Comment on "Origin of Surface Canting within Fe_3O_4 Nanoparticles"

In their Letter [1], Krycka *et al.* discuss the origin of near-surface spin canting within Fe_3O_4 nanoparticles by combining magnetic-energy minimization with polarized small-angle neutron scattering (SANS) data. We comment on the SANS data analysis [specifically, Eq. (1) in Ref. [1]] and on the energy calculations performed in order to find the magnetic ground state of their system.

We start out by commenting the discussion in Ref. [1] regarding the importance of the cross term (CT) in Eq. (1)

$$\mathrm{CT} = -2|M_{\parallel,X}(\vec{Q})||M_{\perp,Y=Z}(\vec{Q})|\sin\theta\cos^3\theta\overline{\cos}(\delta\phi),$$

which is used to explain the "horizontal to vertical suppression" of the experimental spin-flip data at an applied magnetic field of 1.2 T [where, according to Ref. [1], $\overline{\cos}(\delta\phi) = 1$]; $M_{\parallel,X}(\vec{Q})$ and $M_{\perp,Y=Z}(\vec{Q})$ denote the (Cartesian) Fourier coefficients of the magnetization and θ is the angle between the momentum-transfer vector $\vec{Q}$ and the direction of the applied magnetic field $\vec{H}\|\vec{e}_X$ [compare Fig. 1(a) in Ref. [1]]. In the Supplemental Material of Ref. [1], Krycka *et al.* introduce core-shell-type form factors for the functions $M_{\parallel,X}$ and $M_{\perp,Y=Z}$. These single-particle form factors do obviously not depend on the orientation (angle θ) of $\vec{Q}$ on the two-dimensional detector, i.e., $M_{\parallel,X} = M_{\parallel,X}(|\vec{Q}|)$ and $M_{\perp,Y=Z} = M_{\perp,Y=Z}(|\vec{Q}|)$. Consequently, the azimuthal average of the CT vanishes, i.e., $\int_0^{2\pi} CT(\theta)d\theta = 0$, demonstrating that the CT does not contribute to the azimuthally averaged spin-flip SANS cross section or, likewise, to $\pm 10°$ sector averages around the horizontal ($\theta = 0°$) and vertical ($\theta = 90°$) direction. Hence, according to these assumptions made in Ref. [1], the CT cannot explain the "horizontal to vertical suppression" of the spin-flip data, which is, however, a central point of discussion in the Letter. In fact, the main conclusions in Ref. [1] regarding the canting angle of the shell are largely based on the analysis of the horizontal and vertical sector averages.

Furthermore, besides ignoring a term that depends on the polarization of the incident neutrons [2], Eq. (1) in Ref. [1] assumes that the magnitude squares of both transversal Fourier coefficients are equal, i.e., $|M_{\perp,Y}(\vec{Q})|^2 = |M_{\perp,Z}(\vec{Q})|^2$. These assumptions are not mentioned in Ref. [1]. However, and even more important, the assumption that $|M_{\perp,Y}(\vec{Q})|^2 = |M_{\perp,Z}(\vec{Q})|^2$ is questionable, since (for the scattering geometry where $\vec{H}$ is perpendicular to the wave vector of the incident neutrons) the magnetodipolar interaction renders both Fourier coefficients different from each other: this was shown for bulk ferromagnets (two-phase nanocomposites) by means of analytical and numerical micromagnetic simulations [3].

We proceed by commenting on the micromagnetic analysis performed in Ref. [1]. In the first place it should be noted that the spatial discretization used by the authors (0.05 nm = 0.5 Å) is about 17 times smaller than the size of the Fe_3O_4 unit cell (8.4 Å). For such a spatial resolution, the discrete nature of matter should be taken into account when trying to obtain quantitative results, in this particular case, magnetic moments positioned on lattice sites corresponding to the Fe ions. And, even for this (inadequate) spatial discretization, we emphasize that most of the energy expressions used in Ref. [1] for the search of the system's energy minimum are incorrect.

(i) In Eq. (2) in Ref. [1], the magnetic anisotropy energy is assumed to be an uneven function ($\propto \cos\alpha$; for the definition of α see Ref. [1]). This is inadequate (except for the case of a unidirectional anisotropy, not present here), since, due to fundamental symmetry considerations, magnetic anisotropy energies are even functions (e.g., Ref. [4]).

(ii) By analyzing the magnetodipolar interaction energy, the authors claim that for a given nanoparticle "internal dipolar energy is nearly negligible." This is definitely not true here, because the authors assume that each particle possesses a highly nontrivial magnetization configuration, so that the internal magnetodipolar interaction should play a very important role. Furthermore, the interparticle magnetodipolar interaction is computed incorrectly, because the authors cut off this interaction after the 18 nearest neighbors. It is a textbook result that the dipolar interaction is a long-range one [4], so that any cutoff of this interaction may lead to arbitrary error and, correspondingly, to unphysical results.

(iii) When computing the anisotropy energy [Eq. (5) in Ref. [1]] the authors replace the average value of the cosine by the cosine of the average angle, which is clearly an incorrect mathematical operation for any nonlinear function. Moreover, the symmetry of the magnetocrystalline anisotropy is assumed to be uniaxial, although it is well known that Fe_3O_4 possesses cubic anisotropy (which is of leading fourth order in the magnetization components).

(iv) The exchange energy [Eq. (6) in Ref. [1]] is assumed $\propto \cos(T_{d,\mathrm{tilt}})$, where $T_{d,\mathrm{tilt}}$ is defined as the average tilt angle between the T_d Fe sites and the applied magnetic field. This suggests that the Fe core spins align along $\vec{H}$, and are considered as unconditionally fixed—an assumption that may not be made *a priori* if the aim is to study spin canting within a single nanoparticle. In other words, the large exchange energy related to spin canting may lead to significant rotation also of central core spins, so that the correct exchange-energy expression should be used in the energy-minimization procedure.

In conclusion, in view of the substantial criticism raised in this Comment, the conclusions of Krycka *et al.* [1] regarding the spin structure of Fe_3O_4 nanoparticles are supported neither by the neutron-data analysis nor by the theoretical considerations.

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Andreas Michels,[1,*] Dirk Honecker,[2] Sergey Erokhin,[3] and Dmitry Berkov[3]

[1]Physics and Materials Science Research Unit
University of Luxembourg
162A Avenue de la Faïencerie, L-1511 Luxembourg
[2]Institut Laue-Langevin
71 avenue des Martyrs, F-38042 Grenoble, France
[3]General Numerics Research Lab
Moritz-von-Rohr-Strasse 1a, D-07745 Jena, Germany

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*Corresponding author.
andreas.michels@uni.lu

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