

Neutron scattering study of structural and magnetic size effects in NiO

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Abstract. Nickel oxide powders with the grain size of 13-1500 nm have been studied by neutron scattering, scanning electron microscopy and vibrating sample magnetometry. We have found that the atomic structure and the antiferromagnetic ordering are nearly independent of the average size of grains. The existence of the uncompensated spins in nanoparticles with the grain size below 100 nm has been detected.

1. Introduction

Effect of crystallite size on the atomic and magnetic structures of antiferromagnetic (AFM) simple oxides such as MnO [1], CoO [2] and NiO [3] remains an interesting topic of research. In particular, the existence of more than two magnetic sublattices as in bulk antiferromagnetic (AFM) nickel oxide has been proposed in NiO nanoparticles [3, 4] and still remains the topic of discussions. Besides antiferromagnetically ordered core, NiO nanoparticles are supposed to have magnetically disordered uncompensated surface spins [3, 5], which can yield a detectable net magnetic moment.

The existence of AFM ordering at room temperature in NiO nanopowders with the crystallite sizes of 13-1500 nm has been recently confirmed in [6] by several experimental techniques, including neutron diffraction. It was also found that the crystal lattice of nanoparticles in AFM phase experiences weak rhombohedral distortion as in the bulk NiO [6].

In this study we have employed the neutron scattering method to probe a correlation between the size of the coherently scattering structural and magnetic regions in NiO nanopowders.

2. Experimental

Four NiO samples (S1, S2, S3, S4) were prepared according to the procedure described in [6]. The grain average sizes determined from the BET specific surface area measurements were 13 nm (S1), 100 nm (S2), 138 nm (S3) and 1500 nm (S4). The morphology of all samples



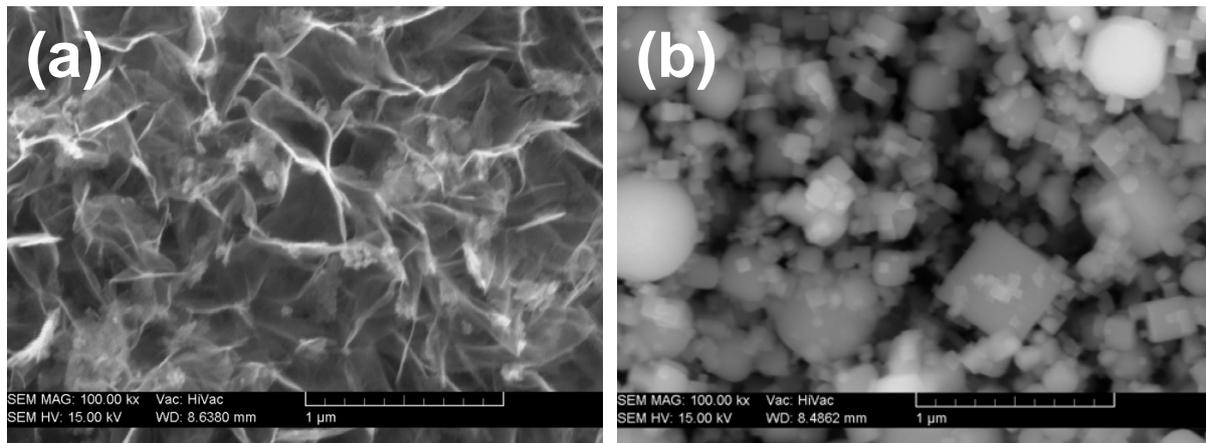


Figure 1. SEM images of NiO samples S1 (left) and S3 (right).

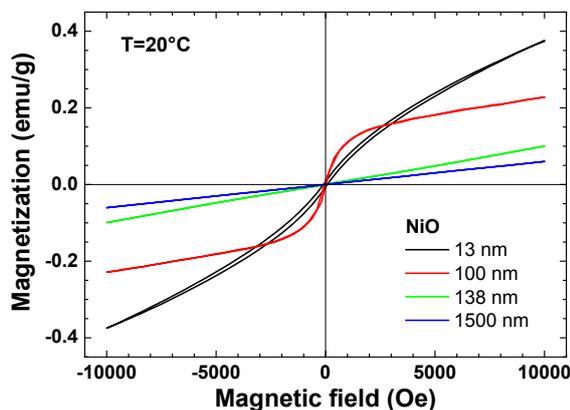


Figure 2. The magnetization curves for NiO samples.

Table 1. NiO grain size L_{BET} (in nm) determined from the BET specific surface area measurements. The sizes (in nm) of coherent neutron scattering regions L_{nuc} and L_{mag} calculated from the width of the nuclear and magnetic reflections, respectively.

Sample	S1	S2	S3	S4
L_{BET}	13	100	138	1500
L_{nuc}	9.3-10.6	94-102	89-123	>380
L_{mag}	<10	37-43	101-133	>280

was studied by scanning electron microscopy (SEM) using TESCAN MIRA microscope with secondary electron detector (Fig. 1). Static magnetization (Fig. 2) was measured by vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., model 7404 VSM) using magnetic field in the range from -10 kOe to $+10$ kOe. The diffraction patterns were measured at room temperature using high resolution Fourier diffractometer (HRFD) at the IBR-2 pulsed reactor in Dubna [7]. Their analysis was performed using the Rietveld method by the MRJA code [8]. The widths of the diffraction peaks were analysed using the UPEAK code [9].

3. Results and discussion

SEM images for two selected samples S1 and S3 are shown in Fig. 1. A homogeneous agglomeration of nanoparticles is observed for the sample S1, however their average size of grains ($L_{BET} = 13$ nm) is too small to be resolved. In the case of the sample S3, the nanoparticles are well visible showing a broad distribution (30-500 nm) of sizes and shapes.

Magnetic field dependence of magnetization, measured at 20°C , is shown in Fig. 2. A hysteretic behavior is observed for samples S1 and S2, having smallest grain size (Table 1). It is consistent with previous findings and can be explained by the presence of the uncompensated

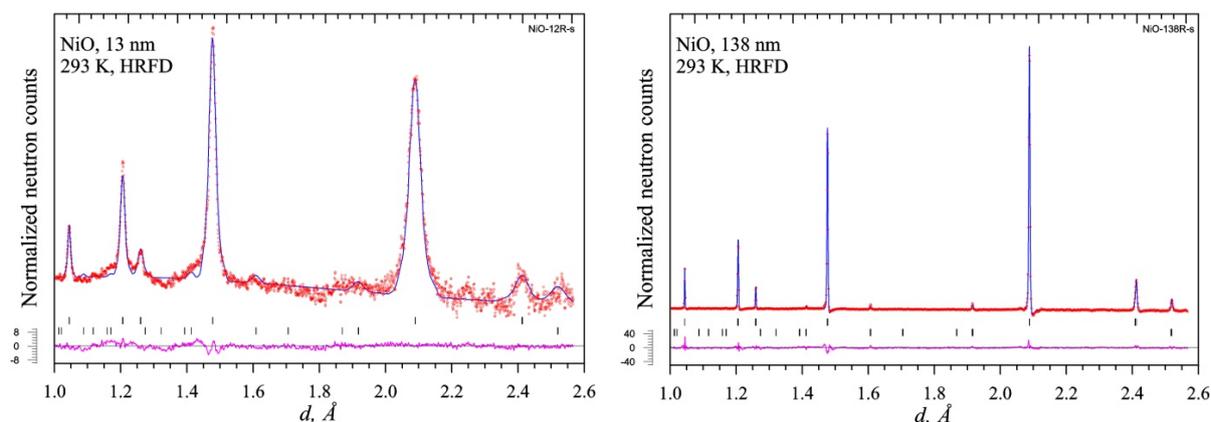


Figure 3. Rietveld refinement of the neutron diffraction patterns measured at room temperature for NiO samples S1 and S3 having the grain size of 13 nm (left) and 138 nm (right). The solid circles correspond to the experimental data, and the solid line – to the calculated pattern. The residual curve is shown at the bottom. The vertical ticks indicate the calculated nuclear (upper row) and magnetic (lower row) reflection positions.

spins in the nanoparticle cores and at the nanoparticle surface [10, 5].

Above the Néel temperature $T_N = 523$ K bulk NiO is in the paramagnetic phase and has a rock-salt cubic structure (space group $Fm\bar{3}m$, No. 255) with the lattice parameter $a_c \approx 4.177$ Å. Below T_N magnetic moments of the Ni^{2+} ions order antiferromagnetically leading to rhombohedral distortion with $a_R \approx a_c/\sqrt{2} \approx 2.954$ Å, $\alpha \approx 60.07^\circ$ (space group $R\bar{3}m$, No.166) [11, 12]. The rhombohedral magnetic cell is twice as large as the crystallographic one $a_{\text{mag}} = 2a_R = 5.907$ Å.

Since the lattice distortion in NiO is very small, it can be detected only using high-resolution diffractometer. In standard operation (Fourier chopper maximum rotation speed $V_{\text{max}} = 4000$ rpm), the resolution of HRFD is $\Delta d/d \approx 0.0015$ for $d = 2$ Å, and it improves with increasing d_{hkl} . At this resolution the reliably determined microstrain in crystallites is $\Delta a/a \approx 0.0008$ and more, and the average size of coherently scattering domains is $L_{\text{coh}} \approx 250$ nm or less.

The HRFD diffraction patterns for two selected NiO samples S1 and S3 are shown in Fig. 3. Both structural and magnetic diffraction peaks are well resolved due to the high symmetry of NiO and high-resolution measurement mode used. No impurity phases have been detected.

Processing of the spectra by the Rietveld method using the MRJA code [8] allowed us to use the experimentally measured line shape. The processing was carried out in a two-phase version (crystal and magnetic structure) in a limited range d_{hkl} with the ability to set different widths of the peaks in phases. The convergence of the minimization process for all spectra was good, except for the magnetic phase in the sample S1.

Upon a decrease of the crystallite size, the unit cell parameter a_R remains practically constant, but the width of the diffraction peaks increases. However, a small (0.16%) increase in the cell volume was observed for the sample S1 with $L_{\text{BET}} \approx 13$ nm. This result agrees with an increase of the lattice parameter in nanosized NiO, which has been found previously by x-ray diffraction [10, 13] and x-ray absorption spectroscopy [14]. Note that while the widths of the structural and magnetic peaks are close in the sample S4, the broadening of the magnetic peaks occurs upon crystallites size reduction (Fig. 4). The sizes of the coherently scattering blocks, estimated from the peak widths of the nuclear and magnetic reflections, are given in Table 1.

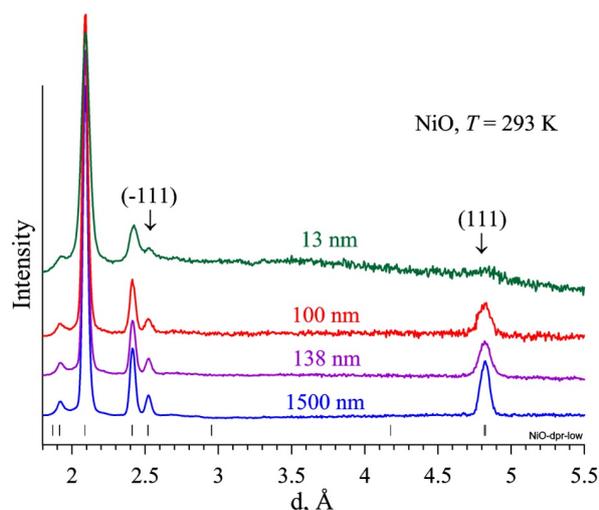


Figure 4. Low resolution diffraction patterns for large d_{hkl} . The positions of the magnetic peaks (111) and (-111) are indicated.

4. Conclusions

Nickel oxide nanoparticles with the average size of grains in the range of 13-1500 nm have been studied by neutron scattering, scanning electron microscopy and magnetometry.

We found that the atomic structure and the type of magnetic ordering are nearly independent of the average size of grains. There is only a small (0.16%) increase in the cell volume when the grain size decreases down to 13 nm. In the samples with the grain sizes of 138 and 1500 nm, the average size of the coherently scattering structural and magnetic regions coincides and is large, but smaller than the grain size. When the grain size is reduced down to 100 nm, it becomes comparable to that of the crystallites, whereas the magnetic coherence length is about 3 times smaller. Finally, the long-range magnetic order becomes largely destroyed in the sample with the smallest grain size of 13 nm.

Acknowledgments

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