

OPTICAL PROPERTIES OF SOLID SOLUTIONS $\text{Ni}_c\text{Mg}_{1-c}\text{O}$

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Pure nickel oxide (NiO) is a classical example of a type-II antiferromagnet having high Néel temperature $T_N = 523$ K [1]. Substitution of nickel ions in nickel oxide by magnesium ions leads to the formation of a continuous series of $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions, having a rock-salt type cubic structure. A magnetic phase diagram of $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ system has been established in the past by elastic magnetic neutron scattering [2] and SQUID magnetometry [2,3]. There are four domains (Fig. 1): (1) a homogeneous antiferromagnet ($0.63 \leq c \leq 1$); (2) a tricritical region or a frustrated antiferromagnet ($0.4 \leq c < 0.63$); (3) a spin-glass state ($0.25 \leq c < 0.4$) and (4) a diamagnet ($c \leq 0.2$) [2]. Complementary information on the magnetic ordering in $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ single-crystals has been obtained from microscopic investigations of the composition and temperature dependence of the domain structure [4].

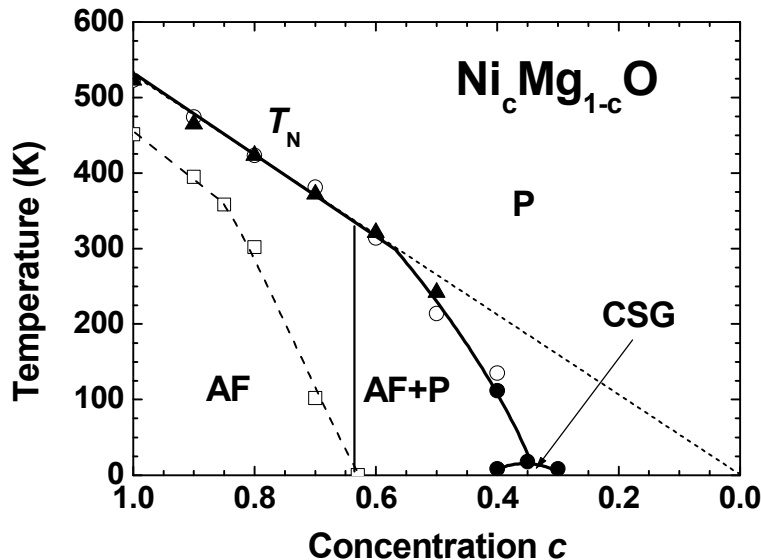


Fig. 1. A magnetic phase diagram of $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ system, according to elastic magnetic neutron scattering [2] and SQUID magnetometry [2,3]. The region of infinite antiferromagnetic cluster [4] is indicated by open squares. **P** means paramagnetic region, **AF** – antiferromagnetic region and **CSG** – cluster spin-glass.

The $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ samples used in the present work were green coloured polycrystalline powders and single-crystals [5,6]. Polycrystalline solid solutions were prepared using ceramic technology from the appropriate amounts of aqueous solutions of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 1200°C in air and then rapidly cooled down to room temperature. $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ single-crystals were grown by the method of chemical transport reactions

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(the “sandwich” technique) on the (100) face of MgO single-crystals. The chemical composition of samples was controlled by instrumental neutron-activated analysis: the content of nickel was in agreement with the stoichiometric one within $\pm 0.01\%$ [7].

The optical absorption spectra of $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ 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 (Fig. 3) are related to parity-forbidden $d-d$ transitions, three of which, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, are spin-allowed ($\Delta S=0$), whereas the others are forbidden. An increase of the nickel ions concentration results in an appearance of new bands and in a shift of the bands maxima. These new bands are caused by spin forbidden electric-dipole transitions: ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$, ${}^3A_{2g}(F) \rightarrow {}^1A_{1g}(G)$, ${}^1T_{2g}(G)$, ${}^3A_{2g}(F) \rightarrow {}^1T_{1g}(G)$ and ${}^3A_{2g}(F) \rightarrow {}^1E_g(G)$, ${}^1T_{2g}(G)$. Their intensity increases rapidly with the nickel content, becoming comparable to the intensity of spin allowed transitions at $c=0.7$. Recently, we have investigated [8,9] the temperature dependence of the three bands – two electric-dipole ${}^1E_g(D)$ at $\sim 13500\text{ cm}^{-1}$, ${}^1E_g(G)$ at $\sim 28000\text{ cm}^{-1}$ and one magnetic-dipole ${}^3T_{2g}(F)$ at 8800 cm^{-1} . The obtained results suggest that all three bands are sensitive to the magnetic ordering in solid solution, moreover the magnetic-dipole band involves the Brillouin zone-centre one-magnon contribution, whereas two electric-dipole bands involve the Brillouin zone-boundary two-magnon contributions [8,9].

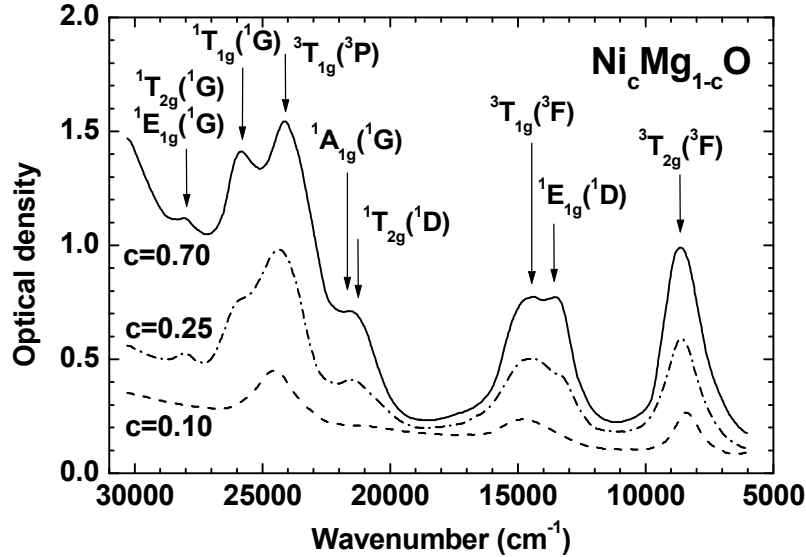


Fig. 2. Room temperature optical absorption in $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ single-crystals [6].

Here we extend our temperature dependent studies to the case of the ${}^3A_{2g}(F) \rightarrow {}^1T_{1g}(G)$ transition (Fig. 3) in two $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions with $c=0.15$ and 0.50 . The analysis of the absorption spectrum in the range $23000\text{--}27000\text{ cm}^{-1}$ indicates that the ${}^1T_{1g}(G)$ band width decreases upon temperature lowering that makes this band better resolved (Fig. 3). Comparison of two solid solutions shows that a decrease of the nickel content results in a decrease of the splitting between ${}^3T_{1g}(P)$ and ${}^1T_{1g}(G)$ bands. This contrasts with an expectation from the energy level diagram, suggesting an increase of the splitting upon lowering of the crystal field Dq parameter in solid solutions with smaller nickel content due to an increase of the lattice parameter [10]. Such contradiction could be explained by a variation of the Racah B parameter, which increases with a decrease of the nickel content due to the change of the Ni–O bonding [6].

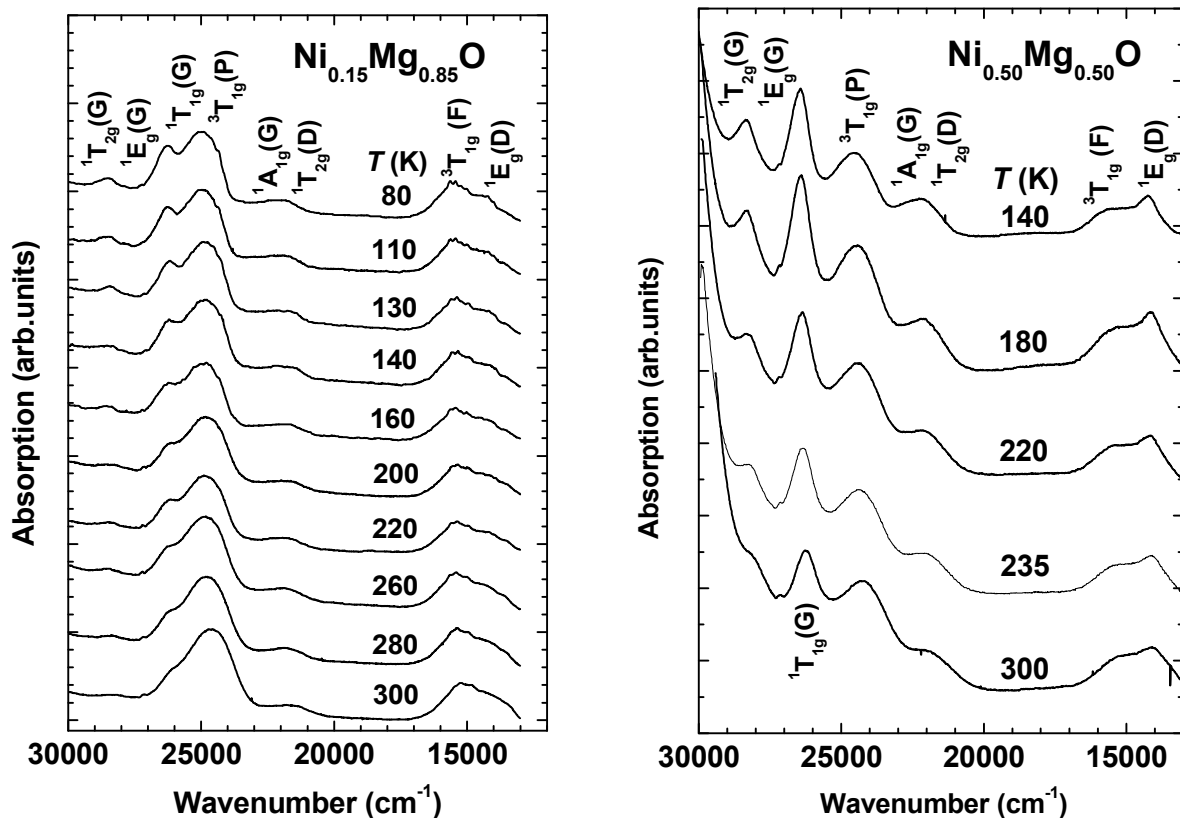


Fig. 3. Temperature dependences of the optical absorption spectra in $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions with $c=0.15$ and 0.50 .

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