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To cite this article: N Mironova-Ulmane *et al* 2007 *J. Phys.: Conf. Ser.* **93** 012039

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Raman scattering in nanosized nickel oxide NiO

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Abstract. Magnetic ordering in nanosized (100 and 1500 nm) nickel oxide NiO powders, prepared by the plasma synthesis method, was studied using Raman scattering spectroscopy in a wide range of temperatures from 10 to 300 K. It was observed that the intensity of two-magnon band decreases rapidly for smaller crystallites size. This effect is attributed to a decrease of antiferromagnetic spin correlations and leads to the antiferromagnetic-to-paramagnetic phase transition.

1. Introduction

Pure nickel oxide NiO exhibit antiferromagnetic magnetic ordering, with planes of opposite spins being repeated in alternating order along the [111] direction. Below the Néel temperature, the magnetic ordering in NiO is accompanied by a slight rhombohedral distortion (at 20°C, $a_0=2.9459$ Å, $\alpha=60^\circ 4.2'$ [1]). Magnon excitations in pure nickel oxide NiO were successfully studied in the past by Raman spectroscopy [2-7]: the strong magnetic Raman response is caused by a Ni-O superexchange mechanism. The temperature-dependent [2,3,5-7] and pressure-dependent [4] Raman scattering in pure NiO allows to identify contributions from one-phonon (TO and LO modes) and two-phonon (2TO, TO+LO, and 2LO modes) excitations and one-, two- and four-magnon excitations. In the paramagnetic phase with the rock-salt structure, no first-order Raman scattering is expected in NiO. However, when NiO is antiferromagnetically ordered or defect-rich, the intensity of one-phonon scattering increases significantly [2]. The magnon contribution in Raman spectra of NiO increases with a decrease of temperature [2,3,7] or increase of pressure [4]. It was also found that the two-magnon (2M) band broadens upon NiO dilution with calcium [8]. Such behaviour of the magnetic subsystem agrees well with that predicted by the theory of light scattering by magnons [9,10]. Recently we have extended these studies to diluted antiferromagnetic system as $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions [11,12], where unpredicted behavior of temperature and composition dependences of one-magnon excitation energies has been observed. In the present work the Raman scattering in nanosized NiO powders, produced by plasma synthesis, was studied for the first time.

2. Experimental

Nanosized NiO powders were produced by evaporation of coarse grained commercially available NiO (99.9%) powder with particle size in the range of 20-40 μm in radio-frequency plasma using

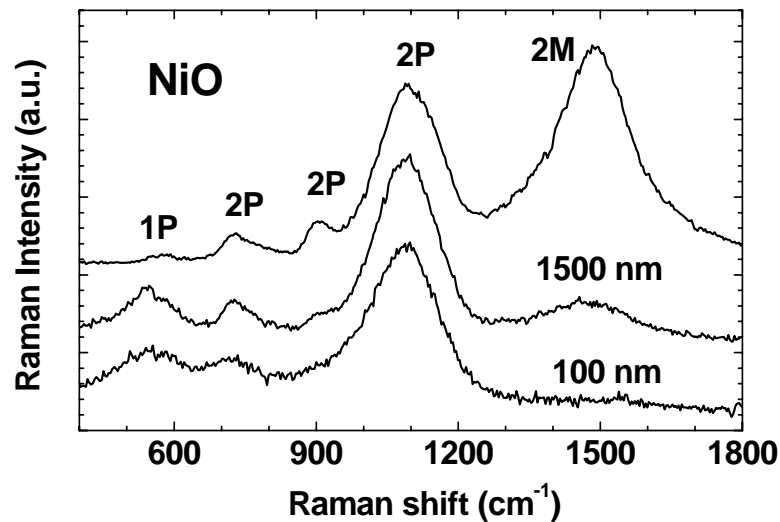


Figure 1 Room temperature Raman spectra ($\lambda_{\text{ex}}=442$ nm) of nickel oxide single-crystal (upper curve) and nanopowders, having the grain sizes of about 1500 nm and 100 nm. Peaks due to one-phonon (1P), two-phonon (2P) and two-magnon (2M) scattering are indicated.

technological apparatus described in [13]. Typical synthesis conditions used in the present case were flow rate of plasma forming gas of 8.0 m³/h, raw feeding rate of 0.6-1.2 kg/h and flow rate of cooling gas of 0.6-50 m³/h. The cooling gas was introduced into vapour region of NiO in order to prevent particle growth and obtain powders with different specific surface area. Change of the flow rate of cooling gas allows to produce NiO particles with specific surface area equal to 6.5 and 9.0 m²/g and having the average particle size of about 125 and 100 nm, respectively. The third NiO sample with specific surface area 0.5 m²/g was prepared by additional calcination of the powder having 125 nm size at 1000°C. According to transmission electron microscopy (TEM), the nanosized NiO particles formed from vapour phase tend to reveal the morphology characteristic of its crystal structure. Green colored single-crystal NiO, grown by the method of chemical transport reactions on MgO(100) substrate, was used for comparison [14].

Raman scattering measurements were conducted using two experimental setups. The Raman spectra at room temperature (RT) (figure 1) were obtained using 3D scanning confocal microscope with spectrometer Nanofinder-S (SOLAR TII, Ltd.) and the He-Cd laser (441.6 nm, 50 mW cw power) as excitation source [15]. The laser power at the sample was regulating by the neutral filter (OD=0.5) to prevent sample heating. The measurements were performed through Nikon Plan Fluor 40x (NA=0.75) objective, mounted on inverted Nikon ECLIPSE TE2000-S optical microscope. The elastic component of scattered light was eliminated by the edge filter. The Raman spectra were recorded by a TE cooled back-thinned CCD camera (ProScan HS-101H) attached to the monochromator-spectrograph Model MS5004i (SOLAR TII, Ltd., focal length 520 mm, 600 grooves/mm grating, a resolution 0.16 nm).

The low temperature Raman studies (figure 2) were carried out by using an home-made micro-Raman spectrometer based on a standard Olympus microscope equipped with single grating Andor Shamrock 303i spectrometer (focal length 303 mm, 600 grooves/mm grating, a resolution 0.33 nm) and TE cooled Andor Newton EMCCD camera. The Nd-YAG 532 nm laser excitation was used with intensity about 5 mW on the illuminated volume. A 50x objective was used, so that sampling volume was a cylinder with diameter 1.5 μm and depth about 14 μm . To carry out the low temperature measurements a special Utreks-type cold finger helium cryostat was designed.

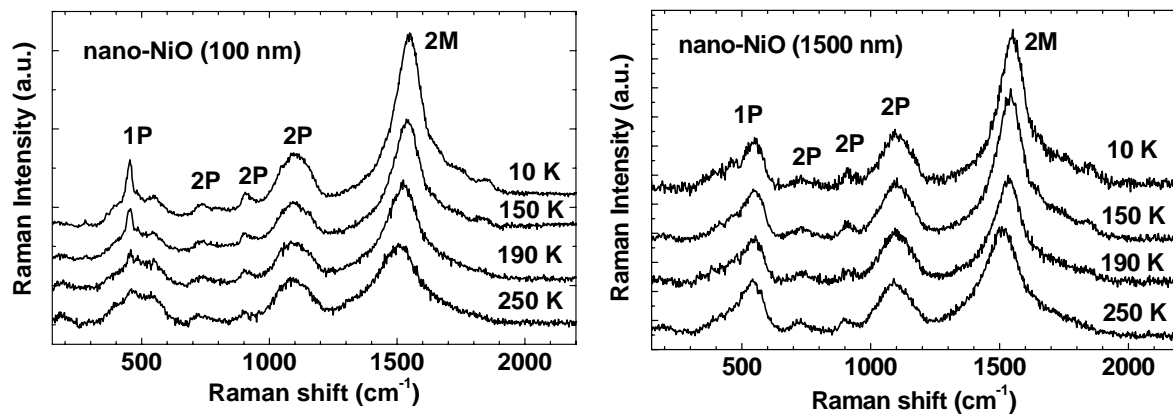


Figure 2 Temperature dependent Raman spectra ($\lambda_{\text{ex}}=532$ nm) of nickel oxide nanopowders, having the grain sizes of about 100 nm and 1500 nm. Peaks due to one-phonon (1P), two-phonon (2P) and two-magnon (2M) scattering are indicated.

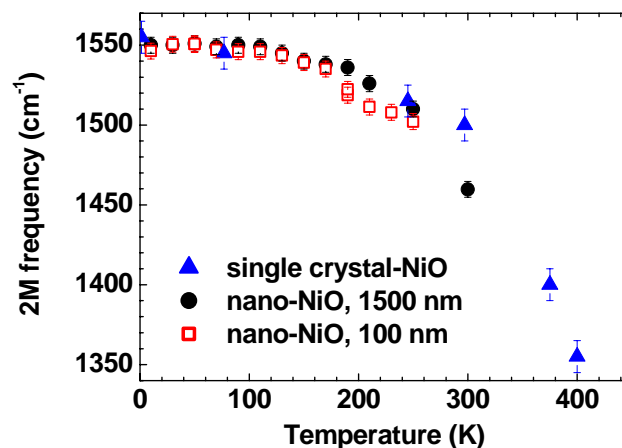


Figure 3 (Color online) Temperature dependence of the two-magnon (2M) frequency in nickel oxide nanopowders, having the grain sizes of about 100 nm (solid circles) and 1500 nm (open squares). The data for single-crystal NiO taken from [2,3] are shown for comparison by solid triangles.

3. Results and Discussion

The RT Raman spectrum of single-crystal NiO shows several bands in the probed region above 400 cm^{-1} (figure 1). The first four bands have vibrational origin and, according to assignment in [3], correspond to one-phonon (1P) TO and LO modes (at ~ 570 cm^{-1}), two-phonon (2P) 2TO modes (at ~ 730 cm^{-1}), TO + LO (at ~ 906 cm^{-1}) and 2LO (at ~ 1090 cm^{-1}) modes. The last strongest band at 1490 cm^{-1} is due to a two-magnon (2M) scattering [3]: it is well observed at RT due to a high value of the Néel temperature ($T_N = 523$ K). Note that the disorder-induced 1P band at ~ 570 cm^{-1} has very small intensity indicating good quality of single-crystal.

The phonon related part of the Raman spectra (1P and 2P bands in figure 1) in nanosized NiO powders is rather similar to that in the single-crystal. However, the 1P band becomes more pronounced in powders due to the presence of defects or surface effect, but the three 2P bands appear to be more broadened, especially the band at 906 cm^{-1} , which practically disappears. At the same time,

the two-magnon (2M) band experiences dramatic decrease of intensity in nanopowders, becoming undetectable for 100 nm crystallites size at RT.

The temperature dependence (10-250 K) of the Raman signal in nanosized NiO powders is shown in figure 2. Here two main effects are observed. First, the two-magnon peak is present in both samples, and its behaviour follows the expected one for three-dimensional, cubic antiferromagnets: upon heating, the peak broadens, and its position shifts to lower energies (figure 3). In bulk NiO the two-magnon peak vanishes at around the Néel temperature [2,3]. Note also that the two-magnon lineshape in nanopowders at 10 K is very close to one that observed in [5,6] for bulk NiO and consist of the main peak and three shoulders at the high energy side. Second, the one-phonon band at $\sim 500\text{ cm}^{-1}$ remains nearly unchanged for 1500 nm size powder at all temperatures, but in 100 nm size powder this band has a different shape and a sharp peak at 450 cm^{-1} grows up on top of the band upon cooling.

Two-magnon Raman scattering in bulk NiO involves Brillouin zone-edge magnons, which interact weakly with phonons [6] that explains rather narrow width of the Raman lineshape, observed also in our nano-powders at low temperature (figure 2). However, in the presence of the substitutional disorder as in $\text{Ni}_c\text{Ca}_{1-c}\text{O}$ [8] and $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ [11], the two-magnon Raman band experience significant broadening. Similar behaviour of the 2M-band appears also in nanosized powders (figure 1). This effect can be explained by a decrease of antiferromagnetic spin correlations [6] leading to the antiferromagnetic-to-paramagnetic transition in nanosized nickel oxides.

Another interesting result, the appearance of the sharp peak at 450 cm^{-1} (figure 2), can be related to the activation of the Raman vibration at low-temperature by magnetostriction effect, known [1] to be responsible for a slight rhombohedral distortion in bulk NiO. The position of this peak remains unchanged due to the TO modes in NiO [21,22] have small dispersion over all Brillouin zone.

4. Conclusions

Magnetic ordering in nanosized (100 and 1500 nm) nickel oxide NiO powders, prepared by the plasma synthesis method, was studied using Raman scattering spectroscopy in a wide range of temperatures from 10 to 300 K. It was observed that the intensity of two-magnon band at $\sim 1550\text{ cm}^{-1}$ decreases rapidly for smaller crystallites size. This effect is attributed to a decrease of antiferromagnetic spin correlations.

Acknowledgments

This work was partially supported by Latvian Government Research Grant No. 05.1718, Latvian National Research Program in Materials Science and the Estonian Science Fondation Grant No. 6999.

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