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# Exciton–Magnon Interactions in $Ni_cMg_{1-c}O$ Single Crystals

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**Abstract**—The effect of chemical composition and temperature on exciton–magnon interactions in $Ni_cMg_{1-c}O$ single crystals was studied using optical absorption spectra in the region of the magnetic-dipole $^3A_{2g}(G) \longrightarrow {}^3T_{2g}(F)$ and electric-dipole $^3A_{2g}(F) \longrightarrow {}^1E_g(D)$ transitions. The two zero-phonon lines at ~7800 and ~7840 $cm^{-1}$ on the low-energy side of the magnetic-dipole transition band were assigned to a pure exciton transition and an exciton–one-magnon transition at the center of the Brillouin zone. The intensity of the exciton–one-magnon peak decreases rapidly with increasing magnesium ion concentration and/or temperature, to vanish altogether at $T = 6$ K for $c < 0.95$ and at $T = 130$ K for $c \geq 0.99$. Thus, the contribution of long-wavelength magnons in optical absorption spectra of $Ni_cMg_{1-c}O$ becomes negligible at temperatures substantially lower than the Néel point $T_N$ (the antiferromagnetic ordering temperature). This observation can be explained as being due to a substantial decrease in the characteristic spin–spin interaction length with increasing concentration of the diamagnetic magnesium impurity ions (static disorder) and/or with increasing amplitude of thermal atomic vibrations (dynamic disorder). At the same time, the peak at ~14500 $cm^{-1}$, which lies in the electric-dipole transition region and corresponds to excitation of an exciton and two magnons at the Brillouin zone edge, remains visible up to the Néel temperature. This is accounted for by the short-wavelength magnons being sensitive to short-range magnetic order, which persists up to $T_N$. © *2002 MAIK "Nauka/Interperiodica".*

## 1. INTRODUCTION

Pure nickel oxide NiO is an antiferromagnet of the second kind with a Néel temperature $T_N = 523$ K. Substitution of a part of nickel ions by magnesium ions produces a continuous series of $Ni_cMg_{1-c}O$ solid solutions [1]. The magnetic phase diagram of the $Ni_cMg_{1-c}O$ system, which has been established earlier by elastic neutron scattering [1] and SQUID magnetometry [2], indicates the existence of four regions (Fig. 1) [1]: (1) a homogeneous antiferromagnet ($0.63 \leq c \leq 1$), (2) a cluster antiferromagnet ($0.4 \leq c < 0.63$), (3) a spin-glass-type structure ($0.25 \leq c < 0.4$), and (4) a paramagnet ($c \leq 0.2$). We note that both of the experimental methods mentioned above [1, 2] are sensitive to long-range magnetic order. Microscopic studies [3] of the effect of composition and temperature on the domain structure of $Ni_cMg_{1-c}O$ single crystals provided additional information. It was established in [3] that a domain structure exists at temperatures substantially below $T_N$ (Fig. 1) and that it is more sensitive to the solid-solution composition than the Néel temperature. Magnetic order in the $Ni_cMg_{1-c}O$ solid solutions was also investigated by optical absorption [4], luminescence [5], and Raman spectroscopy [6].

This publication reports on a study of the contribution of exciton–magnon interactions to the optical absorption spectra of $Ni_cMg_{1-c}O$ single crystals. Attention is focused on the dependence of the one- and two-magnon contributions on the solid-solution composition and temperature.

## 2. SAMPLES AND EXPERIMENTAL TECHNIQUE

$Ni_cMg_{1-c}O$ single crystals were grown by chemical transport reactions [7, 8] on (100)-oriented MgO substrates. The samples were of a greenish color, whose intensity depended on the nickel content and varied from green for $c = 1$ to light green for small $c$. The chemical composition of the solid solutions was checked by neutron activation analysis [9]; it was found that the nickel content was stoichiometric to within ±0.01%. The optical absorption spectra were measured on a Jasco V-570 double-beam spectrophotometer with a tungsten lamp serving as a light source. The absorption spectra were recorded by a photomultiplier tube and a PbS photocell in the energy intervals 11110–18500 and 7600–12500 $cm^{-1}$, respectively. The temperature of the samples, fixed in a helium cryostat, was measured in the 5-to 293-K range to within ±1 K.

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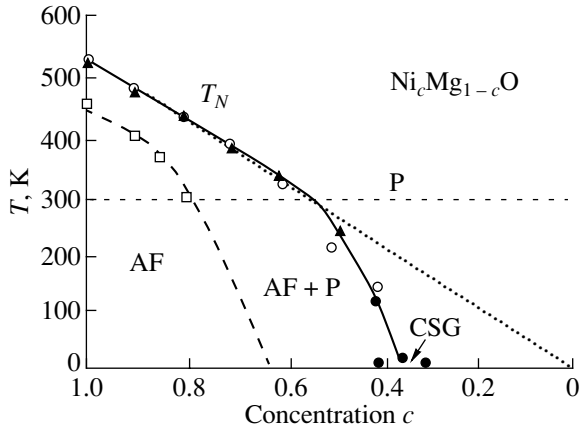


**Fig. 1.** Magnetic phase diagram of the $Ni_cMg_{1-c}O$ solid solutions obtained using elastic neutron scattering [1] and SQUID magnetometry data [2]. The region of an infinite antiferromagnetic cluster [3] is specified by open squares. P denotes the region of the paramagnetic phase, AF is the antiferromagnetic phase, and CSG indicates the cluster spin glass region.

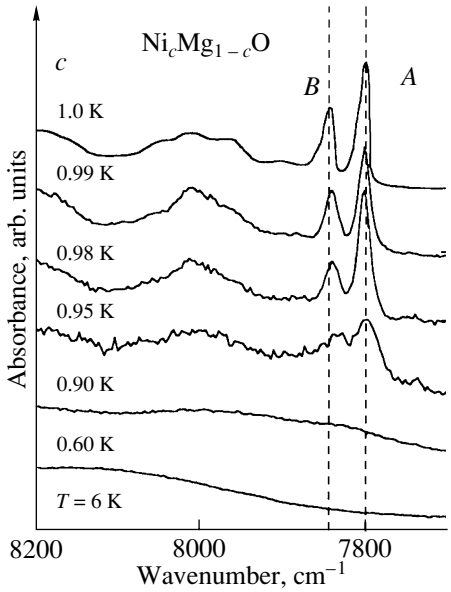


**Fig. 2.** Low-energy part of the $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ magnetic-dipole absorption band in $Ni_cMg_{1-c}O$ single crystals measured at $T = 6$ K. The peaks corresponding to the pure exciton and the exciton–one-magnon transitions are denoted by *A* and *B*, respectively.

## 3. RESULTS AND DISCUSSION

The optical absorption spectra of the NiO nickel oxide and $Ni_cMg_{1-c}O$ solid solutions can be interpreted using the energy level diagram of a free nickel ion $Ni^{2+}$ ($3d^8$) in a cubic crystal field. The observed absorption bands are related to parity-forbidden *d*–*d* transitions, three of which, $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$, are spin-allowed ($\Delta S = 0$), whereas the others are forbidden. We will consider the two lowest bands, which correspond to the magnetic-dipole transition $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ at ~8800 cm$^{-1}$ and the electric-dipole transition $^3A_{2g}(F) \longrightarrow {}^1E_g(D)$ at ~13800 cm$^{-1}$.

At low temperatures ($T < 100$ K), the magnetic-dipole absorption band $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ of NiO consists of two narrow, zero-phonon lines (peaks *A*, *B* in Figs. 2, 3) and a broad vibronic band with several maxima corresponding to simultaneous excitation of an exciton and phonons [4, 10]. Peak *A* at ~7800 cm$^{-1}$ is due to the exciton transition, and peak *B* at ~7840 cm$^{-1}$ is associated with exciton–one-magnon excitation involving a magnon with $k = 0$, i.e., at the Brillouin zone center [4, 10]. The magnon energy is determined by the interval separating peaks *A* and *B* [10]. Variation of temperature and substitution of magnesium for nickel result in homogeneous and inhomogeneous broadening of the absorption band, respectively, which affects the intensity and position of both the *A* and *B* peaks and the vibronic band [11].

Figure 3 displays the temperature dependence of the absorption due to the $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ magnetic-dipole transition in NiO and the $Ni_{0.99}Mg_{0.01}O$ solid solution. In both cases, peak *B* disappears at ~110 K, i.e., substantially below the Néel temperature $T_N$ ~ 523 K. The separation between peaks *A* and *B* (Fig. 4a) does not vary with temperature, which implies a constant magnon energy. Nevertheless, the positions of both peaks, as well as of the absorption band maximum, shift to lower energies, which may be attributed to a change in the crystal field strength resulting from lattice expansion [8]. Another interesting observation is the nonlinear variation of the $I(B)/I(A)$ amplitude ratio of peaks *A* and *B* (Fig. 4b). A comparison of the two graphs in Fig. 4 reveals that the $I(B)/I(A)$ ratio varies faster below 60 K, where the *A* and *B* peaks do not change position. At the same time, the two peaks change position toward lower energies above 60 K, although their amplitude ratio remains constant to within the experimental error.

The absorption originating from excitation of the long-wavelength magnon (at the center of the Brillouin zone) is sensitive to long-range magnetic order; therefore, peak *B* and the magnetic structure of nickel oxide and of the solid solutions are related. Substitution of magnesium ions for nickel (up to 10%, $c > 0.9$) strongly reduces the peak *B* intensity already at $T = 6$ K (Fig. 2), i.e., substantially below the temperature of the phase transition from the antiferromagnetic to paramagnetic state (Fig. 1) [1, 2]. To within the experimental error, the magnon energy in $Ni_cMg_{1-c}O$ for $c > 0.95$ remains constant and equal to the value for pure NiO, $\omega_{1M} \approx 41$ cm$^{-1}$. A decrease in $\omega_{1M}$ by ~8 cm$^{-1}$ was observed to occur for $c = 0.95$ (Fig. 2). While the one-magnon pro-

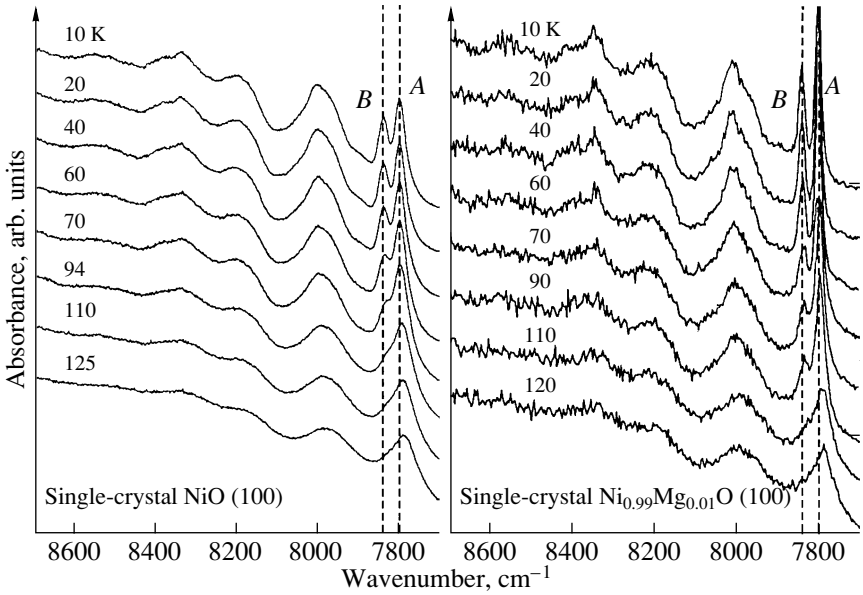


**Fig. 3.** Temperature dependence of the $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ absorption in NiO and $Ni_{0.99}Mg_{0.01}O$ single crystals. Peak *A* corresponds to the exciton transition, and peak *B* corresponds to the exciton–one-magnon excitation.

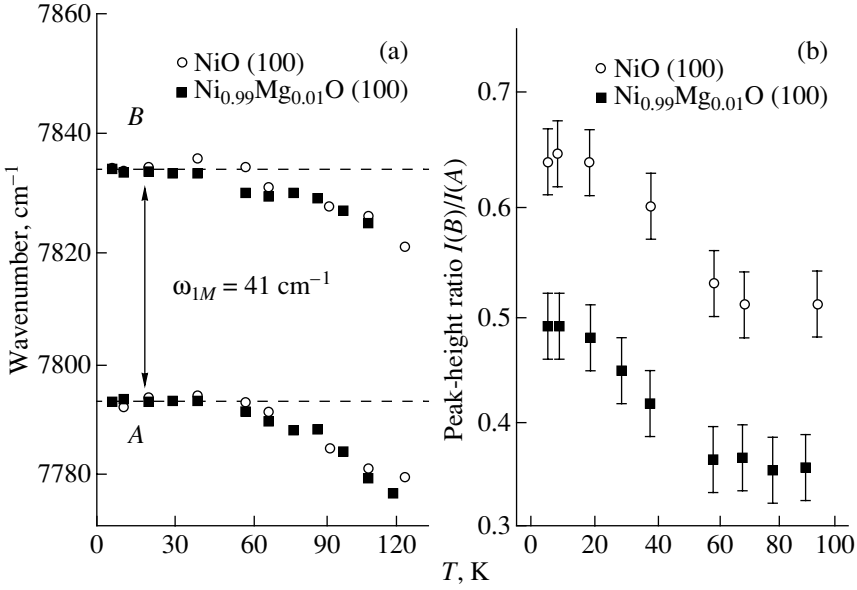


**Fig. 4.** (a) Variation of the *A* and *B* peak positions with temperature in NiO and $Ni_{0.99}Mg_{0.01}O$ single crystals. The separation between the two peaks remains constant and equal to the magnon energy $\omega_{1M} = 41$ cm$^{-1}$. (b) $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$, $^1E_g(D)$ ratio of the *A* and *B* peak amplitudes in NiO and $Ni_{0.99}Mg_{0.01}O$ single crystals.

cess does not produce a contribution in the form of a single peak for $c \leq 0.9$ at 6 K, the $Ni_{0.90}Mg_{0.10}O$ sample nevertheless reveals a strongly smeared feature in place of peaks *A* and *B* (Fig. 2). According to the magnetic phase diagram (Fig. 1), antiferromagnetic order at 6 K is observed in $Ni_cMg_{1-c}O$ solid solutions for $c \gtrsim 0.4$ [1, 2]; moreover, for $c \gtrsim 0.6$, a continuous antiferromagnetic domain structure exists [3]. In pure NiO or in solid solutions with low magnesium content, a continuous antiferromagnetic domain structure is observed to persist up to ~450 K [3], whereas antiferromagnetic order exists substantially above room temperature, up to

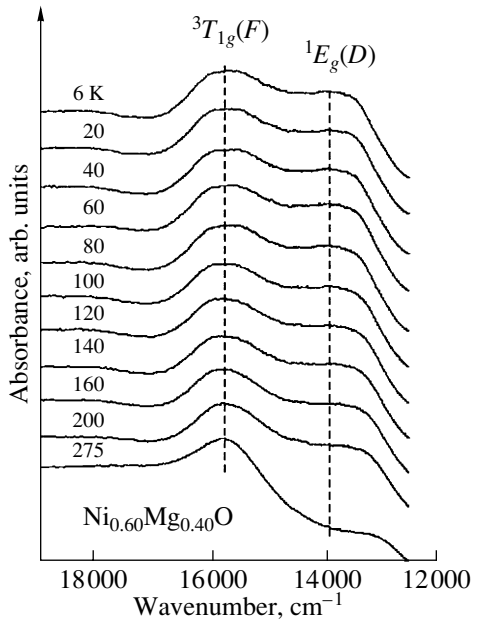


**Fig. 5.** Temperature dependence of the $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ and $^1E_g(D)$ absorption in a $Ni_{0.60}Mg_{0.40}O$ single crystal.

523 K. These results reflect the macroscopic magnetic properties of NiO and $Ni_cMg_{1-c}O$, whereas optical absorption spectra are sensitive to magnetic interactions at a microscopic level. Our observations suggest that the long-wavelength magnons at the center of the Brillouin zone are very sensitive to violations of the long-range spin–spin correlations, which occur with increasing temperature and/or dilution by nonmagnetic ions.

Figure 5 shows the temperature dependence of the absorption due to the $^3A_{2g}(F) \longrightarrow {}^1E_g(D)$ electric-dipole transition in $Ni_{0.60}Mg_{0.40}O$. The $^1E_g(D)$ absorption band is seen to overlap partially with the transition to the $^3T_{1g}(F)$ level lying close to 15700 cm$^{-1}$. The $^1E_g(D)$ band intensity decreases sharply in the 200- to 275-K temperature interval, somewhat below the Néel point $T_N \sim 320$ K. Our previous studies [12] of a similar absorption band in single-crystal $KNiF_3$ permit the conclusion that the shape of the $^1E_g(D)$ band is governed by vibronic processes, in which an exciton and one or several phonons are excited simultaneously, and by an exciton–two-magnon process, which involves excitation of an exciton and two magnons at the Brillouin zone edge. No pure exciton transition is observed in the absorption spectrum, because this transition is both parity- and spin-forbidden; it should lie near 12500 cm$^{-1}$. The zone-edge excited magnons are short in wavelength and, thus, sensitive to short-range magnetic order. Therefore, the absorption corresponding to the exciton–two-magnon process is observed to occur up to the Néel temperature (Fig. 5). The two-magnon contribution was found earlier to behave in a similar way in Raman spectra of NiO [6] and $KNiF_3$ [13]. The energy $\omega_{2M}$ needed to excite two magnons in NiO is approximately ~1400 cm$^{-1}$, i.e., substantially higher than that in $KNiF_3$ ($\omega_{2M}$ = 813 cm$^{-1}$) [12]. The difference between the two energies is due to the superexchange interaction between nickel ions, which is stronger in NiO.

## 4. CONCLUSION

Thus, we have studied the temperature and concentration dependences of optical absorption spectra of NiO and $Ni_cMg_{1-c}O$ single crystals grown on MgO(100) substrates. Attention was focused on the magnon contribution in the absorption bands associated with the magnetic-dipole $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ (~8800 cm$^{-1}$) and electric-dipole $^3A_{2g}(F) \longrightarrow {}^1E_g(D)$ (~13800 cm$^{-1}$) transitions. It was found that the two-magnon absorption contribution varies in close correspondence with the magnetic phase diagram for $Ni_cMg_{1-c}O$, whereas the one-magnon contribution is observed only at temperatures substantially below the Néel point. The results obtained were interpreted as being due to different magnons being involved in the processes. The two-magnon absorption involves zone-edge magnons, whereas the magnon taking part in one-magnon absorption is excited at the center of the Brillouin zone. Because the zone-edge magnons are short in wavelength, they are sensitive to the short-range magnetic order, which persists at fairly high temperatures and for large dilutions of nickel oxide by magnesium ions. At the same time, the zone-center magnon is long in wavelength and, therefore, particularly sensitive to thermal and/or structural magnetic order violations, which arise already at fairly low temperatures and for a 10% substitution.

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