phys. stat. sol. (b) 99, K101 (1980)
Subject classification: 20.3; 13.4; 22.6

Physics Institute, Academy of Sciences of the Latvian SSR, Riga-Salaspils[1])

Temperature Dependences of Near Infrared Luminescence from Isolated and Exchange-Coupled Pairs of Ni^{2+} Ions in MgO

By
G.A. GRINVALD and N.A. MIRONOVA

At present we have thorough knowledge about emission and absorption spectra of the $^3A_{2g} \rightarrow E(^3T_{2g})$ transition of Ni^{2+} in MgO /1, 2/. At low temperatures the spectra consist of zero-phonon lines and a vibrational band. To observe the spectrum of exchange-coupled pairs of Ni^{2+} ions, we have studied MgO single crystals with Ni concentrations of 1, 2, 5, and 10% at. Single crystals were grown by the sandwich technique on MgO single crystal substrates /3/. Some extra zero-phonon lines, apart from lines of isolated Ni^{2+} ions, and also the corresponding phonon sidebands were observed for the first time in the luminescence and absorption spectra of MgO:Ni^{2+} /4/. Due to their non-linear dependence on impurity concentration these extra lines were considered to arise from exchange-coupled Ni^{2+} pairs. Pair spectra were detected most clearly for the sample with Ni concentration of 5 %at.

The zero-phonon line region of the luminescence spectra is shown in Fig. 1 at two different temperatures. The line at 8005 cm^{-1} is the zero-phonon $E(^3T_{2g}) \rightarrow {}^3A_{2g}$ transition of an isolated ion. Other sharp lines at 7937 cm^{-1} (4), 7921 cm^{-1} (3), 7888 cm^{-1} (2), and 7822 cm^{-1} (1) are zero-phonon lines of exchange-coupled Ni^{2+} pairs.

Exchange interaction between Ni^{2+} ions leads to a rise of the set of "spin" sublevels with the total spin $S = S_a + S_b$ equal to 0, 1, 2 both in the ground $^3A_{2g}$, $^3A_{2g}$, and excited $E(^3T_{2g})$, $^3A_{2g}$ states of the pair. Assuming the interaction between the ions to be of the form $H_{ex} = J(S_a S_b)$ the energy levels of the pair are given by the Landé rule

$$W = \frac{J}{2}\left[S(S+1) - S_a(S_a+1) - S_b(S_b+1)\right].$$

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1) 229021 Riga, Salaspils 1, USSR.

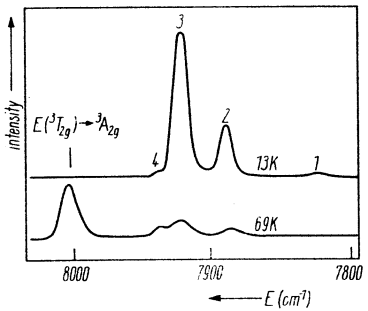

Fig. 1. MgO:Ni^{2+} luminescence spectra (Ni concentration 5% at)

If the selection rule S = 0 is applied, the spectrum should consist of only three lines. The energy differences should be K and 3 K where K is a constant. This rule may be fitted by two sets of lines of the observed spectrum: (1): (7822 cm^{-1}), (2): (7888 cm^{-1}) and (3): (7921 cm^{-1}) where K = 33 cm^{-1} or (2), (3), and (4): (7937 cm^{-1}) where K = 16 cm^{-1}.

We are of opinion that the lines 1, 2, and 3 belong to the transitions between the levels of the total spin 2, 1, and 0,respectively, because the lines 3 and 4 show a similar temperature dependence in absorption spectra and, consequently, the same ground state of the "spin" level S = 0. The temperature dependences of zero-phonon lines of isolated ions and their pairs are shown in Fig. 2. The intensity of the line 4 increases with the rise of temperature from 10 to 20 K, therefore the initial state of the corresponding transition lies probably by 16 cm^{-1} higher than the S = 0 level of the excited $E(^3T_{2g})$, $^3A_{2g}$ state. The scheme of energy levels in the excited state becomes more complicated, which seems to result from spin-orbit splitting of the pair states /5/. Temperature dependences of $E(^3T_{2g}) \rightarrow {}^3A_{2g}$ zero-phonon lines for isolated ions are also shown in Fig. 2. In the sample with Ni concentration 1%at where the number of pairs is relatively small, the intensity of the zero-phonon line of isolated ions is constant at temperatures below 70 K, while at temperatures beyond 100 K it exponentially decreases. On the other hand, in the sample with 5%at Ni the zero-phonon line of isolated

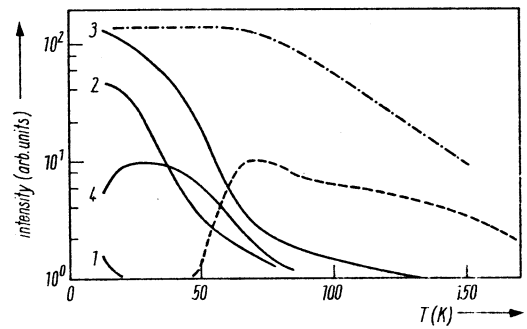

Fig. 2. Temperature dependences of the luminescence zero-phonon lines: — · — single ions in MgO with Ni concentration 1%at; – – – – single ions in MgO with Ni concentration 5%at; —— pairs of Ni^{2+} ions in MgO with Ni concentration 5%at

ions is absent at temperatures below 40 K. This line appears with the growth of temperature, which corresponds to a more drastic decrease of the pair line intensities.

We associate this fact with effective energy transfer from isolated ions to their pairs at temperatures below 40 K.

The authors are grateful to G.V. Bandurkina for her help in growing single crystals and to U.A. Ulmanis for helpful discussions in the course of this work.

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(Received February 8, 1980)