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Structural and Magnetic Properties of Nickel Oxide Nanopowders

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Abstract. Structure and magnetic properties of nickel oxide (NiO) nanopowders have been studied by X-ray/neutron diffraction, SQUID magnetometer, and micro-Raman spectroscopy. Our diffraction data indicate that at room temperature all NiO powders are antiferromagnetically ordered and have a rhombohedral (*R*-3*m*) phase. The SQUID magnetometry and Raman spectroscopy measurements support the presence of the antiferromagnetic ordering.

Introduction

The bulk nickel oxide (NiO), due to its electronic structure and chemical bonding, is a Mott insulator and shows up an easy-plane antiferromagnetic (AFM) ordering of type-II, which has made it a challenge for the theory for decades. In the paramagnetic phase above the Néel temperature T_N = 523 K [1], NiO has a cubic rock-salt crystal structure (*Fm*-3*m*). Below T_N, the magnetic ordering results in that the spins of the Ni^{2+} ions order ferromagnetically in {111} planes [2, 3], and the structure of NiO undergoes a week cubic-to-rhombohedral distortion (*R*-3*m*) due to the magnetostriction effect [1, 4]. The magnetic structure of NiO nanoparticles can differ from the bulk magnetic structure, because of the influence of surface effects [5]. For example, a complex magnetic structure with as many as eight sublattices has been observed in NiO nanoparticles [6], in contrast to the bulk NiO which has a simple two-sublattice structure.

In this work we present the results on the structural and magnetic properties of NiO nanopowders obtained by x-ray/neutron diffraction, SQUID magnetometry and Raman spectroscopy.

Experimental

The nanosized NiO powders have been produced by the two methods. A precipitation method, employing reacting aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and NaOH, was used to prepare particles about 13-23 nm, which were further annealed in air at several temperatures up to T_{an}=450°C. In the second method, particles with a size of 100 and 1500 nm were prepared by evaporation of the coarse grained commercially available NiO (99.9%) powder with a particle size in the range of 20-40 μm in the radio-frequency plasma. The average size of all nanoparticles was estimated from the BET specific surface area measurements.

Structural features of samples were characterized by X-ray Diffraction (XRD) using an DRON-4 diffractometer (Russia) with a Cu Kα monochromatic radiation (λ=1.5418 Å). The neutron diffraction studies were performed at room temperature using a D7a neutron diffractometer (IVV-2M reactor, Zarechny, Russia). The structural parameters were determined by the Rietvield analysis procedure.

SQUID magnetometer measurements of nanosized NiO were performed in the temperature range of 2-300 K and the magnetic field range of 0-50 kOe.

Raman spectra were measured at room temperature using a 50× microscope objective using a Renishaw inVia micro-Raman spectrometer equipped with an argon laser (514.5 nm, max cw power P_{ex}=10 mW). The spectral signal was dispersed by the 2400 grooves/mm grating onto a Peltier-cooled (-60°C) CCD detector. The Raman spectra were acquired with a laser excitation power of 0.1 mW to exclude the sample heating.

Results and discussion

According to our X-ray and neutron diffraction data, all NiO powders are antiferromagnetically ordered at room temperature and have rhombohedral (R-3m) phase as is evidenced from the NiO(422) Bragg reflex splitting located at a high scattering angle of about 130°. The structural parameters, determined by the Rietvield analysis procedure, indicate an expansion of the lattice volume when the size of particles decreases below 30 nm, being in agreement with the results from [7].

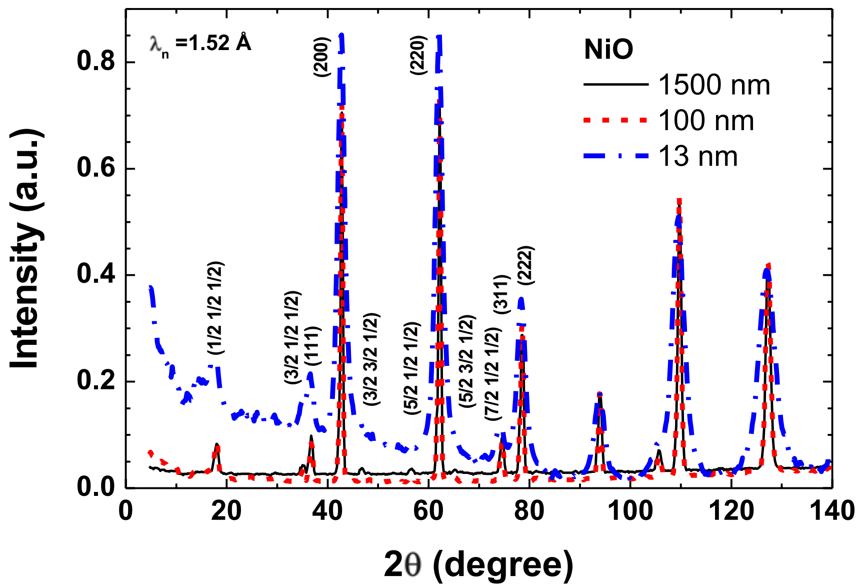

Fig. 1. Neutron diffraction pattern for NiO powders at room temperature.

The results of the SQUID magnetometer measurements of nanosized NiO, performed in the temperature range of 2-300 K and the magnetic field range of 0-50 kOe, evidence the presence, along with an antiferromagnetic particle core, of Ni^{3+} ions.

The room temperature micro-Raman spectra of nanopowders are similar to that of microcrystalline NiO [8]: there are five vibrational bands - one-phonon (1P) TO at 440 cm^{-1} and LO at 560 cm^{-1} modes, two-phonon (2P) 2TO at 740 cm^{-1}, TO+LO at 925 cm^{-1} and 2LO at 1100 cm^{-1} modes; a two-magnon (2M) band at ~1500 cm^{-1}. The presence of the two-magnon band at 1500 cm^{-1} indicates that the powders remain in the antiferromagnetic phase at RT even for such small grains size as 13 nm. Besides, the one-phonon band at about 200 cm^{-1} can be also observed in the rhombohedral phase.

Table 1. Structural parameters (a, c, V) and magnetic moments (μ_B) for the NiO powders obtained from the Rietvield analysis of the X-ray and neutron diffraction patterns. The structural parameters (a, c) correspond to the hexagonal settings of the R-3m space group.

Grain size (nm)	Lattice constants and volume	X-ray data	Neutron data	Magnetic moment (μ_B)
1500	a (Å) c (Å) V (Å^3)	2.95472 ± 0.00003 7.2257 ± 0.0002 54.632 ± 0.002	2.9555 ± 0.0001 7.2247 ± 0.0006 54.654 ± 0.005	0.586
100	a (Å) c (Å) V (Å^3)	2.95474 ± 0.00008 7.2261 ± 0.0002 54.635 ± 0.002	2.9561 ± 0.0001 7.2224 ± 0.0005 54.655 ± 0.005	0.535
13	a (Å) c (Å) V (Å^3)	2.96418 ± 0.00081 7.19740 ± 0.00526 54.77 ± 0.05	2.953 ± 0.002 7.256 ± 0.009 54.80 ± 0.09	0.584

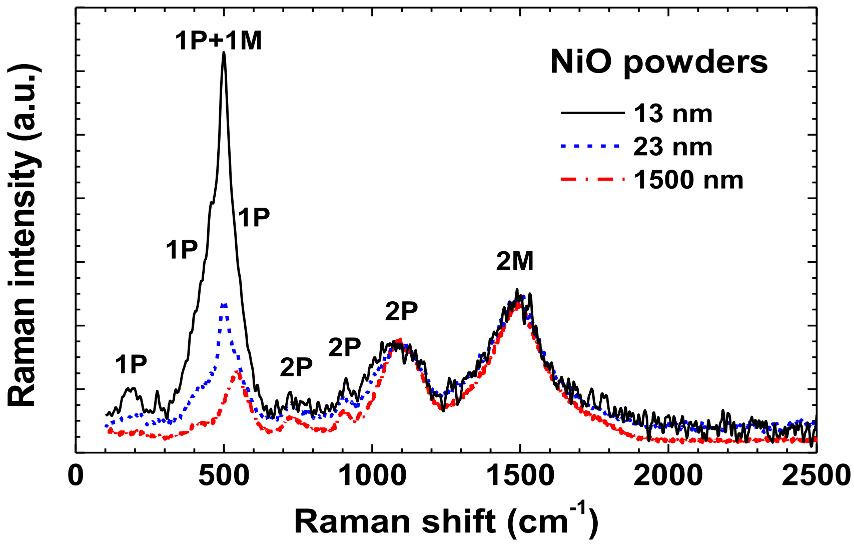

Fig. 2. Room temperature micro-Raman spectra of the NiO powders having grain size 13, 23 and 1500 nm.

A new Raman band at 500 cm^{-1} has been found in nanosized NiO: its temperature and size dependences suggest magnetic origin. We attribute this band to a one-phonon (~440 cm^{-1}) plus one-magnon (~40 cm^{-1}) excitation induced by the strong phonon-magnon interaction at the nanoparticle surfaces or some defects.

Summary

The structure and magnetic properties of the nickel oxide (NiO) nanopowders, having a grain size of 13, 23, 100, and 1500 nm, have been studied by X-ray/neutron diffraction, SQUID magnetometry, and micro-Raman spectroscopy. Our diffraction data indicate that at room temperature all NiO powders are antiferromagnetically ordered and have rhombohedral (R-3m)

phase. The structural parameters, determined by the Rietvield analysis procedure, indicate an expansion of the lattice volume when the particles size decreases below 30 nm. SQUID magnetometry and Raman spectroscopy measurements support the presence of the antiferromagnetic ordering. Besides, a strong phonon-magnon coupling, presumably at the surface of nanograins, has been evidenced in nanosized NiO from the Raman scattering band at 500 cm^{-1}.

Acknowledgements

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