Interaction effects in dilute cluster-assembled magnetic nanostructures

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We have prepared dilute nanostructured magnetic samples by codeposition of preformed cobalt clusters with a narrow size distribution around 40 atoms per cluster in silver matrices. Magnetoresistance measurements are used to derive information about the magnetic structure of the samples. Effects of cluster size distribution or anisotropy can be neglected in our samples. Deviations from simple Langevin-type magnetization are observed as a function of temperature and identified as due to intercluster interactions. Pairwise magnetostatic and indirect exchange interactions as well as the model of interacting superparamagnets are found to be not adequate to explain the observed temperature dependences. We propose an interpretation of a correlated spin glass, which shows that for small clusters, spin glass behavior can be observed even at high dilutions.

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I. INTRODUCTION

Granular magnetic materials have been studied extensively in the past years and promise to play an important role in applied physics. In the ongoing miniaturization of magnetic data storage media, the superparamagnetic limit, as well as intergrain interactions, becomes an issue. It is thus of great interest to develop methods of preparation and characterization of well-defined model nanostructures. On the other hand, a great deal of knowledge has been collected on well-defined gas-phase and supported magnetic clusters. In order to allow technological applications, this know-how must be transferred to nanostructured solid state samples guaranteeing chemical and thermal stability. Developing a detailed understanding of the magnetic properties, especially the interactions, both intergrain and between the localized moment and the conduction electron spin, is important not only to satisfy scientific curiosity but also in order to fully exploit such systems in the development of high performance magnetic materials and spin-dependent electronic devices.1–4

A large number of articles have been published on magnetoresistive properties of granular films, the determination of giant magnetoresistance (GMR) being the simplest spin-dependent transport measurement. Most of the samples described in these studies have been generated by postannealing of metastable alloys of immiscible metals (the first are Refs. 5 and 6). When interactions are observed in these systems, they are usually attributed to direct exchange, especially above the percolation threshold of around 25 at. % of the magnetic element. Irreversible effects such as magnetic freezing below a specific blocking temperature are attributed to the intragrain interaction between macrospin and crystalline anisotropy. The departure from idealized parabolic magnetoresistance curves is explained by either broad size distributions7 or the interparticle interactions.8 The same argument is followed for samples with deposited preformed clusters in the nanometer regime (≥700 atoms). Only concentrated samples (≥10 at. % of Co or Fe) are considered to have interacting clusters; at lower concentration, only the anisotropy is discussed.9–13

For noninteracting superparamagnetic particles, the magnetization follows, in the classical limit, a Langevin behavior: $M(H,T)=M_0 L(S\mu_B H/k_B T)$ with $L(y)=\coth(y)-1/y$, $S$ the macrospin, $\mu_B$ the Bohr magneton, and $k_B$ the Boltzmann constant. A model for the magnetoresistance in granular films has been introduced by Zhang and Levy.14 This model considers contributions from spin-dependent scattering inside the magnetic grains and at the interfaces. It has successfully been used to fit GMR curves of cluster-assembled samples.15,16 Since scattering within the cluster can be neglected,10,14,17 the model boils down to spin-disorder scattering18 with a magnetoresistance $\Delta R \propto -M(H,T)^2$, i.e.,

$$\Delta R \propto -L(H,T)^2 \quad (1)$$

in the classical limit. Deviations from this simple formalism are due to intra- or intercluster interactions (neglecting the quantization of magnetic moment orientation) and manifest themselves as “flat-top” GMR curves in postannealed samples.8,19,20 Magnetic ordering and spin-glass-like behavior have also been observed in rather dilute postannealed granular samples21,22 but the strongly inhomogeneous concentration and large size distributions make an unambiguous interpretation difficult.

We have developed an experimental setup that allows the fabrication of embedded magnetic nanostructures through cluster assembly in a nonmagnetic metallic matrix. This strategy has several advantages, namely, the independent control over cluster size and concentration. In this paper, we present results from magnetoresistive measurements of very small clusters at high dilutions, thereby eliminating influences of large cluster size distributions23 as well as anisotropy effects.

II. EXPERIMENT

Samples were prepared according to the strategy of cluster-assembled materials. The experimental setup is described in detail elsewhere24 and is only sketched briefly. Cobalt cluster ions are generated in the gas phase using a homebuilt magnetron cluster source (based on the principle introduced by Haberland et al.25) and guided by ion optics through several differential pumping stages toward the deposition chamber. The beam can be directed either toward a time-of-flight mass spectrometer for cluster size determina-
tion, beam characterization, and optimization or into a quadrupole mass spectrometer in front of the substrate surface. The conductive polyimide, negligible parallel conductivity

The matrix metal is evaporated in a commercial electron beam evaporator and codeposited simultaneously with the clusters. The cobalt concentration can be adjusted by varying the matrix deposition rate which is monitored with a quartz microbalance. Samples are 50 nm thick and 1 cm² large with a central area of 5 mm diameter of the cluster doped matrix.

For transport measurements, a thin stripe of less than 1 mm width was cut and contacted with silver paste. Transport measurements were performed in a commercial magnetometer (Quantum Design MPMS, USA) at temperatures between 3 and 300 K and fields of up to 5 T. Figure 1 shows magnetoresistance curves at different temperatures for two samples with the same deposited cluster size distribution (⟨n⟩=40, σ≤0.3) but different atomic cobalt concentrations (sample A: 0.8 at. %; sample B: 0.3 at. %). A distinct dependence of both amplitude and shape on the temperature is seen for both samples. In the following, we will focus our discussion on the shape of the GMR curves since these directly reflect the magnetic response at a given temperature. Up to 25 K, no significant change in shape for sample A is discernible; at temperature above 200 K, on the other hand, the onset of saturation in the external field is no longer visible. In sample B, a change in shape of the MR curve can already be seen for low temperature; the curve at 25 K is less saturated. A nearly linear decrease in resistivity with magnetic field is measured already at temperatures below 100 K.

This behavior has been observed for a whole series of samples with different cluster sizes and concentrations. Here, we will focus on two representative samples that clearly support our argument.

III. DISCUSSION

The comparison of the MR curves for samples A and B (Fig. 1) reveals a different approach to saturation, best seen at 75 K. While sample A displays a distinct onset of saturation, no such onset is discernible for sample B. Since the concentration is the only parameter different between the two samples, this already hints toward intercluster interactions, contrary to the common assumption that samples at such high dilution can be considered as consisting of noninteracting superparamagnets.

Figure 2 shows some of the GMR curves for sample A together with fits according to Eq. (1). The agreement seems reasonable at each temperature but the magnetic moment per cluster \( S \) derived from these fits is strongly temperature dependent. This again is contrary to the assumption of non-interacting superparamagnetic particles. We therefore prefer rather to speak of apparent moments. In order to confirm these observations and to make sure that they are not due to some spurious effect of the resistance measurement, we have also measured the magnetization effect in comparable samples via the extraordinary Hall effect. A comparable temperature dependence is observed; we are thus confident in our experiments. In the following, we will estimate and discuss the different possible interactions responsible for our observations.

The anisotropy energy, i.e., the intracluster interaction of the cluster magnetic moment with its own crystalline lattice, can be calculated using \( E_a=KV \) with \( K \) the anisotropy constant and \( V \) the cluster volume. \( K \) has been determined for nanometric cobalt using the micro superconducting quantum interference device technique to be 0.9 and 2.2 \( \times 10^5 \) J/m³ along the hard and easy axes of a cluster of \( \approx 1000 \) atoms. Using a cluster diameter of 9 Å (40 atoms), a measurement time of \( t_{\text{exp}} \approx 10 \) s, and a trial frequency of \( f_0 \approx 10^{10} \) s⁻¹, one can estimate the corresponding blocking temperature according to
FIG. 3. (Color online) Simulated distributions: monodisperse Co clusters distributed randomly in a fcc lattice with 10⁶ sites. Ag matrix atoms are not shown. The number of atoms, the concentration, the characteristic magnetostatic temperatures, and the mean intercluster distances \(d\) are given in the legend. [(a) and (b)] Samples discussed in this paper; [(c) and (d)] simulations of two samples of Ref. 12.

\[
T_b = \frac{KV}{k_B \ln(\tau_{\text{exp}}/\tau_0)}.
\]

This yields a value well below 1 K, meaning that single particle blocking can be definitely ruled out in the samples shown here, independent of possible variations of an order of magnitude in any of the parameters in Eq. (2), e.g., due to an enhanced surface anisotropy.

Consequently, it must be intercluster interactions that are responsible for the observed temperature-dependent apparent moments, an interpretation that is affirmed by the comparison of samples of different concentrations. This is surprising considering the orders of magnitude involved for the two possible types of interaction:

**Magnetostatic dipolar interactions.**

\[
E_{\text{dip}} = \frac{\mu_0}{4\pi r^3} \left[ \mu_1 \cdot \mu_2 - \frac{3}{r^2} (\mu_1 \cdot r)(\mu_2 \cdot r) \right],
\]

where \(r\) is the separation between the magnetic moments \(\mu_1\) and \(\mu_2\). This translates into a characteristic temperature of \(\sim 20\) mK for sample A (assuming a magnetic moment of 70\(\mu_B\) per cluster and a mean separation of 5.7 nm). The same order of magnitude is also found in Ref. 29.

Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions, the indirect exchange interaction \(J\) mediated by conduction electrons polarized by the localized moments. For large distances \(r\), it can be simplified as

\[
J_{\text{RKKY}}(r) \propto \frac{\cos(2k_F r)}{r^3},
\]

with \(k_F\) the conduction electron Fermi wave vector. In Ref. 29, the RKKY interactions between two Co₃O₄ clusters embedded in a Ag matrix have been calculated as a function of separation. Even in a crystalline lattice, this interaction oscillates with an amplitude of several \(\mu\)eV at distances of several nanometers, i.e., of the same order of magnitude as the dipolar interactions. In a disordered structure, the average coupling strength is estimated to be even lower. Consequently, it is not enough to simply estimate pairwise interactions in order to derive blocking temperatures for dilute systems with small clusters. Another way of taking into account interactions between superparamagnetic clusters in metallic matrices has been introduced by Allia et al. [interacting superparamagnet (ISP) model]. Here, the fact that the clusters are not rigidly coupled but still interact has been incorporated via an additional temperature term \(T^*\) in the Langevin function describing the orientation of a magnetic moment in an external field:

\[
M^*(H) = N \mu_L \left( \frac{S^* \mu_B H}{k_B (T + T^*)} \right).
\]

The authors argue that the magnetic moments in their samples fluctuate with frequencies of the order of gigahertz, and thus exert a disordering, random torque which opposes the ordering effect of the external field. It can be considered as equivalent to an elevated temperature.

We can account for all GMR curves by combining Eqs. (1) and (3) and obtain apparent moments \(S^*\) of several hundred Bohr magnetons for sample A (again assuming the bulk value of magnetic moment per atom), equivalent to seven clusters reacting collectively to the external field and to the fluctuations of the other superclusters. The same qualitative behavior has been observed for sample B with an apparent moment of 140\(\mu_B\) per cluster. This is contradictory to the initial assumption of this model that the superparamagnetic cluster is considered to be not coupled rigidly.

In order to estimate the probability of clustering of clusters, we have examined statistical simulations of a random distribution of clusters with 40 atoms in a fcc lattice at the same concentrations as in Fig. 1 [Figs. 3(a) and 3(b)]. It can be clearly seen that all clusters are well separated. It is especially not reasonable to assume an average of seven clusters rigidly coupled in sample A [Fig. 3(b)]. The same simulations have been performed for two samples presented by Binns et al. in Ref. 12, consisting of Fe clusters with a mean diameter of 2.5 nm (=691 atoms) embedded in Ag matrices at 0.8 and 10 at. % [Figs. 3(c) and 3(d)]. The first sample is reported to show purely superparamagnetic behavior (at the
same atomic concentration as our sample A), while the second is interpreted using the ISP model with six to seven clusters being exchange coupled. This number of coupled clusters is comparable to what we derive for our sample A, although the characteristic dipolar temperature of the sample shown in Fig. 3(d) can be estimated to $\sim 5$ K; rigid coupling is thus expected. Consequently, the ISP model, while appropriate for systems as in Ref. 12, cannot be used to explain our observations.

In summary, the following qualitative picture can be drawn for our samples. The magnetic moments are, despite the small cluster size, not isolated; they interact, but neither do they simply misalign each other in a random fashion nor are they coupled rigidly. The system can rather be considered correlated, i.e., the magnetization undergoes smooth stochastic rotations throughout the sample. The sign of the interaction depends on the relative orientation (magnetostatic) and the distance (RKKY); thus, no unambiguous ordering on a large scale is achieved; the moments are frustrated.

This depiction corresponds well to the model of random anisotropy which describes a continuous distribution of weakly coupled, frustrated moments and has been used to interpret correlated spin glasses. The magnetic moments in this model are not coupled rigidly but are rather correlated on a length scale much larger than the pairwise ferromagnetic exchange range. Unlike the typical ferromagnetic domain structure, no sharp boundaries between correlated regions exist. This model of weak anisotropy has to be seen in contrast to the canonical spin glass with strong anisotropy (sometimes called spheromagnetic) where the local magnetization is aligned along the local easy axis and the magnetic properties of which resemble those of randomly stacked ferromagnetic crystallites.

The random anisotropy model has already been evoked in order to explain temperature-independent magnetization curves in samples with nanometer-sized clusters at concentrations of 20%–100%, i.e., for systems of exchange coupled clusters around and above the percolation threshold. Here, the term correlated superspin glass was coined.

Such a correlated spin glass with weak anisotropy is known to be a soft magnet which can initially be easily magnetized. The application of a small field easily rotates the correlated moments to a certain extent; the low-field susceptibility is predicted to be very large. This effect can be seen in Fig. 4, where we compare the low temperature GMR of sample B with the according fit using Eq. (1) for superparamagnetic particles. Clearly, a larger low-field susceptibility than predicted by the simple superparamagnetism model is seen. In order to underline the deviations, only data points for fields $|H| \geq 2$ kOe were used for the fit.

This simple picture can explain the GMR curves of dilute cluster-assembled nanostructures. The magnetic response of the sample is dominated by “droplets” of correlated moments and their response to temperature and field rather than the superparamagnetic behavior of each single superspin. These droplets comprise several clusters; consequently, the magnetic moment derived from GMR curves appears too large. The exact number of correlated clusters cannot be determined since they are not aligned parallel. Upon heating more and more of the droplets become thermally activated and their size may change; the apparent moment consequently changes.

It has been found in annealed granular samples that intermediate magnetic atoms can enhance the RKKY-type interaction between magnetic precipitates. This corroborates our picture where it is the clusters themselves that facilitate correlation over longer distances. The difference in magnetic behavior of the two samples of equal concentration shown in Figs. 3(a) (interactions) and 3(c) (superparamagnetic) is thus due to the small interparticle distance rather than the difference in magnetic moment per cluster.

Further information on the magnetism of granular samples can, in principle, be obtained from the comparison of field cooled–zero field cooled magnetization curves, especially on the anisotropic blocking temperature. We have previously used this technique for samples with higher concentrations and observed a blocking temperature of $\sim 50$ K as well as a coercive field of $>500$ Oe for a sample of Co clusters with $n=15$ atoms at a concentration of 8 at. % in a copper matrix. These observations were attributed to strongly interacting, rigidly coupled clusters. Direct unambiguous magnetization measurements of the more dilute samples presented in this paper were not possible due to the small amount of cobalt. We have, however, compared their low temperature magnetoresistance after field and zero field coolings and found no difference. It is consequently not possible to “freeze-out” a certain orientation of the correlated magnetic moments in dilute samples; even small external fields suffice to turn the local magnetization. This is further confirmed by the negligible coercivity ($<25$ Oe) observed in the GMR curves at 3 K (see inset of Fig. 4). These observations are in agreement with our interpretation of a correlated spin glass with weak anisotropy; only systems with strong anisotropy are expected to show clear differences between field cooled and zero field cooled magnetizations.

**IV. CONCLUSIONS**

We have investigated the magnetoresistive properties of dilute cluster-assembled magnetic nanostructures with a
mean cluster size of 40 atoms. The properties of our samples are determined by the cluster size and the mean intercluster separation:

1. The clusters are too small for anisotropic effects or significant pairwise interactions.
2. Even at dilutions of < 1 at. %, the clusters interact and cannot be considered superparamagnetic.
3. The interactions between clusters manifest themselves not only under extreme conditions; they determine the system’s magnetization even at room temperature.

This has to be seen in contrast to the existing literature where the mean cluster size is generally much larger and, thus, effects of anisotropy, direct exchange, or large separations have to be taken into account. The results presented here clearly show that for small clusters, it is not enough to only consider the atomic percentage of magnetic concentrations. The interparticle distance plays a role at least as important as the absolute magnitude of the magnetic moment.

An interpretation within the framework of correlated spin glasses is proposed, based on the observed low-field susceptibility and interaction effects. The samples shown in this paper do not contain enough magnetic material to directly confirm spin-glass behavior in ac susceptibility measurements; complementary experiments with synchrotron radiation or polarized muons, however, are possible and planned. Preliminary measurements of the extraordinary Hall effect promise the parallel detection of magnetoresistance and magnetization. While further experiments in order to further pin down the exact nature of magnetic interactions are clearly needed and under way, important conclusions can already be drawn. One implication is that it is, due to the interactions, unfortunately not possible to directly infer the evolution of magnetic moment per atom as a function of cluster size for embedded clusters as it has been done in the gas phase.36

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22 The influence of our narrow size distribution on the GMR curves was simulated as described in Ref. 7 and found to be negligible.
27 Below the anisotropic blocking temperature, the magnetocrystalline anisotropy energy is larger than the thermal fluctuations; the magnetic moment aligns along the cluster easy axis. A larger external field is required to overcome this barrier; the cluster can no longer be considered purely superparamagnetic.