligible shape anisotropy effect. Superconducting quantum interference device (SQUID) magnetometry (Quantum Design MPMS magnetometer) is used to characterize the magnetic properties of the embedded clusters, from low-field susceptibility measurements (ZFC/FC protocol, with a 50 Oe magnetic field) and hysteresis loops at various temperatures.

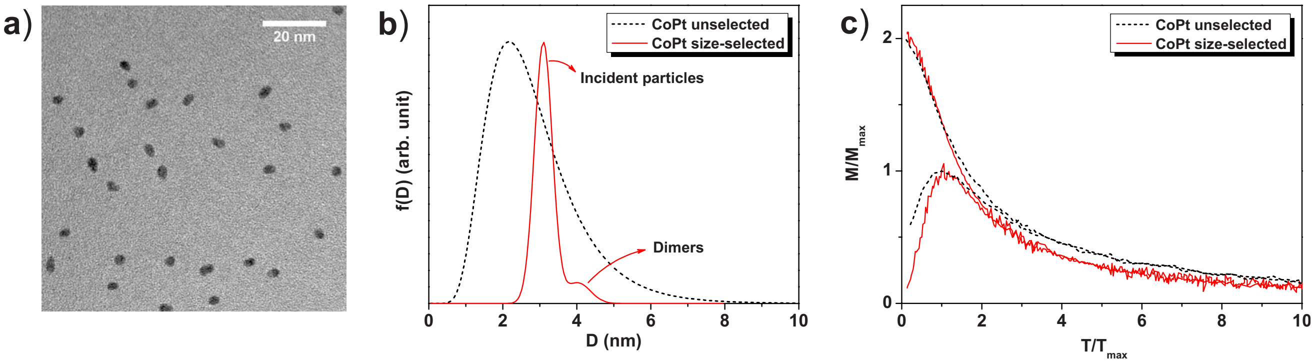

FIG. 1. (Color online) Typical TEM image (a) of a size-selected two-dimensional film of CoPt clusters (equivalent thickness ~0.5 Å) and (b) corresponding size distribution where we can see two contributions: one corresponding to the incident particles, and the other to the few dimers ($\simeq 8\%$) formed on the substrate, simply because of the random nature of cluster deposition. The size distribution of unselected CoPt clusters is shown for comparison (dashed curve). (c) ZFC/FC magnetic susceptibility curves for the samples of unselected (Ref. 16) and size-selected CoPt clusters embedded in amorphous carbon. The curves have been normalized with respect to the maximum point of the ZFC curve ($M=M_{\max}$ for $T=T_{\max}$).

As it can be seen on Fig. 1(c), the width of the ZFC peak is reduced when going from unselected CoPt clusters[16,20] to size-selected ones. However, it is clear that this reduction does not reflect that of the size dispersion which is around six times smaller with size selection [cf. Fig. 1(b)]. If we try to simultaneously adjust the magnetic curves (ZFC/FC curves and a high-temperature magnetization loop) with a semianalytical theoretical model, following the "triple-fit" procedure recently described,[25] no good agreement can be found using the $E_{\mathrm{ani}}=K_{\mathrm{eff}}V$ assumption with a single K_{eff} value and the size dispersion deduced from TEM. Nevertheless, we must stress that this size distribution can perfectly account for the superparamagnetic loops (Langevin fit).

As the triple fit relies on a simple model, where the particles are supposed to behave like noninteracting uniaxial macrospins with a random easy-magnetization direction, one may wonder if its failure could be due to magnetic interactions in the sample. Since the mean first-neighbor distance is around 7 nm, this seems highly improbable. Moreover, the remanence to saturation ratio of the magnetization at 2 K is fully consistent with the model (i.e., it is less than 0.5), and we observe the expected $1/T$ scaling both for the susceptibility curves and the magnetization loops, as long as the temperature is high enough for the system to be in the superparamagnetic regime. This shows that the triple fit failure cannot be explained in this case by the presence of interactions.

On the other hand, the unexpected width of the ZFC peak must be related to an MAE dispersion larger than the one inferred from the TEM size histogram. Within the $E_{\mathrm{ani}}=K_{\mathrm{eff}}V$ model, this could be due to a K_{eff} distribution or to a deceptive evaluation (underestimation) of the magnetic size dispersion. This latter possibility can be ruled out since, as mentioned before, the superparamagnetic magnetization loops can be adjusted with the TEM size distribution. In addition, it is impossible to find a size distribution (by changing the mean diameter, the relative dispersion, the dimer and trimer proportions, etc.), which can adjust simultaneously the three magnetic curves. The use of a size-dependent anisotropy constant, following the $K_V V+K_S S$ model, does not allow a correct fit either. Moreover, it should be noted that a positive surface effect on the MAE, which is usual, corresponds to a higher K_{eff} for the smallest particles than for the largest. This means that the resulting MAE distribution of the cluster assembly will be narrower than for a single K_{eff}, i.e., narrower than the size distribution. This is obviously not the case in these experimental results. In the end, the only physical explanation left to account for the failure of the usual $K_{\mathrm{eff}}V$ model is the existence of a K_{eff} distribution. Indeed, it is fully compatible with the experimental observations since we recall that the magnetic anisotropy has no visible effect on superparamagnetic magnetization loops.

We find that an arbitrary Gaussian dispersion of K_{eff} is able to adjust the curves while keeping the TEM particles' size distribution[26] (see Fig. 2). A best fit then provides the value of the mean anisotropy constant K_0 and the relative K_{eff} dispersion that means $w_K=\sigma_K/K_0$ with σ_K the standard deviation: we find $K_0=218\ \mathrm{kJ/m^3}$ and $w_K=37\%$. The MAE distribution of the clusters assembly is also represented in Fig. 2(c) where it is compared to the one we would have expected with a single K_{eff} value. Interestingly, the mean anisotropy constant is consistent with the value of K_{eff} previously reported for unselected CoPt clusters,[16] which is highly comforting.

In order to get a deeper understanding of the observed K_{eff} dispersion, we have also characterized the magnetic properties of a sample of size-selected pure Co particles [mean diameter $\simeq 3.5$ nm (Ref. 20)] made in the same conditions. This "reference" system should help us to disentangle the various origins of anisotropy dispersion. In this case, a triple fit of the magnetic curves is possible within the simple $E_{\mathrm{ani}}=K_{\mathrm{eff}}V$ model, using a single K_{eff} and the particles' size distribution deduced from TEM measurements (taking into account the slight proportion of dimers and trimers). This shows that even if a small K_{eff} dispersion, not needed here, can exist in the case of pure Co clusters,[18,27] the significant anisotropy constant dispersion in the CoPt sample must clearly be related to the fact that we are dealing with an alloy. The magnetic anisotropy dispersions due to differences in particles' shape or to variations in the clusters' environ-

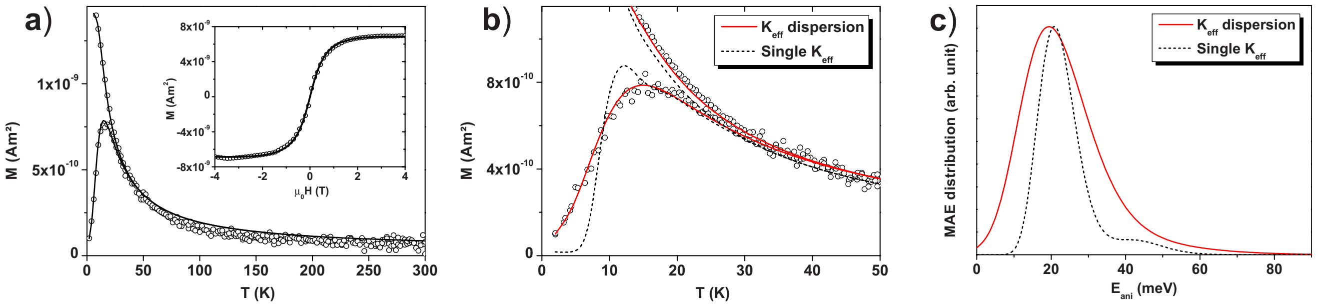

FIG. 2. (Color online) (a) Experimental data points (ZFC/FC curves and superparamagnetic magnetization loop in insert) and best adjustment using the triple-fit procedure (Ref. 25) for size-selected CoPt clusters. (b) Closeup around the ZFC peak where the fit with a K_{eff} dispersion is compared to the one with a single K_{eff} value ($K_{\text{eff}}=K_0$, dashed curve): note that the ZFC peak and the ZFC/FC merging is badly reproduced for a single K_{eff}. The corresponding MAE distributions are displayed in (c).

ment, which are met on every sample, are then negligible as compared to the present nanoalloy effect.

Besides, it is very unlikely that the K_{eff} dispersion in the CoPt assembly comes from a compositional spread around the nominal stoichiometry. Indeed, we can tell that the composition of each particle remains close to the mean 54% Co concentration (energy dispersive x-ray spectroscopy and Rutherford backscattering measurements): according to the statistical sticking process governing the particles formation, the concentration deviation is expected to be around ±2%; we have previously shown[16] that the same particles can transform into the $L1_0$ phase upon annealing, which demonstrates that their composition is in the limited range[28] where the chemically ordered phase can exist; a significant composition dispersion would result in a saturation magnetization dispersion, which is not detected in the fit of the superparamagnetic loop.[29] In addition, according to theoretical MAE calculations on CoPt and FePt clusters,[19] such a moderate stoichiometry variation does not correspond to a broadening of the magnetic anisotropy distribution.

Furthermore, note that contrary to the case of pure Co,[7] the MAE of chemically disordered CoPt particles is quite large even if they have a highly symmetrical shape (regular truncated octahedron).[19] The modifications of K_{eff} by additional facets are then relatively small (around 10%). Therefore, following the theoretical considerations of Ref. 19, we can attribute the K_{eff} dispersion mainly to the multiplicity of atomic configurations. A huge number of chemical arrangements can indeed statistically exist in the case of chemically disordered particles of the same geometry (size and shape), corresponding to different values of E_{ani} and hence K_{eff}.

In fact, the global K_{eff} distribution (not only coming from the chemical arrangements) may evolve with the size since, for instance, the effect of additional facets becomes negligible for large particles. This means that, in a very general way, the response of an assembly of particles can be written as in Eq. (1), but with

$$\chi(V) = \int \chi(E_{\text{ani}} = K_{\text{eff}}V)\rho_V(K_{\text{eff}})\mathrm{d}K_{\text{eff}}, \tag{2}$$

where $\rho_V(K_{\text{eff}})$ is the size-dependent anisotropy constant distribution. In our fit of the magnetic curves for the size-selected CoPt particles, it would then have been legitimate to use a size-dependent K_{eff} distribution instead of a single one. However, several reasons speak against this choice: since the size distribution is quite narrow, the size dependence of the K_{eff} dispersion is not critical as compared to its significant magnitude for a single size; using different K_{eff} distributions for different cluster sizes would have introduced additional parameters in the fit, without adding appreciable physical insight; and the size dependence of the global K_{eff} distribution is difficult to predict in a reliable way but the dispersion due to statistical configurations is expected to be almost size-independent. These later reasons led us to choose a simple Gaussian distribution of K_{eff}, which appears as one of the easiest and most general choices, with only two physically appealing parameters: the mean anisotropy constant and the relative dispersion. One may certainly get little improvement of the fit with more complex distributions of K_{eff} but the purpose was here to show experimental evidence of the K_{eff} dispersion and to provide an estimation of its magnitude, to be compared to theoretical predictions.[19] As a matter of fact, the value of w_K we find is of the same order of the one predicted with the empirical Néel anisotropy model ($w_K \simeq 59\%$). The lower value found experimentally could be due to deviations from a purely random chemical configurations model, implying that some partially ordered geometries are favored.

One may wonder why such a K_{eff} distribution has never been needed before, and especially why is the common $E_{\text{ani}}=K_{\text{eff}}V$ model successful in analyzing the magnetic properties of unselected CoPt clusters.[16] Of course, the anisotropy constant dispersion must still be present but it is masked by the significant size dispersion. We have then tried to adjust the magnetic curves of the unselected CoPt sample, following the triple-fit procedure,[25] using a K_{eff} distribution with $w_K=37\%$. The resulting fit appears to be as good as with a single K_{eff} value.[30] This shows that a K_{eff} distribution cannot be detected for particles assemblies with too large a size dispersion.[31] Small particles with a well-defined size are needed to make this effect visible: this has been achieved thanks to our efficient size-selection device.

In conclusion, we have characterized the magnetic properties of a diluted assembly of CoPt clusters embedded in amorphous carbon, size-selected around 3 nm in diameter, with a sharp size distribution (~8% relative dispersion). The MAE distribution, which controls the shape of the ZFC/FC magnetic susceptibility curves, is found to be much larger than expected just from the size distribution. This can be explained by a significant anisotropy constant dispersion, which has been recently predicted for chemically disordered CoPt nanoparticles. Such a dispersion is usually masked by the size dispersion and is not visible for pure size-selected Co clusters: here a K_{eff} dispersion is experimentally evidenced.

In addition to its fundamental interest, the dispersion of magnetic anisotropy constant that exists in alloy nanoparticles is of particular relevance for their potential applications. Indeed, our results point out that it is almost impossible to avoid a significant MAE dispersion in an assembly of nanomagnets (i.e., a proportion of particles less stable than expected), even if the particle size can be precisely controlled. This may appear as "the other side of the coin" of the exceptional properties of magnetic alloys displaying a very large and promising magnetic anisotropy constant in the bulk:[4] since the anisotropy enhancement is here due to the presence of Pt, the magnetocrystalline anisotropy necessarily depends on the neighborhood of each Co atom.[19,32,33] Note however that, as shown by preliminary results, this dispersion should be strongly reduced upon chemical ordering of the clusters, as long as a well-defined and high-enough degree of chemical order can be reached.

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