Origin of the 4750-Å Emission in KCl:Tl Phosphors

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Some experimental results concerning low-temperature emission intensity, decay times, and activator concentration dependence of the 4750-Å KCl:Tl emission are reported in order to clarify its origin. According to the experimental features, this emission is attributed to the de-excitation of the $^3A_{1u}$ state, directly excited by the transition $^1A_{1g} \rightarrow {}^3A_{1u}$, as an alternative to the several discordant interpretations already given.

The absorption spectrum characteristic of KCl:Tl-type phosphors is qualitatively well explained by the model proposed by Seitz, and quantitative approaches to the problem may be found elsewhere.[1-3] On the contrary, in regard to the emission spectrum, a complete understanding has not yet been reached in spite of the many efforts performed.[4-6] In particular, the origin of the 4750-Å emission of KCl:Tl has not yet been clarified, although several explanations have been given by other authors, as summarized in Table I.

Explanations (a) in the table are able to predict some features concerning the optical spectrum of KCl:Tl, but they are unsuccessful in the interpretation of the double excitation in the A band and of the polarization properties of the emissions.[8,12] Explanations (b)–(f) will be discussed below on the basis of some experiments which were carried out in order to clarify the origin of this emission band. Our experimental results give strong support to Fowler's theoretical prediction[14] of the existence of the weakly allowed transition $^1A_{1g} \rightarrow {}^3A_{1u}$, since they show that very likely the 4750-Å emission arises from the $^3A_{1u}$ state, directly excited by the above transition [explanation (g) proposed here].

TABLE I. Seven explanations for the 4750-Å emission of KCl:Tl.

Excited states responsible for the emission	References
(a) $^1P_1$ or mixing of $^1P_1$ and $^3P_1$.	7
(b) Unspecified level underlying level responsible for 3050-Å emission.	8
(c) X minimum on $^3P_1$ state produced by Jahn-Teller effect.	9
(d) Perturbed exciton state (electron transfer transition).	10
(e) $^3P_0$ after excitation in $^3P_1$ state.	11
(f) States of dimers or clusters of Tl^+ ions.	12, 13
(g) $^3A_{1u}$ (or $^3P_0$) directly excited by $^1A_{1g} \rightarrow {}^3A_{1u}$ transition.	proposed here

Our experiments are concerned mainly with the 4750-Å emission intensity measurement as a function of temperature in the range 18–300°K, and with the excitation spectra for two different Tl^+ concentrations. Moreover, preliminary decay time measurements at low temperature were performed. Ultraviolet light from a 25-W deuterium lamp was chopped and dispersed in a quartz monochromator and focused on the sample placed in a liquid-helium Dewar; the emission was observed at right angles through a 4750-Å filter (bandwidth 500 Å) by a photomultiplier, whose output was sent to a lock-in amplifier. For the decay time measurements, the light produced by an air spark gap was directly focused onto the sample through a 2540-Å filter (bandwidth 150 Å). The samples were single crystals supplied by K. Korth, Kiel, Germany. Use of Smakula's formula, in conjunction with room-temperature absorption measurements of the A band, revealed the Tl^+ concentrations to be 90 and 170 ppm, with an assumed oscillator strength of 0.07.[15] These Tl^+ concentrations are low enough to cause the presence of all but a negligible quantity of Tl^+ dimer.[16]

Figure 1 shows the emission intensity as a func-

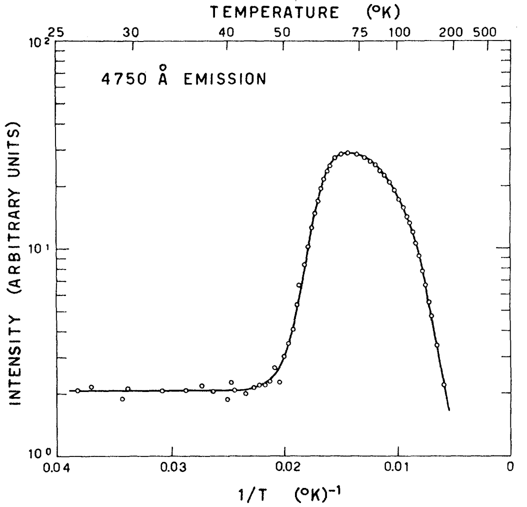

FIG. 1. Temperature dependence of 4750-Å emission intensity of KCl:(1.7×10^{-4} Tl) excited at 2540 Å (4.88 eV). From 18 to 25°K the intensity is unchanged.

tion of the temperature. It can be seen that the emission decreases considerably at low temperatures. This made decay-time measurements difficult for temperatures up to about 60°K, where the decay time was measured to be about 200 μsec. Between 60 and 70°K the decay time diminishes to 20 μsec. Note that the decay time is decreasing while the emission intensity increases. The strong temperature dependence of the intensity and the long decay times suggest that this emission cannot be attributed to dimer centers as supposed in Refs. 12 and 13 [explanation (f)]. In fact, the emission characteristic of dimers shows an intensity weakly dependent on temperature as well as a very short decay time even at low temperature and linear polarization,[17] which is not observed in 4750-Å emission.[18] Furthermore, we have measured the ratio of the emission intensities at liquid-nitrogen temperature (which is near the maximum of the intensity emission, see Fig. 1) with our two Tl^+ concentrations. The obtained intensity ratio 1.8 is coincident with the concentration ratio, within the experimental errors. This result is in agreement with a linear concentration dependence of the emission intensity and with the attribution of 4750-Å emission to single Tl^+ centers as made by Johnson and Williams.[7,19]

Our measurements also show that the maximum of the excitation spectrum for this emission is at 4.88 eV. This value is practically coincident with the energy difference (4.90 eV) between the ${}^3A_{1u}$ excited state and the ${}^1A_{1g}$ ground state of Tl^+ as can be deduced from the data reported in Ref. 3; while the maximum of the excitation spectrum for the 3050-Å emission is at 5.03 eV which corresponds to the energy difference in the ${}^1A_{1g}\rightarrow{}^3T_{1u}$ transition. This suggests that the 4750-Å emission may be attributed to the de-excitation of the ${}^3A_{1u}$ state, directly excited by the transition ${}^1A_{1g}\rightarrow{}^3A_{1u}$, and not after a nonradiative thermal transition between ${}^3T_{1u}$ and ${}^3A_{1u}$, as supposed by Sturge[11] [explanation (e)]. Therefore, our interpretation is in agreement with Knox's proposal [explanation (b)] if it is assumed that his two unspecified levels correspond to the ${}^3A_{1u}$ and ${}^3T_{1u}$ states for the 4750- and 3050-Å emissions, respectively.

The transition ${}^1A_{1g}\rightarrow{}^3A_{1u}$ is forbidden, but the lattice vibrations make it weakly allowed by mixing the ${}^3A_{1u}$ state with the ${}^3E_u$ and ${}^3T_{2u}$ states, which are responsible for the B absorption band[14] (this can be seen, for instance, from the electron-lattice interaction matrix of Ref. 5). This interpretation agrees with the weak emission intensity,[20] its strong temperature dependence, and the long decay time and its temperature dependence.

In order to give a more quantitative approach to the problem, we have computed the adiabatic potential-energy surfaces (APES's) for the ${}^3A_{1u}$ and ${}^3T_{1u}$ states, in a multidimensional coordinate space, assuming the existence of tetragonal minima on the ${}^1T_{1u}$ APES's.[5] First we had to evaluate the electron-lattice interaction matrix element $\langle t_{1u,x}|V_2|t_{1u,x}\rangle$ for the tetragonal mode. A rough estimation of this matrix element has been performed in the point-charge model by assuming the molecular-orbital t_{1u} to be coincident with the $6p$ Tl^+ atomic orbital. The latter approximation is justified because the molecular orbital t_{1u} mainly consists of the $6p$ atomic orbital.[3] Following Toyozawa and Inoue,[2] the electron-lattice coupling constant for the tetragonal mode turns out to to be $b^2=0.69$ eV by assuming the Tl-Cl distance and the $6p$ Tl^+ radial function as in Ref. 3.

Figure 2 shows the cross sections of the ${}^3A_{1u}$ and ${}^3T_{1u}$ APES's, containing the Q_3 axis, computed in intermediate coupling by using the expressions given in Ref. 6 and taking into account the lattice potential energy $[12\zeta(1-\beta)/b^2]x_3^{\,2}$. For the ratio $g=G/\zeta$, between the exchange integral and the spin-orbit coupling constant, the value of 0.406 was obtained from the data of Fukuda.[21] For the constant β, which is the difference in the curvature between the excited and the ground-state APES's, the value of 0.3 was assumed as a

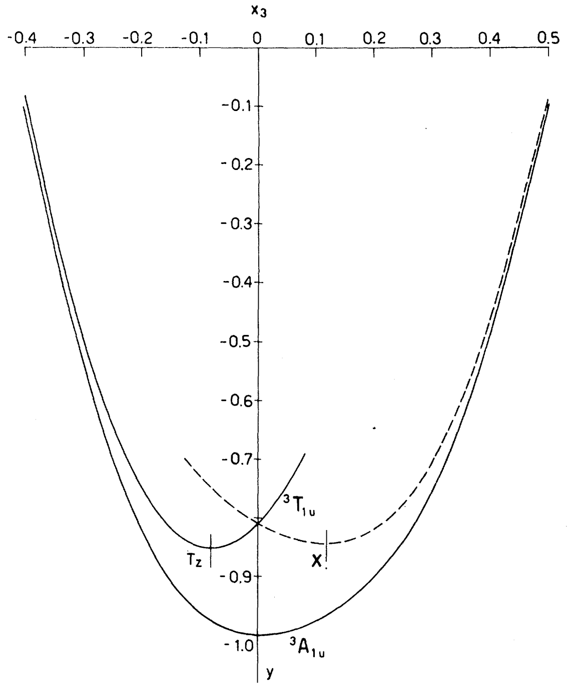

FIG. 2. Cross sections of $^3A_{1u}$ and $^3T_{1u}$ APES's containing the Q_3 axis. Here, $y=E/\zeta$ is the ratio of the energy and the spin-orbit coupling constants, and $x_3 = [-b/(2\sqrt{3}\,\zeta)]Q_3$. Solid lines show nondegeneracy; the dashed line, double degeneracy. There are three equivalent T minima on the $^3T_{1u}$ APES's: The cross sections show the T_z minimum and the X point which is on the cusp between the T_x and T_y minima. The $^3A_{1u}$ APES shows only one totally symmetrical minimum.

reasonable one.[5]

Similar cross sections were obtained by Kamimura and Sugano,[9] who assigned the 4750- and 3050-Å emissions to the transitions from the stationary points X and T_z, respectively [explanation (c)]. However, in this case only the T_z point is a minimum, while the X point is actually only a cusp.[6,17] Thus, in agreement with the experimental results reported above, we assign the 4759-Å unpolarized emission to the totally symmetrical minimum of the $^3A_{1u}$ APES, and the fast component of the 3050-Å emission[22] to the three equivalent T minima of the $^3T_{1u}$ states. This agrees with the partial polarization of the 3050-Å emission which has been explained in terms of the Jahn-Teller effect.[5]

On the basis of the experiments and computations so far performed, we may conclude that the 4750-Å emission of KCl:Tl is due to single Tl^+ centers. In this framework this emission may be reasonably attributed to the de-excitation of the $^3A_{1u}$ state excited by the transition $^1A_{1g} \rightarrow {^3A_{1u}}$. The origin of the slow component of the 3050-Å emission is not yet understood; however, this could be originated by a charge-transfer transition similar to the one suggested by Illingworth,[22] but for this case involving a triplet exciton state. A charge-transfer transition has been invoked by Alderson in order to explain the 4750-Å emission [explanation (d)]. However, in this case it would be hard to explain the strong increase of 4750-Å emission intensity at low temperatures and the corresponding decrease of emission decay time.

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