On the detection of surface spin freezing in iron oxide nanoparticles and its long-term evolution under ambient oxidation

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Abstract

Exchange bias (EB) effects linked to surface spin freezing (SSF) are commonly found in iron oxide nanoparticles, while signatures of SSF in low-field temperature-dependent magnetization curves have been much less frequently reported. Here, we present magnetic properties of dense assemblies of similar-sized (~8 nm diameter) particles synthesized by a magnetite (sample S1) and a maghemite (sample S2) method, and the influence of long-term (4 year) sample aging under ambient conditions on these properties. The size of the EB field of the different sample (fresh or aged) states is found to correlate with (a) whether a low-temperature hump feature signaling the SSF transition is detected in out-of-phase ac susceptibility or zero-field-cooled (ZFC) dc magnetization recorded at low field and with (b) the prominence of irreversibility between FC and ZFC curves recorded at high field. Sample S1 displays a lower magnetization than S2, and it is in S1 where the largest SSF effects are found. These effects are significantly weakened by aging but remain larger than the SSF effects in S2, where the influence of aging is considerably smaller. A non-saturating component due to spin disorder in S1 also weakens with aging, accompanied by, we infer, an increase in the superspin and the radius of the ordered nanoparticle cores. X-ray diffraction and Mössbauer spectroscopy provide indication of maghemite-like stoichiometry in both aged samples as well as thicker disordered particle shells in aged-S1 relative to aged-S2 (crystallographically-disordered and spin-disordered according to diffraction and Mössbauer, respectively). The pronounced diminution in SSF effects with aging in S1 is attributed to a (long-term) transition, caused by ambient oxidation, from magnetite-like to maghemite-like stoichiometry, and a concomitant softening of the spin-disordered shell anisotropy. We assess the impact of this anisotropy on the nature of the blocking of the nanoparticle superspins.

Supplementary material for this article is available online
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(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic nanoparticles (NPs) continue to receive much attention due to a growing number of applications as well as to open questions regarding their rich phenomenology [1–4]. Ferrimagnetic iron oxide NPs with spinel structure (maghemite, \(\gamma\)-\(Fe_2O_3\), and magnetite, \(Fe_3O_4\)) are particularly interesting due to their biocompatibility, which allows their exploitation in medical applications such as magnetic hyperthermia, contrast agents for magnetic resonance imaging and targeted drug delivery [2–9]. An important feature of iron oxide-based NPs is the frequent appearance of surface spin disorder (SSD) or canting, which can be intrinsic, caused by broken exchange bonds at particle surfaces [10–14], or due to surface structural disorder [15]. With decreasing particle size, SSD often becomes more prevalent [16–22] but can also be suppressed due to improvement in (intraparticle) crystalline order [15]. SSD can also become more noteworthy upon moving to a hollow particle morphology [23, 24]. At ambient temperature, SSD can behave as a magnetically dead layer, reducing the overall saturation magnetization [11, 12, 20, 25]. Upon cooling such layers can undergo spin glass-like freezing [26, 27]. Due to the high magnetic anisotropy of such surface spin glass-like phase relative to the magnetically ordered NP cores, an exchange bias (EB) effect—i.e. the displacement of a low-temperature hysteresis loop (recorded after field cooling) along its applied field axis—is often observed in magnetic NPs possessing SSD [28].

A variety of other magnetic features have also been related to SSD. These include open hysteresis loops and large differential susceptibility at high fields [22, 26, 29], irreversibility between field-cooled (FC) and zero-field-cooled (ZFC) dc magnetization curves measured at high field [12, 26, 30], and an increase in the saturation magnetization (relative to an extrapolation based on Bloch’s law) below the surface spin freezing (SSF) temperature [27, 31]. However, in contrast to EB effects, such features are not observed systematically across the vast literature of magnetic oxide NPs with SSD. In particular, the direct detection of SSF via the appearance of a hump (or minor peak compared to that due to particle blocking) in low-field ZFC dc magnetization or in ac susceptibility curves has only rarely been reported [32–35]. The latter technique (ac magnetometry) probes spin dynamics and therefore is capable of distinguishing SSF from conventional particle blocking [13, 15, 32–34, 36–39].

In the present article we review the factors leading to fingerprints of SSF in the thermal dependence of ac and low-field dc magnetization. The approach taken is to study iron oxide NP samples that (as will be concluded) differ essentially with respect to aspects of their spin disordered shells. We correlate the size of such fingerprints with other signatures of SSD—in particular, the EB field but also enhanced coercivity, reduced magnetization values, and high-field FC-ZFC irreversibility. The sensitivity of these factors in the detection of SSF is explored through two types of comparison between ferrimagnetic iron oxide NPs of similar size distribution: (i) the comparison of samples prepared by two different synthesis methods, namely a magnetite (sample S1) and a maghemite (sample S2) method, and (ii) the study of long-term aging (oxidation under ambient conditions) on the SSF effects in the samples. These studies enable us to establish the qualitative conditions, with respect to SSD-shell thickness and anisotropy, required for the appearance of SSF fingerprints in ac and low-field dc temperature-dependent magnetization curves. In addition, the studies suggest that an EB field measurement is more sensitive to SSF than the measurement of the other possible factors (signatures) in pure iron oxide NPs. As well as strongly affecting SSF effects in sample S1, long-term aging is found to affect both the core magnetic moment and the blocking behaviour of these particles, and these effects will be shown to be related to each other.

2. Experimental methods

Sample S1 was prepared by a procedure based on the thermal decomposition of iron oleate in the presence of oleic acid (OA) and hexadecane. This procedure was previously reported to produce magnetite \((Fe_3O_4)\) NPs [40, 41]. Sample S2 was prepared by employing a method that had previously been reported to yield maghemite \((\gamma-Fe_2O_3)\) NPs—namely a procedure based on thermal decomposition of \(Fe(CO)_3\) in the presence of an OA and diocyl ether, followed by oxidation with trimethylamine N-oxide [15]. (Additional information on NP synthesis, particularly on S1, is provided in the supplementary material, available at stacks.iop.org/NANO/32/065704/mmedia). Both S1 and S2 particles were precipitated by adding acetone to their solutions. The particles were then collected by centrifugation to yield powders of OA coated NPs. The OA contents by mass were determined by thermogravimetric analysis to be, approximately, 10% in S1 and 20% in S2. Disk-like samples of these NP powders for use in magnetic measurements were prepared by die pressing under approximately 0.7 GPa. These S1 and S2 samples constitute dense NP assemblies: the magnetic NP packing fraction (\(\phi\)) is assumed to be around 0.5 in S2 (the value previously obtained in a pressed disk-like sample of similar OA-coated maghemite NPs [42]) and is expected to be a little higher in S1 (around 0.55—see section VIII of the supplementary material) due to its lower OA content relative to S2.

Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G2 F20 microscope operated at 200 kV. Magnetic measurements were performed using a Quantum Design MPMS Evercool SQUID (superconducting quantum interference device) magnetometer. Hysteresis loops
were obtained at different (low) temperatures after first performing sample cooling from room temperature to 5 K in a field of 50 kOe applied parallel to the sample (disk) plane. Temperature dependent dc and ac magnetization curves were measured upon heating from 5 K after either the ZFC (in ac and dc measurements) or FC (dc only) state had been prepared. The applied field (and cooling field in FC measurements) was 5 Oe in ‘low-field’ dc measurements, 50 kOe in ‘high-field’ dc measurements, and oscillatory of frequency 10 Hz and amplitude of 2.5 Oe in ac measurements. X-ray diffraction (XRD) measurements were carried out in transmission geometry (using a few milligrams of NP powder mounted on Kapton tape), employing a Bruker D8 diffractometer operating with Cu Kα radiation and a position sensitive (silicon strip) detector. 

57Fe Mössbauer spectra were obtained at 10 K using an applied field of 80 kOe oriented parallel to the incident γ-beam (obtained from a $^{57}$Co/Rh γ-ray source mounted on an electromagnetic transducer controlled according to a triangular velocity waveform).

All SQUID measurements were performed both on ‘fresh’ NPs (particles that had been exposed to ambient conditions for no more than several weeks since being synthesized) and ‘aged’ NPs (particles, from the same sample batches, that had been stored under ambient conditions for a 4 year period), except for the high-field (temperature dependent) magnetization curves, which were obtained only in aged NP samples. TEM images were taken on fresh NPs. XRD and Mössbauer spectroscopy were conducted on aged NPs. In what follows, S1 and S2 (S1a and S2a) refer to the fresh (aged) sample states.

### 3. Results and discussion

Figure 1 shows TEM images of S1 and S2 NPs. In both cases the NPs are found to be approximately spherical and to correspond to a similarly narrow size distribution ($\sigma \approx 2\%$ from log-normal fits of the size histograms), of average diameter ($D_{TEM}$) of 8.6 nm in S1 and 8.0 nm in S2. High resolution TEM suggests a higher degree of crystalline order in S2 than in S1.

Figure 2 presents low-temperature hysteresis loops of S1, S1a and S2. The loop of S2a is very similar to that of S2 and therefore (for clarity in presentation) has been omitted from figure 2 (the S2a loop is provided in figure S1 of the supplementary material). The inset is a close-up indicating where each branch (of each loop) intercepts the applied field axis.

Figure 2. Hysteresis loops recorded at a temperature of 5 K in the S1 sample, when fresh and aged (S1a), and in the S2 sample when fresh (a very similar loop is found in aged-S2—see supplementary material). The inset is a close-up indicating where each branch (of each loop) intercepts the applied field axis.

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Figure 1. Transmission electron micrographs of (a) S1 and (b) S2 nanoparticles. The upper insets are representative high-resolution TEM images of the particles. Each lower inset shows the particle size distribution (extracted from TEM images) fitted to a log-normal function.
‘missing magnetization’) in S1 NPs as compared to S2 NPs. We use the word ‘appears’ due to the presence of the non-saturating (up to the maximum applied field, $H_{\text{max}} = 50$ kOe) component in the S1 loop. Hereafter we refer to the ‘technical $M_S$’ (i.e. the magnetization value corresponding to $H_{\text{max}}$) when discussing this sample.

At room temperature, the technical $M_S$ of S1 is (as expected) around 10% lower than at 5 K and the M(H) dependence in S1 continues to exhibit a non-saturating component (see figure S3 of the supplementary material). In contrast to the magnetic response of S1, near-bulk magnetite $M_S$ values (60–80 emu g$^{-1}$) were found in a recent study of magnetite NPs performed by Kemp et al [43]. In that study, the average particle volume of the NPs was an order of magnitude larger than that of the S1 particle, and a non-saturating component was not detected in room temperature M(H) measurements. The presence of the non-saturating component in S1 is therefore linked to its greatly reduced $M_S$ value with respect to bulk magnetite (in section 3.1, we attribute it to the progressive alignment of spins from disordered particle shells). The $M_S$ value in S2 (figure 2) is lower than the bulk maghemite room temperature value ($\sim 74$ emu g$^{-1}$) but by a lesser extent than the (apparent) discrepancy between the $M_S$ values of S1 and bulk magnetite.

A clear EB effect (displacement from $H = 0$ of each hysteresis loop center) is observed in each loop of figure 2 (see the figure’s inset). The effect is attributed—for each sample in its fresh or aged state—to exchange coupling between a ferrimagnetically ordered iron oxide NP core and a magnetically disordered (and more anisotropic) iron oxide shell. Values of EB field ($H_E$) and coercive field ($H_C$) extracted from these loops are presented in table 1. The correlation between $H_E$ and $H_C$ indicates that coercivity enhancement (by exchange coupling) [44, 45] is significant in the samples. Compared to the range of $H_E$ values reported in the literature on magnetite NPs of similar size to those presented here—which is rather wide and includes the case of no EB effect [16, 17, 46, 47]—the value measured in S1 is relatively large [29]. The $H_E$ value in S2, on the other hand, is typical of maghemite NPs [12, 20, 48, 49]. Our findings are consistent with the presence of relatively thicker (as already suggested above based on the discussion of $M_S$ values) and more anisotropic shells of SSD in S1 NPs relative to S2 NPs. The aging effect on the EB properties and the non-saturating component in S1 is therefore linked to its greatly reduced $M_S$ satursating component was not detected in room temperature magnitude larger than that of the S1 particle, and a non-saturating component in S1 NPs as compared to S2 NPs.

We use the word “ssf” when discussing this sample. Compared to the range of $H_E$ values reported in oxide-based NPs [12, 26, 30]. We observe—figure 4—that S1a exhibits considerably larger EB parameters ($H_E$ and $H_C$ values in table 1) than both fresh and aged S2. The bifurcation temperature corresponding to each irreversibility effect is consistent with the EB onset temperature of each sample ($T_E$ was not measured in S2a but is assumed to be the same as in fresh-S2). We should note that while the hysteresis loops plotted in figure 2 appear to be effectively saturated (i.e. the magnetization appears to be reversible in the high-field regions), our understanding is that with respect to the general criteria provided by Harres et al [55] for the discrimination between minor and major

A low temperature hump feature is clearly exhibited in the $\chi''$ curve of S1. In figure 3(b) this curve is shown fitted to a sum of two Gaussian functions, one representing the NP blocking transition and the other (the weaker Gaussian) representing the hump feature. The position of maximum negative slope of the smaller Gaussian fitting curve of figure 3(b) is located around 65 K, which coincides with the position of the onset of EB $(T_E)$ in S1—figure 3(d). In ac susceptibility studies of canonical spin glasses, the freezing temperature (at a given measurement frequency) is usually determined as either the temperature position of the peak in the in-phase susceptibility $(\chi''')$ or of the inflection in $\chi''$ [54].

It is therefore reasonable to attribute the hump feature in the $\chi''$ curve of S1 to an SSF transition that onsets at $T_{SSF}\approx 65$ K in the S1 NPs. We are aware of just one previous study in which a low temperature peak in a $\chi''$ curve was associated with SSF in an iron oxide-based NPs (the particles being nickel ferrite) [32].

The presence of an albeit less conspicuous SSF hump feature contributing to the $M_{ZFC;50K}$ curve of S1—figure 3(c)—is suggested by the shape of that curve just below $T_{E}$ of S1. This possibility is supported by the shape of the derivative with respect to temperature of that curve—plotted in the inset of figure 3(c)—where a slight minimum is detected around 50 K. That a signature of SSF in a low-field dc magnetization curve should occur at a lower temperature than in an ac measurement is indeed expected from the typical behaviour of the freezing temperature with measurement frequency in a spin glass-like phase [30, 52]. It is therefore plausible to conclude the presence of an SSF hump signature in the low-field $ZFC$ curve of S1. Such signatures have only rarely been reported in oxide-based NPs [33–35].

With both samples (S1 and S2) in their aged states, it was decided to investigate a further effect related to SSF in magnetic NPs—namely high field FC-ZFC irreversibility [12, 26, 30]. We observe—figure 4—that S1a exhibits considerably larger FC-ZFC irreversibility than S2a, which is reasonable since aged-S1 continues to exhibit considerably larger EB parameters ($H_E$ and $H_C$ values in table 1) than both fresh and aged S2. The bifurcation temperature corresponding to each irreversibility effect is consistent with the EB onset temperature of each sample ($T_E$ was not measured in S2a but is assumed to be the same as in fresh-S2). We should note that while the hysteresis loops plotted in figure 2 appear to be effectively saturated (i.e. the magnetization appears to be reversible in the high-field regions), our understanding is that with respect to the general criteria provided by Harres et al [55] for the discrimination between minor and major
Table 1. Summary of SSF-related magnetic results in the S1 and S2 samples in their fresh and 4 year aged ('a') states: EB field ($H_E$) and exchange-enhanced coercivity ($H_C$) at $T = 5$ K from figures 2 and S1 of supplementary material; EB onset temperature ($T_E$) from figure 3(d); brief description of any SSF-related feature in the temperature dependence of the imaginary component of ac susceptibility ($\chi''$) or the ZFC dc magnetization at low applied field ($M_{ZFC,5Oe}$) in figures 3(a)–(c); and a quantification of the degree of irreversibility between FC and ZFC high-field magnetization curves, ($M_{FC} - M_{ZFC})/M_{FC} \times 100$ detected at $[T,H] = [5$ K, $50$ kOe], in figure 4. The penultimate column shows the temperature position ($T_{max}$) of the main peak in each $M_{ZFC,5Oe}(T)$ curve of figures 3(c) and S2 of supplementary material. We conclude (main text) that $T_{max}$, as well as being determined by interparticle dipolar interactions, is affected by high single-particle anisotropy (due to SSD) in S1. The final column gives the ratio between the estimated size of the NPs’ crystallographically-ordered cores ($D_{Scherrer}$), obtained from XRD on aged NPs (figure 5), and the average (geometric) particle size ($D_{TEM}$), obtained from TEM on the fresh NPs (figure 1). NA (not available) indicates that the given parameter was not measured for the given (fresh or aged) sample state. The experimental uncertainty in each value corresponds to $\pm$ one unit in the order of that value’s least significant digit. For comparison with the present results, the last 3 rows of the table present magnetic results from several previous studies, the references of which are provided in their first column entries.

| Sample (this study and previous studies) | $H_E$ (Oe) | $H_C$ (Oe) | $T_E$ (K) | SSF feature in ac or low-field dc $T$-dependent magnetization curve | ($M_{FC} - M_{ZFC})/M_{FC}$ $\times 100$ | $T_{max}$ (K) | $D_{Scherrer}/D_{TEM}$ |
|-----------------------------------------|------------|------------|-----------|-------------------------------------------------|---------------------------------|-------------|---------------------|
| S1                                      | 505        | 953        | 65        | Clear hump in $\chi''(T)$ onsetting at $\sim 65$ K ($=T_E$). Weak hump in $M_{ZFC,5Oe}(T)$ at $\sim 50$ K. | NA                              | 103         | NA                  |
| S1a                                     | 267        | 620        | 65        | Weak hump in $\chi''(T)$ onsetting at $\sim 65$ K. No hump any longer in $M_{ZFC,5Oe}(T)$. | 0.80                         | 116         | 0.76                |
| S2                                      | 106        | 442        | 30        | No SSF feature in $\chi''(T)$ or $M_{ZFC,5Oe}(T)$. | NA                              | 103         | NA                  |
| S2a                                     | 95         | 346        | NA        | No SSF feature in $\chi''(T)$ or $M_{ZFC,5Oe}(T)$. | 0.14                         | 103         | 0.83                |
| 8 nm Ni-ferrite NPs in SiO$_2$ matrix [32] | $\sim 60$ | $\sim 370$ | $\sim 100$ | Clear peak in $\chi''(T)$ onsetting at $\sim 30$ K (below which $H_E$ rises sharply) |                                   |             |                     |
| 10 nm Fe$_3$O$_4$ NP powder [17]         | 0          | 202        | NA        |                                                                 | NA                              |             | NA                  |
| 7 nm $\gamma$-Fe$_2$O$_3$ NPs dispersion [20] | $\sim 30$ | $\sim 300$ | 20        |                                                                 | NA                              |             | NA                  |
hysteresis loops, the size of the high-field FC-ZFC irreversibility observed at $T = 5$ K (figure 4) is small enough to allow any minor loop effect on the $H_E$ and $H_C$ values of S1a and S2a (table 1) to be ruled out, and we expect that the same is true of the samples in their fresh states (despite us having not studied high-field FC-ZFC irreversibility for those states).

As summarized in table 1, the presence (detectability) of the SSF features in the ac and dc (low-field ZFC) magnetization curves of figure 3 correlates with the samples’ EB properties. Namely, the features are best seen in the sample with the largest $H_E$ (S1), are still (barely) visible in that same sample after aging (S1a), where an intermediate $H_E$ value is found, and are absent in the sample with the lowest $H_E$ (S2).

As mentioned, the observation of such a clear SSF fingerprint in the temperature dependence of (dc or ac) magnetization is rather unusual; we are aware of just a few studies reporting such features in the large body of literature devoted to SSD in magnetic oxide particles [32–35], with just one of those studies dealing with NPs of a pure iron oxide (magnetite) [35]. This would suggest that for the detection of such fingerprints in pure iron oxide NPs, disordered shells of a relatively large thickness and high anisotropy not usually present in such (pure) material are required. The size of the FC-ZFC irreversibility (quantified in table 1) also correlates with EB properties for case of the two (aged) sample states.

To gain insight into how the S1 and S2 NPs differ with respect to disordered shell content as well as stoichiometry, XRD and Mössbauer spectroscopy were carried out on aged samples of these NPs. The XRD patterns—figure 5—only contain Bragg reflections corresponding to a spinel ferrite structure. Using the widths of all the reflections of each pattern, we estimate—see section V of the supplementary material—similar values of Scherrer grain size ($D_{\text{Scherrer}}$), namely 6.5 nm (S1a) and 6.6 nm (S2a). Bearing in mind that TEM (figure 1) indicates a slightly larger geometrical particle size for S1 ($D_{\text{TEM}} = 8.6$ nm) compared to S2 ($D_{\text{TEM}} = 8.0$ nm), these grain size estimates imply a larger crystallographically-disordered volume fraction in the S1a NPs relative to S2a NPs (i.e. the ratio $D_{\text{Scherrer}}/D_{\text{TEM}}$ is smaller for S1a, implying a larger disordered volume fraction). Assuming that thicker

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**Figure 3.** Temperature dependence of (a) out-of-phase ($\chi''$) ac susceptibility, (c) low-field FC and ZFC dc magnetization and (d) exchange bias field of the S1 (fresh and aged) and S2 (fresh) samples. (b) Fit to the $\chi''$ curve of fresh-S1 using two Gaussians. The rectangular shaded region indicates the temperature range in which SSF take places in S1 (fresh and aged). Inset of (c): the derivative with respect to temperature of the ZFC magnetization of fresh-S1 (dark blue curve) and aged-S1 (lighter blue curve).

**Figure 4.** FC and ZFC dc magnetization curves measured at high field in both aged samples.
interstitial sites to be distinguished. Detailed analysis of the spectra of figure 6—the fitting parameters of which are presented in table 2—indicates that S1a differs from natural magnetite (where Fe$^{2+}$ ions would be present and characterized by a large isomer shift and a small hyperfine field, and the B site contribution to the spectrum would be complex and asymmetrical [58]). Namely, we find that the isomer shift and hyperfine field values in S1a (as well as in S2a) are more typical of maghemite NPs [59]. Based on this result together with the lattice parameter analysis, we suggest that the effect of long-term aging on the SSF phenomena in S1 is related to a (long-term) transition—caused by ambient oxidation—towards a maghemite-like stoichiometry of NPs (S1) that were initially magnetite-like [60]. This idea is developed further in the following subsection.

In S2a there exists a significant value of $\frac{Fe_{\text{B}}^{3+}}{Fe_{\text{total}}^{3+}}$ at the expense of the value of $\frac{Fe_{\text{A}}^{3+}}{Fe_{\text{total}}^{3+}}$ (table 2), suggesting an excess of octahedral Fe sites at the surface of maghemite NPs. Crucially, both high-field spectra (figure 6) exhibit second and fifth lines of non-zero intensity, which usually indicates a canted structure for Fe$^{3+}$ magnetic moments, with respect to the applied field, i.e. a non-collinear magnetic structure [10, 49, 61, 62]. In S2a we observe a significant spin-canting only at the B site (41°, table 2), which may be related to the aforementioned excess of octahedral sites at the NP surface. In contrast, both A and B sites present a strong spin-canting in S1a. Assuming a simple ordered-core/disordered-shell magnetic morphology in which a spin-disordered shell accounts for all the observed canting, these results support the idea of a relatively thicker spin-disordered shell in S1a compared to S2a.

### 3.1. Ordered-core volume fractions and the effect of aging in S1 on NP core size and disordered shell anisotropy

The non-saturating components in figure 2, although not associated directly with the SSF transition at $T_{\text{SSF}} \approx 65$ K (since such a component is also observed far above $T_{\text{SSF}}$ in the M(H) curves from S1 in figure S3 of the supplementary material), are understood to be due to the progressive alignment of spins from the disordered NP shells. This understanding is based on previous work on iron oxide-based NPs, where such components were observed (at low and room temperature) in hollow maghemite NPs and were attributed to SSD [48], and where, in a very recent study of cobalt ferrite NPs, it was demonstrated that such components are due the progressive alignment of spins from otherwise spin-disordered shells (alignment that extends radially outwards from the interface of each ferrimagnetically ordered core, thus increasing the effective size of that core with field) [63]. The (mass) magnetization value at the point around which each hysteresis loop—of figure 2—closes provides an estimate of the superspin ($\mu_\text{s}$) of each ferrimagnetically ordered NP core (‘uncontaminated’ by a magnetic moment signal from SSD) divided by the total mass (ordered and disordered regions) of the NP. The extraction of these values (denoted as $M_{\text{core}}$) is indicated in section VI of the supplementary material. Dividing the $M_{\text{core}}$ values of S1a and S2a by a typical value

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**Figure 5.** X-ray diffraction from aged nanoparticles of S1 and S2. The solid lines are fits using a profile-matching technique. The inset shows the comparison of the extracted lattice parameters with those of bulk maghemite and magnetite.

**Figure 6.** Mössbauer spectra obtained at 12 K and $H = 80$ kOe in aged nanoparticles of S1 and S2. The solid black (red or blue) lines are total (partial) fits to the data.
of magnetization of bulk maghemite at 5 K (~80 emu g⁻¹) provides estimates for the magnetically ordered volume fraction of each NP type—viz. 0.44 (S1a) and 0.66 (S2a)—which are roughly consistent with the volume fractions of crystallographically-ordered phase obtained from XRD; namely \(D_{\text{Scherrer}}/D_{\text{TEM}}^3\) values of 0.43 (S1a) and 0.56 (S2a).

The reduction in the gradient of the non-saturating component with aging (figure 2) appears to be accompanied by an increase in \(\mu\) (in other words, a slight reduction in ‘missing magnetization’ with aging), which would suggest—since we would not expect an increase in the ‘microscopic volume magnetization’ (\(\mu\) divided by NP core volume) under long-term ambient oxidation—an increase in the radius of the ordered NP core. Using \(M_{\text{core}}\) values for S1 and S1a together with the \(D_{\text{Scherrer}}\) value for S1a, we estimate (see section VII of the supplementary material) that the radius of the ferrimagnetically ordered core increases with aging by \(\Delta r_{\text{core}}\) of between 0.13 and 0.34 nm, which would correspond to the interface between the ordered core and disordered shell ‘swelling up’ to incorporate (approximately) an additional monolayer of iron oxide (from the shell) into the core.

Aging of S1 yields a significant reduction in the EB properties but it is not found—see figure 3(d)—to affect \(T_E\), which is consistent with the appearance of the \(\chi'(T)\) curves of this sample—figure 3(a)—which each possesses a low temperature hump (albeit a weak one in S1a) indicative of essentially the same \(T_{\text{SSF}}\) value (≈65 K). Considering \(T_{\text{SSF}}\) as a property analogous to the ordering temperature \(T_N\) of the high anisotropy (antiferromagnet) component in conventional EB systems [44, 45], and bearing in mind that \(T_N\) (which represents the upper limit value of \(T_E\) in such systems) has been reported to decrease strongly upon moving from nano to subnanometric layer thickness [64, 65], the lack of variation in \(T_E\) (or, equivalently, in \(T_{\text{SSF}}\)) from S1 to S1a would suggest that the thickness of the spin-disordered shells is not significantly altered by aging. This is consistent with the, at most, 0.34 nm growth (reduction) in the NP core radius (in the disordered shell thickness) estimated above. We suggest that it is a softening (decrease) in the anisotropy of the SSD caused by aging in S1 which is the decisive factor accounting for the diminution in the SSF (including EB) effects. Since the magnetic anisotropy is lower in the ferrimagnetic phase of bulk maghemite than in that of bulk magnetite, we suggest that such softening is the result of the gradual transition towards magnetite-like stoichiometry caused by long-term ambient oxidation in S1.

### Table 2. Parameters obtained from the fits of the Mössbauer spectra in figure 6: isomer shift (\(\delta\)), quadrupole shift (\(2\varepsilon\)), effective field \(B_{\text{eff}}\), hyperfine field \(B_{\text{hyp}}\), average canting angle (\(\theta\)) and ratio of the A and B sites. The isomer shift values are referenced relative to \(\alpha\)-Fe at 300 K. The values in parentheses are uncertainties and refer to the least significant digit. The estimated error on each \(\theta\) value is \(\pm 10^\circ\).

| Sample | Site | \(\delta\) (mm s⁻¹) | \(2\varepsilon\) (mm s⁻¹) | \(B_{\text{eff}}\)(T) | \(B_{\text{hyp}}\)(T) | \(\theta(\degree)\) | \(\text{Fe}^{3+}_{\text{A}}/\text{Fe}^{3+}_{\text{B}}\) |
|--------|------|-------------------|-------------------|-----------------|-----------------|-----------------|-----------------|
| S2a    | Fe³⁺ | 0.33(1)           | 0.00(1)           | 59.8(2)         | 52.0(2)         | 11              | 0.29(1)         |
|        | Fe³⁺ | 0.45(1)           | 0.00(1)           | 46.3(2)         | 52.6(2)         | 41              | 0.71(1)         |
| S1a    | Fe³⁺ | 0.38(1)           | 0.04(1)           | 57.3(2)         | 51.7(2)         | 42              | 0.41(1)         |
|        | Fe³⁺ | 0.51(1)           | 0.03(1)           | 46.2(2)         | 52.2(2)         | 43              | 0.59(1)         |

#### 3.2. Impact of SSD on the blocking of nanoparticle superspins

Finally, we discuss the impact of the SSD on the nature of the blocking of the nanoparticle superspins. Both S1 and S2 samples exhibit the same value of main peak position \(T_{\text{max}} = 103\) K in their \(M_{\text{ZFC,50}}\) curves—figure 3(c). Upon first consideration, this may be interpreted (mistakenly) as an indication of identical values of the interparticle dipolar interaction strength parameter, \(E_{\text{dd}}\) \((\propto d^2/3\), where \(d\) is the mean center-to-center separation between nearest-neighbour NPs in each assembly and \(\mu\) is the NP core superspin, defined already), for S1 and S2. However, by more careful consideration (section VIII of the supplementary material) we estimate that the ratio \(E_{\text{dd},\text{S1}}/E_{\text{dd},\text{S2}}\) is at most only around 0.5. This implies a significant contribution to \(T_{\text{max}}\) arising due to a relatively large effective single-particle magnetic anisotropy \(K_{\text{eff}}\), in turn due to a large and highly-anisotropic SSD fraction in S1. The variation in \(T_{\text{max}}\) with aging in S1, namely the value of the ratio \(T_{\text{max},\text{S1}}/T_{\text{max},\text{S1a}}\) (=0.89—see table 1), cannot be explained alone by our estimated value of the ratio \(E_{\text{dd},\text{S1}}/E_{\text{dd},\text{S1a}}\), our upper value of which is 0.79 (see section VIII of supplementary material). This also implies a contribution to \(T_{\text{max}}\) due to \(K_{\text{eff}}\), namely a contribution that weakens with aging \((K_{\text{eff}}\text{ weakens with aging in S1 and hence }K_{\text{eff},\text{S1}}/K_{\text{eff},\text{S1a}} > 1)\) in line with the sample’s aged-induced reduction in SSF effects. Very recently it was suggested, by some of use, that individual (single-particle) magnetic anisotropy impacts on the dipolar collective properties of dense assemblies of magnetic NPs (binary assemblies of maghemite and cobalt-ferrite particles) [66].

As pointed out some time ago by Mørup [51], the interparticle interaction strength in a dense magnetic NP system should be quantified relative to the single-particle anisotropy energy barrier \(K_{\text{eff}} V_{\text{NP}}\), where \(V_{\text{NP}}\) denotes average NP volume). Under such normalization, S2 is yet a stronger interacting system (and hence is yet more likely to be superspin glass-like) than S1, i.e. as well as S2 having an approximate factor of two higher \(E_{\text{dd}}\) parameter than S1, the S2 NPs will have a lower \(K_{\text{eff}}\) value than S1, as a consequence of possessing a lower and less anisotropic SSD fraction. The \(E_{\text{dd}}/(K_{\text{eff}} V_{\text{NP}})\) ratio for S2 is therefore expected to be more than a factor of two larger than the \(E_{\text{dd}}/(K_{\text{eff}} V_{\text{NP}})\) ratio of S1. Our expectation is that S1 is only a moderately interacting system (close to the border of becoming superspin glass) while S2 is more strongly interacting (and hence superspin glass-like). This expectation is confirmed by...
additional SQUID measurements presented in figures S4 and S5 of the supplementary material.

The difference in $E_{\text{eff}}/(K_{\text{eff}} V_{\text{NP}})$ ratio (in part due to the difference in $K_{\text{eff}}$ values) between S1 and S2 is manifest in the difference in shapes of the main peaks in their $\chi''$ curves—figure 3(a). The broad shoulder on the low temperature side of the peak position in the S2 ($\chi''$) curve is attributed to the combination of an asymmetrical line-shape, intrinsic to the physics of superspin glasses (a steeply rising curve—i.e. sudden onset of $\chi''$—on the high temperature side of the peak, and a broad tail on the low temperature side), and demagnetizing field (DMF) effects, which—as was established in a recent study on similarly dense assemblies of maghemite NPs [42]—tend to accentuate such asymmetry. The main peak in the S1 ($\chi''$) curve, in contrast, possesses no such broad shoulder and can be fitted—figure 3(b)—to a symmetrical (Gaussian) function, a consequence of the lower $E_{\text{eff}}/(K_{\text{eff}} V_{\text{NP}})$ ratio in S1 relative to S2. (See section X of the supplementary material for notes on the DMF factors and for $\chi'''(T)$ data—figure S6—measured on a pressed disk-like sample of NPs from the same batch as S2 but coated with silica shells, instead of OA. Figure S6 simultaneously serves to (i) highlight the loss of the intrinsic asymmetrical line-shape as interparticle interactions are reduced relative S2 and (ii) rule out the possibility that DMF effects prevented a hump signature of SSF from being detected in S2. See the text below that figure for more details.)

4. Conclusions

Prior to the present study, several different magnetic effects had been reported as being related to SSD in a large body of literature on iron-oxide based NPs [10–39, 48, 49, 60–62]. By reviewing some of these effects in two samples of similar NP diameter (approximately 8 nm) but synthesized by different methods (one for magnetite and the other maghemite), we have been able to determine why SSF-related hump features in out-of-phase ac susceptibility and low-field dc (ZFC) magnetization curves had been seldom seen in pure iron oxide NPs. Namely, we have found that the requirement for the clear appearance of such features is a relatively thick spin-disordered shell (a shell volume of more than 50% of total NP volume) of a relatively high anisotropy (pertaining more to spin-disorder in magnetite than maghemite). These conditions also give rise to a strong (for iron oxide NPs) exchange-bias effect (EB field, $H_E \sim 500$ Oe, the case of sample S1, produced by the magnetite method). When the conditions are not fulfilled (the case of sample S2, produced by the magnetite method), an EB effect ($H_E \sim 100$ Oe) can still comfortably be detected, suggesting that the measurement of EB field may provide the most sensitive fingerprint of SSF in (pure) iron oxide NPs. The SSF effects in the sample that initially fulfills those conditions (sample S1) have been found to become strongly degraded by long-term (4 year) aging under ambient conditions, which, supported by XRD and Mössbauer analysis, we have attributed to oxidation towards a maghemite-like stoichiometry that results in a softening of the magnetic anisotropy associated with the spin-disordered shells. Finally, we have been able to connect aspects related to the blocking of NP superspins (in S1, S2 and aged-S1) to expected differences in effective single-particle anisotropy (largely governed by SSD) between “samples” (including between the fresh and aged states of the S1 sample). In future work it would be interesting to study a dense assembly of NPs similar to S1 as a function of progressive annealing in air, at moderate temperatures (below the OA boiling point), assessing changes in SSF effects and correlating them with structural information from small angle neutron [63] and total (x-ray) scattering [67].

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