Materials Science, Vol. 20, No. 1, 2002

Review of luminescence and magnetic properties of antiferromagnetic $KMnCl_3$, $RbMnCl_3$, $TlMnCl_3$ and $(C_nH_{2n+1}NH_3)_2MnCl_4$ (n = 1, 2)

MAŁGORZATA PAWŁOWSKA, WALTER WOJCIECHOWSKI

Institute of Inorganic Chemistry and Metallurgy of Rare Elements,
Wrocław University of Technology, Wrocław, Poland

Phenomena connected with the energy transfer in perovskite-type antiferromagnetic materials $KMnCl_3$, $RbMnCl_3$, $TlMnCl_3$ and $(C_nH_{2n+1}NH_3)_2MnCl_4$ (n = 1, 2) dotted with Sm^{3+} and Eu^{3+} ions, are considered and discussed in this paper. The energy transfer in the compounds studied is proved to depend upon the magnetic interactions in them.

1. Introduction

The title compounds belong to a group of magnetically ordered insulating materials. A consequence of their condensed nature is the possibility of excitation energy transfer. This effect dominates the luminescence and absorption behaviour of magnetically coupled manganese salts. In this paper, we present a review of luminescence and magnetic studies of chloromanganates of different crystal structures and magnetic properties of different dimensionalities. All investigated compounds have the perovskite structure which can be simply described as two- or three-dimensional array of $[MnCl_6]$ octahedra.

$KMnCl_3$ has the structure distorted from the ideal cubic perovskite (orthorhombic structure), space group P_{nma}, unit cell parameters: $a = 7.08$, $b = 9.97$, $c = 6.98$ Å, $Z = 4$ (α-phase). This compound manifests an interesting feature of crystallographic polytypism at room temperature, namely, it can simultaneously exist in another orthorhombic crystallographic phase isostructural with $KCdCl_3$, space group P_{nma}, unit cell parameters: $a = 8.79$, $b = 3.883$, $c = 14.42$ Å, $Z = 4$ (β-phase). Mn^{2+} is located in the centre of Cl^- octahedra slightly distorted in case of α-phase and heavily in case of β-phase. Both phases are paramagnetic at room temperature and undergoe a transition to a magnetically ordered state: α-phase at about 100 K and β-phase at about 2.1 K.

$TlMnCl_3$ has cubic perovskite structure at 293 K, space group P_{n3m} (α-phase) lattice constant 5.025 Å, which can transfer into another nonperovskite $KCdCl_3$ structure with space group P_{n3m} and cell parameters: a = 8.93, b = 3.84, c = 14.77 Å. The ideal perovskite structure shows structural phase transition caused by tetragonal and rhombic distortion at 296, 276 and 235 K. Below the last low-temperature transition down to the temperature of liquid nitrogen, the crystal has a monoclinic unit cell. Neel temperature for $TlMnCl_3$ is about 113 K.

$RbMnCl_3$ crystallises in a hexagonal space group $P_{6/mmc}$. Neel temperature is 96 K. No structural transition has been found for this compound.

$KMnCl_3$, $TlMnCl_3$ and $RbMnCl_3$ are 3D Heisenberg antiferromagnets.

$(C_nH_{2n+1}NH_3)MnCl_4$ are perovskite layer compounds and possess two-dimensional magnetic properties. This two-dimensional character is further enhanced in the case of antiferromagnetic alignment of spins within a Mn^{2+} plane. T_N for both compounds investigated are about 43 K. Magnetic properties were reported in details in our previous paper [1].

We investigated pure crystals and crystals doped with Eu^{3+} and Sm^{3+} ions, concentration of lanthanide ions was of the order of 1 wt.%. Figure 1 represents the relevant energy levels of Mn^{2+}, Eu^{3+} and Sm^{3+} and reveals the possibility of resonance of manganese emission levels and the lanthanide ions absorption levels. We could monitor intrinsic manganese, host and trap emission. Energy transfer process could occur between these spectroscopic centres.

The crystal preparation, details about experimental conditions and results were reported in our previous papers [1–8]. In this report, structures, magnetic and spectroscopic properties of the title compounds are summarised and correlated.

2. Manganese(II) luminescence and absorption

Manganese(II) compounds have particularly attracted the interest of spectroscopists. Mn^{2+} ions excited by the absorption of light into higher excited states, rapidly relax to the lowest $^4T_{1g}$ excited state. This is a metastable level, its lifetime is about 30 msec. All d-d transitions are spin- and parity-forbidden but due to the first prohibition they are susceptible to exchange effects. Because of strong Mn–Mn exchange coupling a particular ion do not remain excited, but the excitation energy migrates through the crystal. Excitation transfer, luminescence and absorption are experimentally accessible and can be correctly described by exciton model.

Figure 2 shows a representative absorption spectrum of the compounds investigated. The number and position of the bands are characteristic of octahedry coordinated divalent manganese ions. All those compounds exhibit broad-band luminescence between 14000 cm^{-1} and 19000 cm^{-1}, which strongly depends on temperature, kind of univalent cation and lattice crystal structure. Temperature dependence is mainly associated with additional energy levels induced by lattice defects and impurities, acting as traps for excitation energy. These traps can be divalent transition-metal ions with low-energy electronic states, such as Fe^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, which are unintentionally but inevitably present in trace amounts even in a nominally pure crystal. Consequently, intrinsic emission of regular manganese ion as well as host and trap emission of slightly perturbed manganese sites are observed.

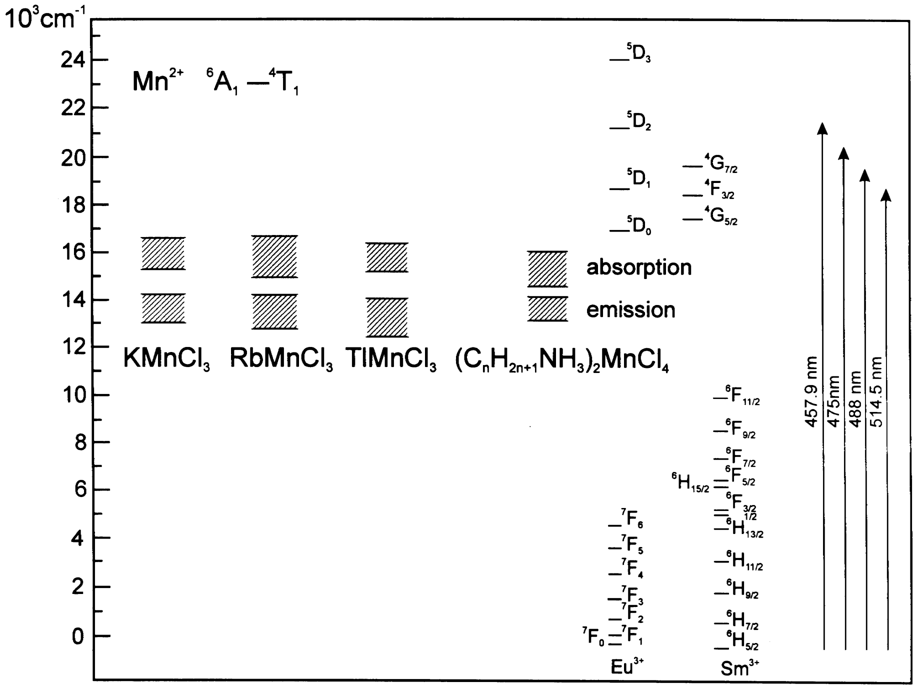

Fig. 1. Relevant energy levels of Mn^{2+}, Eu^{3+} and Sm^{3+}

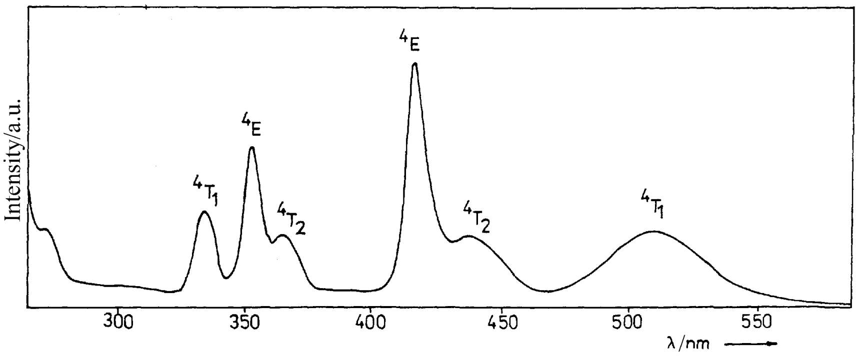

Fig. 2. Absorption spectrum of $KMnCl_3$ at RT

In fluoromanganates energy transfer process occurs at low temperature, so hardly any intrinsic luminescence is observed. This process becomes more efficient when temperature increases and simultaneously deeper traps are feeded. This is the reason for red shift of luminescence spectrum at higher temperature. Some of the traps decay radiatively (host or lanthanide acceptor traps), some are quenching traps. Presence of quenching traps is likely to be responsible for decreasing of the Mn^{2+} donors luminescence intensity at high temperatures. On the subject of energy transfer in fluoromanganates there exist a large body of literature, but there are only few concerning chloromanganates.

Kambli and Güdel [9] investigated antiferromagnets: $RbMnCl_3$, $CsMnCl_3$, $CsMnBr_3$ and Rb_2MnCl_4 doped with Er^{3+} and Nd^{3+}. Emission intensity and time -resolved spectra were measured at different temperatures. The conclusion was that the absence of energy transfer at low temperature is observed for alkalichloromanganates in general. They claim that energy transfer becoms efficient above 50 K.

Our results of Eu^{3+} and Sm^{3+}-doped $KMnCl_3$, $RbMnCl_3$, $TlMnCl_3$ luminescence confirm the above feature of chloromanganates, however weak lanthanide fluorescence was also observed at low temperature (see Fig. 3), hence energy transfer cannot be excluded in low-temperature range.

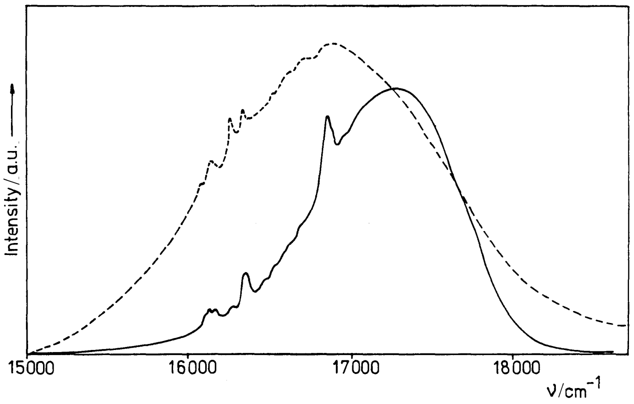

Fig. 3. Luminescence spectrum of Eu^{3+} doped β-phase $KMnCl_3$ at 4.2 K. Dotted line – continuous flow cryostat, full line – stationary cryostat

There is one more effect that could not be explained if we assumed the temperature 50 K to be a critical one for energy transfer process. This is an effect of blue shift of the Mn^{2+} luminescence maximum in chloro-compounds with increasing temperature. It was observed to be of the order of 500–700 cm^{-1} for $KMnCl_3$, $RbMnCl_3$, $TlMnCl_3$ (see Figs. 4, 5) by us and Kambli and Gudel [10] for $RbMnCl_3$. The most probable reason for this shift can be thermal back transfer at high temperature. If it is the case we cannot say that energy transfer is negligible at low temperature.

The luminescence spectra of $(CH_3NH_3)_2MnCl_4$ and $(C_2H_5NH_3)_2MnCl_4$ doped with Nd^{3+} and Eu^{3+} ions were also investigated. A broad-band Mn^{2+} luminescence maximising at ~16500 cm^{-1} at 77 K and at 17100 cm^{-1} at room temperature was observed. Lanthanide ions fluorescence was not detected.

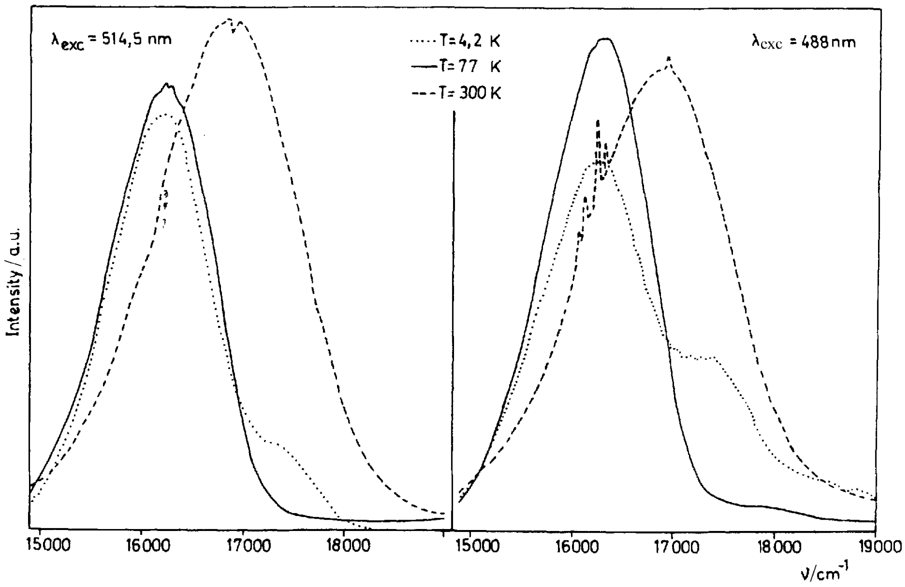

Fig. 4. Luminescence spectra of Eu^{3+} doped α + β-phase KMnC1$_3$ at selected temperatures

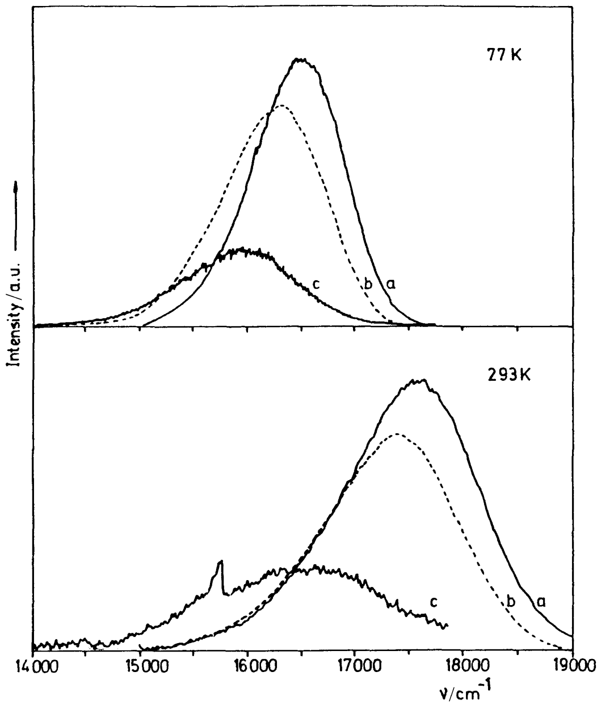

Fig. 5. Luminescence spectra of Eu^{3+} doped TlMnCl$_3$:
a) α-phase, b) α + β-phase, c) β-phase

3. Crystal structure and luminescence characteristic

The $KMnCl_3$ crystal occurs in two crystallographic phases [11]: the orthorhombic perovskite structure – α-phase, and the non-perovskite orthorhombic structure – β-phase. The α-phase is not stable and transforms slowly into β-phase, so in practice two different phases may exist in the $KMnCl_3$ crystal. In Fig. 6 the difference between luminescence spectra of α-phase and β-phase is visible. α-phase emission is observed at 15700 cm^{-1} (635 nm) while this for Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ transition in β-phase lies in the region of significantly higher energy – 17540 cm^{-1} (570 nm). α-phase emission is strong at 77 K while the emission corresponding to β-phase is rapidly quenched when temperature increases to 77 K (Fig. 4).

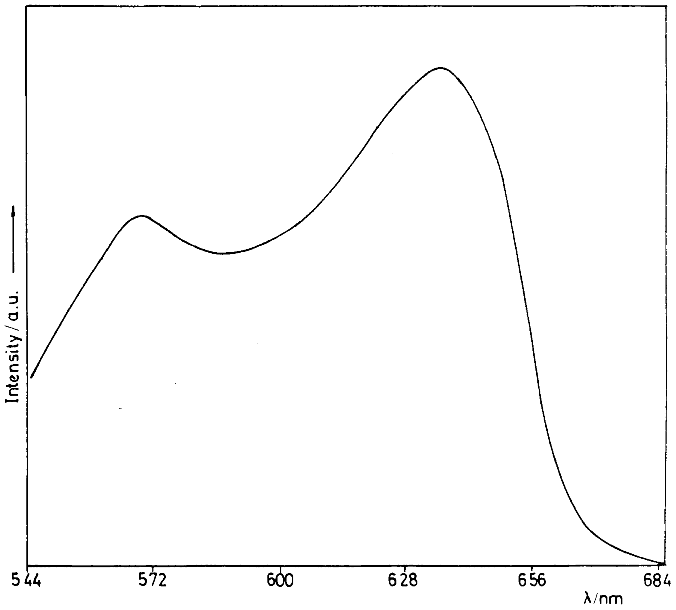

Fig. 6. Luminescence spectrum of $KMnCl_3$ containing α and β crystal phases at 13 K

In $TlMnCl_3$ the dependence of Mn^{2+} luminescence on crystal structure was also observed. We investigated the cubic crystal (α-phase) and orthorhombic (β-phase). The emission maximum in luminescence spectra shifts to the red when the symmetry of the crystal lowers (Fig. 5).

In crystals in which a phase transition occurs, an anomalous luminescence can be observed [7, 11]. Figure 7 presents an evident thermal hysteresis lop of the luminescence lifetime measured at luminescence maximum corresponding to α-phase of $KMnCl_3$ crystal. This effect was not observed for β-phase emission.

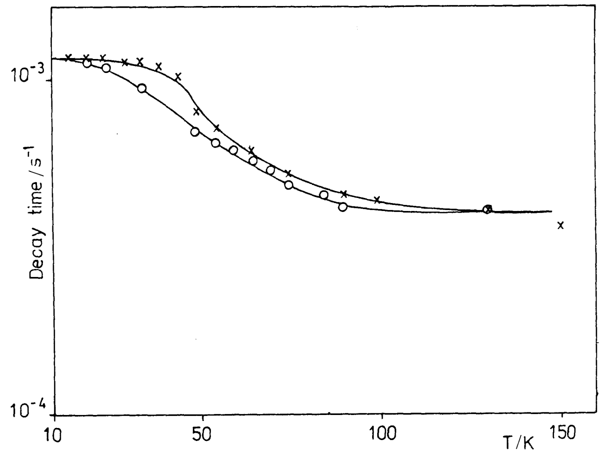

Fig. 7. Temperature dependence of the luminescence lifetimes corresponding to β-phase luminescence of α- + β-$KMnCl_3$ (635 nm). The points marked by × and ¡ were measured for increasing and decreasing temperature, respectively

Another consequence of the structural transitions in this crystal is an interesting dependence of luminescence spectra on the cooling rate of the crystal (Fig. 3). The luminescence spectra of Eu^{3+} doped $KMnCl_3$ crystal for some not closer defined reason depended on cooling rate at 4.2 and 77 K, namely, the spectrum of Mn^{2+} salt placed in a stationary cryostat (rapid cooling) is shifted to the blue by about 400 cm^{-1} in comparison to the spectrum measured in a continuos-flow cryostat (slow cooling); this phenomenon was reversible at LN temperature.

Among the three investigated 3D crystals, $KMnCl_3$ and $TlMnCl_3$ are susceptible to structure transitions. The polytypism and temperature phase transitions significantly influence the luminescence spectra. So the crystal structure should be confirmed for each particular luminescence spectrum. According to our knowledge, no structural changes have been observed for $RbMnCl_3$, so spectroscopy results are synonymous.

4. Trivalent lanthanide ions emission and energy transfer

The investigations of lanthanide ions' luminescence were carried out in such a way that the excitation was only due to energy transfer. The spectra were excited with the argon laser lines: 457.9 nm, 475.5 nm, 488 nm, 514.5 nm. The energy corresponding to these wavelength does not fit the absorption levels of europium and samarium ions (Fig. 1) so direct excitation was negligible. Furthermore, the intensity of lanthanide ions luminescence was of orders of magnitude too high for direct excitation of ions characterized by very small absorption coefficient in low concentrations. Energy transfer could be responsible for excitation of fluorescence of Sm^{3+} and Eu^{3+} ions incorporated into chloromanganates(II) matrices. Figure 8 is a nice illustration of the feeding mechanism of Sm^{3+} emission by long-range and short-range energy transfer from the Mn^{2+} system. Our spectral data [3, 5, 6] and those of other authors [9, 12] give evidence for thermal activation of this process. Efficiency of energy transfer process to lanthanide ions does not only depend on temperature but also on crystal structure and experimental conditions.

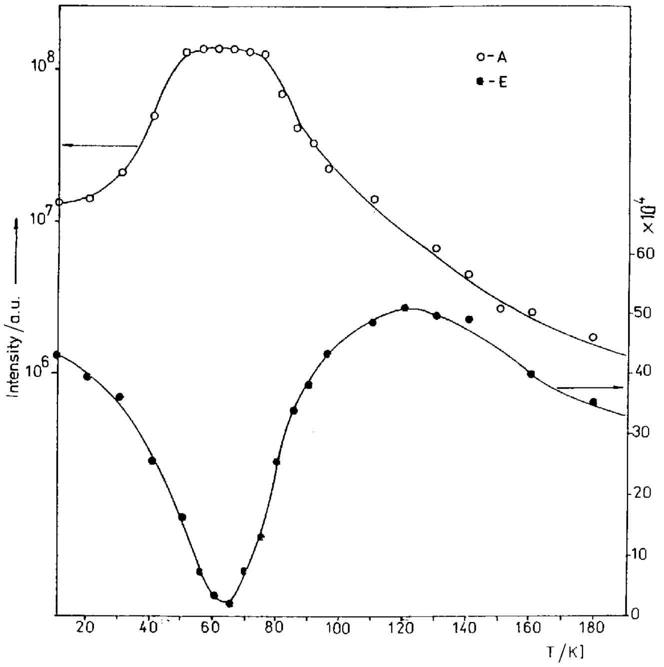

Fig. 8. Temperature dependence of the integrated intensities of $^4T_1$ Mn^{2+} emission (curve *A*) and of ^4G Sm^{3+} (curve *E*) for Sm^{3+}-doped $RbMnCl_3$

Among the investigated salts we have not detected any rare earth emission in case of $(C_nH_{2n+1}NH_3)_2MnCl_4$ and hardly any in case of $TlMnCl_3$. The most effective luminescence centre were created in rubidium and potassium chloromanganates II.

In Figure 4, the luminescence spectra of Eu^{3+} doped $KMnCl_3$ at the temperature of 4.2, 77 and 293 K are presented. The europium luminescence was observed only at room temperature. It consists of single sharp lines at ~16900 cm^{-1} assigned to $^5D_o \rightarrow {}^7F_1$ transition, and of the group of lines of lower energy than that assigned to $^5D_o \rightarrow {}^7F_2$ transition. Note that when 514.5 nm line was used as an excitation source, no Eu^{3+} fluorescence was observed but instead of it the characteristic reabsorption of the $^7F_1 \rightarrow {}^5D_o$ transition resulting from Mn-Eu interaction appeared at the top of Mn^{2+} luminescence broad band. For β-phase $KMnCl_3$ europium luminescence was observed at 4.2 K and 77 K (Fig. 9) Eu^{3+} exhibited several intense sharp multiples. The transitions from the ^5D_o to the $^7F_2$, $^7F_1$, ^7F_o states were observed around 17300, 16900 and

16200 cm^{-1}, respectively. This fine structure in the europium emission spectrum is the result of both electronic and vibronic effects.

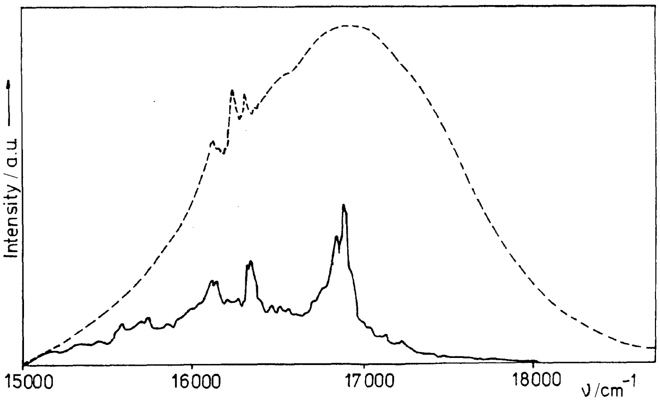

Fig. 9. Luminescence spectrum of Eu^{3+}-doped β-phase $KMnCl_3$ at 77 K. Dotted line – continuous flow cryostat, full line – stationary cryostat

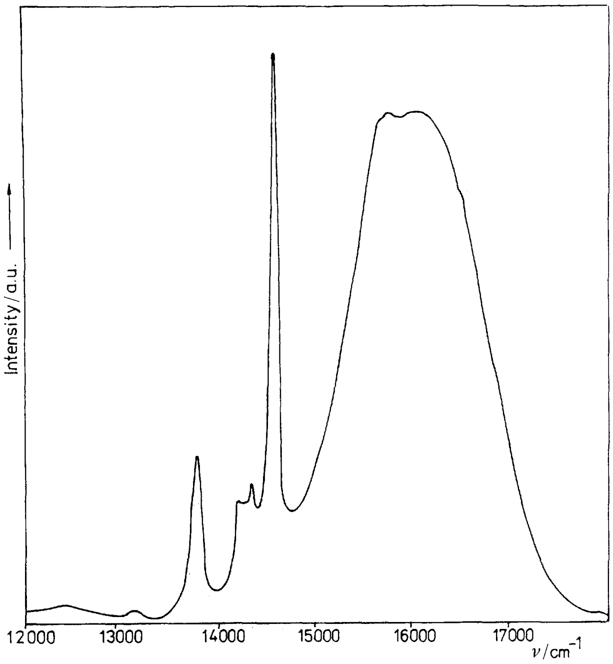

Fig. 10. Luminescence spectrum of Sm^{3+}-doped $RbMnCl_3$ at 130 K

Sm^{3+} fluorescence in Sm^{3+}-doped $RbMnCl_3$ was experimentally accessible at the whole temperature range of 10–180 K. The representative spectrum is presented in

Fig. 10. The Sm^{3+} emission originating from the metastable state $^4G_{5/2}$ was observed. In the measured range of 12000–19000 cm^{-1} at least five bands $^4G_{5/2} \rightarrow {}^6H_{5/2 \text{ to } 13/2}$ should be observed. In practice, only two bands $^4G_{5/2} \rightarrow {}^6H_{13/2}$ and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ located in the range of 12400–13000 cm^{-1} and 14200–14600 cm^{-1}, respectively, were observed. According to the Judd–Ofelt theory [13, 14], $^4G_{5/2} \rightarrow {}^6H_{11/2}$ transition should be more intensive than $^4G_{5/2} \rightarrow {}^6H_{13/2}$ transition as shown in the table for the $<U(\lambda)>$ coefficients [15]. Lack of transitions $^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2}$ located in the range from 15800 to 18000 cm^{-1} of the spectrum may be elucidated by the strong non-radiative energy transfer $Sm^{3+} \rightarrow Mn^{2+}$, since these transitions well match with the absorption band $^6A_1 \rightarrow {}^4T_1$ (Fig 1).

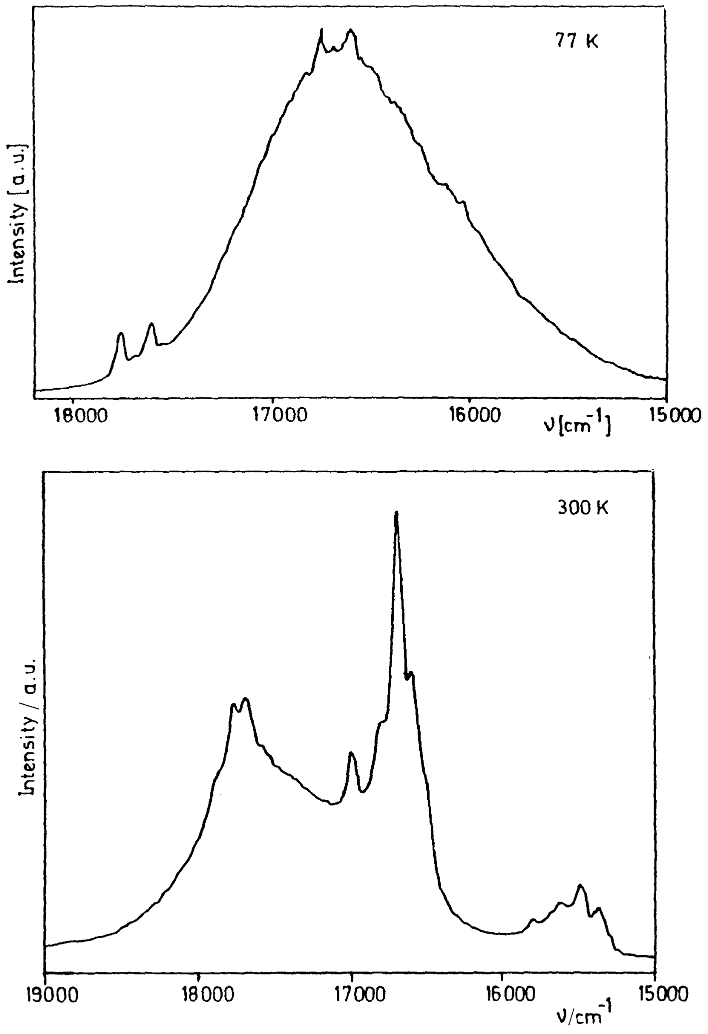

Fig. 11. Luminescence spectra of Sm^{3+}-doped $KMnCl_3$

Sm^{3+}-doped $KMnCl_3$ emission was observed at 77 K and 300 K in the range of 15360–17880 cm^{-1} (Fig. 11). It was assigned to $^4G_{3/2} \rightarrow {}^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$ and $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$. The intensity of Sm^{3+} luminescence was stronger at RT than in LN temperature. This can be associated with the blue shift of manganese luminescence maximum from 16700 cm^{-1} at LN temperature to 17800 cm^{-1} at RT, and hence better overlapping of Mn^{2+} levels with Sm^{3+} ^4G levels.

Lanthanide ions in chloromanganate(II) matrices can be excited via long-range or short-range energy transfer. Short-range means direct energy transfer to earth ions traps from neighbouring Mn^{2+} ions. Long-range transfer takes place when excitation migrates through the host lattice. In such a case the transfer rate increases exponentially with increasing temperature; this relationship is described by an empirical activation law:

$$k_{\mathrm{ET}}(T) = (k_{\mathrm{ET}})_{T\rightarrow\infty} \mathrm{e}^{-\Delta/kT}$$

where k is the Boltzmann constant, Δ is activation energy for energy transfer. The activation energy calculated from experimental data such as intensity and decay time was of the order of several hundreds cm^{-1}, and related temperature at which energy transfer becomes the most efficient process was about 50 K. This common characteristics of all chloromanganates system was confirmed by us and other authors. If the lanthanide ions luminescence is observed below 50 K it may be due to short-range energy transfer from Mn^{2+} to Eu^{3+} or Sm^{3+}. This effect seems to be characteristic of particular crystals and it depends on the structure, monovalent cations and on experimental conditions.

Next to structure and temperature also experimental conditions were found to influence lanthanide ions fluorescence. In Figs. 3 and 9 there are presented the spectra of Eu^{3+}-doped β-$KMnCl_3$ crystal placed in a continuous flow cryostat as well as in a stationary cryostat. The difference between these two experiments consisted in the cooling rate of samples; slow in continuos flow cryostat and rapid in a stationary one. Eu^{3+} fluorescence was much more intensive when the crystal reached quickly the temperature of 77 K.

5. Magnetic properties and luminescence of Mn(II)

The most likely mechanism for excitation transfer in Mn^{2+} compounds with forbidden d-d transitions, is an exchange mechanism. On the other hand, exchange interaction in the ground state generate antiferromagnetic order. Consequently, some relationship between magnetic properties and energy transfer characteristic could be expected.

In the very first investigations [16, 17] these materials distinguished themselves by extensive changes in the fluorescence characteristics below the magnetic ordering temperature. It was suggested that magnetic ordering provides a source of local lattice distortion around the excited ion which, in turn, gives rise to changes in the fluorescence characteristics; intensity and fluorescence maxima below ordering temperature.

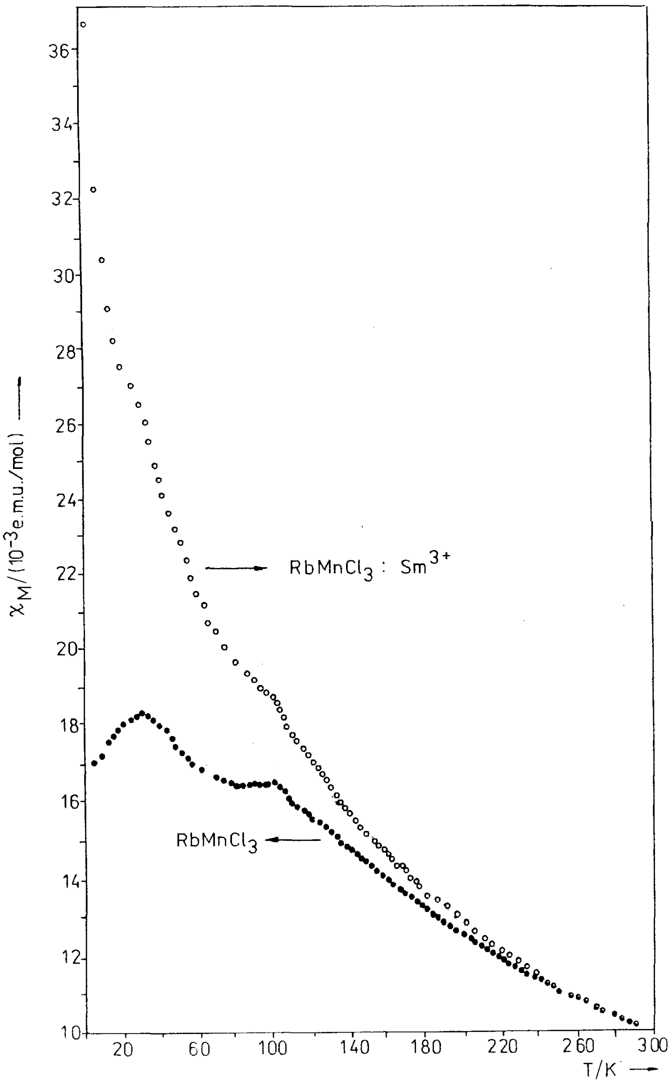

Fig. 12. Magnetic susceptibility χ_M temperature for $RbMnCl_3$ and Sm^{3+}-doped $RbMnCl_3$

Specific energy transfer characteristics were observed for low- and high-dimensional antiferromagnets. In high dimensional MnF_3, and alkali metal fluoromanganates(II) $KMnF_3$ [18], $RbMnF_3$ [19] and $CsMnF_3$ [20] energy transfer is very efficient down to 4.2 K. As a consequence the intrinsic emission is almost not observed. In linear chain compounds (1D): TMMC [21], $CsMnBr_3$ [22], $CsMnCl_3{\cdot}2H_2O$ [23] energy migrates along the chain and the process – indeed one-dimensional – becomes efficient at the temperature above 50 K, so the emission from regular manganese(II) centres dominates the luminescence spectra at low temperature. The layer-structured $NaMnCl_3$ [24] and Rb_2MnCl_4 [25] behave as quasi 2D antiferromagnets and represent an intermediate case.

We investigated magnetic properties of $RbMnCl_3$ [2]. The temperature dependence of the magnetic susceptibility for this crystal and the crystal doped with Sm^{3+} is presented in Fig. 12. The maximum at about 100 K represents transition to long-range antiferromagnetic order in $RbMnCl_3$. The anomaly at approximately 30 K may be connected with another phase transition or only be a mark of the onset of short-range ordering. Magnetic properties of the rubidium chloromanganate crystal doped with Sm^{3+} ion are different, however, this difference does not manifest itself in structural properties. X-ray data [2] shows that both crystals crystallise in a hexagonal system.

Spectroscopic properties of $RbMnC1_3$ have been systematically studied by Kambli and Güdel [10] and two characteristic temperatures for luminescence decay time: ~30 K and ~100 K were distinguished, which match well with two characteristic temperatures 30 and 96 K of magnetic transitions shown in Fig. 12.

In the undoped and weakly doped samples of $RbMnCl_3$ the decay curves of the Mn^{2+} emission are exponential within experimental error [9]. This is not the case of crystal with lanthanide ions' concentration higher than 1%. Traces of samarium ions cause changes in luminescence characteristic, e.g. the temperatures 30 and 96 K are not characteristic of the temperature dependence of Mn^{2+} luminescence intensity. They also influence the magnetic properties of the crystal.

The dimensionallity of the crystal lattice seems to be of minor importance in the luminescence mechanism. We tried to monitore the trap emission in two-dimensional layer compounds $(C_nH_{2n+1}NH_3)_2MnCl_4$ (n = 1,2) doped with Nd, Eu and Sm ions and no lanthanide ions emission was observed. Other low-dimensional manganese compounds such as Rb_2MnC1_4, $CsMnBr_3$ were reported to be an efficient matrix for incorporation luminescence centre of lanthanide ions [9]. Among 3D Heisenberg antiferromagnets in RE doped $T1MnCl_3$ hardly any lanthanide ions luminescence was observed [8] in opposite to RE doped $KMnCl_3$ and $RbMnCl_3$ [3, 4] which produce intense rare earth emission indicating an excitation via effective energy transfer.

References

[1] PAWŁOWSKA M., WOJCIECHOWSKI W., Phys. Stat. Sol.(a), 1991, 127, K125.

[2] PAWŁOWSKA M., WOJCIECHOWSKI W., Bull. Acad. Pol. Sci., 1982, 30, 1–12, 63.

[3] PAWŁOWSKA M., STRĘK W., JEŻOWSKA-TRZEBIATOWSKA B., WOJCIECHOWSKI W., Proc. Inter. Symp. on Rare Earth Spec., 454, Published World Sci., Singapure, 1984.

[4] PAWŁOWSKA M., BRONOWSKA W., WOJCIECHOWSKI W., Phys. Stat. Sol. (b), 1988, 146, K51.

[5] PAWŁOWSKA M., STRĘK W., TRABJERG I., Phys. Stat. Sol. (b), 1989, 154, K89.

[6] PAWŁOWSKA M., STRĘK W., DEREŃ P., J. Sol. State Chem., 1989, 79, 282.

[7] PAWŁOWSKA M., STRĘK W., TRABJERG I., Phys. Stat. Sol. (a), 1991, 124, K63.

[8] PAWŁOWSKA M., ŁUKOWIAK E., STRĘK W., TRABJERG I., Phys. Stat.Sol.(a), 1993, 137, K53.

[9] KAMBLI U., GUDEL H.U., Inorg.Chem., 1984, 23, 3479.

[10] KAMBLI U., GUDEL H.U., J. Phys., C: Sol. State. Phys., 1984, 17, 4041.

[11] HOROWITZ M., MAKOWSKY J., BEN DOR L., KALMAN Z.H., J. Sol. State Chem., 1982, 43, 107.

[12] MORITA M., SEI T., AKASAKA R., MACHII H., SHIBA A., SHOKI T., NARUTOMI S. TSUMBOMARA T., J. Lumin., 1990, 45, 156.

[13] MCPHERSON G.L., TALLITO K., AUERBACH R.A., Sol. State. Com., 1982, 43, 817.

[14] JUDD B.R., Phys. Rev., 1962, 127, 750.

[15] OFELT G.S., J. Chem. Phys., 1962, 37, 511.

[16] LARNALL W.T., CROSSWHITE H., CROSSWHITE H.M., *Energy Level Structures and Transitions Probabilities of the Trivalent Lanthanide in* LaF_3, Argonne National Laboratory, undated.

[17] HOLLOWAY W.W., Jr., KESTIGIAN M., NEWMAN R., PROHOFSKY E.U.I., Phys. Rev. Lett., l963, 11, 82.

[18] HOLLOWAY W.W., Jr., KESTIGIAN M., Phys. Lett., 1969, 29A. 709.

[19] WILSON B.A., YEN W.M., HEGARTY J., IMBUSCH G.F., Phys. Rev. B, Condens. Matter., 1979, 19, 4238.

[20] IVERSON M.V., SIBLEY W.A., Phys. Rev. B, Condens Matter, 1980, 21, 2522.

[21] MANCORGE R., JACQUIER B., MADEJ C., BLANCHARD M., BRUNEL I.C., J. Phys.(Orsay, Fr.), 1982, 43, 1267.

[22] YAMAMOTO H., MCCLURE D.S., MARZZACCO C., WALDMAN M., Chem. Phys., 1977, 22, 79.

[23] MCPHERSON G.L., FRANCIS A.H., Phys. Rev. Lett., 1981, 41, 1681.

[24] MCPHERSON G.L., WILLARD S.C., Chem. Phys. Lett., 1981, 78, 135.

[25] KAMBLI U., GUDEL H.U., BRIAT B., J. Phys. C: Sol. State Phys., 1984, 17, 3113.