FIZIKA 10 (1978) 179—185 YU ISSN 0015-3206

THE PHOTOEXCITATION AND PHOTOLUMINESCENCE OF THE CRYSTALLINE OCTAHEDRAL COMPLEX COMPOUND OF MANGANESE (II) CHLORIDE WITH 3.5-LUTIDINE HYDROCHLORIDE

B. DRAŠKOVIĆ, I. BURIĆ and K. NIKOLIĆ

Institute of Physics, Beograd

Received 22 June 1977

Abstract: In the present paper the experimental and theoreticaly calculated results are reported on the energy structure of the complex compound of $MnCl_2$ with 3.5-lutidine hydrochloride, in which the Mn^{2+} ion is in octahedral symmetry. The excitation spectrum was recorded and all ligand field bands were identified. The Racah parameters B and C, the ground terms, the energy level diagram and the ligand field strength parameter of this complex were calculated. The photoluminescence spectrum was measured, and the effect of temperature on its parameters is analyzed. A configurational coordinate diagram is given for the ground state and for the lowest excited state.

1. *Introduction*

Mangancse (II) chloride combines with 3.5-lutidine hydrochloride to give two crystalline complex compounds, one of which has the Mn^{2+} ion in tetrahedral symmetry and exhibits a green luminescence (the compound being denoted by LUT 2), while the other has the Mn^{2+} ion in octahedral symmetry and displays a red photoluminescence (the compound being denoted by LUT 1). Both complex compounds exist only in crystal form.

The photoexcitation and photoluminescence of LUT 2 have already been investigated[1]. The results obtained have confirmed the proposed mechanism of excitation and luminescence of this type of complex in which the Mn^{2+} ion is the luminescence center[2-3].

In the present paper the experimental and theoretical results are presented concerning the photoexcitation and photoluminescence of he complex compound with the Mn^{2+} ion in octahedral symmetry.

2. Experimental

The procedure for the preparation of the complex compound LUT 1 is similar to that for the preparation of the corresponding tetrahedral complex compound LUT 2[1].

The excitation spectrum was recorded at liquid nitrogen temperature, while the phosphorescence spectra were measured in the temperature range of —22.8° to +88.7 °C.

The experimental procedure is the same as in investigating the complex compound LUT 2[1]. Also in LUT 1 it has experimentally been corroborated that the transition giving rise to emission is made between states of different multiplicity (phosphorescence).

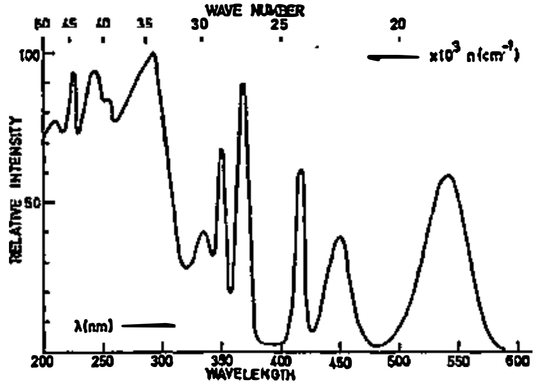

Fig. 1. Excitation spectrum of complex LUT 1 for $\lambda_{em} = 640$ nm at a temperature of 77 K.

3. Results and discussion

Excitation spectrum. The structure and position of excitation spectral bands are independent of the wavelength of the emitted radiation. The excitation spectrum was measured for emission peak ($\lambda_{max} = 640$ nm) (Fig. 1).

All the bands characteristic of excitation transitions of d^5 configuration (the Mn^{2+} central ion benig in octahedral symmetry) were identified (see Table). The spectrum was interpreted in terms of the Orgel weak field matrix for quartet levels d^5 [2,7]. The Racah parameters B and C were calculated, and the energy level diagram was determined for their ratio C/B = 5.259 (Fig. 2). The value of the C/B ratio is larger than those determined by Tanabe and Sugano, Griffith and Stout[4]. The best fit value of the ligand field strength parameter 10 Dq is 7300 cm^{-1}. This is a value larger by a factor of 2 than that for LUT 2.

Table 1 shows the values of ground terms (10 Dq = 0), experimental and calculated positions of excitation bands and their corresponding deviations. The

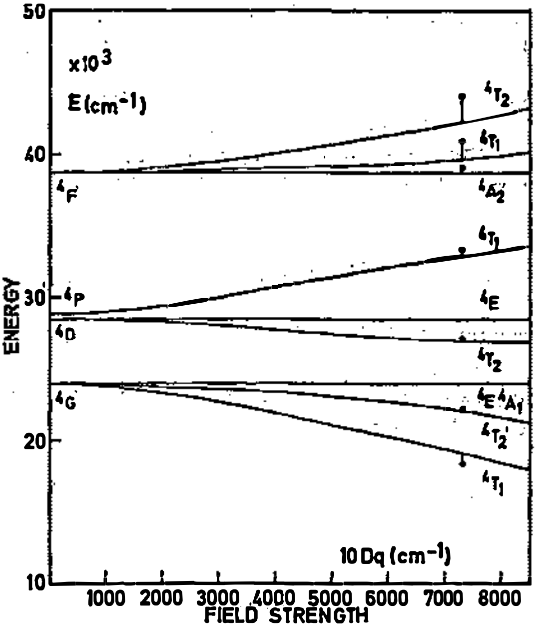

Fig. 2. Energy level diagram (C/B = 5.259).

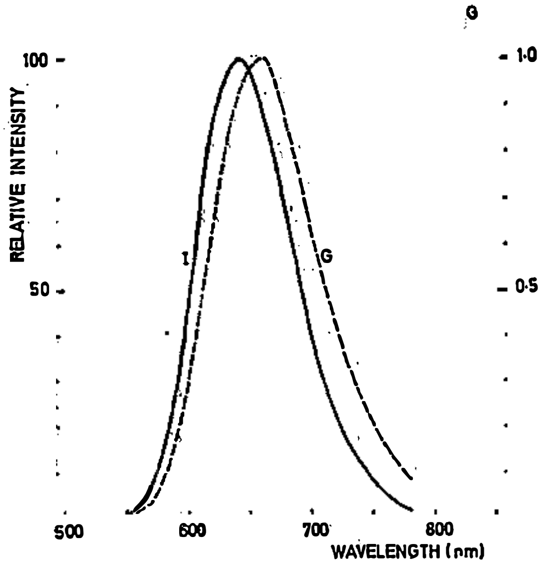

Fig. 3. Photoluminescence spectrum (I) and the distribution function of the matrix factor of dipol transition (G) of complex LUT 1 for $\lambda_{exc} = 540$ nm at $T = 293$ K.

peaks at 210 and 275 nm originate from 3.5-lutidine, while the charge transfer band is at 335 nm, just as in LUT 2 (332 nm) (see Fig. 1).

Emission spectrum. The photoluminescence spectrum of LUT 1 consists of a narrow band with a peak at 640 nm (Fig. 3) the position of which is temperature independent in the temperature range of −22.8° to +88.7 °C.

The maximum radiation intensity varies with temperature according to the Mott-Seitz law

$$I = 608.4 / [1 + 75.2 \exp(-3319/T)],$$

with a maximum relative deviation of the best fit value of 5.2%. Hence the activation energy for quenching is $W = 0.286$ eV.

As the temperature increases, so does the half-width of emission band. By fitting to Payen's formula3) one gets

$$1/L^2 = 0.2 \cdot 10^{-2} \tanh(102.7/T) + 0.11 \cdot 10^{-2} \ (\mathrm{cm}^2),$$

Table

Quartet terms	Calculated position (10 Dq = 0) in cm^{-1} (nm)	Level in O_d symmetry	Experimental positions of excitation bands n_1 in cm^{-1} (nm)	Calculated positions of excitation bands n_2 (10 Dq = 7300 cm^{-1}) in cm^{-1} (nm)	$n_2 - n_1$ 10^3 cm^{-1} (nm)
^4G	23943 (417.7)	$^4T_1$ (G)	18433 (542.5)	19074 (524)	+ 0.641 (− 18.5)
		$^4T_2$ (G)	22222 (450)	22045 (453.6)	− 0.177 (+ 3.6)
		^4E, $^4A_1$ (G)	23952 (417.5)		
^4D	28595 (349.7)	$^4T_2$ (D)	27210 (367.5)	27007 (370.3)	− 0.203 (+ 2.8)
		^4E (D)	28571 (350)		
^4P	28896 (346.1)	$^4T_1$ (P)	33333 (300)	32874 (304.2)	− 0.459 (+ 4.2)
^4F	38802 (257.7)	$^4A_2$ (F)	39063 (256)	38805 (257.7)	− 0.258 (+ 1.7)
		$^4T_1$ (F)	40984 (244)	39714 (251.8)	− 1.270 (+ 7.8)
		$^4T_2$ (F)	44248 (226)	42267 (236.6)	− 1.981 (+ 10.6)
$B = 659.5\ \mathrm{cm}^{-1}$, $C = 3470\ \mathrm{cm}^{-1}$ ($C/B = 5.259$), 10 Dq = 7300 cm^{-1}.					

with a maximum relative deviation of the best fit value of 11.4%. Hence the frequency of the excited state is $\nu_e = 0.428 \cdot 10^{13}\ \mathrm{s}^{-1}$.

The constants a and m were determined for the distribution function of the matrix factor of transition $G(1/\lambda) = \lambda^6 I_\lambda$ (Figs. 3 and 4). The ratio a/m is approximately constant for all temperatures ($\overline{a/m} = -2.09 \cdot 10^{-5}$ cm).

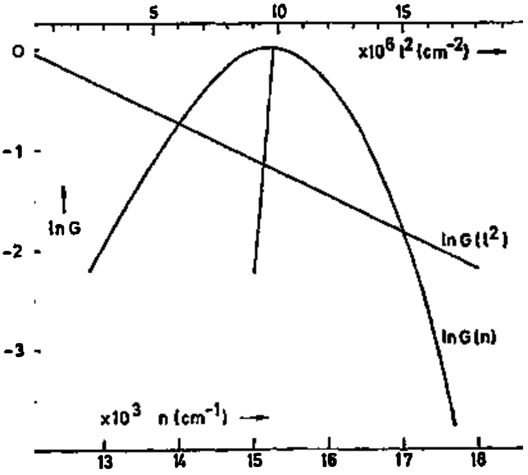

Fig. 4. The ln G — versus — $1/\lambda$ curve and ln G — versus — l^2 curve at a temperature of 293 K for complex LUT 1.

Configurational coordinate diagram. The temperature variation of the emission spectrum parameters makes it possible to present the energy scheme of the emission center Mn^{2+} in the complex compound LUT 1 by the single configurational coordinate method[5,6]. Since the ratio a/m is constant, the following characteristics of configurational parabolas were found by the well-known procedure:

— minimum of the potential energy U_e of the $^4T_1$ (G) level $U_0 = 2.21$ eV;

— configurational coordinate of the minimum of the U_e curve $R_0 = 0.19$ A;

— configurational coordinate of thermal desactivity $R_1 = 0.58$ A;

— fundamental frequency of the ground state $\nu_g = 0.813 \cdot 10^{13}\,\mathrm{s}^{-1}$;

— wave number of the absorption peak $1/\lambda_{ab} = 18431\ \mathrm{cm}^{-1}$.

The equations of the configurational parabolas (Fig. 5) of the ground state (U_k) and of the $^4T_1$ (G) state (U_e) read

$$U_g = 7.42\,R^2\ (\mathrm{eV});\quad U_e = 2.06\,R^2 - 0.79\,R + 2.29\ (\mathrm{eV}).$$

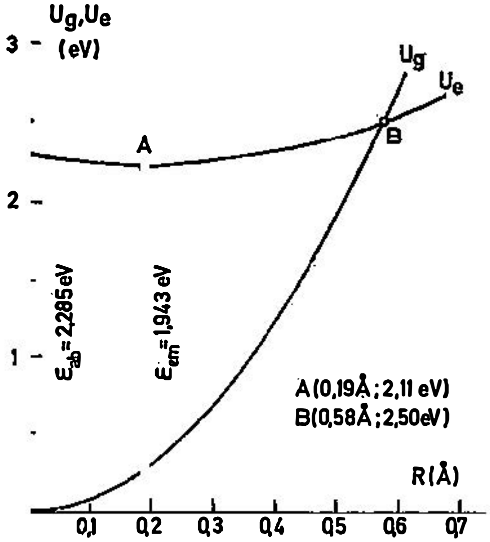

Fig. 5. Configurational coordinate diagram for comp.lex LUT 1.

The experimentally obtained excitation peak for the $^4T_1$ (G) level is $1/\lambda_{ex} = 18433$ cm^{-1}, which is in good agreement with the absorption peak of the configurational curves.

The Stockes separation between the excitation and emission peaks of complex LUT 1 is 2808 cm^{-1} and, according to Furlani's criterion$^{3)}$, is an experimental confirmation that in this complex the Mn^{2+} ion is in octahedral symmetry.

References

1) I. Burić, K. Nikolić and B. Drašković, Fizika **9** (1977) 181;
2) L. E. Orgel, J. Chem. Phys. **23** (1955) 1822;
3) Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9** (1954) 753, 766;
4) D. Curie, C. Barthou and B. Canny, J. Chem. Phys. **61** (8) (1974) 3048;
5) H. Payen de la Garanderie, Thesis, Paris (1964); Ann. Phys., **9** (1964) 649;
6) K. Nikolić, F. Lignou and and H. Payen de la Garanderie, J. of Lum. **8** (1973) 137;
7) K. Bingham and S. Parke, Phys. and Chem. of Glasses **6** (6) (1965) 224;
8) F. Lignou and H. Payen de la Granderie, J. Physique, **36** (1975) 1341;
9) C. Furlani, E. Cervone and P. Cancellieri, Lincei-Rend. Sc. fis. mat. e nat. **37** (1964) 446.

FOTOEKSCITACIJA I FOTOLUMINISCENCIJA KRISTALNOG OKTAEDARSKOG KOMPLEKSA MANGAN (II) HLORIDA SA HIDROHLORIDOM 3.5-LUTIDINA

B. DRAŠKOVIĆ, I. BURIĆ i K. NIKOLIĆ

Institut za fiziku, Beograd

Sadržaj

U radu su referisani eksperimentalni i teorijski rezultati o energetskoj strukturi kompleksa $MnCl_2$ sa hidrohloridom 3.5-lutidina, sa jonom Mn^{2+} u oktaedarskoj simetriji.

Izmeren je ekscitacioni spektar i identifikovane sve trake ligandnog polja. Izračunati su Racah-ovi parametri B i C, osnovni termovi, energetski dijagram i jačina polja ovog kompleksa.

Izmeren je također fotoluminescentni spektar i analiziran uticaj temperature na njegove parametre a prikazan je i kofiguracioni dijagram za osnovno $^4A_1$ (S) i najniže pobuđeno stanje $^4T_1$ (G).