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Spectroscopy of Charge Transfer States in $Mg_{1-x}Ni_xO$

V. N. Churmanov[a]*, V. I. Sokolov[b], V. A. Pustovarov[a], N. B. Gruzdev[b], and N. Mironova-Ulmane[c]

[a] Ural Federal University, Yekaterinburg, 620002 Russia
[b] Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620990 Russia
[c] Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia
*e-mail: v.churmanov@ut.ee

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Abstract—Photoluminescence and photoluminescence excitation spectra of solid solution $Mg_{1-x}Ni_xO$ (x = 0.008) have been analyzed. The contributions of charge transfer electronic states and nonradiative Auger relaxation to the formation of the photoluminescence spectrum are discussed.

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INTRODUCTION

It has already been shown by P.P. Feofilov [1] that the study of charge transfer states is important from both the theoretical and applied point of view. The charge transfer states arise in semiconductors or dielectrics doped with impurities of 3*d*- and 4*f*-transition metals. Many experimental results have been obtained for II–VI semiconductors doped with 3*d* metals, for example, ZnSe : Ni [2]. Impurities replace the atoms of the second group and are doubly charged ions. The energy states of ions are split in the crystal electric field and form a series of intracenter state transitions between which they manifest as narrow, weak peaks in the spectra of light absorption or photoluminescence. Along with these states, states caused by a change in the number of electrons in the *d* shell are possible for the d^n configuration. Transitions to such states are called "charge transfer transitions." Charge transfer transitions are superimposed on the intracenter transitions. They create broad, intense bands of light absorption in absorption spectra. As a rule, they do not appear in the photoluminescence spectra of II–VI:3*d* compounds. The reason for this is that the Auger relaxation is dominant at an impurity center, which results in transformation of the annihilation energy of an electron–hole pair (the electron from the d^{n+1} configuration and the hole from the valence band) into excitation of the d^n configuration [3, 4]. Recently [5], the first data were reported on manifestation of charge transfer in the photoluminescence (PL) spectra and photoluminescence excitation (PLE) of MgO:Ni under pulsed synchrotron excitation. In the PLE spectrum of $Ni_cMg_{1-c}O$ (c = 0.008), a series of equidistant peaks with LO-phonon energy were recorded, which were analogous to a series of vibrational repetitions of the head line in the electronic absorption spectra of II–VI : 3d single crystals [2]. These results were interpreted as manifestations of charge transfer *p*–*d* excitons. For the Ni impurity in MgO, the energy of charge transfer $d^8 + \hbar\omega \rightarrow d^9 + h$ is approximately equal to 3.6 eV and is close to the energies of many intracenter states of the Ni^{2+} ion observed in the absorption spectrum of MgO:Ni [6]. In the present paper, the results of a more detailed investigation of PL and PLE spectra of solid solutions $Mg_{1-x}Ni_xO$ are reported.

EXPERIMENTAL

Nanoparticles of solid solutions $Mg_{1-x}Ni_xO$ were obtained by evaporation of coarse grained (sizes of particles in the range of 20–40 μm) powders of NiO (99.9%) and MgO (99.9%) in a high-frequency plasma. The average size of particles was estimated from the specific area of surface (using the Brunauer–Emmett–Teller theory), which had been calculated from the adsorption—desorption isotherm of gaseous nitrogen at 77 K with a KELVIN 1042 sorptometer. The average size of particles thus obtained was about 50 nm for all compositions of $Mg_{1-x}Ni_xO$.

The PL spectra in the range of 1.25–4.25 eV (excitation energy E_{exc} = 4.65–5.4 eV) at a temperature of 80 K and the PLE spectra (emission energy E_{em} = 2.35–3.38 eV) in the range of 3–5.7 eV at temperatures of 80 and 300 K were recorded using two DMR-4 double prism monochromators (inverse linear dispersion of 10 Å/mm in the region of 5 eV), an R6358-10 photoelectron multiplier (Hamamatsu), and a photon counting system. A DDS-400 deuterium lamp was used for excitation. The PLE spectra were normalized to equal number of photons hitting a sample with the use of yellow luminogen, the PL quantum yield of

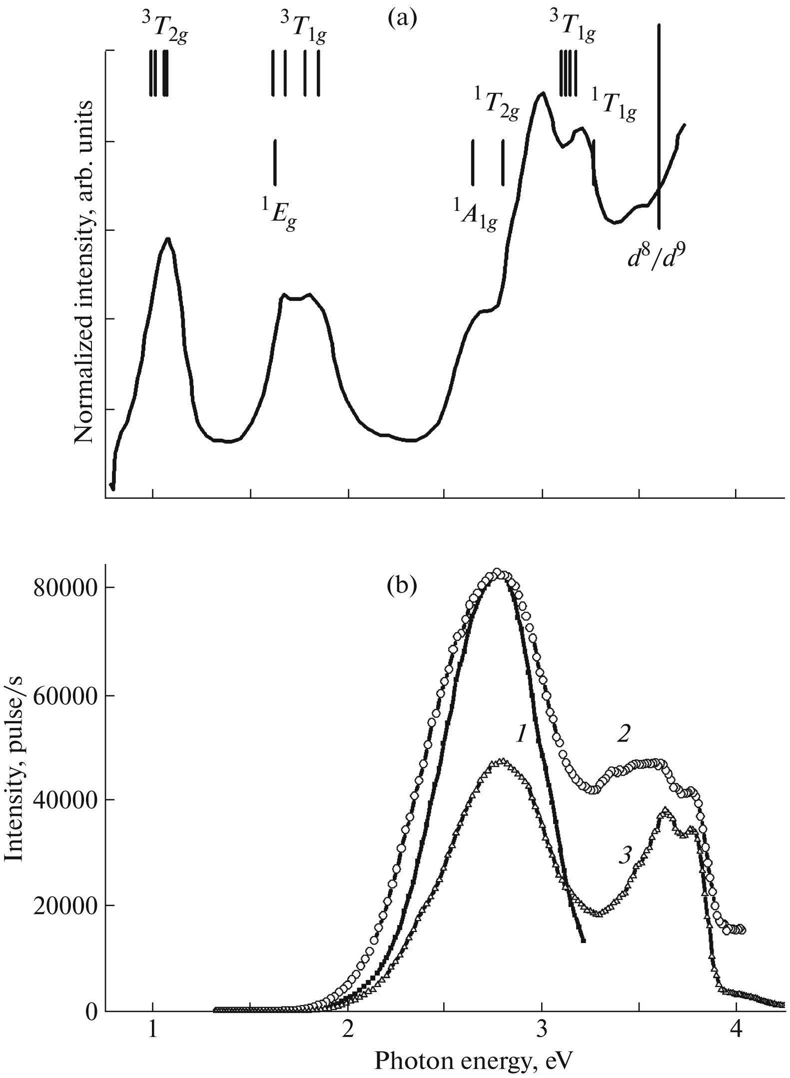

Fig. 1. (a) Absorption spectrum of the Ni^{2+} ions in MgO from [6]. Vertical lines indicate the calculated positions of energy levels of the Ni^{2+} ion and the d^8/d^9 charge transfer state. (b) Photoluminescence spectra of $Ni_{0.008}Mg_{0.992}O$, $T = 80$ K, E_{exc} = (*1*) 3.5, (*2*) 4.35, and (*3*) 5.4 eV.

which does not depend on the energy in the studied energy range. The presented PL spectra have not been normalized to spectral sensitivity of an optical channel.

RESULTS AND DISCUSSION

The low-temperature PL spectra of solid solution $Mg_{1-x}Ni_xO$ ($x = 0.008$) for the excitation energies E_{exc} = 3.5, 4.35, and 5.4 eV are shown in Fig. 1b. For comparison the absorption spectrum of the Ni^{2+} ions in MgO from [6] is presented in Fig. 1a, where the positions of energy levels of the Ni^{2+} ions calculated in [6] and the d^8/d^9 charge transfer states are also shown. One can see that the absorption spectra noticeably differ from the PL spectrum, which has the form of a broad band with a low-energy wing and a maximum at an energy of 3.25 eV resulting from radiative recombination of the charge transfer state [5]. For E_{exc} = 4.35 eV, a distinct, broad band with a maximum at 2.75 eV appears in the PL spectrum, while two very weak peaks at energies of 2.2–2.3 eV were observed in the PL spectrum in [5]. There appear significant changes in the short-wavelength part of the PL band; several emission peaks are seen here. The character of a PL spectrum changes with increasing excitation energy. For E_{exc} = 5.4 eV, two PL bands, close to one another in magnitude and separated by a rather deep minimum, are observed. The second band is seen near 3.7 eV. Figure 2 shows the PLE spectra of crystals $Ni_{0.008}Mg_{0.992}O$ at temperatures of (a) 300 and (b) 80 K with different emission energies. First of all, note that

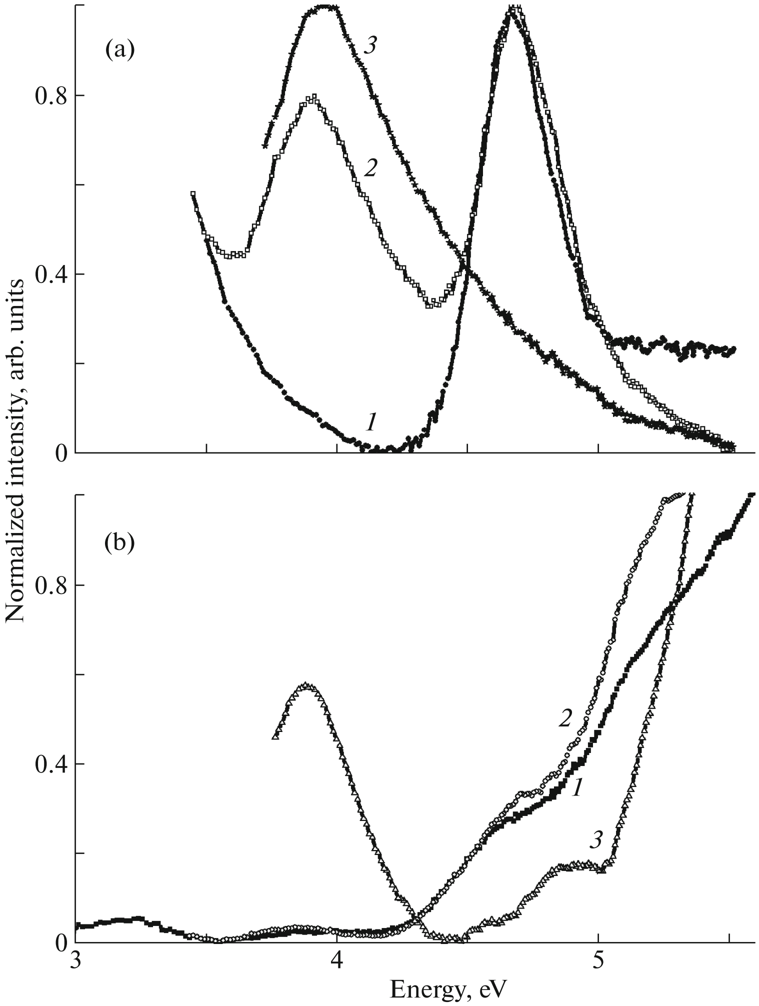

Fig. 2. Photoluminescence excitation spectra of $Ni_{0.008}Mg_{0.992}O$. T = (a) 300, (b) 80 K. (a) E_{emis} = (*1*) 2.43, (*2*) 2.85, and (*3*) 3.35 eV. (b) E_{emis} = (*1*) 2.35, (*2*) 2.85, and (*3*) 3.35 eV.

the PLE spectra significantly differ for two close emission energies, 2.43 and 2.85 eV, which fall onto the smooth long-wavelength slope of a broad PL band observed in [5] under synchrotron radiation excitation. For the emission energy of 3.35 eV, which is coincident with the PL band maximum in [5], the excitation spectrum virtually coincides with the analogous spectrum in [5], but differs from the PLE spectra for the first two emission lines. As the temperature lowers down to 80 K, the PLE spectra for close emission energies transform; however, one can easily see that their spectral features are closely spaced from each other. This suggests that the broad PL bands are sums of contributions made by different transitions.

Comparison with the absorption spectrum shows that the broad PL band is caused by intracenter radiative transitions in the d^8 configuration of the Ni^{2+} ion, but it is impossible to separate these contributions using only the PL spectra. However, the PLE spectra allow the radiative transitions to be distinguished. The PLE spectrum for emission at 2.43 eV has a strong peak in the region of 4.75 eV. The PLE spectrum for emission at 2.85 eV (curve *2* in Fig. 2a) has two maxima at 4.75 and 3.9 eV. The PLE spectrum for emission at 3.35 eV has a maximum in the region of 3.9 eV and a long declining slope at higher energies. This spectrum agrees well with the spectrum in [5] and can be interpreted as a result of excitation of radiative recombination with the *p–d* charge transfer. The common peak in the PLE spectra (curves *1* and *2*) at an energy of 4.7 eV can be due to the $^1T_{2g}$ (^1G) and ^1E_g (^1G) states (Fig. 1 in [6]) with the same energy. Emission at 2.43 eV is excited only via these states, while emission at 2.85 eV is excited via these states and the charge transfer state due to the Auger relaxation at the defect, which is evidenced by a peak in the region of 3.9 eV. The Auger relaxation rate increases on increasing the probability of transition from the $^3A_{2g}$ ground state of the d^8 configuration to its excited state. Transition to the $^3T_{1g}$ excited state with the same spin multiplicity is most probable. Therefore, we suppose that this state is excited via the charge transfer state, while the states with spin multiplicity 1 are not excited via this state. In the octahedral environment, the d and p states are considerably hybridized, the fraction of band states in the d–p hybrids increases, which enhances the radiative recombination via the charge transfer state and, thereby, decreases the Auger relaxation efficiency.

Thus, the energy states with the p–d charge transfer fall into the energy region of intracenter states, which results in the formation of a series of radiative states forming the complicated PL band in $Mg_{1-x}Ni_xO$ (x = 0.008). However, this does not give rise to complete excitation energy transfer to the d^8 configuration, which is the case in II-VI:Ni compounds. The charge transfer state takes part in the formation of a nontrivial PL band in $Mg_{1-x}Ni_xO$ (x = 0.008). The PLE spectrum has a complicated shape, and the same combination of different states is also involved in its formation. A detailed study of changes in the form of $Mg_{1-x}Ni_xO$ spectra with increasing concentration of nickel ions will allow one to better understand the properties of a p–d charge transfer state, which forms the fundamental absorption edge in NiO.

CONCLUSIONS

The results obtained in the study of the system of intracenter states and charge transfer states in $Mg_{1-x}Ni_xO$ may be useful in the investigation of nickel oxide, where the states of the d^8 configuration of the Ni^{2+} ion also coexist with the p–d charge transfer states forming the fundamental absorption edge [5].

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