

STEADY-STATE AND TIME-DEPENDENT LUMINESCENCE OF UO_2MoO_4

W.M.A. SMIT

Physical Laboratory, University of Utrecht, P.O. Box 80.000, 3508 TA Utrecht,
The Netherlands

Luminescence spectra of UO_2MoO_4 between 4.2 - 50 K were studied. The 0 - 0 line splitting is explained. Decay functions were derived reproducing the temperature dependence of the trap emissions. The rate of energy transfer among intrinsic centres and to trap centres is shown to be of similar magnitude.

1. INTRODUCTION

In UO_2MoO_4 (space-group $P_{21/c} - C_{2h}^5$, $Z=4$) the uranyl groups have C_1 site symmetry [1]. The lowest excited state of the symmetric uranyl group is Π_g [2], but due to correlation field splitting ($Z=4$) we expect in UO_2MoO_4 eight levels: $2A_g + 2B_g + 2A_u + 2B_u$. This was investigated by studying the luminescence spectra. The temperature dependence of the trap decay times is studied with regard to energy migration. The experimental set-up is described in Ref. 3.

2. RESULTS AND DISCUSSION

The steady-state emission mainly results from traps which appear to be distorted uranyl groups (see Table 1). The intrinsic emission, observed at 50 ns after the pulse, shows progressions in the A_g correlation field components of the UO_2 stretching modes (see Table 1)[3].

Table 1. Observed emission lines for the intrinsic centres and the two more intensive trapcentres.

$i-av_1-bv_2$ ^{a)}		$t5-av_1-bv_2$ ^{b)}		$t6-av_1-bv_2$ ^{b)}	
position(cm^{-1})	a b	position(cm^{-1})	a b	position(cm^{-1})	a b
19820	0 0	19635	0 0	19548	0 0
19075	1 0	18900	1 0	18815	1 0
18935	0 1	18753	0 1	18677	0 1
18332	2 0	18169	2 0	18085	2 0
18190	1 1	18020	1 1	17946	1 1
18058	0 2	17872	0 2	17807	0 2

a) i = intrinsic centre, v_1, v_2 = A_g correlation field component of UO_2 symmetrical and asymmetrical stretching mode, respectively.

b) $t5, t6$ = trap centres 5 and 6 (see Ref. 3).

The lineshape of the intrinsic 0 - 0 line could be interpreted in terms of four component lines, representing the transitions to the $2A_u + 2B_u$ excited levels, in accordance with the observed temperature dependence of the emission lineshape (see fig. 1)[3].

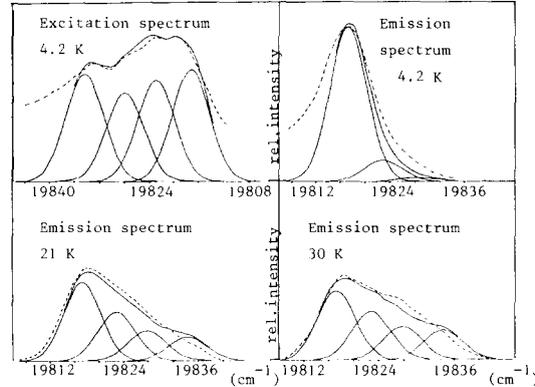


FIGURE 1

Zero-phonon line of UO_2MoO_4 at different temperatures. The Gaussians represent the correlation field components which constitute the observed line. Broken line: observed curve, solid line: sum curve. The positions of the Gaussians are: 19817.3, 19822.9, 19827.9 and 19834.7 cm^{-1} .

The intrinsic emission shows a non-single exponential decay, $\tau = 0.1 > 3 \mu s$. About 10 μs after the pulse the traps attain to maximum intensity. The trap lines show a single-exponential decay, $\tau = 60 - 90 \mu s$. The temperature dependence of τ for traps 5 and 6 follows a decay function based upon a three level system (trap 5)[4] or a four-level (trap 6) system as shown in figs. 2 and 3. The final expressions are for trap 5:

$$\tau_{eff}^{-1} = [w_{21} + w_{t1} \exp(-\Delta E/kT)] [1 + \exp(-\Delta E/kT)]^{-1} \quad (1)$$

and for trap 6:

$$\tau_{eff}^{-1} = [w_{21} + w_{31} \exp(-\Delta \epsilon/kT) + w_{t1} \exp(-\Delta E/kT)] [1 + \exp(-\Delta \epsilon/kT)]^{-1} \quad (2)$$

A detailed discussion of Eqs.(1) and (2) will be given in a forthcoming paper [5]. Using the experimental values $\tau_{21}(t5) = 88 \mu s$, $\Delta E(t5) = 185 cm^{-1}$, $\tau_{21}(t6) = 60 \mu s$, $\Delta E(t6) = 272 cm^{-1}$ the $\tau(T)$ values could be fitted with $\tau_{t1}(t5) = 2.50 \cdot 10^{-10} s$, $\tau_{31}(t6) = 31.5 \mu s$, $\Delta \epsilon = 39 cm^{-1}$, $\tau_{t1}(t6) = 2.17 \cdot 10^{-10} s$. Estimating the hopping time τ_{ij} between intrinsic centres from $\tau_{ij} \approx h/\Delta E_{CF}$ [6], where ΔE_{CF} denotes the correlation field splitting, we find with $\Delta E_{CF} \approx 10 cm^{-1}$ (see caption fig. 1)[3] for $\tau_{ij} \approx 3.33 \cdot 10^{-12} s$. Other estimates [7,8] are in the order of $10^{-8} - 10^{-9} s$. Roughly, τ_{ij} and τ_{t1} seem to be of the same order of magnitude indicating an energy transfer process intermediate between trap-limited migration and diffusion-limited migration.

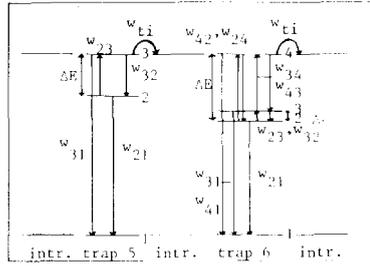


FIGURE 2

Schematic energy level diagram for intrinsic centres and traps 5 and 6. The transition probabilities W_{ij} taken into account in the derivation of the decay functions for the trap levels are indicated in the figure.

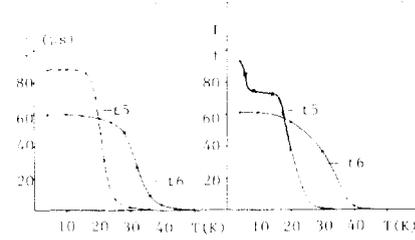


FIGURE 3

τ vs. T and I vs. T curves for traps 5 and 6. The full lines for the τ vs. T curves are the final fitting curves obtained from Eqs.(1,2). The full lines for the I vs. T curves are drawn by hand through the experimental points (indicated in both figures by crosses).

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