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One-magnon Raman scattering in $Ni_cMg_{1-c}O$ solid solutions

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The one-magnon Raman scattering was studied for the first time in antiferromagnetic $Ni_cMg_{1-c}O$ solid solutions as a function of temperature and composition. We found that (i) the one-magnon frequency extrapolated to $T = 0$ K experiences an abrupt change between c = 0.99 and c = 0.9 and (ii) the one-magnon energy for highly diluted nickel oxide vanishes significantly below the Nèel temperature. The obtained dependences are compared to the theoretical predictions within the mean field approximation.

$Ni_cMg_{1-c}O$ solid solutions represent an example of diluted antiferromagnetic system with the rock-salt structure, whose lattice constant varies close to the Vegard's law [1]. Their magnetic phase diagram was established in the past by the magnetic susceptibility measurements [2], neutron scattering [3] and SQUID magnetometry [4]. Pure NiO is a type-II antiferromagnet (AF_2), which becomes paramagnetic above the Néel temperature T_N = 523 K [5]. On the other side, pure MgO is a diamagnet. In $Ni_cMg_{1-c}O$ solid solutions several particular regions can be found upon cooling from paramagnetic phase [3]: the region of homogeneous antiferromagnet exists for $0.63 \le c < 1$, the frustrated antiferromagnet is observed for $0.4 \le c < 0.63$, and the cluster spin-glass for $0.25 \le c < 0.4$. For $c < 0.25$, $Ni_cMg_{1-c}O$ solid solutions remain in paramagnetic state at all temperatures [3].

The antiferromagnetic structure of NiO and $Ni_cMg_{1-c}O$ solid solutions is determined by dominating superexchange interactions ($J_{NNN} \approx 150$ cm^{-1} for pure NiO [6,7]) in the linear atom chains Ni^{2+}–O^{2-}–Ni^{2+} between next-nearest-neighbours (NNN). The magnons dispersion curves have been obtained by inelastic neutron scattering only for pure NiO [6]. Here two modes at ~36.6 cm^{-1} and ~8 cm^{-1} are observed close to the Brillouin zone-centre (BZC) and correspond to antiferromagnetic resonance (AFMR) out-of-plane and in-plane modes [6]. At the same time, the modes dispersion at the Brillouin zone-boundary (BZB) is relatively narrow and peaks in NiO at ~887 cm^{-1} [6].

The magnon excitations in pure NiO have been intensively studied previously by Raman spectroscopy. In particular, the one-magnon [8–11], two-magnons [7, 8, 12–14] and four-magnons [13] scattering has been detected. The observed temperature dependence of the one-magnon scattering is in agreement with the theoretical predictions for the BZC magnon frequency [15, 16]. Temperature dependence of the two-magnon scattering has been studied in [12] and is attributed to the excitation of two BZB magnons [17]. The four-magnons scattering is very weak and has been observed at 1.5 K only in [13]. Besides, pressure dependence of the one-magnon [11] and two-magnon [7] scattering in NiO has been also studied and is explained by a variation of the dominating NNN exchange energy J_{NNN} as a function of the lattice constant.

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The magnetic excitations in diluted nickel oxide have been studied to our knowledge only in two works [14, 18]. In [18], the two-magnon Raman scattering has been measured in calcium doped NiO with calcium content up to 6 mol.%. It was found [18] that upon dilution the position and shape of the two-magnon band follow the expected behaviour [15, 16]. In our recent work on $Ni_cMg_{1-c}O$ solid solutions [14], the dependence of the two-magnon band on the composition and temperature has been studied by Raman spectroscopy in a wide range of compositions ($0.3 < c < 1$) and temperatures (10–300 K). The observed variation of the two-magnon scattering was found to be consistent with the magnetic phase diagram of $Ni_cMg_{1-c}O$ system [3].

In the present work we extend our previous studies to the case of the one-magnon Raman scattering in $Ni_cMg_{1-c}O$ solid solutions as a function of composition and temperature.

A set of polycrystalline and single-crystal NiO and $Ni_cMg_{1-c}O$ (c = 0.99, 0.90, 0.80, 0.60) solid solutions was prepared (i) 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 and (ii) by the method of chemical transport reactions using HCl gas as the transport medium [19]. Thus obtained samples were green coloured. The chemical composition of solid solutions was controlled by instrumental neutron-activated analysis [20], and it was confirmed that the content of nickel in the samples was in agreement with the stoichiometric one within ±0.01%.

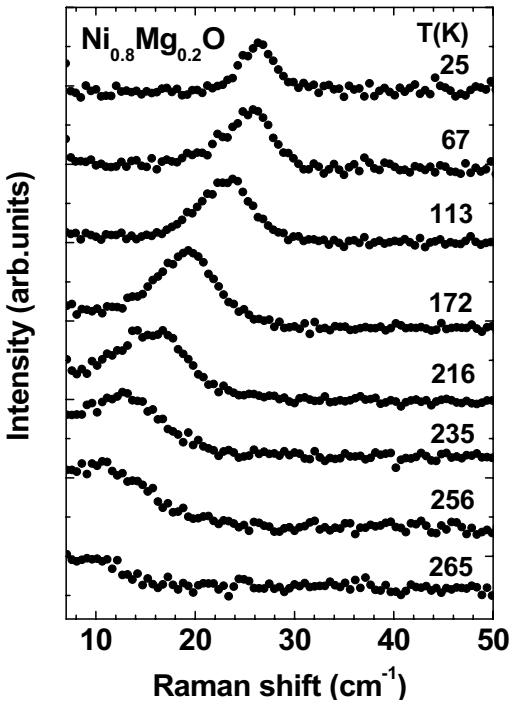

Fig. 1 Temperature dependence of the one-magnon Raman scattering (the Stokes part) in $Ni_{0.8}Mg_{0.2}O$ solid solution.

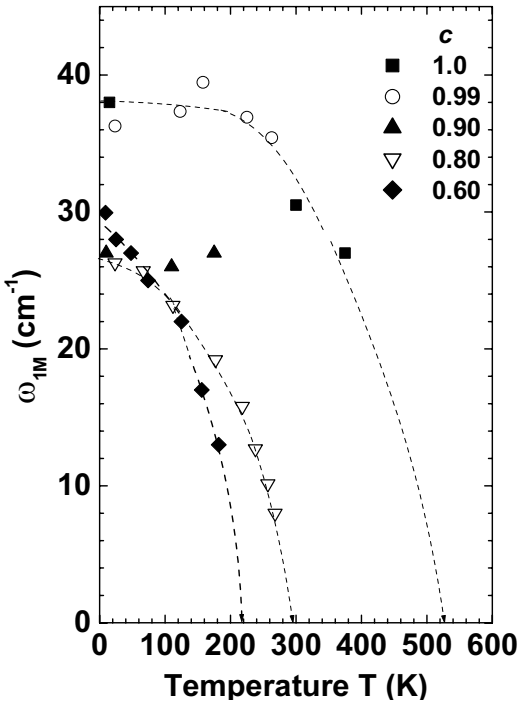

Fig. 2 Temperature dependence of the one-magnon frequency ω_{1M} in NiO and $Ni_cMg_{1-c}O$ solid solutions. Dashed lines are guides for eye.

Raman experiments were performed using standard macro-Raman setup with a right angle scattering geometry in zero magnetic field. The samples were mounted in a liquid helium flux cryostat, and the temperature was varying in the range from 10 to 400 K with the accuracy ±2 K. The Raman spectra were excited by the 514.5 nm line of an argon laser, with a nominal power of 100 mW at the cryostat window. The scattered radiation was focused at the entrance slit of an one-meter focal length double monochromator (Jobin-Yvon, model Ramanor HG2-S), mounting concave holographic gratings (2000 grooves/mm). The experimental resolution was of the order of 3 cm^{-1}. The filtered 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 analyzer and then sent to a microcomputer for the analysis. The Raman spectra were recorded at 0.5 cm^{-1} spectral steps from -80 to 90 cm^{-1}, thus including both anti-Stokes (magnon annihilation) and Stokes (magnon creation) parts.

The representative Raman spectra are shown in Fig. 1 for $Ni_{0.8}Mg_{0.2}O$ solid solution. Here the one-magnon contribution can be detected up to about 270 K, and the one-magnon frequency extrapolated to $T = 0$ K is about 26±1 cm^{-1}. As it is expected, the one-magnon frequency decreases and the peak progressively broadens upon increasing temperature. The extrapolation of the temperature dependence of the one-magnon frequency to $\omega_{1M} = 0$ gives the critical temperature $T_C \approx 300$ K, that is much smaller than the Néel temperature $T_N(c=0.8) \approx 420$ K [3].

Temperature dependences of the one-magnon energy ω_{1M} in NiO and $Ni_cMg_{1-c}O$ solid solutions are shown in Fig. 2. Note that our results for pure NiO are in good agreement with that of [8–10]. The dilution of nickel oxide with magnesium ions leads to a decrease of the one-magnon frequency. However, as one can see in Fig. 2, this decrease is not uniform. In the limit of $T \to 0$ K, the one-magnon frequency is nearly unchanged for $c \geq 0.99$, after that an abrupt lowering of the ω_{1M} value occurs for $c = 0.90$, but no significant variation of ω_{1M} is found for $0.6 < c < 0.9$. In fact, the one-magnon frequency for the samples with $c = 0.6$, 0.8 and 0.9 falls within the interval 27±3 cm^{-1}.

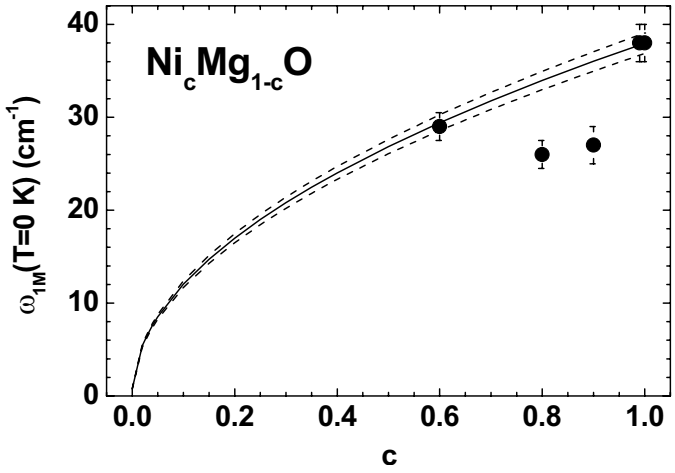

Fig. 3 Composition dependence of the one-magnon frequency in the limit of $T \to 0$ K in NiO and $Ni_cMg_{1-c}O$ solid solutions. The solid line is theoretical prediction for $\omega_{1M} = (2\omega_E\omega_A + \omega_A^2)^{1/2}$ (see text for details). Two dashed lines show an error bar due to an inaccuracy of the exchange constant J_{NNN} and the anisotropy frequency ω_A [6].

The one-magnon frequency in zero magnetic field is given by $\omega_{1M} = (2\omega_E\omega_A + \omega_A^2)^{1/2}$ [21], where $\omega_E = zSJ_{NNN}$ is the exchange frequency, ω_A is the single-ion out-of-plane anisotropy frequency, z is the number of the magnetic neighbours and S is the spin. In the case of solid solutions, the conventional approach is to substitute z with zc [22], so that $\omega_E = zcSJ_{NNN}$. The result of such calculation for $Ni_cMg_{1-c}O$ is shown in figure 3 by solid line. Here we used $S = 1$, $z = 6$, $J_{NNN} = 153\pm3$ cm^{-1} [6] and $\omega_A = 0.785\pm0.03$ cm^{-1} [6]. As one can see, the predicted dependence of the one-magnon frequency on the composition deviates significantly from our experimental observations.

Another interesting result, found in $Ni_cMg_{1-c}O$ solid solutions, is related to the dependence of the critical temperature T_C, at which $\omega_{1M}(T_C) \to 0$, on the composition. In pure NiO, T_C for the one-magnon frequency is close to the Néel temperature T_N (Fig. 2). However, our results clearly indicate that in solid solutions with $c = 0.6$ and $c = 0.8$, T_C is about 100 K smaller than T_N. Close behaviour for one-magnon excitation was observed recently for joint exciton–one-magnon transition in the region of the magnetic-dipole $^3A_{2g}(G) \to {}^3T_{2g}(F)$ optical absorption band in $Ni_cMg_{1-c}O$ single-crystals [23]. However, in the

latter case, the intensity of the one-magnon assisted transition decreases rapidly with increasing magnesium ion concentration and/or temperature: it vanishes at $T = 6$ K for $c < 0.95$ and at $T = 130$ K for $c \geq 0.99$ [23], even faster than in the present Raman results, due to an additional broadening of the exciton excitation. One should note also that in the case of $Fe_{1-x}Zn_xF_2$ solid solution the one-magnon Raman scattering was observed at least up to the Néel temperature [22]. Therefore, it can be concluded that the one-magnon scattering in $Ni_cMg_{1-c}O$ solid solutions is very sensitive to the destruction of the long-range magnetic ordering with increasing concentration of the diamagnetic magnesium impurity ions.

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