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Reply to Comment on Origin of Surface Canting Within Fe3O4 Nanoparticles

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Krycka *et al.* Reply: Measurable suppression of spin-flip scattering, explained by the $M_{\parallel,X}(\vec{Q})M_{\perp,Y}(\vec{Q})$ cross term [1], is used to evaluate the extent of nanoparticle surface canting. We agree with [2] that $|M_{\parallel}(\vec{Q})||M_{\perp}(\vec{Q})|\sin(\theta)\cos^3(\theta)$ in Eq. (1) sums to zero over all θ quadrants. These terms, however, are multiplied by $\cos(\delta\phi)$, which changes sign for $\pm\theta$. In Eq. (1) [1] $|\cos(\delta\phi)| = 1$ for $Q \geqq 0.02$ Å^{-1} since $M_{\perp}(\vec{Q})$ and $M_{\parallel}(\vec{Q})$ are centrosymmetric within each particle. (We incorrectly stated $\cos(\delta\phi) = 1$ [1].) The sign change is a direct consequence of the symmetry present per self-assembled grain of nanoparticles. Specifically, long-range dipolar coupling can create a pattern of the canted shell moments similar to Fig. 2(b) of Ref. [3] ("flower") or Fig. 2(iv) of Ref. [4] over the submicron length scale of a close-packed grain of nanoparticles, involving a net moment along $\hat{X}\|\vec{H}$ and a gradual, average spatial variation among $M_{\perp,Y}(\vec{Q})$ shell moments with mirror symmetry about the X axis. Although we did not discuss the characteristics of the long-range, magnetic, nanoparticle structure in Ref. [1] for brevity, particle clusters with similarly canted shells were required to properly model the spin-flip scattering [5]. The specific distribution, however, does not impact the spin-flip scattering asymmetry ratio as evidenced by the fact that the spin-flip scattering shape was preserved when viewed along any θ cut (Fig. 4 of Ref. [4]).

Additional polarization dependent terms $M_{\perp,Z}(\vec{Q})M_{\perp,Y}(\vec{Q})$ and $M_{\perp,Z}(\vec{Q})M_{\parallel,X}(\vec{Q})$ [Eq. (6) of Ref. [4]] appear only as a difference between spin-flip cross sections. Since our spin-flip cross sections are equivalent within experimental resolution, we summed them together [1] as in Ref. [5], rendering these extra terms irrelevant.

Regarding our isotropic system with magnetic symmetry about $\hat{X}\|\vec{H}$, we clearly state that $|M_{\perp,Y}(\vec{Q})| = |M_{\perp,Z}(\vec{Q})| \equiv |M_{\perp}(\vec{Q})|$ in the Supplemental Material of Ref. [1] and in Ref. [5]. Our system differs from that of the nanocomposite [3] in which magnetostatic dipolar interactions dominate. The $M_{\perp,Y}(\vec{Q})$ and $M_{\perp,Z}(\vec{Q})$ scattering from symmetrically equivalent magnetization components along Y and Z are not identical in this case [3] because the net moments along Y and Z sum to zero over the nanocomposite, resulting in zero spin-flip scattering along the coordinate axes. In contrast, our nanoparticle system exhibits nonzero spin-flip scattering at all θ [4], which implies that the canted shells must have a net uniform moment throughout each particle [5], which is equivalent along Y and Z (on average), and that $|M_{\perp,Y}(\vec{Q})| = |M_{\perp,Z}(\vec{Q})|$. Moreover, any reduction in scattering due to long range coupling between nanoparticles that might suppress $M_{\perp,Y}(\vec{Q})$ scattering would by symmetry considerations suppress $M_{\perp,Z}(\vec{Q})$ equally.

The point of our energetic model was to evaluate the relative contributions of Zeeman, magnetocrystalline anisotropy, exchange, and dipolar coupling to show that T_d tilting is energetically feasible and capable of explaining (a) scattering asymmetry and (b) temperature-dependent, canted shell formation at high magnetic field. When surveying a large collection of nanoparticles, we feel it makes sense to consider the average parameters (i.e., exchange coupling) per unit volume as a function of radial placement. Specifically, 0.05 nm slices were chosen for calculational convenience to be evenly divisible into the nanoparticle diameter.

(i) As labeled, Eq. (2) [1] stems from estimating the minimum size of the anisotropy energy necessary to outcompete the Zeeman energy, irrespective of exchange and the specific anisotropy symmetry. Later, when specific total energy contributions are computed, the simplest appropriate model of anisotropy is included as in Eq. (5) in Ref. [1]. The point remains that in all of these cases, the necessary anisotropy constant would be many times (50–100 times greater) than that of the bulk.

(ii) While in general, dipolar contributions within a nanoparticle and for multiple next nearest neighbors could be important, we found that in this system the individual nanoparticle contribution was negligible in comparison to other energy terms, and considerations of 52 nearest nanoparticle neighbors yielded nearly indistinguishable results from those for 18 nearest neighbors, justifying the truncation.

(iii) As clearly stated in Ref. [1], we perform our calculation using an average shell canting angle as this corresponds to experimental measurement and it represents the global average for a collection of many nanoparticles. We do not dispute that Fe_3O_4 has cubic anisotropy, consistent with Eq. (5) [1]. We consider the tilt away from only the most energetically favorable magnetocrystalline axis (most $\|\vec{H}$), rather than from all remaining axes, which would be a second order effect.

(iv) O_h shell spins were set $\|\vec{H}$ because calculations revealed that only the T_d spins showed appreciable canting away from $\vec{H}$ (Table I of Ref. [1]).

In summary, our small-angle neutron scattering asymmetry analysis combined with this heuristic energy model provides a reasonable explanation for the observed nanoparticle shell canting.

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