Nanoscale measurement of giant saturation magnetization in $\alpha''$-$\text{Fe}_{16}\text{N}_2$ by electron energy-loss magnetic chiral dichroism

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ABSTRACT

Metastable $\alpha''$-$\text{Fe}_{16}\text{N}_2$ thin films were reported to have a giant saturation magnetization of above 2200 emu/cm$^3$ in 1972 and have been considered as candidates for next-generation rare-earth-free permanent magnetic materials. However, their magnetic properties have not been confirmed unequivocally. As a result of the limited spatial resolution of most magnetic characterization techniques, it is challenging to measure the saturation magnetization of the $\alpha''$-$\text{Fe}_{16}\text{N}_2$ phase, as it is often mixed with the parent $\alpha'$-$\text{Fe}_2\text{N}$ phase in thin films. Here, we use electron energy-loss magnetic chiral dichroism (EMCD), aberration-corrected transmission electron microscopy, X-ray diffraction and macroscopic magnetic measurements to study $\alpha''$-$\text{Fe}_{16}\text{N}_2$ (containing ordered N atoms) and $\alpha'$-$\text{Fe}_2\text{N}$ (containing disordered N atoms). The ratio of saturation magnetization in $\alpha''$-$\text{Fe}_{16}\text{N}_2$ to that in $\alpha'$-$\text{Fe}_2\text{N}$ is determined to be 1.31 ± 0.10 from quantitative EMCD measurements and dynamical diffraction calculations, confirming the giant saturation magnetization of $\alpha''$-$\text{Fe}_{16}\text{N}_2$. Crystallographic information is also obtained about the two phases, which are mixed on the nanoscale.

1. Introduction

Permanent magnetic materials are of great importance for applications that include information technology and energy conversion. Rare-earth-free permanent magnetic materials are currently attracting particular attention due to the limited availability of rare earth elements. According to the Slater-Pauling curve and classical cruise magnetic theory [1], the magnetic material with the highest saturation magnetization ($M_s$) is expected to be $\text{Fe}_5\text{Co}_{30}$, with a saturation magnetic induction of 2.45 T. However, in 1972 Kim and Takahashi reported an $M_s$ value of above 2200 emu/cm$^3$ (equivalent to ~2.76 T) in $\alpha''$-$\text{Fe}_{16}\text{N}_2$ thin films using a torque magnetometer, a magnetic balance and a torsion pendulum magnetometer [2]. Sogita et al. measured an $M_s$ value for $\alpha''$-$\text{Fe}_{16}\text{N}_2$ thin films that had been grown using molecular beam epitaxy (MBE) of 2308 emu/cm$^3$ using a vibrating sample magnetometer (VSM) and Mössbauer spectroscopy [3]. Sun et al. further confirmed an $M_s$ value for $\alpha''$-$\text{Fe}_{16}\text{N}_2$ films grown using facing target sputtering of ~2200 emu/cm$^3$ using VSM [4]. Wang et al. verified an $M_s$ value for $\text{Fe}_2\text{N}$ thin films that had an ordering parameter of ~0.35 of 2133 emu/cm$^3$ using VSM and claimed, based on X-ray magnetic circular dichroism (XMCD) measurements, that the observed giant $M_s$ value was correlated with the formation of highly localized 3d electron states [5]. In contrast, Takahashi et al. measured an $M_s$ value for $\alpha''$-$\text{Fe}_{16}\text{N}_2$ films of no more than 1776 emu/cm$^3$ using VSM and conversion electron Mössbauer spectra, which is slightly higher than that of pure Fe [6]. Sakuma determined a value for the magnetic moment of $\alpha''$-$\text{Fe}_{16}\text{N}_2$ of only 1731 emu/cm$^3$ using spin-polarized band structure calculations [7]. Li et al. measured the magnetic moment of $\alpha''$-$\text{Fe}_{16}\text{N}_2$ to be 1850 emu/cm$^3$ using VSM and Mössbauer spectroscopy [8]. Accordingly, although $\alpha''$-$\text{Fe}_{16}\text{N}_2$ is a candidate for use as a rare-earth-free permanent magnetic material [9], there is still uncertainty about its value of $M_s$ [10]. This uncertainty results from the difficulty of phase identification, as $\alpha''$-$\text{Fe}_{16}\text{N}_2$ is readily mixed with the parent $\alpha'$-$\text{Fe}_2\text{N}$ phase in thin films, in combination with the fact that the spatial...
resolution of most magnetic characterization methods is not sufficient to distinguish pure α'-Fe₅N₂ from the parent α'-Fe₃N phase on the nanometer scale.

The technique of electron energy-loss magnetic chiral dichroism (EMCD) [11] in the transmission electron microscope (TEM) offers magnetic characterization with high spatial resolution and therefore a solution to these challenges. EMCD is similar to XMCD, in that it permits the quantitative element-selective determination of spin and orbital magnetic moments in crystalline materials from spectra measured at core-loss edges [12–16]. When compared with XMCD, EMCD offers higher spatial resolution, now reaching the atomic scale, in part due to the short de Broglie wavelength and penetration of high energy electrons in the TEM [17–19]. By combining scanning TEM (STEM) with electron energy-loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy [20–26], structural, compositional and bonding information can be correlated with local spin configurations measured from the very same region [27–30]. In our previous study, the influence of cation ratio and order on local magnetic coupling in ordered and disordered phases of Sr₂Fe₁₋ₓReₓO₃ that were mixed on the nanoscale was investigated [27]. Here, we use a similar approach to study Fe-N that contains mixed phases of α'-Fe₅N₂ and α'-Fe₃N. We record structural and magnetic information from both phases in epitaxial Fe-N thin films. With the help of dynamical diffraction calculations, we use the EMCD measurements to quantitatively determine the ratio of α' in α'-Fe₅N₂ to that in α'-Fe₃N, thereby experimentally confirming the giant saturation magnetization of α'-Fe₅N₂.

2. Materials and methods

Fe-N thin films were grown using MBE with accurate control over their thickness and composition [31] and sizes of 5 mm × 5 mm. Two types of thin films were prepared: one containing mixed phases of α'-Fe₅N and α'-Fe₃N₂ and the other containing primarily α'-Fe₃N. For the films with mixed phases, a 3 nm thick seed layer of α-Fe was first grown on single crystaline MgAl₂O₄ (MAO) (001). A 100 nm thick α'-Fe₃N film was then grown epitaxially, followed by a 4 nm thick Ti capping layer to prevent surface oxidation, as confirmed using X-ray photoelectron spectroscopy. No ordering (i.e., a phase transformation from α'-Fe₅N to α'-Fe₅N₂) was achieved by furnace annealing at 150°C for 50 h. Finally, a 35 nm thick SiO₂ protection layer was deposited using radio frequency (RF) sputtering. For the α'-Fe₅N-dominated films, a 3 nm thick α-Fe and an 85 nm thick α'-Fe₅N layer were grown epitaxially on single crystaline MAO (001) and covered by a 4 nm thick Ti capping layer. A 35 nm thick SiO₂ protection layer was then deposited using RF sputtering.

α'-Fe₅N and α'-Fe₁₆N₂ have tetragonal structures with lattice parameters of a = b = 2.86 Å, c = 3.15 Å and a = b = 5.72 Å, c = 6.29 Å, respectively. The N atoms in blue are distributed randomly in α'-Fe₅N, as shown in Fig. 1a. In contrast, in ordered metastable α'-Fe₅N₂, N atoms in blue occupy half of the octahedral interstices [32], while Fe atoms (Fe I in red, Fe II in green and Fe III in yellow) occupy three different sites that are designated 4d, 8h and 4c, as shown in Fig. 1b. The site occupancy ratio of Fe I (4d), Fe II (8h) and Fe III (4c) is 1: 2: 1, with four Fe atoms on the 4d site, eight Fe atoms on the 8h site and four Fe atoms on the 4c site [8].

X-ray diffraction (XRD) measurements were performed using a high power IP crystal X-ray R-Axis Spider diffractrometer. Magnetic hysteresis (M-H) loops were measured between −15,000 and 15,000 Oe at room temperature (RT) using a superconducting quantum interference device (SQUID) VSM from Quantum Design. Selected area electron diffraction (SAED) patterns, low magnification and dark-field (DF) TEM images were recorded on an FEI Tecnai G² 20 TEM operated at 200 kV. High-angle annular dark-field (HAADF) STEM imaging was performed at 300 kV on an FEI Titan Cubed Themis G2 300 TEM, which is equipped with a double spherical aberration corrector and has a spatial resolution of 0.06 nm in STEM mode. EELS and EMCD spectra were recorded under parallel beam illumination conditions at 300 kV on an FEI Titan 80–300 TEM equipped with a post column Gatan Tridem imaging filter with an energy resolution of ~0.7 eV, a beam size of ~80 nm or less, an incident beam convergence semi-angle of ~0.3 mrad and a collection semi-angle of ~2.5 mrad. Nanodiffraction experiments were performed at 300 kV on an FEI Titan 80–300 TEM using a beam size of ~2 nm [33]. EELS and EMCD experiments under nanobeam illumination conditions were performed at 300 kV on an FEI Titan Cubed Themis G2 300 TEM equipped with a Gatan Quantum imaging filter with an energy resolution of ~1 eV, a beam size of ~2 nm or more and convergence and collection semi-angles of ~0.92 mrad and ~1.98 mrad, respectively. Each EMCD experiment was performed in an optimal two-beam diffraction condition (2BC) based on theoretical dynamical diffraction calculations performed using software that can realize accurate summation over Bloch waves and their plane wave components [34]. EMCD spectra were extracted from differences between pairs of normalized spectra taken at “+” and “−” Thales positions, while corresponding low-loss spectra were acquired under the same convergence and collection angles with the same detection aperture centered on the transmitted beam for estimating the sample thickness. Data processing of the spectra included pre-edge background subtraction, removal of plural scattering using Fourier ratio deconvolution and normalization by integration of the post-edge intensity.

3. Structural characterization of α'-Fe₅N and α'-Fe₁₆N₂

A TEM image and a corresponding SAED pattern of an 85 nm thick film of the α'-Fe₅N-dominant phase on MAO are shown in Figs 1c and 1f, respectively. The SAED pattern reveals an epitaxial MAO(100) // Fe(1 1 0)(001)//α'-Fe₅N(110)(001) orientation relationship, without any superlattice diffraction spots from ordered α'-Fe₅N₂. A TEM image and a SAED pattern of a 100 nm thick film of the mixed phases α'-Fe₅N and α'-Fe₃N₂ on MAO are shown in Figs 1d and 1g, respectively. The SAED pattern reveals superlattice diffraction spots originating from ordered α'-Fe₅N₂ and an epitaxial MAO(100)(001) // α-Fe₁₆N(100)(001)//α'-Fe₅N₁₆N₂(110)(001) orientation relationship. The (12) of α'-Fe₅N₂ superlattice diffraction spot, which is marked by a red circle, was used to form the DF image shown in Fig. 1e. In this image, nanosized α'-Fe₅N₂ regions can be seen to be distributed randomly in the film.

Fig. 2a shows an HAADF STEM image of Fe-N thin films that contain mixed phases viewed along the [100] zone axis of MAO. The image reveals the atomic structures of α'-Fe₅N₂, α'-Fe₃N₂, the Fe seed layer and the MAO substrate, with a perfect MAO(100)(001)//α-Fe₁₆N(100)(001) //α'-Fe₅N₁₆N₂(110)(001) epitaxial orientation relationship. A corresponding diffraction pattern recorded from the MAO substrate is shown as an inset. Regions of α'-Fe₅N₁₆N₂, which are marked by white dashed boxes, are contained within the parent α'-Fe₅N phase. Figs. 2b and c show magnified HAADF STEM images of α'-Fe₅N and α'-Fe₃N₂, respectively. The atomic number (Z) contrast of each column in α'-Fe₅N is almost identical, since the N atoms are distributed randomly. In comparison, there is a modulation of the Z contrast of the columns in α'-Fe₁₆N₂ due to the ordered arrangement of N atoms. The appearance of superlattice diffraction spots originating from ordered α'-Fe₅N₁₆N₂ is visible in the nanodiffraction patterns shown as an inset to Fig. 2c, while there are no superlattice spots in corresponding nanodiffraction patterns of α'-Fe₅N shown as an inset to Fig. 2b.

Supplementary Figs. S1a and S1b show EEL spectra recorded from α'-Fe₅N-dominant and mixed phase films, respectively. The spectra confirm the absence of significant oxidation of both samples, as there is no detectable O K edge.

Figs. 3a and b show raw XRD patterns recorded from the α'-Fe₅N-dominant and mixed phase films, respectively. The degree of N site ordering, D, can be determined from the integrated intensity ratio of the (002) and (004) peaks after background subtraction and peak identification by using the expression [5]
Fig. 1. (a) Crystallographic structure of α'-Fe₈N with randomly distributed N atoms (in blue, while Fe in brown). (b) Crystallographic structure of α''-Fe₁₆N₂ with ordered N atoms (in blue) occupying half of the octahedral interstices and three Fe atoms (Fe I in red, Fe II in brown, and Fe III in yellow) occupying different sites, which are designated 4d, 8h, and 4c. (c) TEM image and (f) corresponding SAED pattern of an 85 nm thick film of the α'-Fe₈N-dominant phase on a MgAl₂O₄ (MAO) substrate (where MAO in white, α-Fe in blue, and α'-Fe₈N in yellow). The SAED pattern reveals an epitaxial MAO[100](001)//α-Fe[110](001)//α'-Fe₈N[110](001) orientation relationship without any superlattice diffraction spots of ordered α''-Fe₁₆N₂. (d) TEM image and (g) corresponding SAED pattern of a 100 nm thick film of mixed α'-Fe₈N and α''-Fe₁₆N₂ on MAO. The SAED pattern reveals superlattice spots of ordered α''-Fe₁₆N₂ (where MAO in white, α-Fe in blue, α'-Fe₈N in yellow, and α''-Fe₁₆N₂ in red) and an epitaxial MAO[100](001)//α-Fe[110](001)//α'-Fe₈N[110](001)//α''-Fe₁₆N₂[110](001) orientation relationship. The (112) α''-Fe₁₆N₂ superlattice spot marked by a red circle in (g) was used to form the dark-field TEM image shown in (e), which reveals nanosized α''-Fe₁₆N₂ regions distributed randomly in the film. The scale bars in (c), (d), and (e) are 50 nm, while those in (f) and (g) are 2 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. (a) HAADF STEM image of interfaces between the MgAl₂O₄ (MAO) substrate and the Fe-N thin films with mixed phases of α'-Fe₈N, α''-Fe₁₆N₂, and an Fe seed layer, revealing a perfect epitaxial MAO[100](001)//α-Fe[110](001)//α'-Fe₈N[110](001)//α''-Fe₁₆N₂[110](001) orientation relationship. A corresponding diffraction pattern from MAO is shown in the inset. Representative α''-Fe₁₆N₂ regions, which are marked by white dashed boxes, are contained within the parent α'-Fe₈N phase. (b) and (c) show HAADF STEM images and corresponding nanodiffraction patterns recorded from α'-Fe₈N and α''-Fe₁₆N₂, respectively. Superlattice diffraction spots are visible from ordered α''-Fe₁₆N₂, but not from α'-Fe₈N. The scale bars are 2 nm in (a) and 0.5 nm in (b) and (c).
4.2. Saturation magnetization determination by nanoscale EMCD measurements

According to sum rules [15, 16], the total magnetic moment $\langle \mu \rangle$ can be determined from experimental EEL spectra $S_+$ and $S_-$ recorded at positions $^+^+$ and $^--$, respectively (as shown in Fig. 4), taking into account the dynamical diffraction coefficients $K$. Assuming that the magnetic dipole term $T_d$ is negligible in the pseudo-cubic Fe-N system:

$$\langle \mu \rangle = -\mu_B (3S + 2S)$$

$$= -\mu_B \left( \frac{2N_0}{K} \frac{5}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE} \int_{-\Delta}^{\Delta} (S_+ + S_-) dE \right) + \frac{2N_0}{K} \left( \frac{3N_0}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE} \int_{-\Delta}^{\Delta} (S_+ + S_-) dE \right)$$

$$= -\mu_B \left( \frac{5}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE} + \frac{3N_0}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE} \right)$$

where $N_0$ is the number of holes, $\mu_B$ is the Bohr magneton and $S_+$ and $S_-$ are the ground state expectation values of spin and orbital moment, respectively. The values of $N_0$ for $\alpha'$-Fe$_{28}$N and $\alpha''$-Fe$_{18}$N$_2$ are equal because they have the same chemical valence. The ratio between the total magnetic moment of $\alpha'$-Fe$_{28}$N and $\alpha''$-Fe$_{18}$N$_2$, which represents the ratio between the $M_s$ values of $\alpha'$-Fe$_{28}$N and $\alpha''$-Fe$_{18}$N$_2$, can be written in the form

$$\frac{\langle \mu \rangle}{\langle \mu \rangle_{\alpha''-Fe_{18}N_2}} = \frac{\int_{-\Delta}^{\Delta} (S_+ - S_-) dE + 4 \int_{-\Delta}^{\Delta} (S_+ - S_-) dE}{\int_{-\Delta}^{\Delta} (S_+ - S_-) dE} = \frac{\frac{5}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE} + \frac{3N_0}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE}}{\frac{5}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE} + \frac{3N_0}{\int_{-2\Delta}^{2\Delta} (S_+ - S_-) dE}}$$

$$\frac{M_s}{M_s_{\alpha''-Fe_{18}N_2}} = \frac{\int_{-\Delta}^{\Delta} (S_+ - S_-) dE + 4 \int_{-\Delta}^{\Delta} (S_+ - S_-) dE}{\int_{-\Delta}^{\Delta} (S_+ - S_-) dE}$$

Since the $M_s$ value of $\alpha'$-Fe$_{28}$N has been determined accurately in
Fig. 4. (a) Calculated thickness-dependent dynamical diffraction coefficients for $\alpha'$-Fe$_8$N (in blue) and $\alpha''$-Fe$_{16}$N$_2$ (in red), the relevant optimal thickness window for EMCD experiment is shadowed by blue and red, respectively. The calculations were performed for $\alpha'$-Fe$_8$N in a two beam condition with $(110)$ systematic reflections excited and for $\alpha''$-Fe$_{16}$N$_2$ in a two beam condition with $(220)$ systematic reflections excited. Distributions of relative dynamical diffraction coefficients for (b) 50-nm-thick $\alpha'$-Fe$_8$N and (c) 40-nm-thick $\alpha''$-Fe$_{16}$N$_2$. Optimal positive and negative positions of the detection aperture in the Thales circle in the diffraction plane are marked “+” and “−”, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Previous studies [5, 35], the ratio $(\mu)_{\alpha'-Fe_{8}N}/(\mu)_{\alpha''-Fe_{16}N_{2}}$ can be used to infer $M_s$ for $\alpha''$-Fe$_{16}$N$_2$.

In order to calculate the coefficients $K$, dynamical diffraction calculations were performed for a 2BC for $\alpha'$-Fe$_8$N with $(110)$ systematic reflections excited and for a 2BC for $\alpha''$-Fe$_{16}$N$_2$ with $(220)$ systematic reflections excited. Fig. 4a shows the resulting thickness-dependent dynamical diffraction coefficients for $\alpha'$-Fe$_8$N and $\alpha''$-Fe$_{16}$N$_2$ obtained from $K$ values averaged within the Thales circles that are marked “+” and “−” in Figs 4b and 4c, respectively. Although the maximum value of $K$ was achieved in $\alpha'$-Fe$_8$N and $\alpha''$-Fe$_{16}$N$_2$ for a thickness of ~11 nm, it was found to be too sensitive to thickness variations between 5 and 20 nm. At the second maximum value, close to which the $K$ value is not that sensitive to thickness variations, the optimized thickness regions for $\alpha'$-Fe$_8$N and $\alpha''$-Fe$_{16}$N$_2$ were selected to be 45–50 nm and 38–44 nm, marked by red and blue frame in Fig. 4a, respectively.

Figs. 4b and c show representative calculated distributions of dynamical diffraction coefficients at 50-nm-thick $\alpha'$-Fe$_8$N and 40-nm-thick $\alpha''$-Fe$_{16}$N$_2$, respectively. Optimal “+” and “−” positions for the detection aperture are marked.

With the aid of the theoretical dynamical diffraction calculations, EMCD experiments were performed from a 49 nm thick $\alpha'$-Fe$_8$N phase in a 2BC with $(110)$ systematic reflections excited, as shown in the inset to Fig. 5a, while EMCD experiments were performed from a 43 nm thick $\alpha''$-Fe$_{16}$N$_2$ phase in a 2BC with $(220)$ systematic reflections excited, revealing the expected superlattice diffraction spots for $\alpha''$-Fe$_{16}$N$_2$, as shown in the inset to Fig. 5b. The $K$ values for 49-nm-thick $\alpha'$-Fe$_8$N and 43-nm-thick $\alpha''$-Fe$_{16}$N$_2$, averaged across the optimized aperture positions, are almost equivalent. Under these circumstances:
Supplementary Figs S2a and S2b show representative low-loss EEL spectra recorded from the α′-FeN-dominant and mixed phase films, respectively, including thickness information about the experimental areas. The magnetic field of the objective lens in the TEM was perpendicular to the plane of the cross-sectional TEM sample, which is equivalent to applying an external magnetic field to the Fe-N thin films in an in-plane direction. During the experiments, the Fe-N TEM samples were saturated magnetically in both TEM and STEM mode in a magnetic field of approximately 2 T, which is much larger than the saturation in-plane magnetic field of ~0.65 T, according to the macroscopic M-H loops shown in Figs 3c and d. Magnetic moments calculated from the measured EMCD spectra therefore correspond to the saturation magnetization of each material. Figs. 5a and b show normalized EMCD spectra plotted in blue and EEL spectra recorded at “+” (black) and “−” (red) positions for α′-FeN and α″-Fe16N2, respectively. According to Eq. (3), in order to compare the saturation magnetizations of α′-FeN and α″-Fe16N2 quantitatively, the EMCD spectra \( S \) were normalized by the intensities of the corresponding isotropic spectra \( \int_{L_{2}} \int_{L_{2}} (S_{\varphi} + S_{\varphi}) dE \), which were calculated by subtracting step functions from integrals of the \( L_{2} \) edges for the sums of the EEL spectra acquired at the “+” and “−” positions [36]. The details of the procedure are described in the Supplementary Fig. S3 and the related section. By making use of Eq. (4), Eq. (3) can be rewritten in the form

\[
\frac{M_{s}(\alpha′-\text{FeN})}{M_{s}(\alpha′-\text{FeN})} = \frac{M_{s}(\alpha′-\text{FeN})}{M_{s}(\alpha″-\text{FeN})} = 1.31 \times \frac{S_{\varphi} - S_{\varphi}}{S_{\varphi} - S_{\varphi}} \times 0.98
\]

(5)

where \( S_{\varphi} \) and \( S_{\varphi} \) refer to the EEL spectra \( S_{\varphi} \) and \( S_{\varphi} \) after normalization by the isotropic spectra \( \int_{L_{2}} \int_{L_{2}} (S_{\varphi} + S_{\varphi}) dE \).

The ratio of the \( M_{s} \) value of α″-Fe16N2 to that of α′-Fe16N2 was determined from the intensities of the \( L_{2} \) edge (from 704 to 712.2 eV) and the \( L_{2} \) edge (from 717.2 to 728 eV) in the normalized EMCD spectra \( (S_{\varphi} - S_{\varphi}) \) for both α′-FeN and α″-Fe16N2 in the form

\[
\frac{M_{s}(\alpha″-\text{Fe16N})}{M_{s}(\alpha″-\text{Fe16N})} = \frac{M_{s}(\alpha″-\text{Fe16N})}{M_{s}(\alpha″-\text{Fe16N})} = 1.31 \pm 0.10
\]

(6)

According to the sum rules [15, 16], the orbital to spin magnetic moment ratios \( m_{O}/m_{S} \) obtained from the EMCD spectra for α′-FeN and α″-Fe16N2 are 0.04 ± 0.01 and 0.09 ± 0.03, respectively.

Errors were estimated from the standard deviations of individual experimental measurements, noise in the spectra, standard deviations of the sample thickness measurements and uncertainty in the measured diffraction coefficient \( K \), following the method of error analysis presented in our previous work [13].

The \( M_{s} \) value of α′-FeN measured using SQUID-VSM, as shown in Fig. 5c, is 1712 emu/cm\(^2\), which is similar to results reported previously [5,35]. The \( M_{s} \) value of α″-Fe16N2\(_{2}\) is therefore inferred to be given by the expression

\[
M_{s}(\alpha″-\text{Fe16N}) = 1.31 \times M_{s}(\alpha″-\text{Fe16N}) = 1.31 \times 1712 \text{ emu/cm}^2
\]

\[
= 2243 \text{ emu/cm}^2
\]

which is close to the value of 2250 emu/cm\(^2\) reported in 1972 [2] and consistent with the value of 2362 emu/cm\(^2\) estimated from XRD and SQUID measurements in this paper. Giant magnetism in α″-Fe16N2 is therefore confirmed using EMCD.

5. Conclusion

Local structural and magnetic information about nanoscale phases of α′-FeN and α″-Fe16N2 in Fe-N thin films has been obtained experimentally using EMCD and analytical high-resolution TEM. Disordered α′-FeN and ordered α″-Fe16N2 phases have been distinguished from each other using nanodiffraction patterns and HAADF STEM imaging. Quantitative EMCD and dynamical diffraction calculations have been used to demonstrate that the \( M_{s} \) value of α″-Fe16N2 is 1.31 times that of α′-FeN. Based on the \( M_{s} \) value for α′-FeN determined using macroscopic SQUID-VSM measurements, the \( M_{s} \) value for α″-Fe16N2 is estimated to be 2243 emu/cm\(^2\), thereby experimentally confirming giant magnetism in α″-Fe16N2. Our approach provides important insight into structure-property relationships in α′-FeN and α″-Fe16N2 phases in Fe-N thin films on the nm scale. The same approach can be applied in future studies of other nanoscale magnetic materials.

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Supplementary materials

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References