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Finite size versus surface effects on magnetic properties of antiferromagnetic particles

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The observation of finite magnetic moment in antiferromagnetic materials is quite unusual and has been immensely investigated in nanoparticle systems. Here, the structural and magnetic properties of NiO particles are explored by x-ray diffraction, extended x-ray absorption fine structure, and magnetization measurements. Using similar-sized particles with different surface defect structure, we show that the observed magnetic enhancement, which is present even beyond finite-size limit, is due to the surface effects. However, the well known spin glass freezing is found to occur only in nano-regime. © 2011 American Institute of Physics. [doi:10.1063/1.3668091]

In spite of their compensated nature, the origin of observed finite magnetic moment in antiferromagnetic (AFM) materials and various unusual phenomena like loopshift upon field cooling, enhanced coercivity in nano-regime have been a debated issue in literature.¹⁻¹³ A clear understanding is awaiting for their technological relevance as well as for basic science. In 1961, Néel proposed that observed magnetic enhancement can be understood by realizing two sublattice uncompensated moment at the surface of the particle. However, observed moment is found to be too large to be expected from the two-sublattice model and that has been extended to *multi-sublattice* model as the new finite size effect in AFM nanoparticles.³ The multi-sublattice ordering has been demonstrated to be true nano-scale phenomenon¹³ and is absent in particles with larger size especially beyond nano-range (>100 nm). Recent observations of spin glass behavior in different AFM nanoparticle systems are not properly understood and have been mostly attributed to surface spin disorder.⁷ The observations of vacancy induced magnetic moment in non-magnetic systems¹⁴⁻²⁰ motivated us to approach the problem from structural studies.¹²

In this context, particle size dependence of magnetic properties is mostly studied; however, magnetic properties of same-sized particles with different surface conditions must be investigated to properly understand the surface effects on the observed magnetic enhancement. For this purpose, we have prepared NiO particles from thermal decomposition of highly pure Ni-nitrate salt at various temperatures (550 °C, 800 °C and 1000 °C). Different synthesis temperatures yield different particle sizes; however, the surface of a fixed size particle (prepared at particular temperature) was modified by varying the cooling rate during synthesis. Some set of samples (Q samples) were quenched to room temperature (RT) from the synthesis temperatures while others (R samples) were allowed to relax for several hours to RT inside the furnace. NiO nanoparticles were prepared by thermally decomposing Ni-hydroxide at 400 °C as described elsewhere.¹² Single phase NiO powders were confirmed by high resolution powder diffraction (XRD) experiments at RT and typical diffraction patterns are shown in Fig. 1(a). XRD experiments were performed at Powder diffraction beamline (MCX) of Elettra synchrotron centre, Italy with a fixed x-ray energy of 8 keV. Crystallite size and morphology of the particles were characterized by transmission electron microscope (TEM). Magnetization data were obtained with a quantum design Superconducting Quantum Interference Device (SQUID) magnetometer. Local structure was characterized by extended x-ray absorption fine structure (EXAFS) measurements at the Ni K edge, in both conversion electron yield mode (CEY) (which is near surface sensitive)^{12,21} and transmission mode (TRANS) (which is bulk sensitive) at XAFS beamline of Elettra synchrotron centre, Italy.

The cell parameters from XRD data are extracted by Rietveld method using the FullProf program suites.²² The observed and calculated diffraction patterns for 800Q (prepared at 800 °C and quenched) and 800R (prepared at 800 °C and relaxed) samples are shown in Fig. 1(a), as an example. Determined lattice constant largely depends on preparation temperature [Fig. 1(b)], expanded in nano-regime. In Fig. 1(b), we also label the average crystallite size as determined from TEM images, which increases with synthesis temperature and nearly saturates (~0.2 μ m) beyond 800 °C. Particle sizes of Q and R samples are found to be nearly same for a particular synthesis temperature, as explicitly shown in the TEM images [Figs. 1(c) and 1(d)] for the samples prepared at 800 °C. In Fig. 1(e), we also present the TEM image of NiO nanoparticles (NP22) prepared at 400 °C.

In Figs. 2(a) and 2(b), we show the phase-corrected magnitude of Fourier transform (FT) of EXAFS signal $(k^2\chi(k))$ for the first two shells (the Ni-O and Ni-Ni shell) measured in CEY mode, as indicated. Background correction and normalization of raw EXAFS data are performed in ATHENA^{23,24} following conventional procedure. Normalized $\chi(k)$ data are then used to model in ARTEMIS with the phase shift and backscattering amplitude calculated from FEFF6 code.²⁵ The first peak around 2.085 Å is due to the scattering from the nearest neighbour shell (Ni-O shell) containing 6 oxygen atoms. The second peak around 2.95 Å is due to the scattering from next shell (Ni-Ni shell) containing 12 Ni atoms. The different FT magnitudes of Q and R samples [Figs. 2(a) and 2(b)] already signify different local environments around Ni sites. Hardly any changes are observed between Q and R samples when

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FIG. 1. (Color online) (a) Typical XRD pattern along with the calculated and difference pattern (as indicated). (b) Effect of synthesis temperature on particle size and lattice constant. TEM images of (c) 800Q, (d) 800R, and (e) NP22 samples.

measured in TRANS mode (not shown). Hence the measurements on microparticles in CEY mode show different surface nature of R samples with enhanced surface disorder or reduced site occupancy compared to Q samples.

To quantify, the experimental data are refined with Fm-3m structural model of NiO within R = 1-3.5 Å range in Rspace (Fourier transformed space), where the influence of multiple scattering is found to be very small. The data sets are also co-refined with multiple k-weight (k and k^3) to break the correlation between σ^2 (disorder parameters) and N (coordination numbers) for different paths. In all cases, we



FIG. 2. (Color online) FT magnitude of EXAFS signal (CEY mode) for the particles synthesized at (a) $800 \degree C$ and (b) $1000 \degree C$. (c) Magnitude and real component of FT of EXAFS signal in R space and (d) the real component of FT in the back transformed k space (for 800R sample). In (c) and (d), the fitting to the data (presented by dots) is shown as solid line.

achieve very good fits; typical fits are shown in Figs. 2(c) and 2(d) for the 800R sample in R-space and backtransformed (Fourier filtered) k-space, respectively, and fitting results are presented in Table I. From this table, it can be noted that for all the R samples Ni co-ordination number is greatly reduced. Near stoichiometric values are obtained from the fitting of the data acquired in TRANS mode. Form these results, we can conclude that the surface of R sample is highly defective (Ni deficient or oxygen excess) and consequently disordered compared to Q sample. This may happen due to vacancy migration to near surface region during slow cooling process for the R samples.

To follow these structural effects on their magnetic behavior, temperature dependent magnetization (MT) measurements were performed under field cooled (FC) and zero field cooled (ZFC) protocols. It can be seen that the FC and ZFC magnetization curves bifurcate near 300 K for the case of nanoparticle NP22 [Fig. 3(a)], while they almost coincide for the microparticles (overlapping FC and ZFC curves are presented by single curve in Figs. 3(c)-3(e)). In Fig. 3(a), we

TABLE I. Fitting results for Q and R samples (CEY data). N_{frac} is fractional occupation of the shells (stoichiometric value is $N_{frac} = 1$), and ss (σ^2) is the disorder parameter.

Bond	N^Q_{frac}	$R^Q({\rm \AA})$	$ss^Q(\text{\AA}^2)$	N^R_{frac}	R^{R} (Å)	$ss^{R}(\text{\AA}^{2})$
		Particle	es synthesize	d at 800 °C		
Ni-O	1.059	2.0848	0.0052	1.0282	2.0857	0.0055
Ni-Ni	0.998	2.9484	0.0052	0.9400	2.9497	0.0051
		Particle	s synthesized	l at 1000 °C		
Ni-O	1.060	2.0851	0.0052	1.0053	2.0856	0.0053
Ni-Ni	0.989	2.9488	0.0051	0.9429	2.9496	0.0052

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FIG. 3. (Color online) (a) FC and ZFC magnetization and (b) MH curve of NP22 nanoparticle. (c)-(e) MT and (f)-(h) MH curves for R and Q samples prepared at different temperatures as indicated. Insets of (c)-(e) show the zoomed view of corresponding ZFC curves with the presence of minima T_m .

observe the usual broad peak around $T_p = 150 \text{ K}$ in the ZFC curve of NP22 sample (a signature of spin glass freezing') which is absent in the magnetization curves with larger particle size (>200 nm, Figs. 3(d) and 3(e)) and even in 60 nm particle (prepared at 550 °C, Fig. 3(c)). Observed hysteric behavior of our NP22 nanoparticle sample [Fig. 3(b)] is quite similar to previous observations.³ The observation of spin glass behavior and enhancement of magnetization in AFM nanoparticle systems have been explained in terms of enhanced surface disorder and interacting cationic vacancy.¹² However, beyond nano-range and even in 60 nm NiO particle, we do not observe any peak (down to 5 K) in the ZFC curve. In all cases, we observe clear minima (T_m) in ZFC-FC curve, which are pronounced for the R samples. Initially the magnetization decreases with increasing temperature and then it increases at higher temperatures after T_m for all R samples (see insets of Figs. 3(c)-3(e)). For the Q samples, low temperature anomaly is less clear; a normal AFM behavior has been observed, i.e., increased magnetization with increasing temperature. Hence from Figs. 3(c)-3(e), we observe a magnetic enhancement at low temperature region for all the R samples compared to Q samples. The MH measurements (at 5K) performed on different Q and R samples are also presented in Figs. 3(f)-3(h). The MH curves for the R samples show a sense of saturation superimposed on AFM contribution (linear nature as in Q samples), which diminishes with increasing synthesis temperature. The low temper-

ature magnetic enhancement enables us to speculate existence of two different magnetic phases over the volume of R samples, one (weak ferromagnet and/or paramagnet like behavior), which dominates in low temperature region and the other one (AFM), which dominates in high temperature region. The competition between these two magnetic phases determines the minima T_m .

In conclusion, structural distortion and defects can modify overall magnetic behavior and introduce finite moments in compensated antiferromagnetic materials. Few previous reports^{10,26} are also in support of our understanding. Here, the highly defective surface shell of relaxed particles (R samples) enhances magnetic moments in otherwise AFM system. In nonmagnetic oxides 16,18,19 (such as CaO, HfO₂), it is shown that the cation vacancy polarizes the surrounding ligand atoms and introduces local moment around the vacancy site. In a similar way, the introduction of a Ni vacancy in NiO host lattice results in hole doping at the oxygen 2p states. Now depending on the charge state of the vacancy, a finite moment arises as discussed in Ref. 12. This dominates the low temperature region of MT curve and is absent in quenched particles (Q samples). The high temperature behavior is determined by the ordered core of the particle (AFM phase). Our experimental observations demonstrate that structurally modified surface of AFM particle can yield magnetic enhancement, which is present even beyond nanorange. Hence the observed magnetic enhancement in AFM particles is not a true nano-scale phenomenon but mostly determined by the surface defect structure.

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