

ENERGY TRANSFER AND BIEXCITON DECAY IN $\text{Cs}_2\text{UO}_2\text{Cl}_4$ CRYSTALS

D.M. KROL

Physical Laboratory, State University Utrecht, 3508 TA Utrecht, The Netherlands

Received 20 May 1980

We have investigated the influence of energy transfer on luminescence properties of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ crystals at low temperatures. Time-resolved emission spectra and luminescence decay times were measured between 1.5 and 15 K with the use of selective excitation techniques. The luminescence of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ depends on the excitation intensity and can be described with a model which includes both energy transfer to traps and biexciton decay.

1. Introduction

We have investigated energy-transfer processes in $\text{Cs}_2\text{UO}_2\text{Br}_4$ [1]. It has been found that migration of the excitation energy has a strong influence on the luminescence properties of this compound. At low temperatures ($T < 10$ K) some intrinsic luminescence is observed, but the greater part of the luminescence originates from uranyl centres near defects. These centres act as traps for the migrating energy. The occurrence of energy transfer also has consequences for the decay curves of both the intrinsic and trap emission and for the quantum efficiency of the luminescence. The decay curves are not single exponentials and show a marked temperature dependence between 1.5 and 25 K. In this temperature region the quantum efficiency varies from $\approx 90\%$ to about 10% and at room temperature it is even less than 1%.

In order to determine whether energy transfer plays a similar role in other uranyl compounds we have investigated the luminescence properties of $\text{Cs}_2\text{UO}_2\text{Cl}_4$. The absorption and emission spectra of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ have been investigated before (see e.g. refs. [2,3]). These studies were, however, concentrated on assignments and no precise information is available about energy-transfer processes in this compound. From the luminescence experiments by Flint et al. [3] it is known that at temperatures above 10 K the luminescence originates mainly from the intrinsic uranyl groups.

In connection with the work on $\text{Cs}_2\text{UO}_2\text{Br}_4$, it should be mentioned that the crystal structures of $\text{Cs}_2\text{UO}_2\text{Br}_4$ [4] and $\text{Cs}_2\text{UO}_2\text{Cl}_4$ [5] are not the same. $\text{Cs}_2\text{UO}_2\text{Cl}_4$ crystallizes in the spacegroup $C2/m$ with two molecules per unit cell. The site symmetry of the uranium ions is C_{2h} . The crystal structure is such that the shortest U-U distance is 5.8 Å (along the c axis), whereas the second shortest U-U distance is 7.1 Å and is situated in the ab plane. The difference between the two distances indicates that energy migration in $\text{Cs}_2\text{UO}_2\text{Cl}_4$ is most probably three dimensional, in contrast to $\text{Cs}_2\text{UO}_2\text{Br}_4$ where it is more likely to be two dimensional [1].

To investigate energy-transfer processes in $\text{Cs}_2\text{UO}_2\text{Cl}_4$, the intensity and decay of the luminescence were measured down to 1.5 K with the use of selective excitation techniques. Furthermore, we have measured time-resolved spectra at low temperatures. The results of these experiments on single crystals of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ are discussed in this paper.

2. Experimental

Single crystals of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ were grown according to the method described by Hall et al. [5]. The apparatus for the optical measurements has been described [1].

3. Results

$\text{Cs}_2\text{UO}_2\text{Cl}_4$ shows a very efficient photoluminescence at 4.2 K under low excitation intensity ($q \approx 90\%$). In contrast with the luminescence of $\text{Cs}_2\text{UO}_2\text{Br}_4$, this luminescence is still relatively intense at room temperature ($q \approx 10\%$).

The emission spectrum of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ was recorded at 4.2 K. Parts of this emission spectrum are shown in fig. 1. Besides the intrinsic emission pattern which was also observed by Flint et al. [3], a second emission pattern is observed, which is ascribed to trap luminescence. This trap luminescence disappears when the temperature is raised. Above about 10 K it cannot be detected. The emission spectrum was also measured at 1.5 K and appeared to be the same as that measured at 4.2 K, except for a decrease in $I(497.58 \text{ nm})/I(497.62 \text{ nm})$ and $I(498.38 \text{ nm})/I(498.41 \text{ nm})$. The positions of the emission lines which are presented in fig. 1 have been tabulated in table 1 together

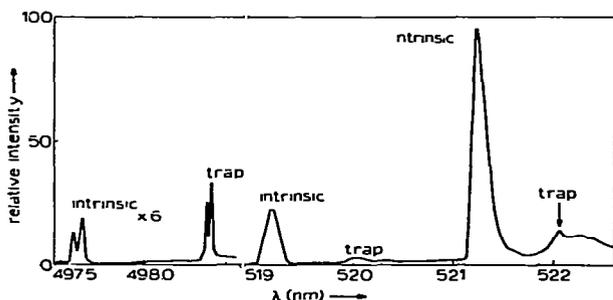


Fig 1 Parts of the emission spectrum of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ recorded at 4.2 K. Excitation takes place in the intrinsic uranyl groups

with their assignments. For the study of the energy-transfer processes we have concentrated on the luminescence behaviour of these lines. In fig. 2 we present the short-wavelength part of the time-resolved emission spectrum, measured after excitation in the intrinsic uranyl centres. Note that the trap luminescence is not observed for short times after the excitation pulse. (We have, in fact, used the time-resolved spectra to assign the emission lines, ascribed in fig. 1, to either intrinsic or trap luminescence.)

The excitation spectra of both intrinsic and trap

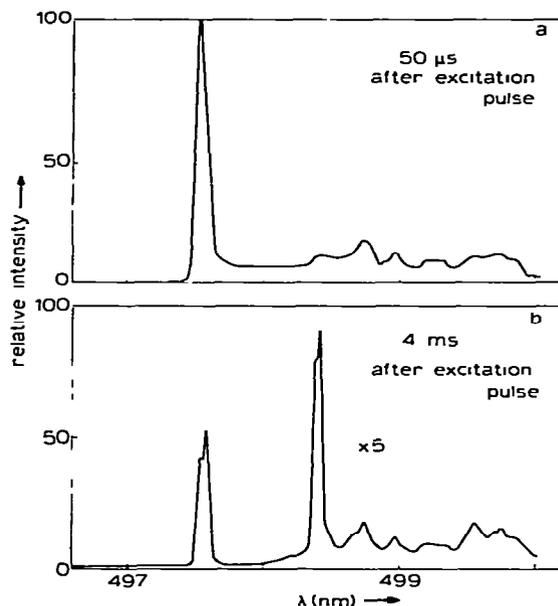


Fig 2 Time-resolved emission spectra of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ recorded at 4.2 K after excitation in the intrinsic uranyl groups

Table 1
Intrinsic and trap emission lines in $\text{Cs}_2\text{UO}_2\text{Cl}_4$

λ (nm) a)	Δ (cm^{-1})	ass b)	λ (nm) c)	Δ (cm^{-1})	ass b)
497.58	0	i	498.38	0	tr
497.62	16		498.41	1.2	
519.18	836	$i + \nu_s$	519.98	834	$tr + \nu_s$
521.23	912	$i + \nu_{as}$	522.06	910	$tr + \nu_{as}$

a) These lines were also found by Flint and Tanner [3]

b) i denotes the electronic origins of the intrinsic emission and tr the electronic origins of the trap emission. ν_s and ν_{as} denote the symmetric and asymmetric stretching modes of the uranyl ion.

c) The energy difference between the trap line at 498.41 nm and the intrinsic line at 497.62 nm is 32 cm^{-1} .

emission were recorded at 4.2 K between 500 and 470 nm. For these spectra a powdered crystal was used. The excitation spectrum of the intrinsic emission showed the same lines as those found by Denning et al. [2] in the absorption spectrum of $\text{Cs}_2\text{UO}_2\text{Cl}_4$. In addition, some other lines are observed when the trap emission is monitored. The energy differences (in cm^{-1}) between these other lines and the electronic origin (tr) are 0(tr), 166, 192(X), 521, 714($\text{tr} + \nu_s$), 733($\text{tr} + \nu_{as}$), 879, 1002($\text{X} + \nu_s$), 1045 and 1228. The intensities of the X lines, situated at 491.22 and 474.68 nm, are stronger than any of the intrinsic excitation lines.

The luminescence properties of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ show a marked dependence on the excitation intensity. The quantum efficiency decreases with increasing excitation intensity. Furthermore the ratio of the intrinsic to trap luminescence (I_i/I_{tr}) shows some variation with the excitation intensity. This ratio increases by a factor of 2 when the intensity is reduced by a factor of 100.

The influence of the excitation intensity is most pronounced for the decay of the intrinsic emission.

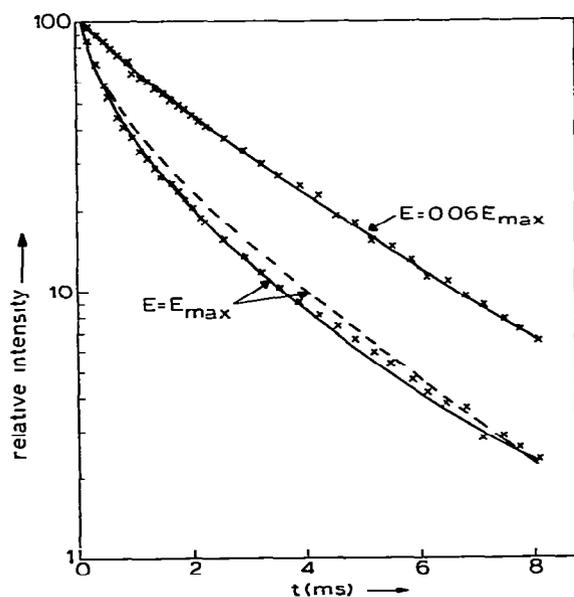


Fig. 3. Decay curves of the intrinsic emission \times experimental curves, measured at 1.5 K with different excitation intensities; — curves fitted with eq. (2), --- experimental curve, measured at 12.5 K.

This is shown in fig. 3. For short times after the excitation pulse, the decay rate decreases with decreasing excitation intensity, whereas the long-time behaviour remains the same. It should be mentioned that the long-time behaviour of the decay curves is not the same for different samples.

When the tail of the decay curve is considered to be exponential, the decay times vary from 1.9 to 2.9 ms at 4.2 K. The value of I_i/I_{tr} is also different for different samples; in samples where τ is shorter I_i/I_{tr} is smaller. The decay of the intrinsic emission was also measured as a function of temperature. The decay curves varied only slightly in the temperature region between 1.5 and 15 K (see fig. 3).

It was not possible to measure the decay of the trap luminescence after excitation in the intrinsic centres. Under these circumstances the trap emission is relatively weak and moreover it coincides with vibronic features of the intrinsic emission. When excitation takes place with either 491.22 or 474.68 nm (X lines) the trap emission is much stronger. In this case a single-exponential decay of the trap is observed with a decay time of ≈ 2.2 ms at 4.2 K.

4. Discussion

The luminescence experiments on $\text{Cs}_2\text{UO}_2\text{Cl}_4$ show that energy transfer occurs from the intrinsic centres to traps (see e.g. fig. 2). The vibrational structure in the emission and excitation spectrum indicates that these traps are also uranyl groups.

The dependence of the luminescence properties on the excitation intensity suggests that non-linear processes occur in $\text{Cs}_2\text{UO}_2\text{Cl}_4$. It is most unlikely that the observed intensity dependence is due to heating of the sample because of the fact that no marked temperature dependence of the intrinsic decay was observed. Furthermore, the temperature dependence of $I(497.58 \text{ nm})/I(497.62 \text{ nm})$ and $I(498.38 \text{ nm})/I(498.41 \text{ nm})$ indicate that local heating does not occur.

We show that the luminescence behaviour of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ at low temperatures can be explained with a model in which both energy transfer to traps and biexciton decay are taken into account. It is assumed that no back-transfer from the traps to the intrinsic levels occurs. In view of the trap depth of 32

cm^{-1} this is a reasonable assumption for the low-temperature region ($T \approx 1.5$ K). In this case the decay of the exciton density (N) can be written as

$$dN(t)/dt = -k_a N(t) - k_b N^2(t). \quad (1)$$

In this expression k_b is the biexciton decay rate and $k_a = n_{tr} k_{tr} + p_r$, in which p_r is the radiative decay rate of the excitons and $n_{tr} k_{tr}$ is the transfer rate to traps. This latter rate depends on the trap concentration (n_{tr}). When biexciton decay does not result in emission of a photon corresponding to the intrinsic emission, the intrinsic emission intensity $I(t)$ will be proportional to $N(t)$ and the solution of eq. (1) can be written as [6,7]

$$I(t) = \frac{k_a}{k'_b} \frac{I(0)}{[k_a/k'_b + I(0)] \exp(k_a t) - I(0)}, \quad (2)$$

where $k'_b I(0) = k_b N(0)$

That we are indeed dealing with a biexciton process in which both excitons are lost for the intrinsic emission can be concluded from the emission spectra. If we were not dealing with such a process, the ratio of the intrinsic to trap emission should increase with increasing excitation intensity. This is, however, not observed for $\text{Cs}_2\text{UO}_2\text{Cl}_4$.

The decay curves of the intrinsic emission, measured at 1.5 K, were fitted with eq. (2). This is shown in fig. 3. The following values were found for k_a and $k_b N(0)$

$$k_a = 265 \text{ s}^{-1}, \quad k_b N(0) = 1600 \text{ s}^{-1} \text{ for } E = E_{\text{max}},$$

$$k_a = 280 \text{ s}^{-1}, \quad k_b N(0) = 120 \text{ s}^{-1} \text{ for } E = 0.06 E_{\text{max}}.$$

The value of the biexciton decay rate (k_b) can be determined when the initial exciton density $N(0)$ is known. The value of $N(0)$ was estimated from the laser power ($E_{\text{max}} \approx 3 \times 10^{-4}$ J per pulse), the laser beam and crystal dimensions and the absorption strength to be about $10^{16} - 10^{17} \text{ cm}^{-3}$ for maximal excitation intensity (E_{max}). With this value for $N(0)$, k_b is found to be $\approx 10^{-13} - 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.

If it is assumed that the biexciton decay rate is limited by the hopping rate of excitons through the lattice, the hopping time τ_H can be determined; τ_H appears to be $\approx 10^{-8} - 10^{-9}$ s. Here we have used $\tau_H = (4\pi/6)R_b^3/k_b$ in which R_b was taken to be 6 Å.

It should be noted that it is not clear that the exciton-decay process is indeed diffusion limited. The decrease of the ratio of the intrinsic to trap emission with excitation intensity could be due to the fact that the trap plays a role in the biexciton decay process.

The value of k_a of about 270 s^{-1} shows that transfer to traps is not very efficient. When p_r is assumed to be about 200 s^{-1} then $n_{tr} k_{tr}$ is 70 s^{-1} , which is a very low value in comparison with the value found for $\text{Cs}_2\text{UO}_2\text{Br}_4$ ($\approx 3000 \text{ s}^{-1}$). The difference between these two values is most probably due to a difference in trap concentration (n_{tr}). The difference in the long-time behaviour of the intrinsic decay of different samples can be explained by a difference in n_{tr} . This is also in line with the fact that in samples with a smaller value of τ (larger n_{tr}) relatively more trap emission is observed.

Finally we note that biexciton decay has also been observed in other uranyl compounds [8] (e.g. uranyl nitrate). In these compounds similar values of τ_H have been found.

Acknowledgement

The author wishes to thank Professor G. Blasse for stimulating discussions and critical reading of the manuscript. Mr. G.J. Dirksen is gratefully acknowledged for the crystal growth of $\text{Cs}_2\text{UO}_2\text{Cl}_4$.

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