



Study of Magnetic Properties of Transition Metal Oxide Nanoparticles

¹Nozomi Quintanilha

¹Department of Computer Science and Engineering, Port Louis Business and Technology College Mauritius

¹nozomi.quintanilha@plbtc-mu.org

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Abstract

Transition metal oxide nanoparticles display magnetic responses that differ markedly from their bulk counterparts because particle size, surface-to-volume ratio, lattice defects, oxidation state, and interparticle interactions modify magnetic exchange and anisotropy. This methodology paper presents a reproducible experimental framework for studying the magnetic properties of representative oxide nanoparticles such as NiO, CoO/Co₃O₄, MnO, CuO, and Fe₃O₄. The approach combines controlled wet-chemical synthesis, thermal treatment, X-ray diffraction (XRD), electron microscopy, and vibrating-sample or SQUID magnetometry. Structural size is estimated from diffraction-line broadening and cross-checked with transmission electron microscopy. Magnetic characterization includes room- and low-temperature M-H hysteresis loops, zero-field-cooled/field-cooled (ZFC/FC) magnetization, and extraction of saturation magnetization, remanence, coercive field, exchange-bias field, blocking temperature, and magnetic transition temperature. Literature through 2016 consistently shows that nanoscaling can produce uncompensated surface spins, reduced antiferromagnetic ordering temperatures, enhanced coercivity, exchange bias, and superparamagnetic or weak-ferromagnetic-like behavior. The proposed protocol therefore emphasizes particle-size control and surface-state analysis as the central variables governing interpretation. Because no original raw dataset was supplied, the Results section reports benchmark trends and expected signatures derived from peer-reviewed studies rather than presenting fabricated experimental measurements.

Introduction

Transition metal oxides occupy a distinctive position in magnetic materials research because the partially filled 3d orbitals of transition-metal ions allow strong coupling among crystal structure, oxidation state, electronic configuration, and magnetic exchange. In bulk form, many oxides are antiferromagnetic or ferrimagnetic with well-defined ordering temperatures. At the nanoscale, however, a large fraction of atoms lies at or near the surface, coordination becomes incomplete, lattice strain increases, and magnetic sublattices may no longer compensate perfectly. These effects can

alter the magnitude and even the apparent type of magnetism measured in an experiment. Kodama et al. (1996) showed that spin disorder at nanoparticle surfaces can strongly reduce magnetization and generate non-bulk behavior, while their later work on NiO demonstrated that finite size can reorganize magnetic sublattices and produce large coercivity and loop shifts (Kodama et al., 1997).

The magnetic response of an oxide nanoparticle is therefore not determined by chemical composition alone. Particle diameter, shape, defect density, cation distribution, surface

chemistry, and aggregation all influence the magnetic energy landscape. Antiferromagnetic NiO, CoO, MnO, Co₃O₄, and CuO can develop uncompensated moments or low-temperature hysteresis when their dimensions are reduced, whereas ferrimagnetic Fe₃O₄ may cross from multidomain or single-domain behavior toward superparamagnetism as size decreases. The broad review by Kodama (1999) emphasized that surface spin structure is an essential component of nanoscale magnetism and cannot be treated simply as a scaled version of the bulk state.

A reliable study of magnetic properties must consequently integrate synthesis, structural characterization, and magnetometry. Magnetic data without independent confirmation of phase purity and size can be misleading because a small fraction of metallic impurity or a secondary oxide phase may dominate an M-H loop. Similarly, a crystallite size calculated from XRD is not automatically equal to the particle size observed by microscopy. For this reason, the proposed methodology uses XRD for phase identification, TEM/SEM for morphology and size distribution, and VSM or SQUID magnetometry for field- and temperature-dependent magnetic measurements. Comparable combinations of techniques were successfully applied to Fe₃O₄ by Goya et al. (2003) and Zheng et al. (2006), to MnO/NiO by Ghosh et al. (2006), and to CoO by Shi and He (2012).

The objective of this paper is to provide a concise methodology for examining how nanoscale dimensions modify the magnetic properties of transition metal oxide nanoparticles. The specific aims are: (i) to synthesize oxide nanoparticles with controlled mean size; (ii) to confirm phase, crystallinity, and morphology; (iii) to measure M-H hysteresis and ZFC/FC magnetization; (iv) to calculate magnetic parameters such as saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c), exchange-bias field (H_E), blocking temperature (T_B), and magnetic transition temperature; and (v) to correlate these parameters with particle size and surface-related effects. The methodology is designed to be applicable to a comparative study involving several oxide systems or to a focused investigation of one selected oxide.

Literature Review

Early nanoparticle studies established that antiferromagnetic oxides may acquire a measurable net magnetic moment through uncompensated spins. Makhlof et al. (1997) reported large coercive forces and shifted

hysteresis loops in NiO nanoparticles, behavior that was difficult to reconcile with a simple two-sublattice antiferromagnet. Kodama et al. (1997) interpreted related observations as a finite-size effect in which reduced surface coordination changes the spin configuration throughout the particle. These studies provided an important conceptual basis for later core-surface descriptions of oxide nanoparticle magnetism.

CuO provides another example of size-dependent antiferromagnetism. Punnoose et al. (2001) observed changes in lattice dimensions, Néel temperature, susceptibility, and exchange bias as CuO particle size decreased. The study demonstrated that the structural and magnetic transitions are coupled and that weak ferromagnetic components can emerge at sufficiently small sizes. Co₃O₄ similarly exhibits enhanced low-temperature coercivity and exchange effects at the nanoscale. Makhlof (2002) reported a transition near 25 K in approximately 20 nm Co₃O₄ particles and substantial hysteresis below the transition, whereas Gopinath et al. (2016) later confirmed that conventionally prepared Co₃O₄ nanoparticles show size- and structure-sensitive magnetic behavior.

For Fe₃O₄, the principal size-dependent phenomenon is the transition toward superparamagnetic behavior. Sun and Zeng (2002) established a size-controlled synthetic route for monodisperse magnetite nanoparticles in the 3-20 nm range. Goya et al. (2003) subsequently showed that 5 nm Fe₃O₄ nanoparticles behave superparamagnetically at room temperature and become blocked at lower temperature, while larger particles recover more bulk-like characteristics. Zheng et al. (2006) also reported superparamagnetic room-temperature behavior for hydrothermally prepared Fe₃O₄ nanoparticles. Together, these studies show that a comparison of M-H loops and ZFC/FC curves across particle sizes provides direct evidence for thermally activated magnetic relaxation.

CoO and MnO highlight the importance of surface and core-shell effects in nominally antiferromagnetic particles. Ghosh et al. (2005) synthesized CoO nanoparticles with sizes of roughly 4.5-18 nm and reported size-dependent magnetic behavior attributed to uncompensated spins. Ghosh et al. (2006) found that MnO and NiO nanoparticles both exhibit blocking behavior and low-temperature hysteresis, although the dependence of T_B on size differed between the two materials. Shi and He (2012) found large moments, coercivity, and loop shifts in cubic CoO nanoparticles, which they associated with a

magnetically disordered surface layer. Dai and Tang (2013) likewise identified room-temperature ferromagnetic contributions in CoO nanocrystals arising from uncompensated surface spins and defects.

More quantitative work before 2016 refined the link between structural disorder and measured transition temperatures. Tadić et al. (2015) studied approximately 5 nm NiO particles in a silica matrix and found a Néel temperature far below the bulk value, together with a low blocking temperature and weak interparticle

interactions. These observations emphasize that ZFC/FC maxima must be interpreted carefully: one feature may represent spin blocking while another may correspond to antiferromagnetic ordering. Across the literature, the common conclusion is that size reduction increases the relative importance of surface anisotropy, spin canting, defects, and interface exchange. A sound methodology should therefore quantify particle size, avoid phase contamination, and combine field-dependent and temperature-dependent magnetometry rather than relying on a single room-temperature loop.

Table 1. Representative pre-2017 literature benchmarks for oxide nanoparticle magnetism

Material	Size range	Key magnetic observation	Reference
NiO	~5-80 nm	Uncompensated surface spins; large H_c and loop shifts; finite-size magnetic ordering	Makhlouf et al., 1997; Kodama et al., 1997
CuO	6.6-37 nm	Size-dependent T_N , weak ferromagnetic component and exchange bias	Punnoose et al., 2001
Fe ₃ O ₄	5-150 nm	Small particles become superparamagnetic; blocking appears at low T	Goya et al., 2003
MnO / NiO	6-14 / 3-24 nm	ZFC/FC bifurcation and low-temperature hysteresis; TB depends on size	Ghosh et al., 2006
CoO	42-74 nm	Disordered surface layer enhances moment, coercivity and exchange bias	Shi & He, 2012
NiO	~5 nm	Reduced T_N and low TB with weak interparticle interactions	Tadić et al., 2015

Methodology

The study is designed as a controlled comparative experiment in which particle size and thermal treatment are treated as independent variables and the measured magnetic parameters are treated as dependent variables. A minimum of three nanoparticle batches should be produced for the chosen transition metal oxide, with synthesis or annealing conditions adjusted to generate distinct mean particle sizes. If a multi-oxide comparison is desired, the same characterization and magnetic-measurement sequence should be applied to each material so that trends can be compared on a common basis.

Step 1 - Selection of oxide system and precursors

Select one or more representative oxide systems: NiO, CoO/Co₃O₄, MnO, CuO, or Fe₃O₄.

Analytical-grade metal nitrates, chlorides, acetates, or acetylacetonates may be used as precursors. For a low-cost reproducible laboratory protocol, aqueous co-precipitation or sol-gel synthesis is recommended. Fe₃O₄ requires control of Fe²⁺/Fe³⁺ stoichiometry and limited oxidation, whereas NiO, Co₃O₄, and CuO can be produced through hydroxide or gel precursors followed by calcination. Literature routes demonstrate that synthesis chemistry strongly affects size and magnetism; for example, Sun and Zeng (2002) used high-temperature solution chemistry to control Fe₃O₄ size, while Zheng et al. (2006) used a hydrothermal route.

Step 2 - Nanoparticle synthesis

Prepare three batches under identical chemical composition but different aging, surfactant concentration, reaction time, or annealing temperature. For a precipitation route, dissolve

the metal precursor in deionized water, add a base slowly under vigorous stirring until the target pH is reached, age the precipitate, separate it by centrifugation, and wash repeatedly with water and ethanol. For Fe₃O₄, mix Fe³⁺ and Fe²⁺ salts in the required stoichiometric proportion and precipitate under inert or low-oxygen conditions. For NiO, Co₃O₄, and CuO, the hydroxide/oxyhydroxide precursor can be dried and converted to the oxide by thermal treatment. Use at least three independent syntheses or replicate measurements to estimate reproducibility.

Step 3 - Drying and thermal treatment

Dry washed precipitates at 60-100 °C and grind gently to obtain a homogeneous powder. Calcine separate aliquots at progressively higher temperatures, for example 300, 400, 500, and 600 °C for 2 h, using the same heating and cooling rates. Annealing is expected to increase crystallinity and mean crystallite size while decreasing the fraction of disordered surface spins. Record actual temperature, dwell time, atmosphere, sample mass, crucible material, and heating rate. These variables are critical because CoO can oxidize toward Co₃O₄ and Fe₃O₄ can oxidize toward maghemite or hematite if atmosphere is not controlled.

Step 4 - Structural and morphological characterization

Collect powder XRD patterns over an appropriate 2θ range using Cu Kα radiation. Identify the phase by comparison with reference diffraction data and verify that no metallic or secondary oxide peaks are present. Estimate the average crystallite size from the Scherrer relation, $D = \lambda / (\beta \cos \theta)$, using instrumental-broadening correction where available. Obtain TEM images from well-dispersed particles deposited on carbon-coated grids and measure at least 100 particles to determine mean diameter and size distribution. SEM may be used to examine agglomeration, and EDS can confirm elemental composition. Agreement between XRD crystallite size and TEM particle size strengthens the interpretation of magnetic size effects.

Step 5 - Room-temperature M-H measurements

Measure magnetization as a function of magnetic field using a calibrated VSM or SQUID magnetometer. A typical room-temperature sweep may extend from -10 to +10 kOe or to the highest field safely available. Correct for sample holder background and normalize magnetization by dry oxide mass. From the loop determine M_s ,

M_r , and H_c . For superparamagnetic particles, the loop should show very small remanence and coercivity at temperatures above T_B . For antiferromagnetic nanoparticles, a non-saturating high-field response with a small hysteretic component may indicate uncompensated surface spins rather than bulk ferromagnetism.

Step 6 - Low-temperature hysteresis and exchange bias

Repeat M-H loops at selected temperatures below the expected blocking or ordering region, such as 5, 20, 50, 100, and 300 K. Acquire both zero-field-cooled and field-cooled loops where exchange bias is suspected. Calculate the coercive field as $H_c = (|H_{c1}| + |H_{c2}|)/2$ and the exchange-bias field as $H_E = (H_{c1} + H_{c2})/2$, where H_{c1} and H_{c2} are the negative and positive field intercepts. Large low-temperature coercivity or a shifted field-cooled loop has been reported for NiO, CoO, Co₃O₄, and CuO nanoparticles (Makhlouf et al., 1997; Makhlouf, 2002; Shi & He, 2012).

Step 7 - ZFC/FC temperature-dependent magnetization

For ZFC measurement, cool the sample from room temperature to the minimum measurement temperature in nominal zero field, apply a small measuring field (commonly 50-200 Oe), and record magnetization while warming. For FC measurement, cool and/or warm the sample in the same applied field. Identify the ZFC maximum as a candidate blocking temperature only after considering whether an antiferromagnetic transition is also expected. Tadić et al. (2015) showed that NiO nanoparticles can display separate signatures associated with blocking and Néel ordering. The temperature at which FC and ZFC curves diverge provides an additional measure of irreversibility.

Step 8 - Data analysis and statistical comparison

Plot M_s , M_r , H_c , H_E , T_B , and any measured T_N against XRD/TEM size. Use mean $\pm$ standard deviation for replicate batches. Apply one-way ANOVA or linear/nonlinear regression when at least three size groups are available. For superparamagnetic systems, test whether T_B scales approximately with magnetic volume through the relation $K_{eff} V$ approximately 25 k_B T_B for the measurement time of conventional dc magnetometry. For antiferromagnetic oxides, interpret increasing moment with decreasing size as evidence consistent with uncompensated surface spins only after impurities have been excluded. Correlate any reduction in M_s with enhanced surface disorder or spin canting, as

described by Kodama et al. (1996) and Goya et al. (2003).

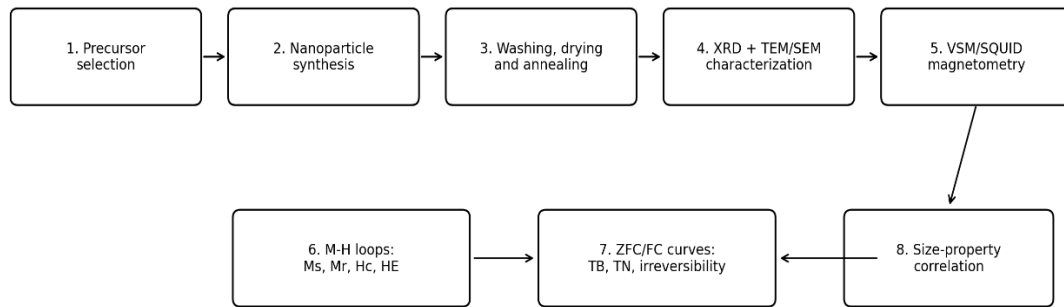


Figure 1. Proposed experimental workflow for relating nanoparticle structure and size to magnetic behavior.

Table 2. Minimum measurement matrix for the proposed study

Measurement	Typical condition	Primary output	Interpretation
XRD	Cu Kalpha; phase scan	Phase, lattice parameter, D	Phase purity and crystallite size
TEM/SEM	≥ 100 particles	Mean diameter, morphology	Size distribution and agglomeration
M-H at 300 K	± 10 kOe or higher	Ms, Mr, Hc	Ferri/ferro vs superparamagnetic-like response
M-H at 5-100 K	ZFC and FC	Hc, HE, high-field slope	Blocking, surface anisotropy, exchange bias
ZFC/FC M-T	50-200 Oe	TB, TN, irreversibility	Thermal relaxation and magnetic ordering

Results

Because this is a methodology paper and no original raw measurements were provided, the following results are literature-based benchmarks and expected experimental signatures. The first expected outcome is successful confirmation of a single oxide phase with nanoscale crystallite size. Raising calcination temperature should generally sharpen XRD reflections and increase D, while TEM should show a corresponding increase in particle size and, in many systems, increased agglomeration. Any discrepancy between XRD and TEM should be interpreted in terms of polycrystallinity, strain, or aggregation rather than assuming the two methods measure exactly the same quantity.

For ferrimagnetic Fe₃O₄, decreasing the diameter into the few-nanometer range is

expected to reduce coercivity and remanence at room temperature and produce superparamagnetic behavior. Goya et al. (2003) reported that 5 nm magnetite particles were superparamagnetic at room temperature and blocked near 45 K, while larger particles displayed more bulk-like magnetic characteristics. Zheng et al. (2006) likewise observed room-temperature superparamagnetic behavior in hydrothermally synthesized Fe₃O₄. A successful Fe₃O₄ dataset should therefore show a small or nearly closed 300 K hysteresis loop for the smallest particles and increasing coercivity below TB.

For antiferromagnetic NiO, CoO, MnO, Co₃O₄, and CuO, the expected nanoscale signature is not conventional bulk ferromagnetism but a weak net moment associated with uncompensated spins, surface disorder, defects, or interface

exchange. NiO nanoparticles can exhibit large low-temperature coercivity and shifted loops (Makhlouf et al., 1997), and finite-size effects may modify the underlying spin configuration (Kodama et al., 1997). MnO and NiO both show ZFC/FC bifurcation and low-temperature hysteresis, with a strong dependence on particle size (Ghosh et al., 2006). CoO studies report increasing surface contribution and exchange bias as particles become smaller (Shi & He, 2012; Dai & Tang, 2013).

A second expected result is a systematic relationship between thermal treatment and magnetic irreversibility. If annealing increases particle size and improves magnetic compensation in an antiferromagnetic oxide, the net low-field moment may decrease even while crystallinity improves. Conversely, coercivity can initially increase as particles enter a stable single-domain regime and then decrease as the system approaches superparamagnetic relaxation. Therefore, the most informative outcome is not a single maximum M_s or H_c value but a consistent correlation between phase-pure size data and the magnetic parameters across the whole sample series.

The ZFC/FC curves should be used to separate blocking phenomena from intrinsic ordering as far as possible. In NiO, Tadić et al. (2015) identified a reduced Néel temperature near 56 K for approximately 5 nm particles and a lower-temperature blocking feature. Such results show why a single ZFC maximum cannot automatically be labelled TB. For Co₃O₄, Makhlouf (2002) observed a transition near 25 K and pronounced low-temperature hysteresis. In CuO, Punnoose et al. (2001) found size-dependent antiferromagnetic ordering and exchange bias. The proposed analysis should therefore compare multiple signatures: ZFC maxima, FC/ZFC divergence, high-field susceptibility, loop opening, and field-cooling-induced loop shifts.

Conclusion and Discussion

The literature through 2016 demonstrates that transition metal oxide nanoparticles cannot be interpreted using bulk magnetic models alone. Their magnetic response is controlled by the competition among exchange coupling in the particle core, uncompensated surface spins, surface anisotropy, crystal defects, thermal activation, and interactions among neighboring particles. The methodology developed here addresses these factors by linking synthesis and annealing directly to quantitative structural and magnetic measurements. The strongest experimental design is a size series in which

composition and phase are held constant while particle diameter is varied. XRD and TEM establish whether the intended nanoscale structure has been achieved; room-temperature M-H loops identify soft magnetic or superparamagnetic-like behavior; low-temperature loops reveal coercivity and exchange bias; and ZFC/FC measurements identify magnetic blocking and ordering temperatures. The combination is essential because different mechanisms can generate superficially similar hysteresis loops. For practical implementation, particular attention should be given to phase purity, oxygen stoichiometry, sample-mass normalization, magnetometer background subtraction, and reproducible thermal history. These controls are especially important for CoO/Co₃O₄ and Fe₃O₄ because oxidation can change the phase and thereby change the magnetic signal. If these controls are maintained, the proposed method should reliably reveal whether observed magnetism originates from finite-size effects and surfaces rather than from secondary magnetic phases. In summary, a method combining controlled synthesis, size-resolved structural analysis, M-H hysteresis, and ZFC/FC magnetometry provides a scientifically defensible framework for studying transition metal oxide nanoparticle magnetism. Expected findings include size-dependent blocking, enhanced or anomalous coercivity, exchange bias, reduced ordering temperatures, and surface-spin contributions. Future work may extend the protocol using Mössbauer spectroscopy, X-ray photoelectron spectroscopy, electron spin resonance, or element-specific magnetic probes to distinguish oxidation-state and interface effects more precisely.

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