VERSITA

Central European Journal of **Physics**

Polarisation dependent Raman study of single-crystal nickel oxide

Research Article

Nina Mironova-Ulmane[1*], Alexei Kuzmin[1], Ilmo Sildos[2], Martti Pärs[2]

1 Institute of Solid State Physics, University of Latvia,
   Kengaraga street 8, LV-1063, Riga, Latvia

2 Institute of Physics, University of Tartu,
   Riia street 142, EE-2400 Tartu, Estonia

Abstract: The magnetic domain structure and Raman scattering have been studied in NiO single-crystals with three different (100), (110) and (111) orientations. Twin-domain structure was observed in NiO(100) and NiO(110) single-crystals using cross-polarized optical microscopy. We found that the ratio of the two-magnon (at 1500 cm^{-1}) to the two-phonon (2LO, at 1100 cm^{-1}) Raman bands intensity is sensitive in a particular way to the type of the twin-domain pattern.

PACS (2008): 71.15.Ap, 71.20.Ps, 75.50.Ee

Keywords: NiO • Raman scattering • antiferromagnetic domains • magnons
© Versita Sp. z o.o.

1. Introduction

Nickel oxide NiO is a type–II easy–plane antiferromagnet ($S = 1$) with the Néel temperature $T_N = 523$ K [1]. In the paramagnetic state, NiO has a rock–salt–type structure (space group $Fm - 3m$) with the crystallographic unit cell parameter $a_0 = 4.1773$ Å. The transition to the antiferromagnetic state below T_N is accompanied by a weak rhombohedral distortion (space group $R - 3m$) with a contraction of the cubic unit cell along the $\langle 111 \rangle$ axes. The rhombohedral cell parameters are $a_0 = 2.9481$ Å, $\alpha = 60.080°$ at 10 K and $a_0 = 2.9533$ Å, $\alpha = 60.037°$ at 295 K [2]. In the antiferromagnetic state, the pres-

ence in NiO of crystallographic twins leads to the formation of antiferromagnetic twin–domains (T–type), having the walls at twin interfaces [3–5]. Spins order ferromagnetically in {111} planes in T–domains, but the antiferromagnetic spins alignment occurs in adjacent planes [6]. Each T–domain splits further into three S–domains with spins pointing along the $\langle 112 \rangle$ directions [7]. T–domains originate from the variety possible for the direction of the easy plane, and S–domains are caused by the variety possible for the direction of the spin axis [4]. Experimentally the domain structure of NiO has been studied in the past using neutron diffraction [4], polarized optical microscopy [4–9], and polarization dependent x-ray photoemission electron microscopy [10]. In the recent work [5], it was shown by studying the NiO(100) surface that the presence of complex assembly of twins predefines the formation of the spin domain walls (S–walls), and the imper-

*E-mail: ulman@latnet.lv

Springer

fect nature of crystallographic twin interfaces gives rise to net moment able to pin the Weiss walls in exchange coupled ferromagnetic layer.

In this work we have studied by cross-polarized optical microscopy and Raman spectroscopy the twin-domain structure in NiO single-crystals having three orientations – (100), (110), and (111). The sensitivity of the Raman scattering spectra to magnon excitations is used to probe the magnetic domain structure.

2. Experiment

Single-crystals NiO(100), NiO(110), and NiO(111) were grown epitaxially on single-crystalline MgO substrates cut along (100), (110) and (111) directions, respectively, by the method of chemical transport reaction using HCl gas as a transport media [11, 12]. Polycrystalline NiO powder, obtained by decomposing $Ni(NO_3)_2 \cdot 6H_2O$ salt at 500-600°C, was used as a source of the material. The single-crystal MgO substrate was placed at 800°C about 1 mm above pressed polycrystalline NiO pellet which was located at 900-1000°C. The whole system was placed in the vacuum reactor with the HCl gas pressure of 40-60 mmHg. Note that due to very small mismatch (< 1%) between the lattice constants of NiO and MgO [13], nickel oxide grows epitaxially on MgO and maintain the substrate orientation. Thus obtained samples were bright green colored.

Domain structure was measured at room temperature using cross-polarized set-up of an inverted Nikon ECLIPSE TE2000-S optical microscope through Nikon Plan Fluor $40\times$ (NA = 0.75) optical objective.

Raman spectra were measured at room temperature through $50\times$ microscope objective using a Renishaw inVia micro-Raman spectrometer equipped with 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.

3. Results and discussion

The projections of the antiferromagnetic twin-domain structure were clearly observed on NiO(100) and NiO(110) single-crystal surfaces using cross-polarized optical microscopy at room temperature (Fig. 1). At the same time, no domain structure was observed for mono-domain NiO(111) sample (not shown). The magnetic domain pattern for NiO(100) is chess-like, whereas it is strip-like for NiO(110). The insets in Fig. 1 provide with the explanation of the domain pattern origin in opti-
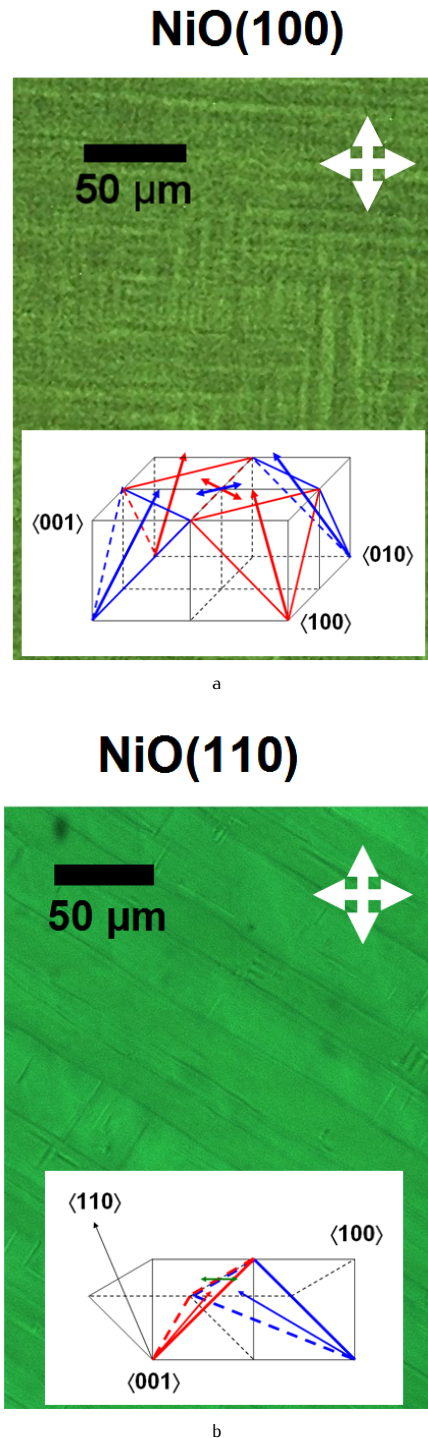

Figure 1. Twin domain structure observed using cross-polarized optical microscopy in (a) NiO(100) and (b) NiO(110) single-crystals at room temperature. The insets show models for the domains and domain walls.
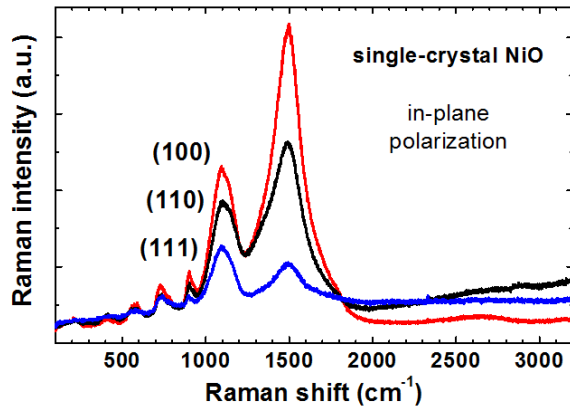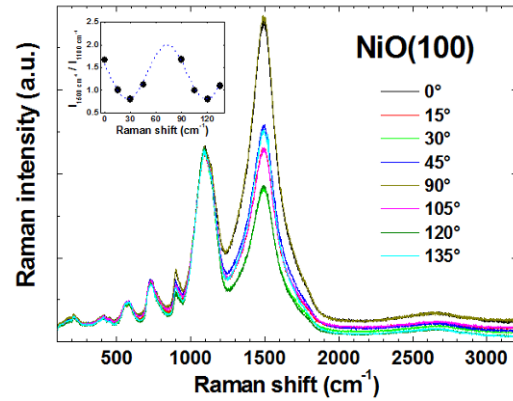
Figure 2. Room temperature micro-Raman spectra of NiO(100), NiO(110) and NiO(111) single-crystals measured with in-plane orientation of the laser polarization.

cal images. The antiferromagnetic ordering in NiO below the Néel temperature 523 K is accompanied by a rhombohedral deformation of the original cubic lattice caused by the antiferromagnetic interaction between (111) planes of ferromagnetically ordered spins [1]. As a results, the single crystal breaks down into twin–domain structure having a compression axis along one of the four [111] directions. For NiO(100), this leads to the formation of a chess–like domain pattern with perpendicular (90°) orientation of the magnetic domains. The size of twin domains platelets in Fig. 1a is about $2-7$ μm, being in agreement with that found in [5]. On the contrary, the strip–like domain pattern has parallel (180°) orientation of the magnetic domains in NiO(110) (Fig. 1b). In case of NiO(111), all spins lie in the ferromagnetic planes parallel to the sample surface, and thus no domain pattern is observed, because the sample is mono-domain.

The difference in the relative domains orientation can be observed not only by cross–polarized optical microscopy but also by the detecting spin related contribution in Raman scattering signals.

The Raman scattering in nickel oxide originates from one-phonon (TO at $400-440$ cm^{-1} and LO at 560 cm^{-1} modes), two-phonon (2TO at 740 cm^{-1}, TO+ LO at 925 cm^{-1} and 2LO at 1100 cm^{-1} modes) excitations as well as one- ($\sim$ 40 cm^{-1}), two- (at $\sim$ 1500 cm^{-1}), and four- ($\sim$ 2800 cm^{-1}) magnon excitations [14–22]. At room temperature, the one–magnon Raman scattering is located very close to the elastic line (at $\sim$ 30 cm^{-1}), being rather difficult to detect, whereas the four–magnon band is very broad (FWHM $\sim$ 400 cm^{-1}). At the same time, the two–magnon band at 1500 cm^{-1} can be easily detected, since it is located far from the elastic scattering line and
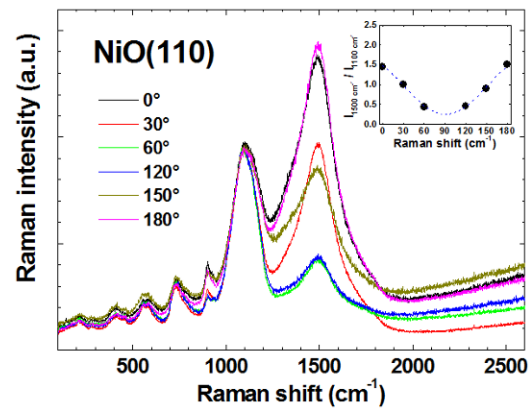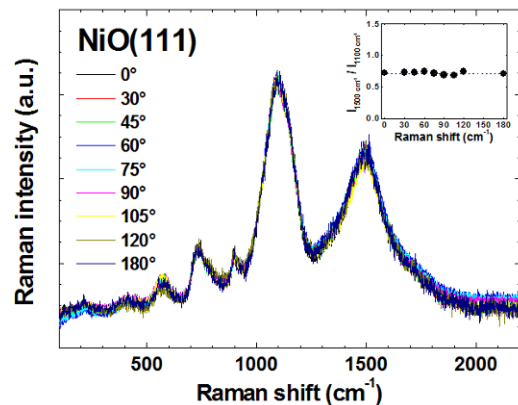
Figure 3. Room temperature micro-Raman spectra of NiO(100), NiO(110) and NiO(111) single-crystals measured for different in-plane orientations of the sample. The polarization of the laser light has in-plane orientation. The insets show the variation of the intensities ratio I(1500 cm^{-1})/I(1100 cm^{-1}) versus the angle of sample rotation. Dashed lines in the insets are guides for eye.

is well separated from phonon contributions. Therefore, it is a good candidate to probe magnetic domain structure. One can expect that the intensity of the magnon Raman scattering should show some dependence on the sample orientation. Since it is difficult to determine the absolute cross section of the Raman signal, one can use the ratio of the magnon-to-phonon bands.

First, the room temperature micro-Raman spectra were measured for NiO(100), NiO(110) and NiO(111) single-crystals with the in-plane orientation of the laser polarization (Fig. 2). The samples orientation was chosen to maximize the intensity of the two-magnon band. As one can see, the ratio between the two-magnon band at 1500 cm^{-1} and two-phonon band at 1100 cm^{-1} decreases from NiO(100) to NiO(100) and, next, to NiO(111).

Next, the room temperature micro-Raman spectra for NiO(100), NiO(110) and NiO(111) single-crystals were acquired for different in-plane orientations of the samples (Fig. 3). The rotation of each sample was performed with a step of 15 degree. In each case, the Raman signals were normalized to the two-phonon band at 1100 cm^{-1}. The insets in Fig. 3 show the variation of the intensities ratio $I(1500$ cm$^{-1})/I(1100$ cm$^{-1})$ versus the angle of sample rotation. As one can see, the mono-domain NiO(111) does not show any sample orientation dependence of the Raman signal, and the ratio of the two-magnon/two-phonon remains constant. On the contrary, the Raman scattering signals of the other two samples, NiO(100) and NiO(110), vary in a particular way upon sample rotation. The Raman spectra coincide after sample rotation by 90° for NiO(100) and by 180° for NiO(110). These values are in good agreement with those expected from the domain patterns in Fig. 1.

4. Conclusions

The magnetic domain structure and Raman scattering were studied in NiO single-crystals with three different (100), (110) and (111) orientations. Twin-domain structure was observed in NiO(100) and NiO(110) single-crystals using cross-polarized optical microscopy (Fig. 1). The ratio of the two-magnon band at 1500 cm^{-1} to the two-phonon band at 1100 cm^{-1} was found to be sensitive in a particular way to the type of the twin-domain pattern (Fig. 3).

Acknowledgements

References

[1] W.L. Roth, Phys. Rev. B 110, 1333 (1958)

[2] D. Rodic, V. Spasojevic, V. Kusigerski, R. Tellgren, H. Rundlof, Phys. Status Solidi B 218, 527 (2000)

[3] R.M. Sabitov, M.M. Faratdinov, Fiz. Tverd. Tela 12, 1661 (1970) (in Russian)

[4] W.L. Roth, J. Appl. Phys. 31, 2000 (1960)

[5] J.N. Armstrong, M.R. Sullivan, H.D. Chopra, Phys. Rev. B 80, 104429 (2009)

[6] H. Komatsu, M. Ishigame, J. Mater. Sci. 20, 4027 (1985)

[7] S. Saito, M. Miura, K. Kurosawa, J. Phys. C Solid State 13, 1513 (1980)

[8] V.S. Mandel, L.T. Emeljanova, M.M. Lebedev, Fiz. Tverd. Tela 12, 1625 (1970) (in Russian)

[9] N.A. Mironova, A.I. Belyaeva, O.V. Miloslavskaya, G.V. Bandurkina, Ukr. Fiz. Zh. 5, 848 (1981) (in Russian)

[10] H. Ohldag et al., Phys. Rev. Lett. 86, 2878 (2001)

[11] V. Skvortsova, N. Mironova-Ulmane, Adv. Sci. Tech. 29, 815 (2000)

[12] N.A. Mironova, G.V. Bandurkina, Latv. J. Phys. Tech. Sci. 4, 14 (1975)

[13] A. Kuzmin, N. Mironova, J. Phys.-Condens. Mat. 10, 7937 (1998)

[14] R.E. Dietz, G.I. Parisot, A.E. Meixner, Phys. Rev. B 4, 2302 (1971)

[15] R.E. Dietz, W.F. Brinkman, A.E. Meixner, H.J. Guggenheim, Phys. Rev. Lett. 27, 814 (1971)

[16] M.J. Massey, N.H. Chen, J.W. Allen, R. Merlin, Phys. Rev. B 42, R8776 (1990)

[17] D.J. Lockwood, M.G. Cottam, J.H. Baskey, J. Magn. Magn. Mater. 104, 1053 (1992)

[18] M. Grimsditch, S. Kumar, R.S. Goldman, J. Magn. Magn. Mater. 129, 327 (1994)

[19] M. Grimsditch, L.E. McNeil, D.J. Lockwood, Phys. Rev. B 58, 14462 (1998)

[20] Y. Mita, Y. Ishida, M. Kobayashi, S. Endo, J. Phys.-Condens. Mat. 14, 11173 (2002)

[21] E. Cazzanelli, A. Kuzmin, G. Mariotto, N. Mironova-Ulmane, J. Phys.-Condens. Mat. 15, 2045 (2003)

[22] E. Cazzanelli, A. Kuzmin, G. Mariotto, N. Mironova-Ulmane, Phys. Rev. B 71, 134415 (2005)