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Influence of diamagnetic impurity on mid-IR absorption in antiferromagnetic insulator NiO

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The influence of diamagnetic magnesium impurities on the absorption band at ~2000 cm^{-1} was studied in polycrystalline Ni$_c$Mg$_{1-c}$O solid solutions with c=0.99, 0.98, 0.97, 0.95, 0.90, 0.80, 0.70 and 0.60. The composition and temperature dependences of the absorption suggest that the band has magnetic origin related to simultaneous excitation of two-magnons at the Brillouin-zone boundary and one phonon.

Nickel oxide NiO is a type-II antiferromagnetic charge-transfer insulator [1] with the Néel temperature T_N=523 K [2] and the band gap about 4 eV [3]. Non-stoichiometric nickel oxide Ni$_{1-\delta}$O exhibit p-type semiconducting properties due to the presence of Ni^{3+} impurities [4]. The absorption spectrum of NiO in mid-infrared spectral range has a band at ~2000 cm^{-1} (0.24 eV), observed previously in [5–10]. This band was attributed to an impurity induced absorption in [5]. However, further studies have shown its connection with magnetic ordering in NiO [6–10]. It was found that upon temperature increase, the band becomes less intensive and its position shifts to lower energies, till the band disappears completely above the Nèel temperature [6, 7, 10]. The energy position of the band was attributed to the joint excitation of two magnons and one phonon [8, 9]. The theoretical description of such transitions was given in [10, 11] and more recently in [12].

The magnetic properties of nickel oxide can be strongly influenced by admixture of non-magnetic ions [13]. For example, Ni$_c$Mg$_{1-c}$O solid solutions represent a nice example of diluted antiferromagnetic system. Its magnetic properties vary from antiferromagnetic-like behaviour for c=1, to diamagnetic-like behaviour for c=0 [14, 15]. For intermediate compositions with c>0.3, paramagnetic-to-antiferromagnetic phase transition occurs upon cooling [14, 15].

In this work, we have studied the influence of diamagnetic magnesium impurities on the absorption band at ~2000 cm^{-1} in polycrystalline Ni$_c$Mg$_{1-c}$O solid solutions.

Polycrystalline solid solutions Ni$_c$Mg$_{1-c}$O (c=0.99, 0.98, 0.97, 0.95, 0.90, 0.80, 0.70 and 0.60) were prepared using ceramic technology from the appropriate amounts of aqueous solutions of Mg(NO$_3$)$_2$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O salts, which were mixed and slowly evaporated. The remaining dry 'flakes' were heated up to 500–600 ºC to remove NO$_2$ completely. The obtained polycrystalline solid solutions were pressed and annealed during 100 hours at 1200 ºC in air and then rapidly 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. These Ni$_c$Mg$_{1-c}$O solid solutions have greenish

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colour, whose intensity depends on the nickel content. For infrared measurements, the samples were prepared from appropriate mixtures of $Ni_cMg_{1-c}O$ and CsI powders, pressed into pellets.

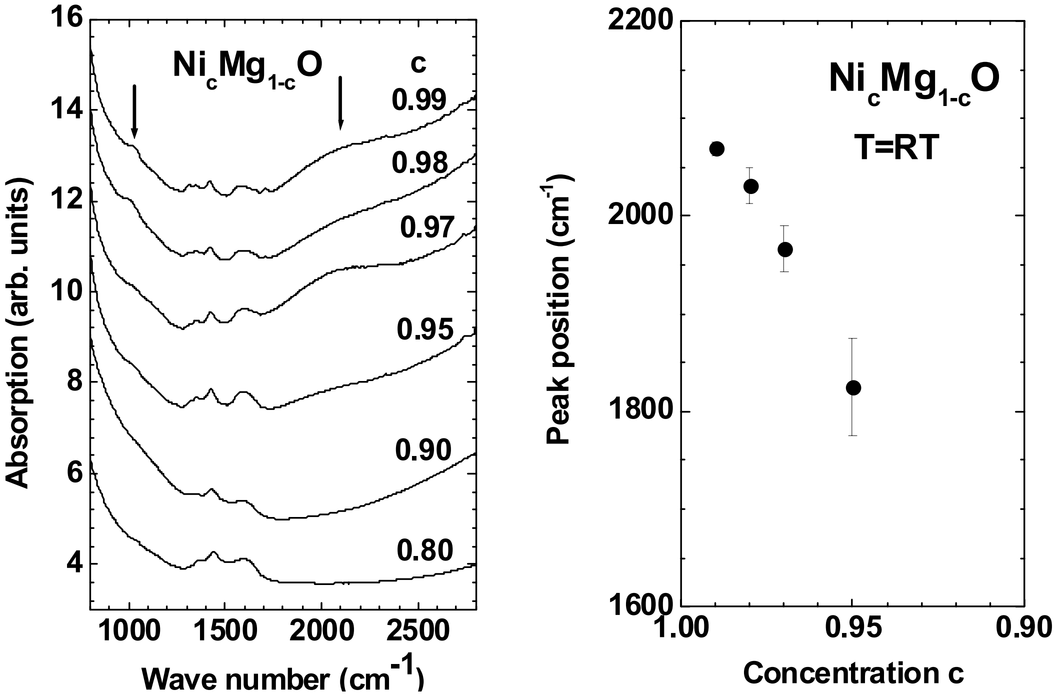

Fig. 1 Left panel: Composition dependence of the absorption bands at 1020 and 2000 cm^{-1} (indicated by arrows) in $Ni_cMg_{1-c}O$ solid solutions at room temperature. Right panel: a variation of the 2000 cm^{-1} band position with composition, determined from the Gaussian model of the band shape.

Mid-infrared measurements were performed using the Brucker Equinox interferometer, modified to work in vacuum, in the range from 800 to 2700 cm^{-1} with the resolution 8 cm^{-1}. The glowbar was used as a light source. Composition dependent measurements were performed at room temperature (293 K) for c=0.99, 0.98, 0.97, 0.95, 0.90, 0.80, 0.70 and 0.60. Temperature dependent measurements were done for c=0.97 using the liquid-helium cryostat in the temperature range from 20 to 330 K. The obtained results are shown in Figs. 1, 2 and 3. The shape of the band at ~2000 cm^{-1} can be well approximated by the Gaussian model, which was used to determine its position, width and intensity, given in Figs. 1 and 3.

In pure NiO the band at ~2000 cm^{-1} has been attributed to the excitation of two magnons (2M) and one phonon (1P) with the total momentum equal to zero [8,9]. The magnon dispersion, obtained by the neutron scattering in [16], indicates high density of magnon states at the Brillouin-zone boundary (BZB) that allows to suppose that two BZB magnons of opposite momentum contribute into the band at ~2000 cm^{-1}. From Raman scattering experiments [8, 17, 18], the two BZB magnon energy is about 1500 cm^{-1} at room temperature, whereas the mean TO (440 cm^{-1}) and LO (560 cm^{-1}) phonon energy is about 500 cm^{-1}. Thus, the sum of two contributions is in good agreement with the infra-red band position. In fact, two absorption lines can be expected in the absorption spectrum at the energies $E_{2M}+E_{1P}$ and $E_{2M}-E_{1P}$, which correspond to the creation and the annihilation of phonons [10]. The second absorption band is weak but still observable at about 1020 cm^{-1} in Figs. 1 and 2. It shows temperature and composition dependence similar to that of the band at 2000 cm^{-1}. The difference between two infra-red bands allows to estimate experimentally the phonon energy, however the accuracy of such estimate is strongly limited by the error in the determination of the 1020 cm^{-1} band position.

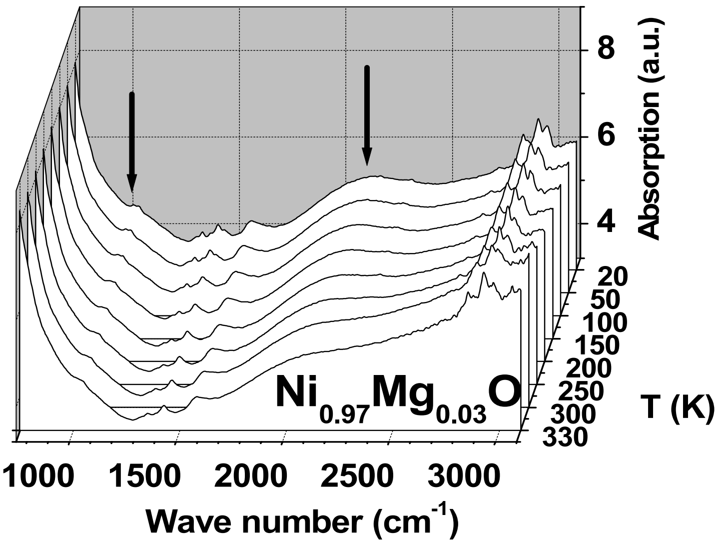

Fig. 2 Temperature dependence of the absorption bands at about 1020 and 2000 cm^{-1} in $Ni_{0.97}Mg_{0.03}O$ solid solution.

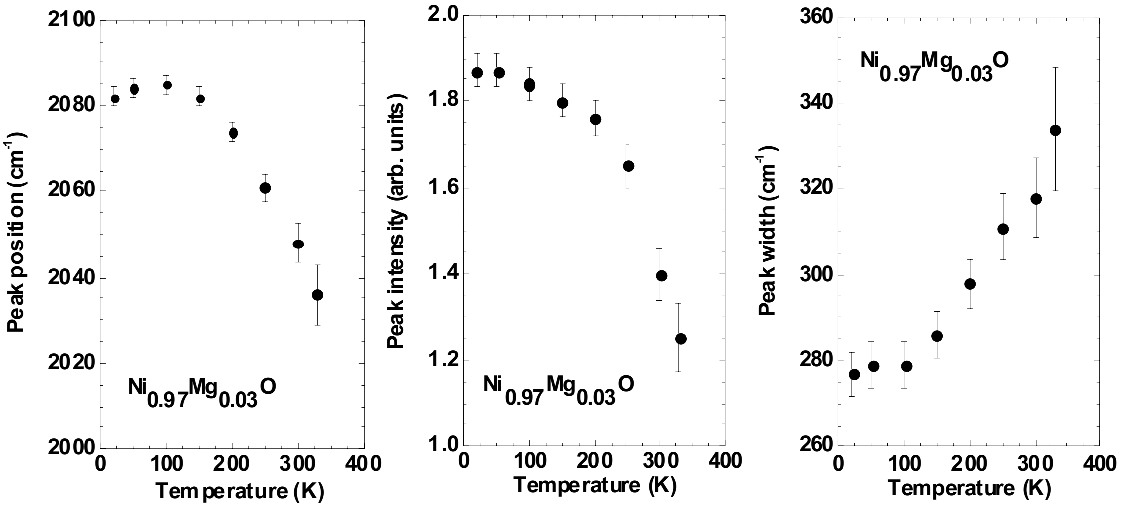

Fig. 3 Variation of the position, intensity and width of the absorption band at ~2000 cm^{-1} in $Ni_{0.97}Mg_{0.03}O$ solid solution with temperature, determined from the Gaussian model of the band shape.

Composition dependence of the band at ~2000 cm^{-1}, measured at room temperature, is shown in Fig. 1 (right panel). The band is well visible for $c \geq 0.95$, and its position shifts to lower energies from 2069±9 cm^{-1} for c=0.99 to 1825±50 cm^{-1} for c=0.95. Note that the band was not detectable at room temperature for c<0.95, in spite of that according to the magnetic phase diagram [14, 15], the paramagnetic-to-antiferromagnetic transition occurs at c~0.6. Since the phonons energy remains nearly unchanged in all $Ni_cMg_{1-c}O$ series [18], the observed behaviour of the band in $Ni_cMg_{1-c}O$ solid solutions is explained by a decrease of the two BZB magnon energy upon an increase of magnesium content [14, 18]. An independence of the phonons energy on the composition [18] explains why a separation between two infra-red lines at ~1020 and ~2000 cm $^{-1}$ remains constant. Note that the composition (c~0.95), at which both bands become invisible at room temperature, is higher than that (c~0.7) found in recent Raman scattering experiments [18]. This means that a slightly different magnetic correlation length plays a role in Raman and infra-red processes.

Temperature dependence of two magnon-assisted bands at about 1020 cm^{-1} and 2000 cm^{-1} for c=0.97 is shown in Fig. 2. Both bands are well visible and change their shape upon increasing temperature. While the band at 1020 cm^{-1} is strongly overlapped with the phonons band tail, the detailed information can be extracted for the band at 2000 cm^{-1}, which was isolated from the background using the Gaussian model for the band shape. A variation of the intensity, position and width of the band at 2000 cm^{-1} is given in Fig. 3. The increase of temperature results in a decrease of the band intensity, a shift of the band position to lower energies and a broadening of the band. Such behaviour supports the explanation of the bands origin as due to the magnon assisted absorption [7,10].

Thus, the mid-IR absorption in antiferromagnetic nickel oxide is strongly sensitive to the dilution with diamagnetic magnesium impurities and provides with an information on the oxide magnetic structure through the sensitivity to the Brillouin-zone boundary magnons.

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