

Low-Temperature Decay-Time Measurements on the Luminescence of Calcium Tungstate (CaWO₄)

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The study of the luminescence of tungstates was begun a long time ago (1) and was reviewed recently by one of us (2). Calcium tungstate (CaWO₄, scheelite) is the best-known representative of this class of phosphors. It shows a broad band emission in the blue with an excitation band in the short wavelength ultraviolet (1, 2). This luminescence is due to the tetrahedral tungstate group (WO₄²⁻). Decay time measurements have been reported by Beard *et al.* (3) and by Treadaway and Powell (4) down to 10 K. No other measurements of this type are known to us. In the course of a study of the luminescence of lanthanide halotungstates (5-8) we observed at very low temperatures ($T < 5$ K) a double decay in the case of LaWO₄Cl. This prompted us to extend the measurements of Beard *et al.* on a classic luminescent material (CaWO₄) to lower temperatures. The results are reported in this Note.

Samples of CaWO₄ were prepared from CaCO₃ and WO₃ by solid-state reaction. They were checked by X-ray diffraction. The optical instrumentation has been described before (5-8). Excitation was into the intrinsic tungstate groups.

The emission and excitation spectra of the blue tungstate luminescence were iden-

tical with those reported on them in the literature (1, 2). Therefore, further discussion will not be necessary. The luminescence intensity is temperature independent up to 280 K.

Figure 1 shows the decay times of the luminescence of CaWO₄ as a function of temperature. Above 5 K all decay curves are single exponential. Below 5 K the decay curves are biexponential and Fig. 1 shows a slow (τ_s) and a fast (τ_f) decay time in this temperature region.

Our decay times show the same temperature dependence as those of Beard *et al.*, but our values are about twice as large. This may be related to the fact that Beard *et al.* used excitation by α -particles, whereas we used ultraviolet excitation.

The τ_s values may easily be explained with a three-level scheme as discussed by Beard *et al.* (3) and, in more detail, by one of us (2). This is shown in Fig. 2. If the nonradiative transitions are fast, i.e., $P_{32}, P_{23} \gg P_{21}, P_{31}$ we expect $\tau_s = [1 + \exp(\epsilon/kT)]/[p_{31} + p_{21} \exp(\epsilon/kT)]$ (Ref. 8). By fitting the experimental data to this equation, we arrived at $\epsilon = 20 \text{ cm}^{-1}$, $p_{21} = 3 \times 10^3 \text{ sec}^{-1}$, and $p_{31} = 1.3 \times 10^5 \text{ sec}^{-1}$. The low values of these transition probabilities have been discussed elsewhere (2). Here we wish to con-

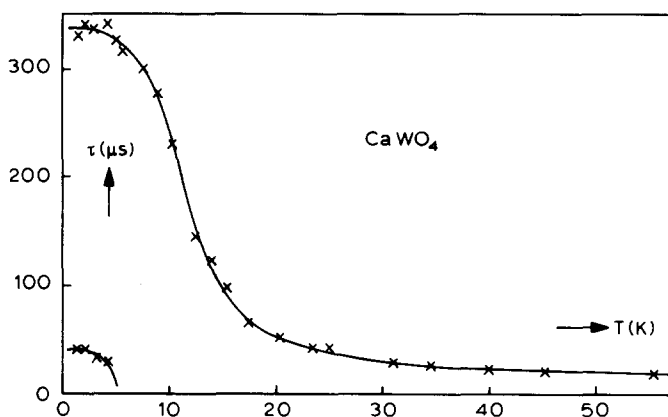


FIG. 1. Temperature dependence of the decay time of the luminescence of CaWO_4 . Excitation is by radiation 250–270 nm. Note the presence of two decay times below 5 K.

concentrate on the $T < 5$ K values which have not been reported to date.

If the nonradiative transitions $p_{32,23}$ do not exceed the radiative ones, two decay times are expected (9). The value of τ_f contains the nonradiative transition probability p_{32} . For $T \rightarrow 0$ the expression for τ_f simplifies to $\tau_f^{-1} = p_{32} + p_{31} - p_{21}$ (Ref. 9). From Fig. 1 it follows that $\tau_f^{-1}(T \rightarrow 0)$ is $2.5 \times 10^4 \text{ sec}^{-1}$, whereas we obtained from τ_s (see above) a value of $p_{31} - p_{21}$ is $1.3 \times 10^5 \text{ s}^{-1}$. This leaves no acceptable solution for p_{32} . Therefore, we have to conclude that the fast decay time cannot be related to a three-level diagram.

It is known, however, that the energy level scheme of the tungstate group is very

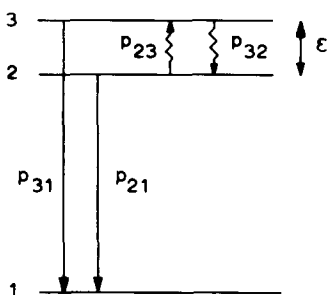


FIG. 2. Three-level scheme with symbols used in the text.

complicated and that photoexcitation is certainly not into the levels 2 and 3, but in higher levels (2): while the emitting levels have a triplet character, the absorbing levels have a singlet character. The observation of a fast decay time at low temperatures is, therefore, ascribed to the processes feeding the emitting levels 2 and 3. A singlet–triplet transition is an obvious possibility.

Similar observations have been made for LaWO_4Cl where the tungstate group is a trigonal bipyramid which is distorted in such a way that the W^{6+} ion has four nearest oxygen neighbors and a fifth further away (7). This coordination is quite similar to that in the tetrahedral WO_4^{2-} group. For octahedral tungstate groups, a fast decay time at low temperatures has not been observed (2, 6).

In closing, we note that the present treatment assumes that energy migration in the lattice does not take place. It has been shown elsewhere that this is a correct assumption (10).

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