

Simplified Configuration Coordinate Model for KCl : Tl<sup>†</sup>

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The configuration coordinate model for KCl:Tl has been modified recently to include the effect of the crystalline field on spin-orbit interaction. We have now re-examined the spectral data on KCl:Tl and related phosphors and propose a simplified configuration coordinate model which also includes this effect. In the simplified model the two excited states are approximately parallel, the upper state being predominantly singlet; the lower, triplet. In contrast to the earlier model, the pure <sup>1</sup>P<sup>0</sup> and <sup>3</sup>P<sup>0</sup> spin states do not cross, and thereby we avoid spin-dependent crystalline interactions which vary rapidly with configuration coordinate. The effects of crystalline interactions on the energy separation of the spin states and on the spin-orbit coupling constants are estimated theoretically. In the quantitative application of the one dimensional model to absorption and emission spectra neglecting configuration interaction with other crystal states, spin-orbit coupling constants which are smaller than the free ion values are used. The application of the model to other alkali halide phosphors and the origin of spectra not readily explained with the simplified model are discussed.

## I. INTRODUCTION

IN a recent publication<sup>1</sup> the 1960 Å and 2470 Å absorption bands and the 3050 Å and 4750 Å emission bands of thallium-activated potassium chloride were interpreted on the basis of a configuration coordinate model including the effect of the crystalline field on spin-orbit interaction. In this model crossing of the <sup>3</sup>P<sup>0</sup> and <sup>1</sup>P<sup>0</sup> pure spin states of the 6s6p configuration of Tl<sup>+</sup> is removed by spin-orbit interaction, and a third emission band in the region of the 2470 Å absorption was predicted. The discovery of the new band tends to confirm the model. In addition, the model is in accord with a large variety of experimental results to within the accuracy to be expected of a single coordinate model.

It is difficult, however, to justify theoretically the strong dependence of the difference in energies of the pure spin states on the configuration coordinate. The extension of the Born-Mayer analysis<sup>2</sup> used for the <sup>1</sup>S and <sup>3</sup>P<sup>0</sup> states of Tl<sup>+</sup> in KCl to <sup>1</sup>P<sup>0</sup> Tl<sup>+</sup> is not consistent with this strong dependence. In fact, the simple theory predicts approximately parallel excited states with, however, too great an energy separation compared to the observed spectra. In addition, the model does not explain the selective excitation<sup>3-5</sup> of the 4750 Å emission band by 2575 Å radiation.

These difficulties plus the existence of the 2470 Å emission, which was unknown at the time the original configuration coordinate model was proposed,<sup>3</sup> suggest that the identification of the transitions responsible for the absorption and emission be re-examined. In the present paper this is done. We first estimate theoretic-

ally the energy separation of the pure spin states and the departure of the spin-orbit coupling constants from their free ion values. We then propose a simpler configuration coordinate model which is consistent with these theoretical parameters and accounts for most of the experimental data on KCl:Tl. Data on other alkali halides, including a new emission band in KI:Tl, are discussed. The theoretical basis for the configuration coordinate model and the background of its application to KCl:Tl have been reviewed elsewhere<sup>1</sup> and therefore will not be duplicated here.

## II. THEORETICAL CONSIDERATION OF SPIN-ORBIT INTERACTION PARAMETERS

The principal effect of crystalline interactions on the spin-orbit interaction of the <sup>3</sup>P<sup>0</sup> and <sup>1</sup>P<sup>0</sup> states of Tl<sup>+</sup> in KCl is on the energy separation 2G<sub>e</sub> of the pure spin states.<sup>6</sup> The parameter 2G<sub>e</sub> involves a term for the difference in interaction of the <sup>3</sup>P<sup>0</sup> and <sup>1</sup>P<sup>0</sup> Tl<sup>+</sup> with the crystal plus a term for the exchange interaction of the 6s and 6p electrons of the Tl<sup>+</sup>.

$$2G_e = 2\Delta G_i + 4e^2 \int_0^\infty \frac{P_{6s}(2)P_{6p}(2)}{r^2} dr_2 \times \int_0^{r_2} r_1 P_{6s}(1)P_{6p}(1) dr_1, \quad (1)$$

where P<sub>6s</sub> and P<sub>6p</sub> are radial wave functions. Since the ions surrounding the Tl<sup>+</sup> have closed shells, exchange interactions are not expected to contribute strongly to 2ΔG<sub>i</sub>. Using approximate free ion wave functions the Coulomb overlap interaction with the nearest-neighbor Cl<sup>-</sup> has been found to contribute -0.4 eV to ΔG<sub>i</sub>.<sup>6</sup>

<sup>†</sup> Presented at the Meeting of the American Physical Society in Cambridge, March 30, 1959 [Bull. Am. Phys. Soc. Ser. II, 4, 147 (1959)].

<sup>1</sup> F. E. Williams and P. D. Johnson, Phys. Rev. **113**, 97 (1959).

<sup>2</sup> F. E. Williams, J. Chem. Phys. **19**, 457 (1951).

<sup>3</sup> P. D. Johnson and F. E. Williams, J. Chem. Phys. **20**, 124 (1952).

<sup>4</sup> K. H. Butler, J. Electrochem. Soc. **103**, 508 (1956).

<sup>5</sup> D. A. Patterson and C. C. Klick, Phys. Rev. **105**, 401 (1957).

<sup>6</sup> F. E. Williams, B. Segall, and P. D. Johnson, Phys. Rev. **108**, 46 (1957).

The second term of Eq. (1) is the same form as for the free ion,<sup>7</sup> and in the approximation of unperturbed free ion wave functions is unaffected by crystalline interactions. Actually, the states of  $Tl^+$  are perturbed upwards by crystalline interactions and the radial wave function  $P_{6p}$  becomes more diffuse. The perturbation of the  $6s6p$  states of  $Tl^+$  in  $KCl:Tl$  to more diffuse charge distributions was discussed qualitatively in the earliest theoretical work<sup>8</sup> on this phosphor, however, the only quantitative theoretical work<sup>2,6,9</sup> has involved free ion wave functions. In the present analysis we depart from free ion functions and estimate  $P_{6p}$  for the  $Tl^+$  in the crystal in order to determine the exchange integral of Eq. (1). The ionization energies  $\epsilon$  of the  $^3P^0$  and  $^1P^0$  states of  $Tl^+$  have been estimated to be reduced by crystalline interactions from 11 and 13 to roughly 4 ev.<sup>10,11</sup> Since for free ion functions only 0.3% of the exchange integral originates inside the last node of  $P_{6p}$  at  $r_0$  and since  $P_{6p}$  beyond  $r_0$  for the crystal functions can be estimated from  $\epsilon$ , the change in  $2G$  arising from crystalline interactions perturbing the  $Tl^+$  can be determined approximately. The radial function  $P_{6p}$  beyond  $r_0$  can be approximated by a function of the form<sup>6</sup>:

$$P_{6p} = Nr(r-r_0) \exp[-(\epsilon)^{1/2}r], \quad (2)$$

where  $N$  is a normalization constant. In Fig. 1 are shown the radial charge densities  $P_{6p}^2$  for  $r > r_0$  for the free ion and for the crystal as approximated by Eq. (2). The points are the Hartree solution for the free ion<sup>12</sup> and indicate the validity of Eq. (2). The exchange integral of Eq. (1) was computed for the  $P_{6p}$  functions of Fig. 1 and found to be a factor of two smaller for the crystal compared to the free ion. In the limit of the

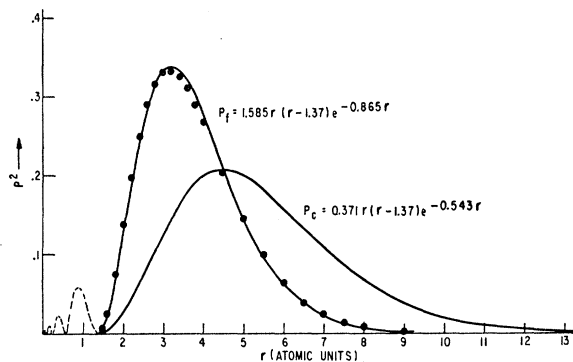


FIG. 1. Approximate radial charge densities for  $Tl:P_f$ , free ion function; and  $P_c$ , crystal function. Points and dashed line are Hartree solutions for free ion.

<sup>7</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), p. 177.

<sup>8</sup> F. Seitz, *J. Chem. Phys.* **6**, 150 (1938).

<sup>9</sup> R. S. Knox and D. L. Dexter, *Phys. Rev.* **104**, 1245 (1956).

<sup>10</sup> P. D. Johnson and F. E. Williams, *J. Chem. Phys.* **21**, 125 (1953).

<sup>11</sup> F. E. Williams, *J. Opt. Soc. Am.* **47**, 869 (1957).

<sup>12</sup> A. S. Douglas, D. R. Hartree, and W. A. Runciman, *Proc. Cambridge Phil. Soc.* **51**, 406 (1953).

effective mass approximation in which the excited electron interacts Coulombically with the  $Tl^{++}$  core in accordance with the macroscopic dielectric constants of  $KCl$ ,  $2G$ , of course, becomes zero. This is a suitable approximation for the  $Z_1$  center,<sup>13</sup> in which an electron is bound to a divalent cation such as  $Ca^{++}$  at a  $K^+$  site in  $KCl$ .

In the final estimate of  $2G_c$  for the  $^3P^0$  and  $^1P^0$  states of  $Tl^+$  in  $KCl:Tl$  we reduce the exchange integral for the free ion, which equals the energy separation of the pure spin states of the free ion, by a factor of two and substitute the value of  $\Delta G_i$  obtained with free ion wave functions into Eq. (1). The experimental value of  $2G$  for the free ion is 2.1 ev. The value of  $\Delta G_i$  of  $-0.4$  ev obtained with free ion functions is not expected to be seriously in error since with the more diffuse crystal functions the overlap with the nearest-neighbor  $Cl^-$  is greater but the difference in overlap between the  $^3P^0$  and  $^1P^0$  states tends to decrease because the radial charge densities for the two states are more nearly the same. From these considerations, real and positive values of  $2G_c$  of the order of several tenths of an electron volt are expected theoretically.

In addition to the effect of crystalline interactions on  $2G$ , the effect on the spin-orbit coupling constants  $\zeta$  and  $\lambda\zeta$  must be considered. These constants depend on the potential  $V$  and on  $P_{6p}$  as follows:

$$\zeta = \frac{e\hbar^2}{2m^2c^2} \int_0^\infty P_{6p}^2 \left( \frac{1}{r} \frac{\partial V}{\partial r} \right) dr, \quad (3)$$

and  $\lambda$  takes account of the difference in  $P_{6p}$  for the  $^1P^0$  and  $^3P^0$  states. Since essentially all contributions to  $\zeta$  originate from within a radius of  $1/20$  A, these parameters have previously been approximated by their free ion values.<sup>1,6</sup> Only 0.015% of the free ion values of  $\zeta$  and  $\lambda\zeta$  arises from  $P_{6p}$  beyond its last node at  $r_0$  so that the direct effect of the crystalline perturbation of  $P_{6p}$  beyond  $r_0$  on  $\zeta$  and  $\lambda\zeta$  is insignificant. However, the renormalization of the inner core region after matching wave functions and their derivatives at  $r_0$  produces an appreciable reduction in  $\zeta$  and  $\lambda\zeta$  from their free ion values.<sup>14</sup> In fact, a Hartree solution for  $P_{6p}$  obtained with the field beyond  $r_0$  modified by an effective dielectric constant consistent with an eigenvalue of 4 ev is found to yield a  $\zeta$  approximately one-half of the free ion value. Since the  $P_{6p}$ 's are expected to be more nearly the same for the  $^1P^0$  and  $^3P^0$  crystal states,  $\lambda$  itself is probably increased from its free ion

<sup>13</sup> F. Seitz, *Phys. Rev.* **83**, 134 (1951).

<sup>14</sup> Our conclusion that the spin-orbit coupling constants for the crystal are less than the free ion values is at variance with the conclusion of R. S. Knox, *Phys. Rev.* **115**, 1095 (1959). His calculation is based on Löwdin-type functions. These do not approach the atomic functions in the inner core region as the crystal functions should [S. Raimes, *Proc. Phys. Soc. (London)* **A67**, 52 (1954)]. In the same report Knox independently suggests a model which has some features similar to the model described in this paper.

value of 0.87 to more nearly unity. The analysis of Owen<sup>15</sup> of the spectra of transition metal ions in solids and solutions indicates spin-orbit coupling constants 70–85% of the free ion values. Configuration interaction of the  $^1P^0$  and  $^3P^0$  states with other crystal states may alter the apparent spin-orbit coupling constants. Knox<sup>16</sup> has most recently considered configuration interaction with electron transfer states.

### III. SIMPLIFIED CONFIGURATION COORDINATE MODEL

The simplified configuration coordinate as applied to KCl:Tl is shown in Fig. 2. Including spin-orbit interaction the upper state is predominantly singlet and the lower excited state is predominantly triplet. As in the model of reference 1, 2470 Å absorption is attributed to the  $^1S_0 \rightarrow ^3P_1^0$  transition, 1960 Å absorption to  $^1S_0 \rightarrow ^1P_1^0$  and 3050 Å emission to  $^3P_1^0 \rightarrow ^1S_0$ . However, the 2470 Å emission in the present model involves an excited state with a greater singlet character than in the model of reference 1. In contrast to the earlier model, the energy separation of the pure spin states,  $2G_c$ , and consequently the mixing by spin-orbit interaction is not strongly dependent on the configuration coordinate. The energies of the  $^3P_0$  and  $^3P_2^0$  states as a function of the configuration coordinate lie parallel to and displaced  $-\zeta$  and  $+\zeta/2$ , respectively, from the pure  $^3P^0$  spin state. The  $^3P_0^0$  and  $^3P_1^0$  states are not shown on Fig. 2 since we are not concerned in this paper with transitions and trapping phenomena associated with these states.

In the quantitative application of the model the energy of each spin state as a function of configuration coordinate is adjusted so that after the application of spin-orbit interaction, using parameters consistent with the theoretical estimates of Sec. II, the experimental

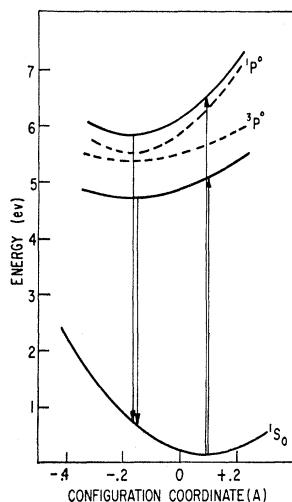


FIG. 2. Configuration coordinate model for KCl:Tl. Dashed lines are the pure spin states. Solid lines are the states with spin-orbit coupling.

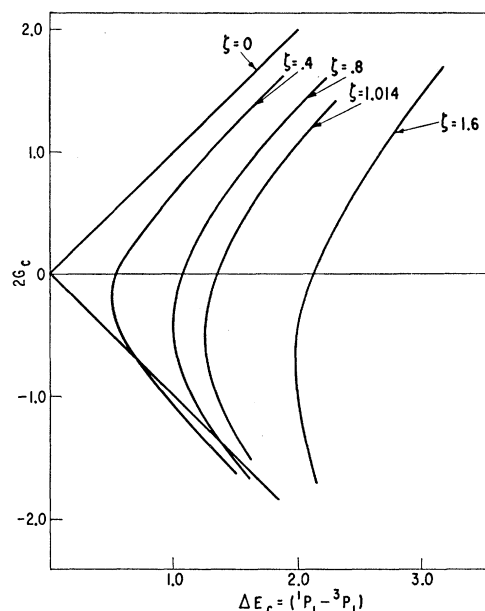


FIG. 3. Energy separation of pure spin states,  $2G_c$ , versus energy separation with spin-orbit interaction,  $\Delta E_c$ , for different values of spin-orbit coupling constant  $\zeta$ , with  $\lambda = 0.87$ .

spectra are reproduced. Also the ratio of oscillator strengths for the absorption transitions are in reasonable agreement with experiment. In Fig. 3 is shown for different values of  $\zeta$  the dependence of  $G_c$  on the separation of the states including spin-orbit interaction. For  $\zeta$  equal to its free ion value of 1.014 eV,  $G_c$  must be negative in order to account for the experimentally observed  $\Delta E_c$  of 1.30 eV at the absorption configuration for KCl:Tl. At the configuration for emission the experimental  $\Delta E_c$  is 1.25 eV and there is no point on the curve for  $\zeta$  equal to 1.014 eV corresponding to this value of  $\Delta E_c$ . For other thallium-activated alkali halides such as KI:Tl the free ion value of  $\zeta$  is unacceptable for both absorption and emission.

In accordance with the theoretical considerations of Sec. II we therefore reduce  $\zeta$  to 0.8 eV<sup>16a</sup> and  $G_c$  becomes real and positive for the experimental values of  $\Delta E_c$  for both absorption and emission in KCl:Tl. Figure 2 is based on this value of  $\zeta$ . In Figs. 2 and 3  $\lambda$  is maintained at its free ion value. If  $\lambda$  is increased, as suggested in Sec. II,  $\zeta$  must be decreased by an approximately equivalent amount in order to maintain the same  $\Delta E_c$ . For KI:Tl a decrease in  $\zeta$  below 0.8 eV is necessary to avoid imaginary values of  $G_c$  even with the free ion value of  $\lambda$ . The larger radial extension of the  $I^-$  wave function, as compared to  $Cl^-$ , is expected to result in a greater perturbation of the free ion  $Tl^+$  wave function which through renormalization yields a greater decrease in  $\zeta$  and  $\lambda\zeta$ . Configuration interaction with other crystal

<sup>16a</sup> Note added in proof.—H. Kamimura and S. Sugano [J. Phys. Soc. Japan 14, 1612 (1959)] from an analysis of the absorption spectra of KCl:Tl independently deduced a value of  $\zeta$  equal to 0.76 eV.

<sup>15</sup> J. Owen, Proc. Roy. Soc. (London) A227, 183 (1955).

<sup>16</sup> R. S. Knox, Bull. Am. Phys. Soc. 3, 358 (1958).

states is also expected to be greater for KI:Tl than for KCl:Tl and thereby to lead to a greater apparent decrease in the spin-orbit coupling constants. In addition, it is evident from the structure in the absorption spectrum of KI:Tl at low temperatures<sup>17</sup> that the activator system does not behave precisely according to the single coordinate model.

In general the one dimensional configuration coordinate model is inadequate to account quantitatively for all phenomena involving impurity systems. As was realized in developing the earlier model the transition energies may depend on more than one independent coordinate. If, as in the analysis based on the previous model, we allow the transition energies of KCl:Tl to depart as much as 5% from the experimental values, a greater  $\Delta E_c$  is obtained and with  $\zeta$  equal to its free ion value,  $G_c$  becomes real and positive for all configurations. Thus, the experimental spectra, except for the 4750 Å emission, are accounted for as accurately by the present model as by the previous model, avoiding in both cases an adjustment of  $\zeta$  from its free ion value. The limitations of the one dimensional configuration coordinate model have been recently discussed by Maeda.<sup>18</sup>

#### IV. DISCUSSION OF SPECTRA

In view of the considerable accumulation of data on the spectra of KCl:Tl since the single coordinate model was first applied quantitatively to this phosphor, it is desirable to reconsider the nature of the impurities responsible for some of these spectra and the detailed assignment of the transitions involved. From the work of Seitz<sup>8</sup> it is clear that the 1960 Å and 2470 Å absorption are characteristic of isolated Tl<sup>+</sup> in KCl. The concentration dependence of emission intensity of the 3050 Å band<sup>19,20</sup> is in accord with the idea that this band arises from isolated Tl<sup>+</sup>. In view of its selective excitation by radiation in the 1960 Å absorption band,<sup>1</sup> the 2470 Å emission is also attributable to isolated Tl<sup>+</sup>.

It should be pointed out that a recent recalibration<sup>21</sup> of the spectrophotometer used for the emission spectra of reference 3 results in the conclusion that the output of 3050 Å emission in KCl:Tl with 1960 Å excitation can be almost entirely accounted for by self-absorption of the emitted 2470 Å radiation. In arriving at this conclusion it is necessary to consider in detail the geometry of excitation and observation. The 3050 Å emission is excited in the region of the crystal observed by the spectrophotometer not only by the 2470 Å

radiation originating in the observed volume but also by 2470 Å radiation originating in parts of the crystal outside the volume of observation.

The energy-configuration coordinate diagram of Fig. 2 explains the 2470 Å and 1960 Å absorption and 2470 Å and 3050 Å emission. However, there remains the problem of the 4750 Å emission and an excitation peak at 2575 Å which preferentially leads to this emission. The problem is first to ascertain the physical identity of the center responsible for this emission. On the basis of an apparent thermal equilibrium between the two emitting states and excitation of 4750 Å emission by 1960 Å excitation we were led to a model which emerged in its most fully developed form as the energy configuration coordinate curves of reference 1.

From excitation spectra Patterson and Klick<sup>5</sup> suggested that 4750 Å emission arises from clusters of Tl<sup>+</sup> ions or of Tl<sup>+</sup> ions associated with other crystalline imperfections. As shown in Fig. 4 excitation at 2450 Å results in practically no 4750 Å emission whereas excitation at 2537 Å yields both bands. It should be pointed out that the temperature dependence of the ratio of the two bands given in reference 3 was obtained using 2537 Å excitation. The temperature dependence of the relative absorption intensity at 2537 Å of the 2470 Å and 2575 Å bands accounts for the variation of relative intensity of the two emission bands with temperature.

The significance of differences in spectra such as shown in Fig. 4 depends on activator concentration and such geometric effects as particle size, if powders are used, or crystal dimensions, if single crystals are used. The ratio of absorption  $A_1/A_2$  in the crystal at two different wavelengths  $\lambda_1$  and  $\lambda_2$  by two different

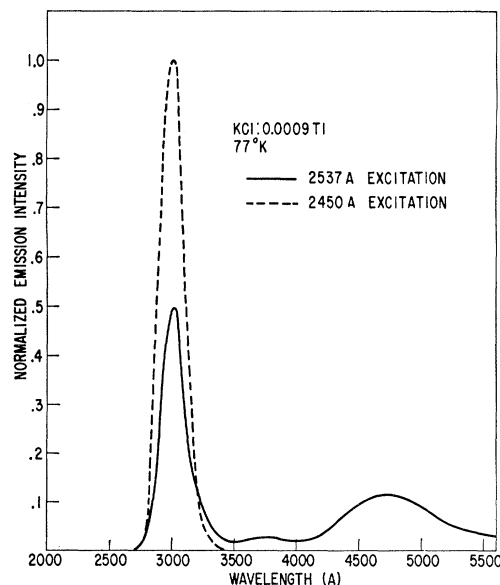


FIG. 4. Emission spectra of KCl:Tl with 2450 Å and 2537 Å excitation.

<sup>17</sup> P. H. Yuster and C. J. Delbecq, *J. Chem. Phys.* **21**, 892 (1953).

<sup>18</sup> K. Maeda, *J. Phys. Chem. Solids* **9**, 335 (1959).

<sup>19</sup> P. D. Johnson and F. E. Williams, *J. Chem. Phys.* **18**, 1477 (1950).

<sup>20</sup> J. H. Schulman, E. W. Claffy, and R. J. Potter, *Phys. Rev.* **108**, 1398 (1957).

<sup>21</sup> Recalibration of the response of the spectrophotometer used to obtain the emission spectra of reference 3 indicates that the 4750 Å band is less intense by a factor of approximately 2.4 relative to the 3050 Å band than the figures of that reference indicate.

centers with concentrations  $c_1$  and  $c_2$  and molar extinction coefficients  $\alpha_1$  and  $\alpha_2$  is:

$$\frac{A_1}{A_2} = \frac{1 - e^{-\alpha_1 c_1 l}}{1 - e^{-\alpha_2 c_2 l}}, \quad (4)$$

where  $l$  is the thickness of the crystal, or the mean path length in a powder.<sup>22</sup> When  $\alpha_1 c_1 l, \alpha_2 c_2 l \ll 1$ , excitation spectra accurately coincide with absorption spectra. However, when  $\alpha_1 c_1 l, \alpha_2 c_2 l \gg 1$ , then  $A_1/A_2 \rightarrow 1$ . Thus with thick crystals, large particles or high concentrations there is no way of distinguishing between significant and minor effects. The data given in Fig. 4 more nearly conform to the first of these two conditions. The fact that excitation at 2450 Å results in no appreciable 4750 Å emission is not in accord with the suggestion in reference 3 that the two emission bands result from excitation to the same state or that there is a high probability of transfer of energy between the two emitting states.

Emission at approximately 3200 Å due to the  $^3P_0 \rightarrow ^1S_0$  transition might be expected if the  $\Delta J$  selection rule were violated. In any case, the 4750 Å emission cannot be explained by this transition for the same center and configuration coordinate of Fig. 2.

However, it cannot be concluded that a different center is involved in 4750 Å emission. The introduction of vacancies by introduction of various divalent ions<sup>3</sup> does not affect the intensities of 3050 Å and 4750 Å emission under 2537 Å excitation, thereby ruling out  $Tl^+$  associated with vacancies as the origin of 4750 Å emission. When cadmium is added, a new emission band appears, and at moderately low  $Tl^+$  concentrations the 3050 Å and 4750 Å bands are both depressed to the same extent.<sup>3</sup> It would seem fortuitous if the same

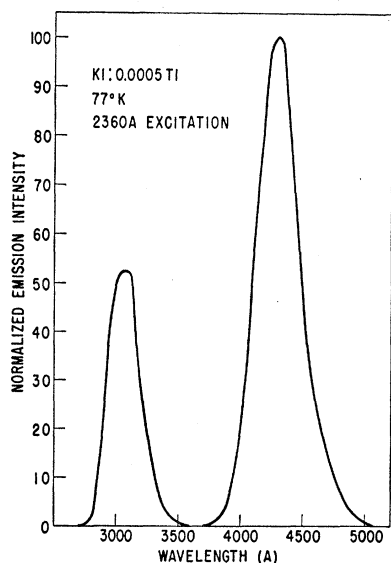


FIG. 5. Emission spectrum of KI:Tl with 2360 Å excitation.

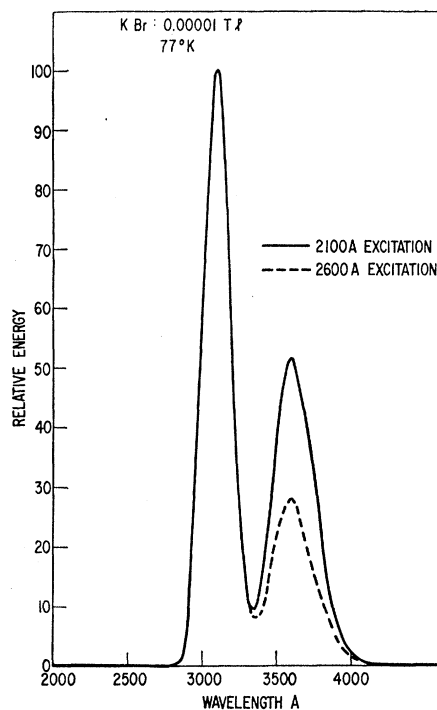


FIG. 6. Emission spectrum of KBr:Tl with 2100 Å and 2600 Å excitation (normalized at 3100 Å).

fraction of two structurally different centers were destroyed by the addition of  $Cd^{++}$ .

From the  $Tl^+$  concentration dependence of intensity of the 3050 Å and 4750 Å bands under 2537 Å excitation it was deduced<sup>19</sup> that both emission bands arise from isolated  $Tl^+$  surrounded only by the KCl lattice. There is some dependence of the ratio of 4750 Å to 3050 Å emission on concentration at lower concentration due to low absorption of the incident 2537 excitation giving rise to selective absorption in the 2470 and 2575 Å bands according to the geometric considerations outlined above.

There is other evidence which indicates that  $Tl^+$  associated with another defect is not responsible for 4750 Å emission. First, quenching or annealing of otherwise identical samples after heating for 6 hours at temperatures ranging from 470° to 670°C resulted in no variation in the ratio of intensities of the 3050 Å and 4750 Å emission. Quenching from various temperatures or annealing would be expected to affect the degree of association of defects with  $Tl^+$ . In addition, Compton and Klick<sup>23</sup> observed no polarization of luminescence in the 4750 Å band with polarized excitation. A permanently asymmetric center would be expected to exhibit polarized emission with polarized excitation. The elimination of other possibilities leads to the suggestion that the 4750 Å emission originates

<sup>22</sup> P. D. Johnson, J. Opt. Soc. Am. 42, 978 (1952).

<sup>23</sup> W. D. Compton and C. C. Klick, J. Phys. Chem. Solids 7, 170 (1958).

from isolated substitutional thallium but that either a different state of ionization or a different configuration coordinate must be involved.

#### V. OTHER ALKALI HALIDE PHOSPHORS

The similarity of the absorption spectra of various alkali halide phosphors activated with  $Tl^+$  or  $In^+$  indicates the desirability of attempting to apply the model of this paper or of reference 1 to these other phosphors. Either model predicts that with excitation in the shorter wavelength absorption band a short wavelength emission band might be observed. In Fig. 5 it is seen that in the case of  $KI:Tl$  this emission does in fact exist. Under 2360 Å excitation the usually observed emission peak at 4300 is accompanied by a shorter wavelength peak at 3080 Å. This peak is, we believe, by analogy with  $KCl:Tl$ , due to the  $^1P_1^0 \rightarrow ^1S_0$  transition. Only at temperatures above that of liquid nitrogen or at high activator concentrations is self-absorption sufficient to depress the short wavelength side of the 3080 Å emission band. Self-absorption may still be sufficient to account for the observed intensity of the 3080 Å band however. The emission bands at 3080 Å and 4300 Å can be correlated with the absorption bands at 2360 Å and 2870 Å, respectively, on the basis of the simple model with the  $^3P_1^0$  and  $^1P_1^0$  states nearly parallel as a function of the configuration coordinate, whereas, a correlation on the basis of the model of reference 1 requires, as for  $KCl:Tl$ , a complicated interaction of the pure spin states.

Under 2300 Å excitation at 77°K,  $KCl:In$  shows no emission at wavelengths shorter than the 4200 Å band. It is possible that the broad multiplet structure in absorption<sup>6,24</sup> results in complete self-absorption of any such emission even at 77°K.

The absorption spectrum of  $KBr:Tl$  with peaks at 2100 and 2600 Å is similar to those of the other alkali halide phosphorus and is intermediate to  $KCl:Tl$  and  $KI:Tl$ . The emission of  $KBr:Tl$  consists of a single broad flat-topped peak centered at 3250 Å at room temperature which separates into two well-resolved

bands at 3100 Å and 3600 Å at 77°K.<sup>25</sup> No emission at wavelengths shorter than the band at 3100 Å was found at 77°K or 300°K. Excitation at 2100 Å results in the 3600 Å band being more intense relative to the 3100 Å emission than is the case with 2600 Å excitation. This is seen in Fig. 6. Because of this fact, the model of this paper is not in accord with the 3100 Å and 3600 Å emission being due to the  $^1P_1^0 \rightarrow ^1S_0$  and  $^3P_1^0 \rightarrow ^1S_0$  transitions, respectively. The absence of emission at wavelengths shorter than the 3100 Å band does not, however, rule out the possibility that the present model may be valid with 3100 Å emission being the  $^3P_1^0 \rightarrow ^1S_0$  transition. As was suggested for  $KCl:In$  shorter wavelength emission may be completely self-absorbed.

#### VI. CONCLUSIONS

It is possible to account for the most prominent features of the absorption and emission spectra of  $KCl:Tl$  by a simple one-dimensional configuration coordinate model in which the excited pure spin states do not cross. The theoretical estimates of the values of the parameters which govern spin-orbit interaction are in accord with the values which are required in order to fit the experimental spectra on the basis of the simple model. The characteristics of the 4750 Å emission and the polarization of the 3050 Å emission suggest that additional coordinates of the same center are required to explain these properties. Many features of the spectra of  $KCl:In$ ,  $KBr$ ,  $Tl$  and  $KI:Tl$  are consistent with the simple model.

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<sup>24</sup> N. E. Lushchik, Trudy Inst. Fiz. i. Astron. Akad. Nauk Eston. S.S.R. 6, 149 (1957).

<sup>25</sup> W. von Meyeren, Z. Physik. 61, 621 (1930).