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Spectroscopy, fluorescence mechanisms and energy transfers in cadmium chloride doubly doped with copper and manganese

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Abstract. We have observed and identified the optical excitation and emission spectra of Mn^{2+} ions in the doubly doped $\text{CdCl}_2:\text{Mn}:\text{Cu}$ system between 77 and 300 K. A comparison is made with the singly doped CdCl_2 system. The temperature dependence of the absorption strength is explained by vibrational electronic interaction, and the quantum efficiency is close to unity for low- Mn^{2+} -concentration crystals. In CdCl_2 the $^1\text{E}_g$ state of Cu^+ lies in the conduction band. By excitation in the main absorption band, $^1\text{A}_{1g} \rightarrow ^1\text{E}_g$, of Cu^+ in $\text{CdCl}_2:\text{Mn}:\text{Cu}$ crystals an energy transfer to Mn^{2+} ions takes place through intermediate metastable states (excimer-like species) which form in the lattice near the Cu^+ centres. Because these states thermally ionize, the energy transfer rate decreases when the temperature increases and above 100 K the photoionization of Cu^+ centres becomes dominant.

1. Introduction

CdCl_2 is a very well known host lattice for iron group transition-metal ions which easily replace the Cd^{2+} cations and thus experience an octahedral environment of halogen anions. This was shown to be true in the case of Mn^{2+} and nearly true for Cu^+ since charge compensation is necessary in this latter case [1].

The fluorescence and photoionization processes of the Cu^+ ion in CdCl_2 have previously been investigated by several workers [1–4]. The main absorption band (4.37 eV) is due to the spin-allowed transition $^1\text{A}_{1g}(\text{d}^{10}) \rightarrow ^1\text{E}_g(\text{d}^9\text{s})$. The fluorescence mechanisms are complicated by the fact that the excited states of Cu^+ lie in the conduction band of CdCl_2 and that photoionization of Cu^+ occurs at low energies. Various channels of relaxation are therefore possible. The UV 'normal' fluorescence (3.33 eV) occurs only at low temperatures and is due to the spin-forbidden $^3\text{E}_g(\text{d}^9\text{s}) \rightarrow ^1\text{A}_g(\text{d}^{10})$ transition. Such emission is usually observed in Cu^+ -doped alkali halides. In addition, two other emission bands were detected in the visible range with a large Stokes shift. The blue band (2.87 eV) was assigned to the recombination of the s electron with an excimer-like species formed after the s electron had been delocalized away from the copper centre, causing the nearest neighbours to relax towards the Cu^+ impurity [3]. Similar species called impurity-trapped excitons were shown to form in other systems such as $\text{MF}_2:\text{Yb}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}$) [5, 6] and $\text{BaF}_2:\text{Eu}^{2+}$ [7], giving rise

to so-called 'anomalous emissions'. The red emission (1.75 eV) was attributed to a self-trapped exciton (STE) resulting from the excitation of the Cu^+ impurity ion [3].

In the case of Mn^{2+} ions in CdCl_2 , it seems that the photoionization does not play any role in the fluorescence mechanism of Mn^{2+} ions. Excitation from the ${}^6\text{A}_{1g}$ ground state to any quartet excited state results in rapid relaxation to the lowest ${}^4\text{T}_{1g}$ (G) level, followed by red fluorescence (at about 1.9 eV) [8].

This paper reports the optical absorption, fluorescence excitation, emission and fluorescence decay time measured in $\text{CdCl}_2:\text{Mn}^{2+}:\text{Cu}^+$ co-doped systems. The experimental data are compared with the data obtained from the singly doped $\text{CdCl}_2:\text{Mn}$ compounds in order to examine and describe the interactions between Mn^{2+} states and the states related to the presence of Cu^+ ions in CdCl_2 , i.e. excimer-like and STE states.

2. Experimental procedure

The single crystals used in this study were all grown in our laboratory using the procedure described elsewhere [9]. Various amounts of manganese and copper ions were introduced in the lattice. The manganese concentration was determined from ESR measurements in singly doped samples and then deduced from absorption measurements in other Mn:Cu co-doped samples. The copper concentration was evaluated from the main absorption band measurements at 4.37 eV using the data from the literature [10].

The optical absorption spectra were performed using a double-beam Varian spectrophotometer model Cary 118.

The emission and excitation spectra were obtained by exciting with a chopped light coming from a 100 W xenon lamp. The fluorescence was analysed with a grating Eu-700 series Heath monochromator and detected with an EMI 9558 QB photomultiplier tube coupled with a gated boxcar averager model PAR 162.

A nanopulser source from Xenon Corporation, model 437 A, was used to analyse the decay kinetics in the microsecond time range.

The spectra were corrected to take into account the wavelength dependence of the lamp intensity and the photocathode sensitivity of the tube.

Low-temperature measurements were made with the crystals mounted in a home-made cryogenic refrigerator. A calibrated iron-constantan thermocouple was used to measure the temperature of the samples in the range 77–300 K.

The hygroscopic crystals were handled with care in a dry nitrogen atmosphere with a fiber-glass-type glove box.

3. $\text{CdCl}_2:\text{Mn}^{2+}$

Our experimental results deal specifically with divalent manganese ions in an octahedral environment (O_h symmetry). At room temperature, the octahedron is slightly compressed along the c axis ($c/a = 0.790$) but, near 380 K, it was shown from ESR measurements that Mn^{2+} occupies a regular octahedral site ($c/a = 0.816$) [11, 12].

$\text{CdCl}_2:\text{Mn}^{2+}$ is characterized by a series of weak absorption bands with oscillator strengths of the order of 10^{-3} . They can be detected only for very large Mn^{2+} concentrations or for relatively thick normal-concentration (up to few per cent) samples

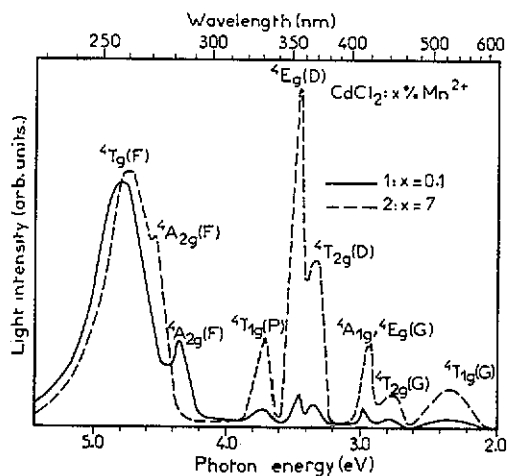


Figure 1. Room-temperature excitation spectra of Mn^{2+} fluorescence in two samples of Mn^{2+} -doped CdCl_2 .

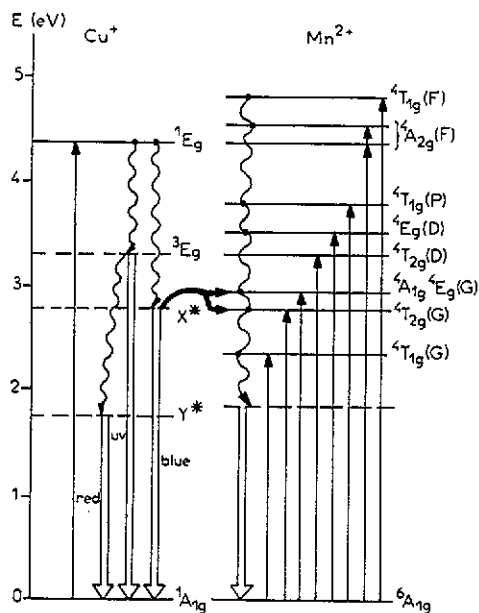


Figure 2. Energy-level diagram of Cu^+ and related species, and Mn^{2+} in $\text{CdCl}_2:\text{Cu}^+:\text{Mn}^{2+}$. The single arrows illustrate the absorption of levels represented by the full horizontal lines. The double arrows illustrate the emission of relaxed excited states represented by the broken horizontal lines. X^* is the triplet state of an excimer-like species ${}^3(\text{CuCl}^+)^-$ and Y^* represents the triple state of the self-trapped exciton ${}^3(\text{Cl}_2^- + e)$ [3]. The thick arrows illustrate the energy transfer channels.

[13]. Indeed, the divalent manganese has a d^5 electronic configuration and all the $d \rightarrow d$ electronic transitions are doubly forbidden (spin and parity) for electric dipole radiation.

Figure 1 shows the excitation spectra of the red emission of Mn^{2+} at room temperature for two variously doped samples. The attribution of the narrow bands in the range below 4 eV (indicated in the figure) is obvious according to the energy-level scheme of Mn^{2+} in O_h symmetry (figure 2). It is well supported by a simple crystal-field calculation using the usual procedure in a strong-field scheme. The observed and calculated values of the excited-state energies are given in table 1. The energies of the

five lowest levels are in good agreement with the experimental data, but discrepancies between 800 and 3500 cm^{-1} are found for UV bands. In addition, the concentration dependence of these latter (shift and intensity) is not clear and cannot be explained in the framework of the crystal approach and their attribution indicated in figure 1 must be considered as a tentative assignment only.

Table 1. Positions and intensities of Mn^{2+} energy levels in the doubly doped $\text{CdCl}_2:\text{Mn}:\text{Cu}$ crystals at 300 K.

Mn^{2+} state	Position (cm^{-1})	
	Observed	Calculated ^a
${}^4\text{T}_{1g}(\text{G})$	19 050	19 526
${}^4\text{T}_{2g}(\text{G})$	22 225	22 242
${}^4\text{A}_{1g}$ ${}^4\text{E}_g(\text{G})$	23 800	23 817
${}^4\text{T}_{2g}(\text{D})$	27 170	26 902
${}^4\text{E}_g(\text{D})$	28 350	28 331
${}^4\text{T}_{1g}(\text{P})$	30 030	32 380
${}^4\text{A}_2(\text{F})$	36 630	38 503
${}^4\text{T}_1(\text{F})$	38 460	39 242

^a Obtained using $B = 662 \pm 31 \text{ cm}^{-1}$, $C = 3453 \pm 72 \text{ cm}^{-1}$ and $10Dq = 7266 \pm 310 \text{ cm}^{-1}$.

The Beer-Lambert law was verified for the bands in the visible range using a series of high-Mn-concentration crystals. The band which corresponds to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$, ${}^4\text{A}_{1g}(\text{G})$ transition is particularly interesting. It has in fact a complicated structure, with six components [8-13]. Except for the component at lowest energy, the rest of the band centred at 23900 cm^{-1} (2.93 eV) verifies the Beer-Lambert law and a vibrational series appears upon cooling to 77 K with a frequency of 240 cm^{-1} . Like the other transitions, its oscillator strength increases with increasing temperature. These transitions are parity forbidden in the free ion but are partially allowed in the crystal by coupling with lattice vibrations of odd parity. This temperature dependence can be described by the well known relation

$$f(T) = f(0) \coth(h\nu/2kT) \quad (1)$$

anticipated for a vibronic mechanism. Experimentally, the increase in the absorption strength of this band, going from 77 K to 300 K, is about 40% [13].

The behaviour of the component at lowest energy (23.665 cm^{-1} or 2.93 eV) of the ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$, ${}^4\text{A}_{1g}(\text{G})$ transition is quite different since its intensity becomes 25% smaller when the temperature increases from 77 to 300 K. In addition its extinction molar coefficient decreases with increasing concentration and becomes zero at very low concentrations. We believe that the source of the intensity of this component in concentrated samples is the exchange coupling between neighbouring ions.

Intrashell excitation of Mn^{2+} gives rise to a broad red emission band centred near 1.9 eV with no fine structure, corresponding to the transition from the lowest excited state ${}^4\text{T}_{1g}(\text{G})$ to the ground state ${}^6\text{A}_{1g}$ of the Mn^{2+} ion (figure 2).

The decay times of the red fluorescence of Mn^{2+} are around 20 ms at room temperature and 40 ms at 77 K. They are typical of electric-dipole-forbidden transitions.

4. $\text{CdCl}_2:\text{Cu}:\text{Mn}$

The optical absorption spectra of $\text{CdCl}_2:\text{Cu}:\text{Mn}$ doubly doped crystals are shown in figure 3. Only the absorption bands due to the copper ion can be detected because of the weakness of the Mn^{2+} absorption bands. The main band peaking near 4.37 eV and the shoulder at higher energy are due to $d \rightarrow s$ transitions of the Cu^+ ion [3]. An additional peak near 3.16 eV is detected in crystal 1 but not crystal 2. After UV irradiation of this latter at room temperature, the same peak appears and also another peak at around 2.1 eV. The band at 3.16 eV is due to Cu^{2+} ions which coexist with Cu^+ ions in as-grown crystal 1 and which are created after UV irradiation in crystal 2 as a result of a photoionization process of Cu^+ ions. The band at 2.1 eV is probably due to colloidal copper particles [1]. It should be remarked that Cu^{2+} is also responsible for another UV band close to the main band of Cu^+ (4.37 eV) and peaking near 4.19 eV [2]. In crystal 1 these two bands coexist; the main band is a convolution of both and is shifted towards a lower energy. UV irradiation of crystal 2 leads to a similar band (curve 2') and the increase in its intensity comes from the creation of the Cu^{2+} band at 4.19 eV but corresponds to a decrease in the Cu^+ band at 4.37 eV. The lack of temperature dependence of the oscillator strength of the main absorption band indicates that the Cu^+ centre experiences a static perturbation which destroys the centre of inversion. As discussed earlier [3], the site symmetry is lowered by an off-centre position of Cu^+ rather than by the charge compensation.

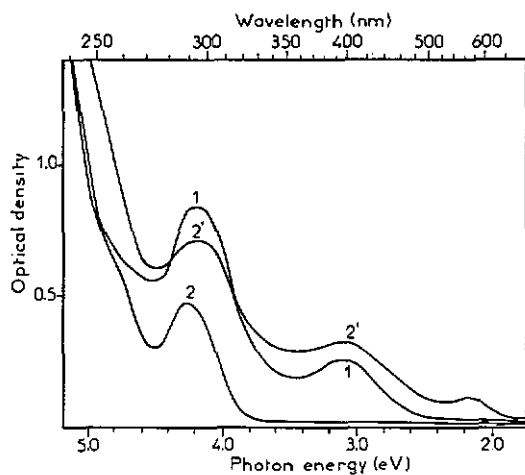


Figure 3. UV absorption spectra of $\text{CdCl}_2 : x\% \text{Cu} : y\% \text{Mn}$ single crystals at room temperature: curve 1 crystal 1, $x = 0.1$, $y = 0.1$; curve 2 crystal 2, $x = 0.1$, $y = 2$; curve 2' crystal 2 after UV (300 nm) irradiation.

The emission spectra of Mn^{2+} in $\text{CdCl}_2:\text{Cu}:\text{Mn}$ can be obtained of course by exciting directly Mn^{2+} ions in the various excited states in the visible range. Under UV irradiation at 4.37 eV in the main absorption band of Cu^+ , emissions of both Cu^+ and Mn^{2+} are obtained. These fluorescences can be easily separated using the technique of time-resolved spectroscopy (TRS) since, for example at 77 K, the fluorescence decay times are a few tens of milliseconds for Mn^{2+} and around 10 μs for the STE near Cu^+ . The emission bands of Mn^{2+} ions and of the red fluorescence of Cu^+ deduced from TRS are shown in figure 4. Their positions are the same as in the singly doped samples.

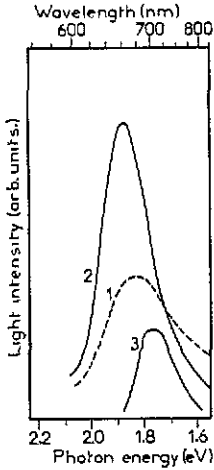


Figure 4. Time-resolved emission spectra of the $\text{CdCl}_2 : x\% \text{Cu} : y\% \text{Mn}$ system at 77 K in the red spectral region, under broad-band excitation at around 4.37 eV: curve 1, emission of Mn^{2+} crystal 1, $x = 0.1$, $y = 0.1$, long delay (> 1 ms); curve 2, emission of Mn^{2+} crystal 2, $x = 0.1$, $y = 2$, long delay (> 1 ms); curve 3, red emission of Cu^+ for both crystals after deconvolution, short delay (about 1 μs).

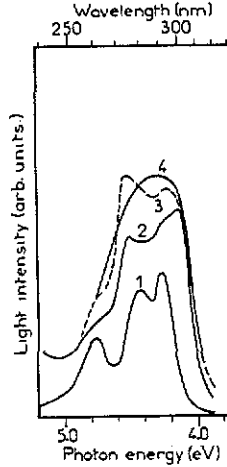


Figure 5. Excitation spectra of $\text{CdCl}_2 : 0.1\% \text{Cu} : 2\% \text{Mn}$ at $T = 77$ K in the UV spectral region: curve 1, blue Cu^+ fluorescence; curve 2, red fluorescence, time-resolved spectrum at short delay (about 1 μs), contribution of both Cu^+ and Mn^{2+} fluorescence; curve 3, red fluorescence, time-resolved spectrum at long delay (> 1 ms), contribution of only Mn^{2+} fluorescence; curve 4, curve for Cu^+ fluorescence deduced from curves 2 and 3.

The relationship between the oscillator strength, f and radiative decay time τ for an electric dipole (ED) process can be written as [15]

$$f_{\text{ED}} = 1.5 \times 10^4 \left\{ \frac{\lambda_0^2}{[(n^2 + 2)/3]^2 n} \right\} (1/\tau) \quad (2)$$

where τ is the fluorescence decay time, λ_0 is the wavelength of the emission in vacuum and n is the refractive index. Using decay time data from table 2 and $n = 1.815$ one finds for f -values ranging from 2.8×10^{-8} to 8.7×10^{-8} . In fact, because of the weakness of the oscillator strength, a more realistic description of the total transition rate has to include both electric dipole and magnetic dipole contributions, as was pointed out for the case of Mn^{2+} in perovskite crystals [16].

It should be noted that the product τf is constant in the 77–300 K temperature range, indicating that the quantum efficiency of the fluorescence is about unity. The decay time for crystal 2 is shorter than the corresponding decay time of the excited single ions in crystal 1 which is 20 times less concentrated. This can be explained by the increase in the absorption intensity and/or by the decrease in the radiative efficiency, e.g. the excitation is shared between coupled Mn ions and the probability of the non-radiative processes increases. Comparing the decay times from table 2 we infer that the optical transitions are more effective in crystal 2 than in crystal 1, and the proof for some non-radiative decay is the temperature dependence of radiative decay rate, which is not dramatic in our case.

The main interest of the $\text{CdCl}_2 : \text{Cu} : \text{Mn}$ co-doped system is of course the possible existence of $\text{Cu} \rightarrow \text{Mn}$ energy transfers. Looking at the energy-level diagram of Cu^+ and Mn^{2+} ions (figure 2), it is clear that the UV and blue emission bands of

Table 2. Decay time constants of Cu^+ red emission (1.75 eV) and blue emission (2.88 eV) and of Mn^{2+} emission in $\text{CdCl}_2:x\% \text{Cu}:y\% \text{Mn}$ crystals as a function of sample temperature. Crystal 1, $x = 0.1, y = 0.1$; crystal 2, $x = 0.1, y = 2$.

T (K)	τ μs					
	Red Cu^+ emission		Blue Cu^+ emission		Mn^{2+} emission	
	Crystal 1	Crystal 2	Crystal 1	Crystal 2	Crystal 1	Crystal 2
77	12.6	7.0	28.6	5.2 ^a 26.0	40.9×10^3	29.4×10^3
95	1.3	1.0	28.6		31×10^3	24.5×10^3
120			24.5			
140			8.9			
300					20×10^3	12.9×10^3

^a Double-exponential decay.

Cu^+ overlap the various absorption bands of Mn^{2+} and therefore energy transfers from ${}^3\text{E}_g$ of Cu^+ and from relaxed excimer-like species (so-called X^*) to Mn^{2+} are expected. The energy difference between the relaxed lowest excited state of the STE (so-called Y^*) and the emitting state ${}^4\text{T}_{1g}(\text{G})$ of Mn^{2+} is too large to consider $\text{Y}^* \rightarrow \text{Mn}^{2+}$ energy transfer even at high temperatures. In the weakly Mn-doped sample (crystal 1), the red fluorescence decay times are similar to those reported elsewhere for singly doped $\text{CdCl}_2:\text{Cu}$ compounds [3]. The red centre, known as a STE (Cl_2^-) centre near a Cu^+ centre, does not interact with the Mn^{2+} ions. In high-Mn-doped sample (crystal 2), the decrease in the STE lifetime can be explained by a perturbation of this centre by a Mn^{2+} neighbouring ion. The rapid shortening of the decay above liquid nitrogen temperature is explained by the ionization of the STE which occurs at $T > 81 \text{ K}$ [3].

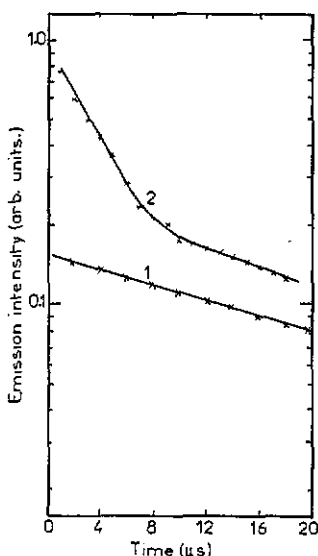


Figure 6. Blue emission decays of $\text{CdCl}_2 : x\% \text{Cu} : y\% \text{Mn}$ at $T = 77 \text{ K}$: curve 1, crystal 1, $x = 0.1, y = 0.1$; curve 2, crystal 2, $x = 0.1, y = 2$.

Let us focus our attention on the $X^* \rightarrow Mn^{2+}$ energy transfer by studying the blue emission of $CdCl_2:Cu:Mn$ systems under UV excitation at 4.37 eV. The first evidence of the occurrence of such a transfer is shown in figure 5. It is clear that the excitation spectra in the UV range of the blue fluorescence of the X^* centres (curve 1) and of the red fluorescence of Mn^{2+} (time-resolved spectrum recorded with a long delay, curve 3) are very similar. However, curve 3, and curve 4 which represents the excitation spectrum of the red Cu^+ fluorescence, are completely different. The comparison of the blue fluorescence decay curves at the same temperature (77 K) and for two different Mn concentrations (figure 6) illustrates the energy transfer. In the case of a weak Mn concentration, the decay is exponential with a time constant of 28.6 μs , a value similar to those found in singly doped $CdCl_2:Cu$ compounds (31 μs [3]). No or a very weak energy transfer occurs in this case. On the other hand, for a highly concentrated sample, the decay is strongly non-exponential with a time constant near 26 μs at long times, close to the value obtained without transfer. The strong temperature dependence of the decay time above 140 K is due to the ionization of the excimer-like species. It is clear that this process then competes with energy transfer which is strongly quenched at room temperature.

5. Conclusion

$Cu^+ \rightarrow Mn^{2+}$ energy transfers have already been observed and studied in alkali halides [17]. The energy transfers occurring in $CdCl_2:Cu:Mn$ are different since they involve as donors excimer-like species rather than Cu^+ centres. Such centres are formed because all the excited states of Cu^+ are degenerate in the conduction band of $CdCl_2$. Work is in progress in order to study in more detail such transfers and also $Cu^+(^1E_g) \rightarrow Mn^{2+}$ transfers which should occur at low temperatures below 40 K.

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