Largely Enhanced Ferromagnetism in Bare CuO Nanoparticles by a Small Size Effect

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ABSTRACT: Magnetic properties of fully oxygenated bare CuO nanoparticles have been investigated using magnetization, X-ray diffraction, neutron diffraction, and Raman scattering measurements. The Langevin field profile is clearly revealed in the isothermal magnetization of 8.8 nm CuO nanoparticle assembly even at 300 K, revealing a 172 times enhancement of the ferromagnetic responses over that of bulk CuO. Surface magnetization of 8.8 nm CuO reaches 18% of the core magnetization. The Cu spins in 8.8 nm CuO order below 400 K, which is 1.7 times higher than the 231 K observed in bulk CuO. A relatively simple magnetic structure that may be indexed using a modulation vector of (0.2, 0, 0.2) was found for the 8.8 nm CuO, but no magnetic incommensurability was observed in bulk CuO. The Cu spins in 8.8 nm CuO form spin density waves with length scales of 5 chemical unit cells long along the crystallographic a- and c-axis directions. Considerable amounts of electronic charge shift from around the Cu lattice sites toward the interconnecting regions of two neighboring Cu–Cu ions, resulting in a stronger ferromagnetic direct exchange interaction for the neighboring Cu spins in 8.8 nm CuO.

1. INTRODUCTION

Fully oxygenated cupric oxide CuO has been characterized as a semiconducting material,1–3 exhibiting great potential for broad applications in photoelectron materials,4 gas sensors,5 lithium-ion electrode materials,6 field emission emitters,7,8 and heterogeneous catalysts.9 CuO crystallizes into a monoclinic structure with a spatial symmetry belonging to the space group C2/c.10,11 There are four formula units in a unit cell, with a crystalline structure that can be viewed as consisting of interconnected zigzag Cu–O–Cu–O chains along the [101] crystallographic direction (Figure 1). Each Cu ion is coordinated by four O ions, forming distorted side-sharing CuO₄ tetrahedrons. The magnetic interaction between the Cu²⁺ ions is mainly mediated through the neighboring O²⁻ ions, with a superexchange strength that depends on the Cu–O–Cu bond angle. The distorted side-sharing CuO₄ tetrahedrons give rise to four different Cu–O–Cu bond angles ranging from 95 to 145° for the Cu–O networks. A complex magnetic structure for the Cu spins can then be anticipated. Neutron diffraction measurements reveal an incommensurate (ICM) antiferromagnetic order for the Cu spins at $T_{N1} = 231 \text{ K}$,10–13 with a magnetic modulation vector that has been suggested to be dependent on the oxygen deficiency.13 Through a first-order transition at $T_{N2} = 212.5 \text{ K}$, the Cu spins reorient into a commensurate (CM) antiferromagnetic arrangement, with the moments aligned along the b-axis direction.12,13 Inelastic neutron scattering
measurements reveal a large spin-wave velocity, showing a strong superexchange interaction for the Cu spins in CuO.13

There are at least two effects that may alter the number of uncompensated spins, hence the magnetic properties, when the size is reduced to the nanometer scale: first, transfer of the outer electrons of surface atoms to the inner core, which has been demonstrated14,15 to be energetically favorable to stabilizing the core; second, the increase of imbalanced spins from the increase of Fermi holes from the image charges of surface electrons.16−18 Magnetization measurements performed on CuO nanoparticles (NPs), fabricated using sol−gel routes, reveal weak ferromagnetic signals that persist up to 330 K in 6.6 nm CuO, which were suggested to be originated from the uncompensated surface Cu2+ spins.19,20 On the other hand, the ferromagnetic responses that persist up to 300 K observed in 14−28 nm CuO NPs fabricated by sol−gel routes were attributed to the appearance of surface oxygen vacancies.21 A giant negative thermal expansion of the crystalline lattice has also been found below a magnetic ordering temperature of 300 K in 5 nm CuO, indicating the existence of strong spin−lattice couplings in CuO NPs.22

There are many ways to fabricate NPs. Chemical reduction processes, such as sol−gel routes, are frequently used, but the resultant NPs are unavoidably capped by the molecules used as reduction agents. The physical properties obtained on surfactant-capped NPs are complicated by the interactions between the NPs and capping molecules, but not reflect those of NPs themselves. In this article, we report the results of studies made on the magnetic properties of capping-free fully oxygenated CuO NPs, with an emphasis on the changes in properties originating from the reduction of particle size but avoiding the complications that may arise from the capping agents. The CuO NP assemblies are fabricated using the gas condensation method.23 The ferromagnetic (FM) component of the Cu spins is greatly enhanced in nanosized CuO. A saturation FM magnetization of 8.8 nm CuO reaches 172 times that of bulk CuO, and the antiferromagnetic (AFM) magnetization increases by a factor of 9. Surface magnetization is visible below 10 K and reaches 18% of the core magnetization. The ordering temperature of the Cu spins in 8.8 nm CuO shifts to 400 K, while the spin reorientation temperature of the Cu spins is greatly enhanced in nanosized CuO. A strong superexchange interaction for the Cu spins in CuO.13

2. RESULTS AND DISCUSSION

2.1. Crystalline Structure. Neutron and X-ray diffractions were used to determine the crystalline structure and chemical composition of the CuO NP assemblies. The General Structure Analysis System (GSAS) program,24 following the Rietveld profile refining method, was used to analyze diffraction patterns. Line profiles of the X-ray diffraction peaks were used to extract mean sizes and size distributions of the NP assemblies. The neutron and X-ray diffraction patterns of all three sets of CuO NP assemblies can be associated with a monoclinic structure. Neutron diffraction is sensitive to the O atom in CuO as the scattering length b of neutron to O is comparable to that of Cu (b = 5.805 fm for O and 7.178 fm for Cu). Neutron diffraction patterns were hence used to determine the O content in the samples. Figure 2a shows the observed (crosses) and fitted (solid lines) neutron diffraction patterns of the representative CuO NP assembly (fabricated using a chamber pressure of 2 torr) at 400 K, revealing that the O sites are fully occupied. It appears that O site occupancy contributes most pronouncedly to the (111) and (002) + (111) neutron diffraction intensities. Refinement analysis assuming a 10% oxygen deficiency generates a fit that fails to satisfactory account for the intensities observed for (110) and (002) + (111) reflections [accounting for 83% of the (110) intensity and 109% of the (002) + (111) intensity], whereas a full oxygen occupancy accounts for 96% of the (110) intensity and 98% of the (002) + (111) intensity. Details of the results of these analyses can be found in the Supporting Information (Figure S2). All four samples are fully oxygenated as the O sites are essentially fully occupied (Table 1). No diffraction peaks other than from the monoclinic CuO can be identified from the diffraction patterns (Figure 2a and Figure S1 in the Supporting Information) in which any impurity phase would be less than 3% of the CuO component. If any capping molecules do appear on the CuO NPs, it would be less than 3%. It appears that widths of the diffraction peaks are much broader than the instrumental resolution, reflecting broadening of the peak profiles from the finite-size effect. The mean particle diameters are determined by fitting the X-ray diffraction peaks, where the angular resolution is better, to...
Table 1. List of the Refined Lattice Parameters and Calculated Cu Bond Valences of the Four CuO Samples Studied

| P (torr) | d  | a (Å) | b (Å) | c (Å) | β (°) | OO | BV |
|----------|----|-------|-------|-------|-------|----|----|
| 2        | 8.8 nm | 4.648(2) | 3.414(1) | 5.101(2) | 99.19(2) | 1.001(6) | 1.98 |
| 1.2      | 25 nm   | 4.681(1) | 3.426(1) | 5.128(1) | 99.29(1) | 0.998(3) | 1.93 |
| 0.05     | 50 nm   | 4.682(2) | 3.423(2) | 5.129(2) | 99.40(2) | 1.002(6) | 1.95 |
| N/A      | 2 mm    | 4.682(2) | 3.422(3) | 5.126(2) | 99.50(1) | 0.999(3) | 1.98 |

N/A = chamber pressure; d = mean particle diameter; BV = Cu bond valence; OO = O site occupancy relative to Cu site occupancy.

The most pronounced feature seen is the extremely large increase of M in the NPs. Two magnetic components are clearly revealed in all three CuO NP assemblies, even in the 2 mm ingots (Figure 3b). In the low-\(H_a\) regime, \(M\) increases rapidly with increasing \(H_a\), becoming saturated at \(H_a \sim 1\) kOe. This component may be satisfactorily described by a Langevin profile \(L(\alpha) = \coth(\alpha) - (1/\alpha)\), where \(\alpha \equiv \mu_p H_a/k_BT\) (\(\mu_p\) is the average particle magnetic moment, \(H_a\) is the applied magnetic field, and \(k_B\) is Boltzmann’s constant). The Langevin profile for \(M(\alpha)\) reflects the alignment of magnetic moments on CuO NPs by \(H_a\). It signifies the existence of FM spin correlations in CuO NPs. This FM component can be expressed in terms of the saturation FM magnetization \(M_0\) as \(M_{FM} = M_0 L(\alpha)\). In the high-\(H_a\) regime, \(M\) increases linearly with \(H_a\), reflecting the existence of an AFM component, which can be expressed in terms of the AFM magnetic susceptibility \(X_{AFM}\) as \(M_{AFM} = X_{AFM} H_a\). The solid curves in Figure 3a,b are the result of the fitting of the data to \(M(\alpha) = M_0 L(\alpha) + M_{AFM} H_a\), with \(M_0\), \(\mu_p\), and \(X_{AFM}\) being the fitting parameters. \(M_0\), \(\mu_p\), and \(X_{AFM}\) obtained from the fits for the four CuO assemblies at 1.8 K are listed in Table 2.

Table 2. List of the Saturation Magnetization of the Ferromagnetic Component \(M_0\), Antiferromagnetic Magnetic Susceptibility \(X_{AFM}\) and Average Particle Moment \(\mu_p\) of the Four CuO Samples Obtained from Fits of the \(M(\alpha)\) Curves to the Expression Discussed in Text

| diameter | \(M_0\) (10^{-2} emu/g) | \(X_{AFM}\) (10^{-6} emu/emu Oe) | \(\mu_p\) (\(\mu_B\)) |
|----------|--------------------------|---------------------------------|---------------------|
| 8.8 nm   | 4.3(7)                   | 172                             | 5.61(1)             |
| 25 nm    | 2.7(2)                   | 108                             | 1.31(2)             |
| 50 nm    | 0.058(1)                 | 2.3                             | 1.12(1)             |
| 2 mm     | 0.025(3)                 | 1                              | 0.62(4)             |

It is remarkable to find that the \(M_0\) of 8.8 nm CuO at 1.8 K reaches \(4.3 \times 10^{-2}\) emu/g, which is a factor of 172 times higher than the \(M_0\) of the 2 mm ingot (Table 2). This extremely large increase of \(M_0\) cannot simply be a result of the increases in the surface moment expected for nanosized particles, but instead, it must be a result of a change of spin arrangement. A large enhancement (108 times) of \(M_0\) is also found for the 25 nm CuO but a considerably smaller enhancement (2.3 times) for the 50 nm CuO (Table 2), showing that a major change in the Cu spin arrangement will occur in particles smaller than 50 nm. In addition, the \(X_{AFM}\) of the 8.8 nm CuO is a factor of 9 times larger than that of the 2 mm CuO (Table 2). The large increases in both the FM and AFM magnetizations cannot solely be a result of the spin rearrangement but are indicative of an increase in the magnetic moment of the Cu ions in CuO NPs. Room-temperature ferromagnetism has also been observed in flowerlike CuO nanostructures with oxygen.
vacancies, prepared by the coprecipitation method and postannealing, but with the ferromagnetism decreasing after annealing in an oxygen atmosphere.\textsuperscript{25} Reduction of Neel temperature to 221 K in 11 nm CuO, prepared by thermal decomposition of the carbonate precursor, has recently been reported and is attributed to the presence of O$^2-$ vacancies.\textsuperscript{26} The present observations of largely enhanced magnetism were from fully oxygenated CuO NPs. Clearly, the particle size and oxygen content of CuO play essential roles in the magnetism of CuO.

2.3. Surface and Core Magnetizations. $M(H)$ taken at temperatures of up to 300 K can all be satisfactorily described by a Langevin plus a linear $H$ dependence (Figure 4a). The thermal profile of the $M_0$ of the 8.8 nm CuO displays a sharp turn at 10 K (Figure 4b). The large difference in the thermal reduction rates of $M_0$ below and above 10 K shows that they are linked to different origins. 11% of the atoms in the 8.8 nm CuO are located on the surface. It can be expected that the magnetic moments developed on the surface of an NP are different from those developed in the core, and their thermal characteristics can be noticeably different. The sharp turn at 10 K separates the effects mainly resulting from the surface moments at low temperatures and from the core moments at high temperatures. The thermal profile of the surface magnetization can be expressed in terms of surface spin freezing temperature $T_s$ as $M_s \propto \exp(-T/T_s)$.\textsuperscript{27,28} On the other hand, the thermal agitation of the core spins can be described by a power law of $M_c \propto \left[1 - \left(\frac{T}{T_C}\right)^b\right]$, where $T_C$ is the transition temperature and the exponent $b$ links to the type of spin ordering.\textsuperscript{29} Accounting for the contributions from both surface and core spins, the saturation magnetization can be expressed as $M_0(T) = M_C\left[\alpha e^{-T/T_s} + 1 - \left(\frac{T}{T_C}\right)^b\right]$, where $M_C$ is the saturation magnetization of the core moment at zero temperature and $\alpha$ specifies the ratio between the surface and core moments at zero temperature. The solid curve in Figure 4a indicates the results of fitting of $M_0(T)$ to the above expression, giving $M_C = 4.31(1) \times 10^{-2}$ emu/g, $\alpha = 0.18$, $T_s = 2.93(3)$ K, and $b = 2.1(2)$. The value of $b = 2.1$ obtained for the 8.8 nm CuO is significantly larger than the $b = 3/2$ expected for creations of thermal magnons in bulk ferromagnets\textsuperscript{30} but reflecting the $b = 2$ expected for finite-size ferromagnetic clusters based on a mean field calculation.\textsuperscript{30} The $\alpha = 0.18$ obtained from the fits shows that the surface moment is 18% of the core moment in 8.8 nm CuO at a temperature without thermal excitation. The Lenz diamagnetic responses are not visible in $M(H)$ but are covered by the strong AFM signals even at 300 K. The values for $X_{AFM}$ deduced from the fits to $M(H)$ do not represent the AFM susceptibility but include the inseparable AFM and Lenz susceptibilities.

2.4. Electronic Charge Redistribution. X-ray diffraction patterns of the 8.8 nm NPs and 2 nm ingots at 77 K were also taken for extraction of electronic charge density (ECD). The ECD maps were obtained by employing the GSAS program, by the calculations of the inverse Fourier transforms of the structure factors, after profile refinements of the X-ray diffraction patterns. The electron density contour map of a specific lattice plane is then obtained by slicing the electron density including 0.025 Å below and above the plane. The changes in the electronic charge distribution are then identified by taking the difference in the ECD plots where the ECD distribution of the 2 nm CuO is subtracted from that of the 8.8 nm CuO. Such difference ECD plots for the Cu sites at (0, 0, 0), the O sites at (0, 0, 0.25), and a representative intermediate region at (0, 0, 0.34) are illustrated in Figure 5. In these plots, the atomic positions with negative values (blue to green) represent the locations where the electronic charges are less in 8.8 nm CuO, which have been redistributed to the positions with positive values (yellow to red).

Considerably less electronic charges (up to $-6$ e/Å$^3$) in 8.8 nm CuO are distributed at and near the Cu lattice sites at (0.25, 0.25, 0) but appear in the interconnecting regions of neighboring ions, as a consequence of an outgoing shift of electrons from near the lattice sites to the interconnecting regions (Figure 5b). There is a significant increase in the number of electronic charges in most of the regions between the two neighboring Cu ions along the [−110] crystallographic direction, while the electronic charges decrease along the [110] direction (Figure 5b). The FM direct exchange interaction between two neighboring Cu ions along the [−110] direction appears to be greatly enhanced by the significant increase in the number of electrons in between. In addition, there is even a larger shift in electrons (up to $-6$ e/Å$^3$) from the O lattice sites at (0, 0.411, 0.25) to the interconnecting regions (Figure 5c). It can be seen that the regions with negative values (blue to green in Figure 5c) in the difference ECD map extend about one-third toward the middle point between the two nearest neighbors along the [110] direction but extend further, to reach two-thirds along the [−110] direction. It is clear that the

![Figure 4](https://dx.doi.org/10.1021/acsomega.9b02913)
distribution of not only the outer electrons but also the inner electrons has been extended toward the interconnecting regions in the 8.8 nm CuO. As we approach the interlayer regions, it is interesting to see that additional electronic charges appear more in the interconnecting regions between the Cu and O ions along the [−110] direction (Figure 5d).

Figure 5. (a) Atom arrangement of monoclinic CuO. The colored planes indicate the positions in the crystallographic c-axis direction where the electronic charge density is plotted. (b–d) Difference of the electronic charge density between the 8.8 nm CuO assembly and 2 mm Cu spheres on the (b) z = 0, (c) z = 0.25, and (d) z = 0.34 lattice planes. The regions marked in yellow-to-red indicate the positions having a positive difference charge density, where the charge density of the 8.8 nm CuO nanoparticles is higher than that of the 2 mm spheres. The regions marked in green-to-blue indicate the positions having a negative difference charge density, where the charge density of the 8.8 nm CuO nanoparticles is lower than that of the 2 mm spheres. The color bars are in units of e/Å³.

Figure 6 displays the contours in a 3D view for a difference ECD of +2.5 e/Å³, showing that more electronic charges shift toward the interconnecting regions between two neighboring Cu–Cu ions than toward that of Cu–O ions, establishing a better electronic connection for the neighboring Cu–Cu ions. Apparently, the change in the spatial distribution of the electronic charge from the reduction of CuO into 8.8 nm does not extend isotopically in all crystallographic directions, but rather some portion of the electrons shift from specific regions to others. The redistribution involves not only spherically distributed s electrons (4s in Cu and 2s in O) but also includes directional 3d electrons in Cu and 2p electrons in O.

2.5. Spin Arrangements. Neutron diffraction patterns taken at low temperatures were collected to identify the diffractions from the magnetic correlation. Several new diffraction peaks developed with intensities increasing upon cooling to below 400 K, showing the ordering of the Cu spins (Figure 7). This reflection can be associated with a magnetic modulation vector of \( q = (0.2, 0, 0.2) \) showing the magnetic unit cell 5 times the nuclear one along the crystallographic a- and c-axis directions. Order parameter measurements reveal a change in the rate of intensity variation at 280 K for the (200) + \( q \) reflection (Figure 8a), showing the appearance of a transition at \( T_{N2} = 280 \) K in addition to the Cu spin ordering temperature of \( T_{N1} = 400 \) K. Additional intensities from
magnetic ordering also appear at the nuclear peak positions, only to reveal downturns in intensity upon cooling below 280 K (Figure 8b,c). No new diffraction peaks were detected, but there was a shift of intensity among the peaks upon cooling below 280 K, revealing the characteristic behavior of the occurrence of spin reorientation at $T_{N2}$ = 280 K without a change in spin structure. The $T_{N1}$ = 400 K for the Cu spins in the 8.8 nm CuO is 1.73 times higher than the 231 K found$^{13}$ in a bulk single crystal, showing a much stronger magnetic coupling strength for the Cu spins in 8.8 nm CuO. The magnetic structure can be described with a magnetic modulation vector of (0.2, 0, 0.2), which differs greatly from the (1/2, 0, 0) + (0.006, 0, −0.017)$^{12}$ or (1/2, 0, 0) + (0.0125, 0, 0.0125)$^{13}$ observed in a single crystal. Spin reorientation, rather than changes in the magnetic modulation vector, occurs at $T_{N2}$ for the Cu spins in 8.8 nm CuO. Figure 9 shows the observed (crosses) and calculated (solid lines) neutron diffraction patterns at 6 K, assuming a monoclinic $C2/c$ symmetry for the monoclinic crystalline structure plus a magnetic structure with a modulation vector of (0.2, 0, 0.2). The set of blue vertical bars on the top marks the calculated Bragg positions of the proposed crystalline structure, and the set of red vertical bars at the bottom marks that of the proposed magnetic structure.

Figure 9. Observed (crosses) and fitted (solid lines) neutron powder diffraction pattern at 6 K, assuming a monoclinic $C2/c$ symmetry for the crystalline structure plus a magnetic component with a modulation vector of (0.2, 0, 0.2). The set of blue vertical bars on the top marks the calculated Bragg positions of the proposed crystalline structure, and the set of red vertical bars at the bottom marks that of the proposed magnetic structure.

between the neighboring double-chain along the c-axis direction (Figure 10) and a ferromagnetic coupling for the Cu spins along the crystallographic b-axis direction. The moments lie along the crystallographic c-axis direction, with an amplitude of 0.78(3) $\mu_B$.

3. CONCLUSIONS

The present study focuses on identifying the effects of spatial restriction on the magnetic properties of CuO. Ferromagnetic responses of 25 nm CuO NPs are $\sim$100 times stronger than that of 2 mm ingots. It is unlikely that the enhancement is from the surface effect since there are only 4% of the atoms in 25 nm CuO located on the surface. The disruption of lattice periodicity at the particle surface, known as small size effect, must have played a role. Ferromagnetic responses, surface magnetization, Cu spin ordering temperature, and Cu spin arrangement are all largely enhanced in 8.8 nm CuO. The present studies show that the enhancements are mainly caused
by charge redistribution triggered by the disruption of lattice periodicity at the surface. Charge redistribution that occurs in the Cu ions must involve both the 4s and 3d electrons for the largely enhanced ferromagnetic responses, reflecting that the 4s and 3d bands of the Cu ions in 8.8 nm CuO are energetically close to each other. An extended 3d and 4s band mixture can then be anticipated to generate the observed anisotropic electronic charge redistribution. The formation of the ferromagnetic double-chain spin density wave for the Cu spins is due to the fact that there are more electronic charges in the interconnecting regions of two neighboring Cu ions and there are less electronic changes in the interconnecting regions of the neighboring Cu and O ions. The former enhances the ferromagnetic direct exchange interaction between Cu−Cu ions, whereas the latter weakens the antiferromagnetic superexchange interaction between Cu−Cu ions mediated by the neighboring O ions. It is the formation of ferromagnetically coupled spin density layers that gives rise to largely enhanced ferromagnetic responses in the 8.8 nm CuO.

4. MATERIALS AND METHODS

4.1. Sample Fabrication. The CuO NPs used in the present study were generated by the annealing of Cu NPs at 323 K in an oxygen atmosphere for 48 h, which progressively transforms the dark-black Cu NPs into dark-green Cu2O NPs and finally into dark-brown CuO NPs. Three sets of Cu NPs were fabricated by employing the gas condensation method, with the mean particle size and size distribution controlled by the appropriate choice of chamber pressure and source temperature. High-purity Cu spheres (0.5 g, 99.99% pure, ∼2 mm in diameter) were heated by a current source of 55 A and were evaporated at a rate of 0.05 Å/s in an Ar atmosphere at the selected pressure (0.05 or 1.2 or 2 torr). A nonmagnetic SS316 stainless steel plate, placed 20 cm above the evaporation source and maintained at 77 K, was used to collect the evaporated particles. The NPs, which were only loosely attached to the collector, were stripped off after the chamber was restored to room temperature. The samples thus fabricated were in powder form, consisting of macroscopic amounts of individual Cu NPs. X-ray diffraction patterns of the samples thus fabricated reveal a face-centered cubic structure of Cu (Figures S3–S5 in the Supporting Information). No traces of oxidation phases or components other than Cu can be identified from the diffraction patterns. There was no substrate or capping molecules on the Cu NPs.

4.2. Instrumentation. The X-ray diffraction measurements were performed on a Bruker D8 ADVANCE diffractometer (Bruker Corporation, USA), employing the standard reflection geometry, with an emission current of 40 mA and an acceleration voltage of 40 kV for the source. The neutron diffraction measurements were conducted at the Bragg Institute, ANSTO, Australia, using the high-intensity powder diffractometer Wombat, employing an incident wavelength of λ = 2.415 Å defined by Ge (113) crystals. For these measurements, ∼1 g of the sample was loaded into a cylindrical vanadium can, which gave rise to no measureable neutron diffraction peak. The sample temperature was controlled using a He gas refrigerator system. The magnetization measurements were performed on a Physical Property Measurement System (PPMS), manufactured by Quantum Design, employing the standard setups. The magnetization M was measured by detecting the induced voltage in the detector coils as the sample moved through them. For these measurements, ∼40 mg of the sample was loosely packed into a thin nonmagnetic cylindrical holder. The holder produced a smooth temperature curve and a background signal that was ∼2% of the signal from the sample. The powdered sample was shaken at 50 Hz for 10 min using a Vortex-Genie mixer to avoid aggregation among the nanoparticles. The mass density was 6% of the bulk density so that the interparticle interaction would be insignificant, mainly revealing the magnetic responses of individual NPs without significant contributions from interparticle interactions. Raman scattering measurements were performed on a Shamrock SR-500i-A (Andor, U.K.), equipped with a double grating of 1200 line/mm each, and a Newton DU940 CCD detector. The Raman spectra were excited using a 514 nm excitation line at 150 mW, with a CCD signal integration time of 90 s.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02913.
X-ray diffraction pattern, neutron diffraction pattern, thermal magnetization and Raman spectrum (PDF)

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Notes
The authors declare no competing financial interest.

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