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Raman scattering by phonons and magnons in $Ni_cMg_{1-c}O$ solid solutions

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ABSTRACT

The Raman scattering by phonons and magnons was studied at room temperature in polycrystalline solid solutions $Ni_cMg_{1-c}O$ and pure NiO. The experimental Raman spectrum of NiO consists of six well resolved bands, whose origin is due to the disorder-induced one-phonon scattering (bands at 400 and 500 cm^{-1}), two-phonon scattering (bands at 750, 900 and 1100 cm^{-1}) and two-magnon scattering (band at 1500 cm^{-1}). In $Ni_cMg_{1-c}O$ solid solutions, a relative increase of one-phonon scattering is observed upon a dilution of nickel oxide by magnesium ions: at room temperature, the two-magnon band becomes invisible for $c<0.7$, whereas the two-phonon contribution disappears at $c<0.5$. Such behaviour is explained by disorder-induced effect, caused by chemical substitution and off-centre displacement of nickel ions.

Keywords: $Ni_cMg_{1-c}O$ solid solutions, NiO, Raman scattering, phonons, magnons

1. INTRODUCTION

Diluted antiferromagnets represent an interesting class of materials, whose crystallographic structure is closely related to magnetic properties [1]. Recently, a correlation between long and short range order in solid solutions with a face-centred-cubic (fcc) magnetic sublattice has been reviewed for a number of zinc-blende and rock-salt type compounds [2]. In these systems, depending on the type of the host-lattice packing, the cation/anion radii ratio and the difference in substituting ions size, the ordered on average crystal lattice experiences local distortions.

$Ni_cMg_{1-c}O$ system is a nice and very useful for theory example of diluted antiferromagnet. It forms a continuous series of solid solutions, whose magnetic properties vary with the composition from antiferromagnetic-like behaviour with the Néel temperature T_N=523 K for pure NiO to paramagnetic-like behaviour for pure MgO [3,4]. For intermediate compositions with $c>0.15$, the paramagnetic-to-antiferromagnetic phase transition occurs upon cooling [3,4].

Due to a small difference (about 0.02 Å) of the ionic radii of Ni^{2+} and Mg^{2+} ions, they can readily substitute each other, and one has been believed for a long time [4], that the lattice parameter of $Ni_cMg_{1-c}O$ system depends linearly on the composition, following the Vegard's rule. However, recent structural investigation by x-ray absorption spectroscopy [5,6] and x-ray diffraction [7], showed that nickel ions move off-centre upon dilution by magnesium ions. In fact, the symmetry lowering at Ni^{2+} sites, due to its off-centre displacement, allowed us to interpret the optical luminescence data [8] and near edge region in Ni K-edge x-ray absorption spectra [9] in $Ni_cMg_{1-c}O$ solid solutions.

One can expect in $Ni_cMg_{1-c}O$ solid solutions that a dilution by magnesium and a displacement of nickel ions should influence the phonon sub-system, which can be probed by Raman spectroscopy. To the best of our knowledge, until now there was no works published on this topic. Most Raman studies have been related to pure NiO [10-15] or MgO

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[16-17] compounds with two exceptions [18,19]. In [18] two-magnon Raman scattering has been investigated in calcium doped NiO with calcium concentration up to 6 mol.%, whereas theoretical and experimental Raman scattering studies of impurity-induced vibrations have been performed in MgO:0.25Co^{2+} in [19]. The temperature [10,11,13-15] and pressure [12] dependent Raman scattering in pure NiO allowed to identify contributions from one- (TO and LO modes) and two-phonon (2TO, TO+LO and 2LO modes) excitations as well as one-, two- and four-magnon excitations. It was also found [10] that the intensity of one-phonon scattering, in particular the LO mode at ~550 cm $^{-1}$, increases dramatically in black NiO, where the nickel vacancy concentration is high. The magnon contribution in NiO increases with a decrease of temperature [10,11,15] or an increase of pressure [12]. In calcium doped NiO the two-magnon band broadens when calcium concentration grows up [18]. Such behaviour of magnetic sub-system agrees well with the one predicted by the theory of light scattering by magnons [20,21]. In pure MgO single-crystals [16], having regular rocksalt structure, no first-order Raman effect can be detected, but the second-order Raman scattering was clearly observed. However, an addition of small amount (0.25 mol.%) of cobalt ions gives rise to one-phonon bands at 278.5, 304.8, 373.8 and 421.4 cm^{-1} [17], which superimpose on the two-phonon spectrum of MgO and have comparable intensity.

In this work, we present for the first time room temperature Raman scattering study of polycrystalline $Ni_cMg_{1-c}O$ solid solutions in a wide range of compositions, starting from c=1 to c=0.3. A contribution of phonon and magnon scattering in the Raman signals will be identified, and their variation with a composition will be discussed.

2. EXPERIMENTAL

Polycrystalline solid solutions $Ni_cMg_{1-c}O$ (c=0.3, 0.4, 0.5, 0.6, 0.7, 0.9) were prepared using ceramic technology from the appropriate amounts of aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ salts, which were mixed and slowly evaporated. The remaining dry 'flakes' were heated up to 500-600°C to remove NO_2 completely. The obtained polycrystalline solid solutions were pressed and annealed during 100 hours at T_{an}=1200°C in air and then quickly cooled down to room temperature. The pure polycrystalline NiO and MgO were obtained using the same method by thermal decomposition of the above mentioned salts. The annealing for several NiO samples was also performed at lower temperatures T_{an}=600 and 1000°C. Thus obtained $Ni_cMg_{1-c}O$ solid solutions have greenish color, whose intensity depends on the nickel content. Pure NiO has green color, and pure MgO is colorless.

The Raman measurements were performed in back-scattering geometry using a micro-Raman set-up, consisting of an Olympus microscope (model BHSM-L-2), mounting an objective 80× with a numerical aperture NA=0.75 and coupled to an 1 meter focal length double Jobin-Yvon monochromator (Ramanor, model HG2-S) equipped with holographic gratings (2000 grooves/mm). The spectral resolution was of the order of 3 cm^{-1}. The scattered radiation was detected by a cooled (-35°C) photomultiplier tube (RCA, model C31034A-02), operated in photon counting mode. The signal was stored into a multichannel analyser and then sent to a microcomputer for the analysis. The Raman spectra were excited by the 488.0 nm line of an argon laser, operated so that the power entering in the microscope was maintained at 20 mW.

3. RESULTS AND DISCUSSION

The Raman spectrum of pure NiO at room temperature consists of several bands: one-magnon (1M) band at 34 cm^{-1} [13], five vibrational bands [11] - 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, and two-magnon (2M) band at ~1500 cm^{-1} [11]. The frequency and shape of the phonon bands do not vary with temperature, whereas the magnon scatterings are strongly temperature dependent - they shift to lower frequencies and decrease in intensity with increasing temperature, disappearing completely close to the Néel temperature T_N=523 K [11,13,15]. Note that a precise measurement of 1M band is normally complicated due to its strong overlap with the elastically scattered exciting laser radiation. We will not discuss 1M contribution in $Ni_cMg_{1-c}O$ here, since this work is in progress.

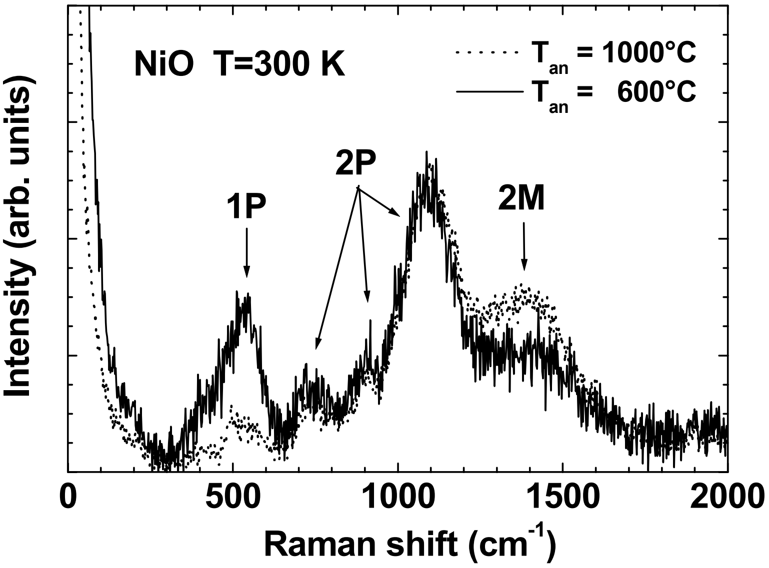

Figure 1: Room temperature (300 K) Raman spectra of green NiO polycrystalline powder, calcinated at two different temperatures 600°C and 1000°C. The spectra are normalized relative to the peak at 1100 cm^{-1} due to two-phonon (2P) scattering. Note that the intensity of two peaks, due to one-phonon (1P) and two-magnon (2M) scattering, changes in opposite direction.

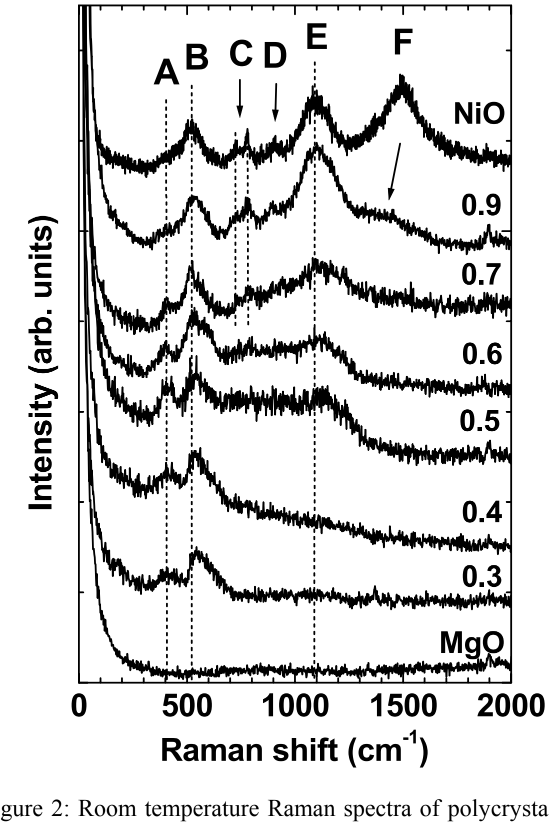

Figure 2: Room temperature Raman spectra of polycrystalline NiO, MgO and $Ni_cMg_{1-c}O$ (c=0.3, 0.4, 0.5, 0.6, 0.7, 0.9) solid-solutions. The origin of the peaks A-F is explained in text.

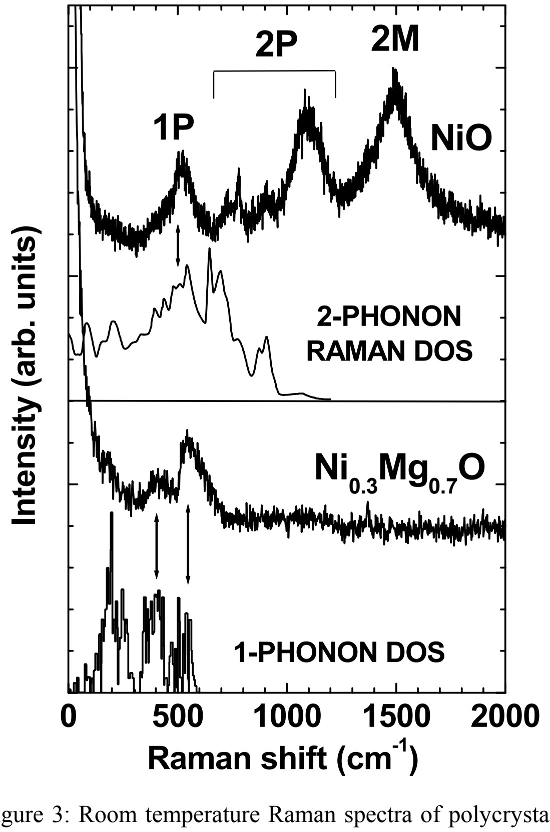

Figure 3: Room temperature Raman spectra of polycrystalline NiO and $Ni_{0.3}Mg_{0.7}O$ in comparison with theoretically calculated one-phonon DOS [25] and two-phonon Raman DOS [24].

First, we will consider an influence of intrinsic defects, nickel vacancies, in pure green NiO on intensity of Raman bands (Fig. 1). The Raman spectra for two samples, annealed at the temperatures T_{an}=600 and 1000°C, were approximately scaled on the 2LO mode, following the approach in [11]. As a result, the main difference is observed for the one-phonon and two-magnon scatterings. Similar but even stronger effect was observed previously for green and black NiO [11]. It was suggested [11] that an enhancement of the first-order phonon scattering occurs in black NiO from parity-breaking defects - nickel vacancies. In our case, we expect that in spite of both samples have green colour, the higher annealing temperature (T_{an}=1000°C) results in a lower concentration of such defects, that is in agreement with a variation of the 1P band intensity in Fig. 1. This explanation is also valid for the magnon induced band: higher concentration of intrinsic defects leads to larger probability of magnon scattering that results in inhomogeneous broadening of the 2M band. Since the concentration of nickel vacancies in green NiO is below 0.1% [22], one can expect even stronger modifications of the Raman scattering in $Ni_cMg_{1-c}O$ solid solutions.

Room temperature Raman spectra of polycrystalline NiO, MgO and $Ni_cMg_{1-c}O$ (c=0.3, 0.4, 0.5, 0.6, 0.7, 0.9) solid-solutions are shown in Fig. 2. Note that all samples were annealed at T_{an}=1200°C due to that some difference is observed between signals for pure NiO in Fig. 1 and Fig. 2. The six visible bands are labelled in pure NiO from A to F for convenience. Note also that our Raman spectrum for polycrystalline MgO does not show any detectable bands, observed previously in single-crystals [16,17]. This means that their intensity is very low, compared to ones in NiO, and the nickel sublattice is the main responsible for the Raman scattering in solid solutions.

According to magnetic phase diagram of $Ni_cMg_{1-c}O$ solid solutions [3,4], the antiferromagnetic-to-paramagnetic transition takes place at room temperature for $c \sim 0.6$ [23]. Therefore we do not expect to see the 2M scattering for more diluted samples. In fact, the band F shows behaviour assignable to 2M scattering: its intensity decreases and position shifts to lower frequencies upon dilution of NiO by magnesium. The 2M scattering becomes not detectable in our experiment for $c<0.7$ due to an overlap with the two-phonon band E. Note that an influence of chemical composition on the magnon sub-system in $Ni_cMg_{1-c}O$ single-crystals was recently studied by us using optical absorption spectroscopy [23]. We found [23] that a contribution of short wavelength magnons, excited at the Brillouin zone-boundary, remains visible till the transition temperature T_N due to persistence of the local magnetic ordering.

The most exciting result in Fig. 2 is related to the strong decrease for $0.4<c<0.9$ and complete disappearance for $c<0.5$ of the two-phonon bands C, D and E. At the same time, the one-phonon bands A and B remain nearly unchanged in intensity but vary slightly in shape: in particular, the band A becomes more pronounced. Since the crystalline structure of $Ni_cMg_{1-c}O$ solid solutions follows that of NiO and MgO (see Introduction), no significant changes of the phonon density of states (DOS) is expected. Therefore, we suggest that at low nickel concentrations, the first order Raman scattering becomes allowed due to local symmetry lowering at Ni^{2+} sites caused by two effects - chemical disorder and off-centre displacement of nickel ions. Thus, in pure NiO and $Ni_{0.9}Mg_{0.1}O$ the first-order scattering is forbidden. The solid solutions in the range of compositions $0.3<c<0.9$ are intermediate, in sence that only for a part of nickel ions the first-order scattering remains forbidden. Finally, the first-order scattering is allowed in $Ni_{0.3}Mg_{0.7}O$.

In Fig. 3 we support our conclusion by the available theoretical calculations. The two-phonon Raman DOS, calculated in [24] within the shell model, is in rather good agreement with our Raman spectrum for pure NiO. The most important point is the shape of the 1P band at 500 cm^{-1}: both our experiment and the theory [25] show asymmetric band. At the other limit, in $Ni_{0.3}Mg_{0.7}O$ solid solution, the 1P band consists of two peaks, which can be related to two maxima in one-phonon DOS, calculated in [25]. Thus, the change in a shape of the Raman bands at 400-500 cm^{-1} provides with a fingerprint for discrimination of an origin of the phonon scattering.

4. CONCLUSIONS

The room temperature Raman scattering by phonons and magnons was studied for the first time in polycrystalline solid solutions $Ni_cMg_{1-c}O$. A comparison of their spectra with that for pure NiO and MgO allowed us to withdraw several conclusions. First, the two-magnon band becomes invisible for $c<0.7$, that agree perfectly with the magnetic phase diagram of $Ni_cMg_{1-c}O$ system [3,4]. Second, upon dilution by magnesium, a relative increase of one-phonon scattering is observed, whereas the two-phonon contribution disappears completely at $c<0.5$. This phenomenon is explained by the local symmetry lowering at nickel sites, caused by chemical substitution and off-centre displacement of nickel ions [5-7].

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