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Magnetization reversal in Nd-Fe-B based nanocomposites as seen by magnetic small-angle neutron scattering

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We have studied the magnetization-reversal process of a Nd2Fe14B/Fe3B nanocomposite using small-angle neutron scattering. Based on the computation of the autocorrelation function of the spin misalignment, we have estimated the characteristic size $l_C$ of spin inhomogeneities around the Nd2Fe14B nanoparticles. The quantity $l_C$ approaches a constant value of about 12.5 nm (~average Nd2Fe14B particle radius) at 14 T and takes on a maximum value of about 18.5 nm at the coercive field of $-0.55$ T. The field dependence of $l_C$ can be described by a model that takes into account the convolution relationship between the nuclear and the magnetic microstructure.

Rare-earth metals are key ingredients of countless technological products, and the global demand for these materials has continuously increased during the last decades. In recent times, geopolitical and strategic issues as well as the danger of a strained supply chain have caused the rare-earth elements to become the focus of attention of a wider public, and the term “critical raw materials” was coined for them.1

One of the most important fields of application of rare-earth metals are in high-performance permanent magnets, which are used, e.g., in electronics devices or motors. Nowadays, permanent magnets made out of the rare-earth transition-metal compounds Nd-Fe-B or Sm-Co possess a worldwide market share of about 65%.2 Essentially, the rare-earth atoms in such alloys provide a high magnetic anisotropy, which results in broad hysteresis loops with intrinsic coercivities of the order of a few tesla, and the 3d transition-metal atoms give rise to a large magnetization along with a relatively high Curie temperature and a remanence of up to 1.5 T.3–8

Given that commercial-grade sintered Nd-Fe-B magnets are rare-earth rich7 and in view of the above sketched situation, it is one of the central problems in the field of magnetic materials to search for strategies to reduce the amount of rare-earth elements by maintaining at the same time the magnets’ performance.3 Hard magnetic nanocomposites9 are considered to be promising candidates for future permanent-magnet applications.10 The microstructure of these materials consists of a dispersion of hard magnetic Nd-Fe-B or Sm-Co based nanoparticles that are embedded in and magnetically exchange-coupled to a soft magnetic transition-metal rich phase. As a consequence of the nanocomposites’ reduced rare-earth content, production costs may be significantly lowered as compared to their sintered counterparts. Due to the technological relevance of such functional magnetic nanomaterials, a better understanding of the microstructure-property relationship is crucial, in particular, the magnetization-reversal process and the role of the thickness of the intergranular soft phase for magnetic hardening.10–14

In the present experiment, we have scrutinized the characteristic magnetic length scales associated with spin disorder during the magnetization-reversal process in a Nd2Fe14B/Fe3B nanocomposite. For this purpose, we have employed the technique of magnetic small-angle neutron scattering (SANS), which provides access to bulk properties on the interesting nanometer length scale.15–28

The SANS experiment was performed at the instrument Quokka at the Bragg Institute, ANSTO, Australia.29 We used unpolarized incident neutrons with a mean wavelength of $\lambda = 5.1$ Å and with a bandwidth of $\Delta \lambda / \lambda = 10\%$ (FWHM). The external magnetic field was provided by a superconducting magnet which had the field direction perpendicular to the wave vector of the incoming neutron beam ($k_0 \perp H \parallel e_z$) and in the plane of the ribbon sample (for sample details, see below). Using three sample-to-detector distances, this setup results in an accessible $q$-range of $0.03$ nm$^{-1} \leq q \leq 1.5$ nm$^{-1}$. SANS raw data were corrected for background scattering and detector efficiency. The autocorrelation function of the spin misalignment $C(r)$ was computed by means of the Fourier-transformation technique within the interval $r_{\text{min}} = 2\pi / q_{\text{max}} \approx 4$ nm and $r_{\text{max}} = \pi / q_{\text{min}} \approx 100$ nm. In order to reduce termination effects in the numerical calculation of $C(r)$, the

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experimental SANS data beyond \( q_{\text{max}} \) were extrapolated to infinity using Porod’s law, \( \frac{\Delta \Sigma}{d\Omega} \propto q^{-4} \), and the extrapolation from \( q_{\text{min}} \) to \( q = 0 \) was carried out using different schemes (linear and constant).

The sample under study was a nanocrystalline hard magnetic composite, which was synthesized by the melt-spinning technique followed by rapid thermal annealing (10 min at 650 °C). The nominal composition of the amorphous precursor material was \( \text{Nd}_2\text{Fe}_{14}\text{B} \). As reported in Ref. 30, the microalloying of \( \text{Cr} \) supports the formation of the hard magnetic \( 2-14 \)-phase and retards the formation of crystallization products with magnetically unfavorable properties. The two-phase microstructure of the nanocomposite consists of hard magnetic \( \text{Nd}_2\text{Fe}_{14}\text{B} \) and soft magnetic \( \text{Fe}_3\text{B} \) crystallites. Specimens that are prepared under such annealing conditions typically contain a \( \text{Nd}_2\text{Fe}_{14}\text{B} \) particle volume fraction of about 45%. Scanning and energy-filtered transmission electron microscopy was employed for the estimation of the respective average crystallite sizes: The average \( \text{Nd}_2\text{Fe}_{14}\text{B} \) (\( \text{Fe}_3\text{B} \)) particle size is about 22 nm (29 nm). For the SANS experiments, several \( \text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B} \) ribbons (thickness: 20 \( \mu \text{m} \); width: 2 mm; length: 10 mm) were stacked and arranged next to each other in order to completely cover the neutron aperture. Neutron absorption was reduced by employing low-capturing \( ^{11}\text{B} \) for the synthesis of the SANS sample.

For the above specified scattering geometry, the elastic SANS cross section \( d\Sigma/d\Omega \) at momentum-transfer vector \( q \) reads

\[
\frac{d\Sigma}{d\Omega}(q) = \frac{8\pi^3}{V} b_H q^2 (|N|^2 + |M_z|^2 + |M_y|^2) \cos^2 \theta + |M_z|^2 \sin^2 \theta - (M_y M_x^* + M_y^* M_x) \sin \theta \cos \theta, \tag{1}
\]

where \( V \) is the scattering volume, \( b_H = 2.9 \times 10^8 \text{A}^{-1}\text{m}^{-1} \), the superscript “c” refers to the complex-conjugated quantity, and \( N(q) \) and \( M(q) = [M_x(q), M_y(q), M_z(q)] \) represent, respectively, the nuclear and magnetic scattering amplitudes. In the small-angle limit \( q \approx q_0 = 0, \sin \theta = \cos \theta \), the angle \( \theta \) is measured relative to \( \mathbf{e} \).

Figure 1 displays \( d\Sigma/d\Omega \) of the \( \text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B} \) nanocomposite at 300 K and at selected applied magnetic fields \( H \). The SANS experiments were performed by first applying a large positive field and then reducing the field to the experimental value, following the course of the hysteresis loop (see inset in Fig. 1). On decreasing the field starting from a value of \( \mu_0 H = +10 \text{T} \) (close to saturation), we observe the emergence of long-range magnetization fluctuations at the smallest momentum transfers. The total nuclear and magnetic \( d\Sigma/d\Omega \) continues increasing up to a negative field value close to the experimental coercive field of \( \mu_0 H_c = -0.55 \text{T} \). Further increase of \( H \) towards more negative values results in a suppression of magnetization fluctuations and in a concomitant decrease of \( d\Sigma/d\Omega \) (open symbols in Fig. 1).

It is the central aim of this study to quantify the length scale and the applied-field dependence of spin-misalignment fluctuations during magnetization reversal in Nd-Fe-B based nanocomposites. From this point of view, and in order to compute the associated correlation function of the spin misalignment, it would be advantageous to separate [in Eq. (1)] the spin-misalignment scattering from the scattering at complete magnetic saturation, where \( d\Sigma/d\Omega = \frac{8\pi^3}{V} (|N|^2 + |M|^2 \sin^2 \theta) \).

For a magnetic two-phase particle-matrix system close to saturation \( |M_z|^2 \propto (\Delta M)^2 \), where \( \Delta M \) is the jump in the magnitude of the magnetization at the interface between the particles and the matrix. This jump is quite small for our nanocomposite, \( \mu_0 \Delta M \approx 0.01 \text{T} \), suggesting that the scattering due to \( |M_z|^2 \) correlations is much smaller than the nuclear SANS. Since \( |N|^2 \) is field-independent and in view of the strong field dependence of \( d\Sigma/d\Omega \) (compare Fig. 1), it is obvious that the dominating contribution to \( d\Sigma/d\Omega \) is due to transversal spin misalignment [compare Eq. (1)]. In order to obtain the associated spin-misalignment SANS cross section

\[
\frac{d\Sigma_M}{d\Omega}(q) = \frac{8\pi^3}{V} b_H q^2 (|M_z|^2 + |M_y|^2 \cos^2 \theta - (M_y M_x^* + M_y^* M_x) \sin \theta \cos \theta), \tag{2}
\]

we assume in the following that the measured \( d\Sigma/d\Omega \) at the highest field of 10 T represents to a good approximation the scattering at saturation (compare magnetization curve in Fig. 1). This assumption is supported (besides the \( \sigma(H) \) data) by the finding that (1) the total \( d\Sigma/d\Omega \) at 10 T exhibits an isotropic intensity distribution (data not shown), in other words, \( d\Sigma/d\Omega \) at 10 T is essentially of nuclear origin; and (2) the total \( d\Sigma/d\Omega \) at 10 T can (asymptotically) be described by a power-law \( d\Sigma/d\Omega \propto q^{-4} \), as is characteristic for particle scattering (compare Fig. 2). Subtraction of the (one-dimensional) 10 T data set from the \( d\Sigma/d\Omega \) at the lower fields then yields \( d\Sigma_M/d\Omega \).

The resulting data for \( d\Sigma_M/d\Omega \) are shown in Fig. 3. Note also that as a consequence of the smallness of the \( M_z \) scattering (relative to the transversal contributions), the cross term \( M_y M_x \) in \( d\Sigma_M/d\Omega \) may be much smaller than the other terms. The magnitude of \( d\Sigma_M/d\Omega \) is comparable to the
magnitude of the total $d\Sigma/d\Omega$ but, remarkably, $d\Sigma_M/d\Omega$ exhibits a significantly different shape than $d\Sigma/d\Omega$. In particular, the shoulder in $d\Sigma/d\Omega$ at $q \approx 0.2$ nm$^{-1}$ (compare Fig. 1) is absent in $d\Sigma_M/d\Omega$. Possible origins for the shoulder in $d\Sigma/d\Omega$ are interparticle interferences and/or diffusion zones around the particles.\(^\text{15}\) Between $+8$ T (data not shown) and $-0.55$ T, $d\Sigma_M/d\Omega$ at the smallest $q$ increases by a factor of about 180. The asymptotic power-law exponent $n$ in $d\Sigma_M/d\Omega = K/q^n$ is at all fields investigated significantly larger than the value $n = 4$ (compare Fig. 2). These findings support the notion of dominant spin-misalignment SANS, which may give rise to power laws as steep as $d\Sigma_M/d\Omega \propto q^{-5}$ (Refs. 32 and 35).

The correlation function of the spin misalignment $C(r)$ was computed from the $d\Sigma_M/d\Omega$ data via\(^\text{36,37}\)

$$C(r) = \frac{\pi}{r} \int_0^\infty \frac{d\Sigma_M}{d\Omega} \sin(qr) \, q \, dq,$$

where $\pi$ is a numerical constant; note that for the determination of the spin-misalignment length $l_C$ the absolute value of $\pi$ is not relevant. The field-dependent $C(r)$ calculated according to Eq. (3) are shown in Fig. 4(a) on a semi-logarithmic scale. In agreement with the previous discussion, it is clearly seen that the spin-misalignment correlations do not decay exponentially, which would yield (asymptotically) $d\Sigma_M/d\Omega \propto q^{-4}$ (compare Fig. 2). From the $C(r)$ data, we determined the spin-misalignment length $l_C(H)$ [see Fig. 4(b)]; $l_C$ at a particular field was identified with the $r$ value for which the correlation function has decayed to $\exp(-1)$ of its value at the origin $C(0)$, where the latter quantity was estimated by extrapolating $C(r)$ from $r_{\text{min}}$ to $r = 0$ according to $C(r) \approx C(0) - ar^2$ [dotted line in Fig. 4(a)]. The neglect of a linear term in the above small-$r$ expansion of $C(r)$ is consistent with the absence of a sharp interface in the magnetic microstructure (scattering from infinitely extended magnetization profiles).\(^\text{34}\)

The length $l_C$ is a measure of the size of gradients (around lattice imperfections) in the spin microstructure.\(^\text{32,35,38}\) In the present case, it is expected that $l_C$ describes the spatial extent of such magnetization inhomogeneities, mainly within the soft magnetic Fe$_3$B grains, that are caused by the jump in the magnetic materials parameters (exchange constant, magnetization, direction, and magnitude of magnetic anisotropy) at the interface between the Nd$_2$Fe$_{14}$B particles and the surrounding Fe$_3$B crystallites [see inset in Fig. 4(b)].\(^\text{39}\) The local perturbation of the magnetization at the phase boundary is transmitted by means of the exchange interaction into the soft phase.\(^\text{38}\) As can be seen in Fig. 4(b), $l_C$ approaches a constant value of about 12.5 nm at the largest positive fields and increases with decreasing applied field to take on a maximum value of about 18.5 nm at the experimental coercive field of $\mu_0H_c = -0.55$ T. Further increase of $H$ towards more negative values results again in a decrease of $l_C$ towards $\sim 12.5$ nm.

The difference between the $l_C(H)$ data obtained at D11 (ILL) and at Quokka (ANSTO) is related to the fact that at D11 the incoming neutron wave vector was parallel to the applied magnetic field, whereas $\mathbf{k}_0 \perp \mathbf{H}$ at Quokka (and KWS 1). This entails a different SANS cross section and results in the slightly different values for $l_C$.\(^\text{40}\) On top of that, one has to take into account the different demagnetizing-field effects for both geometries.

For such a scenario, it was shown that the following expression describes the field dependence of $l_C$:\(^\text{32,35}\)

$$l_C(H) = \mathcal{L} + l_H(H),$$

where the field-independent parameter $\mathcal{L}$ is of the order of the particle size and $l_H = \sqrt{2A/(\mu_0M_iH_i)}$ denotes the exchange length of the field with $A$ the exchange constant and $H_i$ the internal magnetic field. Note that $\mathcal{L} \approx R$ for spherical particles (of radius $R$) with a uniform magnetic anisotropy field.\(^\text{35}\) Equation (4) embodies the convolution relationship between the magnetic anisotropy field microstructure ($\mathcal{L}$) and the magnetic microstructure ($l_H$).

However, due to irregularities in the shape of the ribbon sample and due to nonzero volume divergences of the magnetization, the precise value of the internal field $H_i$ in Eq. (4) is not known. Since in the SANS experiments the applied field $H$ is the control parameter, we set $H = H + H^*$ in Eq. (4) in order to compare the experimental $l_C(H)$ data with the

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**FIG. 2.** Field dependence of the power-law exponent $n$ which was determined by a fit of, respectively, $d\Sigma/d\Omega$ (Fig. 1) and $d\Sigma_M/d\Omega$ (Fig. 3) to $K/q^n$ ($K$ constant). In both cases, the fit was restricted to the interval $0.6 \text{ nm}^{-1} \leq q \leq 0.7 \text{ nm}^{-1}$. Solid horizontal line: $n = 4$.

**FIG. 3.** Applied-field dependence of the spin-misalignment SANS cross section $d\Sigma_M/d\Omega$ of nanocrystalline Nd$_2$Fe$_{14}$B/Fe$_3$B ($T = 300$ K). Solid circles ($\bullet$): $H$ values (in Tesla) decrease from bottom to top: 6, 1, $-0.25$, $-0.55$; ($\square$): $-1$ T; ($\triangle$): $-3$ T. Dashed line: $d\Sigma_M/d\Omega \propto q^{-5.5}$. 

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theoretical prediction; \( H^{*} \) is expected to model the influence of the magnetodipolar field and of the magnetic anisotropy. The solid line in Fig. 4(b) is the result of a fit of the spin-misalignment length \( l_c \). Solid line: fit of the data to \( l_c(H) = \mathcal{L} + \sqrt{2A/[\mu_0 M_s(H + H^*)]} \), where \( \mathcal{L} = 10.9 \text{ nm} \) and \( \mu_0 H^* = +0.60 \text{ T} \) are treated as adjustable parameters; the quantities \( A = 12.5 \text{ pJ/m} \) and \( \mu_0 M_s \) are held fixed. For comparison, \( l_c(H) \) data obtained at the SANS instruments KWS 1 (JCPNS, Germany) and D11 (ILL, France) are included. Dotted horizontal line: average Nd\(_2\)Fe\(_{14}\)B particle radius \( R = 11 \text{ nm} \). Dotted vertical line: experimental coercive field \( \mu_0 H_c = -0.55 \text{ T} \).

In the remanent state, the size of gradients in the magnetization within the soft magnetic Fe\(_3\)B phase is estimated to about 5–6 nm. A modified version of Eq. (4) provides an excellent description of the field dependence of the spin-misalignment correlations.

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**FIG. 4.** (a) Field dependence of the correlation function \( C(r) \) of the spin misalignment of nanocrystalline Nd\(_2\)Fe\(_{14}\)B/Fe\(_3\)B (semi-logarithmic scale). The field values follow the course of a hysteresis loop, starting from a large positive field and then reducing the field to negative values. Dotted line (extrapolating the 6 T data to \( r = 0 \)): \( C(r) = 4.58 - 0.043 r^2 \). (b) Field dependence of the spin-misalignment length \( l_c \). Solid line: fit of the data to \( l_c(H) = \mathcal{L} + \sqrt{2A/[\mu_0 M_s(H + H^*)]} \), where \( \mathcal{L} = 10.9 \text{ nm} \) and \( \mu_0 H^* = +0.60 \text{ T} \) are treated as adjustable parameters; the quantities \( A = 12.5 \text{ pJ/m} \) and \( \mu_0 M_s \) are held fixed. For comparison, \( l_c(H) \) data obtained at the SANS instruments KWS 1 (JCPNS, Germany) and D11 (ILL, France) are included. Dotted horizontal line: average Nd\(_2\)Fe\(_{14}\)B particle radius \( R = 11 \text{ nm} \). Dotted vertical line: experimental coercive field \( \mu_0 H_c = -0.55 \text{ T} \). In the remanent state, the size of gradients in the magnetization within the soft magnetic Fe\(_3\)B phase is estimated to about 5–6 nm. A modified version of Eq. (4) provides an excellent description of the field dependence of the spin-misalignment correlations.

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