Spatially Resolved Disorder Anisotropies in Ferrite Nanoparticles

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Abstract

The technological performance of magnetic nanoparticles is dominated by finite size and disorder effects. However, it is often difficult to isolate intrinsic effects such as magnetic disorder at the particle surface. Despite numerous efforts and advanced techniques, the three-dimensional magnetism of spin disorder and its nanoscale distribution within magnetic nanoparticles remains a key challenge. Here we present the
spatially resolved, non-correlated surface spin disorder in isolated, spherical cobalt ferrite nanoparticles, derived by a combination of polarized small-angle neutron scattering and micromagnetic analysis. The field-dependence of the coherently magnetized particle volume, which is not accessible with conventional integral measurement techniques, illustrates how the nanoparticle magnetization overcomes structural surface disorder. Our results allow us to estimate the magnetic disorder energy, which is required to gradually polarize the surface spins, with spatial resolution within the nanoparticles. Such unprecedented knowledge of the intraparticle spin disorder and associated anisotropies will be decisive for a rational nanomaterials development.

Introduction

The phenomenon of disorder is ubiquitous in structural science, and different qualities of disorder are evident, ranging from the intuitive random disorder to complex types of correlated disorder. Correlated disorder is essential for a large number of functional properties, including polar nanoregions in relaxor ferroelectrics, colossal magnetoresistance in La$_x$Ca$_{(1-2x)}$MnO$_3$, the entropic disorder in thermoelectrics, and correlated spin disorder leading to quasi-particles such as skyrmions and magnetic monopoles. Being intrinsic to nanomaterials, disorder effects such as surface spin disorder and surface anisotropy in magnetic nanoparticles (NP) crucially determine their magnetization properties including coercivity and superparamagnetism, exchange interactions, and spontaneous magnetization. These have a pivotal importance for the diverse technological applications of magnetic nanoparticles, such as in recording media, biomedicine, catalysis, or battery materials.

Surface spin canting or disorder in magnetic NPs is accessible only indirectly using magnetization measurements, ferromagnetic resonance (FMR), Mössbauer spectroscopy, X-ray magnetic circular dichroism and electron energy loss spectroscopy. Spin canting at the NP surface arises from low-coordination sites and a high number of broken exchange bonds.
of the surface atoms\textsuperscript{16}, and causes a field-dependent shift of the superparamagnetic blocking temperature and exchange bias phenomena\textsuperscript{17–19}. Below the spin glass transition, surface spins freeze in a random configuration\textsuperscript{20}. In addition, a strong correlation of magnetic and structural disorder is widely accepted\textsuperscript{21–25}. In order to reliably discriminate bulk and surface contributions to magnetic disorder, spatial resolution of the NP spin structure is required.

Magnetic small-angle neutron scattering (SANS) is a versatile technique to obtain spatially sensitive information of the spin structure in NPs on the relevant nm-length scale. Using half-polarized SANS (SANSPOL), the quantitative magnetization distribution within maghemite NPs has been resolved confirming the presence of spin disorder at the particle surface, but at the same time revealing a significant degree of spin disorder in the entire NP\textsuperscript{26}. Applying SANS with uniaxial polarization analysis (POLARIS) to NP assemblies, a canted magnetic surface shell was reported\textsuperscript{27,28} and the temperature dependence of the spin canting in CoFe\textsubscript{2}O\textsubscript{4} NPs was derived\textsuperscript{29}. More recently, micromagnetic simulations of the magnetic SANS of isolated magnetic NPs in a nonmagnetic matrix demonstrated how the interplay between various magnetic interactions leads to nonuniform spin structures in NPs\textsuperscript{30}.

![Figure 1: Schematic of the structural and field-dependent magnetic NP morphology: structural and magnetic particle sizes are equal in zero-field (left), whereas the initially disordered surface spins are gradually polarized in applied magnetic field such that the magnetic radius increases beyond the structurally disordered surface region (right). The field-dependent NP morphology gives access to the spatially resolved disorder anisotropy (Fig. 5).](image)

Here, we present the field dependence of collinear magnetization and spin disorder in
ferrite nanoparticles. The spontaneous, non-correlated spin disorder at the particle surface is strongly related to structural surface disorder. Remarkably, we observe that with increasing magnetic field the collinear magnetic volume overcomes the structurally coherent particle size. This main result of our work is illustrated in Fig. 1. From the field-dependence of the magnetic particle volume determined using polarized SANS, we extract the spatial extent of spin disorder and estimate the associated disorder energy distribution towards the particles surface based on a free energy calculation.

Results

The precise evaluation of intraparticle morphologies requires highly monodisperse samples of non-interacting magnetic nanoparticles. The oleic acid (OA)-capped cobalt ferrite NPs for our study were synthesized according to Park et al. and stabilized in the non-polar solvent toluene. The sample consists of spherical particles with a log-normal size distribution of 3.1(1)% and a mean particle radius of \( r_{\text{nucl}} = 7.05(5) \) nm as determined using Small-Angle X-ray Scattering (SAXS), which is in excellent agreement with the results obtained from transmission electron microscopy (TEM) analysis (Fig. 2). A Guinier plateau observed in the lower \( Q \) range of the SAXS data further demonstrates the absence of interparticle interactions in toluene dispersion (Fig. 2 c)). The crystal symmetry of the particles determined by powder X-ray diffraction (PXRD) corresponds to the cubic spinel (space group \( Fd\bar{3}m \)) with a lattice parameter of \( a = 8.3618(1) \) Å, which is slightly smaller than for bulk CoFe\(_2\)O\(_4\) (\( a = 8.3919 \) Å), an observation commonly reported for nanosized materials. The determined structurally coherent grain size of 12.8(2) nm is significantly smaller than the particle size, indicating structural disorder near the particle surface.

Refinement of the nuclear scattering cross section obtained by SANS-POL, using the particle diameter and size distribution as obtained by SAXS (Fig. 2 c)), yields an organic ligand shell thickness of \( d_{\text{surf}} = 1.4(1) \) nm (Fig. 2 d)). This is reasonable given the theoretical value
Figure 2: **a)** TEM bright field micrograph (scale bar: 50 nm) and **b)** particle-size histogram based on the evaluation of 200 particles along with log-normal particle size distribution obtained from TEM analysis (red surface) and SAXS refinement (line). **c)** SAXS (red) and nuclear SANS (blue) data along with form factor fit (black lines) and **d)** radial profiles of the nuclear ($\rho_n$, grey) and magnetic scattering length densities ($\rho_{mag}$, red). Our model of the magnetic nanoparticle morphology consists of a coherently magnetized particle core with radius $r_{mag}$ and a magnetically disordered surface shell with thickness $d_{dis}$ within the inorganic NP with radius $r_{nuc}$, stabilized by the oleic acid ligand shell with thickness $d_{surf}$.
of fully stretched OA (2.1 nm) and in good agreement with earlier results on OA-stabilized iron oxide NPs in toluene. From the X-ray and neutron scattering length densities of the particle core \( (\rho_x = 41.61 \cdot 10^{-6} \text{ Å}^{-2} \text{ and } \rho_n = 6.88 \cdot 10^{-6} \text{ Å}^{-2}) \), a Co cation content of 8.4 at.-% is determined according to Végard’s law. Assuming neutral overall charge, we consider the formula \( \text{Co}_x\text{Fe}_{(8-2y)/3}\text{O}_4 \), where \( y = 1 \) represents the cobalt ferrite spinel structure and \( y = 0 \) corresponds to maghemite \( (\gamma\text{-Fe}_2\text{O}_3) \), and derive a composition of \( \text{Co}_{0.22}\text{Fe}_{2.52}\text{O}_4 \). The stoichiometry is based on Mössbauer spectroscopy measurements demonstrating the absence of \( \text{Fe}^{2+} \) in the compound. EDX scans further support a chemically homogeneous crystalline particle core. A line scan reveals 10 at.-% Co content within the entire particle, whereas an average composition of 9.1 at.-% Co is confirmed by TEM EDX mapping, both in excellent agreement with the composition derived by small-angle scattering.

Beyond the nuclear particle morphology including the inorganic particle radius and size distribution as well as ligand shell thickness, polarized SANS gives additional access to the magnetic scattering amplitude that is related to the magnetic nanoparticle morphology. We model the magnetic nanoparticle morphology with a homogeneously magnetized particle core with radius \( r_{\text{mag}} \) and a spin disorder shell of thickness \( d_{\text{dis}} \) towards the surface (Fig. 2d). The magnetic particle size distribution is assumed equal to the nuclear size distribution. The magnetic scattering length density of the particle core \( \rho_{\text{mag}} \) determined using polarized SANS is directly related with the in-field or longitudinal magnetization component \( M_z(H) \).

The nuclear-magnetic interference scattering of our sample (Fig. 3a) is only consistently described by a field dependent variation of both \( \rho_{\text{mag}} \) and \( r_{\text{mag}} \) (Fig. 3c). The magnetic particle radius \( r_{\text{mag}}(H) < r_{\text{inc}} \) increases with magnetic field, starting from \( r_{\text{mag}}(H_{\text{min}}) = 6.3(1) \text{ nm} \) at the lowest applied magnetic field of \( H_{\text{min}} = 11 \text{ mT} \) and attaining \( r_{\text{mag}}(H_{\text{max}}) = 6.76(1) \text{ nm} \) at the highest applied field of \( H_{\text{max}} = 1.2 \text{ T} \) (Fig. 3b,c). The spontaneous \( r_{\text{mag}}(H_{\text{min}}) \) is in excellent agreement with the structurally coherent domain size of 12.8(2) nm from PXRD, indicating a structurally homogeneous and spontaneously magnetized particle.
core smaller than the NP itself. This observation is in line with reports on reduced magnetic domain size in magnetic NPs, revealed by macroscopic magnetization\textsuperscript{23,24,36}, neutron diffraction\textsuperscript{37} and polarized SANS\textsuperscript{27,28}. Several previous studies indicate spatial correlation of spins near the particle surface giving rise to canted spin structures\textsuperscript{27,28}. Simulations propose a variety of different spin canting scenarios, such as collinear, artichoke, throttled and hedgehog spin structures\textsuperscript{38,39}. To distinguish between correlated (spin canting) and non-correlated (spin disorder) spins near the NP surface, spin-resolved SANS (POLARIS) was performed on the non-interacting nanoparticles in dispersion. POLARIS gives access to the Fourier transformation of magnetization correlations along the three Cartesian directions $|\tilde{M}_x|^2$, $|\tilde{M}_y|^2$ and $|\tilde{M}_z|^2$\textsuperscript{34,40}. In our case of spherical nanoparticles, the transversal magnetization correlations $|\tilde{M}_\perp|^2 = |\tilde{M}_x|^2 = |\tilde{M}_y|^2$ are assumed to be equal for symmetry reasons. Based on POLARIS data of two different applied magnetic fields, we conclude that the particles do not exhibit a coherently ordered, transversal magnetization component $|\tilde{M}_\perp|^2$\textsuperscript{34}. Despite low scattering statistics, in particular in the spin-flip data, all further fit parameters of nuclear scattering amplitude, incoherent background, and longitudinal magnetization obtained from the different data sets are in excellent, consistent agreement, including the expected slight increase of the longitudinal magnetization with applied field. The absence of a coherent, elastic scattering originating from transversal magnetization $|\tilde{M}_\perp|^2$ is a strong indication of a non-correlated, randomly disordered spin state at the NP surface for our sample, in contrast to the canted spin structures suggested in the literature.

Whereas the existence of surface spin disorder and canting has been under debate in the past, the field-induced reduction of the magnetically disordered surface shell thickness $d_{\text{dis}}(H) = r_{\text{nuc}} - r_{\text{mag}}(H)$ (Fig. 3 b)) revealed by SANSPOL is an entirely new observation. At the lowest applied magnetic field of 11 mT, 28% of the particle volume is associated to a disordered surface with a thickness of $d_{\text{dis}} = 0.7$ nm. This is in excellent agreement with Mössbauer spectroscopy results, indicating that 28.2% of the Fe$^{3+}$ ions reside in a disor-
Figure 3: a) Nuclear-magnetic scattering interference term $I^+ - I^-$ (points) at various applied magnetic fields (same color code as in c)) and corresponding fits (lines). Inset: zoomed region of $Q = 0.03 \text{ - } 0.065 \text{ Å}^{-1}$. b) Field-dependence of the derived magnetic radius $r_{mag}$ and the disordered shell thickness $d_{dis}$. Nuclear ($r_{nuc}$) and structurally coherent radius ($r_{XRD}$) are indicated in blue and green, respectively. c) Field-dependent magnetic scattering length density $\rho_{mag}$ profiles. d) Macroscopic longitudinal magnetization ($\langle M_{VSM} \rangle$) measured at room temperature in comparison with the longitudinal particle core magnetization ($M_x(H)$) and the particle volume averaged magnetization ($\langle M \rangle$), both derived from SANSPOL. Corresponding fits are shown as lines.
dered state\textsuperscript{24}. The coherently magnetized particle core size, and hence the magnetic particle moment, gradually increases with applied magnetic field, indicating a field-induced alignment of the initially disordered spins even beyond the structurally coherent grain size. At maximum applied field ($\mu_0 H_{\text{max}} = 1.2 \text{T}$), a non-magnetic surface layer of $d_{\text{dis}} = 0.27(1) \text{nm}$ persists, implying a strong degree of spin disorder in 11\% of the particle volume that cannot be overcome by the magnetic field applied in this study.

In the conventional picture, the isothermal magnetization for a superparamagnet is described based on the assumption of a field-independent, constant magnetic particle moment. The relative magnetization is described as:

$$\frac{\langle M \rangle}{M_S} = \langle \cos \gamma(H) \rangle = L(\xi) = \coth \xi - \frac{1}{\xi},$$ (1)

where $\langle \cos \gamma(H) \rangle$ is the orientation average over the particle ensemble, with the angle $\gamma$ between the magnetic moment of a particle and the applied magnetic field $H$. The Langevin parameter is given as $\xi = \frac{\mu_0 H}{k_B T}$ with $\mu_0$ the permeability of free space, $\mu$ the integrated particle moment, $k_B$ denoting the Boltzmann constant and $T$ the temperature. A Langevin fit of the integral magnetization $\langle M_{\text{VSM}} \rangle$ at 300 K (Fig. 3 d)) yields a particle moment of $\mu = 1.2(1) \cdot 10^4 \mu_B$ with a spontaneous magnetization $M_{S,\text{VSM}} = 135(2) \text{kA/m}$. In addition, an excess paramagnetic susceptibility of $\chi_{\text{VSM}} = 6.33(6) \cdot 10^{-5}$ is evident from the non-saturating magnetization at high applied field. Such excess paramagnetic susceptibility along with reduced spontaneous magnetization as compared to the bulk material is commonly associated to misaligned spins. The derived spontaneous magnetization is significantly smaller than for bulk cobalt ferrite (400 kA/m)\textsuperscript{41}. The estimated magnetic particle volume, $V_{\text{mag, VSM}} = \mu/M_{S,\text{VSM}} = 8.3(2) \cdot 10^{-25} \text{m}^3$ is comparable to the magnetic particle volume $V_{\text{mag, SANS}} = 1.05(2) \cdot 10^{-24} \text{m}^3$ derived from the minimal magnetic radius at the lowest applied field. Both magnetic particle volumes are considerably smaller than the morphological NP volume $V_{\text{nuc}} = \frac{4}{3} \pi r_{\text{nuc}}^3 = 1.5(1) \cdot 10^{-24} \text{m}^3$ derived from SAXS. This discrepancy is commonly attributed to
surface disorder effects.

Analyzing the longitudinal magnetization $M_z(H)$ derived from $\rho_{\text{mag}}$ of the coherently magnetized particle core (red dots in Fig. 3 d), a spontaneous magnetization $M_{S,\text{core}} = 200(5) \text{kA/m}$ is extracted, which is larger than $M_{S,\text{VSM}}$, but still substantially smaller than the bulk saturation magnetization of cobalt ferrite. The coherently magnetized particle core contributes an excess paramagnetic susceptibility of $\chi_{\text{core}} = 1.8(8) \cdot 10^{-5}$ that is strongly reduced as compared to $\chi_{\text{VSM}}$. SANSPOL thus reveals a homogeneously magnetized particle core with larger magnetization and less spin disorder than indicated for the entire particle, but still far from bulk CoFe$_2$O$_4$ characteristics. The longitudinal magnetization $M_z(H)$ can be related to the average magnetization of the inorganic particle volume according to $\langle M \rangle = M_z(H)V_{\text{mag}}(H)/V_{\text{nuc}}$ (orange dots in Fig. 3 d)). The good agreement with the integral magnetization confirms the reliability of the refinement for a coherently magnetized core with a magnetically disordered surface shell as further supported by the POLARIS results. In consequence, the observed low NP magnetization as compared to the bulk material is a result of both surface spin disorder and reduced magnetization related to a combined effect of the non-stoichiometric amount of Co in the material and structural disorder within the coherently magnetized particle core. For a composition of Co$_{0.5}$Fe$_{2.5}$O$_4$, a 50% reduced saturation
magnetization compared to nominal CoFe$_2$O$_4$ has been reported$^{42,43}$. For our sample with a composition of Co$_{0.22}$Fe$_{2.52}$O$_4$, a significant decrease in $M_S$ may thus be expected. In addition, high-resolution TEM (HRTEM) indicates structural disorder in the NP interior including dislocations in the (220) lattice plane (Fig. 4). Such structural disorder has been observed before in maghemite spinel NPs$^{22,25}$, and is likely correlated with intraparticle spin disorder leading to reduced spontaneous magnetization as well as excess paramagnetic susceptibility in the coherently magnetized NP core.

The observed field-dependent magnetic radius may originate in either intrinsic magnetic phenomena, such as surface anisotropy, or structural fluctuations such as gradual lattice distortions near the particle surface. We applied a micromagnetic approach in terms of Ginzburg-Landau theory as introduced by Kronmüller and Fähnle$^{44}$ to describe the magnetic scattering amplitude under the influence of spatially random magnetocrystalline and magnetostrictive fluctuations$^{34}$. The refinement based on a core-shell structure for the magnetic perturbation fields converges for an inner anisotropy constant $K_{\text{in}} = H_{\text{K,in}} \cdot M_s = 86(52)$ kJ/m$^3$, suggesting a significant amount of magnetic disorder in the particle core interior. Further relevant parameters obtained include an outer anisotropy $K_{\text{shell}} = 241(91)$ kJ/m$^3$, a shell thickness $d_{\text{dis}} = 1.3(2)$ nm, and a spontaneous magnetization of $M_s = 245(19)$ kA/m. The derived spontaneous magnetization and shell thickness are in good agreement with the spontaneous magnetization in the particle core and the initial disorder shell thickness determined by SANSPOL. The mean anisotropy field inside the particle $\langle H_{\text{K}} \rangle = 0.6(2)$ T corresponds to a magnetocrystalline anisotropy constant of $K_{\text{avg}} = 149(56)$ kJ/m$^3$, which can be considered as an average value over the entire particle. This value is in the range of anisotropy constants reported for CoFe$_2$O$_4$$^{45}$. This indicates that fluctuations of magnetic parameters, i.e. magnetocrystalline anisotropy and magnetostrictive contributions, are the most likely sources of the variation of the magnetic radius with field. In the following, we will consider the magnetic field energy associated to the field dependent variation of the magnetic volume to extract more detailed, model-independent and spatially
resolved information on the extent and strength of the microstructural fluctuations.

The field-dependent increase of the magnetic volume and the corresponding magnetic field energy occurs in excess of disorder energy that has to be overcome to polarize the initially disordered surface spins\textsuperscript{34}. The free energy with respect to the initial volume of the magnetic core is given as

\[ E_{\text{dis}}(H) = \mu_0 H M_z(H)[V_{\text{mag}}(H) - V_{\text{mag}}(H_{\text{min}})]. \] (2)

The gradual growth of the magnetic volume with increasing field is a consequence of a distribution of spin disorder energies such that the spin system is harder to magnetize towards the surface. We attribute this to enhanced structural disorder and significantly reduced exchange interaction near the particle surface. The magnitude of the surface spin disorder energy shown in Fig. 5 a) increases up to a value of \( E_{\text{dis}}(1.2 \text{T}) = 6 \times 10^{-20} \text{J} \). Starting from a negligible magnitude in the spontaneously magnetized particle core \( (r_{\text{mag}} < 6.3 \text{nm}) \), the disorder energy density attains a maximum value of \( K_{\text{eff}} = \frac{\partial E_{\text{dis}}}{\partial V_{\text{mag}}} \approx 10^6 \text{Jm}^{-3} \) close to the NP surface (Fig. 5 b)). We note that the obtained maximum effective energy density value exceeds the bulk magnetocrystalline anisotropy \( K_b = 3.6 \times 10^5 \text{Jm}^{-3} \).\textsuperscript{45}

Figure 5: Dependence of a) disorder energy \( E_{\text{dis}} \) as a function of the coherent magnetic particle radius (black line: spline fit of the data) and b) dependence of the effective disorder energy density \( K_{\text{eff}} \) (black line: derivative of spline in a)).
The derived energy density is understood as the spatially resolved magnetic disorder anisotropy within the particle. According to phenomenological relations, it can be described as an apparent surface anisotropy $K_{S,\text{app}} = K_{\text{eff}} \cdot r_{\text{mag}}/3$ of the nanoparticle. Recent particle size dependent studies indicate that surface anisotropy is not necessarily constant. Further theoretical studies confirm that the effect of surface anisotropy does not scale with the surface-to-volume ratio, but that surface perturbations penetrate to the NP interior transmitted by exchange interactions leading to a reduced coherent magnetic size. Our approach reveals, for the first time experimentally, how the disorder energy anisotropy varies locally within the particle (Fig. 5b), an aspect that is not accessible by common integral approaches correlating volume averaged values from different batches of NP sizes. The maximum apparent surface anisotropy of $K_{S,\text{app}} \approx 2.3 \text{ mJm}^{-2}$ is in excellent agreement with Néel surface anisotropy (0.1 – 1.3 mJm$^{-2}$), resulting from broken symmetry at the particle surface and concomitant structural relaxation into the particle core, and it is in the order of magnitude of ferromagnetic materials, e.g. Co (1 mJm$^{-2}$), Er (14 mJm$^{-2}$), FePt (34 mJm$^{-2}$), YCo$_5$ (34 mJm$^{-2}$). Ferromagnetic resonance estimates a significantly lower anisotropy for maghemite NPs in ferrofluids (0.03 mJm$^{-2}$) or for non-interacting 7 nm maghemite NPs (0.042 mJm$^{-2}$). However, these values are in good agreement with the volume averaged disorder anisotropy of our sample of $K_{S,\text{ave}} = 0.096(32) \text{ mJm}^{-2}$, derived from the maximum disorder energy related to the nuclear particle volume. In this respect, it is noteworthy that the determined values of the surface disorder energies may vary depending on the method and applied magnetic field, as for instance a surface anisotropy of $K_S = 0.027 \text{ mJm}^{-2}$ was obtained from ferromagnetic resonance at 0.1 T.

The gradual decrease of the magnetic disorder parameter (corresponding to enhanced susceptibility) towards the particle interior is likely correlated with reduced structural defect density in the particle core. In addition, spin disorder localized at the particle surface is known to influence the spin configuration in its vicinity via exchange coupling and thus to propagate into the particle interior. In this respect, hollow spherical maghemite nanoparticles
represent interesting model systems to further investigate surface effects on anisotropy and magnetic disorder\textsuperscript{53}. From magnetization measurements for hollow particles, a strength of the surface anisotropy comparable to the results in this study has been observed\textsuperscript{54}. Further, based on Monte Carlo simulations, it has been shown that surface spins tend to a disordered state due to the competition between the surface anisotropy and exchange interactions\textsuperscript{54}.

**Conclusions**

In summary, the field-dependent surface spin disorder of highly monodisperse cobalt ferrite nanoparticles was elucidated with spatial resolution. The nanoparticle magnetization profile determined using polarized SANS is described by a magnetic model consisting of a coherently magnetized particle core with a spin disorder layer at the surface. Spin-resolved SANS indicates non-correlated spins at the surface, which supports surface spin disorder rather than spin canting at the NP surface. The magnetized core size varies significantly with applied field for the studied spherical magnetic NPs indicating that structural surface disorder can be overcome by an increasing magnetic field in order to gradually polarize the surface spins (Fig. 1). Indeed, micromagnetic evaluation indicates fluctuations of magnetocrystalline anisotropy and magnetostrictive contributions as the origins of the observed surface spin disorder. The spin system is characterized by 11 vol-% of spin disorder at the particle surface even at a high magnetic field of 1.2 T. The observed penetration depth of the magnetically perturbed surface region of 0.7 nm into the nanoparticle interior provides a quantitative insight into the thickness of a magnetic nanoparticle surface. Our in-depth analysis further enables to estimate the locally varying disorder energy in the NP, which is not separable from the bulk magnetocrystalline anisotropy by macroscopic characterization methods. The effective disorder anisotropy increases up to $K_{\text{eff}} \approx 1 \cdot 10^6 \text{Jm}^{-3}$ close to the particle surface, corresponding to an apparent surface anisotropy of $K_{S,\text{app}} \approx 2.3 \text{mJm}^{-2}$.

The presented approach can be employed to determine in-depth the particle size depen-
dence of the surface disorder and to characterize the effects of the chemical environment on the surface spins for varying particle coating. By correlating the magnetic surface disorder energy distribution with structural disorder towards the particle surface, the presented approach furthermore provides indirect insight into the defect concentration and depth profile. Looking beyond magnetic applications, such knowledge of the surface morphology of ferrites plays a decisive role in the diffusion-based fields of heterogeneous catalysis and electrochemistry such as solid-state batteries.

Methods

**Synthesis** Cobalt ferrite NPs were synthesized by thermal decomposition of a mixed Co,Fe-oleate precursor according to Park et al.\textsuperscript{31}. The oleate precursors were prepared from the respective metal chlorides and freshly prepared sodium oleate as follows: A solution of sodium oleate was prepared by dissolving 66 mmol (2.64 g) of NaOH in a mixture of 10 mL of H\textsubscript{2}O and 20 mL of EtOH and dropwise addition of 68 mmol of oleic acid. Water solutions of 15 mL of 8 mmol (1.9 g) CoCl\textsubscript{2}·6 H\textsubscript{2}O and 16 mmol (4.32 g) FeCl\textsubscript{3}·6 H\textsubscript{2}O were added to the prepared sodium oleate solution. 60 mL of hexane and 10 mL of EtOH were added to the reaction and it was refluxed at 60°C for 4 hours. After the reaction cooled down, the oleate complex was washed three times with 50 mL of water in order to remove NaCl. A brownish viscous mixed oleate complex was obtained by evaporating all solvents including hexane, EtOH and water. In a second step, the ferrite NPs were synthesized by thermal decomposition of 5 mmol of the prepared oleate precursor with a small amount (1.6 mL) of additional oleic acid in 25 mL of octadecene. A heating rate of 2 K/min was applied up to the reflux temperature of 315°C which was held for a reflux time of 0.5 h. The prepared NPs were precipitated with ethylacetate/EtOH mixture of 1:1 for three times and redispersed in toluene.
**PXRD** Powder X-ray Diffraction (PXRD) was measured with a PANalytical X’Pert PRO diffractometer equipped with Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å), a secondary monochromator and a PIXcel detector. The sample was measured in the 2$\theta$ range of 5 - 80° with a step size of 0.03°. Rietveld refinement was done in FullProf software using a pseudo-Voigt profile function. The instrumental broadening was determined using a LaB$_6$-reference (SR 660b, NIST).

The Rietveld refinement of the PXRD pattern shown in Fig. S 1 reveals two phases, a spinel ferrite phase and sodium chloride. The presence of sodium chloride in the sample was due to a non-perfect washing procedure. For the SANS experiment, the preparation was improved by two more purification steps. Nevertheless, this does not affect the structural and the magnetic sample properties.

**Mössbauer spectroscopy** Mössbauer spectroscopy of $^{57}$Fe was measured on a Wissel spectrometer using transmission geometry and a proportional detector at ambient temperature without magnetic field. An α-Fe foil was used as standard, and spectra fitting was carried out using the Wissel NORMOS routine. The spectogram was fitted with a doublet and a sextet subspectra with implemented Gaussian distribution of hyperfine field.

**HRTEM** High Resolution Transmission Electron Microscopy (HRTEM) was done on a JEOL JEM 2200FS operated at 200 kV with Schottky emitter using bright field (BF) mode, scanning transmission mode (HRSTEM), energy electron loss spectroscopy (EELS) and energy dispersed (EDS) mapping. The samples were obtained by dropping the toluene dispersion on a coated copper grid.

**SAXS** Small-angle X-ray scattering (SAXS) measurements were performed at the Gallium Anode Low-Angle X-ray Instrument (GALAXI) at JCNS, Forschungszentrum Jülich, Germany. Dilute NP dispersions in toluene ($c = 7\text{ mg/mL}$) were sealed in quartz capillaries and measured using a wavelength of $\lambda = 1.3414$ Å at two detector distances of 853 and 3548 mm.
The data were recorded on a Pilatus 1M detector, radially averaged and normalized to absolute units using FEP 1400 Å ($d = 0.35$ mm) as reference material and toluene background subtraction.

**SANSPOL**  Half-polarized small-angle neutron scattering (SANSPOL) was performed at the D33 instrument\textsuperscript{58} at ILL, Grenoble, France. Dilute NPs dispersions in $d_8$-toluene ($c = 7$ mg/mL) were measured at ambient temperature and under applied horizontal magnetic fields up to 1.2 T. Two instrument configurations were used with detector distances of 2.5 m and 13.4 m and collimations of 5.3 m and 12.8 m, respectively. The incident neutron beam was polarized using a V-shaped supermirror polarizer. The efficiencies of the flipper and supermirror were 0.98 and 0.94, respectively, at a neutron wavelength of 6 Å. Data reduction was performed using the GRASP software\textsuperscript{59}.

**POLARIS**  Full polarized small-angle neutron scattering (POLARIS) was done at the KWS-1 instrument\textsuperscript{60} operated by Jülich Centre for Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany. A dilute non-interacting NP dispersion in $d_8$-toluene was measured at ambient temperature and under applied horizontal magnetic fields up to 1.2 T. Measurements were performed at the detector distance of 8 m with a collimation of 8 m. The incident neutron beam (of 5 Å neutron wavelength) was polarized using a supermirror polarizer and the polarization of the scattered neutrons was analyzed using a polarized $^3$He spin filter cell. The incident super mirror gave 0.905 for the wavelength of the experiment with a 0.998 flipper efficiency. The incident beam polarization in this case was slightly reduced by a beam depolarization which was later determined to come from the sample slits. At this time off-line polarized $^3$He cells were used for KWS-1, therefore two different cells named Jimmy and Willy with 8.9 and 10.8 bar cm of $^3$He, respectively, were used\textsuperscript{61}. Both cells provided 100 ($\pm 4$) hours on beam lifetimes. Jimmy and Willy gave starting/ending unpolarized neutron transmissions of about 0.21 down to 0.17 and 0.20 going down to 0.14 after a typical half day of use corresponding to initial to final polarization...
analyzing powers of 0.984 down to 0.976 and 0.995 down to 0.992 for each cell, respectively. Four cell exchanges between the two cells were made during the course of the experiment to maintain good transmission performance.

Data reduction and spin-leakage corrections due to polarization inefficiencies as well as solvent subtraction were performed using qtiKWS software, and extraction of the azimuthal intensities was carried out using GRASP software.

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Author contributions

D.H. and S.D. conceived the study. D.Z. synthesized and precharacterized the sample. D.Z., L.B., E.B., Z.S., A.F. and D.H. carried out the experiments. D.N. performed and analyzed Mössbauer spectroscopy. D.Z., L.B., A.F., D.H., and S.D. performed analysis. D.Z., D.H., and S.D. wrote the paper. All authors commented on the manuscript.
**Competing interests**

The authors declare no competing financial interests.

**Additional Information**

Supplementary information is available in the online version of the paper. Correspondence should be addressed to Sabrina Disch.

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