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Memory effect in Fe-Ag granular multilayers

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Abstract
Magnetic memory effect was measured in Fe-Ag granular multilayers by employing the so-called stop-and-wait protocol in order to reveal super-spin glass (SSG) behavior and explore the role of intra- and interlayer interactions which can influence the superparamagnetic (SPM) behavior of Fe particles separated by Ag layers. Calculations based on the relaxation of two-level systems are made to obtain the evolution of the magnetization of interaction-free SPM particles as a function of temperature and time for arbitrary annealing procedures, e.g., zero-field-cooled (ZFC) and field-cooled (FC) susceptibility (low-field magnetization) or temperature-cycling measurements. In samples with a single Fe layer of different nominal thicknesses, both the observed memory effect and the low-temperature deviation of the measured FC magnetization from the calculated interaction-free FC curve are attributed to the effect of dipolar interactions. Estimates on the anisotropy energy suggest the importance of the surface anisotropy of the Fe particles in the magnetic behavior.

1. Introduction

Fe-Ag multilayers with the Fe-layer thickness in the few-monolayer range [1, 2] show small-particle behavior of Fe islands as indicated by the linear temperature dependence of the magnetic hyperfine field [3] and the deviation of the magnetization of the field cooled (FC) and zero-field cooled (ZFC) sample [4]. The magnetic properties of such so-called discontinuous or granular multilayers resemble those of a superparamagnetic (SPM) ensemble and have been intensively studied [5], similarly to granular alloys prepared by codeposition of the constituents [6–10]. The SPM behavior is influenced not only by the magnetic anisotropy and the size distribution of the ferromagnetic particles but also by the strength of the dipolar and exchange interactions between the particles within and between the layers [11, 12].

In a previous paper [13], we studied the magnetic properties of Fe-Ag multilayers with the general structure: Si substrate/cover layer + (tFe, Fe + tAg, Ag)n + cover layer, where tFe and tAg are the thicknesses of the Fe and Ag layers, respectively, and n is the number of the bilayers given in the parenthesis. At certain values of these parameters, the Fe layers are discontinuous and show the magnetic behavior of a superparamagnetic (SPM) ensemble. Besides the straightforward effect that increasing tFe increases the blocking temperature (Tfl), we found that tAg and n also affect Tfl, however, not only by affecting the interactions between the Fe particles but also through influencing the growth process of Fe. A magnetic ‘phase diagram’ of the Fe-Ag multilayers was constructed in the tFe, tAg, n parameter space, where the onset of SPM behavior can be predicted from the values of these three quantities. This paper [13] did not focus directly on the study of interactions between the Fe particles though with increasing tFe, tAg, and n, an increased flattening of the FC magnetization suggested an increased interaction between the clusters. Binns et al [7] and Gubieda et al [9] studied the ZFC and FC magnetization in nanostructured Fe-Ag granular films and concluded that with increasing Fe content, the FC magnetization becomes gradually flattened, and the flattening was attributed to the increase of interactions between the clusters. However, memory effect, as far as we know, has not yet been investigated in Fe-Ag granular systems although it is an undisputable indicator of the presence of significant interactions between the particles.
Interactions between magnetic nanoparticles have been intensively studied in the last two-three decades [11, 14]. Kleemann et al investigated discontinuous Co80Fe20/Al2O3 multilayers varying the thickness of the magnetic layer separated by a non-magnetic and insulating spacer. With increasing thickness, transitions from superparamagnetic (SPM) to super-spin glass (SSG) and further on to superferromagnetic (SFM) behavior could be observed [15–25]. Non-equilibrium dynamics were explored by Nordblad et al in interacting magnetic nanoparticle systems, e.g., Fe–C [26] and Fe3N [27], and in systems showing similar phenomena such as spin glasses, e.g., CdCr1.3In0.7S4 [28], Ag(Mn) [29, 30] and Cu(Mn) [31]. While in these cases dipolar interactions between the super-spins of the nanoparticles were identified to cause frustration leading to the SSG state, other sources were also proved to bring about this behavior. In magnetic Co–Ag granular films fabricated by cosputtering, a Ruderman–Kittel–Kasuya–Yosida– (RKKY) like exchange interaction between the nanoparticles was suggested to be responsible for the collective SSG dynamics [32, 33]. Similar mechanisms seem to work in Cu97.2Co2.5 alloy prepared by melt spinning [34], Fe50Ag40W10, fabricated by mechanical alloying [35] and annealed Cu–16Fe (at%) solid solutions obtained by high-pressure torsion [36]. The spin-glass phase of the outer shell of a nanoparticle with a core–shell structure may also have influence on the non-equilibrium dynamics of the particle ensemble [37].

There is an agreement in the literature that a genuine method to prove the existence of the SSG (or spin-glass) state of a nanoparticle system (or a canonical spin glass) is to reveal memory effect by the so called stop-and-wait protocol. In a variant of this protocol, the sample is cooled in zero field from above the blocking temperature, $T_b$ (or $T_C$, the spin-glass freezing temperature in case of a spin glass), to a wait temperature, $T_w < T_b (T_C)$, where it is kept for a wait time, $t_w$. Then the sample is cooled further (in zero field) to the lowest measuring temperature and ac susceptibility [26, 28–31] or dc magnetization [19–22, 24, 25, 30, 33, 37] (applying a small ac or dc magnetic field) is measured upon warming. Repeating this procedure without stopping at $T_w$, a reference curve is measured and subtracting the latter from the former, a minimum of the difference curve is obtained close to $T_w$, which is called memory effect. It is connected to the presence of a spin glass or an SSG phase.

The so-called negative temperature-cycling measurements with and without magnetic-field change were also proposed (see detailed description in section 3.4) in order to prove the existence of the SSG phase in a nanoparticle system [38]. Later, this statement was refuted by several authors [27, 39–41], showing that the typical features can be well reproduced by a model of SPM nanoparticle ensemble without interaction.

The aim of this paper is to check if memory effect and superspin-glass properties can be observed in those Fe–Ag multilayers which show FC magnetization incompatible with the interaction-free SPM relaxation model. Measuring memory effect, as described above, is one of the genuine methods to prove the superspin-glass nature of a magnetic small–particle system.

The measured curves will be compared with those calculated from a theoretical model of a superparamagnetic particle ensemble without interaction. The model calculation is able to give the variation of magnetization in any arbitrary experimental procedure to which the sample is subjected. The model is based on the fact that from energetic point of view an ensemble of single-domain particles can be described by an ensemble of two-level systems (TLS) [42]. The two minima correspond to two stable or metastable directions of the magnetic moments between which transitions can occur by thermal excitation. In zero field, the two states has the same energy and the energy barrier between them is proportional to $K V$ where $K$ is the anisotropy constant and $V$ is the volume of the particles. $K$ is assumed to be constant while the distribution of $V$ is approximated by a lognormal distribution. Applying a small magnetic field ($H$) will decrease and increase the respective minima of the TLSs, thus creating a TLS characterized by activation-energy ($E = K V – \mu H$) and splitting ($\Delta = 2\mu H$) parameters. (These expressions are valid if the easy axis of the particle lies in the field direction, otherwise the perturbation is smaller, and approaching zero if the easy axis is perpendicular to $H$).

Here $\mu = VM$, is the magnetic moment and $M$, is the saturation magnetization of the particles. The distribution of $\Delta$ is ascribed to a random distribution of the magnetic-moment directions. See Appendix for the detailed description of the model.

Similar models using the same starting equations for the description of thermally activated processes in an interaction-free superparamagnetic particle ensemble have been described in the literature by Klik et al [43], Sasaki et al [27, 39], Zheng et al [40, 41]. The model of Viddal and Roshko [44, 45] is also similar, using a Preisach formalism. However, the splitting in their case is not solely brought about by the application of a magnetic field but an intrinsic splitting is also assumed which is related to some kind of interactions. The dynamics of an interacting magnetic-particle system can also be studied by Monte Carlo simulations [46].

The paper is organized as follows. In section 2, the experimental details are presented. In section 3.1, the results for the $t_{1/2}$ dependence of the memory effect are shown, together with the ZFC and FC magnetization Versus temperature curves. The relation between the nominal Fe thickness, $t_{Fe}$, and the cluster (particle) size is discussed in section 3.2 where the dipolar interactions between the clusters are also estimated. In section 3.3, the bilayer-number dependence of the memory effect is presented. In section 3.4, the results of the
temperature-cycling measurements obtained with and without magnetic-field change are described. The possible origin of the particle anisotropy is discussed in section 3.5. Finally, the main results are summarized in section 4.

2. Experiment

In this paper, two sample series used also in our previous study [13] were investigated; a series containing only one Fe layer with nominal thicknesses of \( t_{\text{Fe}} = 4, 5, 7 \) and 10 Å \( (n = 1) \) surrounded by buffer and cover layers and samples with 10 bilayers \( (t_{\text{Fe}} = 7, 10 \text{ Å}, t_{\text{Ag}} = 50 \text{ Å}, n = 10) \). In this study the memory effect as a new quantity was measured for them, but for comparison, the temperature dependence of the low-field magnetization was also re-measured.

The multilayer samples were evaporated in a vacuum chamber with a base vacuum below \( 10^{-6} \text{ Pa} \) onto a 0.3-mm-thick untreated Si (111) wafer at room temperature from two independent electron beam evaporation sources with water-cooled copper crucibles (one for Ag and another for B) while \(^{57}\text{Fe} \) or natural Fe was evaporated resistively from a W boat. Two substrate holders (in symmetric position to the W crucible) and an appropriate shutter enable the preparation of two (in some cases four) samples with fully or partially identical layer structure. The evaporation rate was controlled by a quartz crystal thickness monitor. The evaporation rate was varied depending on the thickness of the given layer from 0.1 Å s\(^{-1}\) (for layers with 1–2 Å thicknesses) to 1.5 Å s\(^{-1}\) (for 100 Å). The nominal thicknesses were calculated supposing bulk densities. The general layer sequence of the samples is Si substrate / buffer layer + \((t_{\text{Fe}} \text{ Fe} + t_{\text{Ag}} \text{ Ag})_n + \) cover layer where \( t_{\text{Fe}} \) and \( t_{\text{Ag}} \) are the thicknesses of the Fe and Ag layers, respectively, \( n \) is the number of the Fe/Ag bilayers; ‘buffer’ stands for a nonmagnetic metal layer evaporated directly onto the Si wafer (in our case it is Ag) and ‘cover’ stands for a nonmagnetic layer preventing the oxidation of the multilayer (here it is B or Ag). In the rest of the paper, the Si substrate will be omitted from the sample notations.

The typical layer properties of our Fe-Ag multilayers were investigated earlier by transmission electron microscopy [47]. Epitaxial bcc-Fe and fcc-Ag layers with a columnar-growth structure could be observed for a (15 Å Fe + 26 Å Ag)\(_{25}\) sample but for a multilayer sample with smaller nominal Fe-layer thickness, (2 Å Fe + 26 Å Ag)\(_{15}\), neither Fe layers nor Fe nanoparticles could be identified. In case of very small Fe particles, fcc or face-centered tetragonal (fct) structure cannot be excluded. The determination of the average Fe-particle size from x-ray-diffraction line broadening [48] is prevented by the overlap of some of the diffraction lines of bcc Fe and fcc Ag, while the (111) preferred orientation of the Ag layers could be observed. Binns et al [7] was able to identify pure Fe particles deposited onto Si(111) with \textit{in situ} scanning tunnel microscope (STM). The size distribution of the particles obtained from the STM image was compared to that calculated by fitting Langevin function to the magnetization curves of Fe clusters with 1% volume fraction embedded in Ag matrix by coevaporation and protected by 50 Å Ag capping layer. From the agreement of the size distributions they concluded that the Fe clusters have a morphology in the Ag matrix similar to that observed in the \textit{in situ} STM experiment. Consequently, for capped granular Fe-Ag layers, the magnetic characterization of the particle size seems to be a reliable method.

The magnetization of the samples were measured using a MPMS-5S Quantum Design superconducting interference device (SQUID) in the temperature and magnetic-field range of \( 5 \leq T \leq 300 \text{ K} \) and \( 0 \leq H \leq 50 \text{ kOe} \), respectively. The low-field measurements were performed in \( H = 10 \text{ Oe} \) upon heating after cooling the samples from 300 to 5 K in zero field (ZFC) or in the measuring field of \( H = 10 \text{ Oe} \) (FC). The superconducting magnet is demagnetized by oscillating the field with decreasing amplitude around zero and the minimum field that can be reached by this procedure is around –1 Oe. This is the reason that the magnetization of the ZFC Versus temperature curves shown in this paper can assume negative values. Similar effect has been reported in the literature [49, 50]. One or two pieces of \( \sim 6 \times 6 \text{-mm}^2 \) sample on the Si wafer substrate were pressed between the walls of a drinking straw without using any sample-supporting part. In case of two pieces, they were stacked with the multilayers facing each other. The memory effect is probed by measuring the low-field dc magnetization using the stop-and-wait protocol described in detail in the Introduction. The wait temperatures, \( T_{\text{w},n} \), are selected to be around, slightly below and above the inflexion point of the ZFC magnetization curve where considerable relaxation can be expected. Memory effect Versus temperature curves with wait temperatures giving similar \( T_{\text{w}}/T_{\text{fi}} \) ratio (between 0.67–0.85) are presented here for the sake of quantitative comparability. Negative temperature-cycling measurements (see details in the Introduction) were also performed for the study of the relaxation processes.

3. Results and discussion

3.1. Iron-thickness dependence of the memory effect

Figure 1(a) shows the ZFC and FC magnetizations of the 50 Å Ag + \( t_{\text{Fe}} \text{ Fe} + 50 \text{ Å Ag} + \) cover sample series where only a single Fe layer is evaporated with nominal thicknesses of \( t_{\text{Fe}} = 4, 5, 7 \) and 10 Å. (In this figure and
everywhere in the paper, the magnetization is referred to the total Fe mass of the samples.) As discussed in detail in a previous paper [13], the magnetization of the sample cooled in zero field is small at low temperatures because of the spatially random magnetic moments of the Fe particles (clusters) frozen in during cooling through their respective blocking temperatures. The freezing occurs when the anisotropy energy of a cluster ($K_V$) exceeds the apparent thermal energy ($kT$ multiplied by a factor depending on the time scale of the measurement, see Appendix in detail). Upon warming in an applied measuring field, the clusters gradually turn into the direction of the magnetic field ($H = 10$ Oe) when the apparent thermal energy exceeds their respective anisotropy energies. A size distribution of the clusters results in a smooth peak of the magnetization curve (ZFC curve). The temperature of the peak is called the average blocking temperature of the sample ($T_B$). Above the highest individual blocking temperature of the clusters, the magnetization decreases like it does in a paramagnet. Upon cooling in the same magnetic field ($H = 10$ Oe), the magnetic moments freeze partly aligned to the field, resulting in high magnetization at low temperatures. Upon warming, the thermal excitations become effective...
above temperatures determined by the size distribution and the difference of the FC and ZFC curves disappears above the maximum blocking temperature corresponding to the largest cluster size.

Figure 1(b) shows the memory effect for the same sample series with wait time, \( t_w = 2h \), and wait temperatures, \( T_w \), indicated in the figure (in the inset the ZFC magnetization in the reference and annealed state is plotted as a function of temperature for \( T_{fi} = 5 \) and \( 10 \) Å). Here the sample is cooled in zero field from above the blocking temperature, \( T_B \), to a wait temperature, \( T_w < T_B \), where it is kept for a wait time, \( t_w \). Then the sample is cooled further (in zero field) to the lowest measuring temperature and the dc magnetization is measured upon warming by switching on a small dc magnetic field. Repeating this procedure without stopping at \( T_w \), a reference curve is measured and subtracting the latter from the former, a minimum of the difference curve is obtained close to \( T_w \), which is the memory effect. Two features can be observed in the difference curve: (i) memory effect, meaning that the difference curve shows a dip at \( T_w \), i.e., the sample remembers on the annealing at \( T_w \) when it is reheat; and (ii) rejuvenation meaning that after annealing the sample at \( T_w \) followed by cooling and reheating it, the ac susceptibility or low-field dc magnetization returns to the reference curve and deviates from it only in the vicinity of \( T_w \). These features are impossible in an interaction-free SPM nanoparticle ensemble. Some kind of memory effect can be observed in the interaction-free case, as well, but only if the annealing is made in a nonzero field at \( T_w \) [19]. A distinct feature of this kind of memory effect is that upon reheating the ensemble, the magnetization should always lie above the reference below \( T_w \) since the \( T_B < T_w \) sub-ensemble remembers the field-annealing at \( T_w \).

As seen in figure 1(a), the blocking temperature increases with increasing nominal Fe thickness, which is directly connected to the increase of the average particle size and might also be related to the increase of dipolar interactions between the Fe clusters with increasing \( T_{fi} \). The memory effect shown in figure 1(b) is very small, if any, for \( T_{fi} = 4 \) and \( 5 \) Å while it is clearly present for \( T_{fi} = 7 \) and \( 10 \) Å. An interesting correlation can be observed between the behavior of the FC magnetization and the magnitude of the memory effect. There is a systematic deviation of the theoretical FC curve from the measured one for \( T_{fi} = 7 \) and \( 10 \) Å below \( T_B \), while the theoretical ZFC curves describe relatively well the measured ones. (The calculations do not provide good description in a broad temperature range due to the possible temperature dependence of some parameters, like the anisotropy constant, \( K \) and the frequency factor \( \nu_0 \) [11], therefore, the theoretical curves are not shown above \( T = 50 \) and \( 100 \) K for \( T_{fi} = 4, 5 \) and \( 7, 10 \) Å, respectively.) For \( T_{fi} = 7 \) and \( 10 \) Å, i.e., for increased Fe-cluster size, the measured FC magnetization remains significantly below the calculated curve, becoming more and more flattened without exhibiting any plateau at low temperatures and reaches zero at higher and higher temperatures. The correlation between the magnitude of the memory effect and the flattening of the measured FC magnetization curve suggests that the flattening is connected to the increasing strength of interactions between the Fe clusters. Similar observations were reported by Binns et al [7] studying the magnetic behavior of nanostructured films assembled from preformed Fe clusters embedded in Ag. Similar deviation between the FC susceptibility measured for Co(SiO3) granular films and the corresponding interaction-free theoretical model curve can be seen in the paper of Denardin et al [51]. Their model is static; it assumes a lognormal \( T_B \) distribution and divides the particles into two parts at a given \( T_B \): for blocked ones with \( T < T_B \) and for superparamagnetic ones with \( T > T_B \). The increase of the theoretical FC curve at low temperatures is the consequence of a non-collective behavior of the clusters: the freezing of the individual magnetic moments upon cooling is independent from each other, aligned along the direction of the field. Since the memory effect is weak in our samples (compared to the noise) and the FC magnetization can be measured easily, the temperature dependence of the latter can be informative of the existence of interactions in a particle system even if the memory effect were not measurable.

3.2. Estimation of the dipolar interactions between the Fe clusters

For the estimation of the dipolar interactions between the Fe clusters, the average particle size and the average distance between them should be determined. Since direct determination of the former quantity of our Fe-Ag samples could not be performed, it was estimated from the \( M-H \) curve of the samples by fitting Langevin function to them from which the average magnetic moment of the clusters can be deduced [52] and further on the average cluster volume can be calculated if the atomic magnetic moments are known. However, this can only be done if the \( M-H \) curve can be described by a Langevin function at temperatures far above the blocking temperature (mostly at room temperature). Considering only those samples of our previous paper [13] that satisfy the above condition, the average magnetic moment (\( \mu \)) of the clusters was derived and the average cluster diameter was calculated from it, assuming atomic magnetic moments in the range between 2.2 and 3 \( \mu_B \) spherical form for the clusters and interatomic distance of 2.5 Å between the Fe atoms. Figure 2 shows the so calculated cluster diameter (\( D \)) as a function of the nominal Fe thickness for some Fe-Ag multilayers, in certain cases indicating the nominal Ag thicknesses and the bilayer numbers by labels. The cluster diameters determined from the external-field dependence of the magnetization should be similar to the average cluster volumes.
calculated from the anisotropy-energy distribution fitted to the temperature dependence of ZFC and FC magnetization. As it will be discussed in section 3.5, this circumstance enables to estimate the average anisotropy constant of the clusters.

In case of a given nominal Fe thickness, the cluster diameters depend on $t_{Ag}$ and $n$, as well, similarly to the blocking temperatures discussed in [13]. There are two multilayer pairs whose members have the same $t_{Ag}$ and $n$ parameters ($t_{Ag} = 13\,\text{Å}, n = 75$ and $t_{Ag} = 26\,\text{Å}, n = 10$) and differ only in the nominal Fe thickness (connected by red and green thin solid lines, respectively). According to the slopes of these lines and taking account of all the other data points, the (black) dotted line can be approximated for the $t_{Fe}$ dependence of the cluster size for samples with one Fe layer ($n = 1$). From the trend, we may estimate by linear extrapolation the cluster sizes of samples with larger $t_{Fe}$, which cannot be determined by Langevin-curve fitting. The obtained cluster diameters for large $t_{Fe}$ are obviously unrealistically large, being close to or larger than the nominal thickness of the Ag layer in our sample series studied here ($t_{Ag} = 50\,\text{Å}$). However, the Langevin fit is known to be sensitive to the upper end of the cluster-size distribution, thus overestimating the average cluster volume by at least a factor of 2. Another possible source of this contradiction might stem in the non-spherical shape of the clusters, the in-plane dimensions being larger than the vertical ones.

Nevertheless, in order to estimate the dipolar interaction between the Fe clusters, the average distance between them, $l$, should also be known. The distance between the spherical clusters of one layer can be calculated assuming that the clusters lie only in the layer and are evenly distributed on the layer area with a diameter, $D$, and their total volume should equal to the volume of the layer with the nominal Fe thickness, $t_{Fe}$:

$$t_{Fe} A = N \frac{\pi}{6} D^3$$

where $A = N l^2$ is the area of the layer and $N$ is the number of clusters on this area. Using the above expressions, the average distance between two clusters, $l$, can be calculated from the cluster size, $D$, shown in figure 2. The dipolar interaction ($E_d$) between two clusters is obtained from $l$ and the cluster moment, $\mu$, by

$$E_d = \left( \frac{\mu^2}{k} \right) \text{[cgs]} \quad \text{or} \quad E_d = \left( \frac{\mu_0 \, \mu^2}{k} \right) \text{[SI]}$$

where $\mu_0 = 4\pi \times 10^{-7}\,\text{Vesus/Am}$ is the permeability of empty space. In table 2, the average cluster size ($D$), average distance ($l$) and dipolar energy ($E_d$) between two clusters is given for the 50Å Ag $+ t_{Fe}$ Fe $+ 50\,\text{Å}\,\text{Ag}$ + cover sample series.

For $t_{Fe} = 4$ and 5 Å, $l$ and $E_d/k$ are calculated from $D$ directly obtained from the Langevin-curve fitting while for $t_{Fe} = 7$ and 10 Å, these values (written in italics) are derived from the estimated $D$ values shown in figure 3. Note that $E_d$ is the energy of one dipole pair. In fact, this value should be multiplied by the number of cluster neighbors. Since this calculation is a rough estimation, we attribute more importance to the trends than to the absolute values. It is obvious that the estimated energy of the dipolar interaction increases drastically with increasing nominal Fe thickness. Since the cluster diameters depend slightly on $t_{Ag}$ and $n$ in case of multilayers,

![Figure 2](https://www.etd.tum.de/)
as shown in figure 2, the energy of the dipolar interactions also depends slightly on these parameters, however, it is mainly determined by the nominal Fe thickness. For $t_{Fe} = 1, 2$ and $4 \text{Å}$, the energy of a dipolar pair fall into the range of $E_d \sim 0.6–1, 1.5–4$ and $8–14$ K, respectively, according to calculations similar to those detailed above. The spheroid shape of the clusters with larger in-plane than out-of-plain dimensions, may lead to even larger intralayer dipolar interactions. A plausible explanation for the appearance of a measureable memory effect at $t_{Fe} = 7$ Å might be that the increase of the dipolar interactions causes frustration between the cluster moments.

To sum up, as it is suggested by the estimation of the dipolar interactions between the Fe particles, the increase of the memory effect in the $50 \text{Å} \text{Ag} + (10 \text{Å} \text{Fe} + 50 \text{Å} \text{Ag})_{n} + \text{cover}$ multilayers ($n = 1$ and $10$ denoted by black solid squares and open circles, respectively). The measuring field is $H = 10 \text{Oe}$. (b) Memory effect for the $50 \text{Å} \text{Ag} + (10 \text{Å} \text{Fe} + 50 \text{Å} \text{Ag})_{n} + \text{cover}$ multilayers ($n = 1$ and $10$ denoted by small symbols and large diamonds, respectively) with wait time, $t_w = 2h$, and wait temperatures, $T_w$, indicated in the figure. The ZFC magnetization both in the annealed and the reference states as a function of temperature was measured in $H = 10 \text{Oe}$.

3.3. Connection between bilayer-number and memory effect
Increasing the bilayer number for a multilayer where well defined memory effect was observed for a single Fe layer ($t_{Fe} = 10 \text{Å}$), both the blocking temperature (figure 3(a)) and the memory effect (figure 3b) increase.

![Figure 3](image1.png)
In figure 3(b) the memory effect is shown for several wait temperatures, $T_{w} = 40, 60, 70$ and $80$ K, with wait time, $t_w = 2h$ for the $50$ Å Ag $+ 10$ Å Fe $+ 50$ Å Ag $+$ cover sample. The minimum of each memory-effect curve appears at a somewhat lower temperature than $T_m$ but increases systematically with $T_w$. Therefore, these curves prove that genuine memory effect is measured in this sample. Increasing the bilayer number to $n = 10$, the memory effect increases significantly, which can be attributed partly to the increase of the intralayer interactions due to the increase of the average cluster size with $n$ [13] and partly to the appearance of interlayer interactions. The respective role of these interactions should be further studied since the two examples shown in figure 3(a) are not enough to draw sound conclusions.

3.4. Temperature-cycling measurements with and without magnetic-field change

In one type of such experiment, the sample is cooled in zero field from above $T_B$ to a wait temperature, $T_{w1} < T_B$. A small magnetic field is switched on and the magnetization is measured for a wait time, $t_{w1}$ (first measuring cycle). Then the field is switched off and the sample is cooled to another wait temperature, $T_{w2} < T_{w1}$ where the magnetization is recorded for $t_{w2}$ (second measuring cycle). Subsequently, the sample is reheated to $T_{w1}$ and switching on the same field, the magnetization is measured for $t_{w3}$ (third measuring cycle). In a second experiment of this type, the same protocol is applied without changing the field in the second cycle. It was claimed [38] that in a negative temperature-cycling measurement without field change, at the beginning of the third annealing cycle at $T_{w1}$ the magnetization will resume the relaxation (which has been interrupted at the end of the first cycle by cooling the sample from $T_{w1}$ to $T_{w2} < T_{w1}$) only if there are interactions between the particles causing frustration.

Typical negative temperature-cycling measurements ($T_{w1} = 14$ K, $T_{w2} = 10$ K, $t_{w1} = t_{w2} = t_{w3} = 6600$ s) with (black solid squares) and without (red solid circles) field change ($H = 10$ Oe) are presented in figure 4(a) for the $50$ Å Ag $+ 4$ Å Fe $+ 50$ Å Ag $+$ cover multilayer, together with the corresponding model curves (black open squares and red open circles, respectively) calculated using the interaction-free model of SPM particles described in the Appendix. For the simulation of the relaxation curves, the same lognormal distribution of activation energies was applied as for the description of the ZFC and FC magnetizations (see table 1 for $t_{B} = 4$ Å, $t_{Ag} = 50$ Å, $n = 1$). Here in the measurement, the sample is cooled in zero field from above $T_B$ to a wait temperature, $T_{w1} < T_B$. A small magnetic field of $H = 10$ Oe is switched on and the magnetization is measured for $t_{w1}$ (first measuring cycle). Then the field is switched off and the sample is cooled to $T_{w2} < T_{w1}$ where the magnetization is recorded for $t_{w2}$ (second measuring cycle). Subsequently, the sample is reheated to $T_{w1}$ and switching on the same field, the magnetization is measured for $t_{w3}$ (third measuring cycle). The measured curve is denoted by black solid squares. Then the same protocol is applied without changing the field in the second cycle. The resulting measured curve is displayed by red solid circles.

The simulation curves follow relatively well the measured ones for the sample. The rise of both the measured and simulated magnetization obtained without field change in the middle relaxation cycle (red circles in figure 4(a)) reflects the relatively large increase of the FC magnetization when the temperature is lowered after reaching a given value (here $T_{w1}$). This feature (figure 1(a)) is typical in case of negligible interactions between the clusters. The magnetization at the beginning of the third relaxation cycle, measured without field change (red solid circles in figure 4(a)), continues the relaxation from the value at which it was stopped at the end of the first cycle. The simulated relaxation curve behaves the same way (red open circles in figure 4(a)). In order to illustrate this feature clearly, both curves are plotted in figure 4(b) with the time axis at logarithmic scale where the middle relaxation cycle was removed. These results clearly show that this behavior (sometimes also called memory effect) is not related to the presence of interactions between the clusters, as suggested earlier [38], and supports the counter opinions [27, 39–41].

The temperature-cycling behavior of samples in which genuine memory effect could be found by the stop-and-wait protocol is not yet clear. The transition of the magnetization from the first to the third relaxation cycle (omitting the second cycle measured without field change) was continuous within the experimental error in some cases, while in other samples a jump could be observed to a larger magnetization value. Therefore, it is not clear how this behavior is modified in the presence of interactions. The accuracy of our measurements was not enough to draw sound conclusions in this question.

3.5. Origin of the cluster anisotropy

The question arises whether what value of the average cluster anisotropy ($K$) leads to a meaningful median cluster size ($D_m$). The latter can be obtained from the expressions:

$$V_m = E_m / K, \quad D_m = (V_m / 6 \pi) ^ {1/3}, \quad \mu_m = (\pi / 6) (D_m / L_{Fe-Fe}) \mu_{Fe}$$

where $E_m$ is the median anisotropy energy deduced from the ZFC-FC fit (table 1), $\mu_m$ is the median cluster moment, $L_{Fe-Fe} = 2.5$ Å is the interatomic distance between the Fe atoms and $\mu_{Fe} = 2.2$ $\mu_B$ is the magnetic moment of a Fe atom. Considering the sample with $t_{Fe} = 4$ Å and $n = 1$ for which $E_m = 0.032$ eV (table 1,
Figure 4. (a) Magnetization data as a function of time for the 50 Å Ag + 4 Å Fe + 50 Å Ag + cover sample. Parameters of the three experimental steps: (1) ZFC to $T_{w1} = 14$ K and holding for $t_{w1} = 6600$ s; (2) cooling to $T_{w2} = 10$ K and holding for $t_{w2} = 6600$ s and (3) reheating to $T_{w3} = 14$ K and holding for $t_{w3} = 6600$ s, are indicated in the middle of the figure. In one case (black) the magnetic field ($H = 10$ Oe) is switched on in the first and third annealing cycles and switched off in the middle cycle (squares) while in the other (red) the field is switched on throughout (circles). The solid and open symbols mark the experimental and simulated data, respectively. The calculations were made supposing interaction-free SPM particles with uniaxial anisotropy (see Appendix) using the same lognormal activation-energy (particle-volume) distribution (table 1) which is applied for the calculation of the ZFC and FC magnetizations shown in figures 1(a) and 6. The zero field was modeled by applying a small dimensionless negative field parameter ($h_0 = -0.011$) since in the experiment a small negative field is present when the magnetic field is switched off. $n_0$ is the initial population used in the model calculation (see Appendix). (b) Same as figure 4(a) at logarithmic time scale and the middle annealing cycle removed (vertical line indicates the end of the first cycle). The solid line through the points is guide to the eye.

Table 1. Activation-energy median ($E_m$) and width ($\sigma$) of the lognormal distribution in the interaction-free model of superparamagnetic particle ensemble (see Appendix for definitions) fitted to the ZFC and FC magnetization Versus temperature curves of the 50 Å Ag + $t_{Fe}$ Fe + 50 Å Ag + cover sample series shown in figure 1(a).

| $t_{Fe}$ (Å) | 4   | 5   | 7   | 10  |
|--------------|-----|-----|-----|-----|
| $E_m$ (eV)   | 0.032 | 0.045 | 0.095 | 0.158 |
| $\sigma$ (eV) | 0.3  | 0.2  | 0.22 | 0.22 |
The existence of genuine memory effect was demonstrated in Fe-Ag granular multilayers by measuring the ZFC magnetization with the stop-and-wait protocol. The appearance and the magnitude of the memory effect could be correlated with the deviation of the FC magnetization curves from those calculated for interaction-free SPM particles and with the increasing strength of the dipolar interactions. The interaction–free model calculations were also able to reproduce the negative temperature-cycling measurement, which undoubtedly proves that it is not an indicator of the SSG state. Estimates made on the magnetic cluster size and moments indicate largely increased anisotropy which can be attributed to surface and shape anisotropies. Another possible source of the anisotropy is the shape anisotropy of the clusters which can be expressed as

$$K_{sh} = \frac{1}{2} (N_a - N_c) M_f^2$$

where $K_{sh}$ is the shape-anisotropy constant, $N_a$ and $N_c$ are the demagnetizing factors along the minor ($a$) and major ($c$) axis of the prolate spheroid of revolution, respectively [55]. $N_a$ and $N_c$ can be given as a function of $c/a$ [56]. The calculations show that the cluster anisotropy derived above for the $t_{Fe} = 4 \, \text{Å}$, $n = 1$ sample could be obtained as the shape anisotropy of a prolate spheroid with a ratio of $c/a \sim 6$. It is not realistic to suppose that all the Fe particles are elongated with this $c/a$ ratio, but the calculation shows that shape anisotropy can largely contribute to the increase of the cluster anisotropy.

4. Conclusions

The existence of genuine memory effect was demonstrated in Fe-Ag granular multilayers by measuring the ZFC magnetization with the stop-and-wait protocol. The appearance and the magnitude of the memory effect could be correlated with the deviation of the FC magnetization curves from those calculated for interaction-free SPM particles and with the increasing strength of the dipolar interactions. The interaction–free model calculations were also able to reproduce the negative temperature-cycling measurement, which undoubtedly proves that it is not an indicator of the SSG state. Estimates made on the magnetic cluster size and moments indicate largely increased anisotropy which can be attributed to surface and shape anisotropies.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix

Model of superparamagnetic particle ensemble without interaction for calculating history-dependent relaxation processes (e.g. ZFC and FC magnetization as a function of temperature, relaxation of magnetization as a function of time and arbitrary combination of them).
In a magnetic field (H) opposite (\(\alpha = 180^{\circ}\)) to the initial direction (\(\theta = 0^{\circ}\)) of the magnetization without field, \(K\) is the anisotropy constant, \(M_s\) is the saturation magnetization, \(V\) is the volume, \(\mu = VM_s\) is the magnetic moment of the particle, \(\theta\) and \(\alpha\) are the angles between the easy axis and the magnetic moment and the easy axis and the applied magnetic field, respectively.

**A.1. TLS as a model system for SPM particle ensemble**

Figure 5 shows the schematic view of the energetic relations of a TLS representing a single-domain particle with uniaxial magnetic anisotropy under a small magnetic field lying in the easy axis opposite (\(\alpha = 0^{\circ}\)) to the initial direction (\(\alpha = 0^{\circ}\)) of the magnetization without field. \(\theta\) and \(\alpha\) are the angles between the easy axis and the magnetic moment and the easy axis and the applied magnetic field, respectively. In this case, the energy of the particle is increased and decreased by \(\mu H\) at \(\theta = 0^{\circ}\) and \(180^{\circ}\), respectively. We restrict ourselves to TLSs for which the metastable state of higher energy is always at \(\theta = 0^{\circ}\). Therefore in the general case, the field is applied in a restricted direction with respect to the easy axis, i.e., \(90^{\circ} < \alpha < 180^{\circ}\) and the projection of the field to the easy axis, \(H' = H\cos \alpha\), will appear in the energy. The absolute value is used in this expression because the applied field is regarded as positive when the magnetization of the particles increases under its influence. Thus in general, the TLS can be characterized by two parameters (using cgs system): (i) \(E = KV - |\mu H| = KV - VM_sH\) is the activation energy and (ii) \(\Delta = 2|\mu H| = 2VM_sH\) is the splitting of the energy levels under the magnetic field, where \(|\mu H| = \mu H\cos \alpha\) (\(90^{\circ} < \alpha < 180^{\circ}\)). In zero field the TLS is symmetric with an energy barrier of \(KV\) between the two stable states (\(\theta = 0^{\circ}\) and \(180^{\circ}\)). Both the activation-energy and the splitting parameter have a distribution, creating an ensemble of TLSs. Since the applied field is small, the activation-energy distribution is mainly determined by the distribution of the anisotropy energy \((E_a = KV)\) which can be approximated by one (or more) lognormal distribution(s). If the anisotropy constant, \(K\), is assumed to be invariable, the activation-energy distribution is mainly determined by the volume distribution of the particles, \(V\). The splitting distribution can be related to the random orientation distribution of the easy axes (or magnetic moments) since \(\Delta\) approaches zero if the easy axis of a particle is perpendicular to the magnetic field (symmetric TLS). It can be easily shown that for a TLS with a given \(E\), a constant distribution of \(\Delta\) can be assumed from \(\Delta = 0\) to \(\Delta_{\text{max}} = 2 VM_sH\).

**A.2. Calculation of population change**

The relaxation of a physical property can be related to the population change of an ensemble of TLSs. Such a model, the so-called activation-energy spectrum model was often used to explain the various relaxation phenomena observed in amorphous alloys, where a TLS represents a relaxation center, i.e., an atom (or a group of atoms) that can exist in two configurations of different energies, and transitions are possible between them via thermal activation. Because of the amorphous nature of the material, a quasi-continuous spectrum of \(E\) and \(\Delta\) of the TLSs can be expected and the two parameters vary independently from each other.

In case of single-domain SPM particles, \(E\) and \(\Delta\) are not independent from each other but both depend on the anisotropy energy, \(E_a = KV\) and the magnetic field, \(H\). The activation energy, \(E\), varies between \(E_a = KV\) (for \(\alpha = 90^{\circ}\)) and a minimum value, \(E_{\text{min}} = KV - \mu H\) (for \(\alpha = 180^{\circ}\)), because of the random distribution of the anisotropy axes. In general, \(E\) can be written as:

\[
E = KV - \mu H = KV - VM_sH = KV - |\mu H|
\]
\[ E = KV - |\mu H| = KV - V[M_0, H] = KV - 2KV \frac{M_s H}{2K} = (1 - 2h')E_a \]

where \( E_a = KV \) is the anisotropy energy, \( H_K = 2K/M_s \) is the anisotropy field, \( h = H/H_K \) is a dimensionless field parameter and \( h' = h|\cos \alpha| (90^\circ < \alpha < 180^\circ) \). Consequently, the minimum activation energy is \( E_{\text{min}} = (1 - 2h)E_a \).

Similarly, the splitting parameter, \( \Delta \), varies between zero and \( \Delta_{\text{max}} = 2\mu H \) for \( \alpha = 90^\circ \) and \( 180^\circ \), respectively:

\[ \Delta = 2|\mu H| = 4h'E_a \]

which gives for the maximum splitting \( \Delta_{\text{max}} = 4hE_a \). Since the coercive field of Fe-Ag granular multilayers at \( T = 5 \text{ K} \) can be related to the anisotropy field, i.e., \( H_L \sim H_K \sim 500 \text{ Oe} \) and the magnetic field applied in the present study to measure the ZFC and FC magnetizations is \( H = 10 \text{ Oe} \), in the model calculations \( h = 0.02 \) is used for the relative field parameter.

The relaxation of an ensemble of TLSs characterized by \( E \) and \( \Delta \), initially not in equilibrium, is described by a first-order kinetic process [59]:

\[ \dot{n} = -v_E n + v_{E+\Delta}(1 - n) \]

where \( n \) is the population of the of the higher-energy state with the magnetic moment at \( \theta = 0^\circ \) and \( v_E \) is the rate of transition through the potential barrier with activation energy \( E \). Since the driving force of the relaxation is the thermal energy, an Arrhenius expression is used for \( v_E \):

\[ v_E = v_0 \exp \left( -\frac{E}{kT} \right) \]

where \( v_0 \) is the characteristic frequency of the thermal excitation called frequency factor (\( v_0 = 10^9 \text{ 1/s} \)) [60]. The solution of this differential equation can be written as

\[ n(t) = [n_0(E, \Delta) - n_{\infty}(\Delta, T)]_0(E, T, t) + n_{\infty}(\Delta, T) \]

where the population indices 0 and \( \infty \) refer to the initial and equilibrium states, respectively, and we have introduced a function, \( \theta_0 \), called annealing function characterizing the annealing process:

\[ \theta_0(E, T, t) = \exp \left\{ -v_0 t \left[ \exp \left( -\frac{E}{kT} \right) + \exp \left( -\frac{E + \Delta}{kT} \right) \right] \right\} \]

The equilibrium population is

\[ n_{\infty}(\Delta, T) = 1 / \left[ 1 + \exp \left( \frac{\Delta}{kT} \right) \right] \]

Using the above derived equations connecting \( E_a \) to \( E \) and \( \Delta \), the annealing function can be expressed as a function of \( E_a = KV \) and \( h' = h|\cos \alpha| \) where \( 90^\circ < \alpha < 180^\circ \):

\[ \theta_0(E_a, T, t) = \exp \left[ -v_0 t \exp \left( -\frac{E_a}{kT} \right) \right] \]

where \( \epsilon = \exp \left( \frac{2h'E_a}{kT} \right) + \exp \left( -\frac{2h'E_a}{kT} \right) = 2 \cosh \left( \frac{2h'E_a}{kT} \right) \). \( \epsilon \) assumes its maximum value for \( \alpha = 180^\circ \), i.e., when the easy axis of a particle is parallel to the magnetic field. When the easy axis is perpendicular to the field (\( \alpha = 90^\circ \)), the minimum value of \( \epsilon \) is \( \epsilon = 2 \).

The annealing function starts from zero and turns to 1 very steeply as a function of \( E_a \). The energy of this abrupt change (energy edge) can be estimated from the \( \theta_0 = 1/\epsilon \) condition to be \( E_{\text{edge}} = kT \ln \epsilon_0 \epsilon_\infty \). Above \( E_{\text{edge}} \) practically no relaxation processes take place. Plotting \( \theta_0 \) as function of \( E_a/kT \), we obtain \( E_{\text{edge}} = 26kT \) for \( h' = 0 \) and \( E_{\text{edge}} = 26.5kT \) for \( h' = h = 0.02 \), using the quasistatic time window valid in our experiments (\( t \sim 100 \text{ s} \)). As is obvious, the shift of the energy edge is very small for particles having different anisotropy-axis directions with the magnetic field. Therefore, an average value of \( E_{\text{edge}}/kT = 26.25 \) can be taken for all particles. Using this average value for \( E_{\text{edge}}/kT \), the corresponding \( \epsilon \) values can be calculated to be \( \epsilon = 2 \) for \( h' = 0 \) and \( \epsilon = 3.2 \) for \( h' = h = 0.02 \) from the dependence of \( \epsilon \) on \( E_a/kT \). Taking roughly the average of these two \( \epsilon \) values, \( \langle \epsilon \rangle = 2.5 \) was used for the calculation of the annealing function. Using \( \epsilon = \langle \epsilon \rangle \) in the annealing function, its \( h' \) (or \( \alpha \)) dependence is eliminated, i.e., \( \theta_0(E, T, t) = \theta_0(E_a, T, t) \). An arbitrary annealing procedure, \( T(t) \), is approximated by a series of small kinetics (annealing at temperature \( T_i \) for time \( t_i \) + annealing at \( T_j \) for \( t_j \) and so on). In our SQUID measurements this is not an approximation since the SQUID magnetometer stops at every measuring temperature waiting until the temperature is stabilized.

The population change of one TLS, characterized by \( E \) and \( \Delta \), between the \( i \)th and \( j \)th annealing steps called elementary population change can be expressed as
\[
\Delta n^{(i)}_{\text{elementary}} = n^{(0)} - n^{(i)}
\]

where \(n^{(0)}\) is the population after the \(i\)th annealing step. After the first annealing step (at \(T_i\) for \(t_i\)) the population can be given according to equation (1):

\[
n^{(1)} = (n^{(0)}_0 - n^{(1)}_0) + n^{(1)}_0
\]

where \(n^{(0)}_0\) is the initial population.

In the second annealing step, a similar equation holds with \(n^{(2)} = n^{(1)}\). In the \(k\)th step:

\[
n^{(k)} = \left(n^{(k-1)}_0 - n^{(1)}_0\right) + n^{(k)}_0
\]

Because of the randomly distributed anisotropy axes, \(\Delta\) is evenly distributed from 0 to \(\Delta_{\text{max}}\) for a given \(E\) (or \(E_a\)), therefore, the elementary TLS contributions must be added. Thus, integrating with respect to \(\Delta\), the population of this subsystem of TLSs in the \(i\)th annealing step is given by:

\[
n^{(i)}(E, T_i, t_i) = \frac{1}{\Delta_{\text{max}}} \int_0^{\Delta_{\text{max}}} n^{(i)}(E, \Delta, T_i, t_i) d\Delta
\]

where \(n^{(i)}(E, \Delta, T_i, t_i)\) is the population after the \(i\)th annealing step:

\[
\Delta n^{(i)}(E, T_i, t_i) = \frac{1}{\Delta_{\text{max}}} \int_0^{\Delta_{\text{max}}} n^{(i)}(E, \Delta, T_i) d\Delta
\]

Integrating the equilibrium population with respect to \(\Delta\), its temperature dependence, \(n^{(i)}_\infty(E, T_i)\) is obtained in the \(i\)th annealing step for a given anisotropy energy, \(E_a\) (i.e., particle volume, \(V\)) and magnetic field, \(h\):  

\[
n^{(i)}_\infty(E_a, T_i) = \frac{1}{\Delta_{\text{max}}} \int_0^{\Delta_{\text{max}}} d\Delta \left[ \frac{d\Delta}{1 + \exp(\Delta/kT_i)} \right] = \frac{kT_i}{4h} \ln \left[ \frac{2}{1 + \exp(-hE_a/4kT_i)} \right]
\]

Finally, a simple recursive formula is obtained for the population of a subsystem of TLSs, which has a given anisotropy energy, \(E_a\) with all possible splitting energies, \(\Delta\), after the \(i\)th annealing step:

\[
n^{(i)}(E_a, T_i, t_i) = \gamma (1 - 2n^{(i)}(E_a, T_i, t_i))
\]

where \(\gamma = \exp[-V_{tk}(\varepsilon) \exp(-E_a/kT)]\). (\(\varepsilon = 2.5\) and \(n^{(0)}_0\) is the initial population. During the calculations, \(t_k = \Delta T_k\) is a time interval which the sample spends at temperature \(T_k\).

### A.3. Connection between magnetization (susceptibility) and population

The vector sum of the magnetic moments of the individual particles divided by the total volume gives the magnetization vector of the whole ensemble. The projection of this quantity onto the magnetic field, \(H\) is the measured magnetization \(M\). The relative magnetization of a subsystem of TLSs with activation energy, \(E_a\), \(m = M/M_s\), in the \(i\)th annealing step should be proportional to the population difference of the two energy minima of the system:

\[
m(E_a, T_i, t_i) = \gamma (1 - 2n^{(i)}(E_a, T_i, t_i))
\]

\[
\chi(E_a, T_i, t_i) = \gamma (1 - 2n^{(i)}(E_a, T_i, t_i)) \frac{M}{h}
\]

If the particle subsystem is in the blocked state (\(T = 0\)), the initial population, \(n^{(0)}_0\), is frozen in. If the anisotropy axes are randomly distributed in an ensemble of single-domain particles that are in a blocked state, according to the Stoner-Wohlfarth model [61], the susceptibility is \(\chi_{SW} = M_s^2/3K\). The susceptibility of the blocked subsystem of TLSs should equal to that of the Stoner-Wohlfarth model, which is fulfilled, e.g., if \(\gamma = 2/3\) and \(n^{(0)}_0 = (1 - h)/2\). In this case, if the subsystem is allowed to relax (\(T > 0\)), the susceptibility can be generalized as:

\[
\chi(E_a, T_i, t_i) = \frac{M}{3K} \frac{1 - 2n^{(i)}(E_a, T_i, t_i)}{h}
\]

If other combination of \(\gamma\) and \(n^{(0)}_0\) is used to equal the susceptibility of the subsystem of TLSs to that of the Stoner-Wohlfarth model, the above expression remains valid with a proportionality factor different from 1.
Thus, the normalized susceptibility of a relaxing single-domain particle ensemble with random anisotropy axes is obtained in the $i$th annealing step by integrating over all possible anisotropy energy, $E_a$, i.e., all possible particle volume, $V$:

$$\chi(T_{fi}, t_i) = \frac{1}{\hbar} \int_0^\infty p(E_a)(1 - 2n^{(0)}(E_a, T_{fi}, t_i))dE_a \tag{4}$$

where $p(E_a)$ is the anisotropy-energy spectrum which represents the volume ($V$) distribution of the particles if the anisotropy ($K$) is assumed to be constant. $p(E_a)$ is approximated by one (or more) lognormal distribution(s) of the form:

$$p(E_a) = \frac{1}{\sqrt{2\pi\sigma E_a}} \exp \left[-\frac{1}{2}\left(\frac{\ln \frac{E_a}{E_m}}{\sigma}\right)^2\right]$$

where $E_m$ is the median and $\sigma$ is the width of the distribution.

### A.4. Calculation of ZFC and FC magnetization

The ZFC magnetization is measured upon warming the sample in a constant magnetic field (here $H = 10$ Oe) as a function of temperature after cooling it in zero field through the maximum blocking temperature in the particle system, $T_{Bm}^{\text{max}}$, above which it is in thermal equilibrium, i.e., in a disordered state ($M = 0$). This disordered state is frozen at the starting temperature of the measurement. In the model TLLs, a disordered state means that the population of both states of all TLLs is equal, with the consequence that the magnetic moments of the particles cancel out. Theoretically, this state is brought about by setting the initial population of the TLLs to be $n_0^{(0)} = 1/2$. For the calculation of the ZFC and FC susceptibility, a small field is switched on ($h = 0.02$) which leads to the appearance of a small magnetization corresponding to the Stoner-Wohlfarth susceptibility. This susceptibility can be set using a $n_0^{(0)}$ value slightly below 1/2. In practice, the initial population is adjusted to the measured value of the ZFC magnetization at the start temperature of the measurement. This value is, in general, negative in our measurements because the samples are cooled in the small negative remanent field of the superconducting magnet ($H \sim -1$ Oe) instead of a zero field.

In the first annealing step of a model ZFC measurement, the initial population is set by $n_0^{(0)}$ for all $E_a$, resulting in a small nonzero magnetization if $n_0^{(0)} = 1/2$. Then the temperature is changed instantaneously to the starting temperature, $T_{\text{start}} < T_{Bm}^{\text{max}}$ (usually $T_{\text{start}} = 5$ K) where the relaxation of the TLLs starts. (Here $T_{Bm}^{\text{max}}$ is the highest blocking temperature belonging the largest particle volume.) Switching on the field and heating through small kinetics ($\Delta T = T_{k-1} - T_k = 1$ to 5 K, $\Delta t = t_{k-1} - t_k = 120$ to 220 s) as described above, the magnetization is calculated at each temperature using equations (3) and (4).

The FC magnetization is also measured upon warming the sample in a constant magnetic field (here $H = 10$ Oe) as a function of temperature after cooling it in the same field through $T_{Bm}^{\text{max}}$. The calculation of the FC magnetization is essentially the same with the exception that the frozen-in disordered state (determined by $n_0^{(0)}$) is instantaneously ‘warmed up’ to a state corresponding to the starting temperature, $T_{\text{start}} > T_{Bm}^{\text{max}}$ by setting the temperature to $T_{\text{start}}$. At this temperature all the TLLs will become equilibrated within the measuring time interval. Cooling through small kinetics, the gradual freezing of the magnetization is reproduced by the model. If having reached the lowest temperature and the model experiment is continued by heating again the system above $T_{Bm}^{\text{max}}$, we can model a real FC measurement. The model FC magnetization calculated during cooling and heating can be (slightly) different because of the different temperature rate used in the two procedures.

### A.5. Fitting of the model to the measured ZFC and FC magnetization

Versus temperature curves

Figure 6 shows the measured ZFC and FC magnetizations (black solid and open squares, respectively) of the Fe-Ag multilayer containing only one nominally 4 Å-thick Fe layer between Ag layers ($t_{Fe} = 4$ Å, $t_{Ag} = 1$). (In order not to confuse the population change, $n$, with the bilayer number, the latter is denoted by $n_0$ in the Appendix). These curves represent a typical SPM behavior with a blocking temperature of $T_{B} = 21$ K. Varying the initial population ($n_0^{(0)}$), the median ($E_m$) and the width ($\sigma$) of the lognormal distribution, the red solid (ZFC curve) and open circles (FC curve) are obtained from the model after simulation of the annealing steps applied in the experiment (ZFC heating: $T_{\text{start}} = 5$ K, $T_{\text{end}} = 50$ K, $\Delta T = 1$ K, $\Delta t = 6$ s; FC fast cooling: $T_{\text{start}} = 50$ K, $T_{\text{end}} = 5$ K, $\Delta T = 1$ K, $\Delta t = 120$ s) using $n_0^{(0)} = 0.5205$, $E_m = 0.032$ eV and $\sigma = 0.3$ eV for the initial population and the lognormal parameters, respectively. The value of $n_0^{(0)} > 0.5$ obtained from the fitting reflects the fact that the ZFC magnetization was measured after heating the sample in a small negative magnetic field (instead of zero field) leading to an asymmetric spin configuration with a negative average magnetization. The two model curves were adjusted to the measured ones using the same multiplication factor. The fit is relatively good for both the ZFC and the FC magnetization.
In the inset of figure 6, the activation-energy and the corresponding blocking-temperature distributions are plotted. As seen in the inset, the activation-energy spectrum is almost zero beyond \( E_a = 0.1 \) eV which justifies that only TLSs with \( E_a \leq 0.2 \) eV were considered in the model. Our experience is that the maximum of the \( E_a \) spectrum (\( E_a^{\text{max}} \)) taken in the model should be at least twice of its median value (\( E_m \)) for a correct description of the relaxation of the TLSs.

### A.6. Calculation of time-dependent processes (relaxation)

The relaxation of magnetization of an interaction-free SPM particle ensemble as a function of time at a constant temperature can be calculated with the help of the same model of TLSs which was used above for describing temperature-dependent phenomena. Only appropriate series of annealing steps has to be implemented: \( T = \text{const} \) and \( 2\Delta t \) is the time elapsing between two measuring points. In this case the relaxation can be modeled both with magnetic field switched on and switched off. The switching off the field is simulated by changing the relative field, \( h_r \), instantaneously to \( h_0 = 0.0001 \), thereby making all TLS symmetric. (The relative field, \( h_r \), cannot be set to zero because in equation (2) there appears a division by \( h_r \).) In this case relaxation processes take place only if the TLSs were initially not in equilibrium. In our case, however, a negative \( h_0 \) value is used, corresponding to the small negative remanent magnetic field present in our experiments when the magnetic field is switched off. Finally, note that the calculation of temperature- and time-dependent processes can be combined in the framework of the model, simulating an arbitrary measurement protocol.

### A.7. Calculation of temperature-cycling measurements

A typical measurement protocol to study a magnetic particle system is the temperature-cycling measurement. Here the sample is cooled in zero field through \( T_N \) to a wait temperature, \( T_{w1} < T_N \), where a small field is switched on and the magnetization of the sample is recorded for a wait time, \( t_{w1} \). Then the temperature is changed to a lower one, \( T_{w2} < T_{w1} \), without changing the field, and the magnetization is measured for a time, \( t_{w2} \). Finally also without changing the field, the sample is heated back to the temperature, \( T_{w1} \), and the magnetization is recorded for a time \( t_{w3} \). Another variant of this experiment is when the same protocol is applied but in the middle cycle the field is switched off.

Figure 4(a) shows both variants of the temperature-cycling experiment for the same Fe-Ag multilayer \( (t_{Fe} = 4 \) Å and \( n_{Fe} = 1 ) \) for which using the above model the ZFC and FC magnetization was calculated and fitted to the experimental curves (figure 6). The measured curves \( (H = 10 \) Oe, \( T_{w1} = 14 \) K, \( T_{w2} = 10 \) K, \( t_{w1} = t_{w2} = t_{w3} = 6600 \) s) are denoted by black solid squares (with field change) and red solid circles (without field change). Using the same parameters for the lognormal distribution of \( E_a (E_m = 0.032 \) eV, \( \sigma = 0.3 \) eV) as was applied in figure 6, the relaxation curves denoted by black open squares (with field change) and red open circles (without field change) were calculated from the model using \( h = 0.02 \) and \( h_0 = -0.011 \) for the relative field parameter switched on and off, respectively. (The model curves were adjusted to the experimental ones only.

![Figure 6. Fitting of the model for interaction-free SPM particles to the experimental ZFC (black solid squares) and FC (black open squares) magnetization data of the 50 Å Ag + 4 Å Fe + 50 Å Ag + cover sample measured in \( H = 10 \) Oe. Red solid circles and red open circles denote the simulated ZFC and FC magnetization curves, respectively, using \( n_{Fe} = 5205 \), \( E_m = 0.032 \) eV, and \( \sigma = 0.3 \) eV as fitting parameters. Inset: lognormal activation-energy (bottom axis) and blocking-temperature (top axis) distribution used for the fitting (\( E_m = 0.032 \) eV and \( \sigma = 0.3 \) eV). For the conversion between \( T_B \) and \( E_a \), the expression \( T_B = E_a/(26.25h) \) is used.](image-url)
by a multiplication factor). Here the model curves show the magnetization values also in the transient regions where the temperature was changed (these point were not measured in the experiment). The magnetization calculated from the model reproduces relatively well the measured relaxation curves: (i) in the temperature-cycling experiment without field change, the rise of the magnetization in the middle cycle reflects the behavior of the FC magnetization shown in figure 6; returning to $T_{\text{a1}}$, the magnetization at the beginning of the third cycle continues the relaxation from the value assumed at the end of the first cycle; (ii) in the experiment with field change, the magnetization at the beginning of the third cycle does not attain the value assumed at the end of the first cycle but gradually relaxes towards the curve obtained without field change.

This model is dynamic in contrast to the static models found in the literature [13, 51, 62]. The latter models are based on the a priori assumption of a $T_h$ distribution for the particles, distinguishing only two types of them at a given temperature, $T$: for $T < T_h$ the particles are blocked and for $T > T_h$ they behave as in a superparamagnet. Our present model and those mentioned above [27, 39–41, 43–45] assume a priori a volume or anisotropy-energy ($E_a = K V$) distribution for the particles (which is the same if $K$ is assumed to be constant). The differential equations underlying the model determine whether the magnetic moment of a particle with a given volume becomes blocked or rotates freely or is found in an intermediate state, depending on the thermal history of the system. The particles in the intermediate state excited in an energy range of $kT$ at the steeply increasing edge of the annealing function, $\theta_b$, give rise to the observed relaxation processes. The annealing function, the equilibrium population and the relative equilibrium magnetization as a function of $E_a/kT$ are shown in detail in the Supplement 1, together with the evolution of the population of the TLSs during the measurements displayed in figures 4 and 6. The computer program of the model described above can be freely accessed and used, according to the instructions of the user manual found in Supplement 2.

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