

Near-infrared luminescence of isolated and exchange-coupled Ni²⁺ ions in Ni_cMg_{1-c}O solid solutions

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Abstract

Ni_cMg_{1-c}O (0.01 ≤ c ≤ 1) solid solutions were studied by near-infrared luminescence, optical absorption and X-ray absorption spectroscopies. It was found that Ni²⁺ ions form at c < 0.2 the exchange-coupled pairs, strongly bound via 90° super-exchange interactions, and are displaced at c ≤ 0.6 to the 'off-center' positions. This explains the origin of the zero-phonon line splitting observed in the optical absorption and luminescence spectra. It was also found that the effective energy transfer from the single Ni²⁺ ions to the exchange-coupled Ni²⁺–Ni²⁺ pairs occurs at temperatures below 40 K.

Keywords: Ni_cMg_{1-c}O; Exchange-coupled Ni²⁺ ions; X-ray absorption spectroscopy

The optical absorption and luminescence spectra of the Ni_cMg_{1-c}O single crystals were measured at liquid nitrogen temperature (Fig. 1). These spectra in the energy range 7800–8300 cm⁻¹ correspond to ³A_{2g} → ³T_{2g} magneto-dipole transition at Ni²⁺ sites and consist of two zero-phonon lines (E and T) at 8005 and 8182 cm⁻¹. Previously, these two lines have been explained by the spin-orbit splitting [2]. However, according to the theoretical calculations [2], there should be four zero-phonon lines at 8011, 8177, 8563 and 8720 cm⁻¹ with the relative intensities equal to 0.677, 1.000, 0.790 and 0.235, respectively, while only two of the above-mentioned lines with the relative intensities equal to 0.645, 1.000 were observed in the experiment. We suggest that these lines are due to the splitting of the ³T_{2g} state by a crystal field acting on Ni ions located at the off-center positions. This conclusion is supported by X-ray absorption spectroscopy

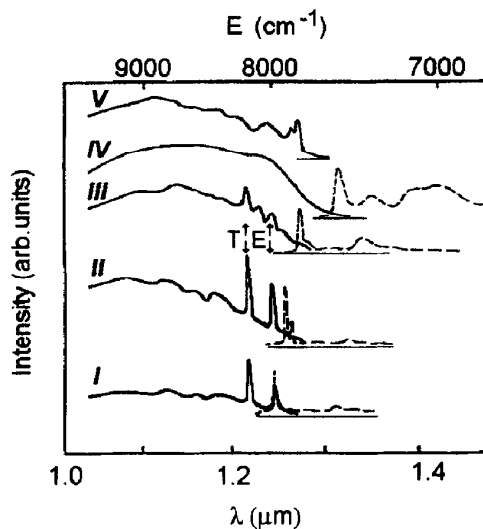


Fig. 1. Optical absorption at $T = 80$ K (solid lines) and luminescence at $T = 10$ K (dashed lines) spectra of Ni²⁺ ions in single crystals Ni_cMg_{1-c}O (I – c = 0.01, II – c = 0.05, III – c = 0.1, IV – c = 0.6, V – c = 1.0) measured at $T = 15$ K.

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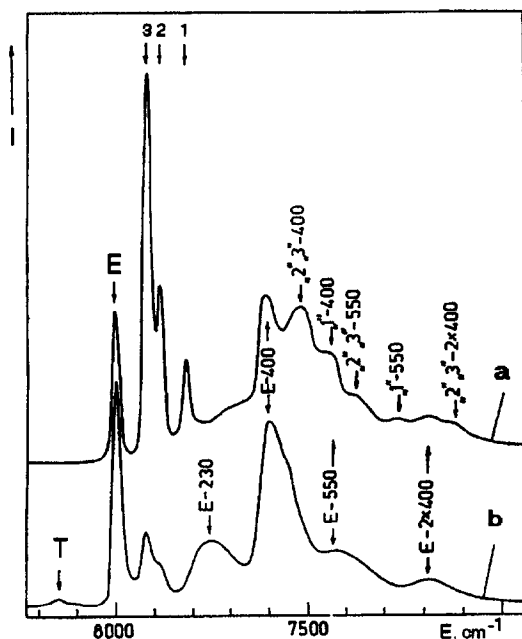


Fig. 2. The luminescence spectra of Ni^{2+} in the region of ${}^3\text{T}_{2g} \rightarrow {}^3\text{A}_{2g}$ transition at 40 K (a) and 80 K (b) in $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ solid solution.

(XAS) [1]: it shows that Ni ions in $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions shift upon dilution to the off-center positions so that the Ni-Ni distance remains nearly constant [1].

Additional sharp lines at 7822, 7888, 7921 and 7937 cm^{-1} appear at the Ni concentrations $0.01 < c < 0.2$. They correspond to the zero-phonon transitions supporting the presence of the exchange-coupled $\text{Ni}^{2+}\text{-Ni}^{2+}$ pairs. The maximum number of isolated pairs appears at $c=0.05$ [3]. Theoretical calculations of the energy levels in the ground and excited states [3] show that the observed sharp lines can be attributed to the so-called '90°-pairs'. Their presence is strongly supported by the XAS results [1].

Temperature variation of the luminescence spectra of Ni^{2+} in the region of ${}^3\text{T}_{2g} \rightarrow {}^3\text{A}_{2g}$ transition in $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ solid solution is shown in Fig. 2. Here the peaks below $\sim 7800 \text{ cm}^{-1}$ correspond to the

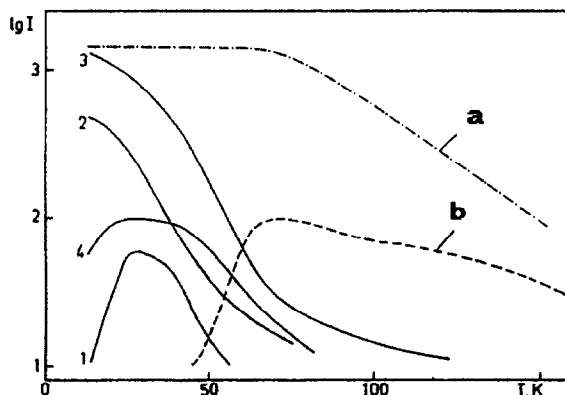


Fig. 3. Temperature dependence of the intensity of zero-phonon luminescence lines: (a) zero-phonon $\text{E}({}^3\text{T}_{2g}) \rightarrow {}^3\text{A}_{2g}$ transition in a single Ni^{2+} ion in $\text{Ni}_{0.01}\text{Mg}_{0.99}\text{O}$; (b) as in (a) for $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$; (1)–(4) zero-phonon transitions in pairs of Ni^{2+} ions in $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$.

phonon transitions. One should point out a redistribution of the zero-phonon lines intensity for the single Ni^{2+} ions (peaks T and E) and the exchange-coupled $\text{Ni}^{2+}\text{-Ni}^{2+}$ pairs (peaks 1, 2 and 3). In $\text{Ni}_{0.01}\text{Mg}_{0.99}\text{O}$, where the number of the exchange-coupled pairs is relatively small, the intensity of the zero-phonon line for the single Ni^{2+} ions remains constant below 70 K and decreases exponentially above 100 K (curve (a) in Fig. 3). In $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$, where the exchange-coupled pairs are present (curves 1–4 in Fig. 3), the intensity of the zero-phonon line for the single Ni^{2+} ions is absent below 40 K (curve (b) in Fig. 3) and it increases when the intensity of the lines for the exchange-coupled pairs decreases.

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