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Journal of Luminescence 72–74 (1997) 231–232

JOURNAL OF LUMINESCENCE

Near-infrared luminescence of isolated and exchange-coupled Ni^{2+} ions in $Ni_cMg_{1-c}O$ solid solutions

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Abstract

$Ni_cMg_{1-c}O$ ($0.01 \leqslant c \leqslant 1$) solid solutions were studied by near-infrared luminescence, optical absorption and X-ray absorption spectroscopies. It was found that Ni^{2+} ions form at $c < 0.2$ the exchange-coupled pairs, strongly bound via 90° super-exchange interactions, and are displaced at $c \leqslant 0.6$ 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 Ni^{2+} ions to the exchange-coupled Ni^{2+}–Ni^{2+} pairs occurs at temperatures below 40 K.

Keywords: $Ni_cMg_{1-c}O$; Exchange-coupled Ni^{2+} 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 $^3A_{2g} \rightarrow {}^3T_{2g}$ magneto-dipole transition at Ni^{2+} 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

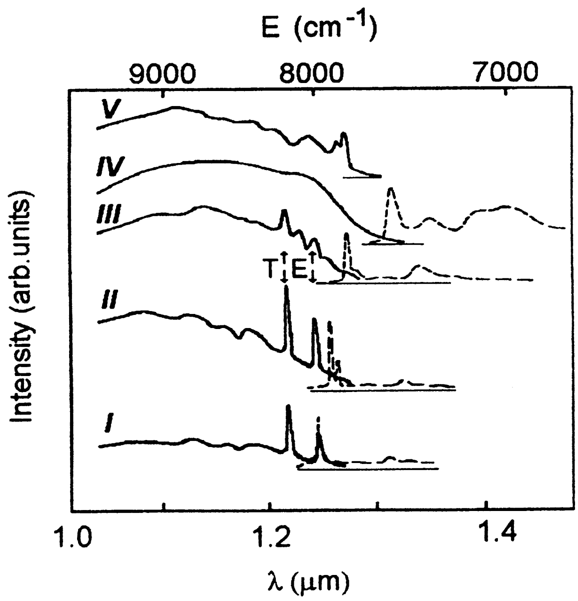

Fig. 1. Optical absorption at $T = 80$ K (solid lines) and luminescence at $T = 10$ K (dashed lines) spectra of Ni^{2+} ions in single crystals $Ni_cMg_{1-c}O$ (I – $c = 0.01$, II – $c = 0.05$, III – $c = 0.1$, IV – $c = 0.6$, V – $c = 1.0$) measured at $T = 15$ K.

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PII S0022-2313(97)00322-5

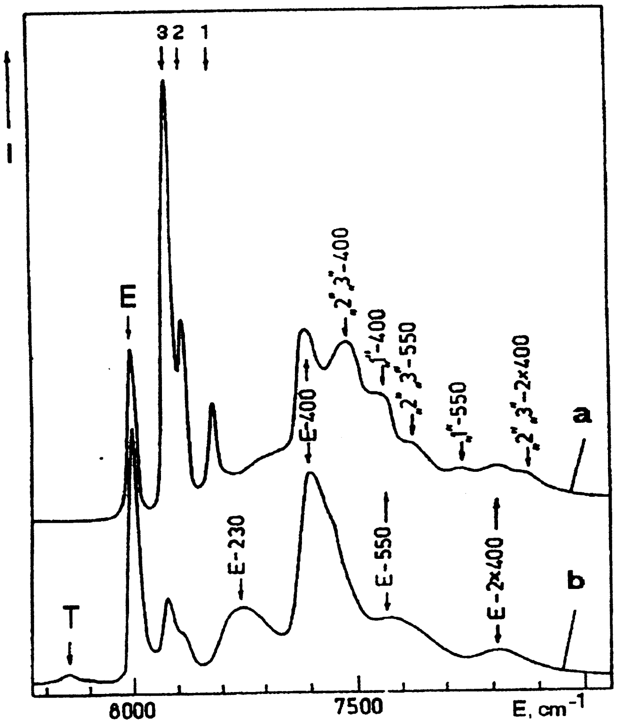

Fig. 2. The luminescence spectra of Ni^{2+} in the region of $^3T_{2g} \rightarrow {}^3A_{2g}$ transition at 40 K (a) and 80 K (b) in $Ni_{0.05}Mg_{0.95}O$ solid solution.

(XAS) [1]: it shows that Ni ions in $Ni_cMg_{1-c}O$ 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 Ni^{2+}–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 $^3T_{2g} \rightarrow {}^3A_{2g}$ transition in $Ni_{0.05}Mg_{0.95}O$ solid solution is shown in Fig. 2. Here the peaks below ~7800 cm^{-1} correspond to the

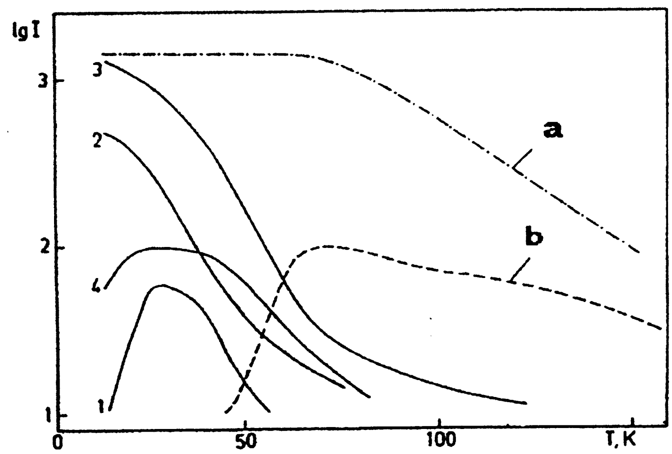

Fig. 3. Temperature dependence of the intensity of zero-phonon luminescence lines: (a) zero-phonon $E(^3T_{2g}) \rightarrow {}^3A_{2g}$ transition in a single Ni^{2+} ion in $Ni_{0.01}Mg_{0.99}O$; (b) as in (a) for $Ni_{0.05}Mg_{0.95}O$; (1)–(4) zero-phonon transitions in pairs of Ni^{2+} ions in $Ni_{0.05}Mg_{0.95}O$.

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 Ni^{2+}–Ni^{2+} pairs (peaks 1, 2 and 3). In $Ni_{0.01}Mg_{0.99}O$, 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 $Ni_{0.05}Mg_{0.95}O$, 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.

References

[1] A. Kuzmin, N. Mironova, J. Purans and A. Rodionov, J. Phys.: Condens. Matter 7 (1995) 9357–9367.

[2] K.Y. Wong, D. Sengupta and E.R. Krausz, Chem. Phys. Lett. 21 (1973) 137–139.

[3] G.A. Grinvald and N.A. Mironova, Phys. Stat. Sol. B 99 (1980) K101–K103.