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Concentration Dependence of Quantum Efficiency of Luminescence in KCl:Tl

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Quantum efficiency measurements for the 3050 A emission band of KCl:Tl under 2470 A excitation are reported and compared with earlier data. In the present work, the average quantum efficiency is found to be 80±5% over a concentration range of 4×10^{-3} to 8×10^{-1} mole percent Tl. Concentration quenching, if it exists in this range, is only slightly greater than the experimental error. This result is consistent with the Dexter-Schulman proposal of the importance of transfer processes in concentration quenching.

I. INTRODUCTION

An interpretation of the quenching of luminescence in solids by increase in activator concentration ("concentration quenching") has been proposed by Dexter and Schulman[1] for nonphotoconducting phosphors. According to this interpretation the excitation energy is transferred from activator to activator by a resonance process until it arrives at a quenching site in the crystal. For this mechanism of concentration quenching to be important, there must be enough overlap between the emission and absorption spectra of the activator to permit energy transfer between activators to take place with high probability. If fair overlap exists, considerable quenching is to be expected for activator concentrations of the order of 10^{-1} to 1 mole percent for an activator transition of the electric dipole or electric quadrupole type. If the activator transition is of a magnetic dipole or higher magnetic or electric multipole type, transfer will occur by exchange rather than by the overlapping of the corresponding multipole fields. Under these circumstances concentrations of the order of a few mole percent will be required in order to obtain appreciable concentration quenching in typical ionic crystals. At concentrations of this magnitude or larger, most activators have other activators as nearest neighbors, and quenching may result from modification of the thermal activation energy for radiationless transitions due to the interactions between nearby activators. In this case quenching can occur at the same activator center that originally absorbs the exciting energy, and no energy transfer mechanism need be involved. Earlier treatments[2,3] of this problem had considered only this case, and had assumed that the cause of concentration quenching was the above-mentioned lowering of the dissipative-process activation energy, either by near-neighbor interactions or by an interaction of the activator with nearby quenching imperfections in the crystal. In these treatments, however, imperfections or other activator atoms within as much as 4000 equivalent sites surrounding a given activator were considered to be "near neighbors" in their effectiveness as quenchers. Modification of the thermal activation energy for radiationless transitions by interaction over such large distances were considered unlikely on theoretical grounds by Dexter and Schulman.

In view of the poor overlap between the absorption[4] and emission[5] spectra of the KCl:Tl phosphor at room temperature (Fig. 1), energy transfer between activators should not take place efficiently. A Tl concentration of the order of a few mole percent should therefore be required to achieve appreciable concentration quenching, if the considerations advanced by Dexter and Schulman are correct. Johnson and Williams,[2] however, have reported that concentration quenching begins in this system at a Tl concentration in the crystal of the order of 10^{-1} mole percent at 25°C, and that there is about 30% quenching at a Tl concentration of 7×10^{-1} mole percent. These investigators used 2537 A light to excite KCl:Tl phosphor powders, and measured the relative intensity of the 3050 A emission band as a function of the Tl concentration of their samples. Their curve of efficiency *vs* Tl concentration is reproduced in Fig. 2, Curve A.

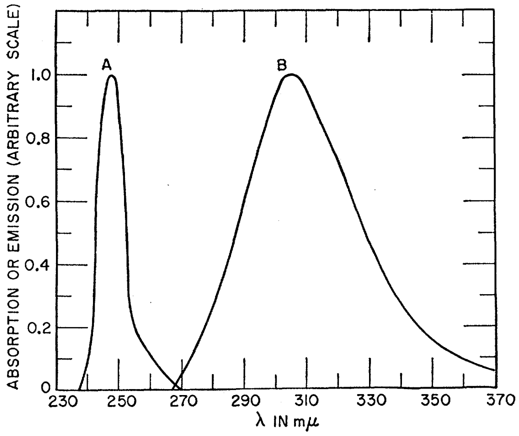

FIG. 1. Absorption and emission spectra of KCl:Tl after references (4) and (5). Curve A = absorption; Curve B = emission.

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[1] D. L. Dexter and J. H. Schulman, J. Chem. Phys. **22**, 1063 (1954).

[2] P. D. Johnson and F. E. Williams, J. Chem. Phys. **18**, 1477 (1950).

[3] J. Ewles and N. Lee, J. Electrochem. Soc. **100**, 392 (1953).

[4] W. Koch, Z. Physik **57**, 638 (1929).

[5] W. von Meyeren, Z. Physik **61**, 321 (1930).

In assessing the significance of Johnson and William's results, two things should be taken into account, however. First, their data are related to the apparent quantum efficiency (quanta emitted per *incident* quantum) rather than to the true quantum efficiency (quanta emitted per *absorbed* quantum). Second, Butler[6] has shown by measurements of excitation spectra, that the long-wavelength Tl absorption in KCl:Tl consists of two overlapping bands, one being the well-known band peaking at about 2450 A, and the other a subsidiary band peaking at about 2600 A at room temperature. The 2600 A absorption leads to an emission in the visible spectral range rather than to the 3050 A emission band. Patterson and Klick[7] have confirmed and extended Butler's results. They suggest that if the 2450 A band arises from substitutional Tl ions at normal cation sites, the 2600 A band is due either to pairs or higher Tl aggregates or to Tl ions at special positions in the crystal. The 2600 A excitation band increases more rapidly with Tl concentration than does the 2450 A band,[6] much as one would expect if Tl-pair formation were responsible. Excitation with 2537 A light, as in Johnson and Williams' measurements, could accordingly result in simultaneous absorption by two different types of centers, one of which emits no luminescence in the spectral region of interest and becomes proportionately more abundant with increase in Tl concentration. If this possibility is neglected and the absorption is ascribed only to one species of Tl bearing centers, the result could be erroneously interpreted as an actual concentration quenching of the luminescence of this species. Measurements with 2537 A excitation could therefore be misleading. Hence quantum efficiency measurements should preferably be made under shorter wavelength excitation, where there is less overlap with the 2600 A absorbing centers.

A result apparently more compatible with the Dexter-Schulman viewpoint had been obtained earlier by Bünger,[8] who had made absolute measurements of quantum efficiency in this system and had found the 3050 A emission band to be excited with essentially constant quantum efficiency over a wide range of Tl concentrations. Bünger employed single crystals with Tl concentrations corresponding to KCl-TlCl melts of 1.5×10^{-2} to 1.83 mole percent TlCl. The crystals themselves were not analyzed for Tl content, which according to Koch's[4] results, could be anywhere between 0.05 to 0.5 of the Tl concentration in the melt. Bünger's data for 2500 A excitation at 50°C are summarized in Fig. 2, Curve B. It will be seen from this figure that the quantum efficiency of the 3050 A emission averaged about 50% throughout the concentration range investigated, with one exceptional crystal giving an efficiency of 76%. The high quantum efficiency of this one sample raises doubts about the quality of the rest of Bünger's crystals and hence about the reliability of the concentration independence of quantum efficiency which he found. Furthermore, the connection between Bünger's results and those of Johnson and Williams is hard to determine, principally because of the uncertainty in the Tl content of Bünger's crystals and because one measurement is a measurement of true quantum efficiency and the other merely of brightness. Because of these uncertainties, a reinvestigation of concentration quenching in KCl:Tl was undertaken.

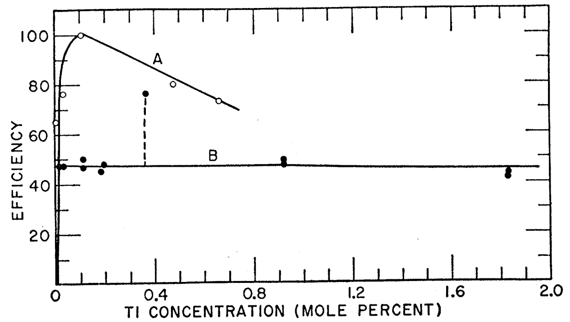

FIG. 2. Luminescence efficiency of 3050 A emission in KCl:Tl *vs* Tl concentration. Curve A: normalized relative efficiency; Tl concentration in solid; 2537 A excitation; $T=25$°C (after reference 2). Curve B: absolute quantum efficiency; Tl concentration in melt; 2500 A excitation; $T=50$°C (after reference 5).

II. EXPERIMENTAL PROCEDURE

Polycrystalline samples of KCl:Tl were prepared from KCl that had been freed from heavy metal impurities by repeated extractions of an aqueous solution with dithizone. After addition of the desired quantity of TlCl to the solid purified KCl, the KCl-TlCl mixture was melted in a fused silica boat in a stream of pure dry HCl gas. The HCl stream was maintained over the sample during the cooling to room temperature. The material obtained in this way was lightly crushed and sieved. Material in the 80–100 mesh particle size range was used for all the measurements except where noted below. Chemical analyses were made for the Tl content of the samples, and the values given in the succeeding graphs refer to the concentration in Tl in the solid phosphor.

Quantum efficiency measurements were made by a method devised by Ginther.[9] Since a full description of this method is in preparation,[10] only a brief summary of the technique will be given here. The powdered phosphor surface is first determined to be a diffuse reflector so that measurements made at an arbitrary angle of observation are representative of the whole surface. Ultraviolet light from a monochromator excites a thick plaque of the powdered phosphor, and measurements are made of the response of a photomultiplier

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[6] K. H. Butler, J. Electrochem Soc. **103**, 508 (1956).

[7] D. A. Patterson and C. C. Klick, Phys. Rev. **105**, 401 (1957).

[8] W. Bünger, Z. Physik **66**, 311 (1930).

[9] R. J. Ginther, J. Electrochem. Soc. **101**, 248 (1954).

[10] R. J. Ginther and E. W. Claffy (to be published).

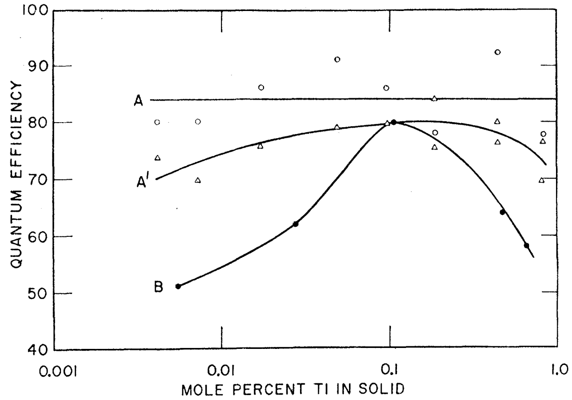

FIG. 3. Quantum efficiency of 3050 A emission of KCl:Tl *vs* Tl concentration, under 2470 A excitation. Curve A: set No. 1, present paper under 2740 A excitation; Curve A′: set No. 2, present paper under 2740 A excitation; Curve B: data of reference (2) (2537 A excitation) normalized to peak value of 80%.

tube to (1) the luminescence emission, isolated by suitable filters, and (2) the sum of the reflected and emitted light. The exciting light reflected from an identical plaque of smoked MgO is also measured. From these measurements the absorbed light is calculated and the quantum efficiency is computed as described by Kröger.[11] Subsidiary data employed in the quantum efficiency determinations are spectral energy distribution of the emission, filter transmission, phototube sensitivity, and reflectivity of MgO.

During the course of this work it was found desirable to make brightness measurements similar to those reported by Johnson and Williams. For this purpose ultraviolet light of any desired wavelength from a monochromator was directed upon plaques of KCl:Tl powder held in a rigidly mounted holder in front of the entrance slit of a spectroradiometer. Emission spectra covering the 3050 A emission band were obtained in this way under constant intensity of incident exciting light. The relative emission intensities of a series of samples under a given excitation were evaluated either by comparing the output at 3050 A peak, or by integrating under the entire emission band. Both methods of comparison gave the same results.

III. EXPERIMENTAL RESULTS

Figure 3 shows the results of two separate series of measurements on the samples under excitation by 2470 A radiation, which is 5 A less than the wavelength of peak absorption in the long-wavelength absorption band of KCl:Tl at room temperature.[4] The first set of measurements (Curve A, measurements by RJP) shows no detectable concentration dependence of the quantum efficiency within the experimental error. The data indicate a quantum efficiency of luminescence in the 3050 A emission band of 84±5%. The second set of data (Curve A′), taken several months later with the same samples but with a steadier ultraviolet source (measurements by EWC), shows a somewhat lower average quantum efficiency, 77±4%, which is again essentially independent of the concentration.[12] Although this second series of measurements is represented in the figure by a curve showing a small concentration dependence, it is not certain that the precision of the method warrants such an interpretation. The average value of all the quantum efficiency determinations given in curves A and A′ is 80% with a 5% average deviation from the mean. Also shown in Fig. 3 is the curve of relative brightness *vs* Tl concentration obtained by Johnson and Williams (Curve B), normalized to 80% quantum efficiency at the concentration of maximum brightness.

The disagreement of our results with those of Johnson and Williams suggested that we redetermine the quantum efficiencies under the same exciting wavelength which they used. The samples were accordingly remeasured under 2537 A excitation, with the results shown in Fig. 4, Curve A. The over-all concentration dependence of efficiency which we observe under 2537 A excitation is somewhat greater than that observed under 2470 A excitation, and appears to be real. The degree of concentration quenching which we observe under 2537 A excitation is far less, however, than that shown by Johnson and Williams' data, reproduced again as Curve B of Fig. 4, normalized to a peak value of 80%.

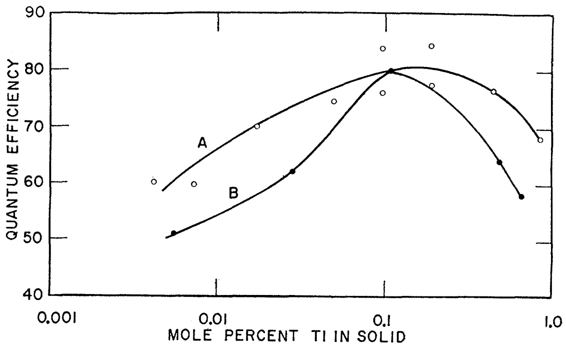

FIG. 4. Quantum efficiency of 3050 A emission in KCl:Tl *vs* Tl concentration, under 2537 A excitation. Curve A: present paper; Curve B: data of reference 2 normalized to peak value of 80%.

In order to clarify the situation further, the samples were remeasured using Johnson and Williams' technique, i.e., the "brightness" or "apparent" quantum efficiency was measured rather than the true quantum efficiency. The results are given in Fig. 5, Curve A, normalized to 80% at the peak, where they may be compared with Curve B, which repeats Johnson and

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[11] F. A. Kröger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, New York, 1948), pp. 257–9.

[12] The difference between the two sets of data is reminiscent of the difficulties reported by Bünger,[8] who found that freshly cleaved or polished crystals gave somewhat better results than specimens that were used many times.

Williams' data again normalized to the same peak value. In this figure both curves represent the same type of measurement, and the agreement between them is fair. Both "brightness" measurements show a pronounced concentration dependence and an apparent "concentration quenching" which is well beyond the experimental error of this type of measurement.

Also shown in Fig. 5 is a corresponding normalized "brightness" curve using 2470 A excitation (Curve C). The concentration dependence of the 3050 A emission band "brightness" is much less under this excitation than under 2537 A excitation. It was further found that the form of "brightness" curves such as those given in the figure depends on the particle size of the sample as well as on the wavelength of the exciting light. An illustration of this point is given in Table I, where the "brightness" (arbitrary scale) and quantum efficiencies of two KCl:Tl samples of different particle size are compared under 2470 A excitation. It will be seen from the table that the quantum efficiencies of all the samples are approximately equal, although the fine fraction of sample *J* is about 10% lower than the corresponding "standard" particle size sample. The relative brightness, on the other hand, differs considerably. The brightness values of the "standard" particle size samples happen to be about equal, while those of the fine samples differ by almost 40%. These results emphasize again the difficulty of interpreting fundamental processes in phosphors from consideration of brightness curves.

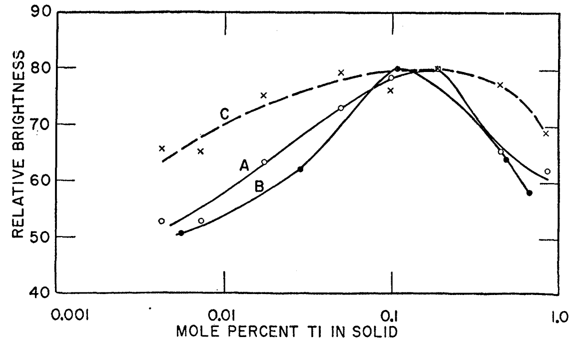

FIG. 5. Relative brightness of 3050 A emission in KCl:Tl *vs* Tl concentration. Curve A: present work, 2537 A excitation; Curve B: data of reference 2; Curve C: present work, 2470 A excitation. All curves normalized to same peak brightness.

TABLE I. Brightness and quantum efficiencies of two KCl:Tl samples.

		"Fines" (through 150-mesh sieve)		"Standard" (80–100 mesh)	
Preparation No.	Tl conc. (mole percent)	Brightness (arbitrary scale)	Q.E.	Brightness (arbitrary scale)	Q.E.
M	1.89×10^{-1}	84	80	47.5	81
J	1.72×10^{-2}	61	68.7	45.0	77.2

IV. SUMMARY AND CONCLUSIONS

Quantum efficiency measurements for the 3050 A emission band of polycrystalline KCl:Tl have shown that the average quantum efficiency under 2470 A excitation at 25°C is 80±5% over a concentration range of approximately 4×10^{-3} to 8×10^{-1} mole percent Tl in the solid phosphor. This average value of quantum efficiency agrees with the highest value found by Bünger[8] on one of his single-crystal preparations. Concentration quenching, if it occurs at all in this concentration range, is only slightly greater than the experimental error of the measurements. The absence of pronounced concentration quenching is consistent with the Dexter-Schulman proposal that an energy transfer process between activators plays an important part in concentration quenching, such transfer being inefficient in KCl:Tl because of the poor overlap of the absorption and emission bands.

Subsidiary experiments were conducted in an attempt to understand the more extensive concentration quenching in KCl:Tl reported by Johnson and Williams.[2] It appears from these experiments that the "quenching" which they observe is, to a considerable extent, a loss of brightness with increasing Tl concentration rather than a decrease in true quantum efficiency. It is possible, also, that a further source of this "quenching" may be the overlapping absorption of other Tl-bearing centers, as pointed out in the discussion of 2537 A excitation in the introduction. The value of the quenching parameters, Z and (σ/σ') derived by Johnson and Williams in their treatment of concentration quenching in KCl:Tl, are therefore of questionable significance. The same question exists concerning the quenching parameters n, α, and K, derived for this system by Ewles and Lee,[3] who applied their own theory of concentration quenching to Johnson and Williams' data.

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